

Degradation of polycyclic aromatic hydrocarbons from coal tar aqueous solutions using photo- biocatalysts

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Overview of the document

This manuscript is prepared for the examination and submitted in completion of the author's doctoral studies at North-West University. The preface contains an overview in the abstract form of the thesis submitted for examination.

General details regarding the published papers and presentations are given along with the papers in this thesis. Some of the papers included in this thesis were published and come submitted in various journals and conference proceedings, each specifying its own formatting and style. These papers are included "as is" and it should be noted that no changes were made to the content thereof.

The preface and appendices include signed statements, acknowledgements and consent to publish from each co-author. The deliverables arising from each study are discussed and a conclusion of the thesis is provided.

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To whom it may concern

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That the thesis entitled: "Degradation of polycyclic aromatic hydrocarbons from coal tar aqueous solutions using photo-biocatalysts", submitted in fulfilment of the requirements for the degree Doctor of Philosophy in Chemical Engineering at the North-West University, is my own work, except where acknowledged in the text, and has not been submitted as whole to any other tertiary institution.

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(27 August 2022)

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I dedicate this thesis to my late grandmother, Yaya Isabelle, who passed away on 17 December 2021.

ABSTRACT

Polycyclic aromatic hydrocarbons (PAHs) are amongst the most predominant pollutants that are currently released into the environment. Despite the myriad of environmental regulations enforced by governments in countries around the world, various industries have continued to release PAHs in various water sources. The petroleum industry has been identified as the industry that released high level of PAHs into the environment. However, a considerable amount of PAH is also released from coal tar produced by the coking industry. The interaction of coal tar with various aqueous solutions in the environment is often a factor determining the release of PAHs into receiving water. In this study, environmental solutions such as acid mine drainage, alkaline mine drainage and sewage wastewater were considered to simulate the release of PAHs from coal tar into the environment. A mass of 5g of coal tar obtained from the coking process was found to contain 2916.47 mg/L of PAHs. The concentration of PAHs in coal tar was determined by using gas chromatography spectrometry. Naphthalene (788 mg/L), phenanthrene (632 mg/L), fluoranthene (395 mg/L), acenaphthylene (356 mg/L), fluorene (327 mg/L), pyrene (266 mg/L), and anthracene (245 mg/L) were the most concentrated PAHs in coal tar. Amongst these PAHs, it has been reported that naphthalene (NAP) is the most abundant PAH in the environment.

The coal tar was immersed in a designed column, containing 300 mL of either acidic mine drainage, alkaline drainage or sewage wastewater. The leaching process conducted over a period of 8 weeks using acidic mine drainage, sewage wastewater and alkaline mine drainage resulted in the leaching of 7.1 mg/L, 1.2 mg/L and 0.32 mg/L of PAHs respectively at room temperature. The PAHs that were highly concentrated were considered to be dissolved at a higher rate. It was also reported that the higher molecular weight of a PAH is life-threatening and more carcinogenic as compared to the lower molecular weight. The dissolution of the PAHs in the different water samples was influenced by the dissolved organic matter and pH amongst others to influence the leaching process. The acidic mine drainage released the most PAHs, followed by sewage wastewater and lastly alkaline mine drainage. After 8 weeks of leaching, 19.3 mg/L, 1.62 mg/L and 1.81 mg/L PAHs in acidic mine drainage, alkaline mine drainage, and sewage wastewater respectively was released. The release of PAHs from the coal tar was observed to increase over time. The PAHs with lower weight between 2 to 4 rings were observed to be highly dissolved in the samples.

The presence of PAHs in the environment demands the implementation of an urgent technique that will remove them completely. Various studies have reported that PAH can only be destabilized under the influence of temperature and photoactive material. Metal oxides were selected as the most effective materials due to their optical, antifouling, and antibacterial properties and thermal resistance to remediate PAH pollutants. In the study, zinc oxide was selected as the photocatalyst for degradation of PAHs. The band gap of ZnO is roughly 3.2eV and in this study, it was recommended to implement agrowastes to improve the photodegradation efficiency of the ZnO/Ag photocatalyst. Various biological agrowastes such as *moringa oleifera* seed (MO), groundnut shells (GS) and apatite (A) derived from cow bones were used

to enhance the desired property of the ZnO. In this study, the band gap of ZnO was found to be 3.35 eV; it was found that due to the relatively high content of metals, including rare earth metals with high photocatalytic activity such as strontium (Sr) that are present in A, GS and MO at a concentration of 387273 µg/kg, 31469 µg/kg and 22730 µg/kg respectively, that they are highly proficient in obtaining a band gap of 1.59 eV and 2.96 eV for ZnO/Ag and MO/GS/A/ZnO/Ag for novel bioheterophotocatalysts. Many photocatalysts were synthesized from the agrowastes, ZnO/A, ZnO/GS and ZnO/MO with a band gap of 2.15 eV, 2.51 eV and 2.74 eV respectively. It was proven from the result that the Sr content in A, followed by GS and lastly MO strongly contributed to a lesser band gap and a higher photoactivity.

MO/GS/A/ZnO and ZnO/Ag materials were tested for the photodegradation of PAHs and it was proven that MO/GS/A/ZnO/Ag was the most effective material to degrade 69.59%, 61.07 % and 61.68% of PAHs as compared to 52.62%, 37.46% and 44.30% using ZnO/Ag in acidic mine drainage, alkaline mine drainage and sewage wastewater in 60 min. Furthermore, another experiment was conducted and this time, a self-made photoreactor was introduced that achieved a photodegradation efficiency of 64%, 55%, and 58%. Without its application, a photodegradation efficiency of 53%, 33%, and 39% was obtained in 60 min under solar irradiation using acidic mine drainage, alkaline mine drainage and sewage wastewater respectively. It was then concluded that the self-made photoreactor was effective even compared with ZnO photocatalyst alone. The photodegradation was conducted with and without a flat-bed reactor or photocatalyst under solar irradiation.

The self-made photoreactor was introduced with the MO/GS/A/ZnO/Ag synthesized photocatalyst. It was found that almost 100%, 97% and 98% degradation were obtained, as compared to 89%, 94% and 92% degradation using ZnO/Ag at 60 min under solar irradiation in acidic mine drainage, alkaline mine drainage and sewage. This indicates that the introduction of MO, GS and A was effective in degrading PAHs in various water sources when using a self-made photoreactor in the presence of solar irradiation. Most significantly, the introduction of the flatbed and even the solar irradiation alone could degrade the PAHs in various water sources.

DELIVERABLES OF THIS STUDY

Paper Title	Synthesis of Bio-Photocatalysts and their Application for the Degradation of Organic Pollutants
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NOMENCLATURE

ACD	Acidic mine drainage
ZnO	Zinc oxide
Ag	Silver
MO	Moringa Oleifera seed
GS	Groundnut shells
A	Apatite
mg/L	Milligram/Litre (PAHs concentration)
g	Gram (mass)
USEPA	United States Environment Protection Agency
EEA	European Environment Agency
AOP	Advanced oxidation processes
NPs	Nanoparticles
CB	Conduction band
VB	Valence band
NAP	Naphthalene
ACY	Acenaphthylene
ACE	Acenaphthene
FL	Fluorene
PHE	Phenanthrene
ANT	Anthracene
FLU	Fluoranthene
PYR	Pyrene
BaA	Benzo[a]anthracene
CHY	Chrysene
BbF	Benzo[b]fluoranthene
Blkf	Benzo[k]fluoranthene
BaP	Benzo[a]pyrene
DahA	Dibenz[a,h]anthracene
Bghip	benzo[ghi]perylene
IcdP	Indeno[1.2.3-cd]pyrene

1. Introduction

Water is the most important resource for humans and living organisms, therefore it is essential to maintain fresh water on a sustainable basis that enriches and satisfies society. The water crises has exacerbated since the growth in pollution and urbanization. There have been major concerns regarding the massive pollution of the environment derived from various industries [1,2]. The pollutants released from these industries have resulted to affect the quality of water. Most of the pollutants derived from these industries have been reported to be given special attention due to their quick turnover in human health concerns [3].

Many industries activities such as as coal conversion, steel mining, pulp, petroleum refining, paper milling, textile processing and organic chemicals among others are responsible for the degradation of water quality trough releasing organic pollutants [4]. These pollutants are found during the incomplete combustion, gasification and pyrolysis of fossil fuels from the release of petroleum [5]. Fatty wastes have also been reported to be a threat to both humans and the environment [3]. Most pollutants such as metal and organic in wastewater are related to human activities and are a risk to health. According to the Environmental Protection Agency (EPA), organic pollutants are the most widely released into the environment [6].

The organic pollutants that are derived from coal tar are the polycyclic aromatic hydrocarbons (PAHs). These organic pollutants are mostly derived from mining- and petroleum-related activities. They are easily concentrated in coal tar which is a by-product of coal [7]. Coal tar is composed of hundreds of organic compounds of different molecular weights, structures, and properties [8]. Coal tar is formed from gasification and other processes which are often carelessly discharged into the environment [9]. The biodegradability of various PAHs has been reported to be a problem, due to their physicochemical properties [10]. The discharge from incomplete combustion or gasification processes contains other compounds such as phenolics (cresols, xlenols), monocyclic aromatic hydrocarbons, and PAHs which are often reported in water sources at higher concentrations [11].

PAHs are organic pollutants mostly found in wastewater, in which their presence causes acute health risks to human life [12,13]. The ubiquity of the PAHs in the environment has made them to persistent and quite challenging to degrade [14]. The number of rings depending on their molecular weight is known to determine their toxicity [8]. PAHs have been reported to have carcinogenic and mutagenic properties and are classified according to USEPA and European Environment Agency (EEA) as the most toxic pollutants that cause cancer and mutations [8].

Pollutants can either be biodegradable or non-biodegradable, depending on their type. Biodegradable pollutants are easily degradable by breaking down their bonds and in this case, it is important to destabilize PAHs by breaking the rings that are bonded on the carbon and carbon bonds. Materials like plants, animals, fruits, flowers, and vegetables are biodegradable, whereas non-biodegradable materials such as rubber, chemicals, paint, and plastic are not easily broken down by microorganisms [4]. There is a need to implement an effective technique that can assist in mineralising these pollutants from the environment. The effectiveness of advanced oxidation processes (AOPs) has been explored for non-biodegradable pollutants such as PAHs under ambient conditions [16].

AOPs are characterized by their catalytic photochemical properties and oxidative degradation reactions, as they have been proven to be successful in the removal of PAH pollutants in water sources [17]. Among the AOPs, photocatalysts have been extensively considered over the previous decades due to their capacity to remove organics pollutants [16]. An advanced technique has also been implemented to enhance photocatalysts by introducing metals, a process known as doping. This results in enhancing the photoactive performance, which also results in favour of photodegradation [18]. Semiconductor-based heterogeneous photocatalysis is an advanced oxidation processes (AOP) that are suitable in the application of water decontamination by solar light emission. ZnO, WO₃, AgBr, Bi₂WO₆, and SrTiO₃ are just a few semiconductors that have been studied for their role in wastewater treatment [19]. ZnO is a metal oxide and also a semiconductor, which is more stable and has a longer life than organic-based disinfectants. Besides, ZnO is regarded as a safe material, and is used in dental, personal care and home care products [20].

ZnO has been synthesized into nanoparticles (NPs) for wastewater treatment with a band gap of 3.37 eV [20]. The incorporation of noble metals with nanomaterials significantly enhances the visible-light absorption via surface plasmonic effects that generate electron-hole pairs for photocatalysis [21]. A photocatalyst is a material that absorbs light to bring it to a higher energy level and provides such energy to a reacting substance to make a chemical reaction occur [22]. Photocatalysis has customarily been considered an indiscriminative process (particularly in water) because these reactions are normally regulated via a free radical mechanism ($\cdot\text{OH}$, O_2^- , HO_2) [23]. Photocatalysis depends on the rule that when a semiconductor is presented to a light source with a degradable wavelength, the electrons from the valence band are elevated to the conduction band, leaving positive gaps in the valence band [24]. It is well known that PAHs are still persistent in wastewater. Several techniques and methods have been utilized for the segregation of organic contaminants from the aqueous solutions, although they are not versatile enough to remove contaminants completely from wastewater [25].

However, photocatalysis degradation has been the most sustainable technique for the removal of pollutants in wastewater. The importance of this technique is simply its rapid reaction, economic feasibility, environmental friendliness, and its complete degradation, which make it more suitable than others [26]. To embrace its capability in the removal of the PAHs, a delay in the electron recombination and other

properties that might influence its performance during the photoreactor (UV) under visible light must be monitored. For a sustainable process, it is of utmost importance to consider a biologically-mediated synthesis of photocatalysts which can allow not only the valorization of wastes but mainly result in the production of a photobiocatalyst with lower toxicity and high efficiency for the degradation of PAHs. In this study, the synthesis of various photobiocatalysts from *moringa oleifera* seed (MO), groundnut shells (GS), and apatite (A) with silver (Ag) to enhance the property of ZnO was conducted and assessed on their compatibility in the enhancement of the degradation of organic pollutants PAHs in a solar-irradiated photoreactor. Therefore, a suitable photoreactor was designed to achieve the objectives. Furthermore, the delay of the recombination of the electrons hole pairs was considered for the selection of a suitable and effective photobiocatalyst to obtain a greater yield in the photocatalytic reaction.

1.1 Motivation for research

According to Wang, *et al.* [27], heterogeneous photocatalysis plays a vital role in the mineralization of the contaminants in water. The rate and the extent of the photocatalytic degradation process are often influenced by the nature of the photocatalyst and the conditions under which the process of photocatalysis is carried out. Therefore, in this research, the enhancement of the performance of the photocatalyst by improving the band gap and delaying the recombination rate of charge carriers was of utmost importance to ensure the effective mineralization of PAHs. Heterocatalysts have been reported to exhibit narrow band gap and delayed recombination of generated gaps; furthermore, biologically-mediated synthesis or green synthesis is a very attractive approach to producing a photobiocatalyst that is eco-friendly and that will allow valorizing waste in the process of developing a suitable photocatalyst. To enable an environment where photocatalysis can be enhanced, a photoreactor is needed for effective exposure of semiconductors to irradiation and to ensure continuous degradation of organic pollutants in water. The building of a photoreactor to assist the degradation was novel, with characteristics such as suitability for photocatalysis in emitting visible light.

1.2 Problem statement

There is still a continuous discharge of coal tar into the environment that causes severe damage to the ecosystems. Further, this coal tar consists of chemical compounds named polycyclic aromatic hydrocarbons that are toxic. Environmental contamination by PAHs derived from coal tar has become one of the major concerns across the world. The scarcity of water resources in South Africa, combined with limited health budgets, pollution by different industries, and lack of proper waste management, call for improved measures to manage the release of PAHs into the environment. The fact that few studies in this area have been conducted in South Africa makes this study important. Exposure of humans and wildlife to PAHs occurs via different pathways; however, exposure through contact and ingestion of water is growing at an exponential rate. The toxicity of PAHs and their widespread distribution have led to more interest in the presence of these compounds in the aquatic and terrestrial environment. Many studies have been done in developing countries but in South Africa, while a few studies have been conducted to determine the

presence and levels of PAHs deriving mostly from pharmaceutical sources. However, very few have focused on the release of PAHs from coal tar into the aquatic environment. Furthermore, the degradation of PAHs by photobiocatalysts in a solar-irradiated photoreactor has not yet received the attention of researchers.

1.3 Research aims and objective

This research aims to synthesize various suitable photocatalysts (photobiocatalysts) that are easily excitable under sunlight (visible light) with delayed recombination of band gap, and to design a photoreactor that can effectively enhance the degradation of PAHs under sunlight. To achieve these aims, the following objectives were considered.

- Assess the influence of the physicochemical properties of receiving water on the release of PAHs from coal tar.
- Synthesize eco-friendly heterocatalysts with enhanced properties to perform under visible light.
- Minimize the formation of toxic by-products during photodegradation of PAHs.
- Design and build a photoreactor that can effectively support the degradation of PAHs under sunlight.

1.4 Research Questions

- How do the physicochemical properties of receiving water affect the release of PAHs from coal tar?
- To what extent do *moringa oleifera* seed, groundnut shells, and apatite influence heterocatalyst properties, like band energy to excite electrons that can enhance photodegradation under sunlight?
- What is the influence of heterocatalysts on the photodegradation of PAHs in acidic mine drainage, alkaline mine drainage and sewage wastewater?
- How does the photoreactor contribute to the photodegradation of PAHs under solar irradiation (visible light)?

1.5 Scope of the study

This research focuses on the organic pollutants (PAHs) that are dominant in coal tar and that have been a major concern in our limited water sources lately. These pollutants were to be removed from aqueous solutions using synthesized photobiocatalysts in an adequately designed and built solar-irradiated photoreactor.

1.6 Significance of research

The benefits of this research are as follows:

- 1) To maximize the use of clean water and reduce the risk of diseases.
- 2) To reduce the cost-effectiveness in the treatment of wastewater.

1.7 Thesis outline

1.7.1 Provisional chapter division

The research presented in the thesis will be conducted at North-West University, South Africa (Department of Chemical Engineering). The thesis comprises eleven chapters.

Chapter 1: Introduction.

Chapter 2: Background.

Chapter 3: Leaching of polycyclic aromatic hydrocarbons from the coal tar in sewage wastewater, acidic wastewater, and alkaline mine drainage.

Chapter 4: Recent advances in photoreactors for water treatment.

Chapter 5: Photodegradation of polycyclic aromatic hydrocarbons using metals oxide under irradiation.

Chapter 6: Synthesis of Bio-Photocatalysts and their application for the degradation of organic pollutants.

Chapter 7: Synthesis of eco-friendly heterocatalysts with enhanced properties to perform under visible light.

Chapter 8: Photodegradation of polycyclic aromatic hydrocarbons from coal tar into mine wastewaters and sewage wastewater on a flat-bed photoreactor.

Chapter 9: Photodegradation of polycyclic aromatic hydrocarbon from coal tar using a heterogeneous photocatalyst on a flat-bed photoreactor.

Chapter 10: Conclusion.

Chapter 11: Appendices.

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2. Background

2.1 Pollutants in the environment compartments

There has been an increased demand for clean water due to various activities that are responsible for releasing pollutants in water, thereby creating wastewater. This action has caused major health concerns to the environment and humans. In addition to that, the growth in population and urbanisation has also contributed to the increases in pollution that has led to a possible water crisis and the lack of clean water [2]. The dumping of pharmaceuticals, pesticides and personal care products also adds to the release of pollutants [3] that promote the presence of parasitic worms, bacteria, viruses, and protozoa [4]; as well as nutrients like phosphates and nitrates; and organic pollutants such as plastics, oil, detergents, dyes, aryl chloride and pesticides [5,6]. Most of these pollutants are generated by the industrial and agricultural sectors and by households [7], and therefore must be removed or treated to ensure a healthy environment [8], although the process in obtaining clean water from this wastewater are costly [10].

The wastes from petrochemicals have largely contributed to releasing persistent organic pollutants that are present in the environment and their destabilisation is a complex matter [11].

Since most of these pollutants are derived from various industries or activities such as mining, coking processes and gasification, their chemical properties are recognised as toxic pollutants that are persistent in the environment [12]. Most of these pollutants are organic pollutants that have been categorised as persistent organic pollutants (POPs) because of their ability to resist any removal techniques. It is very important to keep these organic pollutants away from the environment due to their toxicity and the ability to change the physiochemistry of the wastewater or the water [5]. Before the release of these organic pollutants into various water sources, they come into contact with the surface or underground soil and are adsorbed by the existing minerals, enzymes, and microorganisms in the soil; the remaining pollutants are then channelled into various water bodies [13].

2.2 Analysis of wastewater

There are various parameters such as pH, temperature, chemical oxygen demand (COD), biological chemical demand (BOD), dissolved organic carbons, conductivity and total dissolved solids in water and wastewater that need to be considered when dealing with wastewater treatment [14,15]. Conductivity is the tendency of the aqueous solution to produce and carry an electrical current; it normally occurs due to the presence of certain types of ion, their concentration, and the temperature of the aqueous solution. The most preferred solution conductors that can easily produce electrical current are organic acids, bases and salts. The conductivity of distilled water with no solids is negligible, at a range of 0.5–2.0 $\mu\text{mhos/cm}$. The increase of salts in an aqueous solution increases conductivity, with the conductivity being directly proportional to the amount of dissolved solids in the solution [9,14,15]. The pH must also be considered

when dealing with wastewater. Metal concentrations of 10 mg/L of precious metals and 10,000 mg/L of other metals are found in wastewater. They generally influence the wastewater and can be recovered through a precipitation method [16]. In addition, temperature also plays an important role in the pollutants of wastewater. An increase in temperature tends to increase the solubility of the organic pollutants in the wastewater/water [17]. The higher the concentration of COD and BOD in the wastewater, the more organic pollutants will be adsorbed [18].

2.3 Influence of mines on wastewater

The influence of mines on wastewater has gained interest in the research field. The unintentional releasing of major pollution from various mines has received attention. The most concentrated pollutants are known to be polycyclic aromatic hydrocarbons (PAHs) which is an organic pollutants that can be unleashed from various sources like coal tar and mining-related activities [19]. The reaction that occurs in mines is mostly caused by sulphide-containing ores which are a serious threat to the environment in releasing toxic pollutants [20]. The discharge from the mine reduces the surface of various water sources and groundwater quality. The treatment of this discharge from mines varies regionally and it is costly [21]. Since pH is a major parameter in a mine, a lower pH causes higher electrical conductivity, which greatly contributes to the dissolution and agitation of the metals present in the mines [22]. Various mines have unique properties that vary from region to region, and therefore there is no applicable technique to measure the rankings of these abandoned mines that are responsible for releasing toxic pollutants. The release of acidic mine drainage (AMD) from the mine can be generated at any time during the processing [23].

2.3.1 Acidic mine drainage

Acidic mine drainage is also known as acid rock drainage (ARD). It mainly occurs in mining and is highly concentrated in ferrous and non-ferrous metal sulphates and salts that make it acidic wastewater. Various elements such as Cd, Cu, Fe, Mn, Pb, Zn and toxic elements like As and Se are mostly detected in AMD. Some of these metal concentrations are represented in Table 2.1 for specific regions in South Africa. These elements pose a serious threat to the environment and it has been reported that AMD is likely to be present when the pH measurement is less than 3 [23,24]. The formation of AMD occurs during the oxidation of sulphides in the presence of oxygen, water and micro-organisms (but specially iron-oxidizing bacteria). Therefore, to limit the formation of acidic mine drainage, the components used to form AMD should be reduced [23,25].

Table 2.1: Regional and geochemical characteristics of the AMD in South Africa.

Regions	pH	EC ($\mu\text{S}/\text{cm}$)	Fe (mg/L)	Al (mg/L)	Mn (mg/L)	SO_4^{2-} (mg/L)	References
Mpumalanga (Coal)	2.0	2.0	600	8000	300	300	[26-28]
Witbank (Coal)	2.4	2.4	12,410	6120	506	155	
Witwatersrand (Au)	2.3–6.9	2.3–6.9	520– 10,650	0.05–270	0.03–629	0.01– 120	

Heavy metals with a density larger than 6 g/cm³ are mostly dissolved in AMD which is regarded as undesirable for the environment [29]. The disposal of wastes from various processes such as mining, mineral and metallurgy often require costly treatment processes [30]. There are various ways to prevent the generation of AMD, including introducing an anoxic surfactant and preventing sulphides from being in contact with air and water [21].

2.3.2 Alkaline mine drainage

The hydrolysis of organic matter and dolomite can improve alkaline mine drainage [31]. Alkaline mine drainage is obtained from, amongst others abandoned mines, coal ashes, and materials in the backfill of mines [19]. The environmental pollution is mostly dependent on the pH from the mine drainage which changes both the geology and mines [32]. In addition, various alkaline materials, such as calcium hydroxide $[\text{Ca}(\text{OH})_2]$, calcium oxide $[\text{CaO}]$, sodium hydroxide $[\text{NaOH}]$, sodium carbonate $[\text{Na}_2\text{CO}_3]$, and ammonia $[\text{NH}_3]$ [19] are found in mines. Their concentration will either classify the mine as acidic or alkaline [33]. According to Kefeni *et al.* [32], mines should be managed carefully to keep the environment and the ecosystem safe.

2.3.3 Sewage wastewater

Sewage wastewater is water that has been fouled by various household and human activities. Organic, suspended solids and inorganic wastes contribute to sewage wastewater [34]. In recent years, with a fast-growing population, domestic and commercial activities have led to an increase in the amount of sewage being released into the environment [35]. The release of various mine-related pollutants has also impacted the economy and resulted in activities responsible for this release of toxic pollutants [35]. Sewage water mostly occurs in poorer countries where significant soil pollutants and effluents resulting from other activities are channelled into various waters [36]. Sewage wastewater contains various concentrations of metals such as Fe, Mn, Zn, Cu, Cr, Cd, Co, Zn and Pb which are then released into the receiving soils [35]. Although some PAHs can occur in sewage wastewater, the PAH most commonly and widely found in sewage wastewater worldwide is pyrene. The different PAHs will be described in section 2.6 [37]. From sections 2.3.1 - 2.3.3 is the background of each water sources that have been given less attention in the

discharged of PAHs from coal tar. Therefore it is important to understand their behaviour in nature and components.

2.4 Polycyclic aromatic hydrocarbons

PAHs are organic pollutants that occur in organic substances such as crude oil and petroleum and can also result from the burning of fossil fuels. Their chemical structure makes them resistant and non-biodegradable in almost all circumstances [38,39]. They are semi-volatile compounds that exist both in gas and in particles phase [40,41]. Moreover, they are soluble in organic compounds and insoluble in water. The light molecular weight species are more volatile as compared to the heavy molecular weight species [42]. The PAHs are generated from various processes such as anthropogenic and natural occurrences, as shown in Table 2.2 [37]. Since PAHs are present in petroleum sources, their contact with the aquatic environment can affect various water sources [6]. Acenaphthylene (ACY) is the simplest aromatic hydrocarbon that contains naphthalene with ethylene, and it is mostly used as an intermediate material for various organic compound syntheses, such as polymers and dyes. They can easily react with oxidants (OH), radicals (NO₃), and atoms (Cl) because of their double bonds with carbon atoms. This PAH has a high solubility in water which makes it adsorbable in soil and plants [37].

Benzo[a]pyrene (BaP) consists of high molecular weight and is produced from coal tar and pyrolysis of coal at a temperature range of 300 °C–600 °C. It can also be produced from the combustion of fuels and wood and can be deposited either underground, in the soil or water. Naphthalene (NAP) is derived from the heavy molecular fraction of coal tar and besides the fact that it is slightly toxic, it can also be used as a precursor for dyes. Anthracene (ANT) can be obtained from anthropogenic activities, and it is known to be also insoluble in water and to be less biodegradable. Benzo[k]fluoranthene (BkF) is responsible for affecting organisms. Benzo[ghi]perylene (BghiP) is the most difficult PAH to degrade due to its six-ringed structure. Chrysene (CHY) is a PAH that is slightly soluble in water and polar solvents such as ether and alcohol, however, it is difficult to degrade out of the environment. Fluoranthene is a common PAH that is mostly found in wastewater with a solubility of 0.25 mg/L and just like other PAHs, it can also resist transformation [37]. Phenanthrene (PHE) is also another PAH commonly found in wastewater with a concentration of about 7.6–9.9 µg/L which urgently needs attention as per the United States Environmental Protection Agency (USEPA) regulation [37].

Fluorene is also a PAH, but this organic compound is mostly used in organometallic chemistry. Additionally, these PAHs can also be produced from fuel extraction, coke ovens and roofing tar [37]. The anthropogenic PAHs are produced by humans intentionally and unintentionally and are related to a few processes like pyrogenic and petrogenic processes i.e. oil spills, burning of biomass and the natural process of PAHs release through smoking of cigarettes and driving vehicles that emit gasses like CO₂, CH₄ and N₂O [43].

PAHs can be produced from a gasification and fossil fuel process at a temperature range of 800–1000 °C [37]. PAHs can also be formed through biosynthesis using bacteria, fungi, plants and animals in the geochemical process, and also from some sedimentary rocks that contain buried organic matter [43]. There are over 400 kinds of PAHs that can be released from anthropogenic and natural occurrences and these PAHs are linked together, either in linear or angular relationship, which makes them recognised as hazards, based on their structure and organic ring structures. Some PAHs are white or pale-yellow in solid form but most of them are colourless [44]. PAHs are a by-product that occurs after various activities or processes and are subsequently released to the environment, also due to their solubility in water. The increase in a PAH's molecular weight greatly increases both the boiling and melting point of the species [45].

PAHs are known to be persistent in an environment and thus require an external technique for them to be removed. Their deposition in the environment has a negative impact and should not be sufficiently concentrated to avoid any contact with humans, although some of the releases are inevitable [46,47]. The molecular weight of PAHs can affect their solubility of water: for example, as the molecular weight of the PAHs increase, the water solubility decreases as a result of a deficiency of oxygen demand that will completely change the water physiochemistry. The low molecular weight of 3 aromatic rings will result in the PAHs being lipophilic and more volatile, as compared to 4 ring structures or higher. The increase of the PAH's molecular weight improves the hydrophobic and electrochemical stability of the wastewater. The molecular weight is mainly defined by the number of the rings; however, most of the time, the higher molecular weight species with more than 4 rings are normally insoluble in water, while PAHs are much more soluble with fewer rings in the structure [45].

2.5 Chemical characteristics of PAHs

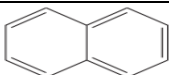
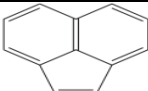
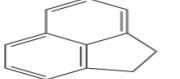
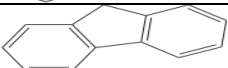
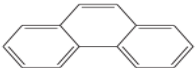
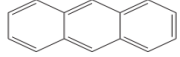
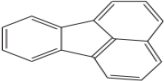
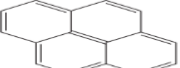
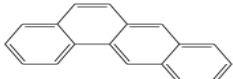
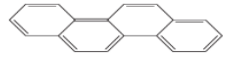
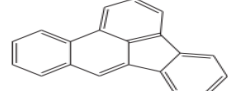
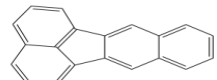
PAHs are constituted of carbons and hydrogen which are semi-volatile, and that are ranged among hundreds of chemical compounds that are abundant in nature as a result of various activities.

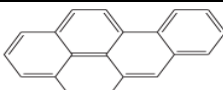
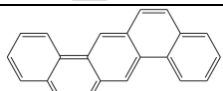
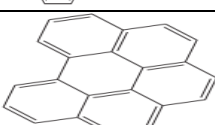
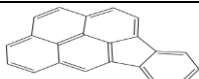
They are not environmentally friendly due to their resistance to change and toxicity [48]. The metabolites of the PAHs can be bonded with DNA and proteins in humans because of epoxide and dihydrodiol presence in the PAH. This can cause severe tumours and cancer through cell modification and biochemical disturbance [49]. The molecular weight is important when analysing the chemical characteristics of the PAHs. The molecular weight defines the toxicity of the compounds and their properties. PAHs can be divided into two categories in terms of molecular weight: low and high. Low molecular weight species consist of four rings maximum, whereas high molecular weight species have five rings or more [48].

The structure and the molecular weight of PAHs vary depending on their physical properties [48]. The characteristics of PAHs can further be identified or observed in their colour. Pure PAHs are usually coloured, crystalline solids at room temperature [50]. The chemical properties of PAHs make them

lipophilic and miscible in organic solvents. The solubility in an aqueous solution for each additional PAH ring decreases as the molar weight increases [51]. Other properties of PAHs that are also of concern are heat resistance, imitability, corrosion resistance, light sensitivity and physiological action [50]. Most of the PAHs are fluorescent and have light-emitting characteristics when they are excited by UV light. Each of the ring structures has a unique UV spectrum that each of the isomers of the ring exhibits, that causes PAHs to have characteristic UV absorbance spectra [46]. Although most organics pollutants such as PAHs are recognized as life-threatening, some PAHs are of greater concern due to their having a particularly severe effect on humans, based on their chemical properties and structures [46]. A summary of the molecular and solubility for these 16 PAHs are presented in Table 2.2, as reported by Nguyen, *et al.* [15,59,60].

Table 2.2: The characterization of the 16 PAHs in wastewater/water

Name	Formula	Molecular weight (g/mol)	Number of rings	Aqueous solubility (mg/L, 25 °C)	Molecular structure
Naphthalene	$C_{10}H_8$	128	2	31	
Acenaphthylene	$C_{14}H_{10}$	152	3	16.1	
Acenaphthene	$C_{14}H_{10}$	154	3	0.8	
Fluorene (FL)	$C_{13}H_{10}$	166	3	1.9	
Phenanthrene (PHE)	$C_{14}H_{10}$	178	3	1.1	
Anthracene (ANT)	$C_{14}H_{10}$	178	3	0.045	
Fluoranthene (FLU)	$C_{16}H_{10}$	202	4	0.26	
Pyrene (PYR)	$C_{16}H_{10}$	202	4	0.135	
Benzo[a]anthracene (BaA)	$C_{18}H_{12}$	228	4	0.011	
Chrysene (CHY)	$C_{18}H_{12}$	228	4	0.0015	
Benzo[b]fluoranthene (BbF)	$C_{20}H_{12}$	252	5	0.0015	
Benzo[k]fluoranthene (BkF)	$C_{20}H_{12}$	252	5	0.0008	

Benzo[a]pyrene (BaP)	$C_{20}H_{12}$	252	5	0.0038	
Dibenz[a,h]anthracene (DahA)	$C_{22}H_{14}$	278	5	2.49×10^{-3}	
benzo[ghi]perylene (BghiP)	$C_{22}H_{12}$	276	6	2.6×10^{-4}	
Indeno[1.2.3-cd]pyrene (IcdP)	$C_{22}H_{12}$	276	6	6.2×10^{-2}	

2.6 Influence of seasons on the occurrence of PAHs

PAHs can be influenced by the weather due to their semi-volatile property [52]. During the rainy season, it was discovered that PAHs such as naphthalene, phenanthrene, pyrene, and benzo[g,h,i]perylene were most abundant on surface water, and about 1.8×10^{-5} mg/L and 4.8×10^{-5} mg/L were dissolved and 15×10^{-5} mg/L – 66×10^{-5} mg/L were precipitated [41]. Since the season influences PAHs, it was found that they were mostly concentrated in winter due to various activities such as domestic heating, human activities and increased atmospheric stability [41]. Since the temperature the PAHs, the summer season is expected to have a lesser PAH concentration. Table 2.3 shows that PAHs were more densely deposited in winter (Argentina) and spring (China).

Table 2.3: Seasonal concentration of PAHs (mg/L)

Countries	Autumn	Winter	Spring	Summer	Reference
Argentina	7.629	10.423	5.793	4.133	[40]
China	0.005	0.007	0.038	0.011	[52]

2.7 PAH pollutants in wastewater

The quality of water worldwide has been exacerbated since 1990 due to an increase in various detrimental effluents derived from industrial and agricultural sectors and human activities [53]. It is important to maintain a freshwater supply for all living organisms, even though there may be still a small volume of micropollutants or salts present that can only be observed with advanced technologies [46]. The leaching of PAHs in wastewater can influence the initial concentration of the wastewater containing dissolved solids, and dissolved carbon that influences the chemical, biological oxygen demand and pH of the wastewater [46]. PAHs such as naphthalene (NAP), acenaphthene, phenanthrene (PHE), and fluorine (FLU) are amongst the 16 PAHs that are rapidly adsorbed in sewage wastewater [54,55].

The higher dissolved organic carbon from the river water studied by Qi *et al.* (2013) resulted in the PAHs dissolving faster [56]. The total dissolved solids (TDS) in wastewater represent both inorganic salts and dissolved organic carbon matter in the wastewater [57]. Amongst the 16 PAHs that have been discovered in wastewater/water, naphthalene is the simplest PAH to be mineralised without a photocatalyst, due to its volatile property and light molecular weight [58]. The existence of PAHs is detrimental to both the aquatic flora and fauna since they are POPs, and also considering the molecular weight of PAHs that influences the medium negatively [61]. According to Qi, Liu, Pernet-Coudrier and Qu [56], the PAHs from the surface river, wastewater plant and sewage in Beijing, China were investigated to be 193×10^{-6} to 1790×10^{-6} mg/L, 245×10^{-6} to 404×10^{-6} mg/L and 431×10^{-6} to 2860×10^{-6} mg/L respectively and this shows that, sewage wastewater was found to be highly concentrated with PAHs. The PAHs in wastewater contribute to

various detrimental factors, but mostly the physiochemistry of that wastewater [56]. The PAHs derived from fossil fuel combustion, petroleum activities, volcanoes and coal were reported by Karyab, *et al.* [62] to be present in drinking water, rivers, lakes, groundwater, wastewater, seawater and sediments.

The presence of PAHs in water bodies also changes the overall pH of the wastewater. Since the chemical composition of crude oil changes according to the region in which it is found, the PAHs also attribute to these changes [63]. Karyab, *et al.* [62,64] reported that individual PAH concentrations in surface water is mostly around 50×10^{-6} mg/L and as soon the concentration is above 0.01 mg/L, it indicates effluent derived from industries [62]. The PAH concentration was investigated by Gutierrez-Urbano, *et al.* [15] in real wastewater and it was found that 16 PAHs, as indicated in Figure 2.1, were identified. The World Health Organisation (WHO) has reported that the concentration of clean water without any influent of PAHs should be as low as 0.00195 mg/L, and with the influent of PAHs it should be 0.0109 mg/l and above [65].

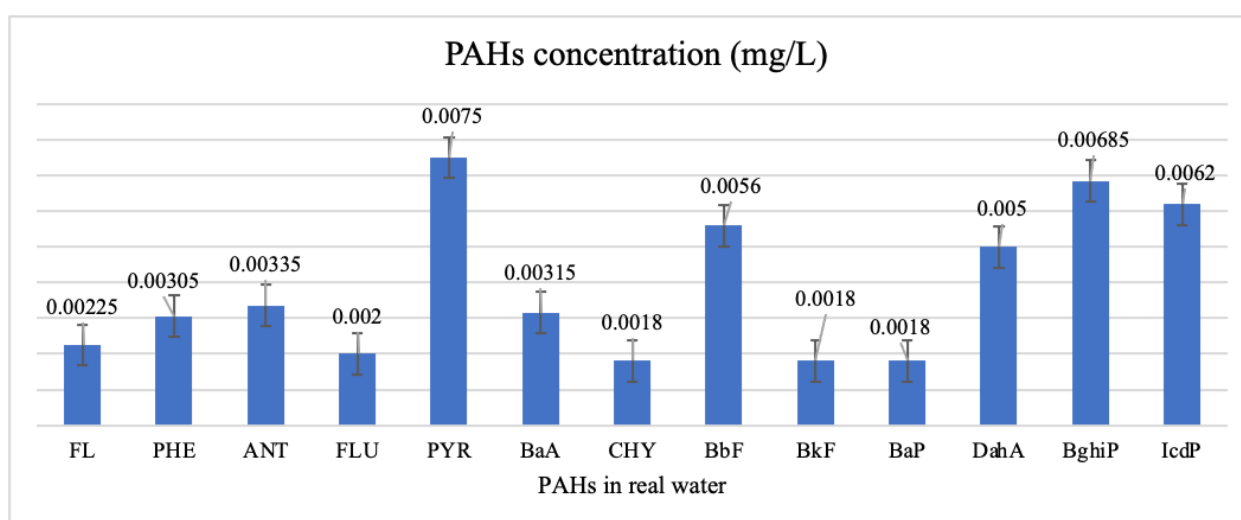


Figure 2.1: The PAHs content in real wastewater [15]

The oxygenated aromatic compounds are mostly observed in a polar substance, like the presence of PAHs that contain oxygen can easily undergo a complete leaching in water where the leaching process is measured over time and also the amount of the pollutants present [66]. The dissolution of PAHs in the soil also depends on the presence of humic acids (HAs) which are known to be complex organics and are produced from the breakdown of plants and animals that have been decaying for years. Additionally, due to PAHs staying under the soil, they inhibit photolysis; it has been suggested by various authors [67-69] that the introduction of a metal oxide can enhance the degradation of the PAHs in the soil [70,71]. Cai *et al.* [66] have reported that the mineralisation of PAHs in the soil is dependent on the quality of organic matter in the soil that can potentially influence the sorption capacity. A similar process can also be conducted in wastewater treatment but in the absence of humic acid.

2.8 The health hazard of PAHs

Various studies by Abdel-Shafy *et al.* [46,47] have reported that the ubiquitous organic pollutants pose a threat to humans, since these organic pollutants consist of fused benzene rings that make them carcinogenic and mutagenic. They are therefore regarded as environmentally unfriendly. Some of these organic pollutants are inevitable [72] and their release into the environment has been massive. To prevent their occurrence in the environment, there is a need to determine the factors that are responsible for stabilising these PAHs [73]. The consumption of organic pollutants such as PAHs by humans can be classified in terms of risk assessment (RI). The level of carcinogenic PAHs for children in drinking water or food range from 0.02×10^{-10} to 4.93×10^{-10} whilst for adults it is between 0.01×10^{-10} and 2.98×10^{-10} [63]. The high molecular weight PAHs are designated as carcinogens [74] that can cause other symptoms such as asthma and heart disease to humans with an inadequate immune system [75]. PAHs with high molecular weight are classified as endocrine-disrupting chemicals (EDCs) due to their health implication [38].

The 16 PAHs found in various water bodies, especially in drinking water, have been reported by Rubio-Clemente, *et al.* [76] to be carcinogenic, mutagenic and teratogenic. These PAHs are genotoxic and can easily be bound with DNA. Anthracene (An), pyrene (PYR), and chrysene (Chr) are high molecular weight PAHs that cause cancer in humans and tumours in animals [77]. Some other health issues are derived from these PAHs, like birth defects, mutations, reproductive effects, cancers of the lung, urinary infection and lung respiration diseases [60]. Since chlorine and fluorine are commonly used chemicals as water disinfectants, they can also easily react with the PAHs to produce halogenated and trihalomethanes, haloacetic acid disinfection by-products [76].

PAHs can suppress the immune system of humans by means of endocrine disrupter abilities (EDs) that can alter the PAH chemical structure and thereby interfere with hormones [78]. PAHs are part of a non-halogenated organic group that includes benzene, phenols and aldehyde [60]. The toxicity of the PAHs differs and depends on their structure and most of the PAHs that are found in wastewater/water belong to the carcinogen group that contains nitrate, methyl and carboxyl groups [60]. Some other health-related issues such as itching of the eyes, mucous membranes, weakened nervous system, reduced bone marrow and various cancer types were also pointed out as a consequence of exposure to PAHs [79]. The consumption of the PAHs can lead to many malfunctioning organs and diseases in humans; however, this occurs mostly in people with a low immune system. These diseases are leukaemia, cancers, neurobehavioral disorders, learning disabilities, cognitive deterioration, mental retardation and many others [80]. The exposure of humans to PAHs is chiefly through polluted air, water and food [81]. These PAHs can readily be absorbed from the gastrointestinal tract of mammals with their high lipid solubility. They are most toxic in the presence of UV light, based on their reactivity to temperature, and do not decompose easily at low temperature. Their toxicity is affected by metabolism and photo-oxidation that can trigger them to settle into the environment. Adverse reactions to organic PAHs can progress to tumours and reproduction, development and immunity problems [46].

2.9 Analytical methods for determination PAHs in aqueous solutions

They are various analytical techniques that can be used to analyse the presence of PAHs in an aqueous solutions and these techniques are used to meet the requirements of the USEPA or the International Organization for Standardization (ISO). Chromatographic, immunoassay and spectrometric techniques are commonly employed in determining the PAHs in wastewater/water or aqueous solutions [45]. The immunoassay technique is not frequently used due to its sensitivity that could prejudice the results, though it is generally cost-effective on a large scale [37]. Spectrometric techniques such as ultraviolet (UV) and infrared (IR) spectroscopy are mostly used for a viscous substances such as lipid compounds (aromatics). Although this is a rapid and cost-effective technique, it requires intensive labour and maintenance. Chromatographic techniques for both liquid and gas chromatography (LC and GC), and are used to quantify the concentration of PAHs in an aqueous solution. They have been used for decades due to their wide applicability and effectiveness [37].

2.10 Methods for removal of PAHs

PAHs in the environment are a challenge that requires an effective method for their removal [63]. This can be conducted in 3 stages, namely primary, secondary and tertiary stages. The primary stage is a pre-treatment stage whereby 40 to 60 % removal efficiency can be expected [77]. The secondary stage involves biological treatment, with the expectation of a 10-90% removal efficiency [54]. In the case of physical methods, the temperature is raised. The heating temperature and treatment temperature at 300 °C and 100 °C are mostly applicable for the physical desorption of PAHs [82].

Conventional methods like coagulation, sedimentation, filtration, ion exchange, flocculation and reverse osmosis have been used during wastewater treatment for the removal of PAHs [15,83]. Photocatalysts are also effective in eliminating the PAHs from wastewater. Their ability to react with the π - π bond and hydrogen is an effective technique that provides low cost, no-toxic release and high-efficiency removal [84]. On the other hand, the biological method has been proven to remove 85 % of the organic pollutant, as compared to the mechanical method of 83 % [85]. Therefore, there is a need to implement natural sorbents known as agrowastes deriving from animals, vegetable wastes or plants in the application of wastewater treatment to remove around 3–15 times the organic pollutants in the soil and 4-20 times better removal than the existing inorganic pollutants in soil. Furthermore, this can also be introduced in wastewater treatment [6].

2.10.1 Photodegradation

Photodegradation is the result of the absorption of UV light or solar irradiation. It causes excitation of electrons from the photons in the material. Photodegradation and biodegradation are used to break the PAH rings from their stable condition, using solar irradiation, which is favoured by a higher temperature and the presence of a photocatalyst [86]. There are various factors like pH, photocatalysts, temperature and irradiated light that can influence the photodegradation of the PAHs [83]. The photodegradation of selected PAHs such as PHE (3 rings), PYRE (4 rings), and BaP (5 rings) was conducted in three types of soils that were acidic, alkaline or neutral. It was found that the photodegradation of the lower molecular weight PAH was rapidly degradable in alkaline soil while the heaviest molecular weight was mostly degradable in an acidic condition [70,71]. Many semiconductors have been studied but TiO₂ and ZnO have attracted a great deal of attention in the study of the wastewater treatment and purification processes. Their efficacy and reliability in ultraviolet (UV) absorbent radiation from the decomposition of contaminants have provided evidence for their value in wastewater treatment [87]. ZnO was deemed the better photocatalyst semiconductor relative to TiO₂ with a higher quantum performance for contaminant depollution [88].

A photocatalytic reaction occurs when the movement of an electron takes place from the positive valence band (VB) to the negative conduction band (CB) of the semiconductor, by leaving holes. The electron recombination hole (e/h) is the time taken for the electron to re-occupy the hole, and that can be obtained from the movement of the electrons to undertake photodegradation spontaneously [89]. For photodegradation to occur, there should be a presence of radicals, which are a group of compounds that contribute intensively to the photodegradation of organic pollutants in wastewater/water or aqueous solutions. These radicals, also known to be oxidants, are shown in Table 2.5 [90]. Although various radicals were considered, the hydroxyl radical was studied to be the best and most effective candidate to interact with organic pollutants at any stage [59]. In addition, photodegradation can only occur if the π electrons on the aromatic pollutants are destabilised [91].

Hydroxyl radicals are known to be chemical scavengers and oxidizing agents that are highly reactive to organic molecules, and are useful for their non-selective nature and ability to degrade organic pollutants in various water media [92]. Traditionally, the hydroxyl radical has been effective in wastewater treatment with potential oxidation of 2.8 eV [93] as shown in Table 2.5. It has been reported by Guerra-Rodríguez, *et al.* [93] that the effectiveness of sulphate radicals is due to their higher oxidation potential. In addition, radical sulphates have a higher oxidation potential and are effective on an organic compound that contains a saturate bond or π - bonds, whereas the -OH can diversely react both in hydrogen abstraction or electrophilic conditions [94,95]; it can only operate at a pH range of 2-8 to achieve a higher performance [96], whereas hydroxyl is preferred due to its diverse operation at a wide pH range [93,97,98]. Table 2.4 is a summary of various oxidants that can be used for the photodegradation of organic pollutants.

Table 2.4: The oxidants oxidation potentials [93,99]

Oxidant	Oxidation potential
Fluorine	3.03
Hydroxyl radical	2.80
Atomic oxygen	2.42
Ozone	2.07
Hydrogen peroxide	1.78
Perhydroxyl radical	1.70
Permanganate	1.68
Hypobromous acid	1.59
Chlorine dioxide	1.57
Hypochlorous acid	1.49
Hypoiodous acid	1.45
Chlorine	1.36
Bromine	1.09
Iodine	0.54

The photodegradation of PAHs is a very complex process that requires specific reactions to occur [83]. A photocatalyst is exposed to irradiation light to provide photons that will produce radicals in the wastewater/water to facilitate the photodegradation of PAHs. Equations 2.1–2.3 can best be used to understand the mechanisms that occur when light is irradiated into a leachate and the electron-hole (h^+), hydroxyl ($\bullet OH$) and superoxide radicals are generated for photodegradation.



Among various oxidizing agents, hydroxyl and superoxide can easily react with the PAH aromatic rings by making them unstable by having to form CO_2 and H_2O as a product. The hydroxyl is thus able to degrade the PAH aromatic compounds [59]. The hydroxyl radical can be produced by having Fenton reagents and hydrogen peroxide, UV reaction and ultrasonic cavitation available for the complete process [76]. The oxidation process can either be conducted directly or indirectly by using ozone (O_3).

Indirect oxidation can only be conducted at a basic pH of 7–14 [100]. Stewart [100] has reported on the advantage of permanganate ions as compared to $\bullet OH$ and O_3 due to their cost-effectiveness, operation at a wide pH, high stability, ability to break the alkene bond and safety in the application of wastewater treatment. Permanganate as oxidant, iron (III) chloride ($FeCl_3$) as a coagulant and sodium hypochlorite ($NaClO$) as disinfectant have been used for the degradation of PAHs in an aqueous solution [15].

The photodegradation of anthracene and benzo(a)pyrene, using a UV lamp ($\lambda > 290$ nm) was also conducted and it was found that 83-93% removal of anthracene and benzo(a)pyrene in groundwater was obtained, whereas only 36–48% removal was obtained on surface water. The groundwater adsorbed higher amounts of PAHs as compared to the surface water and that could result in the presence of biological compounds such as humic acid and minerals in the soil [83]. Besides the humic acid, Table 2.5 shows various chelating agents that can destabilise PAHs as they are persistent in the environment. However, these chelating agents can only be active in the presence of the Fenton oxidation potential [83].

Table 2.5: Various chelating agents that can influence the degradation of PAHs

Chelating agents	Gallic acid (GA)
	Catechol (CC)
	Amino-poly-acetic acids
	Sodium citrate (SC)
	Malic acid (MA)
	Oxalic acid (OA)
	The citric acid (CA)
	Ethylenediaminetetraacetic acid (EDTA)
	Cyclodextrins (CD)

Most studies have focused on the photodegradation of PAHs in the soil as compared to their deposition in wastewater or water sources, because the PAHs initially come into contact with the soil before being channelled to the stream.

2.10.2 Application of a semiconductor for treatment of wastewater containing PAHs

Nanotechnology has been introduced to reduce the presence of pollutants in wastewater. The size of a nanomaterial on a nanoscale can range between 1 to 100 nm [101]. Titanium dioxide (TiO_2) and zinc oxide (ZnO) are two common metal oxide/semiconductors that have been widely used in the application of wastewater treatment, due to their anti-fouling, non-corrosive, non-toxic and excellent photocatalytic properties, and their ability to provide hydrophilic properties. These metal oxides have also been used as nanoparticles to decontaminate wastewater [101]. A smaller size of metal oxide results in a larger surface area, which will strongly promote the photodegradation process [102]. The synthesis of a heterogeneous photocatalyst, where ZnO is combined with other materials, is effective, based on its ability to improve the photocatalytic efficiency by influencing the band gap, crystallinity, surface area, and particle size [103]. Other metal oxides like cadmium sulphide (CdS), tin (IV) oxide (SnO_2), titanium oxide (TiO_2), and

manganese doped (Mn), have been used to obtain heterogeneous photocatalysts, but ZnO is one of the best semiconductors due to its relatively narrow band gap, crystallinity, surface area and particle size [104,105]. A heterogeneous photocatalyst, which is also regarded as an advanced oxidation process (OAP) that can produce hydroxyl radicals ($\text{HO}\bullet$), holes (h^+), superoxide ions ($\text{O}_2^{\bullet-}$) and peroxide radicals ($\text{HO}_2\bullet$), is mostly responsible for the removal of the organic pollutants in wastewater [106]. The radicals are produced during the photocatalytic reaction, and its mechanism can best explain the oxidation of organic pollutants.

Silver has been widely used in various applications like in the medical field, electronic devices, cosmetic products and many others due to its high chemical stability and its antibacterial, antiviral, antifungal and strong conductive properties and has thus attracted interest in wastewater treatment [107]. The combination of Ag with a semiconductor like ZnO will retard the electron-hole pair recombination and therefore improve the photocatalytic activity, and thereby influence the photodegradation of organic pollutants [108]. These semiconductors hold excellent catalytic, electronic and photochemical properties and high quantum performance (converting irradiated light into emitting light) by making them reactive [109]. Semiconductor applications have been preferred for the past two decades in the removal of organic pollutants from wastewater [110,111].

The photon energy released is converted into chemical energy to degrade the organic pollutants and produce carbon dioxide (CO_2) and water (H_2O) [101,112]. The shape and size of the photocatalyst are strongly relevant to achieving the photodegradation of the PAHs [113]. Various studies have been conducted on the different band gaps of ZnO, which depend on how it has been synthesized. The band gap of ZnO ranges from 3.3 eV to 3.6 eV and depends on its modifications [114-116]. The application of ZnO semiconductor nanoparticles in an acidic medium produces Zn^{2+} ions which can rapidly dissolve in an acidic medium with a pH of 4.5 [114]. It is widely applied in electronic devices and wastewater treatment due to its optical property (light-absorbing) [117,118].

The efficiency of ZnO in wastewater treatment is attributed to its enhanced degree of catalytic operation in the ultraviolet zone and its capacity to operate in visible light. It is important to develop new hybrid materials that have narrow band gap energy that will be readily accessible for visible light photons and to boost the overall response in the removal of PAHs [119]. Also, the morphology and high crystallinity of the material can improve the photodegradation of organic pollutants [120]. The photoactivity can be increased by the addition of noble metals such as platinum (Pt) and gold (Au), also to promote the separation efficiency of the electron-hole pairs that can best benefit the photodegradation of the organic pollutants [92,120]. During the photocatalysis reaction, the photons produced by solar radiation split the water molecules into OH^- and H^+ and also generate the photoexcited charge carrier e^-/h^+ pairs on the material (photocatalyst) to undertake a redox reaction. The difference in photogenerated charges on the water splitting will react with H^+ (the electron acceptor) [115].

The reaction of the photocatalytic mechanism is based on the electron-hole pair in the semiconductor and its movement. The band gap energy is the reason why the semiconductor photocatalyst can absorb different light colours and that be used as the photocatalyst because of its ability to electronic configurations, light absorption and excited-state lifetimes [121]. When a photocatalytic surface is exposed to radiation of energy equal to, or greater than the band gap energy of the semiconductor photocatalyst material, it creates a positively charged hole in the valance band and negatively charged electrons in the conduction band by exciting the electrons in the valance band to the conduction band. The delay of the recombination rate of charged electrons-hole pairs can be achieved through the hybridisation of nanomaterials with noble metals such as Pt, Ag and Au, or fabricating composites with various semiconducting photoactive materials that can enhance the photocatalytic performance [122]. Figure 2.2 illustrate the mechanism of the movement of electrons between the bands of the semiconductors.

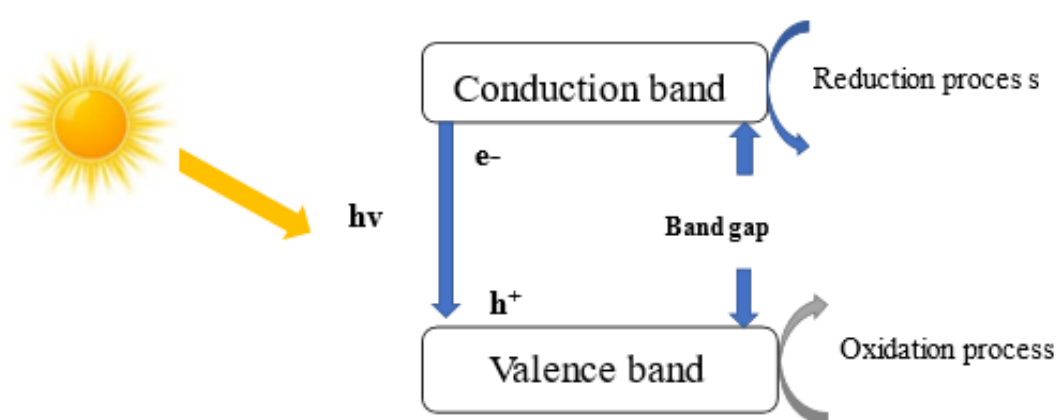


Figure 2.2: Schematic presentation of photocatalysis degradation mechanism of organic pollutants.

2.11 Types of photocatalysis

There are two types of photocatalysis, namely homogeneous and heterogeneous catalysts that can be used in the photodegradation of organic pollutants in water [123]. A high energy source is required for a heterogenous photocatalyst as compared to a homogeneous photocatalyst, which is highly efficient in light absorption [92]. However, the homogeneous photocatalyst can only be used when both the reactants and the photocatalyst are in the same phase such as a liquid or a gas. The two best homogeneous photocatalysts are ozone and the photo-Fenton system (Fe^{+} and $\text{Fe}^{+}/\text{H}_2\text{O}_2$) [124].

The formation of $\bullet\text{OH}$ radical is from the reaction of the excited atomic oxygen ($\text{O}(1\text{D})$) with water vapour [93]. During the reaction, the main objective is to produce the hydroxyl radical ($\bullet\text{OH}$) which can be obtained as can be seen from the reactions in Eq 2.4 – 2.7.





Heterogeneous photocatalysts are semiconductors such as metal oxides, also known as perovskite materials. These metal oxides are light-absorbing materials and mostly need an energy source to react during the photodegradation of the organic pollutants. Their properties, which have been mentioned in section 2.10, make them photoinduced carriers of electrons [124]. The current method of water purification can be accomplished by utilizing heterogeneous photocatalysts that can undergo the removal and oxidation reactions of adsorbed oils, oxygen molecules and hydroxyl anions. It is a system that has less risk and higher water quality yields [125]. The heterogeneous process is known to be more effective than a homogeneous photocatalyst [92].

2.12 Factors that influence the efficiency of a photocatalyst

Photocatalysis is an inexpensive process. Its application for the degradation of organic pollutants requires energy to be generated, but preferably free (solar) energy which will be converted in the system to chemical energy [126]. Various parameters such as pH, the particle size of the photocatalyst, charges of the photocatalyst particles and the position of the conduction and valence band, have been proven to influence the photocatalyst [127]. A photocatalyst with a different morphology has a different photocatalyst activity that influences its efficacy. Zinc oxide and titanium (II) oxide semiconductor photocatalysts on a nanoscale, such as nanotubes, nanospheres, thin porous films, nanofibers and nanowires have been used in many wastewater applications, including high-activity and low-cost applications [128].

The photocatalyst's reaction and the removal efficiency of the pollutants depend on the dose of the photocatalyst, pH and the initial concentration of the pollutants in the wastewater [126,129]. It has been reported that it is important to investigate the initial pH of the medium before an experiment. A greater surface area of the material will enhance photodegradation [127]. The irradiation source plays a very important role in the photocatalyst in the media. The energy emitted onto the media in terms of the photon-producing wavelength must be considered during the degradation of contaminants in water. The photon energy that is emitted is dependent on the intensity of the irradiation, therefore both the wavelength and the intensity of the irradiation are factors to be measured [130].

2.13 Applications of biomaterial photocatalysts in wastewater

In recent years, the emphasis has turned toward safe approaches to remediate wastewater. The applications of a biomaterial provides multiple advantages, such as quick access, strong adsorption efficiency for a range of toxins (even at small concentrations), no manufacturing conditions, environmental safety, being locally accessible at very low cost, limited adsorption of other contaminants such as metal ions and organic

matter, and the ability to be regenerated conveniently. Nevertheless, the effectiveness of such adsorbents is limited in the handling of industrial effluents [131]. Various plant nutrients like tannins, polyphenols, triterpenes, terpenoids, flavonoids, and monoterpenes can act as reducing agents [132,133]. Agrowastes are wastes generated from plants and are widely available at no cost. The use of biomaterials containing phytochemicals, nutrients and functional groups allows quick turnover time in the removal efficiency of organic pollutants [131].

Methods like acid modification, alkali modification, surfactant modification and carbon activation can be used to enhance the property of the nanomaterials [134]. Agrowastes have been used recently to modify semiconductor nanoparticles, where they were shown to improve the photodegradation of organic pollutants (dyes, pharmaceutical compounds and many other organic compounds). The agrowastes happen to be abundant, free and renewable, making them widely available. Their biomolecules and functional groups are responsible for the degradation of organic pollutants, which adds value to wastewater treatment [134]. The low cost, antibacterial activity, availability, and other benefits make the green synthesis process attractive and the photocatalysts produced are proficient in removing harmful organic pollutants. This approach has been selected as a better candidate compared to the traditional method due to its biomaterial reusability, reduced production costs, selectivity for different metals, fast processing period and for not producing chemical sludge [135].

Cellulose is an organic polymer that consists of a linear chain of β -linked D-glucose unit polysaccharides forming an important constituent in plant material. It is the most common natural material derived from plants, making it suitable in various applications in wastewater treatment [136]. Liu, *et al.* [137] reported on the advantages of using natural cellulose in the photodegradation of various carcinogenic pollutants, resulting in a more economical heterogeneous photocatalyst [134]. Nanotechnology has been reported by [138] to be the current application in the remediation of organic pollutants in wastewater. Recent studies have used nanocellulose produced from the transformation of cellulose, which is extracted from plant-based material, to be the most preferred nanotechnology application to combat various organic pollutants in various water bodies [138]. In addition, chemical agents such as sulphuric acid, hydrochloric acid or phosphoric acid in a hydrolysis acid can be introduced in the modification of the agrowastes for wastewater treatment. The modification of the material (agrowastes) is mostly to add more functional groups and active sites, and to increase the efficiency of the material [138,139]. The disposal of wastes can be transformed through methods such as thermal or steam treatment, acid or base treatment, solvent extraction and chemical oxidation that should enhance their stability, functionality, durability and effectiveness [140].

2.14 *M. oleifera* application in wastewater

Moringa oleifera is a plant that has been widely used, especially for medical purposes, due to its phytochemical content [141]. It can reduce cholesterol and other physiological disorders since it affects the

lipid compounds in the body [142]. *Moringa oleifera* (MO) seed is a non-toxic organic and its nutrients contribute to the water-cleaning process [143]. The seed has been used as a coagulant in the removal of organic pollutants in wastewater [144]. Its effectiveness in the reduction of dissolved oxygen, dissolved solids, biological oxygen and alkalinity of wastewater has made it applicable in the photodegradation of PAHs [145]. MO is an agrowaste that contains proteins, peptides, tannins, terpenes and alkaloid phytochemicals that have potential benefit in the medical field [146]. A coagulant is a substance or material that causes pollutants to clot together [147] and MO was used as a coagulant with an antibacterial effect in the removal of the turbidity, alkalinity and gross dissolved solids in wastewater [148]. Santos *et al.* [149] have reported on its application in synthesizing metal oxides such as silver, gold and zinc oxide nanoparticles. Adeniran *et al.* [145] have used MO as a coagulant to remove and reduce water hardness, alkalinity, total solids, suspended solids, dissolve oxygen, dissolved solids, pH, biological oxygen, and chemical oxygen.

2.15 Groundnut shells applications for wastewater treatment

Groundnut shells (GS) are one of the most abundant wastes recommended to add value to wastewater treatment due to their phenolic hydroxyl and carboxyl functional groups that can contribute to wastewater treatment. It is mostly used to feed animals (cattle) and to produce fuel (bio-ethanol) [150,151]. It is highly carbonaceous at a high temperature and an increase in temperature will cause an increase in particle size and surface area that will all contribute positively to wastewater treatment [152]. Carbon is the main constituent at 46%, while hydrogen, nitrogen and oxygen constitute 7.5% 1.25% and 1.45% respectively [153]. The activated carbon can be obtained by the addition of high temperatures either physically or chemically [154,155]. Physically activated carbon occurs when heat is applied in the presence of carbon dioxide (CO₂), nitrogen gas (N₂) or steam at temperatures of 700 to 900 °C. Groundnut shells are a domestic waste that has been widely used as an adsorbent in the removal of organic pollutants. Its main constituents like cellulose (35.7wt.%), hemicellulose (18.7wt.%), and lignin (30.2wt.%) further make it effective in the application of wastewater treatment [152].

Since it is a fibrous waste that contains carbon, it can easily be used as activated carbon to eliminate organic pollutants [156]. Its high surface area can also contribute to the photodegradation of organic pollutants [152]. Due to its high cellulose content, it has attracted interest in the application of wastewater/water treatment [139]. The photodegradation or removal efficiency can be influenced by the particle size, nature of the agrowaste, pH, temperature, and surface area in the application of wastewater treatment [152]. Chemically activated carbon can be obtained with the addition of chemical agents such as sodium hydroxide (NaOH) heated at a specific temperature. The chemically activated carbon has been reported to be highly effective due to the additional sites and functional groups from chemical agents [157,158]. The chemical property of cellulose is hydrophilic which makes it a better material to be used for wastewater treatment [159]. Carbonaceous products such as coconut shells, iron, groundnut shells, wood,

eggshells, snail shells and several other products are used in the manufacturing of activated carbon. Such products disintegrate at a high temperature and may be used for wastewater treatment [152].

2.16 Apatite application in wastewater

Apatite (A) is a short name derived from hydroxyapatite (HAP) which is mostly found in various species like swine bones, fish bones, cow bones and more. The biological compound of this species (HAP) has been used to remove organic pollutants from wastewater due to its biocompatibility, chemical stability and structural strength [160]. However, less attention has been given to this biowaste to remove PAHs from various water bodies. The application of this material (A) to synthesize a metal oxide used as a photocatalytic material to assist in the destruction of PAHs is yet to be considered. These agrowastes have mostly been used in the adsorption of various organic pollutants; however, less attention has been given to the application of these agrowastes in the photodegradation of PAH pollutants or better, to enhance the metal oxides that can be introduced in photodegradation.

2.17 Types of photoreactors

A photoreactor is a system that is used to convert photon energy to assist in the photodegradation of an organic pollutant. According to Shneishil [161], a photoreactor should mostly consist of a cover, reflector and receiver. A cover is a transmission membrane that enables the separation of the receiver and the reflector in a photoreactor, whereas a reflector is a material that has the purpose of directing or reflecting the photon to the receiver, while the receiver on the other hand accumulates/absorbs and is made of a high conductivity material [161]. There are various ways of converting solar energy to useful applications; however, the most common technique is having a photovoltaic collector accompanied by an electrical exchanger that will facilitate the conversion of the solar radiation to electrical energy [162]. There are three types of photoreactors namely batch, semi-batch and continuous can be used in wastewater treatment [163].

The batch reactor is suitable under a sluggish reaction that may be due to the viscosity of the substance in the reactor. The semi-batch reactor is suitable for both slow and fast reaction whereas a continuous reactor is mostly for fast reactions. The reactions can be influenced by certain parameters such as kinetics, catalyst, temperature, pressure and feed state. There are certain specifications like the reaction rate, the multi-pass, multi-bed, multi-vessel or recycle systems that should be considered to obtain the necessary quantity and conversion required from the reactors. Overall, economic viability should be the main focus when designing/building a reactor [164].

2.18 Photoreactor for wastewater treatment

The first photoreactor was developed in 1980 and it was known to be a solar photocatalytic photoreactor, which was used in various applications at the time [165]. A photoreactor is a device that is composed of an

element that absorbs irradiated light and is mostly used for various applications in households, industrial, and wastewater treatment [166]. Some photoreactors have advantages like the ability to receive as much radiated light from either a light source or sunlight, which is mostly influenced by the geometry or material of the photoreactor [167]. There are various types of collectors such as flat plate, parabolic mix, evacuated tank, parabolic trough, Fresnel prism, parabolic dish and heliostat field that can be used to increase the photoactivity of the reaction [168]. The function of these collectors is to accumulate and receive the irradiated photons from a light source and to convert the photon to an energy that can be employed in various applications [169]. It is important to identify which collectors and their temperature range before designing a photoreactor, as shown in Table 2.6.

Table 2.6: Classification of solar collectors efficiency [1]

Category	Example	Temperature range, °C	Efficiency, %
No concentration	Flat plate evacuated tube	75 -200	30-50
Medium concentration	Parabolic cylinder	150 – 500	50-70
High concentration	Parabolic	1500 and more	60-75

2.19 Effectiveness of the light sources

The light source is an important factor to be considered when working with organic pollutants like PAHs in a kinetic reaction in wastewater treatment. The option of lamps may be evaluated by comparing the energy needs of the reaction to the specification of the lamps [130]. Various studies have been conducted, using UV radiation in the removal of organic pollutants (PAHs) from the environment, but the wavelength range that best mitigates PAHs from the environment is 250 nm – 400 nm [46,70]. The sun is the most important source of energy, and is estimated to irradiate the outer earth and the atmosphere at 1367 (W/m²) [170].

The advantages of solar energy are that it is clean, safe, inexhaustible and most of all renewables [171] make it widely accessible to be converted into electrical or thermal energy for various uses [172].

The energy from the sun can be converted to various other energies, as shown in Figure 2.3.

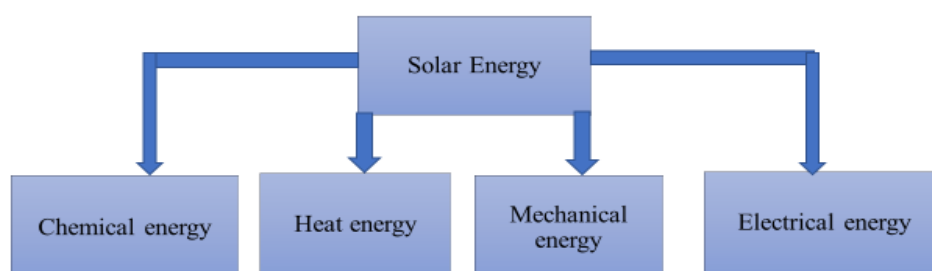


Figure 2.3: Conversion of solar radiation to other energy forms [1]

A study conducted by Rani *et al.* [173] on the photodegradation of PAHs in wastewater proved that benz[a]anthracene and benzo[a]pyrene (BaP) PAHs were more highly degradable in the presence of sunlight than in its absence, and thus the degradation of PAHs is strongly enhanced by sunlight [173].

2.20 Design of a novel photoreactor

When designing a photoreactor, it is important to consider various specifications such as materials, geometry, light source, temperature range and the type of the photoreactor to be able to predict the best outcome [165]. The first steps of the photoreactor design include the choice of the light source and related irradiated materials of the reactor and the most suitable catalyst, if necessary. A variety of types of reactors may need to be studied for design evaluation. Process parameters, such as performance or output pace determine the flow rate or batch period for the conversion or purification process. In the case of modern reactors, the design measurements are very straightforward to facilitate the construction of a suitable photo-reactor. Model equations are accessible to help the designer to analyse all applicable design variables, such as space velocity, reactor scale, catalyst mass, etc. [174].

According to Keane, *et al.* [174], the need to scale up can be an option when working with a photoreactor, though there are modern reactors that need dimensional modelling and computational skills to structure a photoreactor. There are some parameters such as the velocity of the fluids, temperature and concentration field (the material used) that need to be considered whether the photoreactor is being designed dimensionally or non-dimensionally. Other parameters include optimization of the reactor, multi-bed service, new types of reactors, and photoreactors for solar energy [174].

2.21 The fundamental of the photoreactor

Cassano, *et al.* [175] have pointed out the various parameters such as average performance, inlet and outlet of the initial and final concentration of the pollutant in wastewater and selectivity parameters (if applicable) that should be considered when designing a photoreactor. The output system should adhere to the following:

the value of selectivity for raw materials; whether the operating system should be a single or multi-phase system; the hydrodynamic system should be carefully selected as continuous flow, batch, or semi-batch; the photoreactor configuration like its shape, size and geometry is highly dependent on the operating system; the photoreactor temperature(s), pressure(s) and catalytic load (if applicable); and a system that will assist in heating and cooling the reactant(s). The irradiation mechanism plays a very significant function in the photocatalytic effect of the media. The radiation released to the media in terms of the wavelength that emits photons must be recognized during the depletion of pollutants in water. The photons which are the energy released are contingent on the strength of the irradiation, so both the distance and the strength of the irradiation are variables to be determined [130].

2.22 Geometrical configuration

In traditional homogeneous or pseudo-homogeneous reactors, the transfer of a specified reactor volume is independent of geometry, if the results related to the flow characteristics are ignored. Nevertheless, for photoreactors, the configuration of the reactor and the spatial relationship between the reactor and the light source is most significant. The architectural configuration of the photoreactor is typically selected to gain as much as possible from the sequence of irradiation [163].

2.23 Mixing and flow characteristics

In the case of homogeneous photoreactions, the reactants must be put into contact with photons. Homogeneous and heterogeneous photoreactions, the interaction between reactants, photons and catalysts must be investigated to achieve a result. The contact efficiency obtained with the chosen photoreactor model and its interrelationship with the production and processing of the component is a difficult problem that needs to be measured. The issue is extremely complicated for multi-phase photoreactors and cannot be determined independently of the form of reactor configuration used [163].

For photoreactors in which solids are present, the interaction between reactants, photons and catalysts may be facilitated in a variety of ways. Agitation of the reaction mixture may be provided by a stirrer. This is the best approach to obtain a large degree of back mixing, especially for liquid-solid photoreactors. The reactor may also be rotated to allow the catalytic converter to work continuously. It is necessary to use either transverse or axial irradiation [163]. An effective photoreactor and photocatalyst are needed to obtain the photodegradation of PAHs in wastewater. The best photocatalyst that should be considered is heterogeneous, and its specification such as the delay of the recombination of the electrons hole and the narrowing the band gap to enhance the photoactivity should be considered by introducing various agrowastes instead of metals.

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3. Leaching of polycyclic aromatic hydrocarbons from the coal tar in sewage wastewater, acidic and alkaline mine drainage

Authors: Jean Bedel Batchamen Mougno, Frans Waanders, Elvis Fosso-Kankeu, Ali R. Al Alili

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Summary

In this study, the concentration of coal tar was investigated using gas chromatography-mass spectrometry (GC-MS) and 2916.47 mg/L of polycyclic aromatic hydrocarbon (PAHs) was found to be present in 5 g of coal tar. A mass of 5 g of coal tar was immobilized in 300 mL of lixiviant in columns in sewage wastewater and acidic and alkaline mine drainage for 4 weeks. It was found that the ageing of the coal tar in water sources over time increases the release of PAHs. The release of PAHs was highly favoured in acidic mine drainage, followed by alkaline mine drainage and sewage wastewater. The study purposely revealed that the physiochemistry of the water such as pH, dissolved organic carbon amongst water conductivity, dissolved total solids, chemical oxygen demand and biological oxygen demand were considered in favouring the release of PAHs in a water source. Amongst the 16 PAHs that were discovered in coal tar, indeno(1,2,3,c,d-)pyrene and Dibenzo[a,h]anthracene were only leachable in alkaline mine drainage with an initial concentration of 2 mg/L.

The acidic mine drainage of a pH of 2.77, the dissolve organic carbon of 2.25 mg/L, and acidic calcium carbonate (CaCO_3) 672 mg/L happen to release 7.1 mg/L of PAHs followed by the sewage wastewater with a pH of 6.70; the dissolved organic carbon of 113 mg/L and acidic CaCO_3 of 216 mg/L to release 1.1 mg/L and alkaline wastewater of a pH 7.95; and the dissolved organic carbon of 4.35 mg/L, acidic CaCO_3 12.0 mg/L to release 0.32 mg/L of PAHs in water. The higher the acidity of CaCO_3 and the lower the pH influenced the release of PAHs in the study. Although various other considerations such as temperature can also influence the leaching, the experiment was conducted at room temperature and covered with aluminium foil to avoid degradation of the PAHs. It can be confirmed that the release of coal tar in waters can indeed release PAHs over time. The study concluded that it is important to investigate the nature of the water source and to understand the mechanisms of the PAHs in the water.

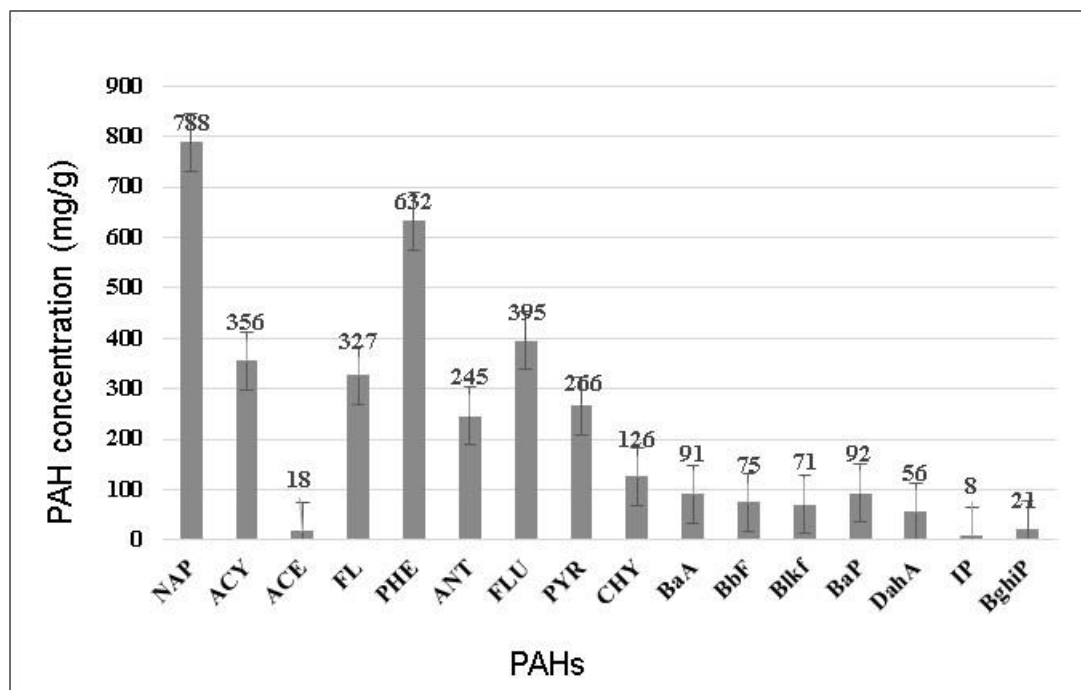


Figure 3.1: Abundance of PAHs in the coal tar as determined by GC-MS analyses in the present experiment



Article

Leaching of Polycyclic Aromatic Hydrocarbons from the Coal Tar in Sewage Wastewater, Acidic and Alkaline Mine Drainage

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Abstract: Polycyclic aromatic hydrocarbons (PAHs) have been a problem in the environment for an extended period. They are mostly derived from petroleum, coal tar and oil spills that travel and are immobilized in wastewater/water sources. Their presence in the environment causes a hazard to humans due to their toxicity and carcinogenic properties. In the study, coal tar was analyzed using Gas Chromatography–Mass Spectrometry (GC–MS) and a concentration of 787.97 mg/L of naphthalene, followed by 632.15 mg/L of phenanthrene were found to be in the highest concentrations in the various water sources such as sewage, alkaline and acid mine drainage. A design column was used to investigate the leaching process and assessments were conducted on 300 mL of the various water sources mentioned, with 5 g of coal tar added and with monitoring for 4 weeks. The influence of the physiochemical properties of the receiving water sources, such as sewage, and acid and alkaline mine drainage, on the release of PAHs from the coal tar was assessed. The acidic media was proven to have the highest release of PAHs, with a total concentration of 7.1 mg/L of released PAHs, followed by 1.2 mg/L for the sewage, and lastly, 0.32 mg/L for the alkaline mine drainage at room temperature.

Keywords: PAH pollutants; acid mine drainage; alkaline mine drainage; sewage wastewater



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1. Introduction

The world's largest energy consumption is produced by coal, making it the second-largest energy source [1]. South Africa (SA) has been ranked the fifth producer and consumer of coal and 86% of the energy produced in SA is derived from it [1]. In SA, coal has been one of the reasons behind the country's improved financial and economic growth due to its availability and cost-effectiveness. The rise in energy demand has exposed the use of coal as a sustainable energy source which causes a potential health hazard to humans and the environment due to the release of a by-product known as coal tar [2]. Thousands of coking processes are responsible for the release of coal tar and gas fuel production, which are being derived from coal transformation [3].



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Figure 1 represents the usage of coal in SA from the year 1980 to 2015 and it has the potential to release a by-product that consists of polycyclic aromatic hydrocarbons (PAHs).

Coal tar is a by-product of coal that is released from various processes of the coal gas and coking process. It is semi-liquid in nature with a density of 1.15 to 1.4 g/cm³ and has a foul smell [4].

Polycyclic aromatic hydrocarbons (PAHs) are a group of organic compounds that are life-threatening because of their chemical structures, that consist of benzene rings bonded in a linear and angular position [5]. Though there are hundreds of PAH compounds, only 16 PAHs are commonly identified in various wastewater and water sources [6]. See also Table 1.

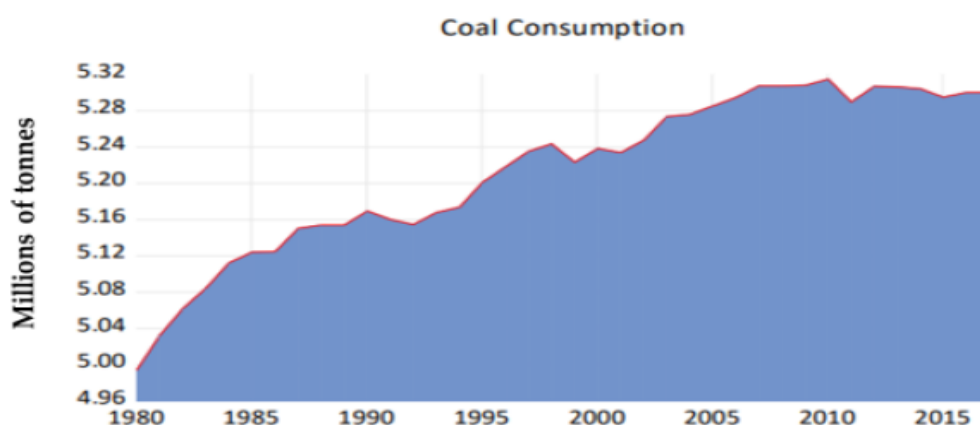


Figure 1. Coal Consumption in SA from 1980 to 2015.

Table 1. Acronyms of the PAHs investigated in this study.

Polycyclic Aromatic Hydrocarbons (PAHs)	Acronyms
Naphthalene	NAP
Acenaphthylene	ACY
Acenaphthene	ACE
Fluorene	FL
Phenanthrene	PHE
Anthracene	ANT
Fluoranthene	FLU
Pyrene	PYR
Chrysene	CHY
Benzo(a)anthracene	BaA
Benzo(b)fluoranthene	BbF
Benzo(k)fluoranthene	Blkf
Benzo(a)pyrene	BaP
Dibenzo(a,h)anthracene	DahA
Indeno(1,2,3,c,-d-)pyrene	IP
Benzo(g,h,i)pyrene	BghiP

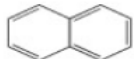
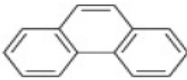
PAHs are released from various industries, from petroleum, coal tar and oil spills that end up settling in the environment and water streams, making them hazardous due to their toxicity level [7]. According to Włodarczyk-Makula [8], the leaching of the pollutants in the various water sources contain PAHs with different chemical properties and concentration ranges from 46 to 70 g/d. Świetlik et al. [9] investigated the photodegradation of PAHs in distilled water and river water. Before the experiment, solids were removed from the river water using a nylon membrane with an opening size of 0.45 μm to prevent any reaction that may occur between the PAHs and the water. It was found that the PAHs were more concentrated in river water compared to distilled water. This was attributed to the physiochemistry of the river water, the temperature and the pH level [9].

Based on the major effluents that occur in various industries, PAHs have attracted a lot of attention due to their presence in wastewater and other water sources. Their deposition into the environment has led to major health concerns such as carcinogenic, mutagenic and teratogenic symptoms. The solubility of PAHs is dependent on various factors such as the temperature, pH, ionic strength and water matrix of the dissolved

organic carbon [10]. It has been reported by Mojiri, Zhou, Ohashi, Ozaki and Kindaichi [5] that the concentration of pyrene in water in South Africa is about $1,118,000 \times 10^{-6} \text{ mg/L}$ and $8,310,000 \times 10^{-6} \text{ mg/L}$ for benzo(b)fluoranthene in sewage wastewater.

This study aims to assess the influence of the physiochemical properties of receiving water sources, such as sewage, and acid and alkaline mine drainage, on the release of PAHs from coal tar. Table 2 shows the molecular weight of the PAHs that are mostly found in water sources and recognized by the World Health Organization (WHO). A few PAHs have been identified to be life-threatening due to their extreme effects on humans, as established by their chemical properties depicted in Table 2.

Table 2. Chemical and structural information of a few common PAHs compounds. Reprinted/adapted with permission from [11]. Copyright 2020, copyright owner's Van-Huy Nguyen.

PAHs	Formula	No. of Rings	Molar Weight (g/mol)	Geometry
NAP	C_{10}H_8	2	128	
ANT	$\text{C}_{14}\text{H}_{10}$	3	178	
PHE	$\text{C}_{14}\text{H}_{10}$	3	178	
CHY	$\text{C}_{18}\text{H}_{12}$	4	228	

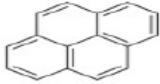
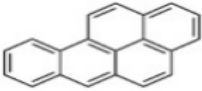
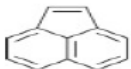
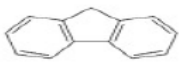
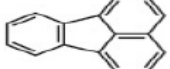
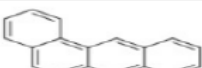
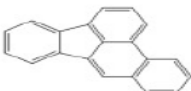
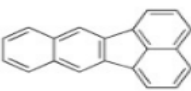
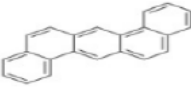
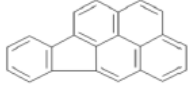
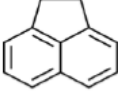
CHY	C ₁₆ H ₁₀	4	202	
BaP	C ₂₀ H ₁₂	5	252	
BghiP	C ₂₂ H ₁₂	6	276	
ACY	C ₁₂ H ₈	3	152	
FL	C ₁₃ H ₁₀	3	166	
FLU	C ₁₆ H ₁₀	4	202	
BaA	C ₁₈ H ₁₂	4	228	

Table 2. *Cont.*

PAHs	Formula	No. of Rings	Molar Weight (g/mol)	Geometry
BbF	C ₂₀ H ₁₂	5	252	
Blkf	C ₂₀ H ₁₂	5	252	
DahA	C ₂₂ H ₁₄	5	278	
BaP	C ₂₂ H ₁₂	6	276.33	
ACE	C ₁₂ H ₁₀	5	154.21	

It has been reported by Mojiri, Zhou, Ohashi, Ozaki and Kindaichi [5] that, in an aquatic environment, the PAHs concentrations were 0.03×10^{-6} mg/L to $83,100,000 \times 10^{-6}$ mg/L. Among these PAHs, the lower molecular weight species, such as naphthalene, which consist of two to three rings, are not as cancerous as other PAHs of four to ten ring structures, such as chrysene, pyrene and others [11,12].

Table 3 shows the PAHs content in various water sources. However, drinking water was pointed out to have a higher PAHs presence compared to groundwater.

Table 3. The PAHs content in various water sources. Reprinted/adapted with permission from [11]. Copyright 2020, copyright owner's Van-Huy Nguyen.

PAHs ($\times 10^{-6}$) mg/L	ACE	ACY	ANT	BaA	BaP	BbF	BkF	BghiP	CHY	DahA	FL	FLU	IP	NAP	PHE	PYR
Drinking Water	3.8 to 478	1.8 to 1210	1.4 to 71	2.29 to 10	1.3 to 8	2.1 to 24	4.6 to 24	2.0 to 8	1.8 to 27	2.0 to 9	4.0 to 41,000	6.5 to 1,430,000	1.6 to 3	4.6 to 14,000	13.1 to 139,000	4.2 to 92,000
Rivers and Lakes	2.6 to 579,000	2.7 to 537,000	1.0 to 256,000	0.6 to 3200	0.5 to 1,239,000	1.2 to 7,800,000	0.8 to 3100	0 to 11,700	1.8 to 4300	4.0 to 11,400	5.6 to 2,480,000	4.2 to 2,498,000	1.0 to 7200.0	52.5 to 6900	13.3 to 126,000	2.9 to 1,138,000
Groundwater	0.4 to 149	0.8 to 13	0.1 to 196	0.1 to 6	3.0 to 123	1.9 to 39	5.1 to 30	0.4 to 9	0.1 to 71	0.1 to 4	0.4 to 168	2.0 to 51	3.6 to 12	2.1 to 281	2.0 to 179	0.3 to 42
Wastewater	28.8 to 100	16.6 to 66	42.0 to 295	46	71.6 to 1,447,000	82.0 to 8,310,000	100.0 to 204	92	20.7 to 112	0	20.0 to 234,000	14.0 to 2,340,000	21	40.0 to 47,000	33.0 to 6,495,000	19.1 to 1,186,600
Seawater	2.6 to 4200	4.5 to 4100	0.1 to 3350.0	0.0 to 17,490	0.0 to 17,490	0.2 to 28,490	0.0 to 32,050	0.2 to 14,790	0.1 to 42,710	0.0 to 32,340	0.2 to 1520	0.0 to 6610	0.0 to 46,600	75.9 to 7800	0.2 to 1080	0.0 to 987
Sediments	0.6 to 1821	1.7 to 13	2.0 to 658	0.2 to 152	0.0 to 739	<1 to 932	3.8 to 17,486	8.9 to 5153	0.9 to 193	1.8 to 999	0< to 52	<1 to 24,857	0.4 to 552	<1 to 69	5.7 to 410	2.8 to 27

During the leaching process, PAHs normally migrate into the soil surface and groundwater where most of the PAHs are adsorbed or biodegraded in the existing minerals or enzymes in the soil. The remaining PAHs then largely channel into the drinking water resulting in it seeming to be more polluted than the groundwater [13,14].

Phase Partition Equilibrium (Raoult's Law) and Dissolution of Kinetics

Raoult's law can be applied for the water samples and the non-miscible organic phase (PAHs), both having an ideal behaviour [15] that best fits the study aim. The ideal behaviour happens to be linear, whereby the more the coal is immersed in the water deposit, will result in more PAHs released in that water. Raoult's law [16] can best describe the influence

on the leaching process of various parameters; however, only pH and contact time were investigated in the study to determine their influence on the leaching process.

The distribution of the pollutant "coal tar", that contains PAHs, into water sources (sewage wastewater, acidic and alkaline mine drainage) is controlled by the molecular diffusion of the coal tar interphase [17]. Since the viscosity of the coal tar is also considered, the global mass transfer is controlled by the slowest rate [18]. This can be attributed to the release of the PAHs in the water source by ageing. The slower the diffusion of the (coal tar) water interface, the higher the concentration of PAHs in the water source [3,14].

2. Materials and Methods

In the present study, the acid mine drainage was collected at Witbank, South Africa, from a river near a large mine; the alkaline mine drainage was collected at a water treatment plant at Middleburg, South Africa; and the sewage wastewater was collected in Cape Town Municipality, South Africa. The coal tar was obtained at a coking oven plant in New Castle KwaZulu-Natal, South Africa.

2.1. Research Methodology

During the leaching process, 5 g of coal tar/water sources were inserted in the columns, having dimensions of 300 cm by 8 cm internal diameter (Figure 1). The columns were filled with 300 mL of the lixiviant of each water source for a 4-week period. Samples were collected weekly using a 50 mL syringe with a syringe filter size of 0.45 μm , to prepare the PAHs for analysis. The system was kept away from light, and it was covered with aluminium foil to prevent light from penetrating. The results of the aliquot were triplicated and analyzed using Gas Chromatography–Mass Spectrometry (GC–MS) with a Thermo Scientific (TSQ 8000) (Cape Town, South Africa) Triple Quadrupole MS.

Figure 2 shows the leaching columns for the three water sources. The acid mine drainage column was observed to have a strong visual colour change (yellowish) compared to the alkaline and sewage water source. The colour shows that a strong interaction between the coal tar and the acid mine drainage occurred, which strongly reveals the release of the PAHs.

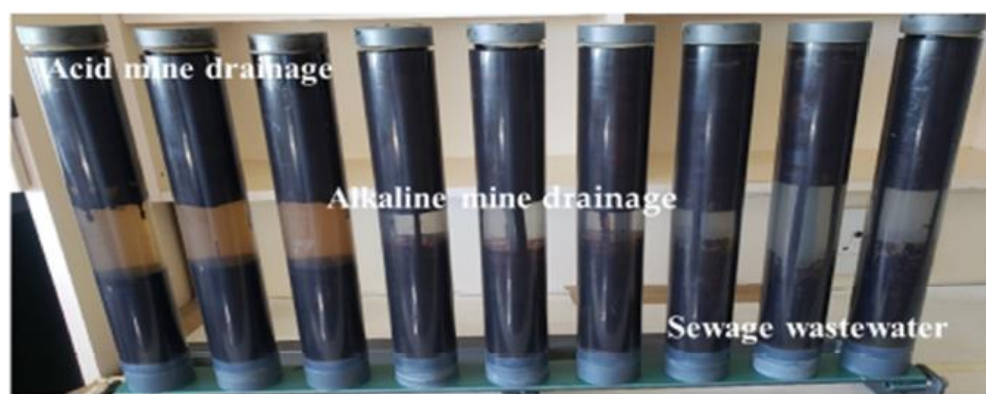


Figure 2. Leaching process of PAHs in acid mine drainage, alkaline mine drainage and sewage wastewater.

Determination of PAHs from GC–MS

There are various techniques such as HPLC–UV, GC–FID and GC–MS–MS or GC–MS that can be used to analyze PAHs. Since GC–MS has been regarded internationally as the gold standard analytical technique, with the ability to analyze and detect tiny amounts of particles in a substance, as reported by Wise, et al. [19], it was used in the study.

An SPE cartridge (SDBL-100 μm Styrene-divinylbenzene) was used to determine the PAHs content in the coal tar and their presence in a leachate. Half volumes of 12 mL of methanol and 10 mL of deionised water were used, and the remaining halves were added

with the sample (coal tar) for calibration. Pressure was applied for about 15 min until the solution with the sample was dried completely.

A standard solution was prepared:

Sodium sulphate was added to a 10 mL Pyrex tube and 2 mL of ethyl acetate was eluted and pressure was applied until the ethyl acetate was transferred into the Pyrex tube. The tube was closed, then vortexed, and 150 μL was measured and then transferred into the GC vial, which was crimped and vortexed.

The prepared standard solution was then used for PAHs analysis using GC–MS.

3. Results and Discussion

In Table 4, the results are shown for the water sources analyzed in the study.

Table 4. Acid mine drainage, alkaline mine drainage and sewage wastewater analysis.

Water Samples	Physical/Aesthetic Parameters	Unit Result	Result
Acid mine drainage	Acidity as CaCO ₃	mg/L	672
	Alkalinity-Total as CaCO ₃	mg/L	<10.0
	Dissolved Oxygen	mg/L	8.00
	Electrical Conductivity @ 25 °C	mS/m	214
	pH @ 25 °C	pH units	2.77
	Organic Parameters		
	Dissolved organic carbon	mg/L	2.25
Alkaline mine drainage	Acidity as CaCO ₃	mg/L	12.0
	Alkalinity-Total as CaCO ₃	mg/L	402
	Dissolved Oxygen	mg/L	8.30
	Electrical Conductivity @ 25 °C	mS/m	352
	pH @ 25 °C	pH units	7.95
	Organic Parameters		
	Dissolved organic carbon	mg/L	4.35
Sewage wastewater	Dissolved organic carbon	mg/L	4.35
	Acidity as CaCO ₃	mg/L	216
	Alkalinity-Total as CaCO ₃	mg/L	438
	Dissolved Oxygen	mg/L	0.50
	Electrical Conductivity @ 25 °C	mS/m	154
	pH @ 25 °C	pH units	6.70
	Organic Parameters		
	Dissolved organic carbon	mg/L	113

Figure 2 represents the PAHs content in the coal tar before the leaching process was conducted. It was found that, from the coal mass of 116.3 mg with 2 mL of hexane added as a solvent, when the PAHs were observed using the GC-MS technique, a total of 16 PAHs were detected. Naphthalene, followed by phenanthrene, fluoranthene and acenaphthylene, were found to be in the highest concentrations, compared to the remaining PAHs. The overall PAHs concentration, identified from the coal tar used, was found to be 2916.47 mg/L.

Naphthalene and phenanthrene were the simplest and most water-soluble molecules of the PAH group observed, and this serves as a model for the dissolution of the light hydroxylated aromatic compounds. The highest dissolution occurred in the acid mine drainage sample. The transfer kinetics of pollutants from the coal tar in the water was the highest at the lower molecular weights of PAHs. The experimental results of this study

also showed ageing between the coal tar and the various water samples, resulting in the progressive release of PAHs. The deposit of coal tar in the acidic mine drainage should be given more attention, as PAHs were proven to be released most effectively with the acid mine drainage, which prompted the release of PAHs hazardous to the environment and to humans. According to Sharma and Lee [20], naphthalene was found to be the most abundant PAH in the coal tar, which was also proven in the present study, as can be seen in Figure 3.

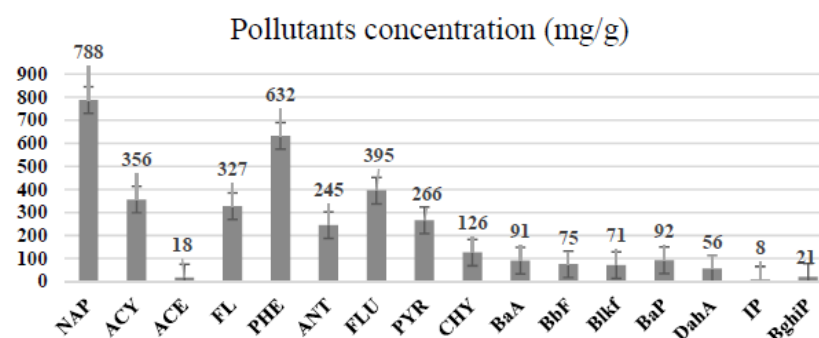


Figure 3. The concentration of PAHs in the coal tar sample, as found in the present study.

According to Makelane et al. [21], pyrene was found to be most concentrated in sewage wastewater, which was also proven in the present study.

All the results on the leaching process of the PAHs from the various water sources are tabulated in Tables 5–7. A total of 16 PAHs were detected in the three water sources; however, acenaphthene was not detected in any of the three water sources used in the present study, albeit a concentration of 18.46 mg/L was found when the coal tar was analyzed. It was noted that the concentration of the PAHs increased with the ageing process. Ageing (or time) was noted to be a factor to be considered in the physiochemical conditions between the water source and the PAHs. The presence of the PAHs in the water source increases as ageing increases. The lower molecular weight PAHs, with two to three rings, were identified to be highly soluble in the acidic media and slightly soluble in the sewage wastewater, and less soluble in the alkaline media (Table 6). Since PAHs are non-polar and have no charge, the electron pairs on the aromatic rings play a role in the physiochemical reaction of the PAHs and the water forming radicals' reaction that triggered the PAHs to be released. Tables 5–7 represent the experimental results obtained during the leaching process. It should also be noted that all experiments were conducted in triplicate.

Figure 4 represents the PAHs dissolution in various water sources and how effective a role Raoult's law plays in the leaching process. The immersion of coal tar in the various water sources used, with their different physiochemistry, resulted in obtaining different PAHs values, as shown in Figure 4. According to Boulangé, Lorgeoux, Biache, Michel, Michels and Faure [3], there are factors such as temperature, ionic strength, pH and dissolved organic carbon. However, in this study, the pH and the dissolved organic carbon were considered in the leaching. There is a need to understand the driving forces of these factors:

The dissolved organic carbon concentration can be influenced by pH [22]; the effect of pH does not influence the neutral organic compound. Neutral organic compounds contain functional groups such as hydroxyl, ether, ketone, lactone, aldehyde and ester because of the oxygen present in them, which can easily react with water to form hydrogen bonds. The presence of these functional groups increases the solubility in water [3].

This study does agree with Boulangé, Lorgeoux, Biache, Michel, Michels and Faure [3], as it labelled the nature of the dissolved PAHs as being acidic by having them dissolved or favored in an acidic mine drainage at a lower pH.

Table 5. The recovery of PAHs in an acidic mine drainage @ 25 °C.

	PAHs Content	Week 1 (mg/L)	Week 2 (mg/L)	Week 3 (mg/L)	Week 4 (mg/L)	PAHs Concentration (mg/L)
Acid Mine Drainage	NAP	0	0	0.332402	0.254163	0.5877
	ACY	0.00232	0.006527	0.023753	0.03721	0.0707
	ACE	0	0	0	0	0
	FL	0	0	0.005651	0.009247	0.0155
	PHE	0.0074534	0.585888	0.0095059	0.0173442	0.620
	ANT	1.548783	0.753182	0.763863	2.669656	5.7355
	FLU	0.0015533	0.001267	0.00161	0.00473	0.0092
	PYR	0.001593	0.001553	0.001507	0.003643	0.0083
	CHY	0.013611	0.013096	0	0.001075	0.0288
	BaA	0.0012033	0.0011733	0.0012	0.0018733	0.0054
	BbF	0.000393	0.000347	0.00037	0.002063	0.0032
	Blkf	0.0001967	0.0001367	0.0001643	0.0019023	0.0024
	BaP	0.00331	0.002507	0.000253	0.002853	0.0098
	IP	0	0	0	0	0
	DahA	0	0	0	0	0
	BghiP	0	0	0	0.002315	0.0023
PAHs Total						7.0944

Table 6. The recovery of PAHs in an alkaline mine drainage @ 25 °C.

	PAHs Content	Week 1 (mg/L)	Week 2 (mg/L)	Week 3 (mg/L)	Week 4 (mg/L)	PAHs Concentration (mg/L)
Alkaline mine drainage	NAP	0	0	0	0.000483	0.0005
	ACY	0.002493	0.00264	0.002393	0.009223	0.0167
	ACE	0	0	0	0	0
	FL	0	0.000506	0.000633	0.004562	0.0057
	PHE	0.0091672	0.0083211	0.00851	0.0233266	0.0493
	ANT	0.019723	0.008446	0.013635	0.052464	0.0943
	FLU	0.004533	0.004873	0.004317	0.010687	0.0244
	PYR	0.004137	0.00459	0.00377	0.008077	0.0206
	CHY	0.001077	0.00192	0.001702	0.004518	0.0092
	BaA	0.0019267	0.00252	0.0022933	0.0046833	0.0114
	BbF	0.001637	0.00322	0.002577	0.00884	0.0163
	Blkf	0.00163	0.003142	0.002957	0.0090683	0.0168
	BaP	0.001993	0.004723	0.004103	0.013353	0.0242
	IP	0.001769	0	0	0	0.0018
	DahA	0	0	0	0.002039	0.0020
	BghiP	0.001521	0.003682	0.00409	0.012656	0.0219
Total PAHs						0.3152

Table 7. The recovery of PAHs in sewage wastewater @ 25 °C.

	PAHs Content	Week 1 (mg/L)	Week 2 (mg/L)	Week 3 (mg/L)	Week 4 (mg/L)	PAHs Concentration
						(mg/L)
Sewage Wastewater	NAP	0	0.00096	0.02564	0.02579	0.0524
	ACY	0.001167	0.008353	0.014387	0.016147	0.0401
	ACE	0	0	0	0	0
	FL	0	0	0.004661	0.005021	0.0097
	PHE	0.005983	0.012669	0.015708	0.012209	0.0466
	ANT	0.013944	0.688642	0.033595	0.128699	0.8649
	FLU	0.001	0.00263	0.002653	0.002507	0.0088
	PYR	0.001223	0.00338	0.001847	0.00194	0.0084
	CHY	0.001336	0.01732	0	0.000317	0.0190
	BaA	0.001	0.00318	0.001023	0.001303	0.0066
	BbF	0.000343	0.00235	0.00035	0.00064	0.0037
	Blkf	0.0001347	0.002133	0.0001453	0.0004623	0.0029
	BaP	0.00024	0.00511	0.000257	0.0006	0.0063
	IP	0	0	0	0	0
	DahA	0	0	0	0	0
	BghiP	0	0	0	0	0
Total PAHs						1.0690

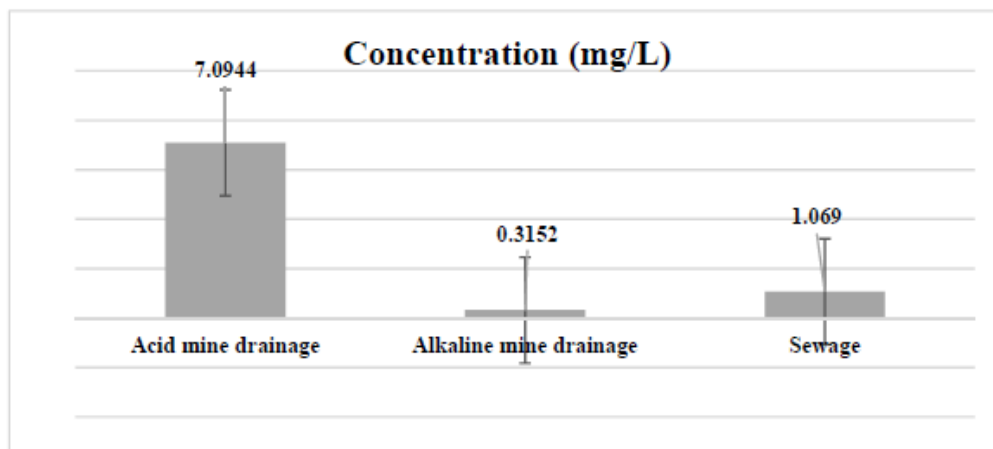


Figure 4. The concentration of total PAHs in the three different water samples studied.

Influence of Ageing of Coal Tar/Variou Water Sources Interphase

Figure 5 represents how ageing influenced the release of the different PAHs and the different water sources. The ageing phenomenon of the coal tar/water sources interphase was found to be an important aspect that has a significant consequence for the long-term fate of coal tar in various water sources, with an increase in the release of higher PAHs concentrations. During the leaching process, anthracene was highly dissolved in the acidic mine drainage and sewage wastewater at week 4. The ageing of PAHs in sewage wastewater agreed with Cai, Ding, Zhang, Wang, Wang, Ren and Dong [14], who mentioned that the longer PAHs are in water, the more they reach an unacceptable level over time. Since time is directly proportional to ageing, as time increases, the PAHs concentration in the coal tar availability reduces, resulting in a greater dissolution.

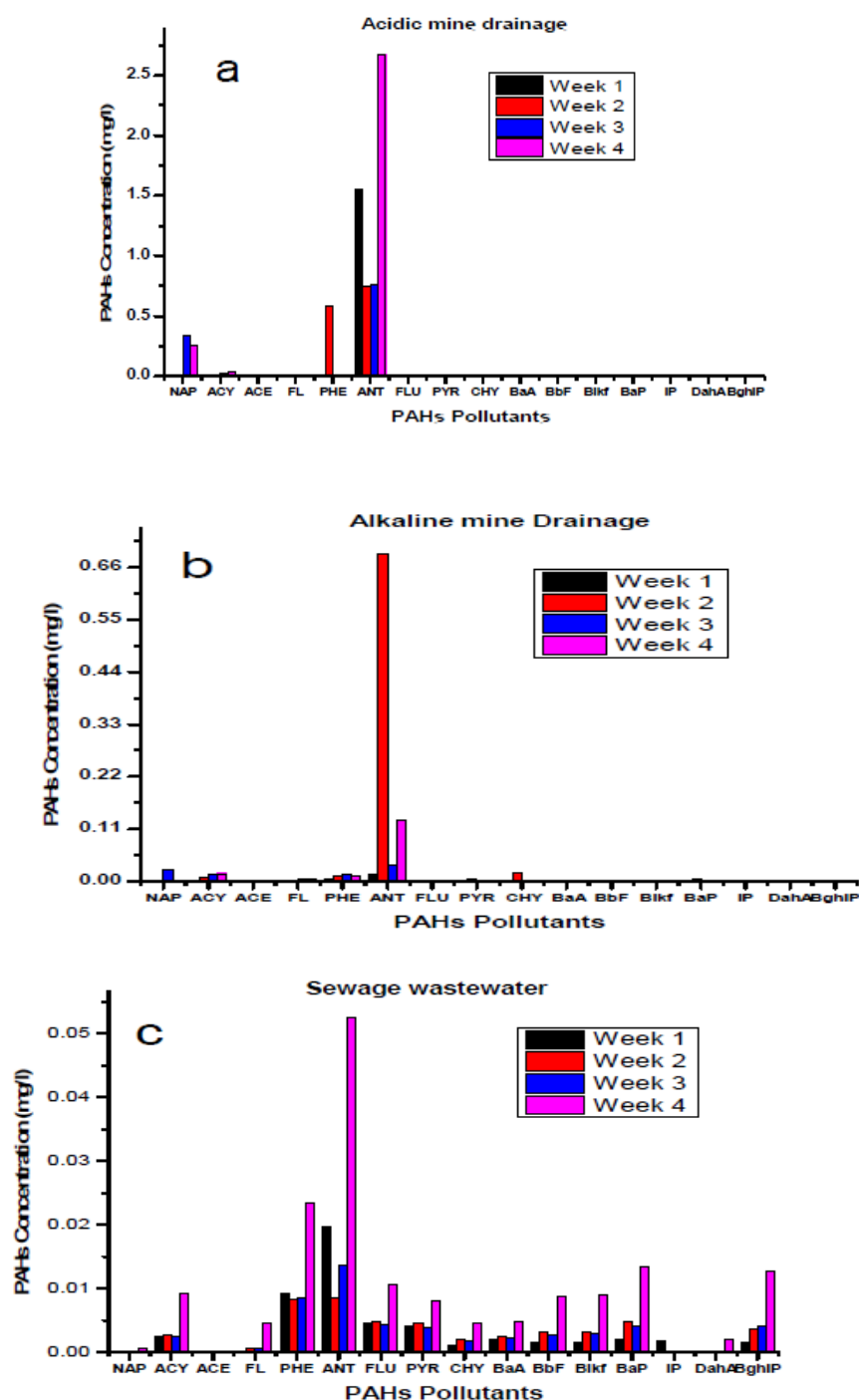


Figure 5. Ageing of PAHs in acidic medium (a), alkaline medium (b), and sewage medium (c).

Since coal is still currently being used as one of the most substantial sources of energy in SA, there is still a prediction of a large release of coal tar that also exhibits PAHs. An intensive consideration should be implemented to avoid coal tar being channeled into various waters. The processes involving the transformation of coal should be conducted far away from water sources, allowing ageing to occur between the by-product (coal tar) and the soil. In doing so, the exposure of PAHs on the surface will be no risk to humans, as

it was reported by Patel et al. [23] that the concentrations of 1 ng/L and 11 µg/L of PAHs in drinking water, as per the WHO regulations, are acceptable.

Since billions of rands have and still are being used on coal for energy consumption and production, millions of rands also play a part in remediating the PAHs from the environment and water.

4. Conclusions

In coal tar-contamination in various water sources, the main mechanism involved in the PAHs release is known to be dissolution; this is described by Raoult's law, which states that the equilibrium concentration of a compound in a water source is a function of the compound's water solubility and its molar fraction in the initial phase in contact with water. The acidic media was proven to have the highest release of PAHs, with a total concentration of 7.1 mg/L, followed by 1.2 mg/L for the sewage, and lastly, 0.32 mg/L for the alkaline mine drainage. Furthermore, it was found that the lower molecular weight PAHs were more soluble in the acidic water as it resulted in releasing a higher PAH concentration.

During the leaching on the acidic mine drainage, it was observed that a pH of 2.77 and dissolved organic carbon of 2.25 mg/L, resulted in the release of 7.1 mg/L of PAHs from the coal tar. The reaction of the π - π bonding also plays a vital role in the reaction of the aromatic compound of the PAHs with the acidic water molecules. PAHs happened to be more soluble in the acidic mine drainage compared to the alkaline, and slightly soluble in sewage depending on the pH and the dissolved organic carbon. Since PAHs are non-polar and only expected to be soluble in an aromatic's solvent however, the pH and dissolved organic carbon are factors to be considered when anticipating the solubility of PAHs in wastewater and water sources.

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4. Recent advances in photoreactors for water treatment

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Summary

Wastewater has gained attention worldwide, and various materials have been recommended to assist in remediating organic pollutants in the environment. A photocatalyst is a common material that has gained attention in wastewater treatment, which can be either homogenous or heterogeneous. It was however proven that a heterogeneous photocatalyst was preferred due to its adsorptive sites, it is easily manipulative, and can be used at a wide range of pH values. However, for the effectiveness of the photocatalyst to be considered for photodegradation, its mechanisms have to be understood. It is important to obtain excitation of electrons that are produced between the valence band and the conduction band, thus producing or promoting the scavengers that will destroy the organic pollutants. Most importantly, the process can also be conducted under an irradiated surface. The process principles between the pollutants and the material (photocatalyst) needs to be carefully understood to best describe the photodegradation. Although the photodegradation can be obtained with either the photoreactor or without, the hydroxyl that forms will interact with the PAHs. However, other species of scavengers can also be used if there is an additional photocatalytic chemical that may improve the photodegradation yield.

It was also shown that the addition of a photoreactor can benefit or improve the photodegradation of the organic pollutants. However, specifications such as the geometry, catalyst, and materials are just a few parameters, among others, to be considered when designing a photoreactor. It is thus important to consider the fundamentals of the photoreactor and the photocatalyst during the photodegradation. The physical geometry, for example, is important to photoreactors because it defines the photon accumulation performance of the overall photochemical process. The photodegradation can only be conducted in the presence of a light source. Most organic pollutants have been found to be persistent at room temperature, therefore they can only be destabilised if an increase in temperature is applied. While various methods have previously been applied, it has been proven that, even with the presence of a light source, photodegradation can occur.

Recent Advances in Photoreactors for Water Treatment

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Abstract

Water pollution and wastewater management is a global issue and gaining attention worldwide. Among several other wastewater treatment technologies, photocatalytic treatment is a promising and sustainable approach to recycle wastewater into clean water for various applications. Several semiconductor photocatalysts have been proven successful candidates to convert the toxic organic and inorganic water contaminant molecules into non-toxic molecules under the irradiation of light. Besides several key parameters of photocatalytic reactions (viz. light intensity, pH, photocatalyst concentration, temperature), the selection or designing of a photoreactor also significantly influence the efficiency of photocatalysis. In this regard, several types of photoreactors, such as slurry/membrane/rotating-drum/annular/closed-loop step photoreactor and microphotoreactor have been designed and employed for wastewater treatment. Heterogeneous, homogeneous, and combined photocatalyst systems have been exploited in the reactors to achieve effective photocatalysis. Therefore, knowledge of photoreactor designing and different photocatalyst systems help to scale up the photocatalysis process at

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an industrial scale. This chapter is mainly focused on the fundamentals of photocatalysis and configurations of different photoreactor for the mineralization of toxic water contaminants.

Keywords: Photocatalysis, photoreactors, monitoring and treatment, water purification, green environment

7.1 Introduction

Photocatalysis has been identified as a promising method for wastewater treatment to break down the organic pollutants and disinfection of toxic microorganisms [1–6]. In the photocatalytic process, reactive species, such as hydroxyl radicals (OH), generates and reacts to degrade the toxic components under light illumination with a suitable catalyst. In spite the discovery of photocatalysis, the application of this technology is still facing some serious challenges, such as degradation rate, reproducibility, and cost [7]. The efficiency of the photocatalysis process is controlled by several factors, such as: (a) by the band gap of suitable photocatalyst [8–11], (b) appropriate light source [12–14], (c) by the recovery of photocatalyst after the reaction for the subsequent reactions [15–17] and (d) by optimizing the photocatalytic reactor and reaction conditions [18].

Photoreactor is a device that has been developed with precise parameters and measurements to be used in different applications of photocatalysis, including wastewater treatment. It is an integral part of the photocatalysis mechanism that is vital to engineering applications. The function of the photoreactor is to enable the photons that will interact with a photocatalyst with an objective to initiate the photocatalytic degradation of pollutants from wastewater. There are two crucial considerations during the dealing with photoreactors: (a) how the photocatalyst can be illuminated effectively (a wide region must be illuminated for high activity) and (b) how photoreactors can be optimized for the use of irradiation from various sources [19]. The first ever used solar photocatalytic reactor were designed and built at the end of the 1980s, which was in the form of a parabolic collector [20]. Thereafter a significant number of photoreactors have been examined and evaluated on the efficacy of their functionality in the elimination of toxins via photodegradation. For industrial-scale purposes, the aimed photoreactors should be a low investment and operating cost with high performance. A suitable designed photocatalytic reactor is one of the crucial challenges in the heterogeneous photocatalysis, which involve development of several mathematical models [21].

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To achieve the high photocatalytic efficiency of a photocatalyst, the designing and fabrication of a photoreactor is one of the extremely important factors. For example, for a wide band gap photocatalyst, the photocatalytic reactor must be configured of the UV-light source, whereas, if the photocatalyst is visible-light-driven, it is configured with the visible light source. Additionally, the position of the light source, material, temperature and dimensions of the photoreactor, along with other parameters, also significantly affects the photocatalysis process [18].

This chapter will be focused on the study of configuration and different types of photoreactors used in wastewater treatment on a laboratory or pilot scale. The main parameters, which are essential during the designing of the photoreactor, is also discussed. Moreover, the special attention is focused on the detailed review of photoreactors used in water treatment.

7.2 Photocatalysis Fundamentals and Mechanism

The term photocatalysis is used to illustrate a photo-induced reaction in the presence of a semiconductor material, which acts as a photocatalyst. It is a popular technique in widespread applications, such as water treatment, cancer treatment, self-sterilization, anti-fogging, CO₂ reduction, water-splitting, and so on [22, 23]. This process was first discovered by Fujishima and Honda to evaluate the photocatalytic characteristics of titanium dioxide (TiO₂) [24]. Recently, photocatalysis has been rapidly expanding and winning more attention from researchers due to the cost efficacy, no secondary waste production, use of renewable source (sunlight) and ease of operational efficiency in rectifying environmental challenges (e.g. wastewater treatment) [25].

Photocatalytic processes can be classified into two categories, namely homogenous and heterogeneous photocatalysis [26, 27]. Homogenous photocatalysis involves the photocatalyst material and the reactants in similar phases. The most commonly used, homogenous photocatalysts are metal complexes, such as complexes of Fe, Cu, and Cr. In homogenous photocatalysis, toxic compounds and water pollutants are degraded by the hydroxyl radicals that are generated by the metal ion complex with a higher oxidation state. In contrast, in heterogeneous photocatalysis, reactants and photocatalysts materials exist in different phases. The chemical reaction is driven by the transfer of electrons from the filled valence band to the empty conduction band, unlike in homogenous photocatalysis where an oxidizing agent is required for chemical reactions to take place and also highly dependent on the continuum electronic states of the metals [28].

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Moreover, heterogeneous photocatalysis can make use of the light from the sun as the source of irradiation, unlike homogenous processes, which uses UV radiation.

On comparing the homogeneous and heterogeneous photocatalysis, heterogeneous photocatalysis is considered a promising and effective technique for the degradation of pollutants from wastewater due to total mineralization, absence of inhibition by water-found ions, easy separation of photocatalyst, low cost, simple operations and easy maintenance of the equipment [29]. TiO_2 , CuO , MoS_2 , WO_3 , ZnO , ZnS , BiVO_4 , Bi_2MoO_6 , BiOCl , ZrO_2 , Fe_2O_3 etc., are the most commonly used semiconductor materials as heterogeneous photocatalysts [30–36]. During the heterogeneous photocatalytic process, semiconducting materials use sensitizers for the light irradiation due to their electronic structure. Figure 7.1 depicts the main steps that are typically involved in heterogeneous photocatalysis. The important steps in heterogeneous photocatalysis are as follows: (a) absorption of reactant species on the photocatalyst surface; (b) adsorption of the photon by photocatalyst; (c) electron-hole pair generation; (d) separation of electron hole-pairs and migration to the surface of the photocatalyst; (e) recombination of electron-hole pairs and/or (f) trapping of electron-hole pairs on the surface via redox reactions; and (g) diffusion or desorption of product from photocatalyst [37, 38].

Nowadays, heterogeneous photocatalysis is the most commonly used technique to degrade the pollutants in wastewater. The fundamental

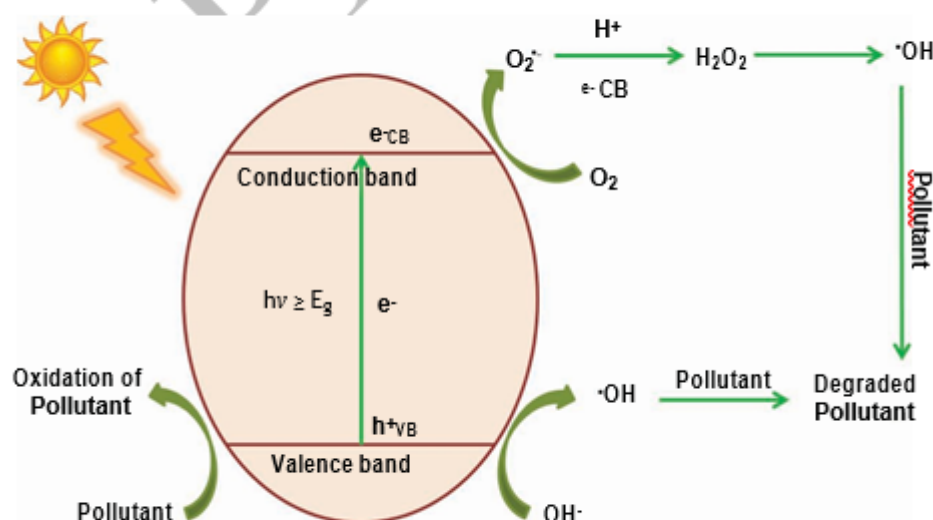


Figure 7.1 General mechanism of photocatalytic wastewater treatment. Reproduced with permission from ref. [38].

mechanism of heterogeneous photocatalysis in wastewater treatment occurs in the following steps:

(a) First, the light radiation with energy equivalent or greater than the band gap energy of the photocatalyst, strike on the surface of the photocatalyst. (b) Second, the electrons in photocatalyst semiconductor material agitated from the valence band and moved to the conduction band, leaving holes in the valence band. (c) These photo-induced electrons and holes either initiate the redox reaction by charge transfer or recombine back and release the energy as heat. The recombination of photo-induced electrons and holes is undesirable as it lowers the efficiency of the photocatalyst and prevents the initiation of the redox reaction. (d) The holes in the valence band can react directly with the pollutant adsorbed on the surface and degrade into smaller nontoxic components. However, the hole is more likely to react with water molecules adsorbed on the photocatalyst surface to degrade the pollutant molecules. The reaction between the hole and water molecules or hydroxide ion (OH^-) is called oxidation reaction and generate the reactive $\cdot\text{OH}$, which in turn degrade the toxic components [39]. Conversely, the electrons in the conduction band reduced the oxygen (O_2) to produce reactive oxygen species (ROS) [40]. These reactions prevent the recombination of electron hole-pairs and allow for the accumulation of ROS that can participate in the degradation of the pollutant. The reduction reaction in the conduction band further produces the intermediate hydroperoxyl radical ($\text{HO}_2\cdot$), which can be protonated to react with hydrogen ions (H^+), and thus produces hydrogen peroxide (H_2O_2). The formed H_2O_2 behaves as an oxidizing agent and produces more hydroxyl radicals, which help in degrading the organic pollutants. The production of more radical enhances the photocatalytic degradation of the pollutants, as these radicals are the ones responsible for the destruction of the pollutant.

7.3 Configuration of Photoreactor

To perform the photocatalytic reaction efficiently, the effectual configuration of photocatalytic reactor is one of the most important steps. Most of the past research was aimed to focus on the configuration of certain basic photoreactors setups [41]. According to Daisey *et al.* (1982), an effective photoreactor for the photodegradation of an organic pollutant is designed with few elements that are inexpensive, hence easy to build and being operational [42]. During the designing of the photoreactor, the following featured should be considered:

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- a) The device should be three-dimensional, which can trap the particles trapped in the air or other gasses during irradiation.
- b) The device should not limit the time of irradiation.
- c) The spectrum of light in the reaction should be as similar as possible to that of sunlight.
- d) It should be possible to assess the light intensity of the reactor.
- e) It should determine the reproductive efficiency of pollutant degradation.

The designing and configuration of the photoreactor determine the efficiency and reproducibility of the photocatalytic reaction. Therefore, it is essential to have an idea of a photoreactor configuration before constructing it. Several parameters, such as light intensity, light reflection, photocatalyst loading, photoreactor temperature, and depth of photolyte, significantly affect the photocatalytic reaction and hence should be considered during the designing of photoreactor. The photoreactors configurations of a photocatalyst reactor must obey the following rules [43]:

- a) emission spectrum of light, the transmitted spectrum of the reactor window and the absorption spectrum of the photocatalyst must all be matched to considered a suitable photocatalyst reactor.
- b) There must be a correlation in the depth of the incident ray and the reactor.
- c) The photoreactor configurations must match with the distribution of the photocatalyst.

The following subsection discussed the few parameters during the configuration of the photoreactor.

7.3.1 Source of Light Irradiation

The purpose of photoreactors configurations is to have a straightforward design that is thoughtful to achieve an effective outcome. However, the design of a photocatalytic reactor and its configurations is not easy as compared to others. The fact that a provision to supply sufficient irradiation to the mass of the photocatalyst in the system makes it complicated. Two types of light irradiation are used in photoreactors: (a) natural solar irradiation (sun) and (b) artificial solar irradiation (lamps). Photoreactors based on

Table 7.1 Characteristics of light sources [47].

Light source	Type	Nominal power [W]	η , %
UV lamp	UV lamp, λ $\frac{1}{4}$ 365 nm	32	25
BL strip	Blue light LED strip	5	50
WL strip	White light LED strip	5	50
BL	Blue light LED	20	50
WL	White light LED	6	50

the solar simulator, mainly for home purposes, is consequently configured in need of a lamp source [44] and a parabolic reflector [45, 46] to establish a suitable photoreactor. A low-pressure mercury lamp (LPML) is the most popular and oldest solar light lamp used in photoreactors. There are different light sources that can engage in photoreactor configurations. Still, these light sources have limitations that vary in wavelength and can undergo photodegrading of organic pollutants with the help of a photocatalyst [47]. Table 7.1 shows the various light sources with different wavelength and $\eta\%$ (electricity into light conversion efficiency). Therefore, it is also essential to know how to use the specific wavelength solar radiation effectively in the photoreactor under various operating conditions [48]. The band gap of the photocatalyst and feasibility of the utilization of solar light of specific spectrum should also be kept in mind during the fabrication of artificial lamp in the photoreactor. Under artificial solar simulated light irradiation, most of the photoreactions are carried out under UV and/or visible part of electromagnetic radiation.

7.3.2 Geometry of Photoreactor

Physical geometry is important to photoreactors because it defines the photon accumulation performance of the overall photochemical system [49]. The high transparent material, shape of the light source and the determination of the pipe diameter should be considered as an important factor while designing the photoreactor. The geometry of the photoreactor should be designed in order to collect the maximum emitted light. For efficient utilization, the diameter (D) of the photoreactor is designed 4 times to the specific depth of heterogeneous radiation. For example, if the penetration of incident light is 1–3 cm, then the pipe diameter should be 4 cm greater. Most importantly, the pipe diameter should not be too large

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and thus internal diameter should be 4 cm. Given all these measurements compiled to an effective and easy photoreactor [43].

7.3.3 Light Source Placement and Distribution

Photo-irradiation can be performed via external illumination [47, 50] or internal illumination [51]. External illumination is carried out by focusing the lens, an IR filter, thermostated bath for cooling and an interference filter or simple Pyrex glass to the reaction cell [52]. External photo-irradiation can be achieved by using one or more LEDs or lamps. Mercury lamps are a popular example of external photo-irradiation. External light irradiating photoreactors are generally used for visible-light-driven photocatalysis reactions. Figure 7.2 exhibits two different configurations for external illumination. However, in internal light irradiation photoreactors (also called as immersion lamp photoreactors), a lamp is fitted inside the quartz jacket and immersed in the reaction solution. These photoreactors consist of three types of cooling configurations: (a) lamp is secured in the additional jacket to circulate the water,

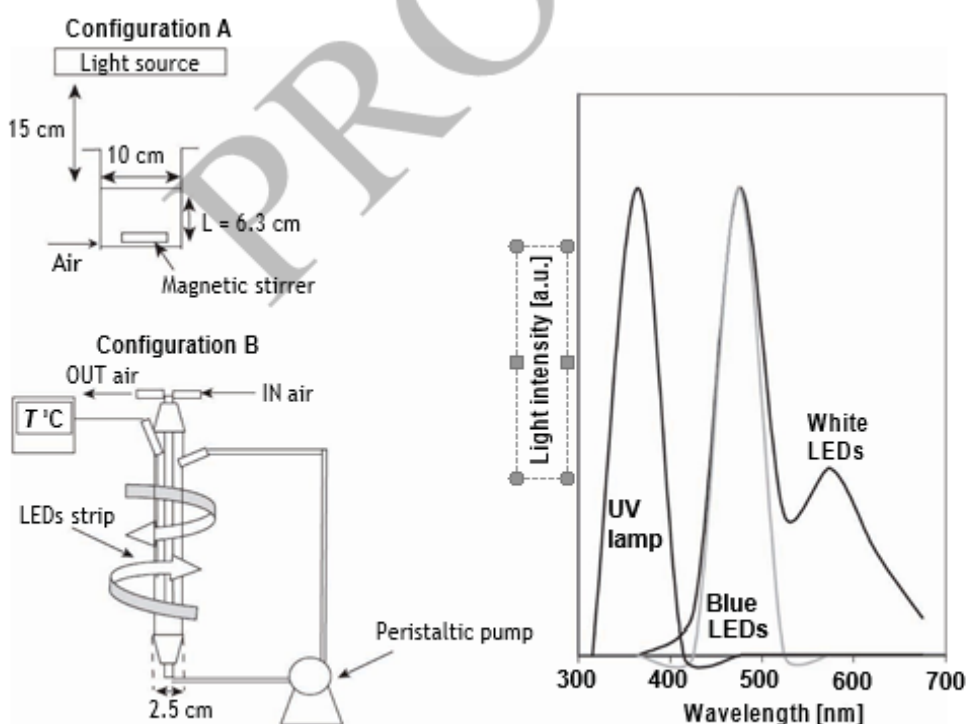


Figure 7.2 Reactor configurations (A and B) and emission spectra of the different light sources. Reproduced with permission from Ref. [47].

(b) the reactor exhibit an additional jacket to circulate the water and
(c) the entire photoreactor system with the light source is placed in the water bath [52]. The used light source can be UV-lamp, visible lamp, blue LEDs or white LEDs (Figure 7.2).

7.3.4 Photoreactor Materials

Since light sources are a critical element to be considered, there are materials and dimensions that can also favour these light sources. Certain materials with specific dimensions have been given preferences to be able to captivate as much radiation as possible. Quartz material has been appointed in photoreactors due to having excellent UV transmittance, good thermal and chemical resistance. Its high excellent UV transmittance is prompted by high iron content. However, the high cost of quartz had made it to be less considered toward an easy built of a photoreactor. Low-iron borosilicate glass is also an alternate material that has the same properties as quartz [53]. Ultraviolet solarization is the process whereby changes in valance of metal ions from a material, preference glass, undergo a transformation during the UV absorption. Based on these radical changes, an addition of 0.1 % silicon (Si) can be added to the melting material (glass) to reduce the melting process and endure the lifespan of the material. Several additional materials, such as aluminium reflectors or glass transmittance, are also introduced in the photoreactor to provide high reflective in the ultraviolet spectrum of solar radiation at a wavelength range of 300–400 nm [53, 54]. Fluorinated, acrylic polymers and several other types of glass material in photoreactor also enhance the ability to absorb as much solar radiation [55]. The fluoropolymers materials have been chosen to be the best due to their high UV and chemical stability. To achieve the minimum operating pressure, the fluorinated wall thickness should be increased, which will also reduce the UV transmittance from the system and make it compatible [56].

The use of photocatalyst during the photoreactor configurations on its reaction can cause wind-down fouling. Wind-down fouling is when the photocatalyst is being stuck or sticking on the photoreactor, therefore to manage or avoids this, an additional metal oxide, preferably TiO_2 which will have a role on the reduction of radiation flux entering the photocatalytic photoreactor is recommended [43, 53]. The selectivity of the material during the design and configuration of the photoreactor is vital for the specific operation of the reactor. The materials must be translucent in order to emit a larger absorbent resulting in size limits, sealing problems and the possibility of breakage [55].

7.4 Types of Photoreactors

Photocatalysis is influenced and affected by several factors, and the reactor type/configuration is one of the many. Therefore, to maximize the efficiency of photocatalytic reactions, a reactor with suitable configurations has to be selected. A good photoreactor must possess the following features and advantages: large surface area per volume unit reactor, unconstrained, mass transfer within the system, permits the photocatalyst to reabsorb photons reflected from the surface and ability to provide UV and/or solar radiation. Photoreactors, such as membrane, slurry, rotating drum, closed-loop step, and annular photoreactors, are some of the reactors that have been developed for use in photocatalysis. An understanding of these reactors is important in the selection a photoreactor for a particular reaction and very useful in scaling-up of the photoreactors. The following section explains the types of various photoreactors.

7.4.1 Slurry Photoreactors

Slurry photoreactors are mostly preferred for the systems with three phases, for an example; a CO₂ reduction process where CO₂ is in gaseous phase, reducing agent in liquid phase and a photocatalyst material in solid phase [57]. For a photocatalyst to remain suspended in slurry reactors there has to be a continuous agitation, or injection of gas to purge the system. To improve the purity of the slurry photoreactor system, air is usually removed from the reactor before any reaction can be started. Slurry photoreactors are also known as fluidized bed photoreactors. These photoreactors can be operated in two arrangements, i.e. batch or continuous process [58]. The difference between batch and continuous slurry photoreactors is that, in batch operation the purging of the system with a gas that will not react with the components of the system is only ran for a limited time i.e. at the beginning of the process and when the purging step is complete, the reactor is tightly closed, then illuminated for a reaction to begin [57, 59].

The configuration of slurry photoreactors has the following benefits: (1) the fluidized particles provide a high surface to volume ratio; (2) the reactor is able to retain fluidized particles, therefore a need to have an external process to separate solid material from the fluid is eliminated; (3) the highly unstable fluid and particles flow reduces mass-transfer limitation. The merits and demerits of slurry photoreactors are clearly populated in Table 7.2. The important factors that determine the reaction rate in slurry photoreactors are; (1) light intensity on the photocatalyst surface;

Table 7.2 Merits and demerits of slurry photoreactor.

Merits	Demerits
Simple design	Reduced penetration depths due to liquid and solid particle absorbing light
Easy to scale up	Large inactive surface sites of the photocatalyst
No mass transfer limitation	Reduced photoactivity due to vigorous stirring
High degradation rate	Solids particles inside the reactor foul the light source
Large surface area for chemical reactions	Separation of photocatalyst from the water is required

(2) adsorption potential of the components in the reactor; (3) the quantum efficiency of the photocatalyst [57].

7.4.2 Photocatalytic Membrane Photoreactors

One of the biggest and common obstacles of using photocatalysis in wastewater treatment is the difficulty of separating the photocatalyst from the treated water for recycling. As a result, a recovery step is usually required to separate and recover the photocatalyst in slurries for reusing. Membrane technology has been successfully used for separation purposes. Thus, the idea to couple photocatalysis with membrane technology has been considered [60]. The combination of membrane technique with photocatalysis makes systems that is known as photocatalytic membrane reactor (PMR). In simple terms, PMR is a reactor system where an effective photocatalysis and recovery of the photocatalyst occur simultaneously using the membrane (Figure 7.3) [61]. The driving force in PMRs can be pressure, concentration or partial pressure difference.

PMRs are environmental friendly equipment as they allow chemical reactions to occur and still allow retention of non-degraded, and undesired molecules in the membrane for further degradation and the retention of the photocatalyst for reuse [62]. The advantages of PMRs mentioned above are beneficial in improving photocatalytic processes in terms of stability, controllability and efficiency, recollection of photocatalyst for further use in consecutive reactions, beneficial in energy saving as well as in reduction of number of units for complete degradation of pollutants because

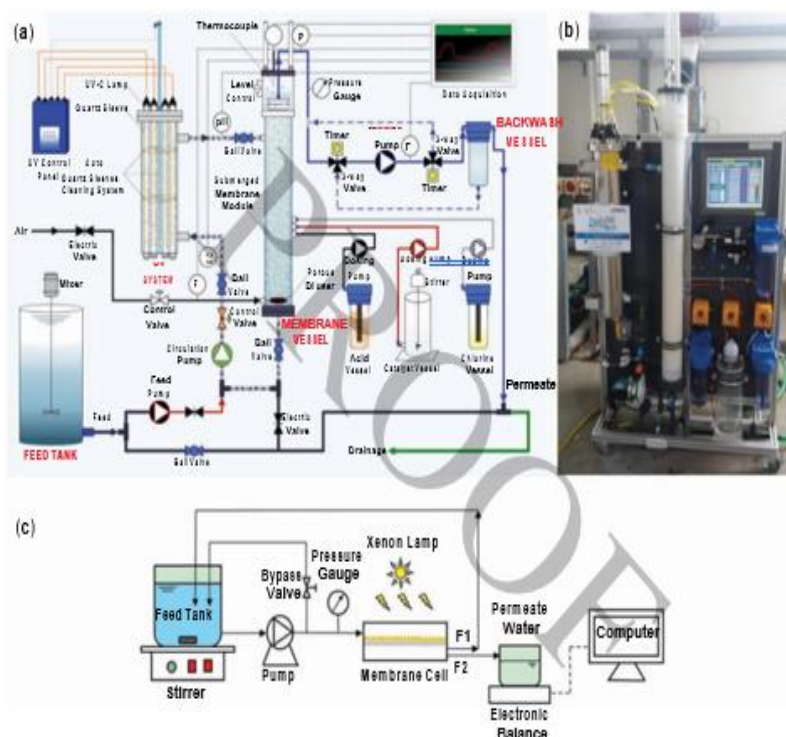


Figure 7.3 Schematic diagram (a) and front side (b) of the pilot scale continuous photocatalytic membrane reactor system with photocatalyst suspended in the feed mixture. (c) Photocatalytic membrane reaction system with photocatalyst immobilized in/on the membrane [61]. Reproduced with permission from [64] (a), and [61] (b).

additional systems for separation purposes, such as coagulation, sedimentation, and flocculation, will not be required [60].

PMRs are normally put into different categories and there are different approaches to classifying PMRs. The common classification of PMRs are based on photocatalyst configuration and on the location of the source of light [63]. On the basis of photocatalyst configurations, PMRs can be categorised into two configurations, namely, (1) PMRs with photocatalyst suspended in the feed mixture (Figure 7.3a); and (2) supported PMRs with photocatalyst immobilized in/on the membrane (photocatalytic membrane) (Figure 7.3b). PMRs with photocatalyst suspended in the feed mixture can be further classified into two subcategories; combined-type PMRs, where photocatalysis and separation system take place in one unit and separated-type PMRs, whereby photocatalysis and membrane separation process take place in two different coupled units, which are the photoreactor and the membrane vessel [62]. Most studies have indicated that PMRs with suspended photocatalyst always attain higher efficiency when compared to PMRs with photocatalytic membrane [63]. The larger surface area in PMRs with suspended photocatalyst ensures an adequate contact between the photocatalyst surface and the target pollutant. Due to the benefits mentioned above, PMRs with suspended photocatalyst have been widely studied and largely used. The disadvantage of PMRs with suspended photocatalyst are: (1) scattering of light by suspended photocatalyst particles; (2) membrane fouling as a result of photocatalyst particles deposition on the surface of the membrane [62].

However, PMRs with photocatalytic membranes has some advantages over PMRs with suspended photocatalyst such easy recovery, regeneration and reusability of the photocatalyst. Furthermore, the use of photocatalytic membranes prevents the challenge of light scattering that occurs in PMRs with suspended photocatalyst. PMRs with photocatalytic membrane give flexibility in the design of the process since the photocatalytic activities can take place on both the feed and permeate side of the membrane [65]. However, the limitation with PMRs with photocatalytic membrane is that the degradation of the pollutant happens within the membrane pores or its surface, as a result in order to initiate photocatalytic reactions, the membrane must be irradiated directly. Due to the latter limitation, it is important that membranes of higher stability under the action of hydroxyl radical and irradiation must be used. The types of membranes that are stable are usually very costly. Moreover the immobilized photocatalyst (photocatalytic membrane) results in mass-transfer limitation, which subsequently decreases the effectiveness of pollutant degradation process [63]. The need

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to change the entire membrane whenever the photocatalyst loses its activity is also a big obstacle of this technology.

On the other hand, on the basis of location of light sources, PMRs can be categorized as follows: (1) PMRs with light source inside/above membrane unit; (2) PMRs with light source inside/above the feed tank; (3) PMRs with light source inside/above an additional unit positioned between the membrane unit and the feed tank [60, 66].

7.4.3 Rotating Drum Photoreactors

A rotating drum is one of the innovative technologies that have gained considerable interest in photochemistry over the few years [67]. The motivation to apply this technology in photocatalysis is to improve and optimize photocatalytic reactions in terms of improving light distribution, surface area to volume ratio and providing mixing inside the photoreactor. Rotating drum photoreactor is a reactor design where a light source/UV lamp is installed inside a drum along the axis and material acting as photocatalyst is coated and immobilized outside the glass-drum [68]. The photocatalyst coated glass drum is partially immersed in contaminated water and rotated with a motor. To maximize the efficiency of rotating drum photoreactors, multiple drums are normally used in one system (usually 5 rotating drums). The drums are usually placed horizontally and parallel to each other, so that the light from the sun outside and/or the artificial UV light from the lamp inside the drum can reach the polluted water. This improves the efficiency of the photocatalyst and the effectiveness of the photocatalytic process in the destruction of the pollutants [69]. The outstanding advantages of introducing rotation in photoreactors are; (1) enhanced mass transfer rate in the system due to the continuous contact between the pollutant and surface of the drum reactor; (2) improved photocatalytic efficiency due to controlled periodic illumination; (3) continuous movement in the system due to rotating drums [68]. Moreover the continuous controlled periodic illumination is important in reducing the build-up of the intermediates and reduce the occurrence of undesirable side-reactions [70]. The other important benefits of rotating drum photoreactors is that, since the water film on the surface of the drum is thin, penetration of light to the photocatalyst surface happens seamlessly [69, 71]. Furthermore the photoreactor system is exposed to the atmosphere to receive solar light and the oxygen from air, the O_2 molecules diffuse rapidly to the photocatalyst surface and cause the formation of $\cdot OH$ and $\cdot OOH$ radicals, which accelerate the photodegradation of water pollutants [72].

7.4.4 Microphotoreactors

Microphotoreactors are devices in which photocatalytic reactions take place in small tubes or micro channels arranged parallel to each other and the tubes usually have an internal diameter of 10 to 50 μm [73, 74]. Microphotoreactors were developed to solve the limitations of conventional photoreactors and improve the effectiveness photocatalytic reactions [75]. Microreactors technology has been successfully utilized in organic chemistry field, and due to its desirous features in photochemistry, such as light penetration, even for concentrated solutions, microphotoreactors were designed. Microphotoreactors exhibit several advantages on photocatalysis, such as better light penetration through the entire reactor depth, higher spatial illumination homogeneity, lower mass-transfer constraints due to the high surface to volume ratio that exists, small amount of photocatalyst can be used, and reduced irradiation time [73, 75]. One of the obvious drawbacks of microphotoreactors is, not being able to scaling-up the process. Therefore if there is a desire to increase the production rate in microphotoreactors, increasing the number of tubes in reactor is one of the solutions [76]. Owing to the fact that the all the tubes are required to have the exact same features, numbering-up of microphotoreactors can be time-consuming and costly [77].

7.4.5 Annular Photoreactor (APR)

An annular photoreactor or tubular continuous reactor is a slurry photo reactor where the lamp is installed inside a vessel in such a way that the suspended photocatalyst or the material to be illuminated surrounds the light source, this arrangement gives the reactor vessel as U-shaped or annulus shape [78] (Figure 7.4). The simple schematic diagram of this configuration is displayed in Figure 7.4 [79]. A pump is configured in the photoreactor to circulate the feed between the reservoir and reactor. These photoreactors have been designed to solve issues and the limitation of the conventional slurry photoreactors [80]. APR allows for continuous mode of operation, which leads to the enhanced performance of the photoreactor in photocatalysis [81]. In this reactor, the light source is positioned inside vessel, which allows the utilization of the irradiation efficiently because the area in which the light directly beams on is very high. Moreover the U-shape that is created by the position of the light source shortens the distance travelled by the light radiation thus making it easier for light to be reflected back to the surface [81].

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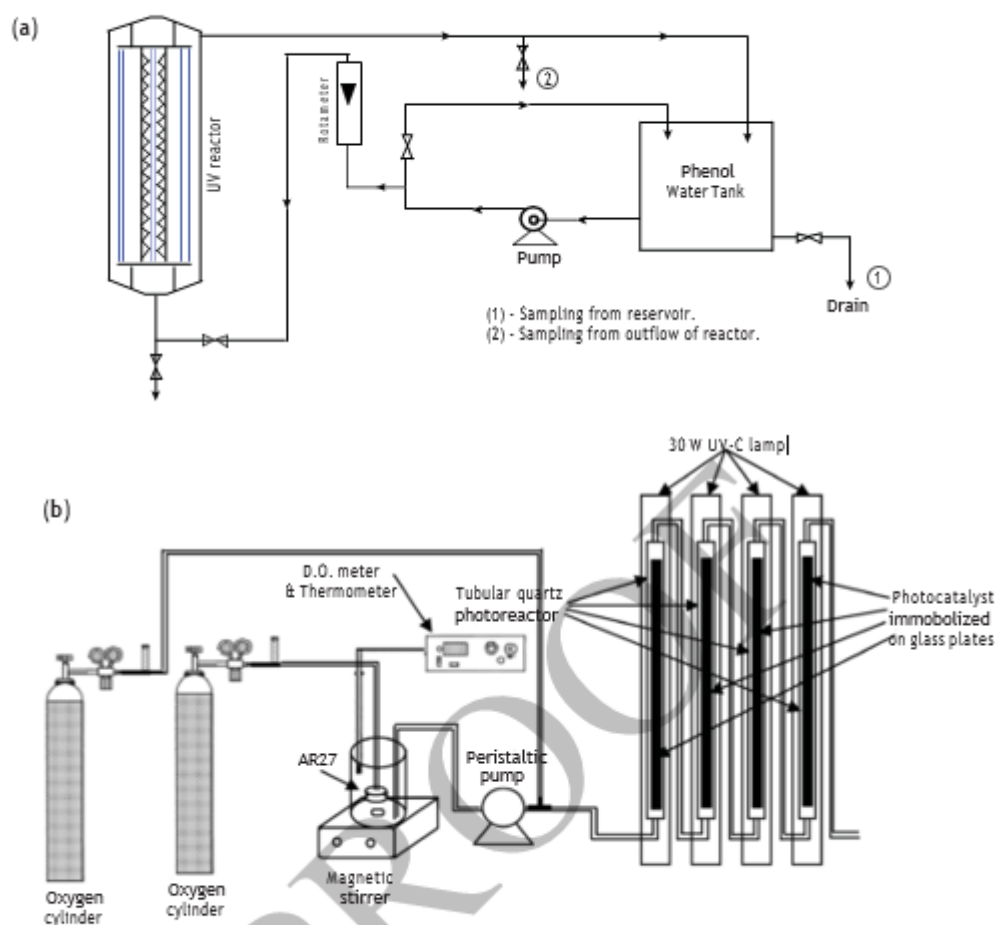


Figure 7.4 Schematic diagram of (a) annular photoreactor [79], and (b) tubular continuous-flow photoreactor with immobilised photocatalyst [82]. Reproduced with permission from [79] (a) [82] (b).

7.4.6 Closed-Loop Step Photoreactors

A closed-loop photoreactor refers to a process whereby no material cross the border of the system boundary once the photocatalytic reaction has started [83]. It is also known as a thin-film cascade photoreactor. Any components participating in the reactions can only enter the system at the beginning of the process and only be withdrawn out of the system when the reaction is complete. Closed-loop photoreactors consist of a flat thin-film where photocatalyst can be deposited, a tank that contains an aqueous solution and a pump for the movement of the liquid. Secondary or external units for separating photocatalyst from aqueous solution is not required in closed-loop systems [83, 84].

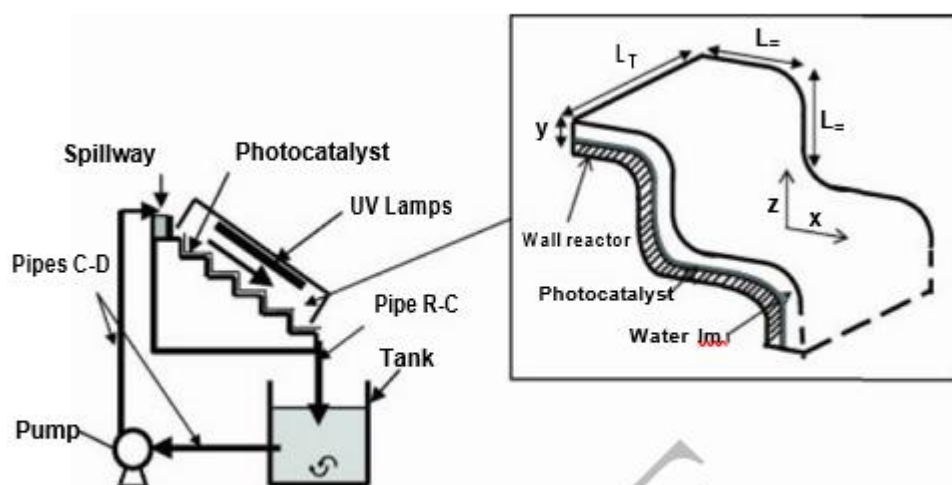


Figure 7.5 A simplified diagram of a closed-loop step photoreactor. Reproduced with permission from ref. [84].

Close loop photoreactors are improved by introducing the step geometry in the system (Figure 7.5). A step geometry provides a more surface for chemical reactions to take place when compared to flat films [84]. The circulation of the liquid in closed-loop photoreactors enhances the mass transfer, but the incorporation of the step further improves the mass transfer rate due to the breaks of the flow that is created by the presence of the steps [85]. Closed-loop step photoreactors offer the following benefits in photocatalysis: illumination zone of higher surface, the thin film of liquid absorbs little UV irradiation, which makes the photo-activation of the photocatalyst to be high, simple configuration and perfect mixing, and easy to scale up [85].

7.5 Photocatalytic Water Purification Using Photoreactors

Photocatalyst within the batch and flow photoreactors can be used by two methods: suspension/dispersed and immobilization/retained forms (Figure 7.6). In suspension approach, photocatalyst is suspended in the liquid phase with the aid of magnetic stirring, toroidal or non-toroidal agitation stimulated by gas molecules. The suspension of photocatalyst in the liquid phase is considered as a slurry system. In immobilization approach, the photocatalyst is bonded to inert support/surfaces via a physical or a chemical bonding [86].

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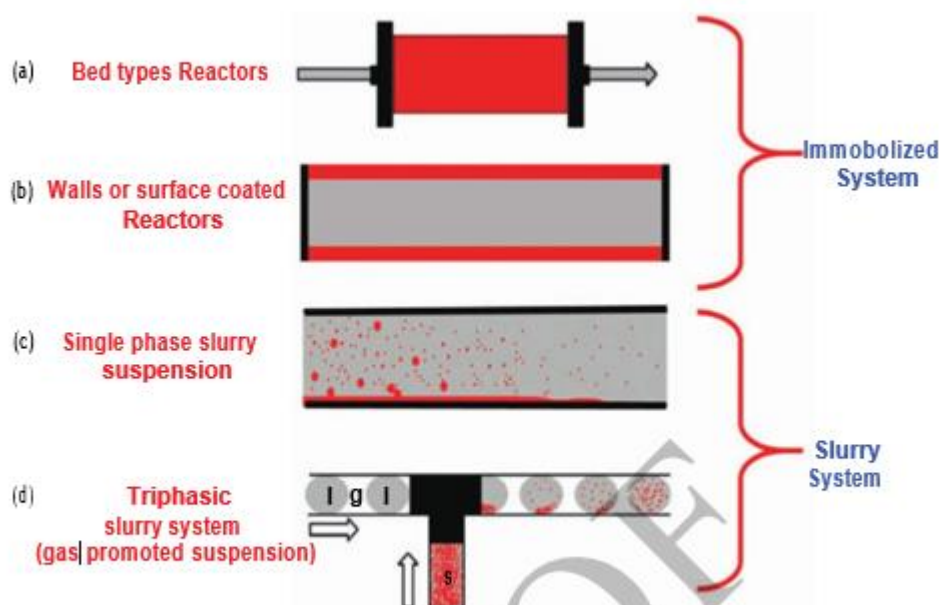


Figure 7.6 Approaches used for the effective implementation of photocatalysts in flow reactors. Reproduced with permission from ref. [86].

The high light absorption and effective reactive oxygen species interaction with pollutants are noticed in photoreactor with suspended/dispersed catalyst, but photocatalyst reuse is obstructed by the laborious recovery of nanocatalyst after completion of the process. Moreover, the toxicity of nanocatalysts and their consequences on the environment are still not completely determined. Other side, photoreactor with immobilized/retained forms of photocatalysts offers reusability of catalyst and high performance. The fluidized-bed photocatalytic reactor is an example of a photoreactor with immobilized/retained forms of the photocatalyst. In this reactor, the light source can be adjusted at the reactor walls or the center of the reactor, considering either LED lights or tubular lamps. For example, Fang *et al.* fabricated TiO_2 nanotube pillared graphene-based macrostructures for photodegradation of bisphenol A (BPA) in a fluidized bed reactor [87]. The composite macrostructures removed 86% of the BPA solution (0.05 mg/L) in the continuous flow system, whereas 97% removal of the BPA solution (5.0 mg/L) over 30 min was achieved in the batch reaction.

Furthermore, immobilization of photocatalyst on a solid, fix support enable long operation time and minimum amount of catalyst loss. Among various supports, polymeric membranes, such as polyvinylidene fluoride (PVDF) and polyethersulfone (PES) have been commonly used to enhance the mass transfer of contaminants to the photocatalytic sites. For instance,

Fischer *et al.* immobilised TiO_2 nanoparticles on PES membrane by dip coating and ultrasound treatment for dye photodegradation. The produced TiO_2 /PES membrane showed almost 100% degradation of methylene blue (13 mg/L) in 40 minutes for nine consecutive cycles [89]. The degradation of toxic components can be explained on the basis of its breakdown into smaller products. Sometimes, it has also been noticed that the degraded products are more toxic and carcinogenic than the parent component. Therefore, the study of degraded products and maximum mineralization of toxic components is essential. Li *et al.* exhibited the usage of double cylindrical shell photoreactor with an immobilized monolayer of silica gel beads coated with TiO_2 [90]. Fouad *et al.* described the use of W- TiO_2 coating on inclined stainless-steel plates to form thin-film fixed-bed reactors, which was irradiated with two metal halide lamps placed above the reactor [91]. Moreover, Stephan *et al.* developed a thin-film cascade photoreactor comprised of fibres steps coated by TiO_2 , where polluted water circulated in the closed-loop [84]. Alternatively, Sun *et al.* proposed a continuous magnetic aggregation bed photocatalytic recycle reactor for dye treatment (Figure 7.7a) [88]. They used a magnetic photocatalyst ($\text{CoFe}_2\text{O}_4\text{-Ag}_2\text{O}$),

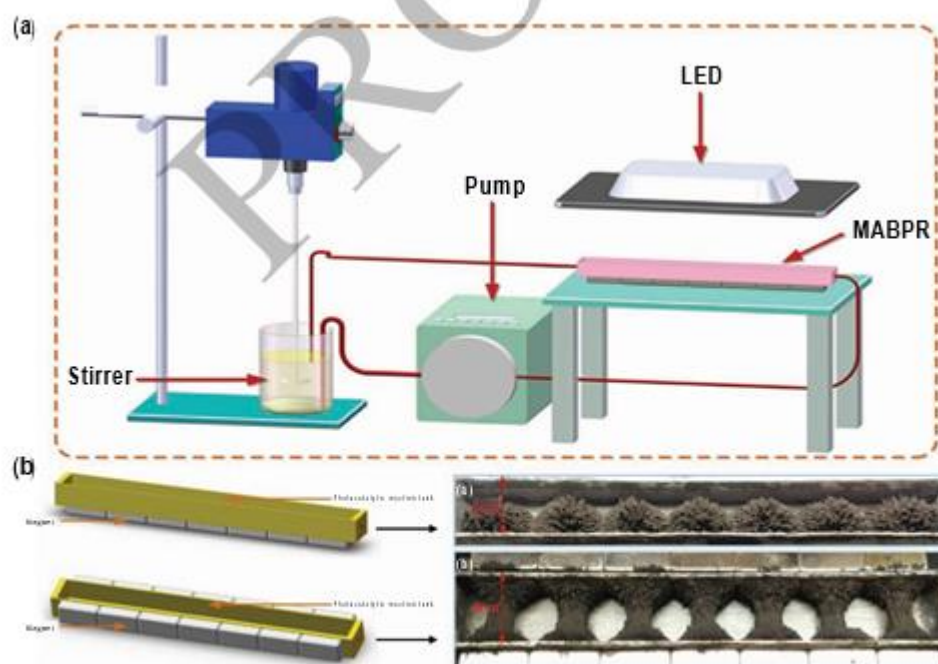


Figure 7.7 (a) Illustration of the assembled continuous magnetic aggregation bed photocatalytic reactor. (b) Different magnet arrangements in photoreactor: bottom and lateral set-up. Reproduced with permission from ref. [88].

Table 7.3 Some recent examples of different photoreactors and their performance.

Reactor	Light source	Pollutant	Photocatalyst	Efficiency	Reaction time	Reuse cycles	Ref.
Micro-meso-reactor	1700 W Xe lamp	Cr(VI)	TiO ₂	100%	60 min	10	[64]
Submerged coated plate reactor	400 W metal-halide lamp	Multiple bacteria	Ru-WO ₃ /ZrO ₂	100%	240 min	4	[93]
Coated plate reactor	400 W metal-halide lamp	Chlorpyrifos	ZrV ₂ O ₇ /graphene nanoplatelets	96.8%	90 min	5	[94]
Fluidized bed reactor	350W Xe lamp	Bisphenol A	TiO ₂ nanotubes/graphene	100%	30 min	5	[87]
Polymer membrane reactor	Solar lamp	Methylene blue	TiO ₂	100%	40 min	9	[89]
Continuous flow slurry reactor	36W Philips PL-L sunlamp UV tubes	Methylene blue	TiO ₂ pellet	98%	60 min	-	[95]
Magnetic aggregation bed reactor	600 W LED lamp	Methyl orange	CoFe ₂ O ₄ -Ag ₂ O	92%	60 min	3	[88]
Photocatalytic PVDF membrane	500 W Xe lamp	Fluvastatin	ZnIn ₂ S ₄	99.75%	180 min	6	[61]
Submerged membrane reactor	500 W Xe lamp	p-nitro-phenol	Fe-ZnS/g-C ₃ N ₄	93.5%	300 min	-	[96]
Immobilized double-cylindrical-shell photoreactor	UV black light lamp	Rhodamine B	TiO ₂ -coated silica gel beads	90.4%	12 h	5	[90]

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which was anchored to the bottom of the reactor via an external magnet (using either at the bottom or lateral arrangement) (Figure 7.7b). The magnetic aggregation in this reactor increased the mass transfer and irradiation surface area. It did not require extra energy input for photocatalyst recovery and mass of photocatalyst remained same over the course of the reaction. However, the performance of magnetic reactor is lower than those of many other reported reactors, whereas it has potential to scale-up for real water treatment. Moreover, continuous slurry reactors with gas promoted suspension are also designed for water treatment. For instance, Rakhshaei *et al.* fabricated a plug flow tubular photoreactor in which catalyst (nano α -Fe₂O₃) were suspended in the liquid phase using air bubbles [92]. It was tested for photocatalytic degradation of different dyes (malachite green, methylene blue, rhodamine B, and bismarck brown Y). Table 7.3 presented some examples of photoreactors and their performance for the treatment of water pollutants.

7.6 Challenges for Effective Photoreactors

Slurry reactors including both solid-liquid and solid-liquid-gas system, are highly beneficial as compared to immobilized reactors due to better photocatalytic performance. The higher catalytic activity of the slurry reactor is attributed to the available high total surface area of photocatalysts per unit volume. As a result, the slurry reactor is very cost-effective in terms of operation and fabrication. Still, it suffers from the drawback of downstream separation of photocatalyst from solution after completion of the reaction. To avoid downstream separation, researchers are inspired to develop/switch toward continuous flow slurry photoreactors without any immobilization. Additionally, recent research efforts are also dedicated to switching the mechanically obtained suspension by air or other gases promoted suspension. This change is essential to match the demand for microreactors, which requires low photocatalyst loading. However, limited research has been done on immobilized reactor systems to improve the irradiation source and required length of scale-up reactors. There are still many challenges, which obstruct the full-scale application of photoreactor with immobilised photocatalyst. Due to inherent kinetics and mass transfer limitations of the photocatalytic process, the processing capacities of the reactor are usually restricted. To achieve enhanced photocatalytic efficiencies, the higher residence time is needed, which can further slow down the complete

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process. Thus, utilisation of immobilized reactors at a large scale for real water treatment is still challenging.

In order to develop an effective photoreactor system, microreactors have gained attention due to their compact design, high surface to volume ratio and better mass transfer compared to the conventionally used large-scale photoreactors [97]. In addition, they offer low catalyst loading, uniform light distribution and improved heat transfers [98].

Furthermore, more studies are needed to investigate the decrease performance in consecutive cycles, intermediate products during photocatalytic degradation, reduction in photocatalyst leaching and applicability of photoreactor in real water matrices (treated municipal wastewaters, river waters, and polluted industrial water) or multi-component pollutants.

7.7 Conclusion

Heterogeneous photocatalyst has been proven the best remediation for the organic pollutants in wastewater with the help of solar radiation. Researches have been accomplished to analyze the efficiency and mechanism of photocatalytic degradation. However, the research that focuses on the configuration and set up of photochemical reactors is limited. There are several types of photoreactors, which employed for the numerous photochemical reactions. For the photoreactors to be operational, they must uphold an effective geometry, preferred light source, materials that have higher reflective property and a thermostat for temperature control. The role of photocatalytic materials and the geometry of the photoreactor have been proved to provide effective photodegradation. Various photoreactor designs such as slurry photoreactor, rotating drum photoreactor, membrane photoreactor, closed-loop step photoreactor, annular photoreactor, micro-photoreactor and magnetic bed photoreactor have been developed for water treatment. Photocatalyst within the batch and flow photoreactors can be used by two methods: suspension/dispersed and immobilization/retained forms. Continuous slurry flow reactors and microphotoreactor are highly advantageous compared to immobilized reactors due to better photocatalytic performance. Furthermore, there is a need to develop photoreactors that are effective for real water matrices and in the multi-pollutants system. More research efforts are required to make photocatalysis technology more commercially viable and environmentally sustainable than conventional processes.

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PROOF

5. Photodegradation of polycyclic aromatic hydrocarbons using metal oxides under irradiation

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Journal of Water Process Engineering

Summary

Polycyclic aromatic hydrocarbons have been the most concerning pollutants in the environment at present and have gained much attention in various research fields. There are still various industries, but especially petroleum-related activities, that are mostly responsible for the release of PAHs into the environment. Knowing their ubiquity and resistance to any removal techniques, various studies have been conducted on the metal oxides' effectiveness in removing these PAHs in wastewater. It is important to assess and monitor the industries that are responsible for releasing these PAHs into the environment. The adverse effect of these pollutants when humans come into contact with them are serious health concerns, due to their carcinogenic and mutagenic properties. These PAHs can be classified on their molecular weight; however the heavier the molecular weight, the more toxic they are, as compared to PAHs with lighter molecular weight. Their sensitivity to heat allows them to be destabilized at a specific wavelength of irradiation.

Various studies have been conducted on how to sustain a healthy environment in view of the persistent organic pollutants. Researchers involved in remediation processes have studied the effectiveness of various metal oxides. The effects of various industries have been discussed with the petroleum industry being mostly responsible for releasing PAHs. Most of the petroleum and mine-related activities that are responsible for releasing PAHs are currently unavoidable, therefore there is a need to investigate, implement or monitor the release of these carcinogenic pollutants, by introducing a method that will enhance the performance of traditional methods used for their degradation. The use of biological applications has been widely considered in the bioremediation of PAHs in soils, and only a few have been considered for wastewater treatment. Various studies on other organic pollutants have been conducted using a biological method and less attention has been given to the photodegradation of PAHs in various water sources. Various processes and techniques are shown in Table 2, whereas Table 3 indicates the most important method to remove PAHs from wastewater.

Photodegradation of polycyclic aromatic hydrocarbons using metal oxides under irradiation

REVIEW

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ABSTRACT

The release of coal tar containing polycyclic aromatic hydrocarbons in various water sources has caused various health repercussions due to their carcinogenic and mutagenic properties. The release of coal tar in an acidic medium of lower pH is a predominant source of higher leachate generation. It was found that the enhancement of a semiconductor by either doping of metals or carbon can improve the photodegradation of PAHs in wastewater. The ubiquitous PAHs can be reduced through physical, chemical and biological methods. Various studies have been conducted on the photodegradation of the PAHs mostly in the soil using a biological method. The delay of the recombination of electrons and narrow bandgap is important, and can be achieved by doping metals into a metal oxide. This review provides a comprehensive overview of various metal oxides used for the photodegradation of PAHs in water under the influence of irradiation surfaces. Green synthesis of material has gained attention due to its being eco-friendly and cost-effective. It has been suggested to introduce agrowastes but the metals in them can perform as metal elements to obtain an effective material that can mineralize PAHs in various water sources at a large.

Keywords: Polycyclic aromatic hydrocarbon; wastewater; coal tar; green synthesis.

1 Introduction

Wastewater treatment has recently gained attention especially in the deposition of coal tar which is composed of various elements and organic pollutants. Coal tar is an organic pollutant that has received attention because of its genotoxic, teratogenic and mutagenic properties that can cause harm to the environment when discharged from activities/industries like mining, coal and petroleum industries. It is a by-product that is predominant in polycyclic aromatic hydrocarbons (PAHs). Its presence has been reported by Ghosal *et al.* [1,2] to be detrimental to the ecosystem. Since petroleum activities have grown over the past decades, it has been predicted that in 2050, the population of 9 billion people around the world will come directly in contact with the PAH pollutants derived from coal tar effluent in wastewater [3]. The fast population growth is responsible for the pollution of large volumes of water along with industries releasing the coal tar that generates harmful PAHs into the environment [4].

The toxicity of these PAHs to the environment should be investigated as it leads to various health concerns [5] and effective methods to remove these pollutants from wastewater need to be considered. The presence of natural organic matter (NOM) also has a role in the ecosystem according to Seopela, *et al.* [6]. NOMs have been proven to be potential inhibitors of the degradation process due to their ability to incorporate light in photochemical reaction energy that will prevent PAHs from degrading and making them resistant to absorption. According to Nadal, *et al.* [7], the photodegradation of PAHs is mostly observed on the lower molecular weight of (1-3 rings) as compared to the heavy molecular weight of 4 rings and more. There are various methods like physical, chemical and biological methods that have been used to assist PAHs remediation [8].

Benzo(a)pyrene is the most unwanted toxic pollutant due to its carcinogenic nature [9]. Parameters like pH, ionic strength, temperature and water matrix components that dissolve the organic carbon are mostly responsible for the solubility of the PAHs in water bodies since their solubility is very low at a concentration level of 31 g/m³ [8]. The release of PAHs from coal tar to wastewater still poses a threat despite the physical, biological, or chemical treatment of wastewater. According to the world health organisation (WHO), the acceptable range of PAHs in drinking water should be 1 ng/L to 11 µg/L. Since benzo(a)pyrene is the most toxic PAH found in wastewater/water, the WHO has recommended a much lower concentration which should be below 0.7 µg/L [9]. They are various metal oxides such as iron oxide, titanium dioxide, silver oxide, zinc oxide and more that have been synthesized into nanoparticles (NPs) for wastewater treatment [10]. Carbon nanotube and nanocomposite have also been introduced as potential candidates to remove pollutants from the wastewater [11]. The use of various plants has been investigated to obtain a green synthesis for the removal or degradation of organic pollutants from wastewater.

This method has been proved to be environmentally friendly and cost-effective. The green synthesis is used to obtain specific morphologies, particle size, photo activities, optical properties or bandgap reduction to enhance properties that should be effective in the remediation of organic pollutants in wastewater [12]. Besides plants, bacteria and fungi can also be used for green synthesis [13].

The biological synthesis of nanomaterial contains no toxic compounds, therefore its application to manufacturing a nanomaterial or nanoparticle makes it effective and has a good overall recovery due to its antibacterial property and functional groups [14]. A study conducted by Denet, *et al.* [15] used various metal oxides: magnesium oxide (MgO), titanium dioxide (TiO₂), cerium(IV) oxide (CeO₂), zinc oxide (ZnO) and zirconium dioxide (ZrO₂) were reported to have antibacterial properties. The synthesis of these metal oxides from a biological method can drastically improve their properties [15]. The main limitation of the study is the application of the physical and chemical treatment due to their drawbacks and cost of assisting to remove the ubiquitous organic pollutants. This can also be achieved under a radiated material and better-synthesized metal oxide from plants or animals or microorganisms mentioned by Denet *et al.* [15] to explore higher efficiencies at a lower cost. There are various methods to synthesize metal oxide nanoparticles as shown in Figure 1.

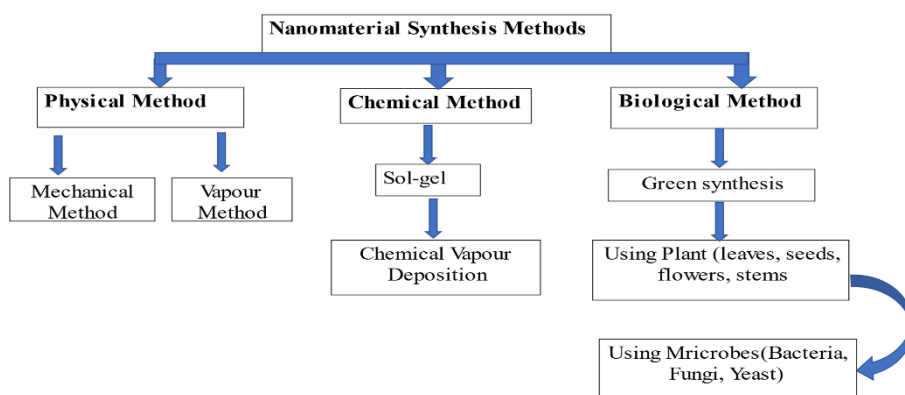


Figure 1: Synthesis method for metal oxide nanoparticle [14]

Various studies have been conducted on the photodegradation of PAHs in soil and other sources; however, less attention has been given to the photodegradation of PAHs in waters. Furthermore, recent studies have shown that the effectiveness of green synthesis in the removal of organic pollutants (dyes) has been successful. Figure 2 reveals various publications and citations on the photodegradation of PAHs but using a photocatalyst thus making it an interesting topic for this review.

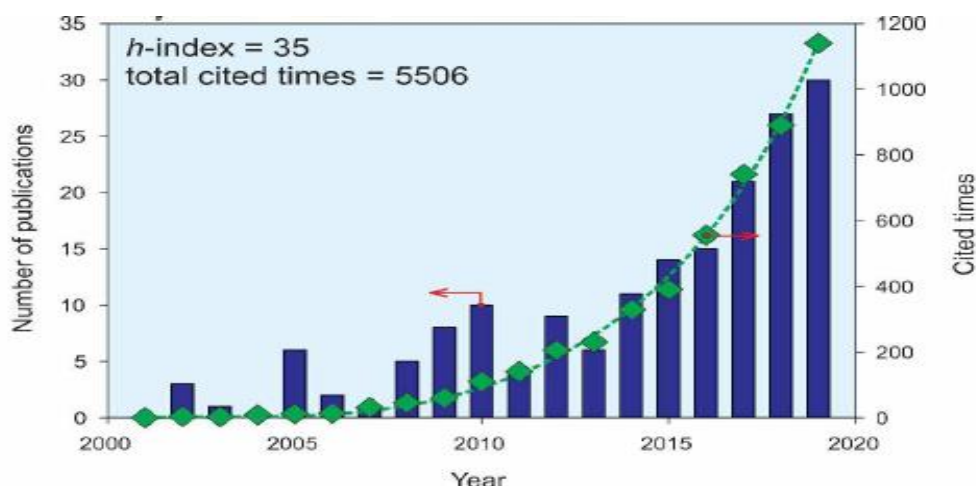


Figure 2: Various studies conducted on the PAHs photodegradation using photocatalysts.

Recent studies have been conducted on the photodegradation of PAHs mostly in soil using biological methods (enzymes, bacteria) and photocatalysts. These biological compounds are derived from plants and animals that have been dead for decades, and later produced micro-organisms that are found underground and in soil. The importance of the plants and animals lies in their availability and medicinal and clinical chemical properties that have been explored in various applications. Their adaptability and biocompatibility for green synthesis have made the biological method effective [16]. The biological method has been widely used for PAHs remediation in soil but it has mostly favoured the lower molecular weight while the heavy molecular weight remained in the soil and become effluent into various water bodies [17]. In this review, the photodegradation of PAHs in water using various techniques and methods is highlighted. No paper has been published on the photodegradation of PAHs derived from coal tar in various water sources such as acidic mine drainage, alkaline mine drainage and sewage wastewater with different physiochemistry properties. Further, the application of agrowastes in narrowing the bandgap and delay of the recombination of electrons has never been performed on the photodegradation of PAHs derived from coal tar.

2 Production of coal tar from various industries

The composition of coal depends on its origin due to the alteration of physicochemistry properties over time [18,19]. Coal tar derives mostly from various coal industrial processes or applications like gasification or heating under specific conditions. Coal is used in various operational technologies that require energy which later produces a by-product like coal tar [18]. Coal is one of the most important sources of energy and is the second largest non-renewable energy source that will remain in use till 2030 [20]. High-quality coal is mostly depleted because of its high demand. South Africa is the 6th largest producer of coal around the world, with around 220 Mt of coal being produced per annum. The use of coal contributes to 95 % of electricity production in South Africa [21,22].

2.1 Characteristics of coal tar

Coal tar is characterised by its black to dark brown colour and it can be either in a highly viscous liquid or in a semi-solid physical state. Its odour is pleasant, but peculiar and naphthalene-like whereby its composition ranges between 0-2% light oils, 16–18% middle, 8-10% heavy oils, 6-20 % anthracene oils, and 50% pitch. Naphthalene is the most predominant PAH in coal tar and is subsequently found in wastewater/water polluted by PAHs [23].

2.2 Sources of PAHs

Besides PAHs being a constituent in coal tar which is produced from various activities mentioned previously like mining, petroleum and oil spills, they can also be derived directly or indirectly from human activities. Most PAHs are discharged into the atmosphere from various processes, especially the use of cigarettes, burning of coal, crude oil, natural gas, gasoline fuel and other organic materials.

The burning of wood is the most common method that widely releases PAHs [18]. The burning of coal and petrochemicals however is considered to be widely responsible for the release of the PAHs at high concentrations [24]. These PAHs also have health repercussions like the PAHs derived from coal tar [25,26]. The composition of the PAHs varies from region to region, depending on the nature of the surroundings like pressure and other factors that may contribute to the coal tar physicochemistry properties [27].

3 General overview of PAHs

PAHs are complex organic pollutants that have a pleasant smell [1]. Naphthalene happens to be one of the various PAHs that are commercially used in the production of chemicals and even in cigarette manufacture [1]. It is important to identify the number of rings in PAHs from coal tar to be able to classify the PAHs as petrogenic or pyrogenic in PAH polluted wastewater/water. The 5 ring structures are more abundant in petroleum hydrocarbons and are regarded as petrogenic, whereby in a pyrogenic substance, the 5 ring structures are easily converted to 6 rings, which makes it stable and more rigid in the environment [28,29].

While there are various PAHs, NAP, ANT, PHE, ACY, ACE, FL, FLU, PYR, BaA, CHY and Bfb are the PAHs that have been identified in coal tar, based on their chemical property or reactivity to the natural environment [6,30,31]. 16 PAHs from coal tar discharged in wastewater and water have been described as mostly responsible for human health disorders United States Environmental Protection Agency (USEPA) [32]. Figure 3 represents the molecular formula of PAHs that are mostly found in coal tar, wastewater and water.

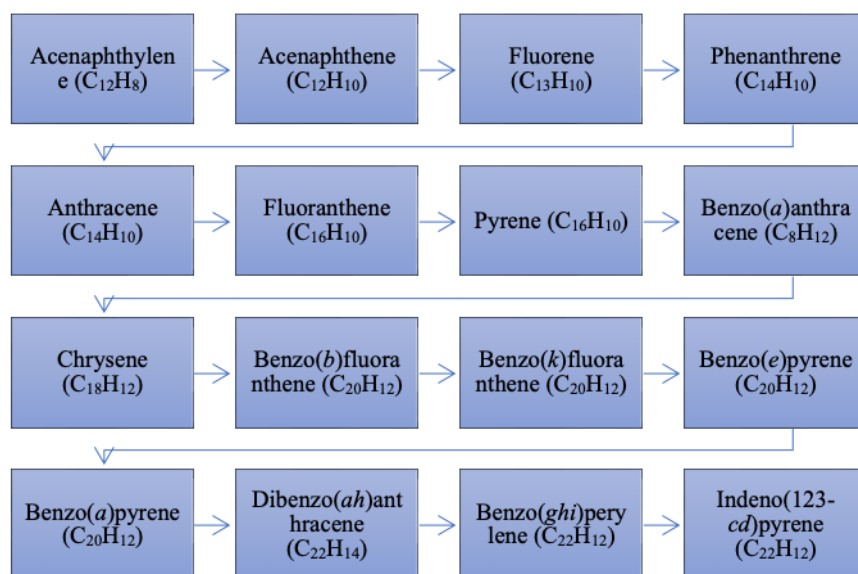


Figure 3: Common PAHS found in wastewater that causes a threat to both the environment and humans.

The petroleum industries are as responsible for releasing large volumes of PAHs from oil spills into the environment causing economic and health challenges [5]. These PAHs can readily be absorbed from the gastrointestinal tract of mammals due to their high lipid solubility. They are most toxic in the presence of UV light due to their temperature reactivity and do not decompose easily at low temperatures. Due to the chemical structure of these PAHs, which are made of at least two attached benzene rings, they are considered toxic [33] and micropollutants [24]. The presence of PAHs in the human body due to inhaling, eating or drinking has serious health consequences such as carcinogenic, oncogenic and mutagenic effects [24,34].

PAHs can be classified according to the number of rings, therefore if the number of carbon rings is less than 5 it can be considered a light PAH [35], with degradation happening more rapidly than heavy carbon rings of 5 or more. The increase in the size of PAHs in coal tar increases the hydrophobicity and electrochemical stability in wastewater/water [31]. The molecular weight of the organic pollutants (PAHs) can determine the toxicity level, therefore the higher molecular weight of PAHs results in higher toxification of the coal tar bearing the PAHs. The physical or chemical properties can change the molecular weight of PAHs [35]. PAHs can be miscible in organic solvents of aromatic substances like acetone, alcohol, hexane, dichloromethane, methyl ethyl ketone and toluene which have a pH below 7 and are lipophilic, conditions promoting the solubility of PAHs [36].

The addition of each PAH ring in a solution reduces the solubility of the water solvent solution, while the molecular weight increases [37]. Most of the PAHs are fluorescent and release light when activated using visible UV radiation. Every ring configuration has a special UV spectrum and each of the ring isomers has an absorbance spectrum of the different PAHs [29].

PAHs with 3 rings or less are more easily degradable according to Sakulthaew, *et al.* [38] and it was also reported that its parent is a non-alkylated compound with lower carbon oxidation that is quick to degrade. Compounds like naphthalene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene and pyrene are a few among hundreds of organics to which humans are most exposed [39].

It has been reported by Mozo, *et al.* [40] that the lower molecular weight PAHs like naphthalene, which consists of 2 rings, are more hydrophilic than Benzo[ghi]perylene which consists of 6 rings, and which is considered to be hydrophobic. The interaction of PAHs with deoxyribonucleic acid (DNA), ribonucleic acid (RNA) and proteins can cause cancer due to the covalent binding mechanism between the PAHs and the DNA [1]. The effluents of coal tar over the last decades have increased tremendously and it is also predicted to increase over time as the population and activities of humans grow [5]. The dispersion of coal tar into the wastewater/water supply constitutes a potential health risk. Therefore an effective technique has to be developed to aid in the degradation of the PAHs that are derived from coal tar so that clean water can be accessible to humans [41].

The discharge of coal tar from various industrial processes into wastewater and water with other pollutants like liquid fat, dirt, floating dust, gasses and minerals adds to higher toxicity in various water sources and is a serious threat to humanity. The presence of the pollutants in a homogenous solution can only be observed using spectrometry equipment [41]. The chemical properties of PAHs as lipophilic and non-polar compounds make them soluble in oil [30]. It has been reported by Iglina, *et al.* [42] that carbon dioxide (CO₂) can absorb PAH pollutants in the soil on a large scale. However considering several factors such as the nature of the soil, temperature, soil nutrients, and presence of other pollutants can influence the removal of the organic pollutants [43].

3.1 Formation of PAHs

The PAHs can be developed through the pyrolysis of lignin, cellulose and hemicellulose. Zhou, *et al.* [44] investigated this by using the pyrolysis/gasification of cellulose and hemicellulose, resulting in a lesser PAH production as compared to lignin, which resulted in a large volume of PAHs. It was also found that an increase in temperature had a greater influence on producing PAHs on a large scale [44]. Attention has been given to the release of coal tar which is mostly responsible for 75% of the release of PAHs in wastewater [27].

3.2 Environmental occurrence of PAHs

PAHs are detrimental due to the health hazard they present. Therefore, their release from coal tar into wastewater has made them a risk to humans through ingestion, inhalation etc. Although some conventional methods have been implemented for PAH removal, there is still room for improvement. The heavier the molecular weight of the PAH, the more difficult it is to remove from the environment [45].

3.3 Health impact of PAHs

The aromatic rings make the PAHs very toxic and unsafe for the environment [29]; for instance, ingesting or inhaling phenanthrene can lead to lung cancer [46]. PAHs like benzoanthracene, benzopyrene, fluoranthene, chrysene, and anthracene have been reported by Cai, *et al.* [47] to be highly dangerous in wastewater. Fluoranthene easily bonds with metabolites and it is easily soluble [10]. A small concentration of PAHs can cause a mutation in some organisms and it is vital to develop an effective technique, that can assist in removing PAHs in wastewater/water. Though there are various conventional methods like reverse osmosis, distillation, filtration and advanced oxidation that have been used to mitigate these issues, drawbacks like byproducts, high cost, operation system and maintenance have resulted in their being ineffective [48].

3.4 Polycyclic aromatic hydrocarbons in coal tar and impact on wastewater

Besides coal tar, PAHs are derived from various channels like thermal cracking, crude oil combustion and other pyrolytic methods, even under a temperature of 100°C [29]. PAHs are constituent of crude oil and those present in petroleum are called petrogenic PAHs [49]. Coal tar is a byproduct of coal produced during the coking process and its maturity over time increases PAH toxicity [29]. The PAHs like naphthalene, acenaphthene, acenaphthylene, fluorene, anthracene, phenanthrene, fluoranthene, pyrene, dibenzothiophene, benzo[a]anthracene, chrysene, benzo[a]pyrene, benzo[e]pyrene, perylene, benzo[b]fluoranthene, benzo[k]fluoranthene, dibenz[a, h]anthracene, benzo[g, h, i]perylene, and indeno[1,2,3-cd]pyrene) have been reported by Hedayati, *et al.* [50] to occur in a range of 1510 to 12500 ng/L PAHs in wastewater and 825 g/d in industrial wastewater. Leaching is a process whereby a liquid or semi-liquid (coal tar) interphase comes into contact with wastewater. The initial properties of the wastewater will be changed due to the addition of the coal tar. The release of PAHs from coal tar into wastewater will depend on the ageing/time of the coal tar contact with the wastewater. The leaching parameters and values reported are given in Table 1.

The lower pH value of the wastewater may be attributed to the presence of coal tar, resulting in lowering the chemical oxygen demand (COD) content and increasing the conductivity [51,52]. Batchamen *et al.* [53] have reported that the deposition of coal tar in various water sources can change the physiochemistry of that wastewater/water [53]. Various techniques have been applied and some methods have been neglected to mineralize toxicity in wastewater/water [52].

3.5 The formation of polycyclic aromatic hydrocarbons from coal tar and transport into wastewater

Coal is one of the major sources of energy, with coal being produced globally as a non-renewable source of energy [33]. Coal is made up of plant components like cellulose, lignin, pitches, seeds, leaves, stems, and roots. The coal is formed when heat and pressure are applied to produce the organic matter coal in the so-called coalification process. This can later produce coal tar which can form an effluent that pollutes wastewater/water [35]. Gasification is one of the processes whereby a large volume of coal tar is produced and normally occurs when coal is burnt and coal tar is released and is channeled into various water sources [54].

3.6 Effectiveness of radicals in wastewater treatment

Stefaniuk, *et al.* [55] reported that zeolites, metal oxides, carbon materials, metals or bimetallic nanoparticles like Fe/Pd, and Fe/Ag have been widely used as metal nanoparticles (NPs) in the remediation of PAHs as organic pollutants. However, nano zerovalent iron (nZVI) has been found to be the most effective and the combined metal NPs success is based on their increased surface area and stabilization [56]. The addition of functional groups or surfactants on the surface can trigger various changes such as the physicochemical properties of the modified material and their cytotoxicity [57]. Advanced oxidation processes are regarded as the most effective in the removal of PAHs in wastewater which is based on their ability to produce hydroxyl radicals ($\bullet\text{OH}$) that can actively react with the PAHs. Some of the various radicals that are being used for the mitigation of PAHs in wastewater are summarized in Table 1.

Table 1: The oxidation potentials of various oxidants [58]

Oxidant	Oxidation potential (VNHE)
F	3.03
$\bullet\text{OH}$	2.80
Atomic oxygen	2.42
O_3	2.07
H_2O_2	1.78
$\text{H}_2\text{O}\bullet$	1.70
MnO_4^-	1.68
HBrO	1.59
ClO_2	1.57
HClO	1.49
HIO	1.45
Cl	1.36
Br	1.09
I	0.54

The application of radicals, or oxidants, can assist in the oxidation of the PAHs by mineralising them. The higher the oxidation potential, the better the ability to produce higher radicals that are recognised as abstraction, electrophilic attack, and electron transfer [59].

A summary of various techniques conducted on the degradation of PAHs in wastewater is being shown in Table 3 [60]. In Figure 4, the photocatalyst mechanism of the electron transfer between the valence band and the conduction band is illustrated. The excitation of electrons from the valence band to the conduction band on a semiconductor leaving an empty hole depends on the light intensity. In wastewater, photocatalyst will be employed that relies on the light intensity and the geometry of the photoreactor material to have a complete reaction.

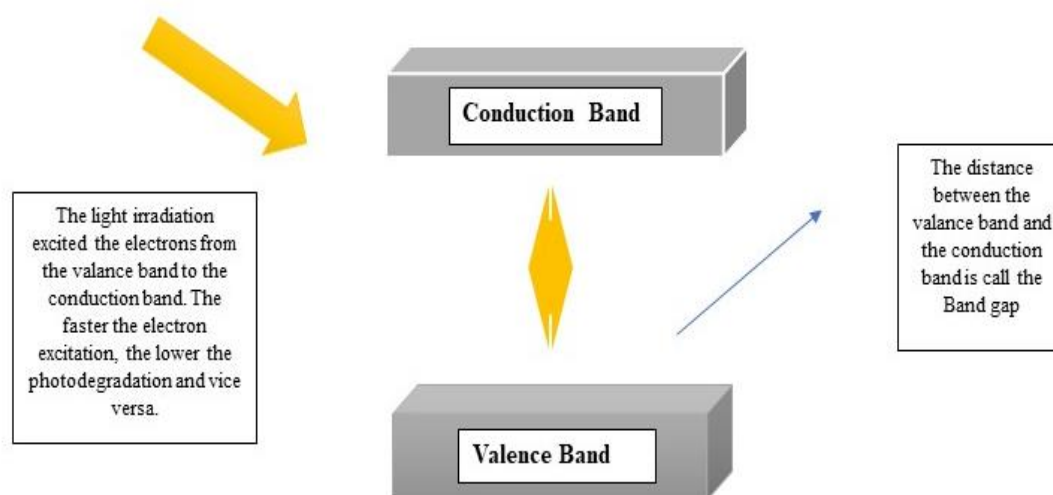


Figure 4: Photocatalyst reaction mechanism for a semiconductor

The photocatalysis process is the application of a material that can attract light and the best semiconductor that has been widely used for environmental remediation. The semiconductor aids to degrade the most unbiodegradable organic pollutants in water [61].

There are three stages for wastewater treatment. The primary stage is whereby solids should be removed to avoid damage to the system, and the physical method is normally conducted at this stage. The secondary stage is the removal of the remaining pollutants and at this stage, the diluted pollutants require oxygen to be decayed. The tertiary stage is whereby the pollutants require a biological method since a mass of the pollutants has been removed resulting in lower pollutant recovery [62]. There are various methods like biological, chemical and physical methods that have been used during PAH remediation from aqueous solutions. However, biological and physical methods have commonly been used to assist in the removal of PAHs. Bioreactor, phytoremediation and bioremediation have been used as biological methods in the removal of PAHs [63,64] and their functions are shown in Table 2.

Table 2: Various advanced techniques of PAH degradation summarised by Eker and Hatipoglu [60].

Techniques	Functions
Solvent extraction	Treatment of single or mixed solvents to reinforce the degradation process of PAHs in wastewater/water.
Chemical oxidation process	Treatment using oxidants shown in Table 1 and few others, like Fenton's reagent, potassium permanganate, to perform oxidization of PAHs in wastewater/water.
Photocatalytic degradation	Treatment in the application of UV light to destroy the PAHs derived from coal into wastewater/water.
Thermal technique	Treatment applies high temperatures to volatilize PAHs derived from coal tar.
Phytoremediation	Microorganisms are derived from plants to treat PAHs from coal tar in wastewater/water.
Biological technique	Treatment uses plants, seeds, leaves or any biological materials to mineralize PAHs from coal tar in wastewater/water.

Conventional methods like membrane filtration (microfiltration, ultrafiltration, nanofiltration, reverse osmosis), flocculation, precipitation, ion exchange and coagulation are used for the removal of PAHs [65]. The drawback of these methods which produce carbon dioxide and methane gas. has prompted the introduction of an advanced method such as adsorption [66], advanced oxidation (ozonation, electrochemical oxidation, photocatalytic [67]) to enhance the traditional methods. This method has good recovery, and it is cost-effective with zero waste. There are various other methods like the Fenton reaction coupled with a biological process, ozonation coupled with biological treatment, direct photolysis coupled with a biological treatment, O_3/H_2O_2 , UV/H_2O_2 , V/H_2O_2 , direct photolysis/ozonation, O_3/H_2O_2 , UV/H_2O_2 , UV/O_3 , and UV/TiO_2 coupled with Fenton's reaction have been applied in the remediation of coal tar PAHs occurring in wastewater/water [9,37,68]. Table 3 shows a summary of various techniques used for PAH degradation [69]. Although various metal oxides presented in Table 3 have been used for PAH photodegradation, TiO_2 has been the most common metal oxide used to remove anthracene, fluorene, and naphthalene at large under an irradiation surface [70]. In addition, further studies [61,71-73] have confirmed the effectiveness of metal doping to improve photocatalytic activity.

Table 3: Various metal oxides used in the photodegradation efficiency of PAHs reviewed

Polycyclic	Photocatalyst	Irradiation	Duration (h)	Photodegradation efficiency %	References			
ANT	ZnFe ₂ O ₄ -CS	Solar irradiation	12	95	[74]			
PHE				92				
ANT	CuO-Fe ₂ O ₃ -CS			93				
PHE				90				
ANT	NiFe ₂ O ₄ -CS			90				
PHE				88				
ANT	Co ₂ O ₃ -Fe ₃ O ₄ -CS			88				
PHE				85				
ANT	FeCr ₂ O ₄ -CS			83				
PHE				81				
BaP	(ZnHCF@ZnO)	Solar irradiation	24	90	[75]			
BaP	ZnO		24	38				
PHE	Cu/N-codoped TiO ₂	Visible light	2	96	[71]			
ANT	α -Fe ₂ O ₃	Light irradiation	7 days	80	[76]			
	Fe ₃ O ₄			40				
	α -FeOOH			30				
ANT	ZnO/emulsion	UV	2.50	90.28	[77]			
ANT	ZnO-NiO	Solar irradiation	12	98	[78]			
PHE				93				
ANT	ZnCo ₂ O ₄			95				
PHE				90				
ANT	MnCo ₂ O ₄			92				
PHE				87				
ANT	CoFe ₂ O ₄			88				
PHE				83				
PHE	La-N-TiO ₂ /AC			Visible light		2	93.5	[79,80]

To enhance metal oxide, it is important to consider doping such as the addition of metal, carbon, transition elements, and solar utilization. This also helps to modulate the bandgap and also to improve its property of solar visibility [81-85]. The oxygen content in material happens to be converted into superoxide and water into hydroxyl which will therefore aid to degrade the PAHs [10].

4 The application of a biogenic photocatalyst for the photodegradation of PAHs

The unique physical and chemical properties of metal nanoparticles which have been reported by Liu, *et al.* [86] to be effective in the remediation of PAHs in wastewater/water could be mainly attributed to their large surface to volume ratio due to their nano sizes. Such characteristics have gained attention due to the fact they exhibit excellent catalytic activity resulting in the oxidation of pollutants and minimization of their presence in water bodies [3]. The application of these metal oxides is often neglected, based on the cost and high energy consumption, though it is effective and easy to produce radicals that react with the molecules of the pollutants [87].

Besides the fact that ZnO has advantages like low production cost, UV resistance, hydrophilicity, eco-friendliness to both humans and the environment (non-toxic), and high photosensitivity and stability, it has also shown greater efficiency, because of its ability to absorb as much light as other metal oxide semiconductors such as TiO₂ and also its better performance due to its photocorrosion [88]. The photodegradation of anthracene was conducted under irradiation using ZnO nanoparticles prepared using an extract of *Coriandrum sativum*. It was found that, in a pH range of 5, 7 to 9, the best degradation was obtained at a neutral pH of 7. Time was also a factor to be taken into account because as time increases the photodegradation proportionally increases. Analysis of the green synthesis using X-ray diffraction (XRD) found that the *Coriandrum sativum* fitted well with the hexagonal structure of ZnO by having a high purity and crystallinity content [88]. According to Sofowora [89], the absorption band of the pure ZnO was 368 nm, although a study by Hassan *et al.* [88] found that the green synthesis of ZnO had an absorption band of 340–390 nm.

The use of ZnO/Ag/GO nanocomposite was employed in the removal of naphthalene [29]. It was proven that the use of Ag and ZnO incorporated with graphene oxide (GO) under light radiation resulted in 92% photodegradation of naphthalene in 50 min. GO alone was less effective, which reveals that the addition of metal oxide NPs in the photodegradation of PAHs improved the results [34]. The application of metal NPs for the photodegradation of organic pollutants (or PAHs) showed that the heterostructure can reduce the bandgap and improve the visible spectrum absorption. This improvement of absorption can occur by doping with another metal or plant [90]. Besides physical and biological methods that are fit for the removal of PAHs from coal tar in wastewater/water [36], chemical methods are the most advanced method for PAH removal. Oxidants like O₃, Fenton reagent (Fe²⁺+H₂O₂), potassium permanganate (KMnO₄), peroxy-acid (R-COOH), hydrogen peroxide (H₂O₂), and activated sodium persulfate (Na₂S₂O₈) have been introduced to produce radicals during the photodegradation of PAHs [9].

It has been proven that nanocomposites of the metal oxides Zn, Fe or Ti oxides with 3.3, 2.23 and 3.2 eV bandgaps respectively have the ability to enhance the photocatalytic effect and influence the electron recombination of charge carriers during the removal of PAHs from coal tar in wastewater/water [75]. However, the reduction of these bandgaps can contribute to increasing photocatalytic activity. The photodegradation of PAHs was influenced at a lower pH of a medium [91]. The photocatalyst reaction can be influenced by hydronium and hydroxyl ions [91]. The classification of PAHs is based on their low water solubility, low vapour pressure, and high melting and boiling point, which only depends on their molecular weight [9]. Okere and Semple [92] also found that the higher the molecular weight of the PAHs the more likely the tendency to decrease the water solubility and increase lipophilicity. An increase in both light intensity and oxygen can increase the photodegradation of the PAHs [93].

5 Conclusion

Various metals have been used for PAH photodegradation and they are preferred in obtaining a higher photodegradation efficiency. There is a need to introduce an effective biological method that will help to remediate the ongoing release of PAHs from various industries but mostly the petroleum industry. These industries release organic pollutants that pose threats to humans. The release of this organic material is inevitable during the fractionation of coal or coking processes. The application of green synthesis using plants on the semiconductors will efficiently reduce the organic pollutants by having a delay of electron recombination and lower bandgap. Its advantages such as non-toxicity, cost-effectiveness, and zero-waste as a by-product make it the best candidate to be considered for future research. The biomolecules and functional groups of most plants could add value to the green synthesis of these metal oxides such as ZnO or TiO₂ for the destruction of PAHs in wastewater.

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6. Synthesis of bio-photocatalysts and their application for the degradation of organic pollutants

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Summary

Wastewater pollution has been the most covered topic concerning the continuous release of organic pollutants into the environment. Various techniques, such as physical and chemical processes have been used over the past decades, although their limitations due to the cost and the release of toxic by-products such as carbon dioxide and methane have made their use unfavourable. To improve these physical and chemical methods to reduce the cost, time and pollution, photocatalysis was seen as a cost-effective and novel approach for the removal of the organic pollutants in wastewater. A photocatalyst is a material that can absorb light, and the energy absorbed has been diversely used in various applications; however, in wastewater treatment it is regarded as an advanced technique. This review regards the application of photocatalyst in wastewater treatment as the best technique to destabilize organic pollutants in wastewater. Since organic pollutants are light sensitive, it is necessary to use a photocatalyst to assist in the degradation of organic pollutants.

Various metal oxides such as ZnO and TiO₂ amongst many, also known as photocatalysts, have been used due to their cost-effectiveness, non-toxic nature, antibacterial properties, and their overall physical and chemical properties that have made them the best candidate to remove organic pollutants. Photocatalysts can further be improved to achieve a better yield and performance in the photodegradation of organic pollutants. The use of additional biodegradable materials has been proven to enhance interaction of metal oxides with organic pollutants. These biogenic applications can influence particle size, and the shape and crystallinity of the metal oxide and will improve photocatalytic performance by producing a photobiocatalyst consisting of the metal oxide and added biodegradable material. The efficiency of this recently introduced photobiocatalyst in wastewater treatment still has space for improvement.

Synthesis of Bio-Photocatalysts and their Application for the Degradation of Organic Pollutants

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Abstract— Photocatalysis is a cost-effective and efficient approach to remove the toxic organic pollutants from wastewater. Eco-friendly approaches, such as the development of photocatalysts using renewable materials, have been discussed in an attempt to follow green technologies. These renewable innovations are of concern because they are low cost and easy to assemble. A great deal of attention has recently been paid to moving towards environmentally friendly and keeping the environment away from pollutants, which is why several reports have been issued. The use of plants (leaves, stems, flowers and fruits) on their process of development and the use of these green synthetic materials in photo-catalysis has been researched and documented on the treatment of wastewater. This paper will focus on the review of the different types of photo-biocatalysts; their synthesis and application for the photo-degradation of organic pollutants.

Keywords- Photo-Biocatalysis; Organics Pollutants; Degradation.

I. INTRODUCTION

Low cost and non-toxic photo-catalysts such as ZnO and TiO₂ have been identified as outstanding candidates for light-duty water depollution [1]. Nevertheless, their use is constrained by the wide bandgap that imposes a UV constraint on the generation of electron-hole pairs [2-5]. For example, to achieve a successful and sufficient energy supply in the system, the following will need to adhere: the semiconductor will need to extend its ability in the lifespan of charge carriers [6]. Environmental remediation has been a challenge for researchers, which is why new treatment approaches, such as photo-catalysis, are being investigated to ensure safe and reliable clean water. Industries such as cosmetics, paper and leather manufacture wastewater containing a variety of organic pollutants such as methylene blue (MB), methyl orange (MO),

dyes, rhodamine blue (RhB) and many others [7].

These industrial effluents pollute natural reservoirs such as rivers, lakes, and dams. There has been substantial growth in the need to develop effective economic approaches for handling water. Several processes, including microbial oxidation, reverse osmosis, adsorption and photo-catalysis, have been used to clear organic pollutants from wastewater. These approaches have one type of downside or another, for example, microbial degradation is time-consuming, unsuccessful for some of the organic pollutants, and may generate carcinogenic materials [8]. Other processes, such as adsorption, although widely studied, appear to be expensive and the regeneration process is difficult [9].

However, the general downside to all these approaches is that they sometimes convert organic pollutants from one step to another and do not fully remove these contaminants, thus producing secondary pollutants. The key advantage of photo-catalysis over other approaches is that it distinguishes organic pollutants from less toxic intermediates. This is an innovative oxidation process that is mainly used because it is cheap and environmentally safe [10].

For the reasons pointed out above, environmentally sustainable methods are required to prevent the degradation of the ecosystem. Eco-friendly approaches, such as the synthesis of nanostructures using green technology, have been investigated to reduce these. These green nanostructures are of concern because they are cost-effective and simple to manufacture. The simplest and safe way to manufacture these nanostructured semiconductor materials is by using plant agents [11]. In the recent past, many materials such as activated charcoal, biochar and low-cost adsorbents produced from a range of resources have been studied for the decontamination of water. Recently, the use of nanostructured materials for scavenging and oxidation of harmful water pollutants has acquired enormous significance due to their peculiar size-dependent properties such as wide surface area, short intra-particle diffusion time, compressibility with marginal surface area reduction, excellent resilience, exceptional reusability and recyclability [12].

Bio-based nanoparticles (NPs) were also used for photocatalytic degradation of toxins in aqueous solutions. Various plant sections, such as leaves, buds, seeds, pods, fruit peels, stems, roots, etc., have been used for NP synthesis [13]. Many types of plant biomass may be used for the synthesis of NPs. Some research groups used fresh biomass for extraction,

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while others used dry/powdered biomass for the same purpose [12]. In recent years, biogenic processing of nano-sized materials has offered an enticing alternative to traditional routes due to their low cost and environmental benignity. However, the optimisation and conservation of key characteristics such as size regulation, monodispersity and durability of biologically derived NPs are of concern [12].

II. ORGANIC POLLUTANTS IN WASTEWATER

More than 0.7 million tons of organic dye are manufactured globally per year. It is known that over 10,000 commercially available dyes are listed as acidic, reactive, dispersive, vat, metal complex, mordant and sulfur dyes. For a variety of factors, reactive dyes have been described as the most environmentally harmful compounds in clothing dye effluents. Second, because of their desired output and their growing market share, reactive dyes are used intensively. Third, they are very soluble and about 10–15% of the weight of the reactive dye added is discharged from various industries and households. Fourth, traditional wastewater treatment systems, which depend on sorption and aerobic biodegradation, have a poor recovery capacity for reactive and other anionic soluble dyes. As a result, they cause tainted water sources and environmental concerns, and contaminants are moved to another process and are not discarded [14].

III. VARIOUS PHOTO-BIOCATALYST

Though many photo-catalyst have been studied and applied in the degradation of organics pollutants, we have come to realize that they are still room for improvement and application of an environmentally friendly technology. Degradation performance of various organic compounds is strongly dependent on experimental conditions such as light irradiation source, reaction time, pollutants form and photo-biocatalyst weight [15]. Any of the contaminants are biologically recalcitrant and inhibitory to tissues, which dramatically decrease the capacity of the microorganism to biodegrade substances before or in practice after treatment [17].

In recent years, a recurring mix of heterogeneous photocatalytic and biological processes for the treatment of various toxic effluents has been proposed. Progress is focused on the achievement of appropriate biodegradability for the shortest photocatalytic degradation (optimal treatment) and the subsequent application of biological degradation, which makes the overall procedure quicker and more desirable. The green synthesis of metal oxides has been studied and concluded in various applications of photo-biocatalyst on the mineralization of recalcitrant organic pollutants in various aqueous solution [14].

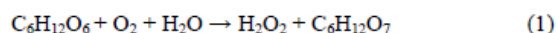
The following sections discuss the different types of photo-biocatalysts used in many applications, their effectiveness and optimisation on the removal of pollutants.

A. GOx/TiO₂/Fe²⁺/Metal Foam Photo-biocatalyst

The formation of the GOx/TiO₂/Fe²⁺/Metal Foam Photo-biocatalyst stated by [17-19] was reported in comparison of the enzymes and the microorganisms. The enzymes were preferred rather than microorganisms based on

their ability to be handled and stored. They are also believed to be highly productive and are produced by microorganisms. The most popular enzyme of interest is glucose oxidase (GOx), which creates hydrogen peroxide in situ in the presence of glucose [15]. FOX1 method can be used to measure the produced H₂O₂ after the production of the photo-biocatalyst, which can later be utilized in wastewater as it holds a strong oxidization affinity. It has several advantages such: a) destroying toxic organics pollutants without pollution transfer to another phase, b) does not produce harmful residues, c) can be combined with other catalysts and other oxidizers, d) efficient in treating almost all organics pollutants and removing some toxic metals, e) works for water disinfection and destruction of microorganisms [20].

One of the most widely used enzymes known as oxidoreductase GOx, catalyzes the reaction by which all electrons (βglucose) are taken from the substrate and transferred to O₂ to produce in situ H₂O₂ [11].



Then, with hydrogen peroxide, ferrous ions respond by producing ferric ions and hydroxyl radicals [21]. A UV-A lamp < 390 nm with an energy band of 3.2 eV was glazed with the TiO₂ semiconductor photo-catalyst to generate a positive charge hole and free electrons [22]. Doing so revealed the photo-catalyst effectiveness under UV-A lamp radiation.

i. Immobilization of TiO₂ nanoparticles on AgO metal-foam

The preparation and the immobilisation of TiO₂ NPs on AgO using Sonoplus Ultrasonic Homogenizer HD 2200 (Germany) was considered. This method was successfully approached where the immobilization of TiO₂ on AgO metal foam was undertaken to generate the photo-catalyst under particular parameters such as temperature, pH and chemical additives. At a selected temperature, a measured concentration of HCl addition to preserve a pH of 5.5 was carefully determined in the production of photo-catalyst [23].

ii. Immobilization of GOx on TiO₂/AgO metal-foam

There are various methods for the immobilization of enzymes, such as physical adsorption, covalent bonding and trapping [24, 25]. The advantages of using the enzymes are, low cost and minimal denaturation which are the most important criteria for selecting the right treatment [26]. Among the various methods mentioned on the immobilisation of enzymes, the physical adsorption of enzyme (GOx) was preferred [27] to be suitable on the immobilisation on the TiO₂/AgO metal-foam to produce a photo-biocatalyst.

The addition of GOx to the preparation mentioned in Section A(i) above the TiO₂ / AgO metal foam immobilization was carried out. Where a new chemical additive phosphate buffer (PBS) was applied, a photo-biocatalyst was obtained at a new temperature and pH value [28, 29].

Table I below displays the data obtained at various periods and the ratio combination with and without the inclusion of UV and GOx, and it has been found that the mixture of the

TiO₂+Fe+GOx+UV has a higher efficiency in the removal of malachite green (MG) from the aqueous solution.

TABLE I: DESCRIPTION OF EXPERIMENTAL EFFECTS OF MG REMOVAL UNDER UV LIGHT WITH [MG]₀ = 20 MG / L; INLET FLOW RATE = 5 ML / MIN [23].

MG Decolourization process	Decolourization (%)		Decolourization rate constant (k, min ⁻¹)
	20 min	60 min	
TiO ₂ +UV	42.17	59.15	2.8×10^{-2}
TiO ₂ +Fe	49.27	55.15	3.3×10^{-2}
TiO ₂ +Fe+UV	55.07	64.67	3.9×10^{-2}
TiO ₂ +GOx	50.03	54.64	3.4×10^{-2}
TiO ₂ +GOx+Fe	58.55	63.54	4.5×10^{-2}
TiO ₂ +GOx+UV	66.09	71.73	5.3×10^{-2}
TiO ₂ +Fe+GOx+UV	84.36	89.85	8.9×10^{-2}

The photo-biocatalyst mixture of Glucose oxidase, titanium dioxide, ferrous iron and metal foam (GOx / TiO₂ / Fe²⁺/MF) had a high tendency to extract 84.37% malachite green (MG) from the aqueous solution under UVA-LED for 20 minutes. It has also been shown that increasing the glucose dose still has a beneficial effect on the elimination of MG as stated by Abdi et al. [23].

B. NiFe₂O₄/T/GOx Photo-biocatalyst

To examine the degree of mineralization of indigo carmine (IC) attained during photo-degradation, a complete organic carbon (TOC) experiment was conducted for NiFe₂O₄ / T / GOx photo-biocatalyst. The use of tannin and GOx was both applied in the synthesis of the NiFe₂O₄/T/GOx photo-biocatalyst. NiFe₂O₄ was prepared using the solvothermal process [26] and

was functionalized with tannin. GOx was then immobilized when NiFe₂O₄ and tannin were modified. This biological approach results in low costs and low environmental risks [31].

i. Synthesis of NiFe₂O₄ magnetic nanoparticles and modification of NiFe₂O₄ MNPs by tannin

Nickel Iron Oxide (NiFe₂O₄) MNPs were synthesized by the solvothermal method [30]. NiFe₂O₄ has a narrow band gap and semiconductors material in a broad application. NiFe₂O₄ exhibits lower photocatalytic activity because of a fast recombination of photoelectron-hole pairs. The morphological and the particle size were determined using a field-emission scanning electron microscope (FE-SEM, SUAPR55, Germany Zeiss) with energy-disperse X-ray spectroscopy (EDS) [32].

ii. Glucose oxidase immobilization and protein assay

During the glucose immobilization, a similar approach was carried out as in Section (A) above and different chemical additive sodium phosphate buffer solutions were used during the glucose oxidase immobilization and protein assay production. Under certain conditions, the desired photo-biocatalyst NiFe₂O₄ / T / GOx was obtained, as stated by Bradford et al. [33].

Table II below indicates various samples and their efficacy, but it was observed that the photo-biocatalyst NiFe₂O₄ / T / GOx-UV had a higher removal ratio after 90 min.

Based on the two Fenton processes and UV light conditions, it was also shown that UV had a good affinity in the higher removal ratio after 90 min relative to Fenton.

TABLE II: KINETICS DATA OF IC REMOVAL IN THE PRESENCE OF A CATALYST [31].

Samples	Rate constants, k (min ⁻¹)	decolourization ratios after 90 min (%)
NiFe ₂ O ₄ -Fe	0.0034	25.3
NiFe ₂ O ₄ -UV	0.0037	29.7
NiFe ₂ O ₄ /T-Fe	0.0040	32.9
NiFe ₂ O ₄ /TUV	0.0047	41.6
NiFe ₂ O ₄ /T/ GOx-Fe	0.0044	37.6
NiFe ₂ O ₄ /T/ GOx-UV	0.0545	98.6

C. ZnAlLDH-HRP biohybrid Photo-biocatalyst

The essential organic compounds with poisonous, mutagenic and carcinogenic effects are phenols and their degradation derivatives [34]. Several methods have also been used for the depollution of organic compounds (phenols and their derivatives) in aqueous solution, such as filtration, flotation, dilution,

adsorption, physicochemical, biological and photochemical approaches [35].

TABLE III: CATALYTIC PERFORMANCES OF PHENOL DEGRADATION FOR PHOTO-BIOCATALYTIC AND ENZYMATIC PROCESSES [35].

	HRP		ZnAlLDH		ZnAlLDH
	ZnAlLDH + hv		-HRP		- HRP + hv
% Phenol degradation	20	41	25	35	
Degradation type	Photo- degradation	Enzymatic polymerization	Enzymatic polymerization	Mainly photo- degradation	

Layered hydroxide layers (LDHs), Horseradish peroxidase (HRP) and Zinc Aluminum Alloy (ZnAl) were used for the synthesis of the photo-biocatalyst. Under solar irradiation, the ZnAlLDH – HRP biohybrid demonstrates an improvement in efficiency relative to ZnAlLDH.

Even if the HRP is an effective biocatalyst in limited amounts, it is toxic, vulnerable to denaturation and inactivation [36]. ZnCrLDH and its derivative formulations have been identified as good materials for photo-degradation of rhodamine B by Liu et al. [37], methylene blue Chen et al. [38], orange II, 4-chlorophenol Paušová et al. [39], 2-nitrophenol, rhodamine 6G Mohapatra et al. [36] and naphthalene Xia et al. [41], photocatalytic reduction of CO₂ Katsumata Wang et al. [38], water splitting Wang et al. [43] and H₂ production Luo et al. [44] under visible light.

i. Synthesis of photo-biocatalysts

The preparation of ZnCr LDH powder was reported by Gunjekar et al [45] with an addition of NaOH at a certain condition in order to obtain ZnCr LDH nanosheets. Since the O_2 generation caused by visible light occurs primarily on the surface of Zn-Cr-LDH. Exciting progress has been made in the development of new synthesis methods; According to Luo, Song [44] composites with a different mass ratio of ZnCr LDH nanosheets modified g- C_3N_4 were obtained [45].

It is revealed on Table III below that ZnALDH- HRP + hv photo-biocatalyst had mainly influence on the photo-degradation of organic pollutants (phenols). The inclusiveness of +hv has greater effectiveness in the depollution and the removal of organics pollutants. Though the HRP also played a vital role as an anti-recalcitrant pollutant, the UV or UV-vis enhanced the process.

D. GOx/TiO₂/PU Photo-biocatalyst

Efforts have been made in recent years to develop heterogeneous catalytic processes by integrating photo-catalysis with biological systems [46, 47]. Later, a photo-biocatalyst containing glucose oxidase immobilized with TiO₂ / polyurethane was successfully used under UV for the removal of orange acid 7 [15]. Biological processes are inexpensive and environmentally sustainable alternatives for the treatment or the disinfection of wastewater [48].

Hybrid techniques, combined with photochemical and biochemical processes, have recently been widely attractive and shown to be more effective for reducing contaminants as well as reported by Shoabargh et al. [15].

Glucose oxidase (GOx) was immobilized with TiO₂ / polyurethane (PU). This process has been tested for the elimination of Acid Orange 7 (AO7). Fast removal efficiency (> 99%) was achieved after 22 min using a GOx / TiO₂ / PU photo-biocatalyst [15].

i. The Immobilization of TiO₂ nanoparticles on PU

According to Shoabargh and Karimi [11] the immobilization of TiO₂ nanoparticles on PU was conducted using the similar approach as section B and C.

A similar approach was adopted by Bulmuş et al. [28] as Section A(i). However, parameters such as temperature, pH and chemical additives used for the immobilization of TiO₂ NPs on PU using the Sonoplus Ultrasonic Homogenizer HD 2200 (Germany) were different.

ii. Preparing GOx/TiO₂/PU photo-biocatalyst

The batch tests were conducted by Gumy et al. [27]. To obtain a successfully synthesized GOx / TiO₂ / PU photo-biocatalyst, as stated by Shoabargh et al. [15] during the immobilization of GOx to TiO₂ and PU.

Table IV below shows the decolourization process and the first-order rate constants which indicate a higher performance of GOx / TiO₂ / PU / UV.

TABLE IV: COMPARISON OF THE FIRST-ORDER RATE CONSTANT (K) AND COEFFICIENT OF DETERMINATION (R^2) OF VARIOUS DECOLOURIZATION METHODS; [AO7] = 20 MG/L, 25 °C; TiO₂/PU = 0.42 G/G, AND RECYCLING RATE = 5 ML/MIN [15].

Decolourization process	k (min ⁻¹)	R ²
GOx/PU	0.009	0.997
TiO ₂ /PU/UV	0.0203	0.999
GOx/TiO ₂ /PU	0.0360	0.998
GOx/TiO ₂ /UV-without glucose	0.0521	0.998
GOx/TiO ₂ /PU/UV	0.207	0.998

E. Corn silk/TiO₂ photo-biocatalyst

The consideration of UV-Vis during the degradation of a pollutant (dye) using photo-biocatalyst was reported by Nadaroglu et al. [49]. The wavelength of a range of 300 to 900 nm was observed [49].

i. Synthesis of corn silk/TiO₂ photo-biocatalyst

The pioneering work of corn silk/TiO₂ as a photo-biocatalyst, was reported by Nadaroglu et al. [49].

Photo-catalyst material of corn silk – TiO₂ was used and successfully applied to the degradation of Reactive Black 5 (RB5) as a typical azo dye under UV radiation. Quick decolouration capability (> 99 %) was achieved after 30 s using corn silk / TiO₂ photo-biocatalyst [49].

Various plant leaves or seeds can be used with a semiconductor to produce a photo-biocatalyst which may be useful during the removal of organic contaminants. The presence of UV contributes to the greater yield of the removal of organics pollutants.

The fact that the green synthesis biomolecules have a functional group that can be related to the ion metals. During this mixture of metal ions and biomolecules, the metal salt is reduced. This greener synthesis thus gives good sensitivity to its applications in diverse ways and further strengthens its assurance that fewer contaminants can be emitted during its biological applications.



Fig. 1: The photo-degradation from the combination of semiconductors and the biologicals products.

The improvement of the efficiency of the removal of pollutants can be achieved from a combination of metals oxide with an agro-waste.

IV. REUSABILITY OF THE PHOTO-BIOCATALYST

Reusability is one of the most significant considerations in catalytic science. It shows the skill and its usefulness in responding to the repetition of how many circles can be used all over again. This also included interactions between the materials used in the construction of the photo-biocatalyst using ion exchanges or chemical processes that could be responsible for holding the bonds among the compounds that are being used during the synthesis. The reusability of the photo-biocatalyst emphasizes its effectiveness during the enhancement on the removal of pollutants in various aqueous solutions, furthermore, it also covers the cost-effectiveness in the production. It is vital to construct a photo-biocatalyst that can have an affinity of being reusable as many times as possible.

V. CONCLUSION

The physico-chemical properties of photo-biocatalysts are determined by the enhancement of biogenic synthesis contributing to the success in the elimination of many organic contaminants. While the photo-biocatalyst can also be effective, several research studies have shown that its efficacy pertains to the agro-synthesis. During the synthesis of photo-biocatalyst

using metal oxides as agents, the organic compounds can potentially be activated by the aqueous solution. The incorporation of biological products has a larger effect with or without the influence of UV or UV-Vis. However, it showed greater yield with additional solar radiation or visible light.

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7. Synthesis of eco-friendly ZnO-based heterophotocatalysts with enhanced properties under visible light

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Summary

In South Africa, there are various abandoned mines and petroleum activities that are often responsible for the release of organic pollutants in water/wastewater. As soon as the PAHs come into contact with humans, it becomes a problem due to the carcinogenic nature of the PAHs. Various techniques and implementation strategies on how to decontaminate the waters have been proposed, with mainly conventional techniques being implemented. In the present study the release of PAHs from coal tar in various water sources was considered, with solutions to remediate the problems proposed. The disposition of the PAHs in wastewater/water has not yet gained enough attention and thus a heterogeneous photocatalyst was suggested, using various agrowastes such as *moringa oleifera* seed (MO), groundnut shells (GS) and apatite (A) with silver metal (Ag) to functionalize with zinc oxide (ZnO) to obtain a number of different photobiocatalysts. In previous studies it was found that the doping of metals, for example in those found in agrowastes, into metal oxide/semiconductors, can effectively delay the recombination of electrons and narrow the bandgap of the photocatalyst. The metal and non-metal content in MO, GS and A contributed to obtaining various photocatalysts, and MO/GS/A/ZnO/Ag and ZnO/Ag with bandgaps of 1.59 eV and 2.59 eV and absorption spectra of 376 nm and 269 nm respectively were developed. It was found that the application of agrowastes and especially apatite influenced the bandgap of the parental ZnO.

These photocatalysts were tested on the photodegradation of PAHs in three water sources, namely acidic mine drainage, alkaline drainage and sewage wastewater, under solar irradiation using a 250 mL beaker as a photoreactor where samples were taken at various interval periods of 20 min, 40 min and 60 min. It was found that the heterobiophotocatalyst MO/GS/A/ZnO/Ag has a higher photodegradation efficiency of about 70% for the acidic mine drainage and 62% for both the mine drainage and sewage waste water, as compared to 53%, 38 and 44% of the ZnO/Ag alone for the respective acidic mine drainage, alkaline mine drainage and sewage wastewater, when exposed for 60 min to visible light radiation. As the time of reaction increased from 20 min to 60 min, the photodegradation of PAHs also increased, as well as the reactivity of the hydroxyl (OH⁻), resulting in a 20% improvement of remediation for the alkaline drainage and sewage wastewater. It was also noticeable that for the acid mine drainage the removal was almost complete within the first 20 min reaction time and only a slight increase was observed for the longest reaction time.

Synthesis of eco-friendly ZnO-based heterophotocatalysts with enhanced properties under visible light

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Abstract: Heterogeneous photocatalysts have been widely used for the removal of various organic pollutants from wastewater. The main challenge so far resides in the sustainability of the process, with regard to the synthesis and the application under visible light. In this study the precipitated materials from the moringa oleifera seed (MO), groundnut shells (GS) and apatite (A) agrowastes were functionalized with zinc oxide (ZnO) and silver (Ag) solution, to produce novel bioheterophotocatalysts. Various analytical techniques such as scanning electron microscope (SEM), energy-dispersive x-ray spectroscopy (EDS), photoluminescence (PL) and x-ray diffraction (XRD) analyses were used for the characterization of the novel photocatalysts. It was proven that, besides the addition of metals into a semiconductor, agrowastes can also enhance the photocatalytic activity of a ZnO-based photocatalyst. The combination of MO/GS/A/ZnO/Ag in a 1:1:1 ratio resulted in a lower band gap of 1.59 eV, as compared to the band gap of 2.96 eV for ZnO/ Ag. These photocatalysts' efficiency was also tested on the photodegradation of polycyclic aromatic hydrocarbon (PAHs) derived from coal leaching in various water sources such as acidic mine drainage, alkaline mine drainage and sewage wastewater. From MO/GS/A/ZnO/Ag, the removal efficiency was found to be 69.59%, 61.07% and 61.68%, compared to 52.62%, 37.96 and 44.30% using ZnO/Ag in acidic mine drainage, alkaline mine drainage and sewage wastewater for 60 min under solar irradiation.

Keywords: heterogeneous photocatalyst; band gap; acidic mine drainage; alkaline mine drainage

1. Introduction

Wastewater impact on the environment is among the main topics studied in recent years due to the continuous release of organic pollutants from various activities such as oil spills, coking processes and gasification [1]. Most of these pollutants end up in various water sources of different physiochemical properties. The pH of these waters can deeply affect the chemistry of the water in the presence of pollutants derived from the aforementioned petroleum-related activities [2].

A number of studies have been conducted using various metal oxides; however, titanium dioxide (TiO₂) and zinc oxide (ZnO) have been widely used as either semiconductors or nanoparticles in various applications and especially in wastewater treatment [3,4]. These metal oxides have recently been used for the photodegradation of polycyclic aromatic hydrocarbons (PAHs). A study conducted by Gupta and

Gupta [5] investigated the effectiveness of iron oxide (Fe_2O_3) added with oxalic acid on the photodegradation of a selected PAH known as benzo [a]pyrene (B[a]P) with regard to its removal from soil. Also, Marquès, *et al.* [6] used Fe_2O_3 to degrade anthracene, benzo(a)anthracene, chrysene, benzo(a)pyrene, and dibenzo(a,h)anthracene in soil and it was found to be successful.

Most soils contain metals such as iron, zinc, titanium, aluminum, and manganese and these metals can also be found as metal oxides in wastewater. Additionally, oxalic and humic acid are also found, which are important chemicals for decomposing PAHs in soil [7]. Metal oxide can further be synthesized by precipitation, hydrolysis, pyrolysis, hydrothermal, electrodeposition, chemical methods and sol-gel processes [8,9]. However, the sol-gel method has been commonly used due to its adaptability, simplicity, reliability and cost-effectiveness [10,11]. By synthesizing metals oxides their size and morphology can be influenced by manipulating the pH, varying the annealing temperature, the rate of the reaction, and the additives in the medium in order to obtain a readily active metal oxide [8]. Also, pH is vital in the wastes and generates hydroxyl radicals [12].

Some of these metal oxides are semiconductors that have inherent electrical conductivity under UV radiation. Their ability to produce electrons from their valence bands to the conduction bands while the electrons are excited is indicative of the band gap that has made them useful in a wide range of various applications, especially in wastewater treatment [13]. The excited electrons will later react with the dissolved hydroxyl in wastewater/water to degrade the organic compounds. The photocatalytic oxidation reaction occurs when the photogenerated excited electron from the valence band moves to the empty conduction band to produce a photon with energy $h\nu$ [14]. The presence of oxygen in the material can interact with the material (metal oxide) to form hydrogen bonds [15].

Figure. 1 is a schematic representation of the process where the photons, with energy $h\nu$, are radiated on the material, creating a band gap that is lower than the excitation energy to ensure the delay of the electron recombination.

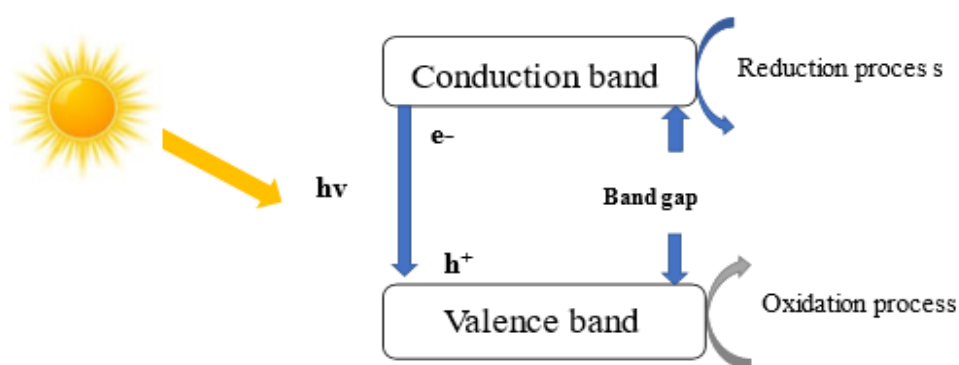


Figure 1. Schematic representation of the photocatalysis process.

Conventional methods like coagulation, flocculation, sedimentation, adsorption and membrane processes have been widely used for the removal of organic pollutants from wastewater [16]. The limitations of these conventional methods such as production costs and the release of by-products such as carbon dioxide and methane gas have made them less applicable. Therefore photocatalysis, bioremediation, biosorption and photodegradation have been introduced to assist in removing the organic pollutants in wastewater [17]. Photocatalysts have been proven to be the best candidates for the degradation of organic pollutants. Their performance can be further improved by introducing a metal which contributes to a delay of electron recombination holes as well as lowering the band gap to obtain a spontaneous photodegradation [13,18].

Wastewater from related mine activities is alarming; however acidic mine drainage and alkaline mine drainage are outcomes that have not been given attention with regard to organic pollutants (PAHs). The decomposition of PAHs in soil has received more attention compared to PAHs in water sources. Therefore, this study focuses on the release of compounds from mining and other effluents that introduce PAHs into various water bodies. Since metals have been proven to delay the electron recombination hole and narrow the bandgap, moringa oleifera seed, groundnut shells and apatite agrowastes have been introduced to replace to enhance the photocatalytic activity of ZnO. In this work, the metals and organic compounds and especially strontium and oxygen from the elementary analysis will be tested on the photodegradation of PAHs in various water sources such as acidic mine drainage, alkaline drainage and sewage wastewater.

2. Material and methods

In this study, chemicals were purchased from Rochelle Chemicals & Lab Equipment, including zinc acetate dihydrate ($\text{Zn}(\text{Ac})_2 \cdot 2\text{H}_2\text{O}$, 98%) and silver nitrate (AgNO_3 , 99.9%). Acidic mine drainage was collected from Witbank, together with alkaline mine drainage from Middleburg, sewage wastewater from the Cape Town municipality and coal tar from Newcastle in KwaZulu-Natal, all in South Africa.

2.1. Synthesis of zinc oxide semiconductor

A mass of 3 g $\text{Zn}(\text{Ac})_2 \cdot 2\text{H}_2\text{O}$ was powdered, using a mortar and pestle and it was calcined for 4 hours at 350°C in a furnace.

2.2. Preparation of moringa oleifera (MO), groundnut shells (GS), and appetite (A)

Biomasses such as *moringa oleifera* seed, groundnut shells and apatite derived from cow bones were sourced at a nearby market in Cape Town, South Africa. Each biomass was ground using a grinder to obtain particles at a size of $100 > 150 \mu\text{m}$ and was washed with deionised water more than 3 times using a centrifuge to remove any impurities. The collected materials were then dried for 24 hours at a temperature of 60°C using an oven.

2.3. Synthesis of ZnO/Ag and MO/GS/A/ZnO/Ag heterogeneous photocatalysts

A mass of 0.2 g of $\text{Zn}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 2\text{H}_2\text{O}$ and 0.1 g of Ag were mixed into a volume of 50 mL of deionised water. The solution of ZnO and Ag was stirred to ensure a homogenous mixture and 1 g each of the selected agrowaste MO, GS and A was added to the mixture. The prepared volume of 2M of NaOH was used to adjust the pH until a pH of 12 was obtained. The overall mixture was stirred at 250 rpm for 2 h. After completing this process, it was centrifuged for 20 min at 6000 rpm whereby the precipitants were obtained, and the material was dried in an oven at a temperature of 80 °C for 24 h.

2.4. Photodegradation of PAHs in various water sources

5 g of coal tar containing a PAH concentration of 2916.47 mg/L was analyzed using the Gas Chromatography Thermo Scientific (TSQ 8000) (Cape Town, South Africa) Triple Quadrupole MS technique. The leaching of 5 g into 300 mL of acidic mine drainage, alkaline drainage or sewage wastewater respectively for 8 weeks was found to be 19.2553 mg/L, 1.6154 mg/L and 1.8125 mg/L. The mass of 2.5 g of MO/GS/A/ZnO/Ag or ZnO/Ag was considerable in the leachate of 300 mL under solar irradiation in 20 min, 40 min and 60 min under solar irradiation. Therefore, Eq 1, 2 and 3 represent reactions that may occur to aid degrading of PAHs in water sources.



Although there are various scavengers that are available when adding a catalyst to a reaction, hydroxyl and superoxide are widely recognized as effective oxidizing agents for organic pollutants. However, hydroxyl is produced with or without a catalyst, even in spilling of water, and it is also highly reactive with organic pollutants [3].

The photodegradation of PAHs is dependent on various parameters such as the physiochemistry of the water (pH, dissolved organic carbon, ionic strength, temperature [19]), the properties of the photocatalyst (narrow band-gap, delay of the electron recombination hole [20]) and solar irradiation [21,22].

3. Results and discussions

3.1 Characterisations

3.1.1 UV-Vis adsorption spectroscopy

UV-Vis adsorption spectrometry was used to determine the optical properties of the synthesized heterophotocatalysts. The adsorption spectra of the MO/GS/A/Ag/ZnO heterogeneous photocatalyst had the lowest wavelength at 376 nm, in comparison to the ZnO/Ag (269 nm) and ZnO (339 nm) respectively, calculated according to the method described by Mukwevho *et al.*, [23]. The broad peaks observed in the MO/GS/A/ZnO/Ag can be attributed to the combination of agrowastes. The optical properties of the material on their band gap is represented in Table 2.

The optical band gap value of the synthesized material can be obtained from the optical absorption spectra by extrapolating the straight line of $(h\nu \alpha)$ the plot versus the energy $(h\nu)$, based on the equation (4), (5) and (6).

$$\alpha = A(h\nu - E_g)^n \quad (4)$$

$$(h\nu \alpha) = A(h\nu - E_g)^{1/2} \quad (5)$$

$$(E_g) = \frac{hc}{\lambda} = \frac{1250}{\lambda} \quad (6)$$

Where α is the absorption coefficient, h is Planck's constant, E_g is the absorption band gap, A is constant and n depends on the type of transition and n may have values $\frac{1}{2}$ (allowed direct), 2 (allowed indirect), $\frac{3}{2}$ (nonradiative direct) and 3 (nonradiative indirect transition). A Tauc plot (graph between $(\alpha h\nu)^2$ vs energy) was used to calculate the band gap energies of the synthesized heterogeneous photocatalysts.

In this study, various agrowastes were synthesized to produce various heterogeneous photocatalysts. In Figure 2 the absorption spectra of ZnO (376 nm), ZnO/Ag (339 nm) and MO/GS/A/ZnO/Ag (269 nm) are shown. It was found that ZnO had a band gap of 3.35 eV, obtained from the Tauc plot, whilst the ZnO/Ag had a band gap of 2.96 eV, with the combined agrowastes and semiconductors MO/GS/A/ZnO/Ag having a narrower band gap of 1.59 eV.

To investigate the influence of the band gap, the following materials, ZnO/Ag (2.96 eV), ZnO/A (2.15 eV), ZnO/GS (2.51 eV) and ZnO/MO (2.74 eV), and the parental ZnO (3.35 eV) were obtained, and it was indicated from the parental ZnO that the apatite was highly effective in narrowing the bandgap followed by groundnut shells and moringa oleifera seed. Various factors such as impurities of the material, temperature can influence the property of the material [24].

This study agrees with Yu, Zhang, *et al.* [25] who reported doping of various elements results in narrowing the band gap. According to Fu *et al.* [26], earth metals are more effective compared to noble metals in enhancing photocatalytic activity. Various studies [13, 27-29] have been conducted and it was proven that the dopant of strontium (Sr) which is rare earth metal has a high photocatalytic activity which can be determined under the visible spectrum [30]. In this study, Sr was highly concentrated in apatite followed by groundnut shells and moringa oleifera presented in Table 2. The metals in these agrowastes are provided to contribute a high photocatalytic activity to the parental ZnO [4,31]. Table 1 shows the synthesized materials and their band gaps.

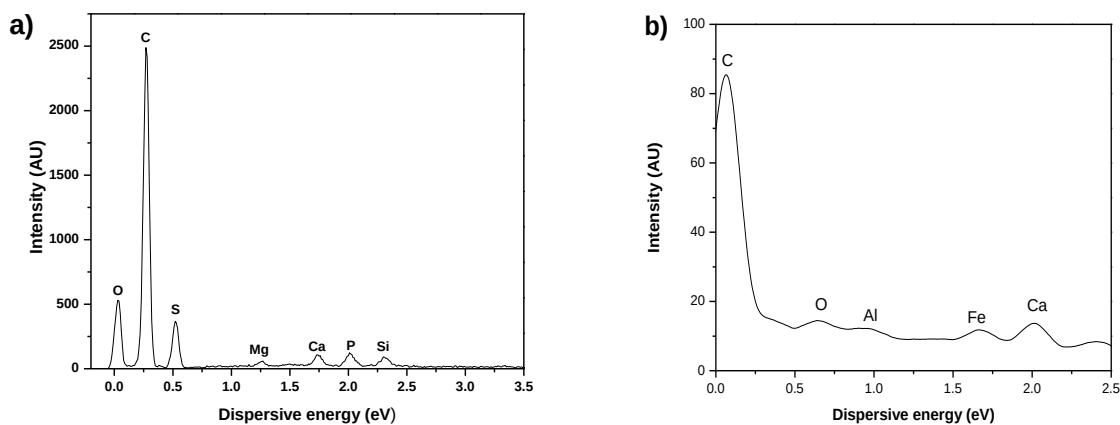
Table 1. The band gaps were obtained for various combinations in the production of a suitable photocatalyst.

Photocatalysts	The bandgap (eV)
ZnO/Ag/MO/GS/A	1.59
ZnO/MO/A/GS	1.63
ZnO/A	2.15
ZnO/MO/A	2.49
ZnO/GS	2.51
ZnO/Ag/A	2.59
ZnO/Ag/GS	2.71
ZnO/MO	2.74
ZnO/Ag/MO	2.80
ZnO/MO/GS	2.85
ZnO/Ag	2.96
ZnO	3.35 (Parental)

3.1.2 Energy-dispersive X-ray spectroscopy

Energy-dispersive X-ray spectroscopy (EDS) (Nova NanoSEM using an Oxford X-max 20mm² detector and INCA software) was used to determine the elemental composition of MO, GS and A presented in Figure 2. The presence of the oxygen element in these materials and the synthesized ZnO from MO, GS, A and Ag will therefore best explain the delay of the electron recombination holes [32]. Figure 2 (e) MO/GS/A/ZnO/Ag show a higher oxygen concentration as compared to ZnO/Ag. In the raw material, the sharp peak in Figure 2 (a) MO is shown to have a high oxygen content, followed by Figure 2 (c) A and Figure 2 (b) GS.

The oxygen content in the raw material and the synthesized material can best be explained as obtaining a delay in the electrons recombination hole and that can be observed in the photoluminescence (PL).



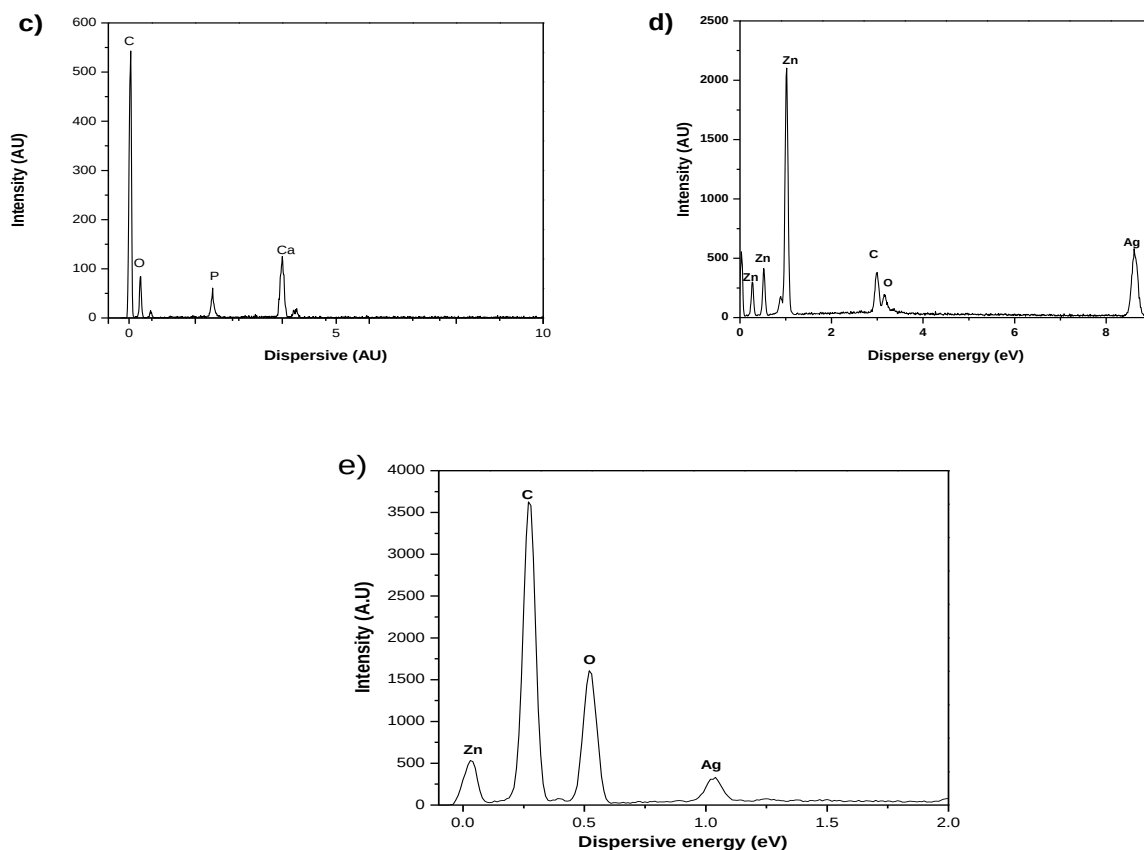


Figure 2: EDS for raw material: a) MO; b) GS; c) A and synthesized material; d) ZnO/Ag; e) MO/GS/A/ZnO/Ag

3.1.3 PL spectra

Photoluminescence was used and recorded on a PerkinElmer LS55 Luminescence Spectrometer. The excitation wavelength (λ) of 310 nm for the raw materials (MO, GS and A) and 300 nm for the synthesized materials (MO/GS/A/ZnO/Ag) and (ZnO/Ag) were observed. Figure 3 shows the PL emission spectra for both the raw materials and the synthesized material at room temperature.

As observed in Figure 3(a) MO provided a broader shoulder sharp peak with a higher PL intensity followed by GS and A. Apatite was observed to have a lower PL intensity which resulted in a higher photoactivity. According to Ji, *et al.* [33], the doping of metals was found to reduce the PL intensity and increase the photocatalytic activity, as shown in Figure 3: MO/GS/A/ZnO/Ag as compared to ZnO/Ag. The incorporation of agrowastes combined resulted in a decrease in PL intensity [34].

It also shows that a higher oxygen content in MO/GS/A/ZnO/Ag is also responsible to influence the electron recombination. This also causes a delay in the recombination of the electrons [35]. This mostly occurs when the electrons are in contact with the material and the oxygen in that material happens to trap the produced electrons from the visible light (solar irradiation) [36].

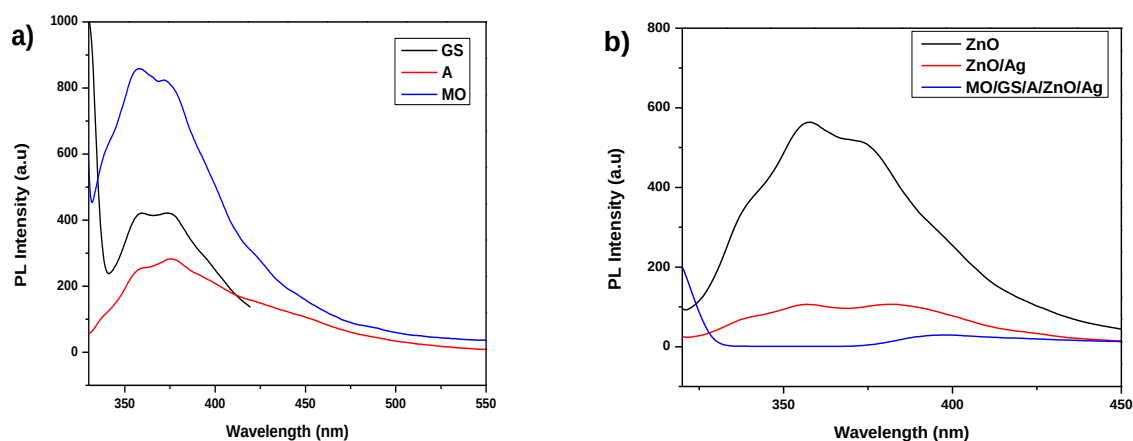


Figure 3: Optical properties of the MO/GS/A/ ZnO/Ag heterogeneous photocatalyst and ZnO/Ag photocatalyst (a) PL of raw materials, (b) PL of the synthesized material.

3.1.4 Scanning electron microscope

A scanning electron microscope NovaNano SEM and the Tescan MIRA3 RISE SEM was used to determine the structure and the morphology of the material presented in Figure 4. MO showed the plant cells that constituted fairy pores and GS showed the fibres (stems) ,whereas A shows a smooth structure derived from lipid compounds known as phospholipids. The image of the heterogeneous photocatalyst MO/GS/A/ZnO/Ag shows tissue cells (stem plant) and ZnO/Ag shows nanocrystals.

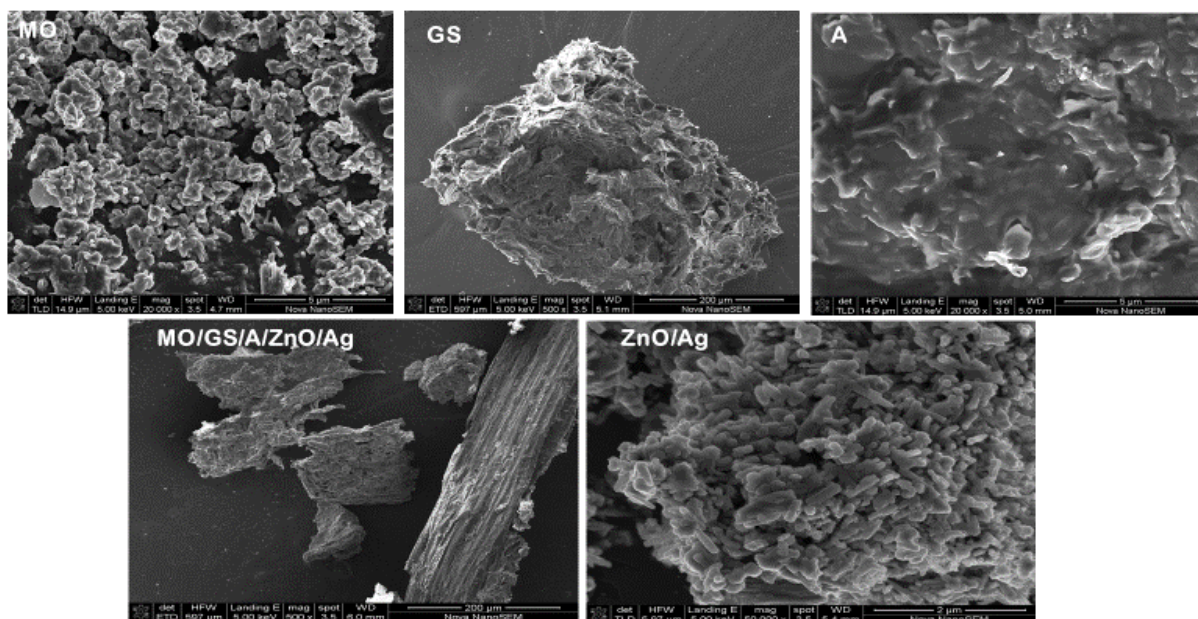


Figure 4: SEM images of the raw materials (MO, GS and A) and synthesized materials (MO/GS/A/ZnO/Ag and ZnO/Ag)

3.1.5 X-ray diffraction

X-ray diffraction (XRD) Powder XRD measurements were recorded on an Analytical XPERT-PRO diffractometer, using Ni filtered CuK α radiation ($\lambda = 1.5406 \text{ \AA}$) at 45 kV/40 mA which was used to determine the crystal structure of the materials. The diffraction measurements in Figure 5 were collected at room temperature in a Bragg-Brentano geometry. The XRD of MO/GS/A/ZnO/Ag and ZnO/Ag did not completely corroborate with the hexagonal structure of the raw reference pattern: ZnO, 00-036-1451 and Ag, 00-004-0783. Since the studied ZnO and Ag were used in combination with the biomasses, the impurities could have interfered with or influenced the diffraction peak.

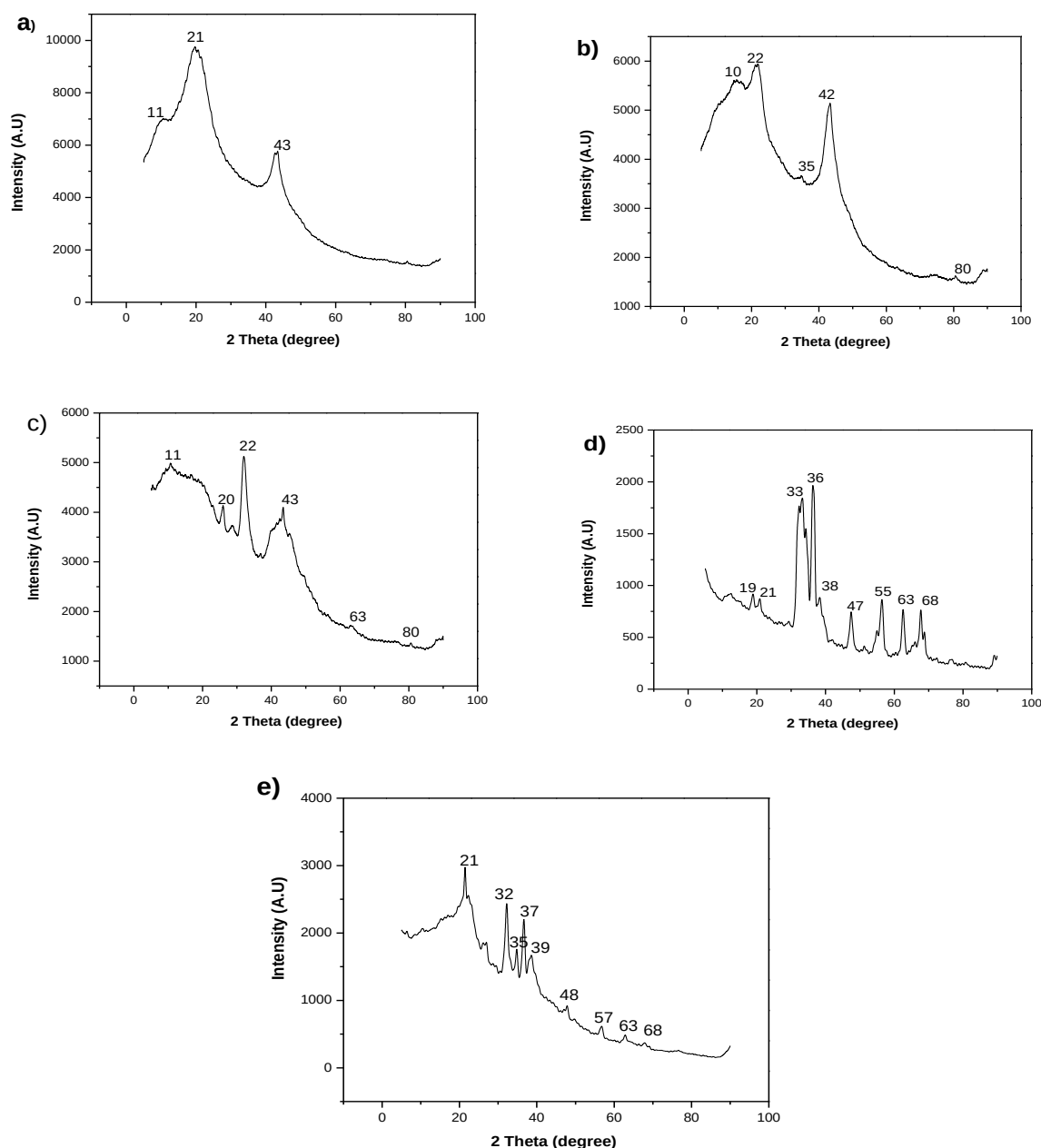


Figure 5: XRD spectra of raw material a) MO; b) GS; c) A and synthesized material d) MO/GS/A/ZnO/Ag; e) ZnO/Ag

The synthesis of MO/GS/A/ZnO/Ag was found to be the best candidate due to its narrow band gap (1.59 eV) with absorption spectra of 376 nm followed by ZnO/Ag with a band gap of 2.96 eV and absorption spectra of 269 nm, while the parental ZnO band gap was 3.35 eV with absorption spectra of 339 nm. Based on the synthesis of these complex heterogeneous photocatalysts, ZnO/MO (2.74 eV), ZnO/GS (2.51 eV), ZnO/A (2.15 eV), and the parental ZnO (3.35 eV), it was found that A was effective compared to others agrowastes in obtaining a narrow band gap and their absorbance in the visible region.

Various studies [37-40] have reported that doping of metals can potentially enhance the photocatalytic process and achieve a spontaneous photodegradation outcome. In this study, the elementary analysis of the existing metals in apatite, groundnut shells and moringa oleifera seed using Thermo ICap6300 ICP-AES is represented in Table 2.

Table 2: Raw material elementary analysis using ICP-MS

Elements	Rare metals (ug/kg)		
	Apatite	Groundnut shells	Moringa oleifera seed
Boron (B)	4886	14040	3345
Aluminum (Al)	286978	1379257	335251
Vanadium (V)	857	2464	972
Chromium (Cr)	47821	5375	13577
Manganese (Mn)	29085	49766	13797
Iron (Fe)	3305754	1626773	624167
Cobalt (Co)	749	491	179
Nickel (Ni)	12202	2585	2437
Copper (Cu)	14339	9104	10354
Zinc (Zn)	112006	81561	54864
Arsenic (As)	612	249	79
Selenium (Se)	71	50	801
Strontium (Sr)	387273	31469	22730
Molybdenum (Mo)	579	261	269
Cadmium (Cd)	67	30	54
Tin (Sn)	3083	593	232
Antimony (Sb)	125	21	19
Barium (Ba)	61927	51511	11780
Mercury (Hg)	13	13	10
Lead (Pb)	6433	1479	947
Elements	Metals (mg/g)		
	Apatite	Groundnut shells	Moringa oleifera seed
Sodium (Na)	4435644	80587	30317
Magnesium (Mg)	3245487	1414007	1352569
Silicon (Si)	115349	302102	398638
Phosphorous (P)	108054240	1083471	7167605
Potassium (K)	343351	2654548	777148
Calcium (Ca)	221203248	4871463	3061091
Elements	Non-metals (%)		
	Apatite	Groundnut shells	Moringa oleifera seed
Nitrogen (N)	3.72	1.11	4.36
Carbon (C)	20.01	44.58	54.18
Hydrogen (H)	4.41	8.59	10.41
Sulphur (S)	1.65	2.93	2.36

3.2 Photodegradation of PAHs in various water sources

Table 3 illustrates the decomposition of PAHs from coal tar using Gas Chromatography-Mass Spectrometry (GC–MS) with a Thermo Scientific (TSQ 8000) (Cape Town, South Africa) Triple Quadrupole MS.

Table 3: Concentration of PAHs concentration in coal tar at room temperature

PAHs (pollutants)	Concentration (mg/L)
NAP	788
ACY	356
ACE	18
FL	327
PHE	632
ANT	245
FLU	395
PYR	266
BaA	91
CHY	126
BbF	75
Blkf	71
BaP	92
DahA	56
IP	8
Bghip	21

The photodegradation of PAHs using a MO/GS/A/ZnO/A and ZnO/A synthesized photocatalyst was tested in acidic mine drainage, alkaline mine drainage and sewage wastewater. It was undertaken in a 250 mL beaker under solar irradiation. After the photodegradation, a 0.45 µm syringe filtered PDVP (0.45 µm) was used to collect each water sample at 20 min, 40 min and 60 min. The samples were analyzed using GC-MS and the data representation is in Tables 4, 5 and 6 and their removal efficiency using Eq. 7 is also represented in Table 7.

Tables 4, 5 and 6 represent the photodegradation of PAHs in acidic mine drainage, alkaline mine drainage and sewage wastewater.

$$\text{PAHs removal efficiency (\%)} = \frac{C_o - C_t}{C_o} \times 100 \% \quad (7)$$

The initial and residual concentrations are given a symbol C_o and C_t that is related to the contact time (t) between the pollutants and the catalyst under solar irradiation. The photodegradation of PAHs was better in acidic mine drainage followed by sewage wastewater and alkaline mine drainage under solar irradiation over time. It was observed that the lowest PAH compounds of 2 to 3 rings such as naphthalene, anthracene, phenanthrene and phenalene of a lower molecular weight were rapidly degraded as time increased [41]. These PAHs are highly volatile, therefore the application of solar irradiation was able to destabilize them from their normal condition.

MO/GS/A/ZnO/Ag delay of electron recombination and its lower band gap had an influence on the photodegradation of the three water sources over time under solar irradiation. Radicals such as $\bullet\text{OH}$ and $\bullet\text{O}_2^-$ from the material [42] and the morphology [43] strongly contributed to the photodegradation of PAHs.

visible light

Table 5: Photodegradation of PAHs in acidic mine drainage

PAHs	Initial concentration	Catalyst	20 min	40 min	60 min	Catalyst	20 min	40 min	60 min
NAP	0.0031	MO/GS/A/ZnO/Ag	0.0014	0.0011	0.0012	ZnO/Ag	0.0015	0.0013	0.0013
ACY	0.1302		0.0967	0.1068	0.0931		0.1105	0.0097	0.1001
ACE	0		0	0	0		0	0	0
FL	0		0	0	0		0	0	0
PHE	0.0181		0.0067	0.0063	0.0057		0.0072	0.0084	0.0070
ANT	18.9847		5.8110	5.7913	5.7010		9.0047	9.1091	8.9122
FLU	0.0020		0.0015	0.0012	0.0011		0.0016	0.0015	0.0015
PYR	0		0	0	0		0	0	0
BaA	0.1114		0.0503	0.0510	0.0496		0.1018	0.0981	0.0974
CHY	0.0012		0.0008	0.0001	0.0001		0.0009	0.0002	0.0002
BbF	0		0	0	0		0	0	0
Blkf	0		0	0	0		0	0	0
BaP	0.0046		0.0037	0.0026	0.0023		0.0039	0.0030	0.0031
DahA	0		0	0	0		0	0	0
IP	0		0	0	0		0	0	0

visible light

Bghip	0		0	0	0		0	0	0
PAHs photodegradation	19.2553		5.9856	5.9604	5.8540		9.2321	9.2313	9.1228

Table 6: Photodegradation of PAHs in alkaline mine drainage

PAHs	Initial concentration	Catalyst	20 min	40 min	60 min	Catalyst	20 min	40 min	60 min
NAP	0.7615	MO/GS/A/ZnO/Ag	0.5005	0.5013	0.3780	ZnO/Ag	0.5253	0.5102	0.4955
ACY	0.2596		0.0419	0.0291	0.0210		0.1974	0.0976	0.1003
ACE	0.0020		0.0010	0.0001	0.0001		0.0014	0.0012	0.0012
FL	0.0030		0.0009	0.0010	0.0009		0.0019	0.0012	0.0011
PHE	0.0447		0.0297	0.0270	0.0261		0.0371	0.0318	0.0211
ANT	0.5388		0.2119	0.2005	0.2004		0.4724	0.3816	0.3799
FLU	0.0039		0.0021	0.0016	0.0011		0.0026	0.0025	0.0017
PYR	0.0019		0.0013	0.0012	0.0012		0.0017	0.0016	0.0014
BaA	0		0	0	0		0	0	0
CHY	0		0	0	0		0	0	0
BbF	0		0	0	0		0	0	0

visible light

Blkf	0		0	0	0		0	0	0
BaP	0		0	0	0		0	0	0
DahA	0		0	0	0		0	0	0
IP	0		0	0	0		0	0	0
Bghip	0		0	0	0		0	0	0
PAHs photodegradation	1.6154		0.7893	0.7618	0.6288		1.2398	1.0277	1,0022

Table 7: Photodegradation of PAHs sewage wastewater

PAHs	Initial concentration	Catalyst	20 min	40 min	60 min	Catalyst	20 min	40 min	60 min
NAP	0.0069	MO/GS/A/ZnO/Ag	0.0045	0.0041	0.0032	ZnO/Ag	0.0051	0.0051	0.0044
ACY	0.0489		0.0308	0.0261	0.0247		0.0391	0.0265	0.0271
ACE	0		0	0	0		0	0	0
FL	0.009		0.0043	0.0042	0.0009		0.0050	0.0049	0.0045
PHE	0.0961		0.0223	0.0219	0.0193		0.0767	0.0743	0.0731
ANT	0.1758		0.1202	0.1125	0.1083		0.1411	0.113	0.0976
FLU	0.1706		0.1052	0.1015	0.1004		0.1491	0.1205	0.1073
PYR	0.1389		0.0119	0.0110	0.0109		0.1196	0.1174	0.0843
BaA	0.1888		0.1329	0.1171	0.1066		0.1046	0.1021	0.0981

visible light

CHY	0.1170		0.0716	0.0673	0.0642		0.1002	0.0901	0.0860
BbF	0.2216		0.1222	0.1217	0.0898		0.1929	0.1001	0.1001
Blkf	0.1563		0.0593	0.0875	0.0981		0.1052	0.0909	0.0998
BaP	0.2185		0.1005	0.1001	0.0193		0.1852	0.1087	0.1005
DahA	0.1278		0.0110	0.0101	0.0095		0.1108	0.0897	0.0655
IP	0.0345		0.0051	0.0037	0.0038		0.0195	0.0162	0.0171
Bghip	0.1018		0.0530	0.0429	0.0275		0.0824	0.0487	0.0441
PAHs photodegradation	1.8125		0.8548	0.8317	0.6946		1.3465	1.0965	1.0095

The higher oxygen content in the material traps the electrons and prevents them from recombination [44]. The modification of the material MO/GS/A/ZnO/Ag was found to provide a low PL intensity which contributed to poorer recombination rates of photo-induced charge carriers as compared to ZnO/Ag [23,35,45]. The removal efficiency was better in acidic mine drainage, followed by alkaline mine drainage and sewage wastewater over time under solar irradiation.

Table 8: Removal efficiency of PAHs in contact time

Water sources	Removal efficiency (%) MO/GS/A/ZnO/Ag			Removal efficiency (%) ZnO/Ag		
	20 min	40 min	60 min	20 min	40 min	60 min
Acidic mine drainage	68.91	69.05	69.59	52.05	52.06	52.62
Alkaline mine drainage	51.14	52.84	61.07	23.25	36.38	37.96
Sewage wastewater	52.84	54.11	61.68	25.71	39.50	44.30

Since oxygen is an anion and electron acceptor, it was highly responsive to attracting electrons during the electron-carrier charge. The study found that the application of a biological method in combination with various agrowastes for the synthesis of heterogeneous photocatalysts contributed to narrowing the band gap in agreement with literature studies [25,46]. MO was an effective material due to its high hydrocarbon content and slightly lower metal content enabling the synthesis of an elastic, strong, high resistance and viable material [47]. Besides the oxygen molecules, the impurities of the material can also deflect electrons and reduce the photocatalytic activity of the material by having a lower photon efficiency. The presence of OH⁻ and O₂ in the environment or (material) can easily generate radicals such as •O₂⁻ and •OH that will prevent the recombination of h⁺ and e⁻.

A study conducted by Tong *et al.* [48] reported that the narrow band gap of a photocatalyst resulted in rapid recombination of electrons and holes which restricted the photocatalytic efficiency. However, this study had contrary findings, in agreement with Guo *et al.* [20], that MO/GS/A/ZnO/ZnO provided a delay in recombination of electron hole-pairs and narrow band gap. Its application in the photodegradation of PAHs in different water sources under solar irradiation drastically improved over time. The application of this heterogeneous photocatalyst generated high photons, also by being able to produce reactive scavengers in comparison to ZnO/Ag. In this study, it was found that agrowastes that contain various metals (including Sr which is reported to have high photocatalytic activity and can be naturally found in a few agrowastes) obtained a higher removal efficiency than metals without agrowastes.

4. Conclusion

The application of agrowastes was found to be a better candidate as compared to metals in obtaining a higher removal efficiency. The synthesis of complex heterogeneous photocatalysts resulted in narrowing the band gap and its oxygen content resulted in retarding electron recombination. Free energy in the form of solar irradiation was effective in destabilizing the aromatic ring in PAHs in water sources. The superoxide and hydroxides were also responsible for destabilizing the aromatic rings from the PAHs. Since PAHs were highly concentrated in acidic mine drainage due to the water physiochemistry but mostly pH and total organic carbon, removal efficiency was also favoured. Time was also observed to be an important factor in obtaining an acceptable photodegradation. The heterogeneous photocatalyst MO/GS/A/ZnO/Ag was found to be effective as compared to ZnO/Ag. Their application in wastewater treatment was evaluated and it was proven that the synthesized MO/GS/A/ZnO/Ag was highly effective under solar irradiation, with a removal efficiency of 69.59%, 61.07% and 61.68% using MO/GS/A/ZnO/Ag as compared to 52.62%, 37.96%, and 44.30% using ZnO/Ag. The free energy solar irradiation was effective for the photodegradation of PAHs. Since various metals can improve photocatalytic activity and photodegradation, the metal contents and organic content in various agrowastes can alternatively be suggested as a novel application due to their metals content, abundancy, availability and cost-effectiveness in future.

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8. Photodegradation of Polycyclic Aromatic Hydrocarbon from Coal Tar Using a Heterogeneous Photocatalyst on a Flat-bed Photoreactor

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Water, Air, & Soil Pollution

Summary

The photodegradation of polycyclic aromatic hydrocarbons (PAHs) was investigated but was conducted with a self-made photoreactor, operating under solar irradiation. The time interval for sampling was at 20 min, 40 min and 60 min reaction time. PAHs such as ACE, FL, BbF, DahA, IP and Bghip in acidic mine drainage, BaA, CHY, BbF, BbF, Blkf, BaP, DahA, IP, Bghip in alkaline mine drainage and ACE in sewage wastewater were not observed in the leaching process. Beside ACE, most of the PAHs represented in the Figure below were observed in the sewage wastewater

The effectiveness of a flat-bed photoreactor was tested and it was found that 64%, 55%, and 58% degradation occurred with the flat-bed photoreactor, whilst only 53%, 33%, and 39%, without the flat-bed reactor for photodegradation efficiency were obtained for the acidic mine drainage, alkaline mine drainage and sewage wastewater in 60 min under solar irradiation. The PAHs can further be destabilized under the influence of heat/temperature, and the lower molecular weight PAHs were observed to be completely degraded, as compared to the heavy molecular weight PAHs. It was indicated that the flat-bed photoreactor was effective under solar irradiation to reduce by at least about 50% of the toxic carcinogenic pollutants in the various water sources over time. The water physiochemistry, such as total organic carbon, pH and various others contributed to the photodegradation. As time increased, the photodegradation efficiency of the PAHs also increased.. The photodegradation of PAHs was also influenced by environmental issues such as solar irradiation. Higher removal efficiency was obtained at 60 min under solar irradiation and various radicals were responsible for the photodegradation of PAHs; however, hydroxyl was predominant among $\text{H}_2\text{O}^\bullet$ and $\text{O}_2^\bullet$ radicals.

Article

Photodegradation of Polycyclic Aromatic Hydrocarbon from Coal Tar Using a Heterogeneous Photocatalyst on a Flat-bed Photoreactor

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Abstract

Polycyclic aromatic hydrocarbons (PAHs) have been the most alarming organic pollutants derived from petroleum industries, mining and oil splitting. Their deposition to the environment has caused a severe threat to humans, resulting in a quest for an effective technique for its degradation from the environment. The presence of PAHs is unfriendly to the environment and humans, due to their toxicity potential when they are consumed. A number of photocatalysts were manufactured from different agrowaste namely *moringa oleifera* seed (MO), groundnut shells (GS) and apatite (A) aiming to reduce the bandgap of the parental zinc oxide that was obtained in the study to be 3.35 eV. These photocatalysts properties were investigated using analytical techniques such as PL, UV, SEM, XRD, EDS, GC-MS and FTIR. MO/GS/A/ZnO/Ag and ZnO/Ag were selected to participate in the photodegradation of polycyclic aromatic hydrocarbons on a self-made photoreactor. Photodegradation efficiencies of 99.72%, 97.04% and 98.21% using MO/GS/A/ZnO/Ag as compared to 89.48%, 94.35% and 92.44% using ZnO/Ag were obtained at 60 min under solar irradiation in acidic mine drainage, alkaline mine drainage and sewage. The functional groups such as amine using MO/GS/A/ZnO/Ag and carboxylic acid group using ZnO/Ag were highly involved in the photodegradation of PAHs for the three water sources even during the presence of scavenger radicals such as superoxides and hydroxyl. The combinations of the agrowastes (MO/GS/A) in narrowing the bandgap and retarding the recombination of the electrons were effective in achieving spontaneous photodegradation and relatively so in acidic mine drainage over time. The adsorption and kinetic isotherm that mostly described the study was Freundlich and pseudo-first order.

Keywords: Photodegradation; photocatalyst; wastewater; acidic mine drainage; alkaline mine drainage

1 Introduction

Water pollution is caused by various activities such as petroleum, textile, mining, and dumping of wastes that release pollutants and travel to the environment and into water sources (Ali *et al.*, 2019). Wastewater has become an issue around the world and common organic pollutants such as polycyclic aromatic hydrocarbons (PAHs) derived from various industries but mostly the petroleum industry (Haripriyan *et al.*, 2022) have been found to damage the environment. The increase in industrialization and urbanization has led to a continuous PAH release (Obotey Ezugbe and Rathilal, 2020) and also negatively impacted the ecosystem (Vickers, 2017). Coal is a source of energy and millions of barrels are produced and consumed every year (Al-Sabahi *et al.*, 2017) which also contributes to the release of a vast volume of PAH pollutants (Nacheva and Sotelo, 2016). In addition, abandoned mines also highly contribute to the release of PAHs (Mhlongo and Amponsah-Dacosta, 2016).

The inherent properties of PAH are organic pollutants that are persistent in the environment (Adeniji *et al.*, 2019, Zhang *et al.*, 2022) and can also cause carcinogenesis, teratogenesis and mutagenesis (Allan *et al.*, 2016, Zhang *et al.*, 2022). The presence of PAHs in the aquatic environment is influenced by metabolism and photo-oxidation. They are sometimes concentrated in the environment, hence the alleviation of these pollutants from the environment is necessary due to their toxicity. These organic pollutants have the potential to impair the aquatic ecosystem by causing tumours and destabilizing the reproduction, development, and immunity systems of the biota and humans (Dong *et al.*, 2012). The colourless, white or pale-yellow PAHs are pervasive and persistent in the environment. They affect the organisms through inhalation, dermal contact, and ingestion (Abdel-Shafy and Mansour, 2016). Most of the PAHs are fluorescent which poses challenges in the environment by exhibiting wavelength characteristics in presence of solar radiation or light sources. The molecules within the PAHs can absorb the light rays, which will therefore make them resist the degradation. Each ring structure from these PAHs consists of a unique UV spectrum (Abdel-Shafy and Mansour, 2016).

Naphthalene is the first PAH among 16 PAH found in various waters and also reported to be the most unwelcome and threatening PAH by the Environmental Protection Agency (EPA) and International Agency for Research on Cancer (IARC) (Farhadian *et al.*, 2016). PAHs are found in wastewater/water (Özdemir, 2020) at the concentration range of (0.9-1.547 ng/g) (Johnson *et al.*, 2002) which are undesirable due to their aromatic fused rings that make them toxic. The most commonly PAHs found in wastewater/water are naphthalene (NAP), phenanthrene (PHE), fluoranthene (FLT), anthracene (Ant), pyrene (PYR), fluorine (FLU), benzo(b)fluoranthene, 2-methyl naphthalene, benzo(k)fluoranthene, 2-methyl naphthalene, benzo(a)pyrene, acenaphthylene (ACY), indeno(1,2,3-cd)pyrene, acenaphthene, benzo(a)anthracene, dibenzo(ah)-anthracene (DahA), chrysene and benzo(g,h,i)perylene (Torretta, 2012).

Naphthalene (NAP), acenaphthene, phenanthrene (PHE), and fluorine (FLU) are the PAHs found in municipal sewage wastewater as reported by Katsou *et al.* (2018). A study by Katsou *et al.* (2018) has reported that the pre-treatment and the primary treatment are between the ranges of 40 % and 60%. The secondary treatment, which is biologically the most preferred method has a broad range of 10 % to 90 % of removal efficiency (Katsou *et al.*, 2018). There is a need for future consideration to suggest a tertiary treatment to promote ongoing PAH removal (Gaurav *et al.*, 2021). The United States Environmental Protection Agency (USEPA) reported 16 PAHs in wastewater in 1983 (Patel *et al.*, 2020) which are presented in Table 1. Their presence in the environment brings complications and health concerns that have been addressed. It is important to remove PAH pollutants completely from various water sources and to prevent them settling in the environment or wastewater. These PAHs are recalcitrant and their presence in wastewater/water reduces the solubility and increases the lipophilicity of water (Patel *et al.*, 2020).

Table 1: Physicochemical properties of 16 polycyclic aromatic hydrocarbons (Patel *et al.*, 2020).

Name	Formula	Molecular weight (g/mol)	Solubility in water (g/mL)
Naphthalene	C ₁₀ H ₈	128.17	31
Acenaphthene	C ₁₂ H ₁₀	154.21	3.8
Acenaphthylene	C ₁₂ H ₈	152.20	16.1
Anthracene	C ₁₄ H ₁₀	178.23	0.045
Phenanthrene	C ₁₄ H ₁₀	178.23	1.1
Fluorene	C ₁₃ H ₁₀	166.22	1.9
Fluoranthene	C ₁₆ H ₁₀	202.29	0.26
Benzo(a)anthracene	C ₂₀ H ₁₂	228.29	0.011
Chrysene	C ₁₈ H ₁₂	228.29	0.0015
Pyrene	C ₁₆ H ₁₀	202.26	0.132
Benzo(a)pyrene	C ₂₀ H ₁₂	252.32	0.0038
Benzo(b)fluoranthene	C ₂₀ H ₁₂	252.32	0.0015
Benzo(k)fluoranthene	C ₂₀ H ₁₂	252.32	0.0008

The application of the conventional method has the major drawback of releasing secondary pollutants like carbon dioxide and methane gas (Gong *et al.*, 2017). Traditional methods, also known as conventional methods, such as membrane oxidation, electrolysis, filtration, ion-exchange reverse osmosis, ozonation, flocculation, membrane filtration and coagulation (Kuppusamy *et al.*, 2017) have been used to assist the removal of PAHs.

Advanced methods like photochemical, thermal, biological, adsorption, photocatalytic, photolysis, and Fenton oxidation have been introduced to enhance the conventional methods of removing PAHs from wastewater (Sahu *et al.*, 2020, Ali *et al.*, 2019). The biological process has been effective in the removal of PAHs because of its ability to undertake higher molecular weights but mostly applies in soil. The biological process and photocatalysis are environmentally friendly processes that can economically eliminate PAHs in the environment and wastewater (Shanker *et al.*, 2017).

Photodegradation has been described as the most effective technique among the conventional and advanced techniques to be used in the removal of PAHs (Saeed *et al.*, 2013). Photodegradation is a process where a light source is used on an effective material to challenge the organic pollutant (PAH) in a reaction that will produce scavenger radicals. These radicals are reactive and soluble in water; the most effective radical in photodegradation is known to be a hydroxyl radical (Shao, 2017). The photodegradation of the organic pollutants can be activated in the presence of light on the photocatalytic material (Nguyen *et al.*, 2020). In a previous study, the photodegradation of PAHs was conducted using a laboratory photoreactor and it was found that fluorine (FLU, 4.17 min), phenanthrene (PHE, 3.79 min) and pyrene (PYR, 4.77 min) were highly concentrated and effectively removed from an aqueous solution under UV-light (Shao, 2017).

Zinc oxide (ZnO) is a well-known semiconductor that has been widely used for wastewater treatment due to its chemical and physical properties: it is non-toxic, anti-fouling, antibacterial, inexpensive and thermally stable (Chauhan *et al.*, 2020, Shaba *et al.*, 2021). Various studies (Sescu *et al.*, 2020, Mbiri *et al.*, 2019, Zhang *et al.*, 2021, Tsuzuki *et al.*, 2019) have reported the doping of metals into a metal oxide which improves photoactivity to bring about spontaneous photodegradation. It has also been reported by Zhao *et al.* (2020) that a photocatalyst in the dose range of 2.5g/L-10g/L was used for the photodegradation of PAH pollutants. Further, the doping of metals has been found to narrow the band gap of semiconductors (Dou *et al.*, 2015, Yoo *et al.*, 2012). The novelty of this study is the application of agrowastes to obtain delayed recombination of free electrons with a narrower bandgap for successful photodegradation. In this study, various agrowastes *moringa oleifera* seed (MO), groundnut shells (GS) and apatite (A) derived from the cow bones were considered to assist in narrowing the parental ZnO bandgap that was reported in the literature reviewer to be in the range of 3.10 eV to 3.37 eV (Davis *et al.*, 2019).

2. Materials and methods

Heterogeneous photocatalysts were synthesized using various agrowastes such as *moringa oleifera* seed, groundnut shells and apatite (cow bones). The use of these agrowastes combined in a ratio of 1:1:1 into a mass of 0.2 g of the synthesis $\text{Zn}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 2\text{H}_2\text{O}$ and 0.1 g of Ag were mixed into a volume of 50 mL of deionised water.

The solution of ZnO and Ag was stirred to ensure a homogenous mixture, and 1 g of each of the agrowaste was added to the mixture. The prepared volume of 2M of NaOH was used to adjust the pH until the pH of 12 was obtained. The overall mixture was stirred at 250 rpm for 2 h. After completing this process, it was centrifuged for 20 min at 6000 rpm whereby the precipitants were obtained, and the sample was dried in an oven at a temperature of 80°C for 24 h. A self-designed photoreactor made of Perspex glass material (dimensions: length 40 cm, width 35 cm and height 15 cm) as illustrated in Figure 1, was assembled to undertake PAH degradation in various water media under solar irradiation. The photoreactor was inserted inside a box with the following dimensions: length (70 cm), width (60 cm) and height (40 cm) to prevent the photons escaping.

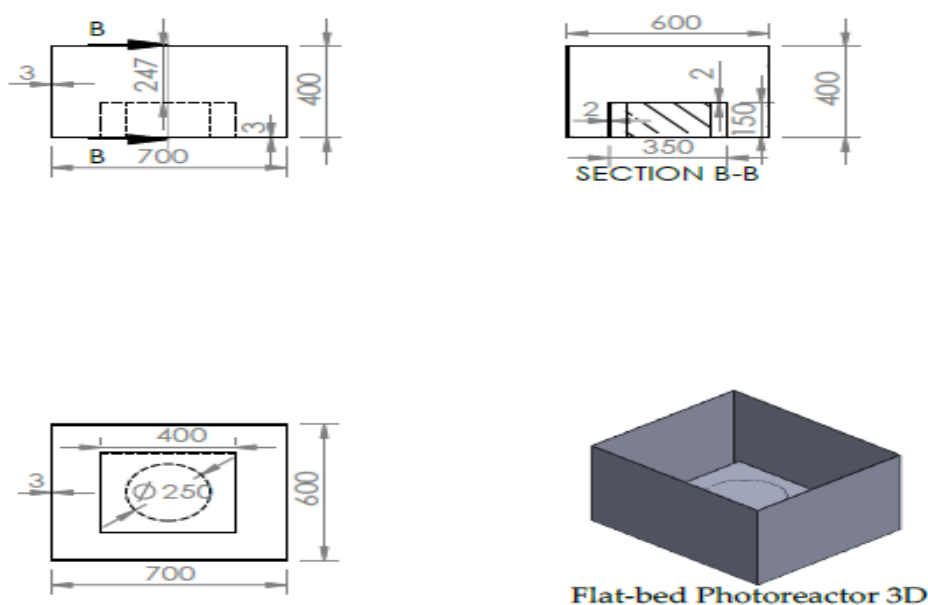


Figure 1: Flat-bed photoreactor for the photodegradation of PAHs on various water sources

2.1 Synthesis of MO/GS/A/ZnO and ZnO/Ag

Synthesis of MO/GS/A/ZnO was manufactured from 1 g of MO, GS and A at a ratio of 1:1:1 with 0.2 g of ZnO and 0.1 g of Ag into a 250 mL beaker with deionised water. Various pH ranges of 9.8 -11.8 were observed and therefore sodium hydroxide (NaOH) was used to adjust to a pH 12 to obtain a synthesized bioheterophotocatalyst.

2.2 Adsorption and photodegradation of polycyclic aromatic hydrocarbons

Coal tar containing 2916.47 mg/L of PAHs was analyzed using Gas Chromatography-Mass Spectrometry (GC-MS) with a Thermo Scientific (TSQ 8000) (Cape Town, South Africa) Triple Quadrupole MS. The coal tar was immersed in various water sources such as acidic mine drainage, alkaline mine drainage and sewage wastewater for 8 weeks. For the collection of the sample, a syringe and filtered PDVP (0.45 µm) were used and analyzed using GC-MS. The data are presented in tables 2, 3 and 4. Afterwards, the photodegradation was conducted, whereby, a mass of 2.5 g of the synthesized photocatalyst was immersed in a self-made flat-bed photoreactor.

The photodegradation efficiency of the PAHs in various water sources under an effective photoreactor using MO/GS/A/Ag/ZnO and ZnO/Ag was calculated with the following equation below:

$$\text{Photodegradation efficiency (\%)} = \frac{C_0 - C_t}{C_0} \times 100 \% \quad (1)$$

Where C_0 and C_t (mg/L) are the initial and residual concentrations respectively, of PAHs in solution at the time (t). The photodegradation efficiency of these water sources is presented in Table 5.

2.2.1 Adsorption kinetic

To investigate the adsorption in a system it is required to have the kinetic data that can best describe the adsorption kinetics of the pollutants onto the material. To achieve that, many kinetic models are available, although the most commonly applied are the pseudo-first-order (PFO) and pseudo-second-order order (PSO) models (Vieira *et al.*, 2022).

The PFO equation is presented as follows:

$$q_t = q_s (1 - \exp(-k_1 t)) \quad (2)$$

Where q_t represents the amount of the pollutant (PAHs) adsorbed by the material at the time (t); q_s and k_1 in PFO are obtained from the data analysis through linear regression. Most importantly, the higher k_1 , the sooner it will reach equilibrium. Most of the time the k_1 is mostly dependent on the pH of the solution, and in this study it will be wastewater, temperature and the initial concentration of the material.

The adsorption kinetic PSO equation is presented as follows (Kumar *et al.*, 2019) and can be calculated by using equation 3 below:

$$q_t (\text{mg/g}) = \frac{k_2 q_s^2 t}{1 + k_2 q_s t} \quad (3)$$

Since the k value is the time scaling factor, a similar parameter as PFO is considered; however this time the higher K_2 will result in a shorter time required for the reaction to reach equilibrium in the system. The value of K_2 is also influenced by the same factor for k_1 .

2.2.2 Adsorption isotherm

The adsorption isotherm is one of the most important tools in adsorption for understanding the process of a reaction between the pollutants and the material. Various isotherms have been used to describe the adsorption equilibrium, although the Langmuir and Freundlich isotherms have been most widely used to best describe the adsorption isotherm (Ayawei *et al.*, 2017, Stromer *et al.*, 2018).

The Langmuir adsorption is the simplest model that is used mostly for gas and liquid (Mahmoodi *et al.*, 2018, Fallah *et al.*, 2020). However, the Freundlich isotherm occurs on a heterogeneous surface (Khayyun and Mseer, 2019). The Langmuir in (4) and Freundlich isotherms (5) can be described as:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (4)$$

$$q_e = K_F + C_e^{1/n} \quad (5)$$

where q_e represents the adsorbed pollutants expressed in per unit mass (mg/g); q_m is the monolayer adsorption; K_L is the adsorption Langmuir isotherm constant (mg/L); K_F is the adsorption Freundlich isotherm constant and C_e is the equilibrium of the adsorbed pollutants (PAHs) in a solution, and it is express in a unit (mg/L).

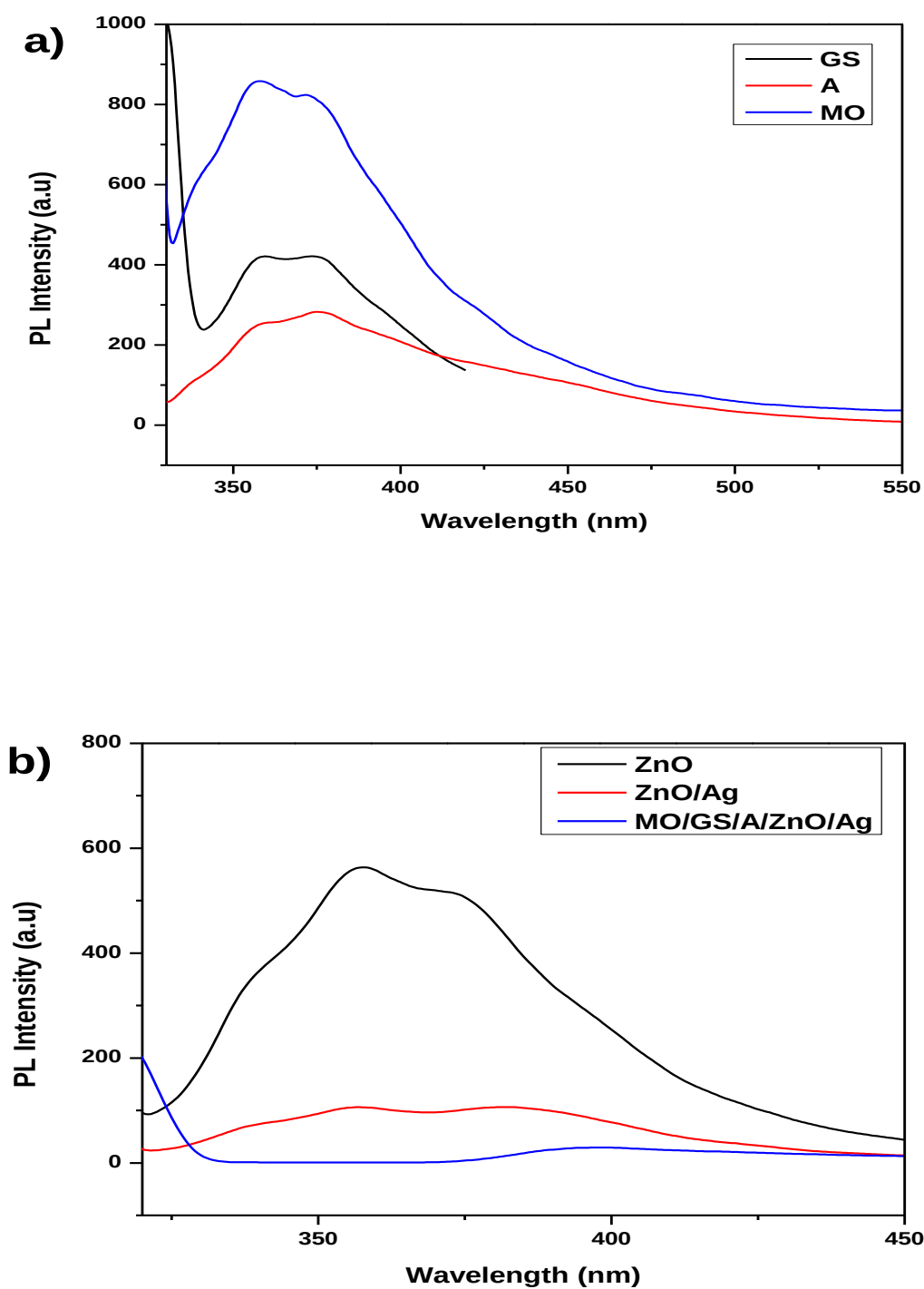
3 Results and discussions

3.1 Characterizations

3.1.1 Photoluminescence spectroscopy

A Photoluminescence PerkinElmer LS55 Luminescence Spectrometer was used at the excitation wavelength (λ) of 310 nm for the MO, GS and A agrowastes in Fig 3a and excitation of 300 nm for the synthesized materials (MO/GS/A/ZnO/Ag), ZnO/Ag and the parental ZnO, conducted at room temperature as shown in Fig 3b. MO indicates a higher PL intensity in comparison to GS and A whereas the synthesis bioheterophotocatalyst (MO/GS/GS/A/ZnO/Ag) indicated a lower PL intensity that was attributed to the combination of the agrowastes and the impurities followed by the parental ZnO/Ag and ZnO in Fig. 2b.

The electron recombination was obtained in MO/GS/GS/A/ZnO/Ag followed by ZnO/Ag and the parental ZnO. The delay of the recombination charge carrier is dependent on the lower PL intensity and that is indicated in Fig 2a A and Fig 2b MO/GS/A/ZnO/Ag.



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Figure 2: PL spectra for agrowastes MO, GS and A (a) and Synthesized photocatalyst ZnO/Ag and MO/GS/A/ZnO/Ag (b)

3.1.2 Scanning electron microscopy

NovaNano SEM and the Tescan MIRA3 RISE SEM were used on the morphology of MO/GS/A/ZnO/Ag and ZnO/Ag before and after the photodegradation of PAHs was obtained, as shown in Fig. 3. The SEM images of MO, GS and A morphologies are shown in Fig. 3a, b, and c. The MO in Fig. 3a presents a rough cavity distributed over the surface by showing few microcells on the MO while GS is shown in Fig. 3b as a fibre structure, and A is shown in Fig. 3c as a viscous image confirming the fatty acid. Before the photodegradation, MO/GS/A/ZnO/Ag in Fig. 3d and ZnO/Ag in Fig. 3e indicate free adsorptive sites and the availability of the pores and even structure. The presence of ZnO exhibited a smaller nanoparticle of 40–160 nm that was equally distributed to the agrowastes (Kumar *et al.*, 2015).

After photodegradation, the samples were collected from acidic mine drainage using MO/GS/A/ZnO/Ag in 60 min (Fig. 3f); ZnO/Ag in 40 min (Fig. 3g); alkaline mine drainage using MO/GS/A/ZnO/Ag in 40 min in (Fig. 3h); ZnO/Ag in 60 min (Fig. 3i); sewage wastewater MO/GS/A/ZnO/Ag in 20 min (Fig 3j); and ZnO/Ag in 40 min (Fig 3k) displays the PAHs occupying the pore size, which reveals slight adsorption occurring.

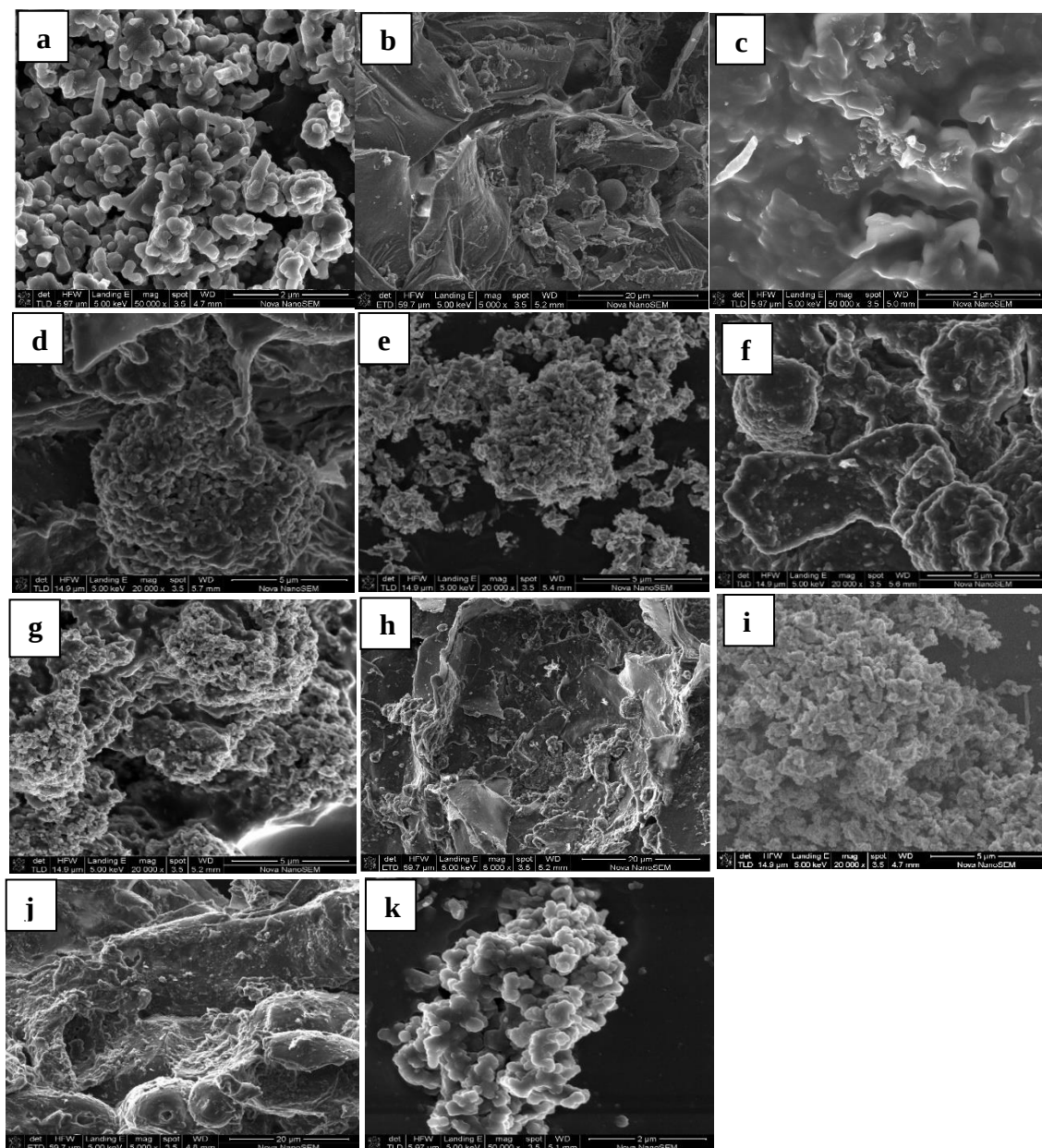


Figure 3: SEM of MO (a), GS (b), A (c), MO/GS/A/ZnO/Ag (d), ZnO/Ag (e), MO/GS/A/ZnO/Ag (60 min) (f), ZnO/Ag (20 min) (g) in acidic mine drainage, MO/GS/A/ZnO/Ag (40 min) (h) and ZnO/Ag (60 min) (i) in alkaline mine drainage, MO/GS/A/ZnO/Ag (20 min) (j) and ZnO/Ag (40 min) (k) in sewage wastewater.

3.1.3 Fourier transform Infrared (FTIR)

The FT-IR PerkinElmer Spectrometer was used to determine the existing functional group in MO, GS and A (cow bone) agrowastes before and after the photodegradation of PAHs using MO/GS/A/ZnO/A and ZnO/Ag.

Before the photodegradation of PAHs (Fig. 4), the MO spectrum illustrated a peak stretching at 3293 cm^{-1} which was ascribed to the alcohol. The vibration at 2854 cm^{-1} and 2923 cm^{-1} indicated the alkanes. The long and sharp peaks at 1742 cm^{-1} and 1647 cm^{-1} indicated the carbonyl group (C=O) that was attributed to the tertiary amines (N-H) and the presence of the amide revealed the protein compounds.

The peak at 1543 cm^{-1} indicated the presence of nitro compound (N-O). The peaks at 1452 cm^{-1} , 1236 cm^{-1} , 1160 cm^{-1} and 1020 cm^{-1} strongly indicated the aromatics amine and aliphatic amine (C-N) (Shanmugavel *et al.*, 2018, Bouchareb *et al.*, 2021).

The GS spectrum indicated a peak at 3342 cm^{-1} that was assigned to the -OH and this was presented from the macromolecules such as cellulose, hemicellulose, and lignin. The peak at 2895 cm^{-1} indicated the methyl group (CH) and the peak at 1243 cm^{-1} indicated the OH in-plane bending in cellulose. The peak at 1020 cm^{-1} indicated the carbonyl group (C=O) in carboxylic and alcoholic groups (Wang *et al.*, 2016).

Furthermore, A in Fig. 4 revealed a peak at 3286 cm^{-1} that indicated the -OH while 2854 cm^{-1} and 2923 cm^{-1} indicated the alkanes group. Also, the peak at 1742 cm^{-1} indicated the aldehyde and 1647 cm^{-1} indicated the carboxylic acid and 1543 cm^{-1} indicated the N-H. The three intensive peaks at 1243 cm^{-1} , 1160 cm^{-1} and 1020 cm^{-1} were assigned to fatty acid (phospholipids) and 727 cm^{-1} and 881 cm^{-1} indicated the aromatic groups (Forero-Sossa *et al.*, 2021).

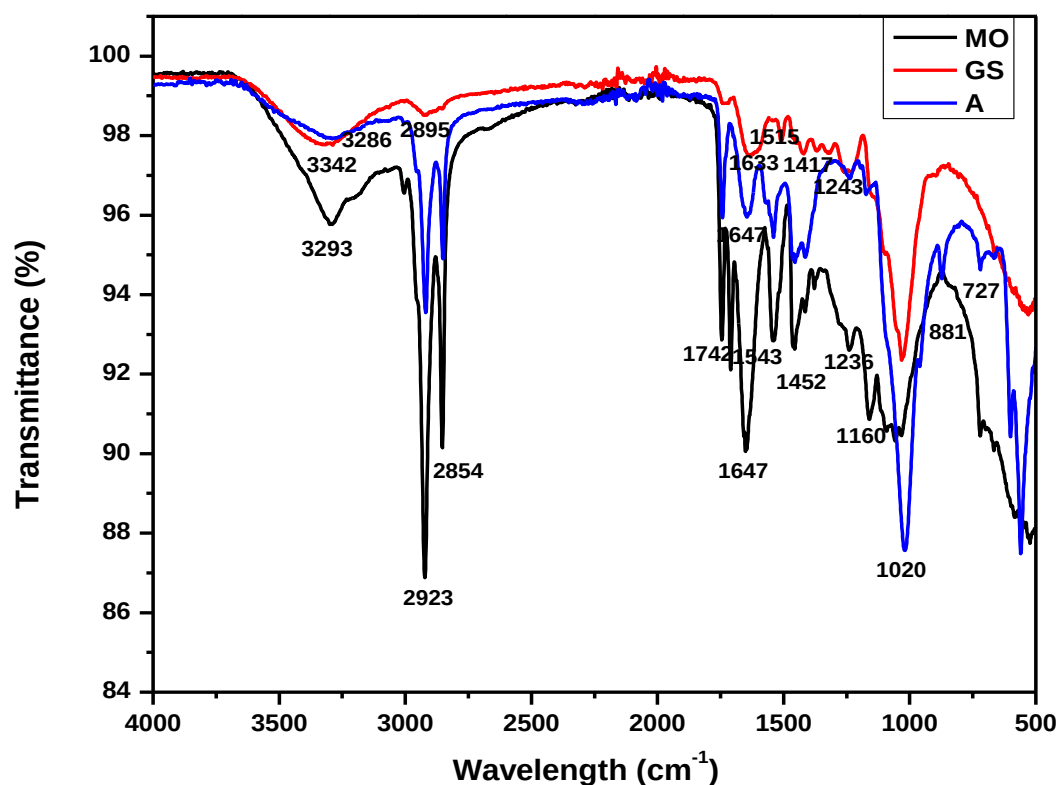


Figure 4: Fourier transforms infrared of MO, GS and A.

The synthesized MO/GS/A/ZnO/Ag and ZnO/Ag exhibited various functional groups presented in Fig 5. The MO/GS/A/ZnO/Ag revealed a peak at 3649 cm^{-1} that was assigned to the -OH. The vibration at 2854 cm^{-1} and 2972 cm^{-1} indicated the CH_2 and CH_3 whereas 1383 cm^{-1} indicated the N-H. The peaks at 948 cm^{-1} and 1158 cm^{-1} indicated the polysaccharides.

A few functional were observed which could be attributed to various agrowaste combinations having low-level radioactive waste and hazardous waste. The ZnO/Ag exhibited a peak at 3340 cm^{-1} that indicated the -OH and 2972 cm^{-1} indicated the alkane. The peak at 1728 cm^{-1} indicated the carboxylic acid and 1553 cm^{-1} and 1670 cm^{-1} indicated the C=C and the peaks at 1161 cm^{-1} , 1239 cm^{-1} , 1383 cm^{-1} and 1448 cm^{-1} indicated C-O, and 950 cm^{-1} indicated the aromatic group.

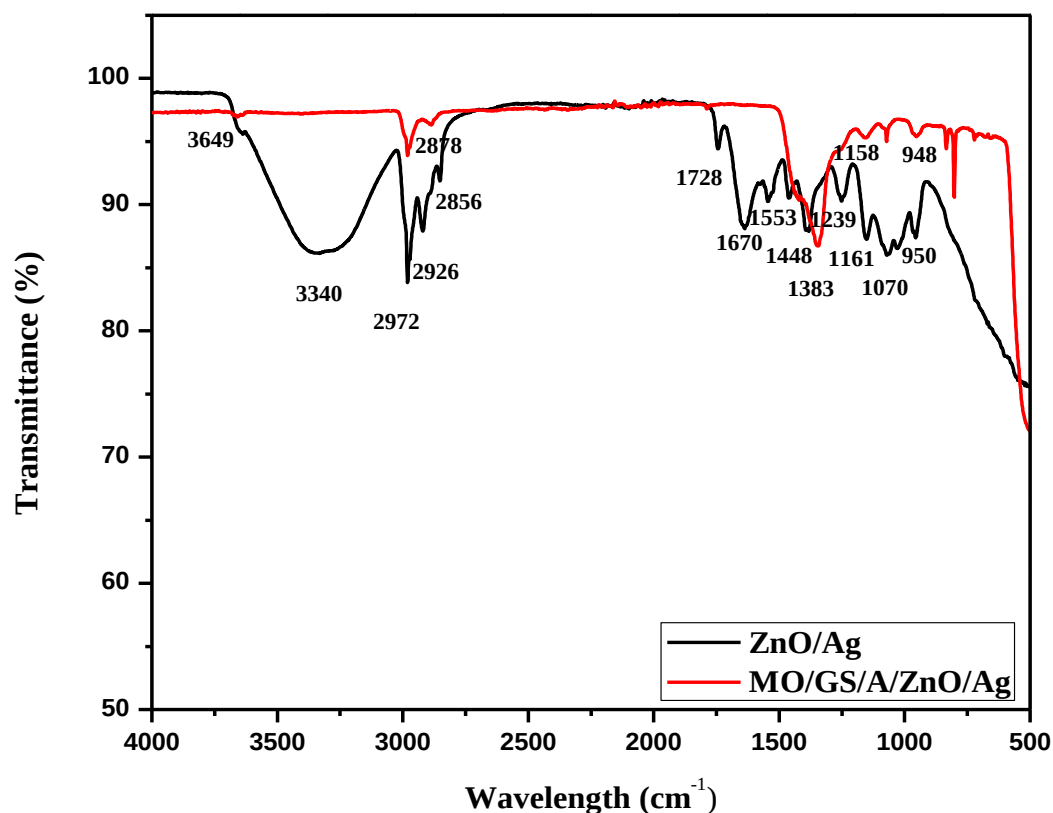


Figure 5: FT-IR of ZnO/Ag and MO/GS/A/ZnO/Ag before photodegradation

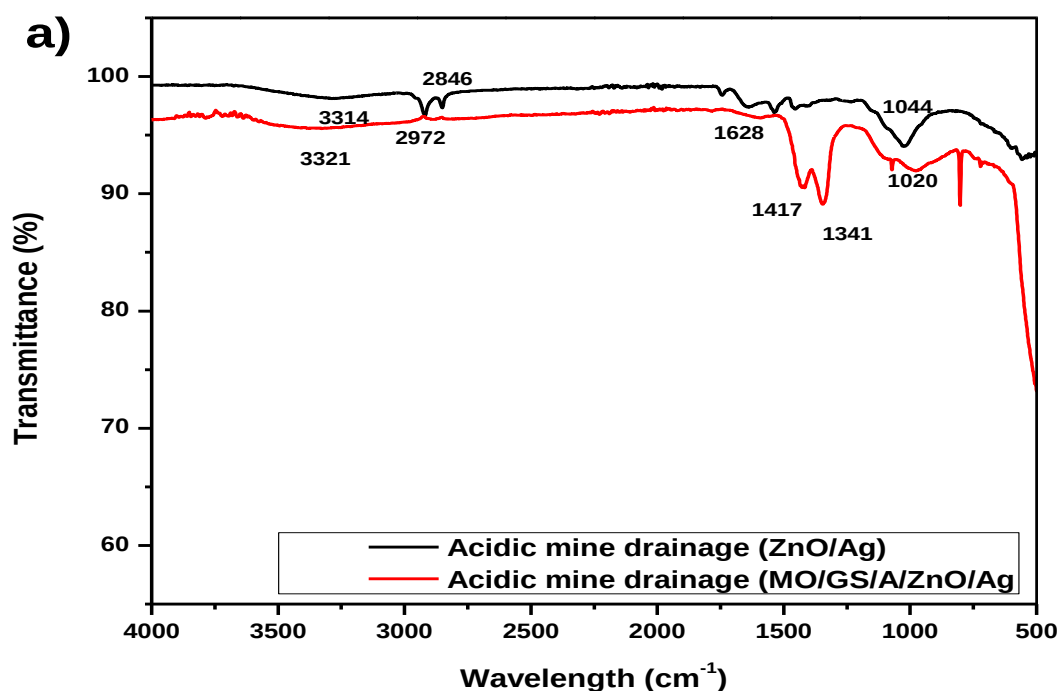
After the photodegradation, it appears that few functional groups were involved in the photodegradation of PAHs. This was observed by fairly dim and diminishing peaks in Fig 6 and 7. Before the photodegradation in Fig 6a using MO/GS/A/ZnO/Ag, a peak at 3649 cm^{-1} indicated the -OH and after the photodegradation, a broader and disappearing peak at 3314 cm^{-1} on the acidic mine drainage was observed (Fig. 6a); a peak at 3321 cm^{-1} on the alkaline mine drainage was diminished (Fig. 6b) and the -OH was completely involved in the sewage wastewater (Fig. 6c).

Before the photodegradation of PAHs, a peak at 2854 cm^{-1} and 2972 cm^{-1} indicated the alkanes, while after the photodegradation no alkanes were involved in photodegradation of PAHs in acidic drainage (Fig. 6a). A peak at 2859 cm^{-1} and 2907 cm^{-1} on an alkaline mine drainage (Fig. 6b) and sewages wastewater were diminished (Fig. 6c).

Before the photodegradation a peak at 1383 cm^{-1} indicated the N-H and after the photodegradation the amine was completely involved in the photodegradation of PAHs in an acidic mine drainage (Fig. 6a), the alkaline mine drainage (Fig. 6b) and the sewage wastewater (Fig. 6c).

Lastly the peaks at 948 cm^{-1} and 1158 cm^{-1} indicated the polysaccharides and after the photodegradation a small broader peak at 1020 cm^{-1} , 1041 cm^{-1} and 1034 cm^{-1} were diminished on the acidic mine drainage (Fig. 6a), alkaline mine drainage (Fig. 6b), and sewage wastewater (Fig. 6c).

In Fig. 6a using ZnO/Ag before the photodegradation, a peak at 3340 cm^{-1} indicated the -OH and after photodegradation, a broader and disappearing peak at 3314 cm^{-1} was observed in the acidic mine drainage (Fig. 6a) and the -OH was completely involved in the photodegradation of PAHs in alkaline mine drainage (Fig. 6b) and at a peak at 3307 cm^{-1} that was diminished (Fig. 6c). The peak at 2856 cm^{-1} , 2926 cm^{-1} and 2972 cm^{-1} indicated the alkanes and after the photodegradation, the alkanes were observed to be involved completely in the photodegradation on the acidic mine drainage (Fig. 6a), and at two small peaks at 2846 cm^{-1} and 2917 cm^{-1} of alkanes was also involved slightly in alkaline mine drainage (Fig. 6b), and a small broad peak at 2917 cm^{-1} was observed to be diminishing. The peak at 1728 cm^{-1} indicated the carboxylic acid that was completely involved in the acidic mine drainage (Fig. 6a), alkaline mine drainage (Fig. 6b) and sewage wastewater (Fig. 6c). The peaks at 1553 cm^{-1} and 1670 cm^{-1} indicated the C=C and after the photodegradation, a peak at 1628 cm^{-1} diminished on the acidic mine drainage (Fig. 6a), and a peak at 1640 cm^{-1} both on the alkaline mine drainage (Fig. 6b) and sewage wastewater also was diminished (Fig. 6c). The peaks at 1161 cm^{-1} , 1239 cm^{-1} , 1383 cm^{-1} and 1448 cm^{-1} indicated C-O and were involved in the three water sources.



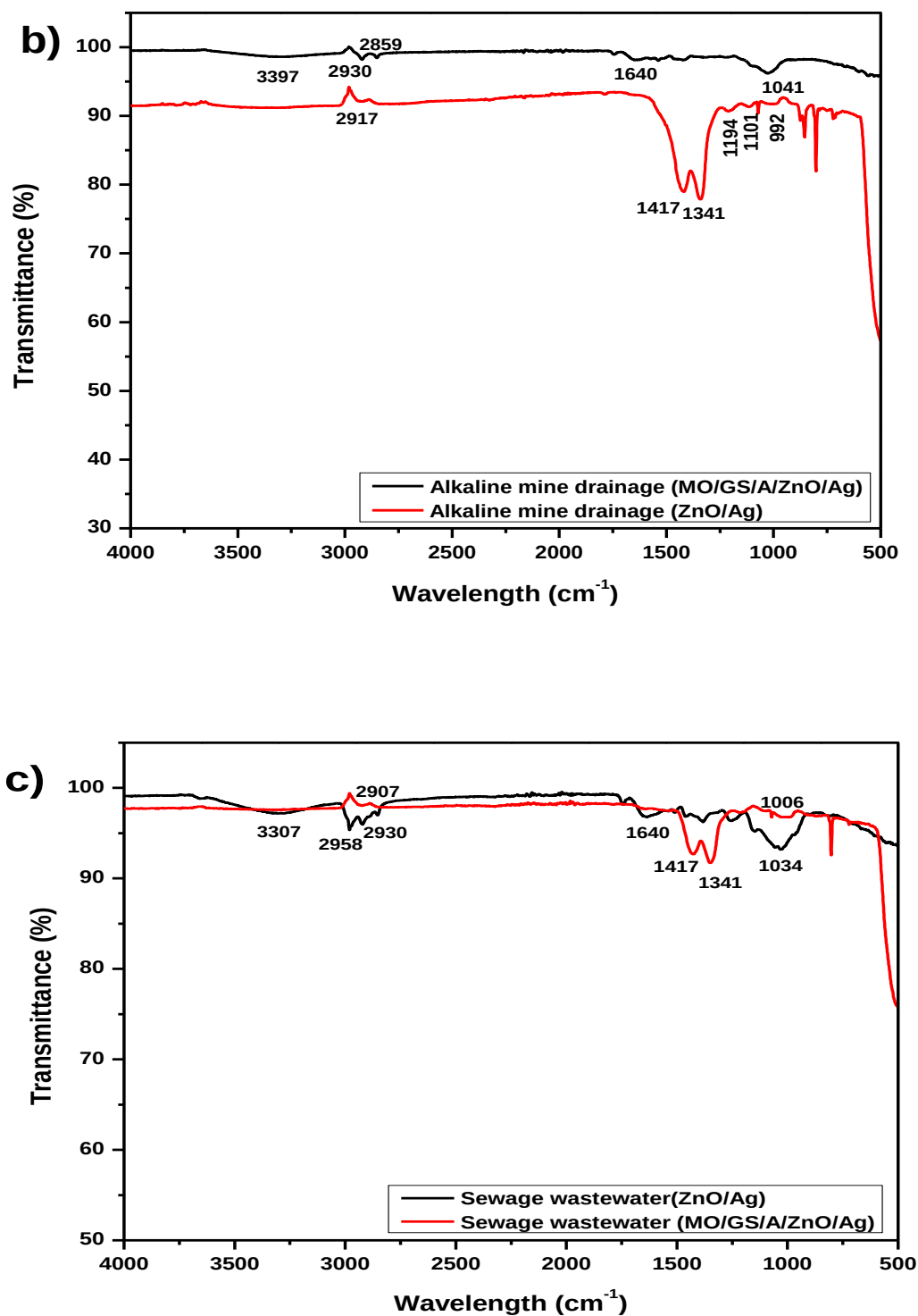


Figure 6: FT-IR of ZnO/Ag and MO/GS/A/ZnO/Ag after photodegradation

3.1.4 Energy-dispersive X-ray spectroscopy analysis

An EDS Nova NanoSEM using an Oxford X-max 20mm² detector and INCA software was used to identify the organic component present in an agrowaste. It was confirmed that the synthesized bioheterophotocatalyst MO/GS/GS/A/ZnO/Ag was richer in both carbon and oxygen content. The combination MO/GS/GS/A/ZnO/Ag of the agrowastes provides a bigger, broader peak that reveals smaller crystal sizes (Fig. 7a) whereas a less broad peak revealed a bigger crystal size showing the presence of zinc and silver (Fig. 7b).

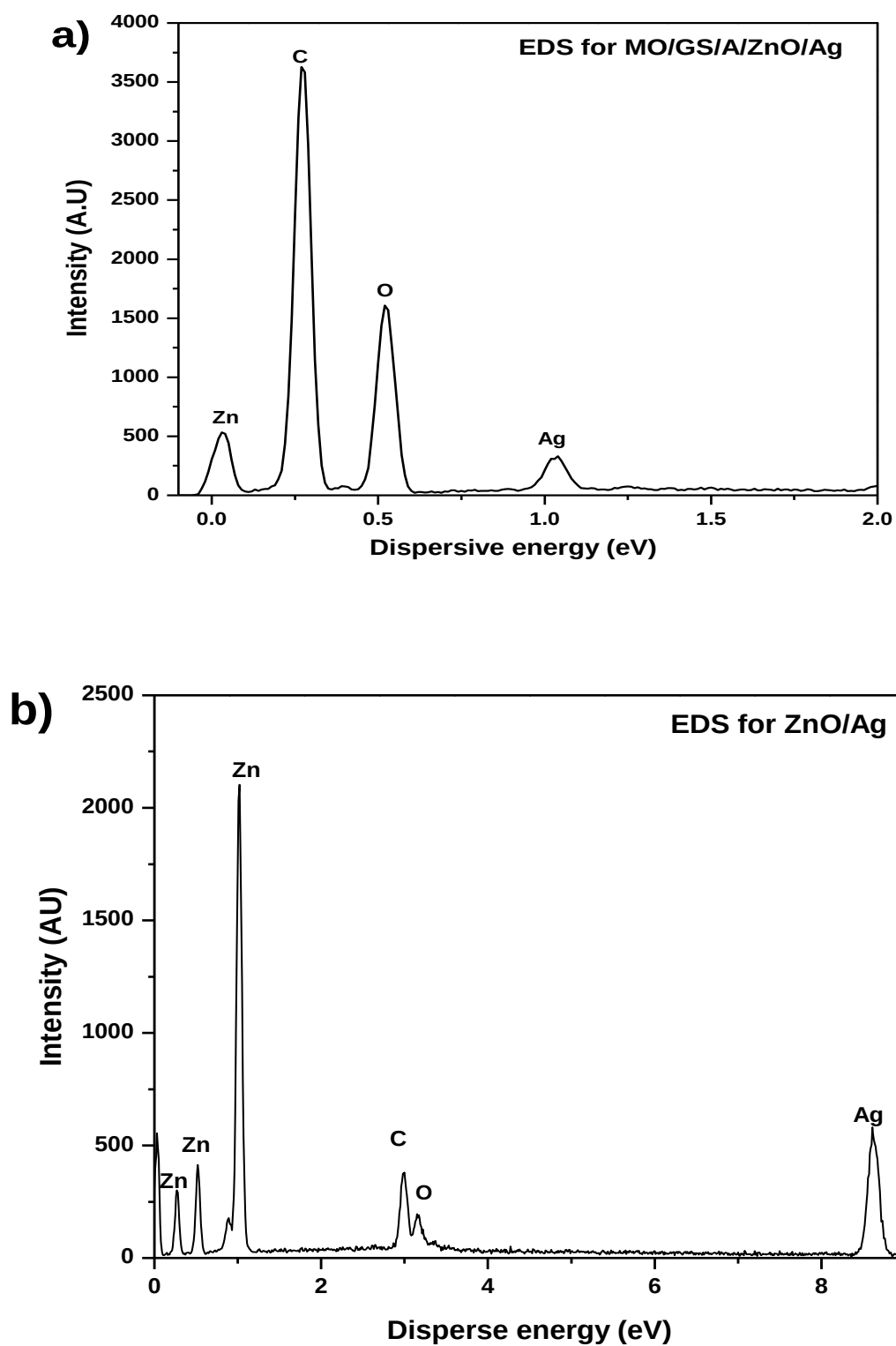
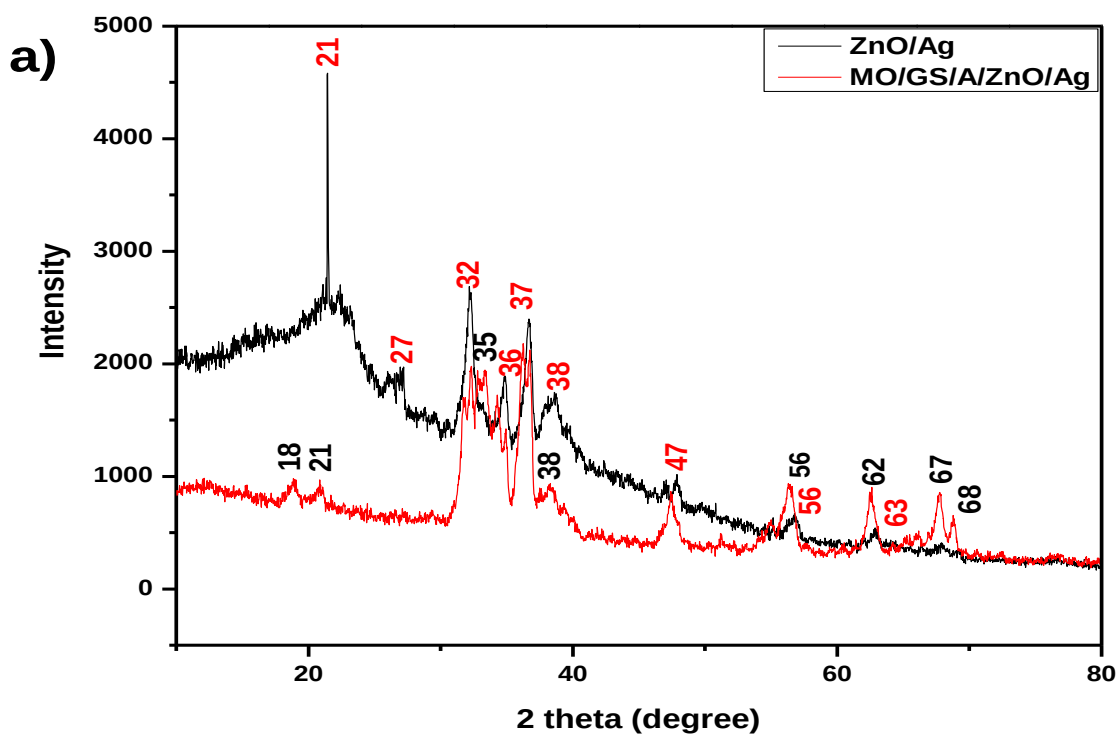
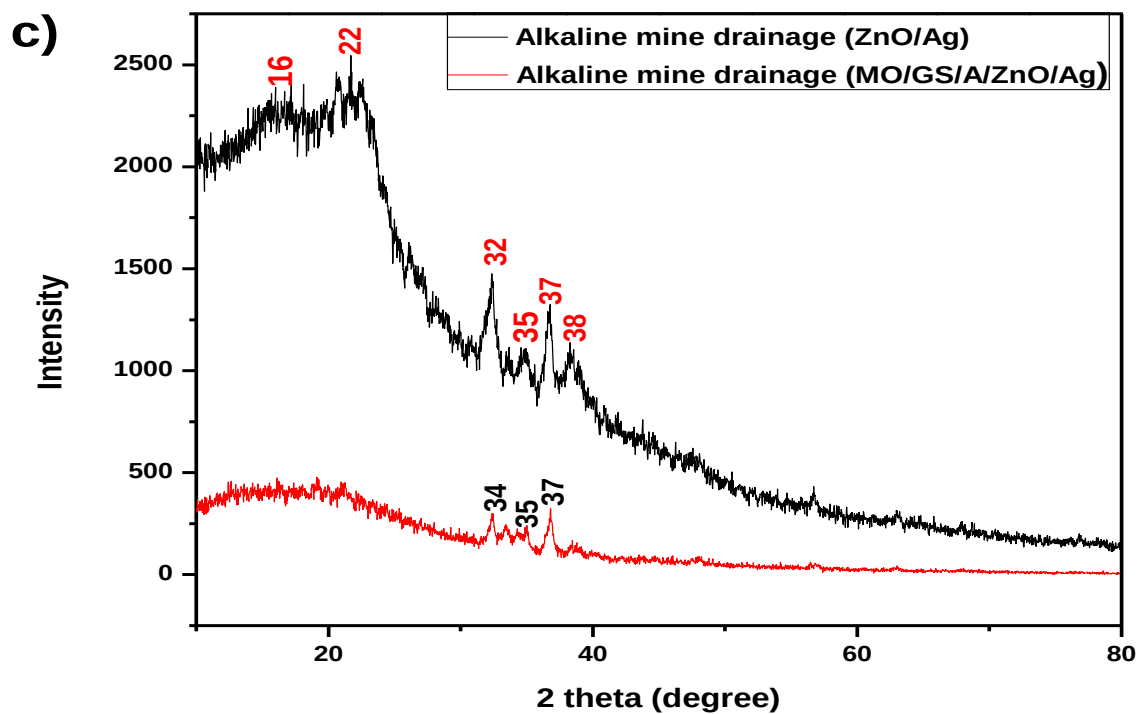
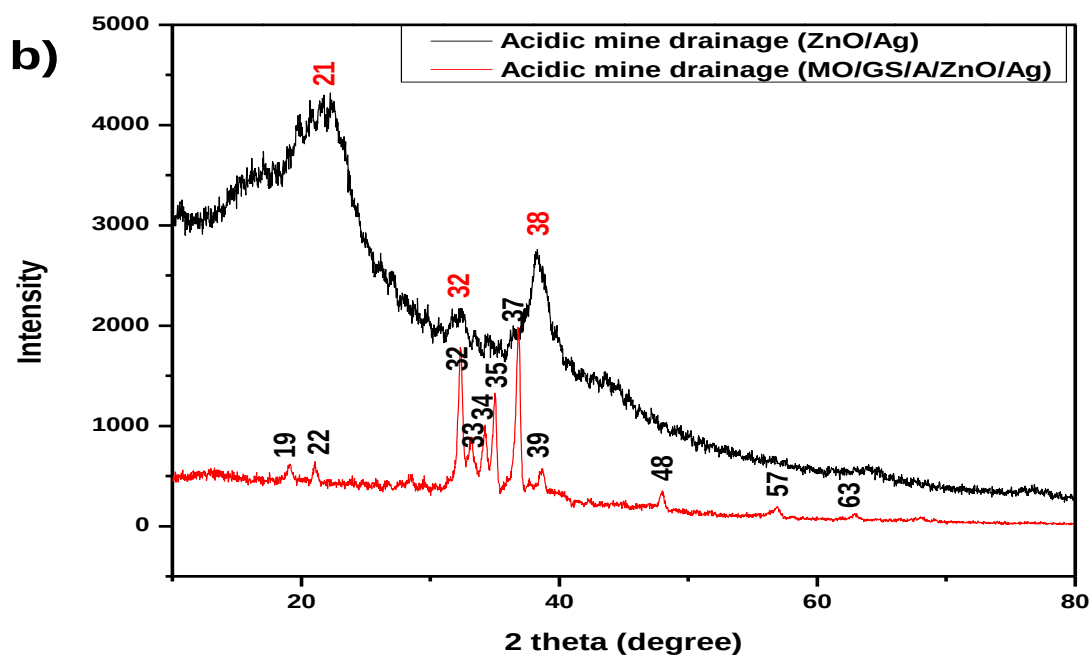


Figure 7: EDS for synthesized photocatalyst ZnO/Ag (a) and MO/GS/A/ZnO/Ag (b)

3.1.5 XRD analysis

X-ray diffraction (XRD) Powder XRD measurements were recorded on an Analytical XPERT-PRO diffractometer, using Ni filtered CuK α radiation ($\lambda = 1.5406 \text{ \AA}$) at 45 kV/40 mA to determine the crystal structure of the materials. The XRD pattern of MO/GS/A/ZnO/Ag and ZnO/Ag is illustrated in Fig. 8 and from MO/GS/A/ZnO/Ag and ZnO/Ag, it partially agreed with the hexagonal structure of the raw reference pattern: ZnO, 00-036-1451 and Ag, 00-004-0783. The high impurities of these agrowastes influenced the diffraction peak of the material. Additionally, various factors such as crystal structure, elements, occupations, substitutions, thermal vibrations, diffractometer geometry, variable or fixed apertures, homogeneity of the sample and texture of the material could have defected the diffraction peak and the crystallinity of the material.





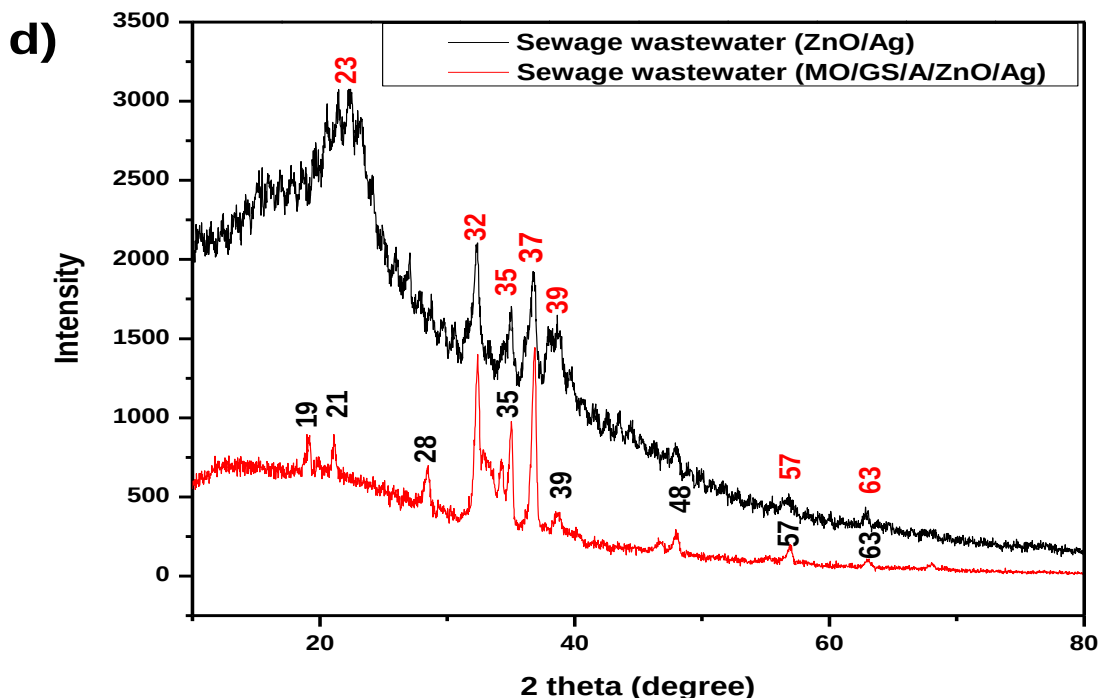


Figure 8: XRD of MO/GS/A/ZnO/Ag and ZnO/Ag before PAHs photodegradation (a), MO/GS/A/ZnO/Ag (60 min) and ZnO/Ag (20 min) in acidic mine drainage (b), MO/GS/A/ZnO/Ag (40 min) and ZnO/Ag (60 min) in alkaline mine drainage (c), MO/GS/A/ZnO/Ag (20 min) and ZnO/Ag (40 min) in sewage wastewater (d).

Tables 2, 3 and 4 represent the results obtained after the photodegradation. The photodegradation was highly favoured using MO/GS/A/ZnO/Ag in acidic mine drainage in 60 min. Since the experiment was conducted in an open space, various factors such as inconsistent solar irradiation, wind, the environment, and the weather could have influenced the experiment.

The property of the water such as the temperature, pH, ionic strength and water matrix of the dissolved organic carbon also contributed to the photodegradation of PAHs (Batchamen Mounol *et al.*, 2022).

The findings presented in Table 5 agree with Cai *et al.* (2019) and Huang *et al.* (2021) that as time increases, the photodegradation efficiency also increases because of the prolonged contact between the pollutants and the photocatalyst.

The light molecular weight was almost completely degraded due to its volatility properties. Shao (2017) and Li, *et al.* (2020) have reported that -OH and -COOH are the most predominant functional groups

involved in the photodegradation of organic pollutants; in this study it was proven that -NH and -COOH were involved in degrading PAHs in various water sources.

It has been proven that the photodegradation of PAHs with higher molecular weight is strongly promoted by H⁺ whereas those with lower molecular weight are favoured at -OH under solar irradiation (Eker and Hatipoglu, 2018, Zhang *et al.*, 2008). The bioheterophotocatalyst MO/GS/A/ZnO/Ag was proven in this study to be eco-friendly and cost-effective for the photodegradation of PAHs. The presence of the oxygen content, the band gap of 2.3eV and the delay of the electron recombination holes resulted in spontaneous photodegradation. A photodegradation efficiency of <90% for PAHs was obtained using MO/GS/A/ZnO/Ag.

It was important to determine the bandgap to ensure that the material is usable in the solar spectrum at a wavelength range from 100 nm to 1 mm (Makula *et al.*, 2018). The performance of photocatalytic reactions depends greatly on the capacity of electron excitation from the valence band to the conduction band in such a way that the energy input is bigger than the band's energy difference. This excitation contributes to the development of holes that connect with adsorbed hydroxyl species or water molecules that create reactive hydroxyl radicals. These radicals were able to react or disintegrate the PAH pollutant molecules into CO₂ and H₂O (Nezamzadeh-Ejhi and Ghanbari-Mobarakeh, 2015). The narrow band gap promotes an increase in the rate of photodegradation, making possible the excitation under visible light; however, it also implies that doping of various elements like nitrogen, boron, iron, molybdenum, titanium, magnesium, zinc or manganese decreases the band gap of the parental ZnO drastically and enhances photodegradation even further (Yu *et al.*, 2016). These metal elements were strongly present in the agrowaste materials and thus the use of agrowastes was found contribute strongly to the reduction of the band gap.

Table 2: Photodegradation of PAHs in acidic mine drainage

	Initial concentration	Catalyst	20 min	40 min	60 min	Catalyst	20 min	40 min	60 min
NAP	0.0031	MO/GS/A/ZnO/Ag	0.0024	0.0021	0.0019	ZnO/Ag	0.0025	0.0025	0.021
ACY	0.1302		0.0478	0.0447	0.0320		0.0555	0.041	0.0322
ACE	0		0	0	0		0	0	0
FL	0		0	0	0		0	0	0
PHE	0.0181		0.0096	0.0087	0.0080		0.0109	0.0107	0.0086
ANT	18.9847		1.1048	1.0003	0.3117		2.0869	1.9707	2.0232
FLU	0.0020		0.0006	0.0005	0.0001		0.0008	0.0007	0
PYR	0		0	0	0		0	0	0
BaA	0.1114		0	0	0		0	0	0
CHY	0.0012		0	0	0		0	0	0
BbF	0		0	0	0		0	0	0
Blkf	0		0	0	0		0	0	0
BaP	0.0046		0	0	0		0	0	0
DahA	0		0	0	0		0	0	0
IP	0		0	0	0		0	0	0

Bghip	0		0	0	0		0	0	0
PAHs photodegradation	19.2553		1.1652	1.0563	0.3537		2.1566	2.0850	2.0256

Table 3: Photodegradation of PAHs in alkaline mine drainage

PAHs	Initial concentration	Catalyst	20 min	40 min	60 min	Catalyst	20 min	40 min	60 min
NAP	0.7615	MO/GS/A/ZnO/Ag	0.0039	0.0084	0.0035	ZnO/Ag	0.0105	0.0174	0.0094
ACY	0.2596		0.0522	0.0395	0.0307		0.0415	0.0432	0.0372
ACE	0.0020		0	0	0		0	0	0
FL	0.0030		0	0	0		0	0	0
PHE	0.0447		0.0139	0.0150	0.0136		0	0	0
ANT	0.5388		0	0.0056	0		0.0523	0.0298	0.0456
FLU	0.0039		0.0012	0.0008	0		0.0005	0.0009	0.0017
PYR	0.0019		0	0	0		0	0	0
BaA	0		0	0	0		0	0	0
CHY	0		0	0	0		0	0	0
BbF	0		0	0	0		0	0	0
Blkf	0		0	0	0		0	0	0
BaP	0		0	0	0		0	0	0

DahA	0		0	0	0		0	0	0
IP	0		0	0	0		0	0	0
Bghip	0		0	0	0		0	0	0
PAHs photodegradation	1.6154		0.0712	0.0693	0.0478		0.1048	0.0913	0.0939

Table 4: Photodegradation of PAHs in sewage wastewater

PAHs	Initial concentration	Catalyst	20 min	40 min	60 min	Catalyst	20 min	40 min	60 min
NAP	0.0069	MO/GS/A/ZnO/Ag	0.0044	0.0054	0.0028	ZnO/Ag	0.0087	0.0143	0.0067
ACY	0.0489		0.0088	0.0107	0.0087		0.0302	0.0308	0.0159
ACE	0		0	0	0		0	0	0
FL	0.0090		0	0	0		0	0	0
PHE	0.0961		0.0195	0.0148	0.0165		0.158	0.0173	0.0121
ANT	0.1758		0	0.0036	0.0032		0.0659	0.095	0.0520
FLU	0.1706		0.0064	0.001	0.0013		0.0047	0.0049	0.0027
PYR	0.1389		0.0049	0	0		0.0033	0.0033	0.0019
BaA	0.1888		0.0036	0	0		0.01	0.0089	0.0058
CHY	0.1170		0.0009	0	0		0.0051	0.003	0.0014

BbF	0.2216		0.0046	0	0		0.0304	0.0174	0.0106
Blkf	0.1563		0.0015	0	0		0.0221	0.0132	0.0053
BaP	0.2185		0.0022	0	0		0.037	0.0175	0.0073
DahA	0.1278		0	0	0		0.0273	0.0199	0.0077
IP	0.0345		0	0	0		0.0065	0.0045	0
Bghip	0.1018		0	0	0		0.0251	0.0187	0.0076
PAHs photodegradation	1.8125		0.0568	0.0355	0.0325		0.4343	0.2687	0.1370

3.16 Photodegradation efficiency

Table 5 represents the photodegradation of PAHs in various water sources. It shows that MO/GS/A/ZnO/Ag was more effective in acidic mine drainage. Nearly 100% photodegradation was obtained at 60 min under solar irradiation. The flat-bed photoreactor also contributed to the photodegradation yield throughout.

Table 5: Photodegradation efficiency of PAHs in contact time

Water sources	Photodegradation efficiency (%) MO/GS/A/ZnO/Ag			Photodegradation efficiency (%) ZnO/Ag		
	20 min	40 min	60 min	20 min	40 min	60 min
Acidic mine drainage	93.95	94.51	99.72	88.80	89.17	89.48
Alkaline mine drainage	95.59	95.71	97.04	93.51	94.19	94.35

Sewage wastewater	96.87	98.04	98.21	76.06	85.18	92.44
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3.17 Adsorption isotherm analysis

The adsorption isotherm results are presented in Table 6 and it was found that the data analysis obtained was best described by the Freundlich isotherm.

Table 6: Adsorption isotherm parameters for PAHs adsorption using 8.3 g/L of MO/GS/A/ZnO/Ag and ZnO/Ag

Water sources	Photocatalyst	Langmuir		Freundlich	
Acidic mine drainage	MO/GS/A/ZnO/Ag	R ²	0.984	R ²	0.990
		Q max	2.136	1/n	0.339
		K _L L/mg	-48.79	K _f (mg/g)	2.185
	ZnO/Ag	R ²	0.999	R ²	0.999
		Q max	1.835	1/n	-0.121
		K _L L/mg	-4.406	K _f (mg/g)	2.253
Alkaline mine drainage	MO/GS/A/ZnO/Ag	R ²	0.998	R ²	0.997
		Q max	0.179	1/n	-0.024
		K _L L/mg	-480.38	K _f (mg/g)	0.196
	ZnO/Ag	R ²	0.998	R ²	0.999
		Q max	0.170	1/n	-0.064
		K _L L/mg	-16.756	K _f (mg/g)	0.156
	MO/GS/A/ZnO/Ag	R ²	0.988	R ²	0.997
		Q max	0.206	1/n	-0.024

Sewage wastewater	ZnO/Ag	K_L L/mg	-953.512	K_f (mg/g)	0.196
		R^2	0.745	R^2	0.928
		Q max	0.157	1/n	-0.166
		K_L L/mg	-32.354	K_f (mg/g)	0.145

3.17 Adsorption isotherm analysis

The kinetic isotherm results were presented in Table 7 and it was found that the data analysis obtain was best described in PFO.

Table 7: Pseudo-first order and second-order kinetic parameters for PAHs solutions using 8.3 g/L MO/GS/A/ ZnO/Ag and ZnO/Ag

Water sources	Photocatalyst	PFO		PSO	
Acidic mine drainage	MO/GS/A/ZnO/Ag	Q_t mg/g	2.268	Q_t mg/g	2.268
		K_1 mg/g/L	0.029	K_2 mg/g/L	-0.009
		R^2	0.622	R^2	0.724
	ZnO/Ag	Q_t mg/g	0.483	Q_t mg/g	2.067
		K_1 g/min/L	1.908×10^{-4}	K_2 mg/g/L	-0.001
		R^2	0.995	R^2	0.994
Alkaline mine drainage	MO/GS/A/ZnO/Ag	Q_t mg/g	0.449	Q_t mg/g	0.188
		K_1 g/min/L	3.75995×10^{-4}	K_2 mg/g/L	-0.040
		R^2	0.621	R^2	0.622
	ZnO/Ag	Q_t mg/g	0.182	Q_t mg/g	0.182
		K_1 mg/g/L	1.7944×10^{-4}	K_2 mg/g/L	-0.019

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		R^2	0.159	R^2	0.160
Sewage wastewater	MO/GS/A/ZnO/Ag	Q_t mg/g	0.213	Q_t mg/g	0.213
		K_1 g/min/L	0.013	K_2 mg/g/L	-0.032
		R^2	0.73	R^2	0.679
	ZnO/Ag	Q_t mg/g	0.201	Q_t mg/g	0.201
		K_1 g/min/L	0.028	K_2 mg/g/L	-0.536
		R^2	0.931	R^2	0.973

3.18 Comparison to other studies

Table 8 shows the comparison of various studies on Ant and PHE PAH pollutants. It was revealed that MO/GS/GS/A/ZnO/Ag photobiocatalyst was effective on the photodegradation of ANT in 1 h. The contact between the pollutants and the material surface and especially under solar irradiation indicates higher efficiency of the photodegradation.

Table 8: Photodegradation efficiency comparison with other catalysts in water

PAHs	Photocatalyst	Irradiation	Duration (h)	Photodegradation efficiency (%)	References
ANT	ZnFe ₂ O ₄ -CS	Solar irradiation	12	95	(Rani and Shanker, 2020)
PHE				92	
ANT	ZnO-NiO			98	(Rani and Shanker, 2019)
PHE				93	
ANT	MnCo ₂ O ₄			92	
PHE				87	
ANT	CoFe ₂ O ₄			88	
PHE				83	
ANT	ZnCo ₂ O ₄	Solar irradiation	12	88	Present
PHE				83	
ANT	MO/GS/A/ZnO/Ag	Solar irradiation	1	98.36	
PHE				55.80	
ANT	ZnO/Ag			89.34	
PHE				52.48	

4 Conclusion

The properties of water such as the temperature, pH, ionic strength, and water matrix of the dissolved organic materials are responsible for influencing the photodegradation of PAHs. The acid mine drainage was proven to have influenced the photodegradation of PAHs at the largest scale using both photocatalysts. The oxygen concentration in the photocatalyst synthesis was responsible for the photodegradation of PAHs through electrons transfer. The synthesized MO/GS/A/ZnO/Ag was proven to be effective in the photodegradation of PAHs and was most effective in order of acidic mine drainage, alkaline mine drainage and sewage wastewater in 60 min. Photodegradation efficiencies of 99.72%, 97.04% and 98.21% using MO/GS/A/ZnO/Ag as compared to 89.48%, 94.35% and 92.44% using ZnO/Ag were obtained at 60 min

under solar irradiation in acidic mine drainage, alkaline mine drainage and sewage respectively. The functional groups like amine and carboxylic acid were responsible for the PAH photodegradation; these functional groups potentially produce superoxide radicals (O_2^-), hydroxyl radicals (OH), and hole (h^+) to enhance the photocatalytic activity of the reaction. The combination of the agrowastes (MO/GS/A) on the parental ZnO has proven to be effective to narrow the band gap in comparison to Ag. The most favoured media whereby coal tar was dissolved at a faster rate was acidic mine drainage. The flat-bed photoreactor and the solar radiation also achieved a spontaneous photodegradation efficiency of about <85%.

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9. Photodegradation of Polycyclic Aromatic Hydrocarbons from Coal Tar into Mine Wastewaters and Sewage Wastewater on a Flat-bed Photoreactor

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Pollutants MDPI

Summary

The photodegradation of the polycyclic aromatics (PAHs) into various water sources such as acidic mine drainage, alkaline mine drainage and sewage wastewater was conducted using synthesized heterogeneous photocatalysts. The application of the synthesized heterogeneous photocatalyst on the 2916.47 mg/L of PAHs observed in the coal tar was conducted and it was found that 7.0944 mg/L, 0.3152 mg/L and 1.0690 mg/L leached out in the acidic mine drainage, alkaline mine drainage and sewage wastewater respectively over a period of 8 weeks. Different photocatalysts were manufactured and analysed by means of several analytical techniques, such as photoluminescence (PL), scanning electrostatic microscopy (SEM), X-ray diffraction (XRD), energy-dispersive X-ray spectroscopy analysis (EDS), gas chromatography-mass spectrometry (GC-MS) and Fourier transform infrared analyses (FTIR). MO/GS/A/ZnO/Ag photocatalyst was selected as the best candidate in the quest to find a photocatalyst having a narrow band gap ensuring recombination of the electron-hole pairs at the lowest/best, whereas ZnO/Ag was used as a comparison. The photodegradation of PAHs was conducted on a self-made photoreactor (flat-bed) under solar irradiation..

The functional groups, such as the amine and carboxylic groups, were found to be responsible for the degradation and were found to be highly reactive, as was determined by the FTIR analyses. The morphology of the material before and after the photodegradation process was used to identify its free adsorptive sites. The XRD analysis was used to investigate the crystallinity of the material and EDS analyses was used to identify its elementary composition. During the photodegradation of the PAHs in the flat-bed photoreactor, the removal efficiency, using MO/GS/A/ZnO/Ag as photocatalyst, was almost 100%, 97% and 98% for acidic mine drainage, alkaline mine drainage and sewage wastewater respectively, in comparison to almost 90%, 94% and 92% when using the ZnO/Ag. It was also observed that aromatic compounds having 2 or 3 rings degraded due to their molecular weight and volatility properties. From the experimental observations, the use of a flat-bed photoreactor and solar irradiation were both necessary to cause spontaneous photodegradation. The MO/GS/A/ZnO/Ag photocatalyst was the best candidate due to its higher photodegradation efficiency compared to ZnO/Ag.



Article

Photodegradation of Polycyclic Aromatic Hydrocarbons from Coal Tar into Mine Wastewaters and Sewage Wastewater on a Flat-Bed Photoreactor

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Abstract: Wastewater treatment has been widely focused on the undesirable pollutants derived from various activities such as coking, coal gasification, oil spills, and petroleum. These activities tend to release organic pollutants, however polycyclic aromatic hydrocarbons (PAHs) happen to be highlighted as the most carcinogenic pollutant that easily comes into contact with the environment and humans. It causes major challenges due to its lingering in the environment and chemical properties. Although various techniques such as ions exchange, advanced oxidation, and reverse osmosis have been conducted, some of them have been ignored due to their cost-effectiveness and ability to produce a by-product. Therefore, there is a need to develop and implement an effective technique that will alleviate the organic pollutants (PAHs) in various water sources. In this study, a self-made flat-bed photoreactor was introduced to degrade PAHs in various water sources such as acidic mine drainage, alkaline mine drainage, and sewage wastewater. A previous study was conducted, and only 7.074 mg/L, 0.3152 mg/L and 1.069 mg/L in 4 weeks and thereafter 19.255 mg/L, 1.615 mg/L and 1.813 mg/L in 8 weeks in acidic mine drainage, alkaline mine drainage, and sewage wastewater leachate from a 2916.47 mg/L of PAHs in coal tar, was analysed. It was found that the flat-bed photoreactor was highly effective and able to obtain a removal efficiency of 64%, 55%, and 58%, respectively; without the flat-bed photoreactor, the removal efficiency was of 53%, 33%, and 39%, respectively, in 60 min in acidic mine drainage, alkaline mine drainage, and sewage wastewater. The photodegradation of PAHs was favoured in the acidic mine drainage, followed by sewage wastewater and alkaline mine drainage respectively, showing time and solar irradiation dependence.

Keywords: photoreactor; polycyclic aromatic hydrocarbons; solar irradiation



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1. Introduction



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Wastewater treatment is a well-studied topic concerning the release of organic matter (dyes, pharmaceuticals, etc.) and suspended solids (salts, metals, etc.) [1–3]. This wastewater is mostly derived from water pollution that is obtained from various activities such as mining, oil spills, agriculture, burning of coal, etc. These activities happen to release major pollutants, however, most developing countries are responsible for releasing large amounts of pollutants from their extensive production [4]. The petroleum industry is one of the contributors to the release of organic pollutants during energy production through gasification and coking [5], and it is also used to manufacture various products [6]. Coal tar is a by-product of coal that can be formed from fractionation or coking and has polycyclic aromatic hydrocarbons (PAHs) that are predominant and harmful when found in water

sources [7]. The PAHs are known as persistent organic pollutants (POPs) that can be distinguished by their solubility, vapor pressure, and high boiling and melting point [1].

It is important to identify their molecular weight when considering the removal of the pollutant, and their increase in molecular weight contributes to the oxidation and reduction [8]. The maturity of the crude oil or coal tar supposedly increases the molecular weight of PAHs over time [9]. Anthropogenic activities such as oil seeps, volcanic eruptions, human activities, crude oil, coal tar, and petroleum spills can also contribute to the release of PAHs in the environment [5]. The stability of the PAHs in the environment can be described by their molecular weight and structures [5]. It was reported by Cai et al. [10] that a lower number of molecular rings of 2 and 3 of PAHs mean that they have greater solubility in water and easily undergo destabilization and degradation as compared to the heavy molecular rings of 4 rings and above. The PAHs mostly consist of carbon and hydrogen, and their structure can be configured in a linear, angular, or cluster formation [10]. It was discovered by Batchamen Mognol et al. [11] that the leaching of PAHs is quick in the acidic mine drainage as compared to the alkaline mine and sewage wastewater, which was caused by pH and the total dissolved organic carbon in the water sources.

There are more than 100 PAHs that are derived from various activities, however, only 16 PAHs have been recognized by the United State Environmental Protection Agency (U.S. EPA, Washington, DC, USA) and European to be human carcinogens and also widely present in various water sources [12]. The 16 PAHs, as presented in Table 1, have been discussed in various studies with regard to their molecular weight and toxicity level [13]. It has been reported by Smol et al. [14] that the PAHs with a lower molecular weight (LMW) undergo a faster degradation as compared to those with a heavy molecular weight (HMW). Moreover, the solubility of PAHs is dependent on their molecular weight [14]. Table 1 represents the characteristics of the 16 PAHs that are found in the environment and various water sources based on the U.S. EPA.

The potential health-related issue resulting from the excessive consumption of PAHs such as skin irritation, inflammation, immune dysfunction, and damage to both kidneys and liver have made them unwanted and unfriendly to the environment. These PAHs also lead to the biological destruction of human cells due to their carcinogenic and mutagenic properties [5,15,16]. Because of their adverse effects, it has been prioritized as the pollutant that is in contact with humans the most, according to the U.S. Environmental Protection Agency (USEPA) [16–19].

The release of these PAHs can also homogeneously change the physio-chemistry of the sewage wastewater, alkaline mine drainage, acid mine drainage, and possible other water sources. Sewage wastewater contains various other pollutants that have been studied in conversion to energy [20]. Most organics such lipids, fats, oils, and heterogeneous and inorganic materials are mostly found in sewage wastewater [21]. The viscosity of sewage wastewater is due to its hydrophobic property [22]. Some metals, such as arsenic (As), cadmium (Cd), chromium (Cr), copper (Cu), mercury (Hg), manganese (Mn), nickel (Ni), lead (Pb), and Zinc (Zn) have similar carcinogenic and mutagenic properties as PAHs [23]. Sewage properties can allow for the adsorption of suspended particles that represent a threat to ecosystems [24]. Various parameters such as total dissolved solids (TSD), pH, temperature, nitrate, nitrite, phosphate, chloride, biologic oxygen demand (BOD), sulphate, ammonium ion, chemical oxygen demand (COD), and alkalinity [25,26]. The deposition of PAHs in acidic mine drainage, alkaline mine drainage, and sewage wastewater has not received attention [11].

Acidic mine drainage has been widely noted to be the world's largest problem, and this has been revealed by various studies [27]. The term AMD has been recently used instead of acidic rock drainage (ARD) and sulphide oxidation, which was previously used [28]. AMD is formed in a process that occurs in most mining activities due to sulphide reactions, often in the presence of microorganisms, temperature, water, and oxygen in a mine region through a geology function. These mechanisms are variable for different mine regions [29]. The destruction of the mineralized material also leads to AMD and is detrimental to the

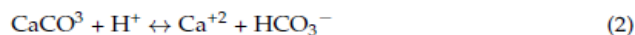
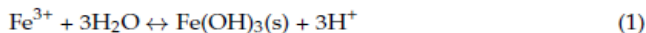
environment and humans by damaging various agro species such as plants, fauna, and water, leading to a major cost. AMD is a strong acidic wastewater that contains both ferrous and non-ferrous materials, as well as salts. Among the ferrous materials, there are also some other toxic metals such as As, Cd, Cr, Cu, Zn, Ca, Mg, Al, Mn, Ni, and Pb that contribute to the acidic mine drainage; these are found in small concentrations in the ppm range [29–31]. The alkalinity can be generated through a process of sulphate reduction and carbonate dissolution. On the other hand, a sufficient concentration of carbonate (CaCO_3), bicarbonate (HCO_3^-), and silicate minerals, can change wastewater to be alkaline [32,33].

Table 1. The 16 PAHs that are commonly found in various water sources [13]. Copyright 2020, copyright owner's A.O. Adeniji.

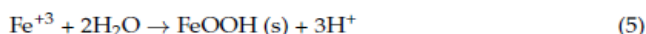
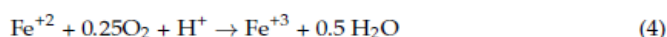
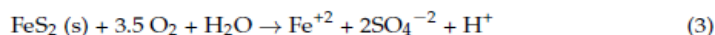
Table 1. The 16 PAHs that are commonly found in various water sources [13]. Copyright 2020, copyright owner's A.O. Adeniji.

PAHs	Chemical Formula	Molecular Weight (g/mol)	Rings Number	Melting Point (°C)	Boiling Point (°C)	Structures
Naphthalene (NAP)	C ₁₀ H ₈	128	2	80.2	218	
Acenaphthylene (ACY)	C ₁₂ H ₈	152	3	92.5	280	
Acenaphthene (ACE)	C ₁₂ H ₁₀	152	3	93.4	279	
Fluorene (FL)	C ₁₃ H ₁₀	166	3	115	295	
Phenanthrene (PHE)	C ₁₄ H ₁₀	178	3	99.2	340	
Anthracene (ANT)	C ₁₄ H ₁₀	178	4	215	340	
Fluoranthene (FLU)	C ₁₆ H ₁₀	202	4	108	384	
Pyrene (PYR)	C ₁₆ H ₁₀	202	4	151	404	
Benzo[a]anthracene (BaA)	C ₁₈ H ₁₂	228	4	167	435	
Chrysene (CHY)	C ₁₈ H ₁₂	228	4	258	448	
Benzo[b]fluoranthene (BbF)	C ₂₀ H ₁₂	252	5	168	481	
Benzo[k]fluoranthene (BkF)	C ₂₀ H ₁₂	252	5	217	480	
Benzo[a]pyrene (BaP)	C ₂₀ H ₁₂	252	5	177	495	
Dibenzo[a,h]anthracene (DahA)	C ₂₂ H ₁₄	278	5	270	524	
Indenol [1,2,3-cd] pyrene (IP)	C ₂₂ H ₁₂	276	6	164	536	
Benzo[g,h,i]perylene (Bghip)	C ₂₂ H ₁₂	276	6	278	550	

The measure of pH can be used to determine the acidity and alkalinity of the wastewater, and it is in the range of pH 2–8 [32]. The acidic and alkaline reactions are presented in Equations (1) and (2)



AMD is formed by reduced sulphur oxidization in the presence of oxygen and water during destruction [33], and the formation of AMD can be represented in Equations (3)–(5)



Presently, there are still major industries and activities that release PAHs, and according to Rodríguez-Galán, et al. [30], special treatment should be implemented to either treat or monitor the deposition of compounds or by-products that contain PAHs, like the coal pollution in the environment, which cause problems and result in a lot of necessary maintenance and high costs to reduce or treat the pollution.

The increase in the number of rings increases the molecular weight of PAHs and their hydrophobic nature [10]; this has been suggested as an effective method to remove these organic pollutants from living things [34,35]. There are methods such as biological, physical (filtration, precipitation, flocculation, reverse osmosis methods, and adsorption) and chemical (advanced oxidation, ion exchange, coagulation, advanced oxidation, and ozonation) approaches [36] that have been conducted to assist in degrading these PAHs from various water sources [7,37]. There are disadvantages to these, such as the maintenance cost and the release of a toxic by-product when using physical and chemical methods. However, it was pointed out that the biological method is a better candidate to approximately remove 92% of PAHs that are mostly in soil [38,39].

Sunlight is composed of three components that provide a range of wavelengths, namely visible light (400–700 nm), UVA light (320–400 nm), and UVB (280–320 nm), which can be used to degrade PAHs in water sources [40]. The degradation of PAHs can best be monitored using visible light and UVA [40]. The application of the light source can be accommodated with a photoreactor. A photoreactor is a device that is mostly composed of elements that are designed with a specific dimension and geometry to be used for various applications, but this study is aimed at the photodegradation of PAHs. The photoreactor can either be designed with a single channel (the fluid is flowing in one direction) or multiple channels (the fluid is flowing in various directions) [41]. Various photoreactors, such as photocatalytic reactors, have been used for the degradation of organic pollutants. These reactors have been designed to accommodate a catalyst and light source. In this conventional photocatalytic reactor, an additional solar converter, timer, recycler, cooler or heater exchange, etc, can be mounted to enhance its effectiveness [42,43].

Some photoreactors have advantages and disadvantages in converting energy from solar irradiation to photons [44]. The use of collectors is important in case the photoreactor is unable to provide enough of the necessary energy / photons [45]. However, it all depends on the range of operating temperatures and the efficiency. Collectors such as the flat plate, parabolic mix, evacuated tank, parabolic trough, Fresnel prism, parabolic dish, and heliostat field collectors can be used to enhance the photoreactor effectiveness. The advantages of these collectors, when combining them with optical, thermal and thermodynamic devices, can enhance their performance [46]. A study conducted by Matamoros et al. [47] illustrated that the nature of the environment drastically influences the removal efficiency of pollutants. It was observed that during a warm season, a higher temperature resulted in a higher removal efficiency as compared to a cold season. It was proven that the longer the reaction between the photon and the pollutants, the higher the photodegradation of the pollutants (PAHs) [48].

In this study, the aims are to investigate the effectiveness of a self-made photoreactor on the photodegradation of PAHs in acidic mine drainage, alkaline mine drainage, and sewage wastewater, assisted by solar irradiation. The purpose of this work is to introduce an effective material that is harmless and cost-effective for the photodegradation of PAHs. Therefore, to achieve this, it is important to improve the effectiveness of solar irradiation by implementing a material that will enhance viability.

2. Materials and Methods

In this study, three water sources, namely acidic mine drainage, alkaline mine drainage, and sewage wastewater, were collected at the Witbank (25.8728° S, 29.2553° E), Middleburg (25.7699° S, 29.4639° E) and Cape Town Municipality (33.9249° S, 18.4241° E) in South Africa. The coal tar was obtained at New Castle KwaZulu-Natal (27.7138° S, 29.9972° E), South Africa (30.5595° S, 22.9375° E). These water sources were analysed as previously reported by Batchamen et al. [11].

2.1. Degradation Experiments

A 5 g mass of coal tar was added in each water sample, i.e., acidic mine drainage, alkaline mine drainage, and sewage wastewater, for the leaching process [11]. A concentration of 2916.47 mg/L of PAHs in coal was identified using the Gas Chromatography Thermo Scientific (TSQ 8000) apparatus (Cape Town, South Africa) using a Triple Quadrupole MS technique.

The leaching process of the PAHs was conducted, and it was found that 19.255 mg/L, 1.615 mg/L, and 1.813 mg/L of PAHs out of 2916.47 mg/L were dissolved in the acidic mine drainage, alkaline mine drainage, and sewage wastewater, respectively, in 8 weeks. A volume of 300 mL of each of these water sources was used for the photodegradation of the PAHs under solar irradiation respective to time with or without the flat-bed photoreactor. Without the flat-bed photoreactor, 250 mL volume solution was stirred with a magnetic stirrer operated at 250 rates per minute (RPM), as illustrated in Figure 1. A similar procedure was also conducted but this time, with the flat-bed photoreactor being used.

The water samples were collected at each interval of 20 min, 40 min, and 60 min using a 0.45 µm syringe filtered PDVP after the photodegradation. The GC-MS was used to determine the remaining PAHs in each of the water sources so as to investigate the degraded PAHs, and the results are presented in Tables 3 and 4. The degraded PAHs were calculated using Equation (6) and the removal efficiency using Equation (7).

$$\text{PAHs}_{\text{initial}} - \text{PAHs}_{\text{final}} = \text{PAHs}_{\text{degraded}} \quad (6)$$

$$\text{PAHs removal efficiency (RE) (\%)} = \frac{C_o - C_t}{C_o} \times 100\% \quad (7)$$

where C_o is the initial concentration of PAHs and C_t is the concentration after the photodegradation respective to time (t).

A similar experiment was conducted but this time with a flat-bed photoreactor. The flat-bed photoreactor was made of Perspex material (AXSC0230502050I) and used for the study. Their dimension unit is given in millimetres (mm) (Figure 2). The box was used to maintain the photon energy within the system.

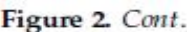
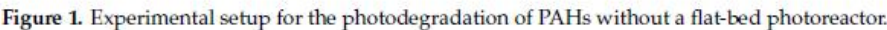




Figure 2. Different views of the dimensions of the photoreactor.

The introduction of the flat-bed photoreactor was highly efficient by collecting as much photon energy from the sun and destabilizing the π - π bonds from the PAHs. The process of photoelectrochemical water splitting, which is also known as the electrolysis process using solar energy to split water molecular (H_2O) and form H^+ and OH^- should be considered for spontaneous photodegradation of PAHs. These radicals can effectively destroy organic pollutants, however, these radicals were highly reactive when using the flat-bed photoreactor.

2.2. Photodegradation Mechanism

There are various species, also known as oxidants or radicals, such as $\text{O}_2^{\cdot-}$ and $\text{HO}_2^{\cdot}$; however, their oxidation potential is not as high as the hydroxyl ($\cdot\text{OH}$) that can contribute to the photodegradation [49]. These species can be derived naturally under solar irradiation from the water molecule.

During the photodegradation of PAHs, the water molecules are broken down by forming radicals, and these radicals interact with the pollutants by degrading them. According to Li et al. [50], h^+ , $\text{HO}_2^{\cdot}$, $\text{O}_2^{\cdot-}$, and $\text{OH}^{\cdot}$ are the most active reagents with regard to degrading organic pollutants. Although they are several scavengers, also known as active reagents, that can degrade the PAHs, $\text{OH}^{\cdot}$ happens to be widely effective and generable from the water molecule splitting [43]. Its high oxidation potential of $E(\text{OH}/\text{H}_2\text{O}) = 2.80 \text{ V/SHE}$ makes it better and more effective [51]; although it is the second after fluorine $E = 3.0 \text{ eV}$ to be commonly responsible for interacting with the PAHs, it can easily be generated from water splitting. Figure 3 demonstrates the mechanism of the splitting of a water molecule triggered by solar irradiation to aid in the photodegradation of PAHs.

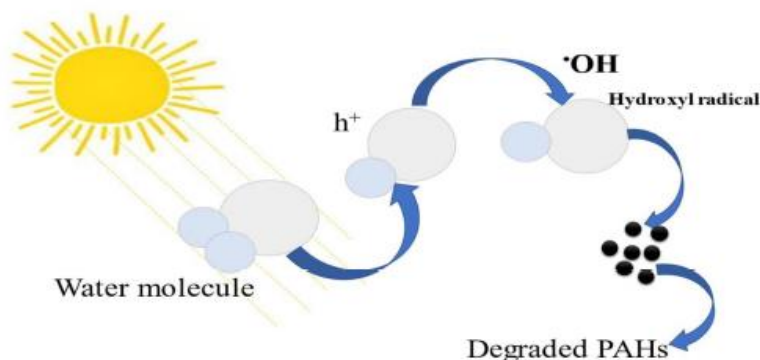


Figure 3. The mechanism of the photodegradation of PAHs.

Since organic pollutants have recently gained attention and various techniques have been applied and the application of the photocatalytic has been proven to be highly effective, and eco-friendly; in undertaking complex organic compounds and for spontaneous photodegradation, a presence of light should be acquired [52–54].

A Study by Rani and Karthikeyan [55] was conducted using a self-made photoreactor that was composed of a photocatalytic membrane reactor which was coupled with a

membrane process to assist in the photodegradation of selected PAHs such as PHE, NAP, and ACE under UV light. The photodegradation of PHE, NAP, and ACE at 180 min without the catalyst (TiO₂) and the membrane ultrafiltration (UF) was found to be 8.1, 43.3, and 42.0%, respectively. Afterwards, the addition of a catalyst and membrane resulted in the removal efficiency that varied individually as compared to a sample. A removal efficiency of 83.5, 76.8, and 80.1% individually was found, as compared to the removal efficiency of 85.6, 79.1, and 83.4% for PHE, NAP, and ACE, respectively, that was observed in a sample.

3. Results and Discussion

A mass of 116.3 mg with 2 mL of hexane was used to extract and analyse the PAHs in a coal tar using the GC-MS. It was discovered to have a concentration of 2916.47 mg/L of PAHs in total. Table 2 represents the concentration of 16 PAHs found in coal tar. Naphthalene happens to be highly concentrated with 788 mg/L as compared to Indenol[1,2,3-cd] pyrene of 8 mg/L.

Table 2. PAHs concentration in a coal tar.

PAHs (Pollutants)	Concentration (mg/L)
NAP	788
ACY	356
ACE	18
FL	327
PHE	632
ANT	245
FLU	395
PYR	266
BaA	91
CHY	126
BbF	75
Blkf	71
BaP	92
DahA	56
IP	8
Bghip	21

Tables 3–5 represent the photodegradation of these 16 PAHs in 20 min, 40 min, and 60 min with and without the flat-bed photoreactor on the acidic mine drainage, alkaline mine drainage, and sewage wastewater.

During the photodegradation of PAHs in various water sources, the water was treated in time periods of 20 min, 40 min, and 60 min, and it was observed that the remaining PAHs in each water source were degraded with a lesser removal efficiency in the shorter time periods. Naphthalene with a lower ring number and lower boiling point, as presented in Table 1, was completely degraded. Acenaphthene, fluorene, dibenzo[a,h]anthracene, pyrene, indenol[1,2,3-cd] pyrene, Benzo[g,h,i]perylene, benzo[b]fluoranthene, and benzo[k]fluoranthene with initial concentrations of 18 mg/L, 395 mg/L, 56 mg/L, 266 mg/L, 8 mg/L, 21 mg/L, 75 mg/L, and 71 mg/L, respectively, in an acidic mine drainage were not degraded. In addition benzo[a]anthracene, chrysene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, dibenzo[a,h]anthracene, indenol[1,2,3-cd] pyrene, and benzo[g,h,i]perylene with initial concentrations of 91 mg/L, 126 mg/L, 75 mg/L, 71 mg/L, 92 mg/L, 56 mg/L, 8 mg/L, and 21 mg/L, in an alkaline mine drainage were also not degraded; moreover, acenaphthene

with an initial concentration of 18 mg/L in sewage wastewater was also not degraded. These PAHs were not degraded at any stage of the photodegradation process; although they were identified in coal tar, they were not dissolved in the water sources left for 8 weeks of dissolution time. The higher molecular weight PAHs happen to have a lower decomposition rate, which was observed in alkaline mine drainage.

Table 3. Photodegradation of PAHs in acidic mine drainage (concentrations in mg/L).

PAHs	Initial Concentration	20 min	40 min	60 min	20 min	40 min	60 min
NAP	0.0031	0.0030	0.0017	0.0025	0.0019	0.0016	0.0029
ACY	0.1302	0.1092	0.1267	0.1031	0.1271	0.1098	0.1277
ACE	0	0	0	0	0	0	0
FL	0	0	0	0	0	0	0
PHE	0.0181	0.0083	0.0091	0.0133	0.008	0.0143	0.0176
ANT	18.9847	7.7006	6.7824	6.7014	10.7141	9.5481	8.7359
FLU	0.0020	0.0017	0.0013	0.0013	0.0018	0.0013	0.0016
PYR	0	0	0	0	0	0	0
BaA	0.1114	0.1049	0.1062	0.0517	0.1109	0.1089	0.1093
CHY	0.0012	0	0	0.0007	0.0010	0.0003	0.0009
BbF	0	0	0	0	0	0	0
Blkf	0	0	0	0	0	0	0
BaP	0.0046	0.0042	0.0036	0.0032	0.0042	0.0037	0.0040
DahA	0	0	0	0	0	0	0
IP	0	0	0	0	0	0	0
Bghip	0	0	0	0	0	0	0
PAHs photodegradation	19.2553	7.932	7.031	6.889	10.969	9.788	8.999

Table 4. Photodegradation of PAHs in alkaline mine drainage (concentrations in mg/L).

PAHs	Initial Concentration	20 min	40 min	60 min	20 min	40 min	60 min
NAP	0.7615	0.5943	0.5280	0.4212	0.6802	0.6212	0.5212
ACY	0.2596	0.0419	0.0363	0.0139	0.2281	0.1081	0.1281
ACE	0.0020	0.0012	0.0001	0.0001	0	0	0
FL	0.0030	0.0013	0.0012	0.0014	0.0027	0.0019	0.0021
PHE	0.0447	0.0381	0.0216	0.0218	0.0418	0.0359	0.0237
ANT	0.5388	0.2329	0.2194	0.2584	0.5071	0.4112	0.3972
FLU	0.0039	0.0027	0.0019	0.0012	0.0037	0.0028	0.0031
PYR	0.0019	0	0	0	0	0	0
BaA	0	0	0	0	0	0	0
CHY	0	0	0	0	0	0	0
BbF	0	0	0	0	0	0	0
Blkf	0	0	0	0	0	0	0
BaP	0	0	0	0	0	0	0
DahA	0	0	0	0	0	0	0
IP	0	0	0	0	0	0	0
Bghip	0	0	0	0	0	0	0
PAHs photodegradation	1.6154	0.9122	0.8085	0.7180	1.4636	1.1811	1.0754

Table 5. Photodegradation of PAHs in sewage wastewater (concentrations in mg/L).

PAHs	Initial Concentration	20 min	40 min	60 min	20 min	40 min	60 min
NAP	0.0069	0.0053	0.0045	0.0047	0.0067	0.0062	0.0053
ACY	0.0489	0.0359	0.0310	0.0224	0.0379	0.0358	0.0302
ACE	0	0	0	0	0	0	0
FL	0.009	0.0067	0.0058	0.0015	0.0011	0.0010	0.0065
PHE	0.0961	0.0177	0.0153	0.0121	0.0821	0.0773	0.0758
ANT	0.1758	0.1502	0.0957	0.1019	0.1508	0.1395	0.1059
FLU	0.1706	0.0197	0.0049	0.0347	0.1607	0.1370	0.1134
PYR	0.1389	0.0149	0.0123	0.0333	0.1297	0.1033	0.0927
BaA	0.1888	0.0158	0.0937	0.1171	0.1251	0.1222	0.1193
CHY	0.1170	0.1002	0.0713	0.0943	0.1078	0.0931	0.1091
BbF	0.2216	0.1506	0.1474	0.1004	0.2004	0.1017	0.1099
Blkf	0.1563	0.0753	0.1132	0.1007	0.1390	0.1031	0.1013
BaP	0.2185	0.1073	0.1175	0.0372	0.2012	0.1109	0.1197
DahA	0.1278	0.0137	0.0109	0.0273	0.1224	0.1006	0.0710
IP	0.0345	0.0063	0.0045	0.0065	0.0217	0.0194	0.0205
Bghip	0.1018	0.0676	0.0507	0.0451	0.0978	0.0501	0.0612
PAHs photodegradation	1.8125	0.7872	0.7787	0.7572	1.5844	1.2002	1.1113

According to Qiao [56], these PAHs emit a specific wavelength, and in this study, these persistent PAHs in each water source were slightly degraded at their specific wavelength.

The photodegradation of the PAHs was conducted at an interval period of 20 min, 40 min and 60 min in acidic mine drainage, alkaline mine drainage and sewage wastewater. It was observed that, as time increases, the removal efficiency of PAHs also increased due to the longer contact time between the photons and the pollutants (PAHs) in the flat-bed photoreactor. The higher removal efficiency occurred in acidic mine drainage as compared to alkaline mine drainage with and without the introduction of the flat-bed photoreactor. The greater the remaining PAHs in each of these water sources, or the closer they are to their initial concentration, the lesser the removal efficiency, and vice versa. In this study, the acidic mine drainage should be given more attention due to its higher PAHs dissolution respective to time. The higher removal efficiency depends on the PAHs' dissolution in the water sources. Besides this, sewage water was the water source where 15 PAHs out of the 16 recognized PAHs were dissolved, and this could be attributed to the water's physiochemical properties, such as total dissolved solids and dissolved organic carbon.

Figure 4A,B represent the photodegradation of the PAHs with (A) a flat-bed photoreactor and (B) without a flat-bed photoreactor, showing better degradation efficiency when the flat-bed photoreactor was used.

Since two sets of experiments were conducted aiming for the photodegradation of PAHs in three water sources, it was discovered that the photodegradation of PAHs in acidic mine drainage was better to dissolve the PAHs rapidly in the leaching process, as reported by Batchamen et al. [11]. The photodegradation was also favoured by both solar irradiation, as shown by Li et al. [50,57], and the time taken for degradation [48]. The photodegradation of PAHs was directly proportional to time and best performed using a flat-bed photoreactor. As shown in Figure 4, the removal efficiency of the PAHs indicates that the flat-bed photoreactor provided a higher removal efficiency. The scavenger ($\text{OH}^\bullet$) was highly reactive in acidic mine drainage as compared to alkaline mine drainage, and this was attributed to the physiochemical properties of the water reported by Batchamen et al. [11].

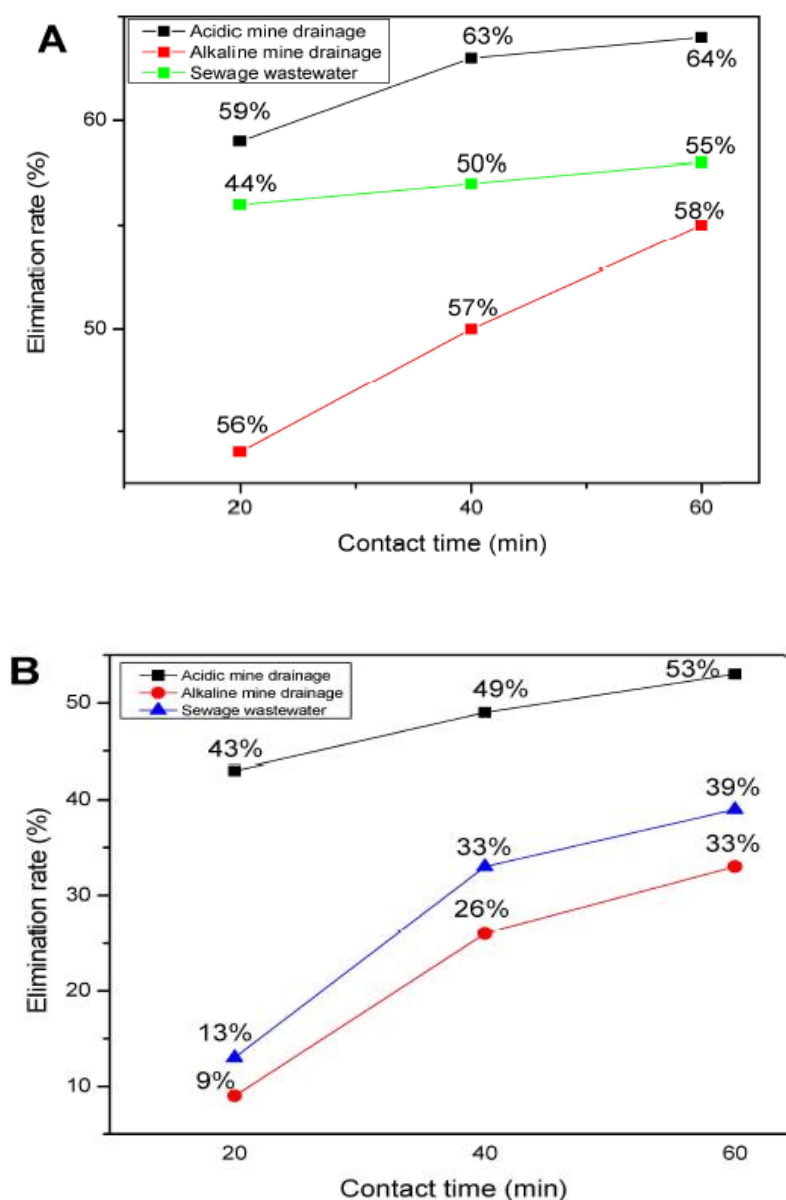


Figure 4. Photodegradation of PAHs with (A) a flat-bed photoreactor and (B) without a flat-bed photoreactor.

A comparison of the experiments conducted by Rani et al. [55] on the photodegradation of PAH in an aqueous solution and the results obtained in the present experiment for the AMD, shows that the results of this current study agree with those obtained by Rani et al. [55], which showed that the removal efficiency was higher as compared to the individual PAHs. The introduction of TiO_2 and UF (UV) in a photoreactor could enhance a 85.6% PHE, 79.1% NAP, and 83.4% ACE removal, whereas with the application of the flat-bed, as was done in the present experiment, almost 100% removal was possible in the three water sources studied.

The photodegradation of PAHs was favoured in the acidic mine drainage, followed by sewage wastewater and alkaline mine drainage. The results reveal that, as time increases, more energy is required from the photon to the chemical energy to destabilize the π - π bonds rings in PAHs to anticipate its degradation. The flat-bed photoreactor was able to adapt enough energy due to the materials used and the geometry. The photodegradation after

60 min was not enough to obtain a removal efficiency of 100%, therefore, it is recommended for the photodegradation to go beyond 60 min.

In this study, it was proven that the flat-bed photoreactor was effective, and it was able to decrease both the hydrophobic and immobility of the PAHs by destabilizing them with the help of solar irradiation [53]. However, since the reaction occurred in a system, a few factors, such as the nature of the environment, might influence the reaction, as reported by Matamoros et al. [47]. After the photodegradation, the physiochemical property of these waters, like the total dissolved organic carbon, decreases along with the PAHs pollutant [58]. The application of the flat-bed photoreactor can be recommended as an efficient method for the photodegradation of persistent organic pollutants at any stage and water sources. This flat-bed shows a higher removal efficiency under solar irradiation without any addition of a catalyst; therefore, it can be recommended to be tested with an additional catalyst to enhance the photodegradation of PAHs in various water sources.

4. Conclusions

The photodegradation of PAHs was proven to be spontaneous in the acidic mine drainage, followed by the alkaline mine drainage and sewage wastewater, because of the pH and the total dissolved organic content of these waters, as shown by Batchamen et al. [11]. Solar energy, which is a renewable energy source, was effective in reducing the PAHs in acidic mine drainage, alkaline mine drainage, and sewage wastewater with or without the flat-bed photoreactor. It was also highlighted that as time increased, more contact between the PAHs and the photon took place. The flat-bed photoreactor was effective in producing enough photons to challenge the aromatics rings to degrade the PAHs over time. The removal efficiency was found to be 64%, 55%, and 58% using a flat-bed photoreactor and 53%, 33%, and 39% without the flat-bed photoreactor over time in acidic mine drainage, alkaline drainage, and sewage wastewater, respectively. The hydroxyl species from the water splitting was responsible for taking control of the persistent organic pollutants (PAHs) in the experimental waters. The solar irradiation and the flat-bed photoreactor were highly effective in achieving the aim. The highest removal efficiency was observed in acidic mine drainage, followed by sewage wastewater and alkaline mine drainage.

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10. Conclusion

The study of the photodegradation of the polycyclic aromatic hydrocarbon (PAH) group of organic pollutants has been reported to be life-threatening, therefore their photodegradation were assessed in various water sources.. Their presence in water and contact in the environment has made them pollutants that should be removed, or limited, with regard to their release into the atmosphere and all water sources. There are 660 known species of PAHs, but only 16 of these PAHs are widely abundant in the environment and wastewater; they are known as toxic pollutants according to the USEPA, because of their chemical nature. Their molecular structure determines their solubility in water, with a higher molecular weight PAH resulting in more strongly carcinogenic action, as compared to the lower molecular weight PAHs.

It was proven that naphthalene, phenanthrene, and acenaphthylene with concentrations of 788 mg/L, 632 mg/L and 356 mg/L respectively were the most concentrated species found in the coal tar investigated. These PAHs have lower molecular weight and fewer rings, which makes them volatile and soluble in wastewater, as compared to the heavy molecular weight PAHs. It was previously reported that the concentration of PYR in water in South Africa was at 1.118mg/L and 8.31mg/L for BbF in sewage wastewater. However, in this study, the concentration of PYR in acidic mine drainage, alkaline mine drainage and sewage wastewater was found to be 0.0083 mg/L, 0.0206 mg/L and 0.0084 mg/L, whereas the concentration of BbF was found to be 0.0288 mg/L, 0.0092 mg/L and 0.0190 mg/L in the same water samples. This confirmed that the petroleum industry and mine related activities can contribute to a higher PAH solution in waters and also result in change in the water physiochemistry.

The influence of the leaching of coal tar into these wastewaters resulted in a change in the physiochemistry of wastewater. From the experimental date it was apparent that the higher molecular weight PAHs are less hydrophobic and water-soluble, as compared to the lower molecular weight PAHs.

The dissolution of the coal tar was influenced by the pH and the total organic carbon present, which are a few amongst many factors which could influence the leaching reaction at room temperature. Having obtained the leachate, there was a need to implement a technique that could improve on the traditional methods that have been previously used for the degradation of PAHs. Various metal oxides have been used in semiconductor experiments, but the addition of agrowastes to these catalysts has not been widely used. Agrowastes have been used in various other application, like the green synthesis of nanoparticles and their precipitates, and in the present investigation they were used in conjunction with a metal oxide semiconductor for the study of the photodegradation of the PAHs in various water sources. Agrowastes such as groundnut shells, *moringa oleifera* seed and apatite, including silver to enhance the properties of the ZnO semiconductor were used to make a heterogeneous photobiocatalyst, with the MO/GS/A/ZnO/Ag photobiocatalyst degradation properties of the PAHs, compared to those of a traditional ZnO/Ag photocatalyst.

The main reason for adding these biological wastes was to increase the photoactivity of the ZnO. They were added in various concentrations, with a ratio of 1:1:1 resulting in the best properties and lowest bandgap for the photocatalyst. It was found that the biogenic application on the ZnO/Ag resulted in a lower bandgap, as compared to the parental ZnO. From the ICP-MS analysis it was revealed that the agrowastes had a relative high metal content and further contributed to the better performance of the heterobio-photocatalyst, as compared to Ag metal doping alone of the ZnO. Various studies have reported the doping of metals to reduce the bandgap of metal oxide and alternatively, in this study, the presence of the metals in the agrowastes was investigated and proven to reduce the ZnO bandgap. The combination of these agrowastes at a ratio of 1:1:1 resulted in a 1.96 eV bandgap, as compared to the parental ZnO which was found to be 3.35 eV and 2.96 eV for ZnO/Ag. The effectiveness of the agrowastes used in different ratios individually was found to be ZnO/MO (2.74 eV), ZnO/GS (2.51 eV) and ZnO/A (2.15 eV).

The agrowaste apatite was highly effective in lowering the bandgap and increasing the photoactivity of ZnO. These materials were later used to determine their effectiveness in minimizing the PAH concentrations in the 3 wastewater samples tested. It was found that 70%, 61% and 62% degradation was obtained for the acidic mine drainage, alkaline mine drainage and sewage wastewater respectively by using MO/GS/A/ZnO/Ag, while 53%, 38% and 44% degradation was possible using ZnO/Ag alone. All the experiments were conducted under solar irradiation in a period of 60 min. It was thus proven that MO/GS/A/ZnO/Ag was a better candidate as compared to ZnO/Ag. Lastly, a self-made flat-bed photoreactor was constructed, since the PAHs can be better destabilized from the environment under a light source.

It was therefore imperative to use a material that would absorb enough energy to degrade the PAH pollutants. As indicated in Table 1, the effectiveness of the self-made flat-bed photoreactor was highly effective as compared to the other experimental set-ups.

Table 1: Comparison of the different results obtained on the PAH photodegradation efficiency

Material	Photodegradation efficiency (%)		
	Acidic mine drainage	Alkaline mine drainage	Sewage wastewater
Photoreactor	64.0	58.0	55.0
ZnO/Ag	52.62	37.96	44.30
MO/GS/A/ ZnO/Ag	69.59	61.07	61.68
Photoreactor/ ZnO/Ag	89.48	94.35	92.44
Photoreactor /MO/GS/A/ ZnO/Ag	99.72	97.04	98.21

The combination of the catalyst and the photoreactor gave the best results. The mechanism involved in the photodegradation, when using the flat-bed photoreactor, the hydroxyl radicals produced from the water resulted in the hydroxyl radicals produced from the water resulted in faster degradation of the PAHs. By combining both the photocatalyst and the flat-bed photoreactor the best higher degradation efficiency was

achieved. Thus, when using MO/GS/A/ZnO/Ag with a flat-bed photoreactor, nearly 100% photodegradation efficiency of the PAHs was obtained. The flat-bed photoreactor alone was even found to be more effective when compared to the ZnO/Ag photocatalyst alone. The photodegradation efficiency of about <50%-60 using only the flat-bed photoreactor, compared to <35%-50%% efficiency using ZnO alone, is proof of the advantage of using the flat-bed photoreactor.

The flat-bed photoreactor was able to provide the sufficient energy to degrade the PAHs. The excitation of the electrons from the valance band (VB) to the conduction band (CB) to produces hydroperoxyl radical ($\text{HO}_2\bullet$) reacting with hydrogen ions (H^+) in the solution produced hydrogen peroxide (H_2O_2) radicals that behaved as an oxidizing agent. This later produced a secondary strong radical, an hydroxyl radical, that is slightly less oxidising than for example fluorine. In the absence of the photocatalyst, $\text{OH}\bullet$ was still produced from the dissolution of the water when using the flat-bed photoreactor. The oxygen present in the agrowastes transformed to $\text{O}_2\bullet$ from accepting delocalized electrons from between VB and CB, and $\text{O}_2\bullet$ was then promoted to interact with PAHs. The superoxide ($\text{O}_2\bullet$) was only produced during the introduction of the photocatalyst. However, the presence of the metal in the apatite contributed to a lower band gap and the oxygen in the MO contributed to the delay recombination of electron charge carrier that overall played an important role to the photodegradation process. It was also revealed that, as time increased, the rate of the reaction between the pollutants and the photocatalyst also increased.

The leaching and subsequent photodegradation of the PAHs were both favoured in acidic mine drainage. FTIR analyses indicated the functional groups, such as amine and carboxylic acid, that contributed to the degradation of the PAHs. The SEM analyses revealed the morphological structure of the material before and after treatment. The material surfaces indicated the occupation of the active sites by the PAHs. The most preferred adsorption isotherm and kinetic that best represented the study were the Freundlich and Pseudo-first-order theorems.

The release of PAHs into the environment has resulted in the manufacture of a novel application that successfully alleviated the resultant pollutant problems occurring in various water sources. The addition of solar irradiation was able to assist in degrading the 16 PAHs found in the present investigation. The introduction of agrowastes was an effective way to further eradicate the pollution of the PAHs to ensure a safer and cleaner environment.

RECOMMENDATIONS

The following are recommendations for further research:

- The study investigated only a few types of leaching lixivants and should be extended to other lixivants such as the various AMD sources, as well as sea water, that can be tested to see how they can influence the leaching process of PAHs.

- Prolonged testing periods are needed to determine how the concentration and the constituents in the leachate change after a prolonged period of time.
- Since all photodegradation experiments in this study were conducted on a laboratory scale, it is necessary to investigate the feasibility on large scale set-ups.
- Other materials, such as glass, can be used in the construction of a flatbed reactor, as the present reactor was made of Perspex with a reduced transmission of light.
- Since this study investigated a PAH removal process from water using naphthalene as the representative of PAHs, more degradation and adsorption experiments can be conducted using other heavier and toxic PAHs such as benzo(a)pyrene, phenanthrene and pyrene.
- Different agrowastes should be used and detailed analyses undertaken of their organic compounds, such as carbon and hydrogen, as some agrowastes were not effective due to their mineral content. It can be recommended in future, that other agrowastes, ratios or metal oxides can be considered to improve the study on the photodegradation of PAHs derived from coal tar or any other related petroleum substance. The biogenic application provided a better performance and can even be further improved to obtain the best method in the degradation of these organic pollutants.

11. Appendices

Paper Title	Synthesis of Bio-Photocatalysts and their Application for the Degradation of Organic Pollutants
Authors	Jean Bedel Batchamen Mougno, Elvis Fosso-Kankeu, Ali R. Al Alili, Neeraj Kumar, Rashi Gusain, Hemant Mittal and Suprakas S. Ray
Document type	Conference Paper and presentation
Journal	18th JOHANNESBURG Int'l Conference on Science, Engineering, Technology & Waste Management (SETWM-20) Nov. 16-17, 2020 Johannesburg (SA)
Year	Published (2020)
Co-authors: Elvis Fosso-Kankeu Signature	
Co-authors: Ali R. Al Alili Signature	
Co-authors: Neeraj Kumar Signature	
Co-authors: Rashi Gusain Signature	
Co-authors: Hemant Mittal Signature	
Co-authors: Suprakas S. Ray Signature	

Paper Title	Photodegradation of polycyclic aromatic hydrocarbons using metals oxide under irradiation
Authors	Jean Bedel Batchamen Mougno; Frans Waanders; Seteno Karabo Obed Ntwampe; Elvis Fosso-Kankeu; Ali R. Al Alili
Document type	Review paper
Journal	Journal of Water Process Engineering
Co-authors: Frans Waanders Signature	
Co-authors: Seteno Karabo Obed Ntwampe Signature	
Co-authors: Elvis Fosso-Kankeu Signature	
Co-authors: Ali R. Al Alili Signature	

Paper Title	Recent Advances in Photoreactors for Water Treatment
Authors	Jean Bedel Batchamen Mougnot, Shelter Maswanganyi, Frans Waanders, Rashi Gusain, Neeraj Kumar, Elvis Fosso-Kankeu, Suprakas Sinha Ray
Document type	The Future of Wastewater Treatment Ch. 7
Journal	Scrivener Publishing, SCI Journal
Year	Accepted. Ready for publication.
Co-authors: Shelter Maswanganyi Signature	
Co-authors: Frans Waanders Signature	
Co-authors: Rashi Gusain Signature	
Co-authors: Neeraj Kumar Signature	
Co-authors: Elvis Fosso-Kankeu Signature	
Co-authors: Suprakas Sinha Ray Signature	

Paper Title	Leaching of polycyclic aromatic hydrocarbons from the coal tar in sewage wastewater, acidic and alkaline mine drainage
Authors	Jean Bedel Batchamen Mougno; Frans Waanders; Elvis Fosso-Kankeu; Ali R. Al Alili
Document type	Article
Journal	International Journal of Environmental Research and Public Health. MDPI.
Year	Published (2022)
Co-authors: Frans Waanders Signature	
Co-authors: Elvis Fosso-Kankeu Signature	
Co-authors: Elvis Fosso-Kankeu Signature	
Co-authors: Ali R. Al Alili Signature	

Paper Title	Synthesizes of eco-friendly heterocatalysts with enhanced properties to perform under visible light
Authors	Jean Bedel Batchamen Mougol, Frans Waanders, Seteno Karabo Obed Ntwampe; Elvis Fosso-Kankeu, Ali R. Al Alili
Document type	Article
Journal	Environmental Systems Research. Springer Journal.
Year	Submitted (2022). It is currently under review by the Journal.
Co-authors: Frans Waanders Signature	
Co-authors: Seteno Karabo Obed Ntwampe Signature	
Co-authors: Elvis Fosso-Kankeu Signatur	
Co-authors: Ali R. Al Alili Signature	

Paper Title	Photodegradation of Polycyclic Aromatic Hydrocarbons from Coal Tar into Mine Wastewaters and Sewage Wastewater on a Flat-bed Photoreactor
Authors	Jean Bedel Batchamen Mougol, Frans Waanders, Elvis Fosso-Kankeu, Ali R. Al Alili
Document type	Article
Journal	Pollutants. MDPI.
Year	Published (2022)
Co-authors: Frans Waanders Signature	
Co-authors: Elvis Fosso-Kankeu Signature	
Co-authors: Ali R. Al Alili Signature	

Paper Title	Photodegradation of Polycyclic Aromatic Hydrocarbon from Coal Tar Using a Heterogeneous Photocatalyst on a Flat-bed Photoreactor
Authors	Jean Bedel Batchamen Mougol, Frans Waanders, Elvis Fosso-Kankeu, Ali R. Al Alili
Document type	Article
Journal	Water, Air & Soil Pollution. Springer Journal.
Year	Submitted (2022). It is currently in process.
Co-authors: Frans Waanders Signature	
Co-authors: Elvis Fosso-Kankeu Signature	
Co-authors: Ali R. Al Alili Signature	