

Microstructural properties and persulfate activation evaluation of cobalt-doped copper bismuth oxide

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ABSTRACT

Co-doped CuBi_2O_4 has been successfully prepared by a facile hydrothermal process. The microstructural properties of the ternary oxide were studied using Williamson-Hall and Rietveld analyses, while the persulfate activation activity was evaluated for tetracycline degradation. The effect of Co composition on the lattice strain, crystallite size, and cell volume of the compounds was systematically studied. The crystallite size calculated from Scherrer's equation and Williamson-Hall analysis was in the range of 23.8–28.1 nm and 22.4–25.7 nm respectively. The cell volume calculated from the Rietveld analysis was in the range of $420.9\text{--}421.5 \times 10^6$ pm. No significant alteration in the lattice parameters of the Co- CuBi_2O_4 was observed when compared to pristine CuBi_2O_4 . These relatively constant microstructural properties were accounted for by the small amount of Co in the CuBi_2O_4 crystal. The persulfate activation study showed an increase in activity with doping concentration. The highest efficiency of 91.5 % was achieved over 120 min with 5 mM of persulfate and 10 mg of $\text{Cu}_{0.93}\text{Co}_{0.07}\text{Bi}_2\text{O}_4$. A maximum degradation activity was achieved at pH of 7, while the radical scavenging studies showed that the mechanism was through a non-radical process involving the generation of 1O_2 . The influence of Co doping on the microstructural properties of CuBi_2O_4 and its positive influence on the persulfate activation activity for tetracycline degradation have been established in this study.

1. Introduction

The rapid increase in industrialization and population growth has resulted in increased release of pollutants into water bodies [1]. This has led to deterioration in the quality of both surface and underground water reserves, which has resulted in a significant strain on the available water resources [2]. The threat posed by climate change and global warming implies that significant efforts need to be invested in maximizing available water reserves. The recent discovery of several pharmaceuticals in underground water has raised the level of concern for the treatment of wastewater containing these compounds [3]. This is due primarily to their toxicity to both animals and humans and the inability of current wastewater treatment techniques to effectively handle this class of pollutants [4]. Recently, high concentration of antibiotics has been detected in various environmental matrices, such as underground

and surface water. The importance of these compounds in human medicine and their consumption rate implies that their concentration in the environment will continue to increase. This poses a serious ecotoxicological risk to the environment, arising from the inducement of antibiotic resistance in bacteria, which may lead to the emergence of super-bacteria [5,6]. Therefore, urgent steps need to be taken to mitigate the presence of these compounds in the environment.

Advanced oxidation processes (AOPs) have shown excellent efficiency against many recalcitrant organic pollutants because they generate highly reactive radicals such as $\bullet\text{OH}$, $\text{O}_2^{\bullet-}$ and $\text{SO}_4^{\bullet-}$, which are able to initiate the degradation of many organic pollutants. Persulfate (PS)/peroxymonosulfate (PMS) based AOPs, which could dissociate PS or $\text{PMS}(\text{S}_2\text{O}_8^{2-})$ into highly oxidizing $\text{SO}_4^{\bullet-}$ radicals are a cost-effective method for contaminant degradation in water; however, the dissociation process requires high energy (140–213.3 KJ/mol) [7–9]. This

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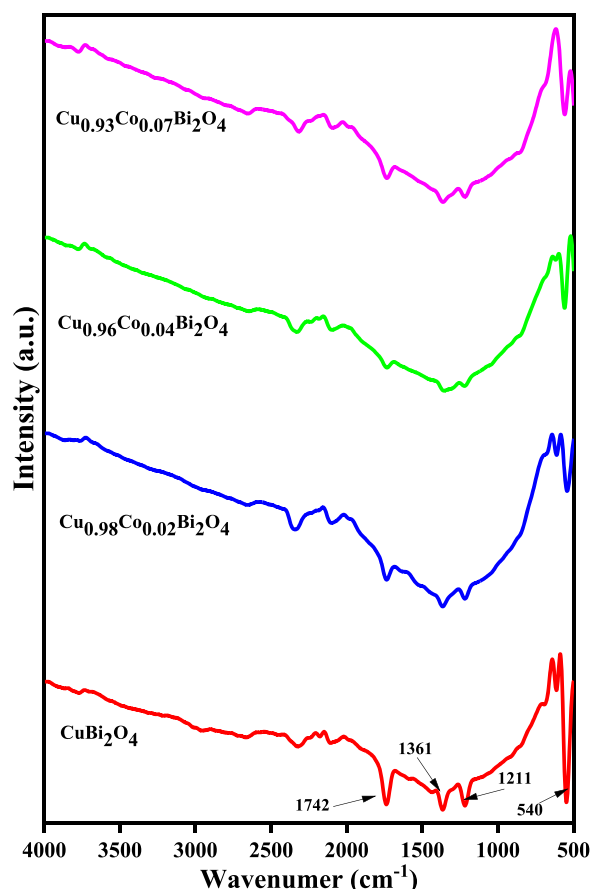


Fig. 1. FTIR spectra of CuBi_2O_4 and Co-doped CuBi_2O_4 nanoparticles.

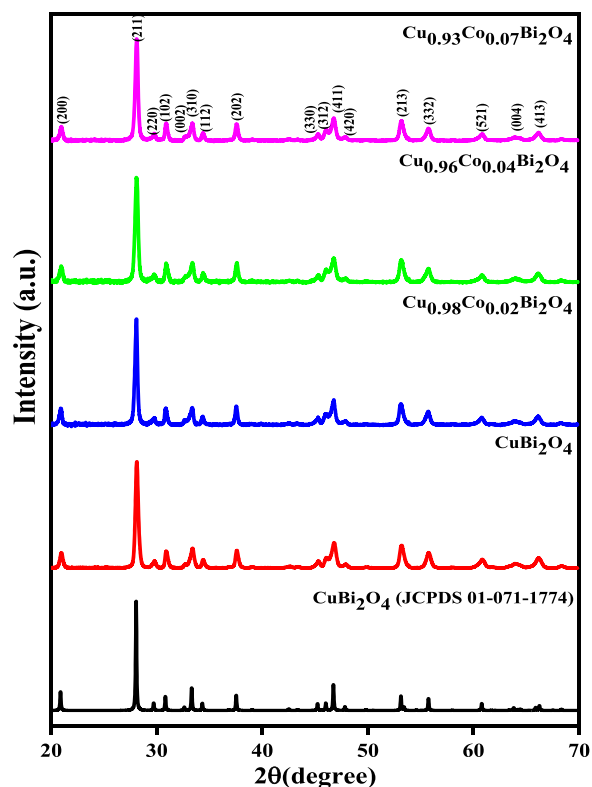


Fig. 2. XRD patterns of pristine CuBi_2O_4 and Co-doped CuBi_2O_4 (at different dopant concentrations).

PS/PMS activation process has therefore become a well-researched area in recent times.

Transition metal oxides have been confirmed to be highly suitable for PS activation. For example, copper bismuthate (CuBi_2O_4), an interesting semiconductor material belonging to a class of materials called spinel oxides, has been reported to show potential for PS activation [10,11]. It is a p-type semiconductor material with a tetragonal structure and possess both octahedral and tetrahedral phases with Bi_2O_3 and CuO composition, respectively. Due to its unique structural, optical, and reducing properties, it has attracted much interest recently [12]. The spinel structure of the oxide prevents the leaching of Cu and Bi, while the divalent copper could also undergo valence change during the PS activation, which promotes the activation process [13]. In addition, the presence of large surface hydroxyl group, improves its PS activation potential [14]. Unfortunately, CuBi_2O_4 suffers from high charge carrier recombination, which limits its ability to significantly drive any redox process. This is often mitigated by either coupling CuBi_2O_4 with other semiconductor materials or by doping with other metal ions to form mixed-metal oxides [15,16]. The synthesis of mixed metal oxides is often desirable, as it improves the stability of the catalyst and reduces metal ion leaching during the PS activation process [16].

Since cobalt (Co) is often regarded as one of the most catalytically active transition metals, cobalt oxide is often employed in the formation of heterostructures for PS activation [17]. The metal oxide, however, suffers from high Co^{2+} leaching [16]. The formation of mixed-metal oxide provides a simple route to improving the catalytic property of CuBi_2O_4 by doping the spinel oxide with Co^{2+} . Metal ion doping often results in the alteration of microstructural properties [18,19]. Therefore, in this study, Co-doped CuBi_2O_4 was prepared for PS activation in the degradation of tetracycline. The effect of Co^{2+} concentration on the microstructural properties of CuBi_2O_4 and the persulfate activation efficiency was studied. The reactive radicals generated and the mechanism of PMS activation by the Co-doped CuBi_2O_4 catalyst were also investigated.

2. Methods

Copper(II) nitrate pentahydrate ($\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$), bismuth(III) nitrate hemipentahydrate ($\text{Bi}(\text{NO}_3)_3 \cdot 2.5\text{H}_2\text{O}$), cobalt(II) nitrate hexahydrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), sodium hydroxide (NaOH), sodium persulfate ($\text{Na}_2\text{S}_2\text{O}_8$), tetracycline, and ethanol, were obtained from Sigma Aldrich and used without further purification.

2.1. Synthesis of copper bismuth oxide (CuBi_2O_4) and cobalt-doped copper bismuth oxide (Co- CuBi_2O_4)

The hydrothermal method of synthesis was used for the preparation of CuBi_2O_4 and Co-doped CuBi_2O_4 nanoparticles. In a typical synthesis, 0.348 g of $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$, 1.358 g of $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, and 1.68 g of NaOH were mixed together in 50 mL of distilled water and stirred together for 1 h. The solution was transferred into a 100 mL autoclave and heated at 180 °C for 6 h in a furnace. Thereafter, the set-up was allowed to cool down naturally to room temperature, and the dark brown product was washed by vacuum filtration with water and ethanol and dried at 60 °C overnight. For the synthesis of Co-doped CuBi_2O_4 , $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was introduced into the reaction setup while keeping the mole ratio of Cu and Co to 1. The mole ratio of Co^{2+} was 0.02, 0.04, and 0.07 in the product obtained, and they were labelled as $\text{Cu}_{0.98}\text{Co}_{0.02}\text{Bi}_2\text{O}_4$, $\text{Cu}_{0.96}\text{Co}_{0.04}\text{Bi}_2\text{O}_4$, and $\text{Cu}_{0.93}\text{Co}_{0.07}\text{Bi}_2\text{O}_4$, respectively.

2.2. Characterization of CuBi_2O_4 and co- CuBi_2O_4 catalysts

A D8 advance diffractometer with a secondary graphite monochromated Cu K α radiation ($\lambda = 1.5460 \text{ \AA}$) at 40 KV/50 mA was used for X-ray diffraction (XRD) measurement. Fourier transformed infrared spectroscopy (FTIR) was carried out on a spectroquant® prove 300

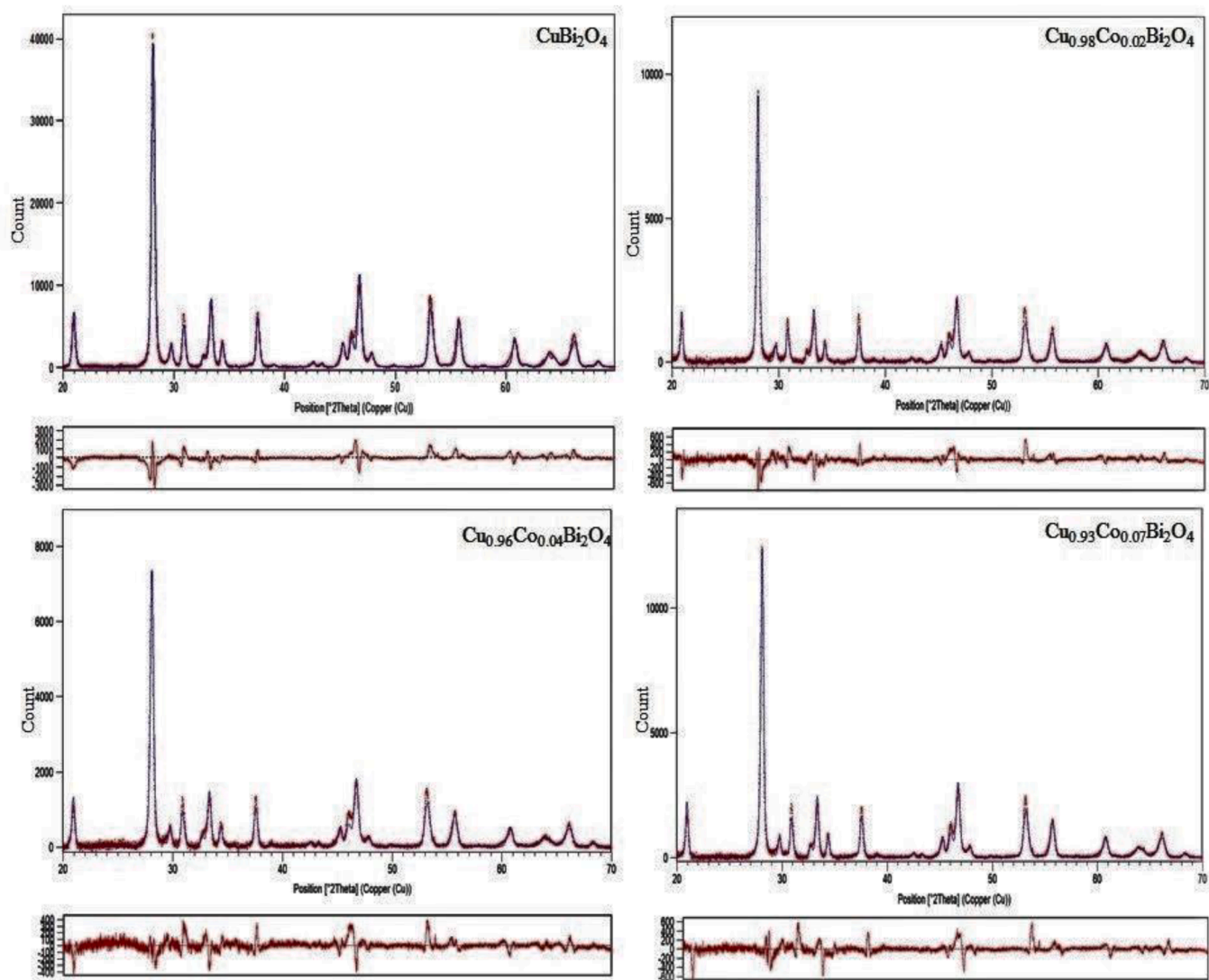


Fig. 3. Rietveld analysis plot for CuBi_2O_4 and Co-doped CuBi_2O_4 . The red lines show the line profile from the experimental measurement, while the blue line shows the simulated pattern. The bottom plot showed the difference between the experimental and simulated profiles.

Table 1
Lattice parameters, cell volume, and agreement parameters for the Rietveld analysis of pristine CuBi_2O_4 and Co-doped CuBi_2O_4 .

Material	Lattice parameters (Å)			Cell volume (10^6 pm^3)	Rietveld parameters		
	A	B	C		R_{exp}	R_p	R_w
CuBi_2O_4	8.519	8.519	5.805	421.3	1.44	4.85	6.89
$\text{Cu}_{0.98}\text{Co}_{0.02}\text{Bi}_2\text{O}_4$	8.515	8.515	5.805	420.9	2.58	3.87	5.37
$\text{Cu}_{0.96}\text{Co}_{0.04}\text{Bi}_2\text{O}_4$	8.524	8.524	5.806	421.9	2.62	3.73	4.84
$\text{Cu}_{0.93}\text{Co}_{0.07}\text{Bi}_2\text{O}_4$	8.520	8.520	5.806	421.5	2.43	3.69	5.13

Table 2
Crystallite size and lattice strain calculation using Scherrer equation and the Williamson-Hall analysis.

	Scherrer Crystallite size (nm)	Williamson-Hall analysis Crystallite size (nm)	Strain (%)
CuBi_2O_4	24.8	23.4	-4.58×10^{-5}
$\text{Cu}_{0.98}\text{Co}_{0.02}\text{Bi}_2\text{O}_4$	28.1	25.7	-4.97×10^{-5}
$\text{Cu}_{0.96}\text{Co}_{0.04}\text{Bi}_2\text{O}_4$	23.8	22.4	-4.40×10^{-5}
$\text{Cu}_{0.93}\text{Co}_{0.07}\text{Bi}_2\text{O}_4$	26.1	24.7	-4.82×10^{-5}

spectrophotometer. The morphology of the materials was determined using scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The images were taken on a Fe-SEM FEI 430 Nova NanoSEM System and FEI Tecnai G2 Twin at 20 kV. The surface charge of the materials was determined through zeta potential measurement using a Malvern Nano ZS instrument.

2.3. Evaluation of persulfate-activation activity of CuBi_2O_4 and co-doped CuBi_2O_4

The persulfate activation activity of CuBi_2O_4 and Co-doped CuBi_2O_4 was evaluated for tetracycline (TCE) degradation. In a typical process, 10 mg of the material was measured into a beaker containing 10 mg/L of

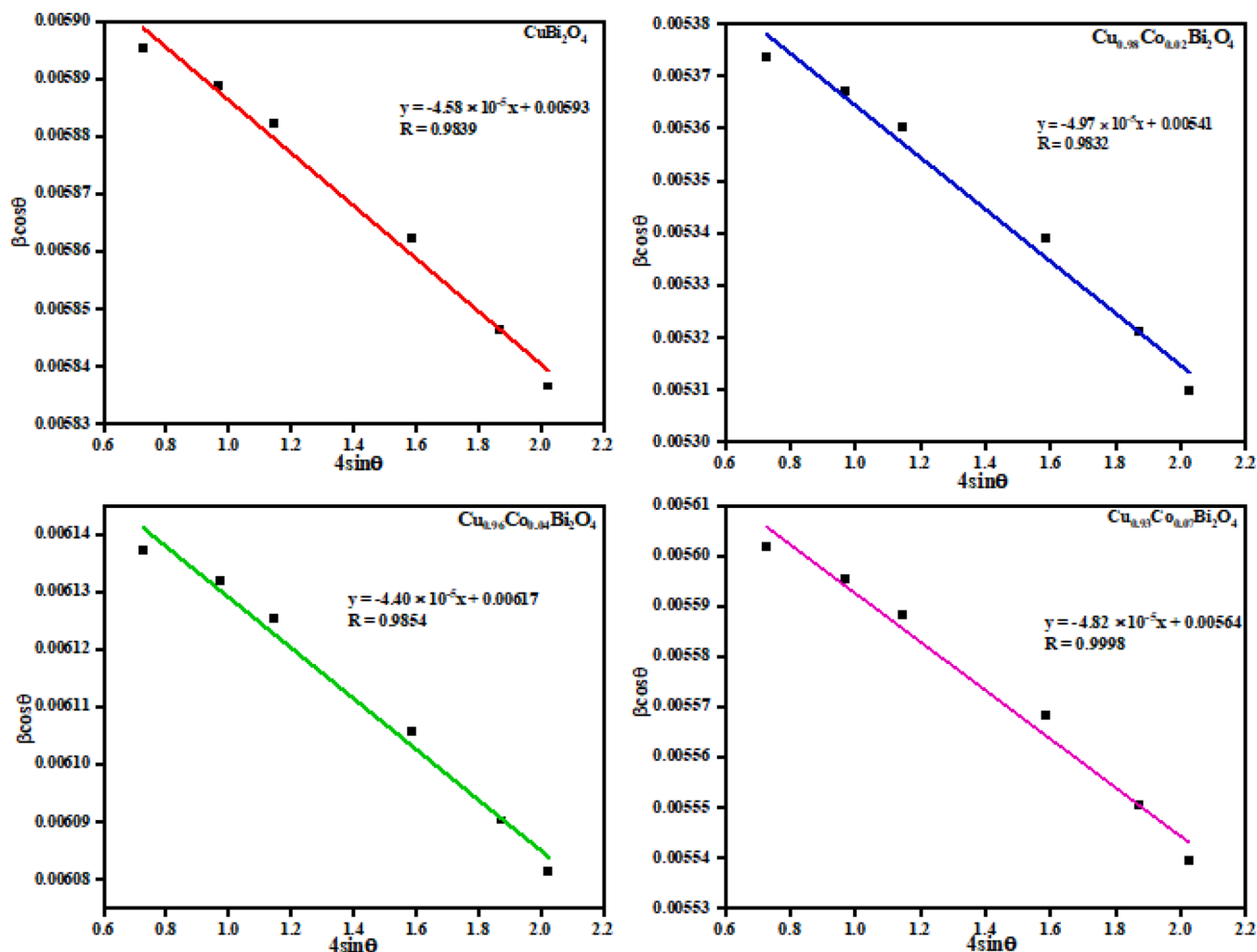


Fig. 4. Williamson-Hall plots for pristine CuBi_2O_4 and Co-doped CuBi_2O_4 .

TCE. This was followed by the addition of 5 mM of $\text{Na}_2\text{S}_2\text{O}_8$ to the mixture and stirred continuously. Aliquots were taken from the set-up at intervals of 15 min and the concentration of TCE in the solution was measured using a spectroquant® probe 300 UV-spectrophotometer at 360 nm. The concentration of TCE was evaluated using Eq. (1),

$$\% \text{degradation} = \frac{C_o - C_t}{C_o} \times 100 \quad (1)$$

where C_o and C_t are the initial and final concentrations of the solution, respectively. The degradation data was fitted into the linear form of the pseudo first order kinetic plot using Eq. (2),

$$\ln(C_i) = \ln(C_o) - kt \quad (2)$$

The effect of process parameters such as pH (2–12), TCE concentration (5–40 mg/L), PS concentration (1–10 mM) and catalyst concentration (5–30 mg) on the degradation process was further evaluated. To study the radical species responsible for the degradation, radical scavengers (5.0 mM) were added to the reaction system. Methanol was added as $\bullet\text{OH}$ and $\text{SO}_4^{\bullet-}$ scavenger; *tert* butyl alcohol (TBA), and p-benzoquinone were added as $\bullet\text{OH}$ and $\text{O}_2^{\bullet-}$ scavenger, and furfural (FFA) was added as 1O_2 respectively.

3. Results and discussion

3.1. Characterization and microstructural studies of CuBi_2O_4 and $\text{Co-doped CuBi}_2\text{O}_4$

The FTIR spectra of the samples are shown in Fig. 1. In the spectra, prominent peak at 540 cm^{-1} can be assigned to the Cu-O vibrational frequency of CuBi_2O_4 [20]. The stretching vibrations of Cu-O and Bi-O bonds were observed at around 1211 and 1361 cm^{-1} respectively. The bending vibration of H_2O was observed at 1741 cm^{-1} [21,22]. A significant reduction in the Cu-O and Bi-O peaks was observed in the Co-doped CuBi_2O_4 , which could be attributed to the effect of the introduction of Co.

The XRD patterns of CuBi_2O_4 and Co-doped CuBi_2O_4 , overlapped on the standard pattern for CuBi_2O_4 , are shown in Fig. 2. All the samples show diffraction patterns consistent with the tetragonal primitive crystal lattice with JCPDS No: 720,493 [23]. No impurity peaks were observed in the patterns, confirming the formation of pure CuBi_2O_4 . In the Co-doped CuBi_2O_4 , no additional peaks were observed; however, there was a significant reduction in the intensity of the 121 peak. The closeness of the ionic radii of Cu^{2+} (0.60 Å) and Co^{2+} (0.65 Å), means no change in the crystalline structure of the doped materials is observed at long-range [24]. Hence, suggests that the level of Co^{2+} dopant in the structure was not significant enough to induce structural changes in the lattice of CuBi_2O_4 [25]. This was confirmed by the lattice parameters and cell volume of pristine CuBi_2O_4 and Co-doped CuBi_2O_4 obtained

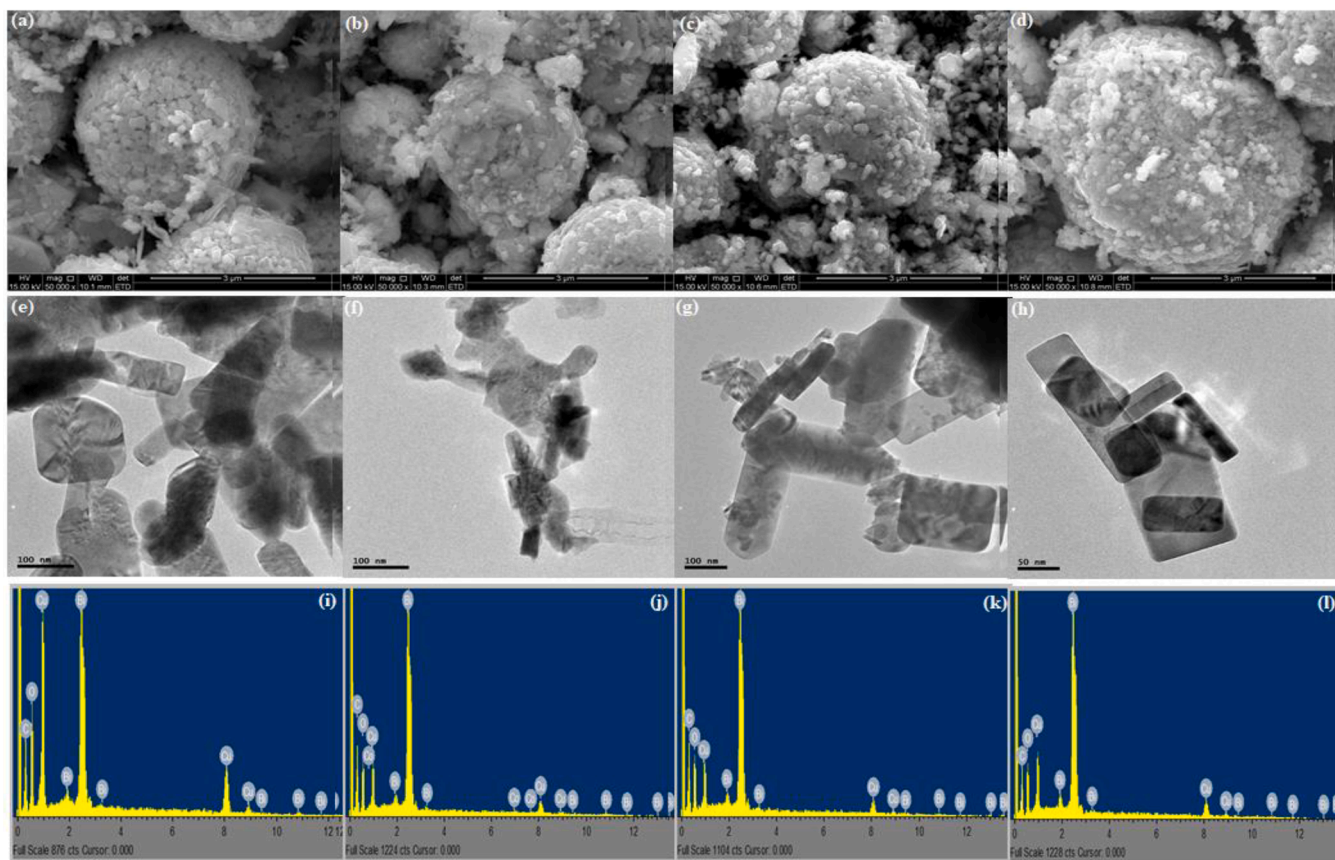


Fig. 5. SEM, TEM, and EDX images of (a, e, i): CuBi_2O_4 ; (b, f, j) $\text{Cu}_{0.98}\text{Co}_{0.02}\text{Bi}_2\text{O}_4$; (c, g, k) $\text{Cu}_{0.96}\text{Co}_{0.04}\text{Bi}_2\text{O}_4$; (d, h, l) $\text{Cu}_{0.93}\text{Co}_{0.07}\text{Bi}_2\text{O}_4$.

from the Rietveld analysis of the XRD data. Fig. 3 shows a good agreement between the experimental (red line) and simulated pattern (blue line) obtained from the Rietveld analysis, confirming the purity of the obtained materials. As shown in Table 1, the values obtained for the lattice parameters and cell volume of the samples agreed with reported values in literatures. The slight increase in the cell volume showed the doping-induced distortion in the lattice of Co-doped CuBi_2O_4 and increased defects compared to pure CuBi_2O_4 . The agreement parameters from the Rietveld analysis (R_{exp} , R_p and R_w) show the obtained values were reliable as they were within acceptable limits.

The crystallite sizes of the materials were evaluated using both the Scherrer's equation (Eq. (3)) and Williamson-Hall analysis (Eq. (4)).

$$D = \frac{k\lambda}{\beta \cos \theta} \quad (3)$$

$$\beta = \frac{k\lambda}{\beta \cos \theta} + 4\epsilon \tan \theta \quad (4)$$

where D is the crystallite size (nm), K is the shape factor (0.94), λ is the $\text{CuK}\alpha$ radiation wavelength (1.5406 nm), θ is the diffraction angle, ϵ is the strain, and β is the peak broadening.

As shown in Table 2, crystallite size in the range of 23.8–28.1 nm was obtained for the materials using the Scherrer equation, while the Williamson-Hall analysis gave a range of 22.4–25.7. Both analyses gave very close values for the crystallite size and followed similar trends. No significant difference in the crystallite size was observed for both pristine CuBi_2O_4 and Co-doped CuBi_2O_4 . This confirms the earlier assertion that the presence of Co^{2+} had no significant influence on the lattice of CuBi_2O_4 . The observed result could be attributed to the low concentration of Co^{2+} and the close similarity between the ionic radii of Co^{2+} and Cu^{2+} . Fig. 4 shows the Williamson-Hall plot for the nanomaterials. A slight increase in the lattice strain was observed in the Co-doped

CuBi_2O_4 and the negative slope of the linear plot shows the strain in the lattice was due to lattice contraction [26].

The morphology of the materials was studied with electron microscopy, and Fig. 5 shows the SEM, TEM, and EDX micrographs of the nanomaterials. Pristine CuBi_2O_4 appeared as highly aggregated, rectangular shaped nanoparticles with an average particle size of 152 ± 20 nm. Co-doping significantly influenced the morphology of the material, both in terms of shape and size. The shape of the materials was observed to become more rounded as the doping level increased. As observed in the TEM images, the particles of the Co-doped CuBi_2O_4 were more disposed to agglomeration, resulting into larger plate-like materials. The average particle size of the nanomaterials showed a significant increase with Co concentration. For $\text{Cu}_{0.98}\text{Co}_{0.02}\text{Bi}_2\text{O}_4$, $\text{Cu}_{0.96}\text{Co}_{0.04}\text{Bi}_2\text{O}_4$, and $\text{Cu}_{0.93}\text{Co}_{0.07}\text{Bi}_2\text{O}_4$, the evaluated particle size was 284 ± 41 , 899 ± 71 , and 725 ± 89 nm, respectively. The influence of metal-ion doping on particle size is observed to be dependent on the nature of the metal ion. Both increased and reduced particle sizes have been reported for such doped materials [27]. The EDX spectra show the elemental composition of the nanomaterials and confirm the doping of Co into the CuBi_2O_4 lattice.

3.2. Persulfate activation study for TCE degradation

To understand the influence of adsorption on the degradation of TCE, the zeta potential of the catalyst and the amount of TCE adsorbed were measured. Fig. 6a shows that all the catalysts exhibited a positive surface charge, which increased with the Co^{2+} dopant level. The amount of TCE adsorbed by the catalysts is shown in Fig. 6b, and the adsorption potential of the catalyst increased with the incorporation of Co^{2+} . After 1 h, Co-CBO(0.04) adsorbed about 32.5 %, which was followed closely by Co-CBO(0.07) with 31.0 % adsorption. The percentage of TCE adsorbed by the catalyst followed a similar trend with the zeta potential. Fig. 6c

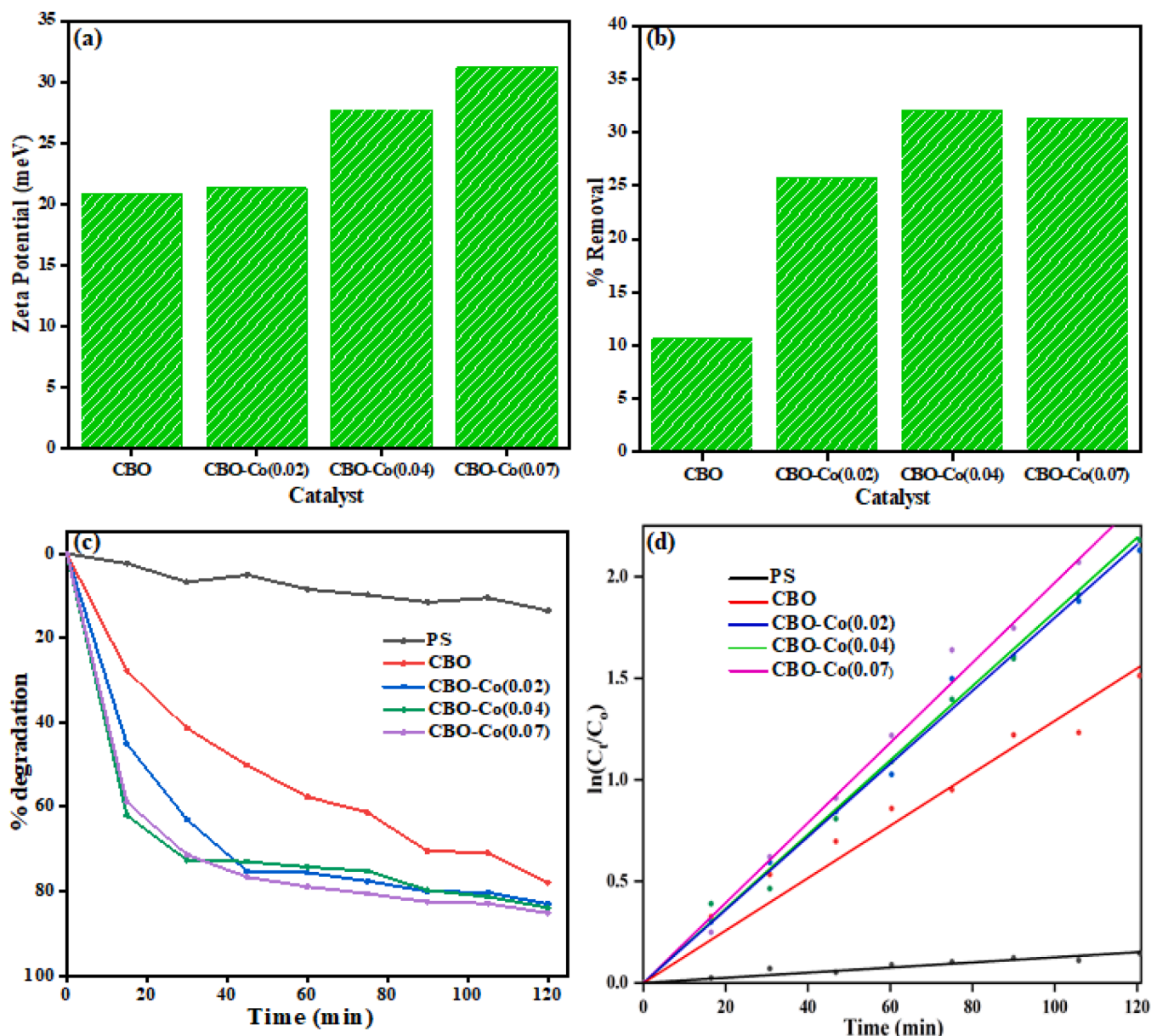


Fig. 6. (a) Zeta potential of catalysts; (b) percentage adsorption of TCE; (c) degradation profile of TCE by PS, CuBi_2O_4 and Co-doped CuBi_2O_4 ; (d) Pseudo first order kinetic plot for the degradation of TCE.

shows the degradation profile for the degradation of TCE by PS, CuBi_2O_4 , and Co-doped CuBi_2O_4 . In the presence of only PS, a very low concentration of about 13.5 % of the TCE was degraded. This was significantly improved to 77.9 % in the presence of CuBi_2O_4 . The result shows the significant effect of persulfate activation of CuBi_2O_4 in enhancing the degradation process, which was also reported by Tian, et al. [28]. The doping of CuBi_2O_4 with 0.02, 0.04 and 0.07 mmols of Co were observed to further improve the persulfate activation activity of CuBi_2O_4 , with degradation efficiencies of 83.1, 83.9, and 91.5 % achieved, respectively. The ability of PS to react with surface Mn^{+} (Fe^{2+} , Co^{2+}) species to yield M^{n+1} has been identified as an important process in enhancing PS-based processes[29]. This was observed in the efficient degradation of sulfane by persulfate activation using Co and Zn co-doped magnetite nanoparticles. Co-doped Mn_2O_3 was also reported to enhance persulfate activation for tetracycline degradation[30]. The improved activity of Co-doped CBO for TCE degradation could therefore be attributed to the introduction of Co^{2+} into the lattice of CBO. Fig. 6d shows the pseudo-first-order kinetics plot for the degradation process.

The kinetic rate constant for the process was 1.3×10^{-3} , 1.29×10^{-3} , 1.80×10^{-2} , 1.83×10^{-2} and $1.97 \times 10^{-2} \text{ min}^{-1}$ respectively.

3.3. Effects of process variables on TCE degradation

The effect of process parameters such as TCE concentration, pH, PS dosage, and catalyst dosage on the rate constant of the degradation process was studied. The effect of TCE concentration on the degradation process was studied from 5 mg/L to 40 mg/L. As shown in Fig. 7a, the rate constant was reduced from 2.6×10^{-2} to $1.2 \times 10^{-2} \text{ min}^{-1}$. Also, the effect of PS dosage was studied from 1 to 10 mM (Fig. 7b), with an increase in k value of 1.8×10^{-2} to $2.6 \times 10^{-2} \text{ min}^{-1}$ recorded. The study on the effect of Co- CuBi_2O_4 dosage on the degradation process (Fig. 7c) showed an initial increase in k from 1.2×10^{-2} – $2.6 \times 10^{-2} \text{ min}^{-1}$ with an increase in dosage from 5 to 20 mg, however, a further increase to 30 mg resulted in a decrease in the value of k to $1.9 \times 10^{-2} \text{ min}^{-1}$. Finally, the effect of pH was studied using pH values of 2–11 (Fig. 7d). The value of k was observed to reach a maximum at neutral to alkaline pH. This

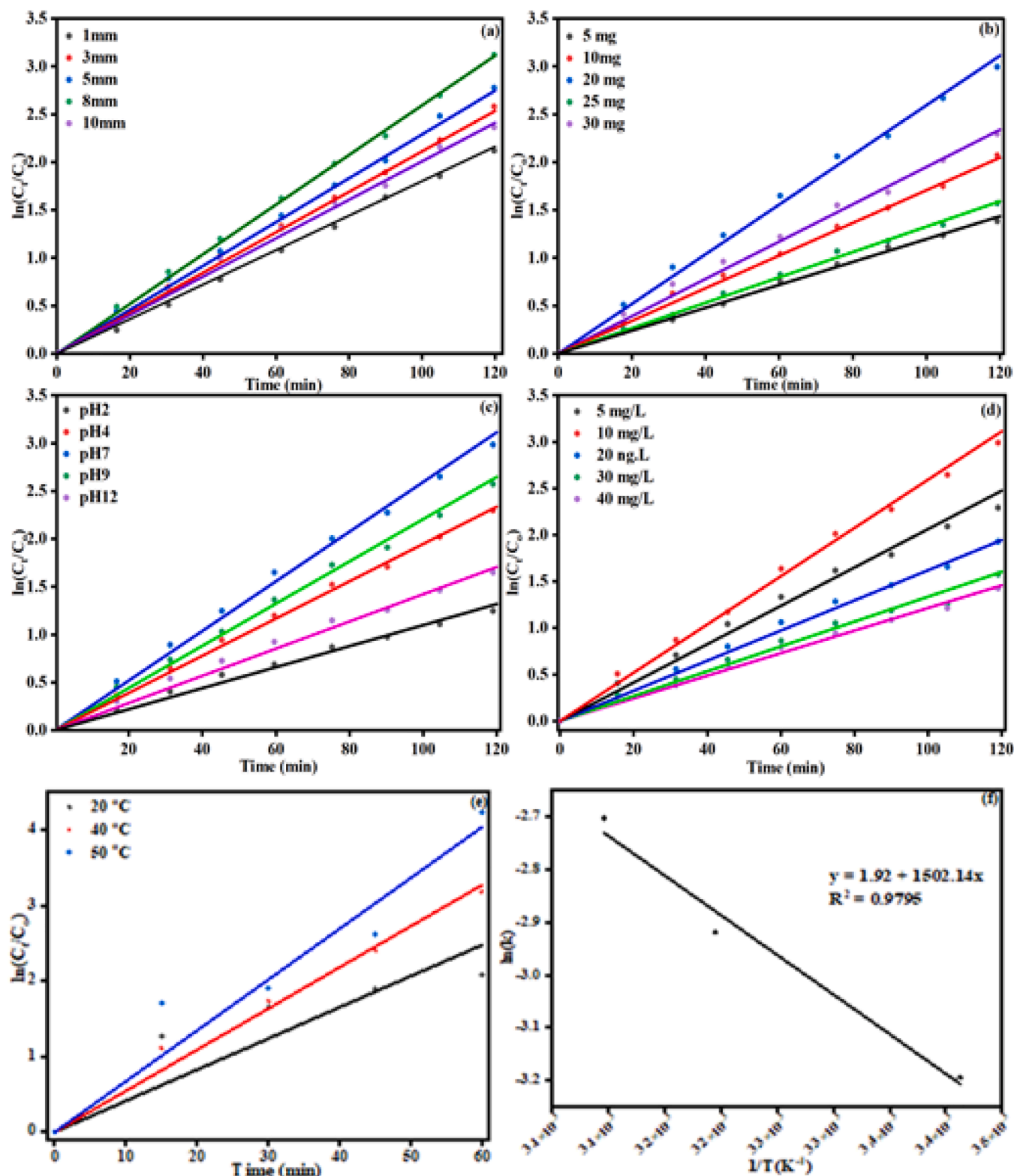


Fig. 7. Effect of process parameters: (a) PS concentration; (b) catalyst dosage; (c) pH; (d) TCE concentration; (e) temperature on the degradation of TCE, and (f) Arrhenius plot for TCE degradation at 20–50 °C.

observation was similarly reported by Liang, et al. [31]. The influence of pH on the degradation process could be attributed to the change in the surface charge of the catalyst and the adsorption of TCE. As shown by the zeta potential, the surface charge of Co-CuBi₂O₄ is positive, while at alkaline pH, TCE exists as a negatively charged ion [32], which could enhance TCE adsorption on the Co-CuBi₂O₄ surface and a subsequent

enhancement in the degradation efficiency. Also, above a pH value of 9.4, the SO_5^{2-} form of PS is the most dominant specie in solution, while the HSO_5^- is the most dominant at pH values below 9.4. The lower redox potential of SO_5^{2-} (1.22 V vs. NHE) compared to that of HSO_5^- (1.75 V vs. NHE) implies that it is more difficult to react with [33,34].

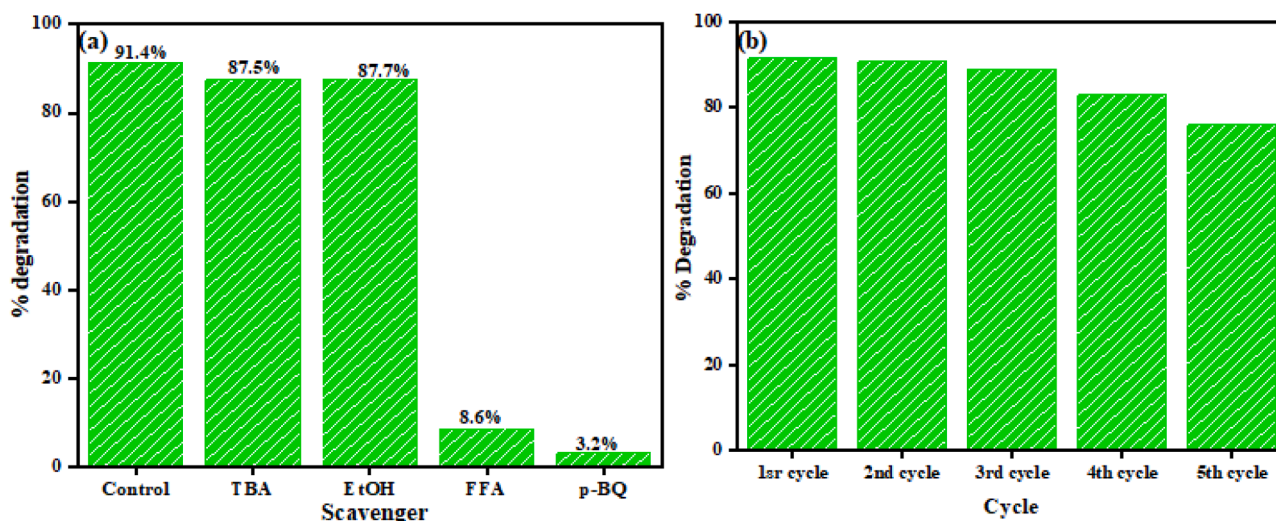


Fig. 8. (a) Radical scavenging experiment and (b) stability test of Co-CuBi₂O₄ for TCE degradation.

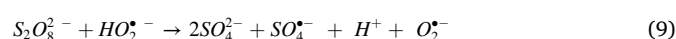
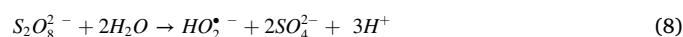
The effect of reaction temperature (20, 40, and 50 °C) on tetracycline degradation rate is shown in Fig. 7e. The temperature of the system was maintained at the target temperature throughout the degradation process, with the rate constant of TCE degradation estimated to be 0.041, 0.054, 0.067 min⁻¹ at 20, 40 and 50 °C, respectively. The activation energy (E_a) was evaluated using the Arrhenius equation (Eq. (5)),

$$\ln(k) = \ln(A_o) - \frac{E_a}{RT} \quad (5)$$

where k , A_o , R , T , and E_a represent the rate constant, pre-exponential factor, gas constant, temperature, and activation energy, respectively. Fig. 7f shows the plot of $\ln(k)$ against $1/T$ and negative gradient indicates that the catalytic reaction process is endothermic. The activation energy of the reaction was evaluated to be 12.5 KJ/mol.

3.4. Radical scavenging experiment

To explore the reactive species generated during the PS activation, radical scavenging experiments were carried out. MeOH was used as $SO_5^{\bullet-}$ and $\bullet OH(K_{SO_5^{\bullet-}} = 1.6 - 7.1 \times 10^7 M^{-1} S^{-1}$ and $K_{OH} = 1.2 - 2.8 \times 10^7 M^{-1} S^{-1}$ [35] scavenger, while TBA was used to scavenge $\bullet OH$ ($K_{OH} = 1.9 \times 10^9 M^{-1} S^{-1}$) [36]. As shown in Fig. 8, the addition of MeOH and TBA had a negligible effect on the degradation efficiency of the process. It shows that the degradation of TCE by Co-doped CuBi₂O₄ followed a non-radical process [37,38]. This non-radical process was initially limited to carbon-based catalysts; however, several reports have shown that perovskite oxides and metal-based catalysts are capable of initiating persulfate activation through the non-radical process [34,39]. In non-radical PS activation processes, $1O_2$ has been identified as the main oxidized specie for the degradation of pollutants [38]. In the generation of $1O_2$, recent reports have shown that highly oxidized metal centres can generate $O_2^{\bullet-}$ by accepting an electron from PS molecule. The $O_2^{\bullet-}$ plays an intermediate role in the generation of $1O_2$ by undergoing direct oxidation as shown in the sequence of reaction in Eqs. (6)–(10) [40]. To confirm the role of $O_2^{\bullet-}$, the degradation was carried out in the presence p-Benzoquinone (p-BQ) ($K_{O_2^{\bullet-}} = 0.9 - 1.0 \times 10^9 M^{-1} S^{-1}$) and furfuryl alcohol (FFA). The degradation of TCE was almost completely inhibited by p-BQ and FFA, confirming the significant role played by $O_2^{\bullet-}$ and $1O_2$ in TCE degradation. This observation was similarly reported by Zhang et al. [41] for C@Fe₃O₄ activation of persulfate for tetracycline degradation.



Furthermore, the stability of the catalyst for TCE degradation was explored by recycling the catalyst for five (5) degradation cycles. Fig. 8b shows that after 5 cycles, the catalyst still maintained a significant efficiency of about 78 %. Hence, confirms the stability of the Co- CuBi₂O₄ catalyst for the degradation process.

4. Conclusion

The microstructural and persulfate activation properties of Co-doped CuBi₂O₄ synthesized by a hydrothermal method are reported in this study. Using the Williamson-Hall and Rietveld analyses, no significant alteration in the microstructural properties of the Co-CuBi₂O₄ was observed, which could be attributed to the interstitial doping of Co²⁺ ions in the CuBi₂O₄ crystal. The doped ternary oxide nanomaterials exhibited higher persulfate activation for tetracycline degradation compared to its pristine form. The efficiency of the process reached 83.1, 83.9, and 91.5 % for dopant levels of 0.02, 0.04 and 0.07 mol%, respectively. The radical quenching experiment showed the persulfate activation by Co-doped CuBi₂O₄ followed a non-radical process, as the efficiency of the process was not significantly impeded by radical scavengers. The positive influence of Co²⁺ doping on the catalytic activity of CuBi₂O₄ is therefore established in this study.

CRedit authorship contribution statement

Olalekan C. Olatunde: Conceptualization, Formal analysis, Writing – original draft. **Hela Ferjani:** Formal analysis, Methodology. **Damian C. Onwudiwe:** Conceptualization, Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper

Data availability

Data will be made available on request.

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