Removal of COD from Biodiesel Wastewater using a Hydrophobic Polymer

Elvis Fosso-Kankeu*, Marcelle Van den Berg, Frans Waanders and Sadanand Pandey

Abstract—Biodiesel production is increasing internationally as an alternative fuel. This is due to the rapid depletion of non-renewable energy sources. Pure biodiesel product can be obtained by washing the product with hot water. This results in a huge quantity of wastewater that is unsafe for disposal in normal drainage systems. Treatment of this wastewater is thus important for reuse or safe disposal in the environment. There are a lot of existing treatment methods, but they are costly, produce large quantities of excessive sludge and are not economically feasible. Flocculation is widely used in water treatment as it is easy to use and affordable. Flocculants can be synthesized to treat the specific wastewater type focusing on the reduction of certain impurities.

The reduction of Chemical Oxygen Demand (COD) in the biodiesel wastewater was investigated through jar-tests using hydrophobic, non-hydrophobic and a combination of hydrophobic and non-hydrophobic polymers that were synthesized.

Almost 68% COD removal was obtained with the non-hydrophobic polymer and about 56% COD removal was obtained with the hydrophobic polymer. The non-hydrophobic polymer has a better removal efficiency, as the wastewater contains a large quantity of hydrophilic organic matters. Although the hydrophobic polymer also removes COD, it could be seen that the hydrophobic polymer attracted the unreacted oil in the biodiesel wastewater.

Keywords — Biodiesel wastewater, hydrophobic polymer, non-hydrophobic polymer, COD, flocculation

I. INTRODUCTION

Biodiesel production is increasing internationally since fossil fuels are non-renewable energy sources which are depleting fast. Global warming and climate change are also affecting the environment in a negative way [1-11]. Biodiesel quality is dependent on its refinement process, which produces large volumes of wastewater which cannot be disposed of in normal drainage systems [12].

Biodiesel wastewater is produced after the washing phase and is a viscous fluid that is organic with a white colour. The effluent has high pH levels. The high pH levels are unfavourable for the growth of microorganisms, thus complicating the natural degradation of the oil in the wastewater [13]. Due to impurities in the biodiesel wastewater, the wastewater can be characterized by chemical oxygen demand and biological oxygen demand [12].

The wastewater effluent consists of water, residual biodiesel, soap, salts, methanol, un-reacted oil, and glycerol (main by-product) [1]. The discharge of such water in the environment will exacerbate the problem of water in a country considered as water scarce [14-24].

Flocculation is widely used in water treatment. Flocculation has advantages in treating wastewater containing oil, as it has no phase transition, operation is easy, affordable, and has an overall good treatment efficiency [25]. Flocculation is also convenient, environmentally friendly, easy to handle, and energy efficient [26-32].

Adding cationic polyacrylamide (CPAM) as polymer to the wastewater will affect the viscosity and permeability of the water by increasing and decreasing it respectively, which will result in a lower mobility ratio [33].

Hydrophobically associated polyacrylamide polymers (HAPAMs) have unique structures with thickening properties. HAPAMs have shear thinning abilities, anti-polyelectrolyte behaviour as a mobility control agent and with rheology modifiers [34]. Hydrophobic groups that are part of the polymer can enhance the interaction with hydrophobic oily colloids in the wastewater [25]. Hydrophobic monomers will temporary form intra- and intermolecular forces, minimizing their exposure to the water [33].
II. MATERIALS AND METHODS

A. Materials

Biodiesel was prepared with used cooking oil (UCO), methanol and potassium hydroxide (KOH) as catalyst.

For the polymer synthesis, acrylamide (AM) was used as a base. Benzylidimethyl(2-hydroxyethyl) ammonium chloride (BMAC) was the monomer used to synthesize the hydrophobic polymer, and for the non-hydrophobic polymer [2-(Methacyryloxy)ethyl] trimethyl ammonium chloride (MTAC) was used for synthesis. Both monomers were purchased from Rochelle Chemicals.

Potassium peroxodisulphate was added as initiator for the co-polymerization to take place. Hydrochloric acid (HCl) and sodium hydroxide (NaOH) were used for pH adjustment, and a combination of acetone and ethanol was used to wash the polymers.

B. Biodiesel production and obtaining the biodiesel wash water

A total of 4 L biodiesel was prepared in five batches. Each batch contained 800 mL UCO, 3.92 g KOH and 160 mL methanol. The UCO was pre-heated to 55°C in a water bath. After the KOH was dissolved in the methanol, it was added to the UCO and continuously stirred for 1 h at 55°C. After the 1 h reaction time the mixture was poured into a separation funnel to allow the complete separation of biodiesel from glycerol within 24 h. After the glycerol was removed from the separation funnels, the remaining biodiesel was washed with deionised water. The water was heated to 40°C and added to the separation funnels. Each funnel was gently flipped for a couple of times, then returned to the stand to let the biodiesel separate from the water. The water, at the bottom of the funnel, was tapped into a plastic bottle, and the colour of the water was white. This washing process was repeated 5 times for each funnel. A total of 12 l wash water was obtain

C. Polymer synthesis

A total of five polymers were synthesized, namely a hydrophobic polymer (HP 100%), non-hydrophobic polymer (CP 100%) and the other three polymers were a combination of the hydrophobic and non-hydrophobic polymers with 75/25%, 50/50% and 25/75% ratios of the hydrophobic and non-hydrophobic monomers respectively.

1 g AM and 0.4 g monomer [BMAC/MTAC/comboination] were dissolved in 20 mL of deionised water. The pH of this solution was adjusted to 4 ±0.2 with HCl or NaOH. A 1 M solution both of HCl and NaOH was prepared and used for the synthesis process.

After the pH adjustment, the solution was purged with nitrogen gas for 15 min. After 10 min of purging, the initiator (Potassium peroxodisulphate) was added. One g of initiator was dissolved with 3 mL of deionised water. For each polymer 100 μl of the initiator mixture was added.

After completion of the purging, the solution was mixed using the Labcon 5082U shaking incubator at 60°C and 250 rpm for 1 hr. The increase of solution density was observed over time, confirming the formation of gel and therefore successful copolymerization taking place; the density of the gel varied depending of the ratios.

The polymers were washed with an ethanol-acetone mixture. The wash mixture was prepared in a 1:2 ratio, and the polymers were washed for 5 min. When the wash mixture was added, one could see it becoming white as the unreacted reagents were washed from the polymer. It is important to let the solution settle before decanting the ethanol-acetone mixture containing unpolymerized monomers and homopolymers. The washed mixture settled on top of the polymer. The polymers were dried for 2 days in an oven at 60°C.

D. Flocculation tests

For the flocculation tests 10, 20,30,40 and 50 mg/L dosages of flocculant were used to determine the COD and turbidity removal from the biodiesel wastewater.

Five beakers of 1 L volume each were used in which 200 ml of wastewater was added. The different dosages of the flocculants were added. Flash mixing took place for 1 min 30 s at 200 rpm, followed by slow mixing for 15 min at 40 rpm. After the slow mixing, the beakers were left to settle for 30 min. After the settling time, the pH, turbidity and COD could be measured.

E. Biodiesel wastewater and treated water parameter measurements

The pH values were measured with a pH meter from Hanna Instruments. The pH electrode was placed in the water sample to record the pH. After each pH measurement the electrode was washed with deionised water and dried.

Turbidity was measured with a HACH 2100Q turbidity meter. The turbidity meter has a glass vial that has a volume of 10 ml. This vial was filled with the water sample and inserted into the turbidity meter. The reading obtained was then noted as the sample’s turbidity.

COD testing kits were ordered from Hanna Instruments. An aliquot of 0.2 mL of the water sample was added to the COD testing kit and digested at 150°C for 2 hours using a Hanna digester. The digested mixture was then left at room temperature to bring the temperature down at around 120°C, and the tubes was inserted in the photometer for COD measurement. The photometer used was a HI 83099 COD and Multiparameter Photometer from Hanna Instruments.

F. The characterization method of the polymers

The hydrophobic, non-hydrophobic and combine polymers were characterized with FTIR and SEM techniques. The IRAffinity-1S Fourier transform infrared spectrophotometer from the University of Johannesburg was used with a spectral range of 4000 to 500 cm⁻¹. The JEM-2100 multipurpose electron microscope (SEM) was used to determine the morphology of the polymers and the SEM image sizes ranged from 500 to 50 μm.

III. RESULTS AND DISCUSSION

A. Morphology of polymers

SEM images of the HP 100%, CP 100%, HCP 75/25%, HCP 50/50% and HCP 25/75% are shown in Fig. 1. The morphology
of the HP 100% is lumpy and has a homogeneous surface. CP 100% (Fig.1d) is smooth and has a homogenous surface. HCP 75/25% (Fig.1e), HCP 50/50% (Fig.1b) and HCP 25/75% (Fig.1a) exhibit the properties of both the HP and CP polymers. Their morphology consists of a heterogenous and irregular surface. HCP 75/25% are more in sync with HP 100% and HCP 25/75% are closer to CP 100%, which is due to the ratio’s used in synthesis of the copolymers.

**B. Binding groups of polymers**

FTIR spectroscopy was used to identify the binding groups on five synthesized polymers. Fig. 2 shows the spectrum of each of the five polymers. The acrylamide backbone could clearly be seen in all five polymers. Between the spectrum values of 3312.93 and 3174.68 cm\(^{-1}\) a N-H stretch exists, while a C-C=C symmetric stretch can be responsible of the peak between 1655.96 and 1603.17 cm\(^{-1}\). The backbone is completed with a C-C stretch, C-N stretch and =C-H bend in the ranges of 1448.02 – 1407.17 cm\(^{-1}\), 1316.40 – 1049.08 cm\(^{-1}\) and 988.92 – 719.30 cm\(^{-1}\) respectively.

An O-H stretch related to the peak between 3043.80 – 2866.49 cm\(^{-1}\), can be found in the HP 100%, HCP 75/25% and HCP 50/50% due to the alcohol group in the BMAC. The HCP 25/75%, HCP 50/50% and HCP 75/25% contains a C=O stretch and C-H rock due to the combination of BMAC and MTAC with spectrum ranges of 1733.59 – 1729.91 cm\(^{-1}\) respectively. The CP 100% polymer contained a C-H stretch of 1454.35 cm\(^{-1}\) and a N-H bend of 2936.15 cm\(^{-1}\).

![Fig. 1. SEM Images of synthesized polymers (a) HCP 25/75% (b) HCP 50/50% (c) HCP 75/25% (d) CP 100% (e) HP 100%](image1)

**C. Flocculation results**

The characterization done on the biodiesel wastewater showed a pH of 8.15, turbidity of 728 NTU and a COD measurement of 14370 mg/l.

Tables 1 and 2 show the results obtained from flocculation of the HP 100% and CP 100% polymers respectively.

**TABLE I: FLOCCULATION RESULTS FOR HP 100%**

<table>
<thead>
<tr>
<th>Flocculant dosages (mg/l)</th>
<th>pH</th>
<th>Turbidity (NTU)</th>
<th>COD (mg/l)</th>
<th>% COD removed</th>
<th>% Turbidity removed</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2</td>
<td>6.72</td>
<td>671</td>
<td>6850</td>
<td>52.33</td>
<td>7.83</td>
</tr>
<tr>
<td>0.4</td>
<td>6.95</td>
<td>653</td>
<td>6666</td>
<td>53.61</td>
<td>10.30</td>
</tr>
<tr>
<td>0.6</td>
<td>7.11</td>
<td>649</td>
<td>6490</td>
<td>54.84</td>
<td>10.85</td>
</tr>
<tr>
<td>0.8</td>
<td>7.25</td>
<td>644</td>
<td>6440</td>
<td>55.18</td>
<td>11.54</td>
</tr>
<tr>
<td>1</td>
<td>7.38</td>
<td>638</td>
<td>6380</td>
<td>55.60</td>
<td>12.36</td>
</tr>
</tbody>
</table>

**TABLE II: FLOCCULATION RESULTS FOR CP 100%**

<table>
<thead>
<tr>
<th>Flocculant dosages (mg/l)</th>
<th>pH</th>
<th>Turbidity (NTU)</th>
<th>COD (mg/l)</th>
<th>% COD removed</th>
<th>% Turbidity removed</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2</td>
<td>5.23</td>
<td>604</td>
<td>5239</td>
<td>63.54</td>
<td>17.03</td>
</tr>
<tr>
<td>0.4</td>
<td>5.84</td>
<td>596</td>
<td>5170</td>
<td>64.02</td>
<td>18.13</td>
</tr>
<tr>
<td>0.6</td>
<td>5.97</td>
<td>590</td>
<td>5118</td>
<td>64.38</td>
<td>18.96</td>
</tr>
<tr>
<td>0.8</td>
<td>6.09</td>
<td>562</td>
<td>4875</td>
<td>66.08</td>
<td>22.80</td>
</tr>
<tr>
<td>1</td>
<td>6.31</td>
<td>537</td>
<td>4658</td>
<td>67.59</td>
<td>26.24</td>
</tr>
</tbody>
</table>

With both polymers, the pH increased as the flocculant dosage was increased. CP 100% was more effective at removing COD from the biodiesel wastewater. Flocculation tests with the HP 100% polymer showed oily colloids clumping together on the surface of the water after treatment. HP 100% removed both COD and turbidity, but the CP 100% had a better removal efficiency. One could say that HP 100% focuses more on the oil in the wastewater, whereas CP 100% was better at removing the organics in the wastewater.

With the combination polymers, the results observed after the jar tests, indicate that there is an increase in COD removal as the ratio of the non-hydrophobic part in the different polymers increase. Fig. 3 and 4 show the impact of degree of hydrophobicity on the COD removal.

**Fig. 3. COD results obtained for the hydrophobicity of the different polymers used**

![Fig. 2. FTIR result obtained and the comparison is shown of the different synthesized polymers used](image2)
This was not the case with the non-hydrophobic polymer. The synthesized polymers used as flocculants showed effective removal of COD from the biodiesel wastewater. After treatment of the biodiesel wastewater, the pH increased as the flocculant dosage increased. Turbidity decreased as well as the COD. The hydrophobic polymer was found to react mostly with oil resulting in the formation of clumps at the surface of the water. This was not the case with the non-hydrophobic polymer. The non-hydrophobic polymer had better COD removal efficiency, implying that it reacted mostly with the hydrophilic organic matter in the wastewater.

IV. CONCLUSION

In this study, five polymers including a hydrophobic, a non-hydrophobic and three intermediate polymers were synthesized using the sol-gel method. The characterization of these polymers using the FTIR analytical technique showed a variety of binding groups confirming the successful grafting of the initial ingredients. The synthesized polymers used as these polymers using the FTIR analytical technique showed a variety of binding groups confirming the successful grafting of the initial ingredients. The synthesized polymers used as flocculants showed effective removal of COD from the biodiesel wastewater. After treatment of the biodiesel wastewater, the pH increased as the flocculant dosage increased. Turbidity decreased as well as the COD.

The hydrophobic polymer was found to react mostly with oil resulting in the formation of clumps at the surface of the water. This was not the case with the non-hydrophobic polymer. The non-hydrophobic polymer had better COD removal efficiency, implying that it reacted mostly with the hydrophilic organic matter in the wastewater.

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REFERENCES


M. van den Berg was born and raised in a small town located in the Northern part of Kwa-Zulu Natal, Vryheid, South Africa. Marcelle is currently a final year student at the North-West University, studying chemical engineering.

She had opportunities through her years of study to learn project management skills through the opportunities the university gave her. She was fortunate to be part of the start of a small-scale biodiesel production plant situated in Benoni. Her love for water treatment started in 2016 after finishing vacation work at a water treatment consultation company.