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Synthesis and Performance Evaluation of a New Polymeric Composite for the Treatment of Textile Wastewater

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ABSTRACT: Azo dyes are synthetic colorants widely used in textile industry and are considered to be major contaminants in dye wastewater. Coagulation–floculation is most preferred techniques to treat dye wastewater. A N,N-diisopropylamine-based new polymer was synthesized by polycondensation of epichlorohydrin, N,N-diisopropylamine, and ethylenediamine. The chemical and thermal properties of the polymer were investigated by FTIR, XRD, TG, and viscosity measurements. The flocculation efficiency of the polymer was evaluated at different coagulant dose, organic load, and pH. The flocculation efficiency of this polymer was found to be higher over a pH range of 2–10 at its optimal dose of 80 mg/L. Morphological changes in the floc were studied by light and scanning electron microscopy. The zeta potential results clearly indicated that flocculation at the optimum doses is the result of charge neutralization and adsorption bridging. This study demonstrates the successful synthesis of the polymer, its excellent color removal efficiency (>98%) at lower doses, and effectiveness in dye wastewater treatment.

1. INTRODUCTION

Refractory organic compounds are often present in the effluents of pharmaceutical, textile, pesticide, and herbicide manufacturing industries. Effective treatment of such nonbiodegradable compounds are challenging and energy intensive, thus making it inordinately costly to treat.1–5 The increased worldwide demand for manufactured textile products has predictably led to a proportionally higher quantity of textile effluent being released into the receiving environment. These colored textile effluents regularly contain high concentrations of the nonbiodegradable refractory organic compounds, particularly in the form of azo dyes. Most of these dyes and their degradation byproducts are highly toxic to the flora and fauna of the receiving aquatic ecosystem.6

Approximately 50% of dyes produced globally each year (700,000 tons) are azo dyes, and the majority of these are used in the textile manufacturing process.7,8 Alarming, a major proportion (≥15%) of these dyes is released into the waste effluent stream as part of the normal textile manufacturing process, where they primarily enter the receiving environment in a very reactive state.9 Such effluents contain high concentrations of azo dyes which are highly carcinogenic. In addition to high toxicity and physiological effects to the aquatic life, dye wastewater also leads to eutrophication and is aesthetically unacceptable. Congo red is one such biologically recalcitrant azo dye, with the chemical formula 3,3′-((biphenyl)-4,4′-diylbis (azo))bis (4-amino-1-naphthalene sulfonic acid) disodium salt. It is primarily used to color textile and wood pulp, but is also a useful biological indicator since it changes from red-brown in basic solution to blue in acidic solution.5,9 The effective removal of dissolved dyes and suspended particles from dye wastewater is an important task and efficient remediation of effluent textile wastewater still represents a critical need in the textile manufacturing processes.

Recently, the development and use of cationic polymer composites for color removal from dye wastewater is one of the preferred treatment technologies. Combined coagulation and flocculation processes are more extensively used for the pretreatment of textile effluents than biological processes.5,10–13 Lower cost and higher efficiency are the major advantages of coagulation and flocculation in comparison to other treatment methods. As such, significant efforts are being made to develop low cost, highly efficient polymeric composites for advanced decolorization of textile effluents.14 Alum and other inorganic coagulants have been used extensively in conventional wastewater treatment; however, these have been shown to not be very effective for the removal of organic dyes by flocculation.15–17 Moreover, efficient removal of reactive or azo dyes from effluents using conventional flocculants is still somewhat difficult and ineffective.18,19 Since the current level of flocculant technology necessitates the addition of large amounts of coagulants, the generation of excessive volumes of sludge is unavoidable; thus the routine application of inorganic flocculants is limited. The development and use of cationic polymer composites for color removal from dye wastewater is among the preferred treatment technologies that have recently come into vogue. Consequently, multiple efforts are being
made to develop low cost polymeric flocculants for the treatment of anionic dyes.

Cationic polymeric flocculants effectively destabilize the dye molecules as well as other charged suspended particles by charge neutralization and the compression of the electrical double layer. Additionally, adsorption and formation of particle–polymer–particle bridges also play an important role in the flocculation phenomenon. Investigation into cationic polymers has been increasing over the past decade, and quaternary amine salts of polyamine-based cationic polymers have proven to be effective flocculants for the charged, highly reactive dye molecules. Earlier studies have shown that polyamine-based flocculants have significant advantages over their counterparts as they are easy to use, instantly water-soluble, and effective over a wide range of pH. Furthermore, cationic polymers and composites possess excellent color removal at lower doses, with the added advantages of lower cost and comparatively small volumes of sludge production, making them highly effective options. To date, limited studies have been conducted on the application of polyamine-based flocculants for the treatment of wastewater and textile effluents. In this study, a quaternary ammonium salt-based EPI-DIPA-EDA flocculant was synthesized as a potential method for textile effluent remediation. It was characterized by different analytical methods, and was further evaluated for its performance efficiency in the removal of Congo red from a simulated dye wastewater.

2. MATERIALS AND METHODS

2.1. Chemicals and Reagents. Ultrapure analytical grade chemicals used in this study were procured from Sigma-Aldrich (South Africa). All the stock solutions were prepared with ultrapure water.

2.2. Preparation of Cationic Polymer (Quaternary Ammonium Salt of Polyamine). The high viscosity cross-linked EPI-DIPA-EDA flocculant was synthesized by the polycondensation of ethylenediamine, N,N-diisopropylamine, and epichlorohydrin. In brief, epichlorohydrin (22.5 g), N,N-diisopropylamine (4 g), and water (40 g) were mixed and stirred continuously in a glass reactor at constant temperature (30 °C) followed by addition of 15.5 g of ethylenediamine at elevated temperature (70 °C). The temperature of the reactor was further raised slowly to 85 °C, and the reaction was continued for next 1 h. Later on, an excess of epichlorohydrin was added to the reactor. The reaction continued through the next 12 h at 95 °C and then was stopped by concentrated H2SO4. The detailed synthesis process is provided elsewhere.

2.3. Characterizations of the Polymer. 2.3.1. Viscosity Measurement. The flocculation performance of the polymer is greatly affected by its viscosity. The viscosity measurement of the EPI-DIPA-EDA flocculant was carried out at 750 rpm and 25 ± 0.05 °C using a Brookfield Viscometer (model no. CAP 2000, Spindle 05, USA).

2.3.2. Infrared Spectrometric Characterization. The FT-IR spectra of the polymer were analyzed using the KBr dispersion method on a Spectrum Bx FTIR System (PerkinElmer) to identify possible chemical bonding and the presence of different functional groups in the EPI-DIPA-EDA composite. The EPI-DIPA-EDA flocculant powder was mixed with KBr in a 1:10 ratio, and pellets were formed using a stainless steel mold. The FTIR spectrum was recorded with a resolution of 4 cm⁻¹ in the range of 4000–400 cm⁻¹ in transmittance mode.

2.3.3. X-ray Diffraction Analysis. The formation of polymer networks was studied by X-ray diffraction (XRD). The diffraction pattern was recorded in an X'Pert Pro (model PW3040/60, PANalytical (Netherlands) using a 2θ of 10–50° angle (Cu radiation, k 1/4 0.1546 nm) at 40 kV and 30 mA.

2.4. Preparation of Synthetic Dye Wastewater. A 100 mg/L sample of Congo red dye wastewater was prepared with tap water for the coagulation and flocculation studies. The pH of the experimental dye wastewater was adjusted with dilute (1 N) NaOH or H2SO4 as necessary.

2.5. Flocculation Experiment for Simulated Dye Wastewater. The stock solution (5000 mg/L) of the EPI-DIPA-EDA flocculant was prepared in deionized water. The absorbance of dye wastewater was measured using a spectrophotometer (SpectroquantPharo 300, Merck) at a λmax of 497 nm. Coagulation and flocculation experiments were carried out by adopting the method of Granados et al, 2012. In brief, rapid mixing of dye wastewater and selected doses of flocculent was carried out for 2 min at 150 rpm followed by slow mixing at 20 rpm for 5 min for flocc development. A set of Congo red dye wastewater devoid of any flocculent was used as a control. A 10 mL aliquot collected from each set was used for absorbance measurements. The spectrophotometer was calibrated using ultrapure water as a blank for all optical density measurements, and all samples having optical density 1.0 were subjected to the successive dilutions. The efficiency of the polymer was evaluated on the basis of the percentage of color removed, as follows:

\[
\% \text{color removal efficiency} = \frac{OD_{t0} - OD_t}{OD_{t0}} \times 100
\]  

where ODt0 is the optical density at time zero and ODt is the optical density of the simulated dye wastewater at time t.

The charge neutralization potential of EPI-DIPA-EDA flocculant was studied using a zeta potential/particle sizer (NICOMP 380 ZLS, PSS.NICOMP, USA).

2.6. Floc Analysis. 2.6.1. Light Microscopy. After flocculation, the flocs were allowed to settle under gravity for 4 h. The supernatant was discarded and a few drops of settled flocs were carefully taken with the help of a dropper. An oil-emulsified slide was prepared with a single floc droplet and observed under a light microscope (Nikon eclipses 80i, Nikon, USA). The physical adhesion and formation of dye aggregates were studied.

2.6.2. Scanning Electron Microscopic (SEM) Analysis. A small volume of settled flocs was transferred to a watch glass and oven-dried at 80 °C overnight. The dried Congo red flocs were powdered, and a small volume was placed onto carbon ribbon which was held down by a sample holder. The surfaces of the flocs were made electrically conductive with a gold/palladium coating at a sputter current of 3 mA for 60 s, using a Quorum (Q 150R ES). The ultramicroscopic structural changes during flocculation were studied using scanning electron microscopy (Zeiss Ultra Plus FEG SEM).
3. RESULTS AND DISCUSSION

The viscosity obtained for the EPI-DIPA-EDA flocculant was 1040 cps. It has previously been reported that the adsorption-bridging efficiency of epichlorohydrine-based flocculants improves with increasing viscosity; thus the higher viscosity of the flocculent in the present study contributes to the higher flocculation efficiency of the polymer. The main fractions of quaternary ammonium salt of amine-based polymer were characterized by FT-IR spectroscopy (Figure 1), which revealed the presence of amine, alkane, carboxyl, and hydroxyl functional groups in the current polymer. The FT-IR spectra showed characteristic absorption bands (in cm$^{-1}$) around 3000 cm$^{-1}$ (C−H stretches); around 2663 cm$^{-1}$ (most probably due to a hydroxyl group); and around 1616 cm$^{-1}$ (C=O stretching of the ester bond). The quaternary ammonium groups (R−N$^+$ (CH$_3$)) bending band are positioned at 3401 cm$^{-1}$ (N−H stretching). In previous studies, the presence of RNH$_2$ amine group bands in the range of 3419−3468 cm$^{-1}$ in newly synthesized polymers containing polyaluminum chloride, epichlorohydrin, and acrylamide has been reported.

The X-ray diffractogram profile of the polymer sample is presented in Figure 2, with the prepared flocculant exhibiting a distinct crystalline peak. In contrast the quaternary ammonium salt of amine-based polymers showed a dispersive broad peak, thus signifying the amorphous nature of the flocculant.

The thermal stability of the EPI-DIPA-EDA flocculant was determined by thermogravimetric analysis. The TGA profile of the synthesized polymer indicated a two-step mass loss: almost 3−5% of total mass was lost in the temperature range up to 148.6 °C, while a sharp decrease in mass of 80.26% in the temperature range between 148 to 461 °C was observed. This may be attributed to moisture loss due to the hygroscopic nature of the polymer, with the residual mass (17.23% at 461.53 °C) shown in Figure 3. These results indicate that the EPI-
DIPA-EDA flocculant has a degradation temperature threshold around 148 °C.

Figure 3. TGA analysis of polyamine polymer.

3.2. Flocculation Behavior of the EPI-DIPA-EDA Flocculant. A new quaternary ammonium salt of amine-based polymeric composite was designed and developed by the polycondensation of epichlorohydrin, N, N-disopropylamine and ethylenediamine and evaluated for the removal of azo dye by flocculation from dying wastewater. We modified the thermal polycondensation process for the development of a new polymeric composite based on the distinctive chemical properties and high flocculation efficiency of the aforementioned materials. The flocculation/coagulation efficiency of EPI-DIPA-EDA flocculant was examined by flocculation tests using Congo red simulated dye wastewater. The results were expressed as the color removal efficiency and are shown in Figure 4. The first experiment was carried out with simulated dye wastewater containing 100 mg/L of Congo red without any adjustment of the pH of the wastewater. The findings showed that with an increase of the polymer doses up to the optimal level, the residual dye concentration in the simulated wastewater gradually decreased to a minimum. The dye removal efficiency (Figure 4) increased gradually with an increase in EPI-DIPA-EDA flocculant dosage reaching a maximum up to 95% at 80 mg/L. The results showed that >80% of dye removal was achieved at 60 mg/L of flocculant dose and the highest dye removal (94.8 ± 0.73%) was obtained at a dose of 80 mg/L. The measurement of zeta potential provides information on the charge of the flocs. The zeta potential changed from −34.06 ± 0.03 mV to −17.87 ± 0.91 mV at 80 mg/L flocculant dose, whereas at 250 mg/L flocculant dose, it reached the value of −2.37 ± 0.64 mV.

Therefore, our study confirms a typical appearance of the charge neutralization as well as adsorption bridging mechanism in the case of EPI-DIPA-EDA based coagulation-flocculation phenomenon. We also observed that for the optimal dose of polyamine polymer, effective flocculation occurred and resulted in the formation of larger aggregates and thus visible flocs of Congo Red, showing effective removal of anionic and reactive dyes by charge neutralization with cationic polyamine based polymers. Wang et al., 2009 showed that the viscosity and high cationic potential of the polymer are directly proportional to charge neutralization during flocculation. The effective agglomeration and flocculation of Congo red is not possible without charge neutralization or adsorption bridging. The polymer showed excellent coagulation during flocculation of the dye at its optimal dose (80 mg/L). Therefore, it can be assumed that the polymer effectively neutralizes the negative charges of the dye, thereby improving the agglomeration and hence flocculation. Previous studies demonstrated successful flocculation due to the charge neutralization of the negatively charged functional groups with a positive charge density of the cationic flocculant. Congo red is an anionic dye that bears sulfonic groups. Electrostatic attraction neutralizes negatively charged sulfonic groups of Congo red dye with protonated amine groups of the polyamine-based cationic flocculent which help them to bind together to form flocs. Such flocs get settled due to gravitational forces. Therefore, the removal of the azo dyes is optimal only when the amount of protonated amine groups is sufficient to completely neutralize the anionic charges. On the other hand, an excess of protonated amine groups leads to restabilization of the suspension when large doses of polymer are added to the simulated dye wastewater, which results in no further increase in dye removal efficiency of the process.

We also observed that at a dose of 100 mg/L there was no further improvement in dye removal efficiency (94.31 ± 1.60%). The effectiveness of the flocculation process is enhanced due to the reaction between various negatively charged sulfonic groups of the Congo red with inter- and intrachain associated different protonated amine groups of the EPI-DIPA-EDA flocculent as well as due to its high molecular weight. Similar findings (Table 1) were reported by other investigators for various cationic polyamine polymers with different chemical compositions.

The quaternary ammonium salt of amine may play a dual role during the flocculation process: the coagulation of Congo red molecules due to charge neutralization in the first step followed by flocc formation by adsorption bridging at the second step. However, electrostatic adsorption rather than bridging of the polyamine-based polymers is more important and plays a crucial role in the flocculation of azo dyes. It is therefore observed that in the present study at optimal EPI-DIPA-EDA flocculant concentration, electrostatic adsorption results in the formation of larger flocs, leading to maximum color removal. Figure 8 shows a floc and floc aggregates. An SEM image presented in Figure 9 shows the (A) morphological difference between actual Congo red molecules and (B) demonstrates the morphological compactness of Congo red flocs which are tightly packed with low porosity and solid and smooth structure due to the action of the polymer.

3.3. Effect of pH on Flocculation Performance of EPI-DIPA-EDA flocculant. The flocculation performance of EPI-DIPA-EDA flocculant for Congo red dye wastewater was assessed under varying pH conditions (Figure 5). The results showed that the flocculation efficiency of the EPI-DIPA-EDA...
The EDA produced condensed and tighter ammonium salt of amine of the EPI-DIPA-EDA from 4.0 to 10.0, which indicates that the quaternary to 60 mg/L of the trend of decreased decolorization at lower doses from 10 mg/L DIPA-EDA pH 10.0. Interestingly, at the optimal dose (80 mg/L) of EPI-  

Table 1. Comparison of Various Dye Removal Studies

<table>
<thead>
<tr>
<th>flocculent</th>
<th>type of dye</th>
<th>optimum concentration</th>
<th>% removal</th>
<th>ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>epichlorohydrin–dimethylamine polymers</td>
<td>Reactive Brilliant Red K-2BP (RBR)</td>
<td>60%</td>
<td>&gt;95%</td>
<td>8</td>
</tr>
<tr>
<td></td>
<td>Disperse Yellow RGFL (DY)</td>
<td>60%</td>
<td>&gt;95%</td>
<td></td>
</tr>
<tr>
<td>polyferric chloride–poly-epichlorohydrin–dimethylamine polymer</td>
<td>Reactive Red (K-2BP)</td>
<td>120 mg/L</td>
<td>90%</td>
<td>34</td>
</tr>
<tr>
<td>polyamine–polyferric chloride polymer</td>
<td>Reactive Disperse</td>
<td>80 mg/L</td>
<td>&gt;98%</td>
<td>32</td>
</tr>
<tr>
<td>polyaluminum chloride–poly(3-acrylamido-isopropanol chloride)</td>
<td>RCB dye</td>
<td>50 mg/L</td>
<td>92%</td>
<td>20</td>
</tr>
<tr>
<td>polyferric chloride (PFC) and epichlorohydrin–dimethylamine</td>
<td>DYT dye</td>
<td>50 mg/L</td>
<td>96%</td>
<td></td>
</tr>
<tr>
<td>dimethylamine and epichlorohyd and 1,2-diaminoethane</td>
<td>Reactive Blue (K-GL)</td>
<td>120 mg/L</td>
<td>90%</td>
<td>23</td>
</tr>
<tr>
<td>polyferric chloride and poly-epichlorohyd–dimethylamine with</td>
<td>Reactive Red (K-2BP)</td>
<td>120 mg/L</td>
<td>98%</td>
<td></td>
</tr>
<tr>
<td>triethylenetetramine</td>
<td>Reactive Red liquor</td>
<td>100 mg/L</td>
<td>96%,</td>
<td>35</td>
</tr>
<tr>
<td>dimethylamine, acetone and formaldehyde was grafted onto</td>
<td>Reactive Blue liquor</td>
<td>100 mg/L</td>
<td>97%</td>
<td></td>
</tr>
<tr>
<td>hydroxymethylated lignin</td>
<td>Reductive Yellow liquor</td>
<td>60 mg/L</td>
<td>96%</td>
<td></td>
</tr>
<tr>
<td>epichlorohydrin–N,N-diisopropylamine–ethylnediamine</td>
<td>Reactive Brilliant Red</td>
<td>120 mg/L</td>
<td>&gt;75%</td>
<td>33</td>
</tr>
</tbody>
</table>

Figure 5. Effect of pH on Congo red removal efficiency of EPI-DIPA-EDA flocculant.

Flocculant increased at pH 4.0 and >95% color removal was achieved at 20 mg/L flocculant dose, whereas at the same concentration, 52% removal was achieved at pH 7.0 and 42% at pH 10.0. Interestingly, at the optimal dose (80 mg/L) of EPI-DIPA-EDA flocculant, the color removal was 98%, 96%, and 96% at pH 4.0, 7.0, and 10.0, respectively, which may be due to initial charge neutralization between the negative charge of the sulfonic group of Congo red and the positive charges of quaternary polyamine of EPI-DIPA-EDA flocculant. A clear trend of decreased decolorization at lower doses from 10 mg/L to 60 mg/L of the flocculant was noticed with increasing pH from 4.0 to 10.0, which indicates that the quaternary ammonium salt of amine of the EPI-DIPA-EDA flocculant produced condensed and tighter flocs of Congo red dye with smaller variation in the distribution of floc size. It is possible that the bridging between flocculant and Congo red molecules, as well as charge neutralization, may have significantly contributed to the flocculation phenomenon. However, it seems that the charge density of the quaternary ammonium salt of the EPI-DIPA-EDA flocculant at higher pH may be less than bridging, resulting in better flocculation at a lower pH and lower doses. The finding of ref 28 suggests that even though this hybrid polymer contains a varying molar ratio of epichlorohydrin, the solution pH had a significant effect on the performance. Similar observations were made by Yeap et al., 2014 while evaluating the flocculation performance of an inorganic–organic hybrid polymer for Reactive Cibacron Blue F3GA and Disperse Terasil Yellow W-4G dyes. They reported that these cationic polymers were effective in the range of pH 7.0 to 10.0 at optimal doses. There was a minor difference (i.e., <2%) in the Congo red dye removal efficiency of the EPI-DIPA-EDA flocculant over pH 2 to 10 at the optimum dose of the flocculent (80 mg/L). Wang et al., 2009 also reported similar results with epichlorohydrin–dimethylamine-based cationic flocculant. The results suggested that adsorption-bridging between dye and polymer molecule as well as charge neutralization mechanism were involved in the flocculation of Congo red dye by EPI-DIPA-EDA flocculant. Gao et al., 2011 proposed that the adsorption-bridging mechanism was responsible for the effectiveness of the epichlorohydrin–dimethylamine polymer in the pH range of 2.0–10.0 for the removal of brilliant red and disperse yellow dye by flocculation.

3.4. Effect of Substrate Concentration on Flocculation Performance. The effect of the initial dye concentration was assessed on flocculation behavior and dye removal efficiency of EPI-DIPA-EDA flocculant at its optimal dose of 80 mg/L. Figure 6 shows the variations in the absolute dye removal versus the initial dye concentration. The results revealed that at the optimum flocculant dose (80 mg/L), the absolute dye removal increased constantly 26 mg to 250 mg for initial concentrations 50 mg/L to 400 mg/L, respectively. The results

Figure 6. Effect of Congo red concentration on absolute dye removal of EPI-DIPA-EDA flocculant.
shown in Figure 6 clearly indicated that for Congo red, the absolute dye removal of the EPI-DIPA-EDA flocculant first increased linearly with increasing dye concentration. The findings suggest that up to a 400 mg/L dye concentration, the adsorption-bridging between polymer and Congo red dye was optimum, whereas a decrease of absolute dye concentration was observed upon a further increase of the dye concentration from 400 mg to 500 mg (Figure 6). The results demonstrated that EPI-DIPA-EDA flocculant showed similar removal efficiencies as reported earlier (Table 1); however, it was found highly effective with reference to absolute dye removal up to 400 mg of Congo red concentration. This may be associated with the effect of additional adsorption of the polymer on the flocs which could increase the positive charge of the aggregates. In turn, this could increase the positive charge over the flocs instead of achieving charge neutralization, thus resulting in repulsion between the flocs.

### 3.5. Effect of Time on Floc Settling

The effect of time on the settling of the flocs is presented in Figure 7. The results revealed that over 95% floc settling was achieved in 6 h of flocculation at optimal dose of flocculant. Less than 25% floc settling was observed below 40 mg/L flocculant doses. Very low to moderate floc settling (9%–89%) was observed at 60 mg/L of flocculant dose. However, 70% floc settling was recorded even in 1 h at optimal dose of EPI-DIPA-EDA flocculant, which gradually increased with the time and reached >95% in 6 h. Yeap et al., 2014 reported that the epichlorohydrin-dimethylamine/PFC based polymer produces larger and condensed flocs in less time thus resulting in higher color removal efficiency. The finding of our study is also in agreement with those of Yeap et al., 2014 and as indicated in Figure 7, > 95% color removal was achieved through floc sedimentation within the 6 h.

![Figure 7. Effect of time on floc settling.](image)

![Figure 8. Light microscopy image of Congo red flocs formed by EPI-DIPA-EDA composite.](image)

### CONCLUSION

The present study has demonstrated the successful synthesis of a new quaternary ammonium salt of amine-based polymer which demonstrated high coagulation–flocculation potential for the anionic Congo red dye. Therefore, the use of suchflocculant could be an effective method for treatment of dye wastewater. The flocculation efficiency of this synthetic flocculant was evaluated for the removal of Congo red dye at different pH, substrate concentration, and flocculation time intervals. The coagulation–flocculation efficiency of this flocculant for the removal of Congo red dye was effective over a wide pH range, that is, 4.0–10.0. We observed that the flocculation efficiency of the synthetic flocculant was greatly dependent on the initial dye concentration and flocculant dose. At higher pH levels, optimum dye removal was obtained at thylamine composite flocculant in terms of floc formation vs separation efficiency and concluded that the formation of larger and condensed flocs improves the separation efficiency. The results of our study revealed that in the case of EPI-DIPA-EDA flocculant, the formation of large flocs was due to charge neutralization between sulfonic groups of the Congo red dye and quaternary amine. This was followed by adsorption-bridging which resulted in a larger size of aggregates at optimal doses of the flocculent and improved the floc settling. The coagulation and flocculation efficiency greatly depends on several factors such as floc size and shape, floc aggregation time, floc density, and sedimentation. In their study, Yeap et al., 2014 reported that the epichlorohydrin-dimethylamine/PFC based polymer produces larger and condensed flocs in less time thus resulting in higher color removal efficiency. The finding of our study is also in agreement with those of Yeap et al., 2014 and as indicated in Figure 7, > 95% color removal was achieved through floc sedimentation within the 6 h.
comparatively high doses of the flocculant. Quaternary ammonium salt of amine-based synthetic flocculant has shown a dual advantage in flocculation; charge neutralization that leads to coalescence between Congo red molecules followed by flocculation through the adsorption-bridging mechanism. However, the doses of the flocculant and its cationic potential, solution pH, and chemical properties of the colloids significantly control the flocculation process. The findings of this study have clearly demonstrated that the synthetic flocculant is quite effective between pH 4 to 10, whereas very low doses are required for optimum removal of Congo dye below pH 7.0. The results showed a high color removal efficiency >98% of the EPI-DIPA-EDA flocculant for Congo red at optimal conditions.

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Notes
The authors declare no competing financial interest.

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