Characterization of textile dyeing effluent and its treatment using polyaluminum chloride

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Abstract
The study aimed to expose the level of pollution owing to textile dyeing effluents and assess the coagulant efficiency of polyaluminum chloride (PAC) for treating the textile dyeing effluents. The discharged of untreated textile dyeing effluents have severely polluted water and soils, threatened the entire environment. The study analyzed the discharged and treated effluents using standard methods of analysis. The optimized parameters of the coagulant PAC were the dose, contact time, temperature, and agitation speed. The color removal efficiency study observed that the coagulant PAC removed the color from 85 to 95% of three dyeing effluents at optimum conditions. The result showed that the maximum reduction of EC, TDS, COD, BOD, Cl\textsuperscript{-}, HCO\textsubscript{3}\textsuperscript{-} and SO\textsubscript{4}\textsuperscript{2-} were found to be 83.66, 85.7, 82.05, 82.05, 83.45, 66.91, 66.91 and 72.88%, respectively. It also showed that the coagulant efficiently reduced heavy metals and the highest percentage of reduction achieved was 72.7 and 98.52 for Fe and Pb, respectively, from the effluents. Hence, the PAC would be a potential coagulant for treating the textile dyeing effluents that help to build a sustainable environment.

Keywords BOD · Coagulant · COD · Effluents · PAC · Treatment

Introduction
Textile and dyeing factories play an incredibly imperative role in deteriorating the water quality by releasing their effluents in ponds, rivers, lakes, and oceans. Even a few amounts of dyes in water are vastly observable and objectionable (Crini 2006). Pollutants from textile dyeing industries change significantly and depend on the chemicals used in different dyeing and printing processes. The discharged untreated or poorly treated or diluted textile dyeing effluents on land surface and exterior water bodies could relocate a huge cost to the environment as well as to ecological disturbance and associated human health problems. Generally, industrial pollutants often differ the physicochemical characteristics, for example, temperature, acidity, salinity, turbidity of water bodies, leading to ecology alterations resulting in water becomes brackish. A study observed that high sulfate (SO\textsubscript{4}\textsuperscript{2-}) content in industrial effluents discharged near the drinking water supply can cause invigorating action (Agarwal 1996). Besides, the chloride (Cl\textsuperscript{-}) ion, which has always been used as a pollution pointer, might scratch the metallic pipes and agriculture products (Kumar, 1989; Lalove et al. 2000). As the textile dyeing effluent deteriorated the surface water quality, hence, it should be treated before discharging nearby surface water bodies. Recently, various treatment techniques, including adsorption (Makia et al. 1999; Ahmad and Ram 1992), precipitation (Duizbek and Kowal 1983), ozonization (Lin and Lin 1993), oxidation (Tan et al. 2000), and coagulation-flocculation (Bennett and Reeser 1998; Belukar and Jekel 1993) are developed for treating the effluents. Adsorption, flocculation, coagulation, precipitation, ozonization, irradiation, etc. are used as physical and chemical methods for the treatment of textile dyeing effluents (Soares et al. 2006; Wang et al. 2009a, b; Ozer et al. 2006; Shi et al. 2007). Coagulation is one of the most effective chemical methods to remove dyes and pigments from textile dyeing effluents (Gao et al. 2007; Golob et al. 2005). Chemical coagulation in textile dyeing effluent treatment involves the adding of chemicals to change the physical state of dissolved and suspended solids and assist their elimination by sedimentation. The coagulation process has been applying for many years because it is technologically suitable and cost-effective (Islam and Mostafa 2018a;
Anjaneyulu et al. 2005; Golob et al. 2005). The study considered polyaluminum chloride (PAC) as an effective coagulant for removing the color from the textile dyeing effluents. The study selected three dyeing industries located in Narsingdi, Gazipur and BSCIC area of Rajshahi District as the areas have the hubs of textile dyeing and printing industries in Bangladesh. The objective of the study is to characterize the textile dyeing effluent and assess the color removal efficiency of the coagulant polyaluminum chloride (PAC).

Materials and methods

Sample collection

The study collected three textile dyeing effluents, namely Ef1 (Effluent of Narsingdi District), Ef2 (Effluent of Rajshahi District), Ef3 (Effluent of Gazipur District), from sampling locations of Narsingdi, Rajshahi and Gazipur Districts of Bangladesh. The samples were collected in a one-liter double cap acid-washed polythene bottles from three locations. Before sampling, every bottle was washed with watery acid and double distilled water and before real sampling, the bottles were rinsed with effluents to be sampled.

Sample treatment

All textile dyeing effluent samples were treated with coagulating agent PAC (Analytical Reagent Grade). A jar test apparatus was used in this study to determine the optimum condition. The color removal efficiency of the coagulant PAC was determined using optimized the parameters such as pH (3 to 11), doses (50 to 600 mg/L), agitation speed (30 to 150 rpm), initial dye dose (50 to 300 mg/L) and temperature (30 to 50 °C). A definite dose of coagulant PAC were added to the desired volume of effluent containing beaker and immediately mixed with a magnetic stirrer for 1 to 2 min. Then mixed slowly and finally, the mixed solution was allowed to settle for 30 min. The solution was then filtered (Arnold et al. 1992). All these tests were performed at temperature 30 °C because the temperature is one of the important parameters on concentration, viscosity and therefore retained the volume of coagulant used. The temperature has a significant effect on pH calculation (APHA 1989). During the effluent’s treatment, the PAC coagulant was controlled by the hydrolysis speciation (Dennett et al. 1996). Many monomeric and polymeric species of PAC coagulant have been produced during coagulation such as $\text{Al}_{13}$$(\text{OH})_{34}^{5+}$, $\text{Al}(\text{OH})_{17}^{7+}$, $\text{Al}(\text{OH})_{20}^{4+}$, $\text{Al}(\text{OH})_{27}^{3+}$, $\text{Al}_{2}(\text{OH})_{2}^{4+}$, $\text{Al}_{2}(\text{OH})_{5}^{3+}$, $\text{Al}_{2}$$\text{O}_{4}$(OH)_{2}^{3+}, $\text{Al}_{5}(\text{OH})_{10}^{6+}$, $\text{Al}_{13}$(OH)$_{32}^{7+}$, and $\text{Al}_{14}$(OH)$_{8}^{8+}$, to name but a little bit (Amirtharajah and Mills 1982). The tri-positive aluminum ion is converted into the negative aluminum ion in the aqueous solution gradually and is shown in Fig. 1 (Stumm and Morgan 1962).

Sample analysis

The collected samples were analyzed for some major parameters of the textile dyeing effluents including pH, EC, TSS, TDS, COD, BOD, chlorides, bicarbonates, sulfates, and heavy metals. TDS and TSS of the effluents were measured by the gravimetric oven drying method at 105 °C. BOD of the effluents was determined by incubating the sample at 20 °C for 5 days followed by titration. COD was measured by the closed reflux method. Bicarbonates, chlorides, and sulfates were determined by complexometric titration, argentometric titration, and turbidity method, respectively. All the parameters after the treatment with PAC coagulants were measured, followed by the same methods, as discussed above. The textile dyeing effluent samples were preserved for analysis of heavy metals (Cr, Cu, Fe, Mn, Zn, and Pb) by acidification with concentration HNO$_3$ and HCl (2 ml HNO$_3$ and 3 ml HCl) of the solution and then stored at 5 °C till analyzed. All the metals were examined by the atomic absorption spectrophotometer using the air-C$_2$H$_2$ flame, as suggested by Chrislarsen (1982). The analytical results of all the water samples were thus evaluated following the norms prescribed under EPA standards.

Results and discussion

The study optimized the color removal efficiency of the coagulant PAC considering the parameters including coagulant dose, agitation speed, pH and temperature. It also analyzed some physicochemical parameters of textile dyeing effluents and the results were compared with the national standard discharge limits of the effluents. The study results are described below:
Optimized color removal efficiency

Effect of coagulant dose

In the study, the effect of coagulant dose on color removal efficiency of doses of PAC on three effluent samples. The results showed that the color removal efficiency increased in the beginning with dose concentration and then decreased slowly with doses for all the effluents (Fig. 2). It is noted that the color removal efficiency at low doses resembled well with the neutralization ability of coagulants. A number of reports showed that the coagulation-flocculation phenomenon was likely to be recognized to charge neutralization (Sharp et al. 2006; Wei et al. 2010). By increasing doses, the positive charge of the coagulants became more dominant, which led to electrostatic repulsion between particles. As a result, the color removal efficiency of the coagulants decreases with the increasing of doses because of destabilization of colloids (Cohen and Hannah 1971). The maximum efficiency of coagulant PAC was observed to be near about 93% at a dose 100 mg/L. The results indicated that PAC has potentially remove color from the effluents.

Effect of mixing speed

Mixing speed is one of the important factors in achieving higher color removal efficiency of the coagulants during the coagulation process. In this study, the effects of agitation speed between 30 and 150 rpm were investigated. The results showed that the color removal efficiency of PAC in three different effluent samples increased with the increasing mixing speed between 30 and 70 rpm, except for the effluent Ef3 (Fig. 3). These results might be caused by the effect of fast flocs formation and sludge precipitation rate of the inorganic coagulant with azo bone structure in drimarene red. A similar observed was made by Tasti et al. (2003).
color removal efficiency of PAC gradually decreased as the agitation speed increased. This trend showed that floc formation and breakage were intensely affected by the mixing rate (Xu et al. 2010). The highest color removal might be caused of increasing of the shear stress and breakage of flocs with increasing agitation speed. The results showed that the optimum speed achieved was at 60 rpm and the color removal efficiency was about 94% for effluent Ef3.

Effect of pH

The pH has a major role in the unaccompanied coagulation process (Perng and Bui 2014). The pH variation influences the charge on hydrolysis products and precipitation of metal hydroxides. It must be required to control the pH of the solution to get the optimum efficiency of the coagulants (Li and Gregory 1991). The illustrated that the color removal efficiency of the coagulant as a function of pH. The maximum color removal efficiency of the coagulant obtained was about 93.84% at pH 5. The coagulant showed the highest color removal efficiency among the three effluents was about 94% at pH 4.5 and 8 (Fig. 4). However, the results showed that the coagulant, PAC was more active in an acidic pH range for all the three effluents to remove color from the wastewater.

Similar observations were reported by Jiang (2001) and Ye et al. (2007), which supported the present findings.

Effect of temperature

Temperature affects the solubility of the metal hydroxide precipitate and the rate of formation of the metal hydrolysis products. The results illustrated that the color removal efficiencies of the coagulant increased with increasing temperature for all the effluent samples (Fig. 5). The highest color removal efficiency of the coagulants PAC was about 94%. The results indicated that the suitable temperature to flocculate of reactive dye wastewater was at room temperature (30 °C). A report showed that temperature has significantly affected the turbidity and particle counts during coagulation (Braul et al. 2001). A number of researchers reported that the color removing and dissolved organic carbon (DOC) of the dyeing solution are not sensitive to temperature (Knocke et al. 1986; Randtke 1998). Therefore, PAC is more suitable for the color removal from synthetic dyeing wastewater as compare to FeCl₃ coagulants at room temperature.

The color removal efficiency study observed that the coagulant PAC removed the color from 85 to 95% of three dyeing effluents at a 300 mg/L coagulant dose, 60 rpm
speed, 30 °C temperature, and acidic range between 6 and 7 indicated the potentiality of the coagulant.

**Characterization and removal efficiency of physicochemical parameters**

**pH**

The pH is one of the most significant effluent discharge quality parameters of an industry (Banerji 1993). Some chemical reactions such as solubility and metal toxicity are affected by the pH of the discharged effluents. The pH of the effluents also helps to establish the equilibrium between free $\text{CO}_2$, $\text{HCO}_3^-$, and $\text{CO}_3^{2-}$ (Patel et al. 2015). Table 1 shows that the pH of textile effluent samples varied from 6.70 to 8.10 with a mean value of 7.48 indicating the alkalinity of the effluent samples. The results were similar to the study conducted by Imtiazuddin et al. (2012). The pH was found to be neutral range after treating the samples with PAC.

**Electrical conductivity**

The EC is indicating dissolved substances in an aqueous system. It depends on the dissociation of ions, their concentration, temperature, and migration in the electric field, but it does not give any idea about the type of ions present (Rump 1992). The electrical conductivity (EC) of textile dyeing effluents before and after treatment is given in Table 2. Before treatment, it was 5640, 4590 and 4150 μS/cm, respectively, those were higher as per DoE (Department of Environment) standards permissible limits indicating the high levels of pollution. The results are similar to the report published by Kamal et al. results (2016). After the treatment, EC values went below the discharge limits of the DoE standards indicating the suitability of the coagulant PAC for the dyeing effluent.

**Total dissolved Solids (TDS)**

The amount of total dissolved solids (TDS) in different textile dyeing effluent samples were found to be 3778, 2937.5 and 3350 mg/L, respectively (Table 3). The results showed that the TDS of the effluents was found higher indicating the discharged effluents have the potential to deteriorate the surface water quality and aquatic life as well. A similar observation was made by Imtiazuddin et al. (2012). The highest level of TDS was found in the EF1, which was collected from Norsindi area indicated that the area is severally polluted.

**Table 1** pH of textile effluents before and after treatment

| Sample name | pH before treatment | pH after treatment with PAC | DoE Standard |
|-------------|---------------------|----------------------------|--------------|
| Ef1         | 7.65                | 6.5                        | 6–9          |
| Ef2         | 6.70                | 6.75                       |              |
| Ef3         | 8.10                | 7.10                       |              |

*Department of Environment, Bangladesh

**Table 2** Electrical conductivity (EC) of textile effluents

| Sample name | EC (μS/cm) before treatment | EC (μS/cm) after treatment with PAC | DoE standard EC (μS/cm) | % of decrease of EC after treatment with PAC |
|-------------|-----------------------------|-----------------------------------|-------------------------|--------------------------------------------|
| Ef1         | 5640                        | 1080                              | 1200                    | 80.85                                      |
| Ef2         | 4590                        | 750                               | 83.66                   |
| Ef3         | 4150                        | 1138                              | 72.57                   |

**Table 3** Total dissolved solids (TDS) of textile effluents

| Sample name | TDS (mg/L) before treatment | TDS (mg/L) after treatment with PAC | DoE standard (mg/L) |
|-------------|-----------------------------|-----------------------------------|---------------------|
| Ef1         | 3778                        | 910                               | 2100                |
| Ef2         | 2937.5                      | 470                               |                     |
| Ef3         | 3350                        | 479                               |                     |

Fig. 5 Effect of temperature on the color removal efficiency of the coagulant from the textile dyeing effluents (pH = 7.65, 6.70 and 8.10 of the Ef1, Ef2 and Ef3, respectively, coagulant dose 300 mg/L and agitation speed 60 rpm for PAC coagulant)
compared to the other two areas. The textile dyeing effluents with high TDS value may raise salinity troubles due to discharge to irrigation water (Kolhe and Pawar 2011). After treatment, the effluent samples with PAC, a decrease in TDS level was found to be 75.91, 84, and 85.70%, respectively (Fig. 6). The TDS removal percentage of the present study was higher than the other two studies conducted by Solanki et al., (2013) and Khatmode and Thakare (2015) reported that the percentage of TDS removal of the textile dyeing effluents was about 62.5 and 27 by using PAC coagulant and sawdust adsorbent, respectively. Kumar (1989) stated that the allowable range of TDS in textile dyeing effluents was 1850–2000 mg/L for agriculture uses. The results illustrated that the TDS values in the effluents might change the taste and/or odors. The textile dyeing effluent must be treated before releasing it to the surface water bodies.

### Total suspended solids (TSS)

The total suspended solids (TSS) of various textile dyeing effluent samples was found to be in the range of 401–233 mg/L, which was notably higher than the permissible limit of TSS (150 mg/L) as per DoE and EPA standard in textile dyeing effluents (Table 4). Several reports showed that the TSS of some textile dyeing effluents was varied from 100 to 390 mg/L (Mannuf et al. 2014). The TSS value of the treated effluent samples showed tremendous results reduced from 43 to 82% in three different effluent samples. (Fig. 6). Aleem et al. (2016) stated that the TSS removal by Alum was about 62% of textile effluents of Pakistan, which was lower than the results of the present study. PAC has a better TSS removal capacity.

| Sample name | TSS (mg/L) before treatment | TSS (mg/L) after treatment with PAC | DoE standard (mg/L) |
|-------------|-----------------------------|-----------------------------------|--------------------|
| Ef1         | 401                         | 88                                | 150                |
| Ef2         | 340                         | 61                                |                    |
| Ef3         | 233                         | 132                               |                    |

### Biological oxygen demand (BOD)

Biological oxygen demand (BOD) measures the amount of oxygen used by microorganisms in the biological process in water. The results shows that the BOD value of Ef1, Ef2, and Ef3 were 272, 117, and 197 mg/L, respectively, obtained before treatment (Table 5). This observation was found to be similar to the study conducted by Intiazuddin et al. (2012). After treatment, the BOD values were 83.45, 75.21 and 76.14% for Ef1, Ef2, and Ef3, respectively. Patel and Vashi (2010) stated that the BOD of textile effluent was reduced to 51.4% after treatment with ferric sulfate coagulant which is lower than the present study. Hence, PAC is the most efficient coagulant for the textile dyeing effluents.

### Chemical oxygen demand (COD)

Chemical oxygen demand (COD) shows the presence of all organic and inorganic matter content in the textile dyeing effluents. It comprises both the biodegradable and non-biodegradable portions of live bacterial attack, but it can be oxidized by strong chemical oxidants (Abbasi 1998; Tan et al. 2000; Chiron et al. 2000). Table 6 illustrates the total COD in various textile effluents was found to be 784, 340, and 512 mg/L, respectively, indicating a higher level
of pollution. Morshed et al. (2016) reported that the COD of untreated textile effluents was found between 301 and 359 mg/l, which were lower than the present findings. The highest COD value was observed in sample, Ef1 and the lowest was found in sample Ef2. After treating the effluent samples with PAC, the reduction of COD was found to be 77.55, 82.05, and 75%, respectively (Fig. 6). The removal of COD from the textile dyeing effluents was higher than the studies conducted by Patel and Vashi (2010), where the removal was 55.2% treated with ferric sulfate coagulant.

Concentration of chloride ions

Almost all-natural waters contain chloride and sulfate ions. The EPA standard recommends a maximum concentration of chloride in water is 250 mg/L. The lower and higher than the permissible limits might create harm for human beings. Table 7 shows that chloride contents of textile dyeing effluents were 654.95, 337.96, and 126.74 mg/L, respectively,

Table 7 Concentration of chloride ions of textile dyeing effluents

| Sample name | Chloride ions (mg/L) before treatment | Chloride ions (mg/L) after treatment with PAC | DoE standard (mg/L) |
|-------------|--------------------------------------|---------------------------------------------|--------------------|
| Ef1         | 654.95                               | 304.91                                      | 400–600            |
| Ef2         | 337.96                               | 111.83                                      |                    |
| Ef3         | 126.74                               | 78.92                                       |                    |

in three effluent samples. The chloride concentration in the effluent samples found lower than the DoE standard except for the Ef1.

Aleem et al. (2016) reported that the concentration of chloride of the untreated effluents was 432 mg/l, which was lower than the study results indicating a lower level of pollution. After treating the effluent with PAC, the chloride concentration in all the effluents was found below the DoE standard limit and these were 53.45, 66.91, and 37.73% for Ef1, Ef2, and Ef3, respectively (Fig. 7). A report showed that the removal percentage of chloride was 53.94% after treated with ferric chloride coagulant (Metha 2013), which was almost the same as the present study findings.

Concentration of bicarbonate ions

The lower amounts of bicarbonate ions in water are not considered for pollution but the higher concentration decreases the water quality level. The DoE standard recommends a maximum concentration of 300 mg/l for bicarbonate ions (Dey and Islam 2012). Table 8 shows that the bicarbonate ion concentration in textile dyeing effluents was 654.95, 337.96, and 126.74 mg/L, respectively, indicating a low level of pollution.

Only the effluent sample (Ef1) exceeded the DoE standard limits. After treating the effluent with PAC, the concentration of decrease in bicarbonate concentration was considerable and was 44.4, 56.5, and 51.6%, respectively, for different

Table 8 Concentration of bicarbonate ions of textile dyeing effluents

| Sample name | Bicarbonate ions (mg/L) before treatment | Bicarbonate ions (mg/L) after treatment with PAC | DoE Standard (mg/L) |
|-------------|-----------------------------------------|-----------------------------------------------|--------------------|
| Ef1         | 360                                     | 200                                           | 300                |
| Ef2         | 425                                     | 185                                           |                    |
| Ef3         | 475                                     | 230                                           |                    |

Anionic parameters
effluent samples (Fig. 7). Hussian et al. (2004) studied that the higher concentration of bicarbonate ions was found in four textile dyeing effluents, and this observation is similar to the present findings.

**Concentration of sulfate ions**

Most of the natural water supplies contain sulfates (SO$_4^{2-}$), which has no color and odor. These are compounds of sulfur and oxygen and stay as a dissolved salt in water. Sulfates can be more worrying because they usually take place in larger concentrations. The amount of sulfate ions in various textile effluent samples was shown to be in the range of 448, 638, and 434 mg/L, respectively (Table 9). According to WHO, the maximum permissible concentration of sulfate is 400 mg/L and except for the sample (Ef2), the sulfate concentration in the other two samples was well below the permissible standard. After treating the effluent samples with PAC, the sulfate ions concentrations found in the samples were 64.06, 65.72, and 72.88%, respectively, indicated that the coagulant PAC successfully reduced sulfate ions from the effluents (Fig. 7). Aleem et al. (2016) depicted that the concentration of sulfate ion in textile dyeing effluents was increased after coagulation with alum; however, the present study results showed the reduced concentration after treated with PAC.

Agarwal (1996) stated that the textile effluents containing sulfate ions should not be discarded into water bodies from where water is supplied for consumption, as a higher concentration of sulfate ions might change the taste. The sulfate ions have a laxative effect on domestic animals and humans and are generally related to high hardness levels.

**Some heavy metals of textile dyeing effluents**

The concentration of heavy metals including Cr, Mn, Fe, Cu, Zn and Pb in dyeing effluent samples is shown in Table 10. The concentrations of these heavy metals were lower than the national quality discharge standard limits for the textile dyeing effluents expect the concentration of Fe and Pb as stated by Dey and Islam (2012). The Fe concentrations of the samples Ef1, Ef2, and Ef3 were 4.2826, 3.6188, and 2.891 mg/L, respectively. Before treatment, the Pb concentration of Ef3 was 0.2900 mg/L, which was higher than standard limits. The concentrations of Fe of the samples Ef1, Ef2, and Ef3 decreased to 72.7, 64.85, and 71.92%, respectively, and the concentration of Pb of the samples were decreased to 79.2, 47.7 and 98.5%, respectively, after treatment with PAC coagulant (not shown in Table). The study optimized the parameters of the coagulation process and illustrated that coagulation with PAC was potentially reduced Fe and Pb. Hence, the PAC coagulant is very much active against heavy metals removing from the dyeing effluent.

**Conclusions**

The color removal efficiency study observed that the coagulant PAC removed the color from 85 to 95% of three dyeing effluents at a 300 mg/L coagulant dose, 60 rpm speed, 30 °C
temperature, and acidic range between 6 and 7 indicated the potentiality of the coagulant. The study results revealed that the concentration of different parameters of textile dyeing effluents such as EC, TDS, TSS, BOD, COD, and anions was found higher than the standard guidelines for effluent discharged. The study results showed a noteworthy decrease in all physicochemical parameters including pH, EC, TDS, TSS, COD, BOD, Cl\(^{-}\), HCO\(_3\)\(^{-}\), and SO\(_4^{2-}\). Among the heavy metals of the textile dyeing effluents, Fe and Pb exceed the national discharge standard limits of the effluents. The coagulant PAC also successfully reduced heavy metals like Fe and Pb by 65 to 72% and 48 to 95%, respectively. After treatment with PAC, the concentrations of heavy metals in the textile dyeing effluents were found lower than the DoE standard for the discharge limits of the textile effluents. The study results showed that the PAC is a potential coagulant for reducing the concentration of several physicochemical parameters from textile dyeing effluents. It is difficult to degrade the dyeing effluent using a single treatment unit such as physical, chemical, and biological. Therefore, the study suggested a combination of the units for achieving a higher degradation of the effluents.

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