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Decolorization and COD removal from synthetic and real textile dye bath wastewater containing Reactive Black 5

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ABSTRACT

Treatment of textile wastewater containing reactive dyes is highly important as dyes and their breakdown products are toxic. The application of chemical coagulation and Fenton oxidation on the color and the chemical oxygen demand (COD) reduction of Reactive Black 5 (RB 5) dye solution, the synthetic textile wastewater (STW), and the real dye bath real textile wastewater (RTW), was investigated. Among three coagulants used, polyaluminium chloride (PAC) decolorized more than 98% of RB 5 dye at a dosage of 200 ppm and pH = 5, while most common coagulants, alum, and $FeSO_4$, removed only 11% and 6% of RB 5 dye, respectively. PAC removed also 80% of the COD at 300 ppm dosage. All the three coagulants failed to decolorize highly saline STW containing RB 5 dye, but 80% decolorization was successfully achieved for the real textile dye bath wastewater by the polyaluminium coagulant dosage of 400 ppm while alum and $FeSO_4$ of the same dosage reduced only about 66% and 75%, respectively. Fenton oxidation reduced 98% of the color and 61% of the COD in 100 ppm RB 5 dye at pH = 3 and dosage of 0.2 mM Fe^{2+} and 2.0 mM H_2O_2. The COD was reduced by 90% when Fe^{2+} dose was increased to 0.5 mM keeping the Fe^{2+}:H_2O_2 ratio 1:10. When pH was increased from 3 to 7, the color reduction decreased from 91% to 78%. STW was decolorized to 87% by 0.25 mM Fe^{2+} and 2.0 mM H_2O_2 at pH = 3. For the discoloration of RTW, the optimum Fenton condition was 0.1 mM Fe^{2+} and 0.5 mM H_2O_2 at the same acidic condition. The current study reveals that the coagulation with PAC and Fenton oxidation can be successfully used to treat the real textile dye bath wastewater containing reactive dyes.

Keywords: Textile wastewater; Reactive dyes; Coagulation; Fenton oxidation

1. Introduction

The demand for durable, colorful, and fancy finishing products is continuously increasing with the rapid growth of the world's population. To meet such customers' demands manufacturers use improved raw materials in their production processes. Currently, textile, printing, plastic, etc. are the rapidly growing dye consuming industries [1]. The textile industry uses a huge amount of dyes and chemicals in its production process and consequently generates a large amount of colorful wastewater [2]. It is estimated that around 150–350 L of water is required to produce 1 kg of finished apparel [3]. Among the various types of dye, reactive dyes are widely used to color wool, cotton, nylon, and silk [4]. It is also estimated that around 40% of the dye is lost during the washing and rinsing steps [5] which are ultimately released with wastewater. If such wastewater is not properly treated before discharge to the environment, it can cause several environmental problems including the destruction of aquatic life [6,7]. Consumption of water containing dyes and their breakdown products can cause an adverse effect on human health [8,9]. Discharge of even a

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very small amount of colorful dye to the water streams is not acceptable, as it can disturb the photosynthetic process by interfering with the light penetration [10]. The treatment of the textile wastewater containing the reactive dyes is highly important as the reactive dyes are widely used in the dyeing process due to the good lightfast and excellent wash-fast properties [11]. Reactive dyes are very stable towards the sunlight and the other environmental factors making them difficult to treat by conventional biological treatments [12]. In general, an excess amount of salt is used in the dyeing process that causes the treatment of wastewater difficult due to the high salinity.

Currently, there are various techniques adopted for the treatment of textile wastewater. Coagulation, adsorption onto activated charcoal and chemical and biological oxidation techniques have been widely used to treat the colorful effluents [13–16]. The biological oxidation and the adsorption onto the activated carbon have several limitations due to the wastewater toxicity and the requirement of a higher dosage. Highly saline textile effluents may be toxic to the microorganisms and reduce the efficiency of the biological degradation of dyes present in wastewater. There are advantages and limitations of all these techniques, and the selection of the appropriate treatment method depends on several factors including wastewater quality and quantity [17]. Recently, we communicated our findings on the adsorptive removal of reactive dyes using low-cost adsorbents prepared from sawdust and rice husks [18]. The major disadvantage of the adsorption process is the requirement of adsorbent regeneration that may be costly and requires vacuuming, steaming, or other chemicals.

Advanced oxidation processes are being widely studied to degrade industrial wastewaters because of their low cost, high efficiency towards non-biodegradable wastewater, and easy operational processes [19]. The modern textile dyes are resistant to mild oxidation conditions such as aeration existing in the biological treatment systems. Therefore, an efficient color removal method must be accomplished by more powerful oxidizing agents. In the Fenton process, under acidic conditions, a Fe^{2+}/H_2O_2 mixture produces hydroxyl radicals [Eq. (1)] with a high electrochemical oxidation potential in a very cost-effective manner [20–22]. The hydroxyl radicals generated react with dye molecules in wastewater to convert them into less harmful colorless species. H_2O_2 regenerates the Fe^{2+} [Eq. (2)] and the catalytic cycle continues to produce more OH radicals. The effectiveness of these methods largely depends upon several factors that may include the type of dye, wastewater quality, Fe^{2+}, and H_2O_2 molar ratio, reaction pH, and contact time [23–28].

$$H_2O_2 + Fe^{2+} \rightarrow Fe^{3+} + OH^- + HO^\bullet \quad (1)$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2^\bullet + H^+ \quad (2)$$

Yadav et al. [29] reported the treatment of simulated textile wastewater containing reactive orange 6 dye using Fenton's oxidation with H_2O_2/Fe^{2+} molar ratio of 20 at the pH range 3–3.5 and achieved a 99% color reduction. Solmaz et al. [30] examined the biologically pretreated textile wastewater and reported a 95% color reduction when the H_2O_2/Fe^{2+} ratio is 1:2 at pH 3 [29]. Fenton oxidation is usually carried out at acidic conditions (pH 3–4) as at higher pH, Fe^{2+} easily converts into $Fe(OH)_3$ and significantly reduces the efficiency of the degradation process.

The coagulation process is a conventional treatment technique widely used in wastewater treatments. It has been widely tested for color removal, and several coagulants and the optimum reaction conditions have been reported [30,31]. The coagulation process is simple and cost-effective compared to other methods and often used as a pretreatment of wastewater. One major advantage of the coagulation process is the complete removal of dye molecules rather than partial decomposition to produce several harmful aromatic intermediates. The selection of an appropriate coagulant, its dosage, and various other operational parameters, such as the stirring time and the appropriate pH control, may significantly affect the coagulation-flocculation process. Alum, $Al_2SO_4{\cdot}14H_2O$, is among the most widely applied coagulant in water treatment. Recently, researches have focused on an alternative coagulant called polyaluminium chloride (PAC), a polynuclear form of $AlCl_3$ [32]. PAC is being more popular due to its lower dose requirement and less alkalinity consumption compared to the other common coagulants [33]. Alum and PAC behave differently in water. Alum hydrolyzes to yield several monomeric alumina species such as Al^{3+}, $Al(OH)^{2+}$, $Al(OH)_4^-$ and $Al(OH)_3$. The composition of these species depends on alkalinity, pH, and other contaminants present in the wastewater. In contrast, PAC is pre-hydrolyzed and forms highly charged polymeric aluminum species including $Al_2(OH)_2^{4+}$, $Al_3(OH)_4^{5+}$, and $Al_{13}O_4(OH)_{24}^{7+}$ [34]. As it is pre hydrolyzed, it consumes less alkalinity and acts faster in the coagulation process.

The coagulation process has been successfully applied to reduce chemical oxygen demand (COD) and other water quality parameters of industrial wastewater [35]. Greater than 90% reduction of COD and color of pulp and paper industry effluents was achieved by coagulation with alum [36]. Effectiveness of the coagulation process was evaluated using Alum, PAC, and $MgCl_2$ to treat textile wastewater containing reactive dyes [37] and PAC showed better performance over alum and $MgCl_2$.

Most of the previous studies on textile waste treatment have been carried out for synthetic or laboratory simulated textile wastewater. In general, these simulated wastewater conditions deviate significantly from the real textile dye bath wastewater. The aim of the current study was to use two physicochemical treatment methods namely the coagulation and Fenton oxidation to decolorize synthetic and real textile wastewater (RTW) containing reactive dyes. The optimum reaction conditions were determined for both synthetic and real dye bath wastewater.

2. Materials and methods

2.1. Materials

Reactive Black 5 (RB 5) was obtained from the local textile industry and used without further purification. Sulfuric acid, hydrogen peroxide, PAC, hydrated salt of iron, and magnesium were obtained from Mark chemicals (Mumbai, India). Alum, potassium dichromate, sodium azide, mercurous sulfate were obtained from BDH England. Sodium chloride, potassium iodide, manganese sulfate, manganese dioxide were obtained from Sigma-Aldrich, USA.

2.2. Experimental methods

2.2.1. Preparation of RB 5 dye solution

1.00 g of RB 5 dye was dissolved in a 1 L of distilled water to prepare a 1,000 ppm stock solution.

2.2.2. Preparation of synthetic textile wastewater

STW was prepared by dissolving 1.00 g RB 5 dye, 117 g NaCl, 0.16 g of Na_2CO_3, and 0.1 g of NaOH in 1 L of distilled water. Then the dye solution was hydrolyzed by heating at 50°C for 1 h [38]. 100 mL of 100 ppm STW sample was used in each experiment.

2.2.3. Decolorization of RTW

Real textile dye bath wastewater containing only RB 5 as the dye was collected from a textile industry located in an industrial zone in Sri Lanka. Characteristics of the RTW are given in Table 1. As we reported earlier for the adsorption studies [18], collected real dye bath wastewater samples were ten times diluted before the analysis and 100 mL of the diluted samples were used in each experiment. The color reduction was measured at a maximum absorbance wavelength (λ_{max} = 595 nm).

2.2.4. Coagulation studies

A known amount of each coagulant was mixed with wastewater samples using a mechanical shaker at 150 rpm for 1 min. The speed was reduced to 40 rpm and the content was stirred further for 30 min. Then the solution was kept undisturbed for 20 min for sedimentation. The supernatant was filtered through a Whatman filter paper (Grade 4) and the filtrate was used for the color and COD measurements. The coagulation experiments were performed using PAC, alum, and $FeSO_4 \cdot 7H_2O$ as coagulants. A jar test was carried out to find the most suitable coagulant and its optimum conditions. The coagulant dose was changed from 200 to 500 ppm at a constant pH. The optimum pH value for the coagulation process was determined using a constant concentration (200 ppm) of the coagulant with 100 mL of textile wastewater at different pH values.

Table 1
Characteristics of real dye bath wastewater

pH	9.24
Conductivity, μs/cm	1,414
Total dissolved solids, mg/L	714
Total suspended solids, mg/L	193
Chemical oxygen demand, mg/L	787
Biochemical oxygen demand (BOD_5), mg/L	146
Color, Abs at 595 nm (100 times diluted)	0.351

2.2.5. Fenton oxidation

All the Fenton experiments were carried out at 30°C as it is close to the daytime room temperature at the laboratory as well as to the wastewater in the equalization tank. Oxidation experiments were conducted under different H_2O_2 and $FeSO_4$ doses at different pH values. pH was changed using dilute H_2SO_4 acid. 100 ppm RB 5 solution/wastewater was used in each experiment and experiments were carried out in 250 mL Erlenmeyer flasks covered with an aluminum foil to avoid any sunlight. Samples were stirred mechanically at 200 rpm for 30 min and a small amount of MnO_2 was added to stop the reaction. The absorbencies were recorded after filtering (or centrifuging) the samples and the percentage color reduction was calculated at the maximum absorbance wavelength (595 nm).

2.3. Analytical methods

Initial and residual dye concentrations were measured using the UV-visible spectrophotometer (HITACHI UH 5300, Japan) at the λ_{max} = 595 nm. COD was measured by the closed refluxed colorimetric method using a COD reactor (Lovibond MD 100, Germany). A multi-parameter water analyzer (Hanna, HI 98194, Romania) was used to measure other water quality parameters.

3. Results and discussions

3.1. Coagulation studies of RB 5 dye solution

Coagulation is the most common technique being used in the wastewater treatment process. Alum ($Al_2(SO_4)_3$), $FeSO_4$, and PAC coagulants were used in the current study under different pH conditions and discoloration efficiency was evaluated. The best coagulant doses corresponding to each of the three coagulants were determined by measuring the color reduction with the variation of the concentration of each from 50 to 400 ppm at three different pH. Fig. 1 gives the graphical representations of pH and dosage dependence of color reduction of 100 ppm RB 5 dye solution for three different coagulants. Figs. 1a and b and Fig. 2a reveals that regardless of the pH of the medium, PAC has an intense color reduction compared to the alum and $FeSO_4$. Discoloration by PAC is more than 98% at the dosage of 200 ppm in accordance with the previous report by Perng et al. on PAC at pH 7 [40] on PAC at pH 7, while the most common coagulants, alum, and $FeSO_4$ decolorized only about 11% and 6% of RB 5, respectively. With the increase of PAC dose, discoloration increases showing a maximum at 200 pm, there on the discoloration shows a decrease with PAC dose and the reduction is about 62% at 600 ppm. As PAC produces several relatively large hydrolysis polymeric species carrying high positive charges, a lower dosage of PAC is sufficient to neutralize the negative charges of dispersed dye molecules. The amount of positively charged coagulant species present in the solution determines the amount of destabilization of the dyes. Alum and Fe coagulants are less effective in forming highly charged polymeric species and are therefore less effective in the coagulation of reactive dyes. The low performance of PAC at high coagulant concentration may be due to the

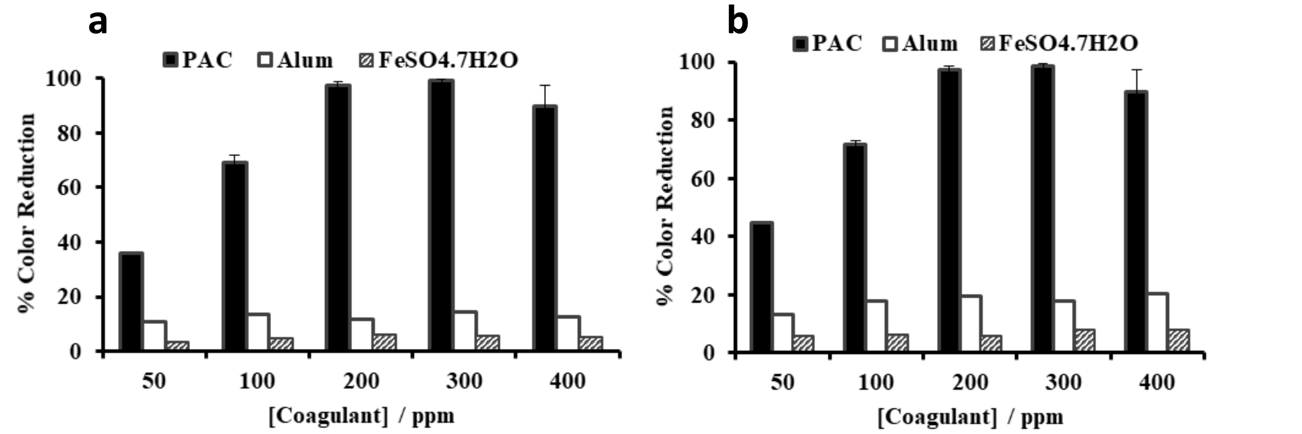

Fig. 1. Variations in the color reduction of 100 ppm RB 5 dye solution by three different coagulants with coagulant dosage and pH (a) pH 5 and (b) pH 7.

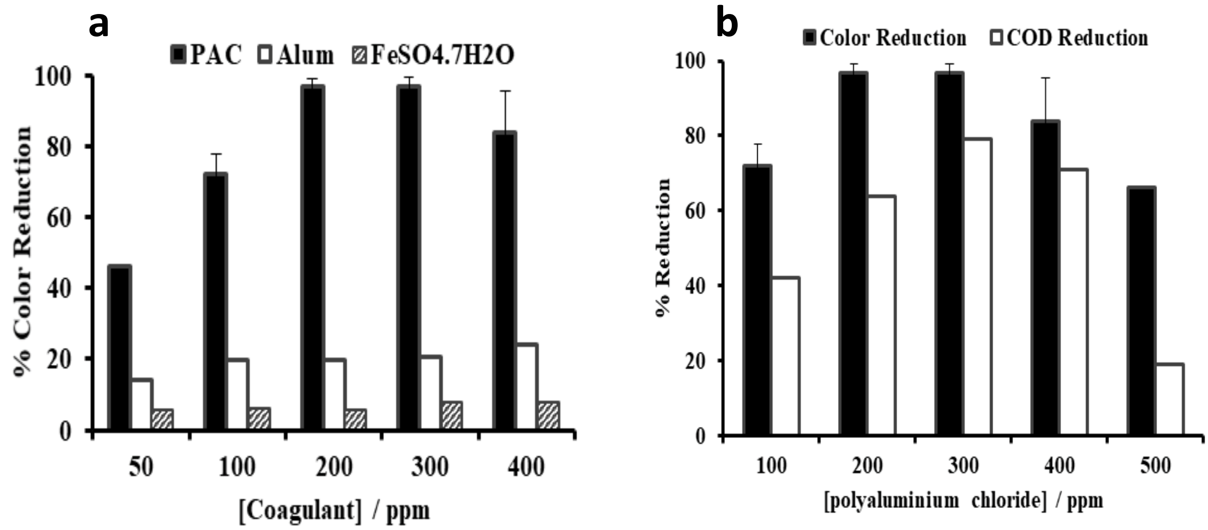

Fig. 2. (a) Color and (b) COD reduction of RB 5 with polyaluminium chloride at pH 9.

charge reversal on the colloidal particles resulting in a stabilization of the suspended dye molecules, additionally, at higher concentrations, PAC forms several polymeric species bearing positive charges. These species which have repulsive interactions have hindered the coagulation process. In general, as pH plays an important role in coagulation, the conclusion on the optimum pH condition for PAC also is important. It is interesting to note that the discoloration of RB 5 dye by PAC coagulant does not significantly vary with pH changes as shown in Figs. 1 and 2.

If we revisit Figs. 1 and 2 and compare the pH dependence of the color reduction by all three coagulants, interestingly only 11% of RB 5 discoloration was achieved by 200 ppm alum coagulant at pH 5 and it increased only up to 20% when the pH was increased up to 7 or 9 under the same reaction conditions. The Fe based coagulant ($FeSO_7 \cdot 7H_2O$) was the least effective, at all pH conditions and its discoloration is always below 10% RB 5 regardless of the coagulant dosage. As only the PAC showed an effective color reduction, further studies were carried out using this coagulant. As RTW is generally basic and PAC showed no pH dependence, COD reduction was measured at a pH value of 9. As indicated in Fig. 2b with the color reduction, the COD reduction shows an increase with the PAC dose and reaches a maximum at 300 ppm, and there on the reduction decreases with PAC dose at a pH of 9.

At the 300 ppm PAC dose where the maximum COD reduction observed (80%), the color reduction is about 97%. When the PAC dose was increased to 500 ppm, color, and COD reduction dropped to 66% and 18%, respectively at a pH of 9. As reported in previous studies by Verma et al. [41], coagulation is less efficient in the reduction of COD compared to the color reduction of dye-containing wastewater.

3.2. Fenton oxidation of RB 5 dye solution

The degradation of RB 5 dye solution using the Fenton oxidation was investigated at 30°C by changing the parameters affecting the Fenton process: pH and doses of Fe^{2+}

and H_2O_2. Hydroxyl radicals produced during the Fenton process react with the pollutants more rapidly than the other conventional oxidants and reduce the pollutant load present in wastewater.

3.2.1. Effect of H_2O_2 dosage

The impact of H_2O_2 dosage was studied by stirring 100 mL of 100 ppm RB 5 solution with 0.5 mM Fe^{2+} solution in a series of H_2O_2 solutions with concentrations ranging from 0.5 to 5 mM at pH of 3. The optimum H_2O_2 concentration corresponding to the maximum COD and color reduction was determined as shown in Fig. 3a. RB 5 degradation, which is mimic by the color reduction, increased with the H_2O_2 concentration. While 93% color reduction was observed at 1.0 mM H_2O_2, only a 4% increase of color reduction was observed when the H_2O_2 concentration was doubled to 2.0 mM. Further increase of H_2O_2 concentration up to 4 mM had no effect on the color reduction. When the experiment was carried out in the absence of H_2O_2, less than 5% discoloration was observed confirming the contribution of OH radicals in the Fenton process. The low or negative impact of H_2O_2 dosage on color reduction beyond the 2 mM dosage may be due to the potential OH radical scavenging reaction [Eq. (3)] occurring at higher H_2O_2 concentrations [41].

$$^{\bullet}OH + H_2O_2 \rightarrow HO_2^{\bullet} + H_2O \quad (3)$$

Similarly, in the increase of H_2O_2 dosage from 0.5 to 5 mM, first an exponential increase and then a flattening of COD reduction (from 16% to 90%) could be observed. The best COD reduction was achieved when the Fe^{2+}:H_2O_2 ratio was 1:10.

3.2.2. Effect of Fe^{2+} dosage

The effect of Fe^{2+} concentration on the discoloration was also investigated by changing the Fe^{2+} concentration from 0.01 to 0.5 mM while keeping H_2O_2 concentration at 1.0 mM and a pH of 3. Percentage RB 5 discoloration at the optimum H_2O_2, pH conditions, and different concentrations of Fe^{2+} is shown in Fig. 3b. When the Fe^{2+} concentration increased, the color reduction increased and reached a maximum value of 94% at 0.1 mM Fe^{2+} concentration (Fe^{2+}:H_2O_2 = 1:10). Further increase of Fe^{2+} concentration had no effect on the discoloration of the RB 5 solution.

As most of the previous Fenton studies have been performed at Fe^{2+}:H_2O_2 ratio of 1:10, both Fe^{2+} and H_2O_2 concentrations were varied maintaining the ratio at 1:10 and the color, and COD reduction was determined. As shown in Fig. 4a, 98% color reduction was observed at 0.2 mM Fe^{2+} and 2 mM H_2O_2, but under these reaction conditions, COD reduction is only about 61%. However, at 5 mM H_2O_2 concentration COD was reduced by 90%. For the discoloration process, it is only required to break the conjugation of the chromophore, but for the COD reduction, complete mineralization is required [42]. Therefore the COD reduction requires much stronger conditions than for color reduction.

3.2.3. Effect of pH on color reduction

The study was continued to understand the effect of pH on color reduction, the Fenton reaction was carried out within the pH range 3–7 and the results are shown in Fig. 4b.

Fe^{2+} and H_2O_2 concentrations were kept at their optimum levels for this study based on the conclusion drawn above. In the Fenton reaction, pH plays a critical role and the maximum color reduction was achieved at a pH of 3. The color reduction decreased from 91% to 78% with the increase of pH from 3 to 7. Fenton oxidation is usually carried out at low pH to avoid precipitation of Fe^{2+} and Fe^{3+} as oxyhydroxides in alkaline conditions. These precipitates inhibit the reaction between Fe^{2+} and H_2O_2 and prevent the OH radical formation. In addition, at higher pH values, H_2O_2 undergoes the dissociation and auto decomposition reactions to form oxygen gas and water [Eq. (4)]. Further, the oxidation potential of OH radicals is known to decrease with the increase of pH of the solution [43].

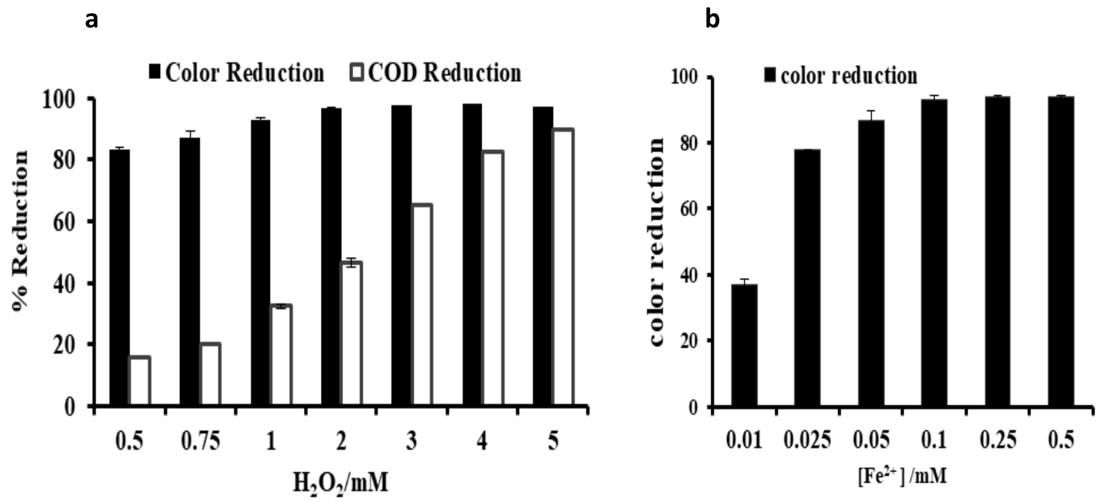

Fig. 3. Percentage color and COD reduction under different Fenton conditions: (a) variation with H_2O_2 concentrations at [Fe^{2+}] = 0.5 mM and (b) variation with Fe^{2+} concentrations at [H_2O_2] = 1.0 mM.

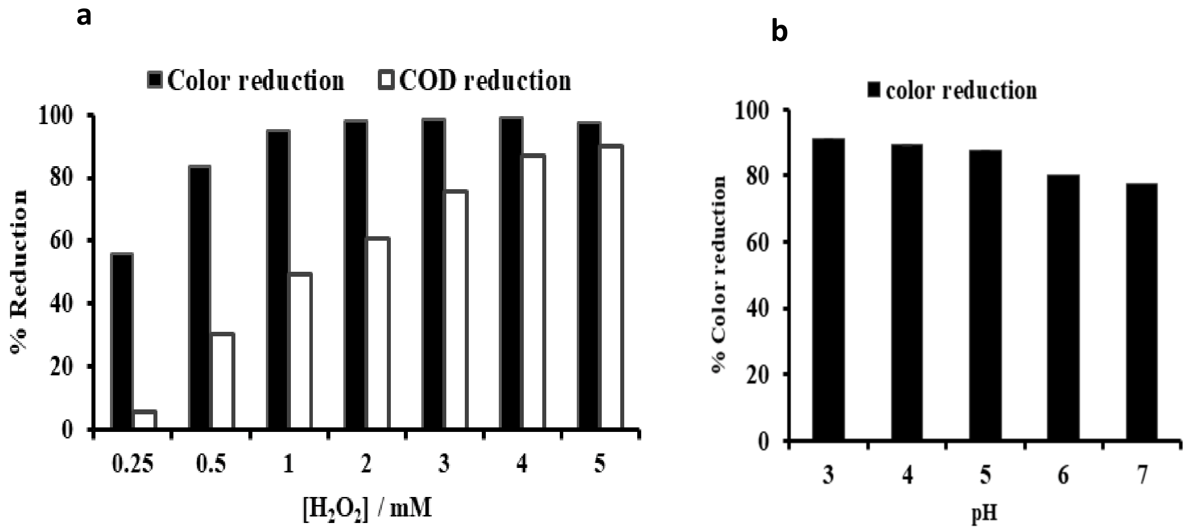

Fig. 4. (a) Variation of color and COD reduction at $[Fe^{2+}]$:$[H_2O_2]$ = 1:10 ratio and (b) pH dependence of color reduction at $[Fe^{2+}]$:$[H_2O_2]$ = 1:10 ratio.

$$2H_2O_2 \rightarrow O_2 + 2H_2O \quad (4)$$

3.3. Treatment of STW

The coagulation and the Fenton oxidation were performed for the hypersaline STW containing RB 5 dye.

3.3.1. Coagulation studies of STW

The discoloration studies of synthetic wastewater containing RB 5 dye were carried out using the same three coagulants as described above in section 3.1. All three coagulants showed less efficiency in color reduction and failed to decolorize STW regardless of the dosage or the pH of the dye wastewater. This may be due to the high stability of dispersed dye molecules in the highly saline wastewater solution. High NaCl concentration present in wastewater causes a charge reversal on dye molecules and restabilizes the dye suspension. As shown in Fig. 5, the $FeSO_4$ coagulant was the least effective and it decolorized only about 10% of dye regardless of the dose applied. Both PAC and alum, show a similar efficiency with the maximum color reduction about 35% of RB 5 present in STW although the PAC reached the maximum at 50 ppm while alum reached the maximum at 100 ppm.

The color reduction by PAC showed no change after its maximum (35%) with the increase of its concentration while alum showed a decrease with its concentration after the maximum. $FeSO_4$ coagulant mainly produces $Fe(OH)_2$ or $Fe(OH)_3$ upon hydrolysis while alum produces several monomeric species. PAC produces several highly charged polymeric Al species. Accordingly, strength in the color reduction of the three coagulants varies in the order of PAC > Alum > $FeSO_4$.

3.3.2. Fenton studies of STW

The Fenton oxidation was successfully applied to decolorize highly saline RB 5 synthetic wastewater. In each

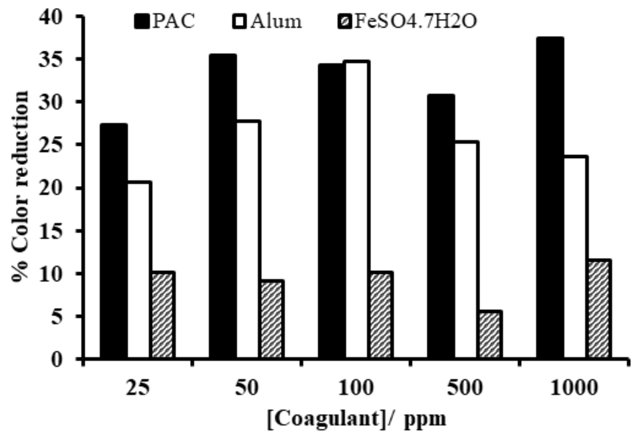

Fig. 5. The color reduction of 100 ppm STW with three different coagulants at pH = 9.

experiment, 100 mL of 100 ppm STW solution was used and all the experiments were carried out at pH = 3 in 250 mL Erlenmeyer flasks covered with aluminum foil. The optimum H_2O_2 concentration was determined by changing the H_2O_2 concentration from 0.25 to 3.0 mM keeping the Fe^{2+} concentration constant at 0.5 mM.

The effect of Fe^{2+} concentrations on oxidation was then studied by measuring the color reduction in the series of Fe^{2+} concentration from 0.01 to 0.5 mM keeping the H_2O_2 concentration at its optimum level (2.0 mM). As shown in Fig. 6a, at 0.025 mM Fe^{2+} concentration, 76% of color reduction, which is about a 67% increase from 0.01 mM Fe^{2+} was achieved and it was increased up to 87% when the Fe^{2+} dose was increased to 0.25 mM.

This is only about an 11% increase for a 10 times increase of the Fe^{2+} concentration. Further increase of Fe^{2+} concentration showed no considerable effect on the color reduction. This maximum discoloration observed for synthetic wastewater at the Fe^{2+}:H_2O_2 of 1:10 is in accordance

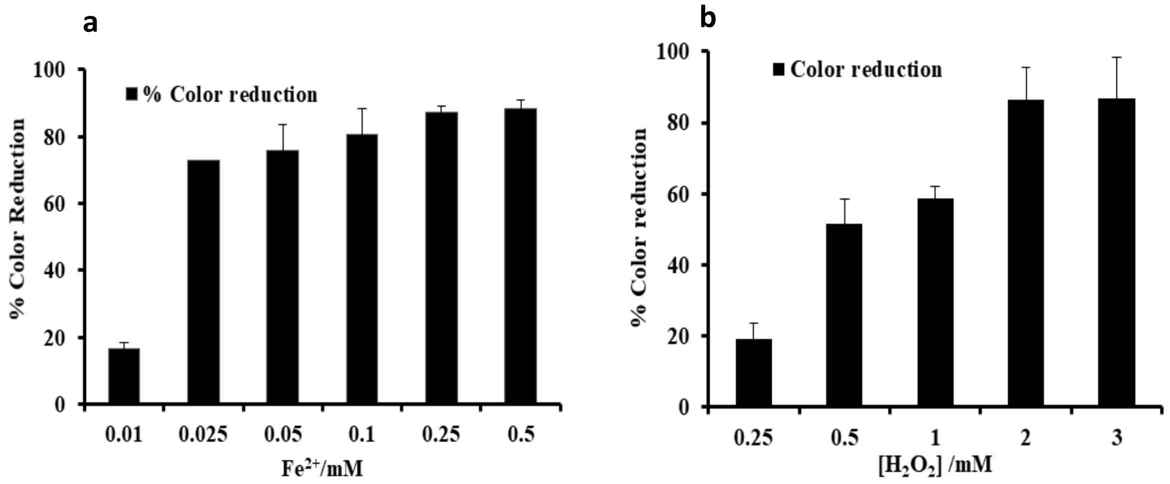

Fig. 6. The color reduction of STW with different Fenton conditions at pH = 3, temperature = 30°: (a) with different Fe^{2+} dosages at 2.0 mM H_2O_2 concentration and (b) with different of H_2O_2 dosages at 0.5 mM Fe^{2+} concentration.

with the observation made for the discoloration of the RB 5 dye solution. However, the percentage discoloration of synthetic wastewater was low compared to the RB 5 dye solution. As shown in Fig. 6b, the maximum color reduction of 86% was yielded at 2.0 mM H_2O_2 solution. Further increase of H_2O_2 concentration up to 3 mM had no effect on the discoloration.

The synthetic wastewater solution is hypersaline and contains 71 g of NaCl in 1 L. This low discoloration may be due to the complex formation between Fe^{2+} and Fe^{3+} in the presence of Cl^- ions in wastewater and also Cl^- ions act as scavengers of OH radicals as shown in Eqs. (5)–(7) [44]. Due to these two reasons, the amount of the available OH radicals decreases and hence reduces the color reduction of RB 5 synthetic wastewater.

$$HO^{\bullet} + Cl^{-} \leftrightarrow HOCl^{\bullet -} \quad (5)$$

$$HOCl^{\bullet -} + H^{+} \leftrightarrow H_2O + Cl^{\bullet} \quad (6)$$

$$Cl^{\bullet} + Cl^{-} \rightarrow Cl_2^{\bullet -} \quad (7)$$

3.4. Discolorization of RTW

Most of the colorful pollutants present in the textile wastewater come from the dyeing step. Usually, dye bath wastewater is directly drained to the sewage tank which contains a large amount of wastewater received from other various operations of the production and finishing steps. Discoloration of the dye present in wastewater is the most challenging step and works with a huge amount of wastewater present in the sewage tanks makes the treatment process more complex and expensive. If the colorful dye bath wastewater can be decolorized before sending it to the sewage tanks, that would dramatically reduce the treatment cost making it simpler for treatment. Therefore real dye bath wastewater containing RB 5 dye released by a textile industry was collected for the discoloration studies. UV-Visible spectra of pure RB 5 and the dye bath wastewater showed a peak at 595 nm confirming the presence of RB 5 in dye bath waste. COD and pH of the untreated wastewater were measured as 787 ppm and 9.24 respectively. The coagulation and the Fenton oxidation techniques were performed for the real dye bath wastewater collected.

3.4.1. Coagulation studies on real wastewater

The coagulation studies were carried out with 100 mL of 10 times diluted real textile dye bath wastewater at pH = 9 and 30°C. The coagulant dosages of the three coagulants, alum, PAC, and $FeSO_4 \cdot 7H_2O$ were changed from 100 to 500 ppm and the samples were centrifuged before analysis. The percent color and COD reductions are shown in Figs. 7a and b for the three coagulants. In contrast to the observation made for the synthetic RB 5 wastewater, the $FeSO_4$ coagulant showed a good color reduction at the lower dosage and it decolorized 65% of the RB 5 at 200 ppm dose. Alum was the least efficient up to 300 ppm dosage which showed only the reduction of 17% dye present in the wastewater. All three coagulants showed around 80% color reduction at 400 ppm coagulant dosages. Further increase of alum and PAC doses up to 500 ppm increased the color reduction to 92% while the increase of $FeSO_4$ coagulant dose reduced the color reduction to 64%. The reduction of COD by the three coagulants showed the same variation as the color reduction. Again, alum was the least efficient in COD reduction at 300 ppm dose counting about to a 29%. PAC and $FeSO_4$ coagulants reduced COD by 69% and 71% at 300 ppm dose, respectively. At 400 ppm coagulant dose, alum, $FeSO_4$, and PAC coagulants reduced 66%, 75%, and 84% of COD, respectively. Based on the color and the COD reduction performance, it can be concluded that the PAC coagulant at the 400 ppm dosage is the most effective coagulation conditions to treat the real textile dye bath wastewater containing reactive dye.

3.4.2. Fenton studies of real wastewater

In the Fenton studies, the dye bath wastewater samples were diluted 10 times before they were used in the experiments. The procedures similar to sections 3.2 and 3.3.2 were adopted to determine the optimum conditions at pH of 3 and 30°C. A series of mixtures with H_2O_2 concentrations from 0.25 to 2.0 mM keeping the Fe^{2+} concentration constant at 0.5 mM were prepared to determine the optimum H_2O_2 concentration. The optimum Fe^{2+} concentration was determined by preparing a series of mixtures with the Fe^{2+} concentrations from 0.01 to 0.5 mM keeping the H_2O_2 concentration constant at 0.5 mM. The percent color reductions at different H_2O_2 and Fe^{2+} concentrations are shown in Fig. 8.

From Fig. 8a it can be seen that the discoloration efficiency increased with the H_2O_2 concentration and reached an optimum at 1.0 mM H_2O_2 dose with 96% discoloration of dye at 0.5 mM Fe^{2+} concentration. In Fig. 8b, the five times increase of the Fe^{2+} dose from 0.01 to 0.05 mM increased the color reduction from 31% to 85% and the effect of Fe^{2+} concentration on the color reduction reached an optimum value at 0.1 mM with the percentage color reduction of 91%.

In a previous study maximum COD and color removal of 51.2% and 52.3% were achieved respectively when H_2O_2:Fe^{2+} molar ration of 8:1 after 120 min of reaction time [45]. Another study reported the best discoloration percentage of 95% when the H_2O_2:Fe^{2+} molar ration of 36:1 after 60 min reaction time [46]. As revealed by Fig. 8 in the present study, more than 80% color reduction was observed when Fe^{2+}:H_2O_2 molar ratio of 1:10 after 60 min reaction time. All these studies used RTWs having different characteristics and the optimization of the reaction conditions are required to limit the excessive usage of Fe^{2+} and H_2O_2 during the treatment process. For all three types of RB 5 wastewaters treated in the current study by the Fenton method, this optimum 1:10 ratio between Fe^{2+} and H_2O_2 concentrations could be observed.

4. Conclusions

Two physicochemical wastewater treatment techniques were studied namely the coagulation and the Fenton oxidation to treat textile wastewater. Three commonly used coagulants, alum, PAC, and $FeSO_4$ were used to decolorize the

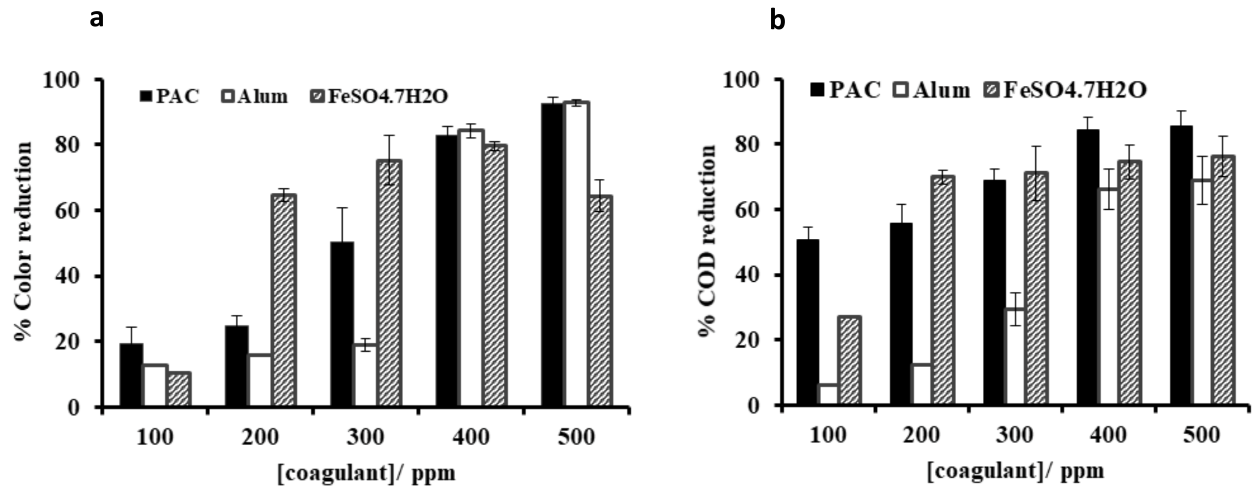

Fig. 7. (a) Color and (b) COD reduction of real textile wastewater by different coagulants at pH = 9, temperature = 30°C.

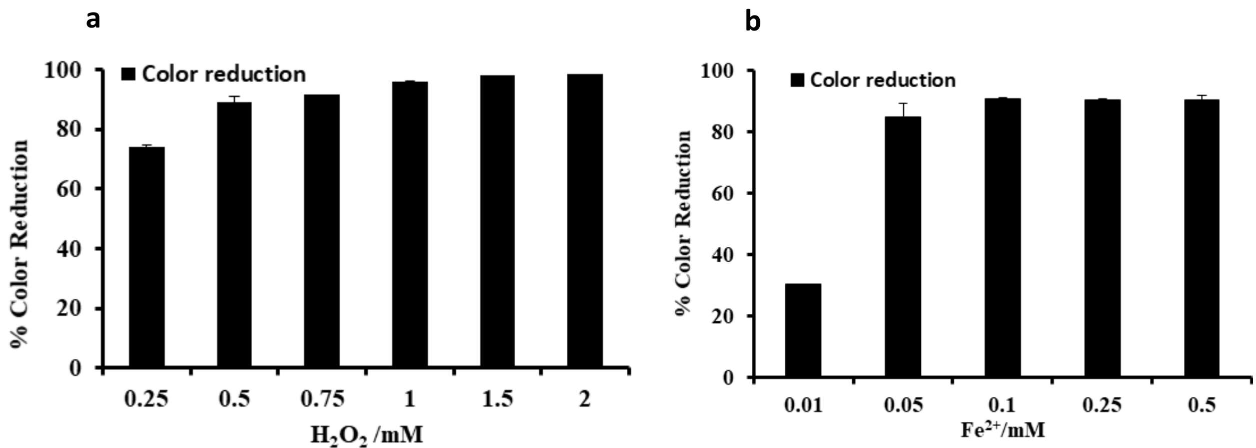

Fig. 8. Percentage color reduction of the real textile water (RTW) at different: (a) H_2O_2 and (b) Fe^{2+} concentrations at pH = 3, T = 30°C.

RB 5 dye solution, STW containing RB 5 dye, and the real textile dye bath wastewater. Among these coagulants, only PAC reduced the color and the COD of the RB 5 solution. PAC decolorized more than 98% of RB 5 dye at a dosage of 200 ppm and pH = 5, while the most common coagulants, alum, and $FeSO_4$ removed only 11% and 6% of RB 5 dye present in RB 5 solutions. The color reduction of RB 5 dye by all three coagulants was not significantly different within the pH range of 5–9. All three coagulants failed to decolorize the hypersaline STW containing RB 5 dye. The Fenton oxidation successfully decolorized 87% of hypersaline STW at pH 3. All three coagulants successfully decolorized real dye bath wastewater and showed around 80% color reduction at 400 coagulant dosages. The Fenton oxidation with 0.5 mM H_2O_2 and 0.05 mM Fe^{2+} decomposed more than 80% of real dye bath wastewater. According to the results of the current study, the Fenton oxidation can be successfully used to decolorize highly saline dye bath wastewater containing RB 5 dye.

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