

Decolorization of Reactive Dyes from Aqueous Solution Using Combined Coagulation-Flocculation and Photochemical Oxidation (UV/H₂O₂)

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Abstract: Removal of reactive dyes from wastewater is a great environmental concern. Attempts were made to study the performance of a coupling process of coagulation-flocculation (CF) and photochemical oxidation (PCO) for the removal of two reactive dyes (Reactive Black 5 (RB 5) and Reactive Orange 12 (RO 12)) from aqueous solution. The CF experiments were conducted using alum as coagulant and polyacrylamide as coagulant aid whereas the PCO tests were carried out using H₂O₂ in the presence of UV light irradiation. Effects of various process parameters such as pH, coagulant dose and coagulant aid dose on the CF process, and H₂O₂ dose and UV exposure time on the PCO method have been studied. The study reveals that only the CF process is not sufficient to treat the dye solution. The CF step could remove 52.30% and 41.38% of RB 5 and RO 12, respectively. At the best conditions of process parameters, the combined CF-PCO method results in color removals of 87.10% and 82.53% for RB 5 and RO 12, respectively. The combined process of CF and UV/H₂O₂ may be a useful treatment technique for wastewater contaminated with reactive dyes.

Keywords: reactive dye, combined process, coagulation-flocculation, UV/H₂O₂

1. Introduction

Dyes are widely used in textile industries to color their products. The textile industries consume a large volume of water and produce a huge amount of wastewater during all phases of textile production and finishing ^[1]. The dye effluents generated from these industries may pose a serious problem to the environment as most dyes are synthetic compounds with complex aromatic molecular structures, which make them resistant to light, heat and oxidizing agents, non-biodegradable, and toxic to life with carcinogenic and mutagenic effects ^[2-5].

Among different types of dyes used in textile industries, 60-70% are azo compounds. Reactive dyes, one of the prominent and most widely used types of azo dyes, are characterized by a fiber-reactive component bonded to an appropriate azo, anthraquinone, phthalocyanine or metal complex dye ^[6]. These dyes are highly soluble in water and also have low levels of fixing to fibers. About 50% of the reactive dyes are lost through hydrolysis during the dyeing process and a large quantity of the dyes appears in wastewater. Moreover, these dyes are considered to be the most problematic compared to other forms of dyes, as they tend to pass through conventional treatment systems unaffected ^[7-9]. Consequently, the treatment of wastewater containing reactive dyes is a practical environmental challenge, and there is a constant need to develop an effective method that can efficiently remove these ecotoxic dyes.

Many attempts have been made for the removal of reactive dyes in wastewater using conventional treatment methods such as biological treatment ^[10], adsorption ^[11,12], membrane filtration ^[13], chemical coagulation ^[14] and advanced oxidation. Despite several advantages, there are some disadvantages and limitations for various dye treatment methods, and up to now there is no single and cost-effectively attractive method that can efficiently decolorize the dye effluent ^[11,15,16]. Through the biological treatment method, the removal of reactive dyes is difficult due to low biodegradability and/or low level of absorption of the dye onto activated sludge during treatment. The other limitations of this method are the longer duration of treatment, toxicity of dyes, large operational area, post-treatment of sludge, and requirement of specific bioreactors ^[17]. The color removal through the adsorption method is based on the affinity of dyes towards the adsorbents. Various adsorbents such as activated carbon ^[18], carbon microspheres ^[19], sulfur-doped carbon sphere ^[20], Fe₃O₄@SiO₂@NH₂

nanocomposite [21], sawdust [22], Pará chestnut husk [23], zeolite [24], Silica [25], and alginate-montmorillonite-polyaniline [26] have been studied for the adsorption of dyes and other organic pollutants from wastewater. However, the most commonly used adsorbent is activated carbon but it is expensive and neither the regeneration nor the disposal of used adsorbent is straightforward [27,28]. Polymeric membranes or nanoparticles/polymer composite membranes have been used for the removal of dyes from colored wastewater [13,29-32]. The basic problem involved in any membrane-based process is the decline in flux and the fouling of the membrane surface [6]. The coagulation-flocculation (CF) method for dye removal usually consists of destabilization of the colloids by coagulation-flocculation followed by phase separation of dye-loaded sludge through sedimentation [33-35]. This method is relatively cheap [27, 36] and effectively decolorizes insoluble dyes (such as disperse dyes), but does not work well for soluble reactive dyes [37-39]. Chemical oxidation with ozone, and photochemical oxidation with a combination of UV radiation, ozone or H₂O₂ are promising methods based on the generation of reactive free hydroxyl radicals that react with organic pollutants to form carbon dioxide, water, and other oxidation products during the oxidative degradation. These methods are suitable to deal with highly toxic and low biodegradable wastes, but their costs are very high for effluent treatment [37, 40].

The combined treatment techniques can be applied in a complementary manner, in such a way as to compensate for deficiencies of the single processes when used independently. To reduce the load on the costly photochemical oxidation (PCO) method, CF can be used as a pretreatment step with subsequent PCO using UV/H₂O₂. To overcome the disadvantages of individual processes, some other combined processes such as membrane bioreactor (MBR [41], MBR coupled with reverse osmosis [42], electrocoagulation coupled with adsorption [43], ozonation coupled with electrocoagulation [44], hydrodynamic cavitation or acoustic cavitation combined with chemical oxidation [45], nanofiltration coupled with electrolytic oxidation [46], CF followed by nanofiltration [6], ultrasonication coupled with microbial removal [47], CF combined with electrocoagulation [48], CF coupled with adsorption [49], and chemical oxidation followed by adsorption and microbial techniques [50] have been studied over past few years. So far, there is only a little information on the combined treatment process of CF and UV/H₂O₂ for the removal of reactive dyes.

The objective of the present work was to study the performance of the CF process in combination with the PCO (UV/ H₂O₂) method for the removal of reactive dyes from aqueous solution. Alum and polyacrylamide were used as coagulant and coagulant aid, respectively while hydrogen peroxide was used as the oxidant. The most effective operational conditions for CF and PCO methods were determined.

2. Materials and methods

2.1 Materials

The experiments were performed using two commercially available reactive dyes namely, Reactive Black 5 (RB 5) and Reactive Orange 12 (RO 12), collected from a local textile industry, Bangladesh. The structures, molecular weight and wavelength of maximum absorbance (λ_{max}) of the dyes are shown in Table 1. Polyacrylamide was obtained from Chemitec Properties Ltd., Bangladesh. Alum [Al₂(SO₄)³.18 H₂O], hydrochloric acid (HCl), sodium hydroxide (NaOH) and hydrogen peroxide (H₂O₂) (30% w/w) were purchased from MERCK, Germany.

Table 1. The general characteristics of RB 5 and RO 12 [6,51,52]

Dye	Structure	Molecular weight (g/mol)	λ_{max} (nm)
RB 5		991.82	598
RO 12		739.98	416

Separate stock solutions of the two dyes were prepared by dissolving 1000 mg of respective dye (RB 5 or RO 12) in 1 L distilled water. The experimental ‘fresh dye solutions’ were prepared by diluting stock solutions to the desired concentrations. The pH of 100 mg/L fresh dye (RB 5 or RO 12) solution was recorded as 5.5. For adjusting the pH of dye solution to the required value, sodium hydroxide (NaOH) 0.1M or hydrochloric acid (HCl) 0.1M was used.

Dye concentration in aqueous solution was evaluated using a UV spectrophotometer (UV-1601, Shimadzu, Japan) at λ_{max} (i.e., 598 nm and 416 nm for RB 5 and RO 12, respectively). A pH meter (HI8014, HANNA Instruments, Singapore) was used for measuring the pH and a Jar Test apparatus was used to conduct the CF process. A UV lamp (100 watt) was used as the UV irradiation source.

2.2 Coagulation-flocculation method

To explore the best operational conditions of process parameters (dose of coagulant and coagulant aid, and pH) for the CF method, experiments were conducted in a jar test apparatus containing six jars. Each jar was filled with 1 L of fresh dye solution (initial dye concentration, $C_0 = 100$ mg/L) and necessary doses of coagulant (alum) and coagulant aid (polyacrylamide) were added. Just after the addition of coagulant and coagulant aid, the solution was mixed rapidly (300 rpm) for 3 min to disperse the chemicals followed by slow mixing (60 rpm) for 30 min to aid floc formation. Then stirring was stopped and flocs were allowed to settle down for 70 min. The remaining dye concentration (C) of the supernatant was measured at the end of the sedimentation period. The experimental conditions for the CF process were selected based on previous studies and primarily study. During the study of the influence of pH on the CF process, the initial dye solution was adjusted to the pH in the range of 2-9 before being subjected to the jar test. The dye removal efficiency was defined as C/C_0 , where C_0 was the initial concentration of dye, and C was the remaining concentration dye in the solution.

2.3 Photochemical Oxidation (UV/ H_2O_2) studies

The residual dye solution concentrations were 47.70 mg/L (pH 6.3) and 58.62 mg/L (pH 5.9) for RB 5 and RO 12, respectively at the end of CF step conducted at the best operational conditions of process parameters (e.g., initial dye solution pH, and doses of coagulant and coagulant aid). The effluent dye solution obtained from the CF process was the raw solution for the second step of the coupled process, i.e. PCO (UV/ H_2O_2). Figure 1 shows the outline of coupling of the CF process with the PCO step.

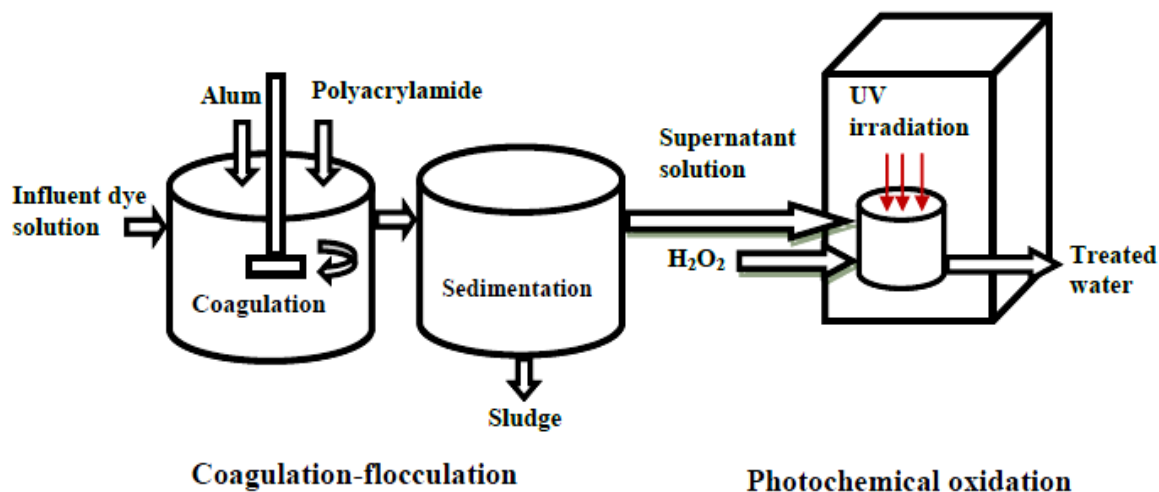


Figure 1. Coupling of coagulation-flocculation and photochemical oxidation methods for the removal of reactive dyes

The PCO tests were performed in a batch photoreactor system. The reactor consists of a beaker placed in a rectangular box and a UV lamp (100 watt) was hanged at 10 cm apart on the overhead of the beaker. The penetration of UV light to the outside was prevented using a loose and removable reflective aluminum foil around the reactor.

In each experimental run, 250 mL of dye solution was taken into the beaker and a certain dose of H_2O_2 was added into the solution followed by UV lamp irradiation (at 254 nm) from the top of the reactor. After a certain period, the remaining concentration (C) of the dye solution was measured. To determine the most effective dose of H_2O_2 for color removal, the PCO process was first analyzed with different doses of H_2O_2 at a constant UV irradiation time of 60 min. Then the PCO tests were carried out at the best dose of H_2O_2 varying the UV irradiation time. In this case, 5 mL of the sample was withdrawn from the beaker at a regular time interval of 10 min and after analyzing the dye concentration, the solution was returned into the beaker.

The overall system efficiency of the combined process was evaluated from the difference in dye concentration between the influent of the CF process and the effluent of the PCO process.

3. Results and discussion

3.1 Coagulation-flocculation method for dye removal

3.1.1 Effect of dose of coagulant and coagulant aid on dye removal

An insufficient dose or overdosing of coagulant and coagulant aid would result in poor performance in the CF process. It is crucial to determine the most favorable dose to minimize the dosing cost and obtain the best performance in the treatment.

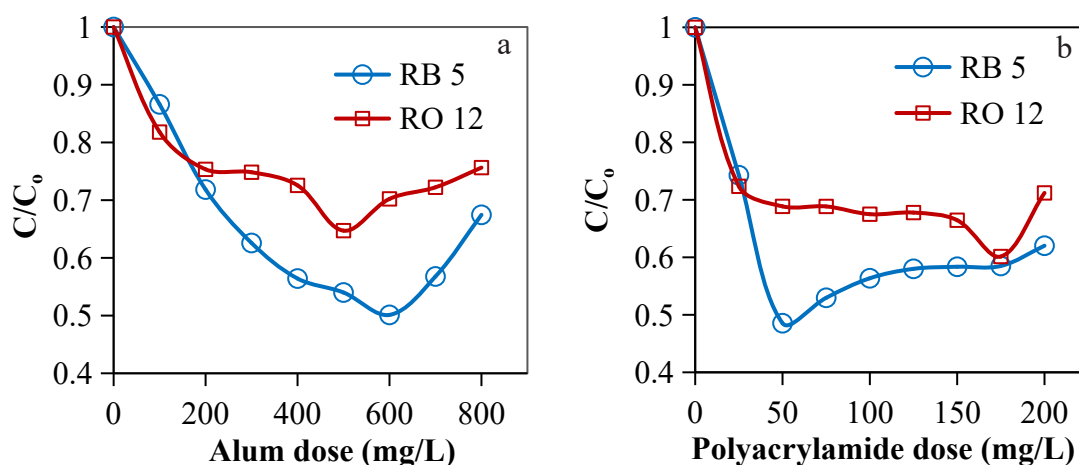


Figure 2. Effect of (a) alum dose (at polyacrylamide dose of 150 mg/L) and (b) polyacrylamide dose (at alum doses of 600 mg/L and 500 mg/L for RB 5 and RO 12, respectively) on the removal of dyes in CF process

The CF tests were first conducted at pH 5.5 (natural pH of dye solution), initial dye solution concentration (C_0) of 100 mg/L and an arbitrary dose of coagulant aid (150 mg/L), varying the dose of coagulant from 100 mg/L to 800 mg/L. Figure 2a shows the removal efficiencies of RB 5 and RO 12 as a function of coagulant (alum) concentration at a constant dose of polyacrylamide (150 mg/L). As shown in Figure 2a, the dye removal performance increased up to a certain dose of coagulant and after that the performance decreased. At the fixed-dose of polyacrylamide (150 mg/L), the maximum dye removal of 49.88% and 35.28% were achieved respectively at the coagulant doses of 600 mg/L and 500 mg/L for RB 5 and RO 12, respectively. The difference in maximum removal performance may also arise from the different molecular masses and chemical structures of two reactive dyes. As shown in Table 1, RB 5 has a higher molecular mass compared to RO 12. Moreover the RB 5 dye has four sulfonic acid groups whereas the RO 12 dye contains three of these groups. When alum is dissolved in water, the formation of cations occurs which combine with dye anions to form an insoluble complex. Consequently the dye removal using the CF process was more efficient for RB 5 which settles easier than RO 12.

To explore the most effective dose of coagulant aid for color removal, CF experiments were carried out at pH 5.5, the initial dye concentration of 100 mg/L, and the alum dose of 600 mg/L and 500 mg/L for RB 5 and RO 12, respectively, varying the dose of polyacrylamide from 25 mg/L to 200 mg/L. The dye removal efficiency as a function of different doses of polyacrylamide is shown in Figure 2b. It was noticed from the findings that the removal of dyes increased for the coagulant aid dose up to a certain dose. As shown in Figure 2b, the most effective doses of coagulant aid for color removal were 50 mg/L and 175 mg/L for RB 5 and RO 12, respectively. One of the largest uses of polyacrylamide is to flocculate solids in a liquid. Trivalent metal salt like aluminum sulfate is bridged by the long polymer chains of polyacrylamide. This polymeric coagulant aid causes the formation of flocks more quickly and increases the rate of sedimentation by bridging and connecting the already-formed flocks. Further, with that network formed during sedimentation, this coagulant aid takes other tiny particles, which couldn't form flocks inside them and make them sediment along with themselves^[53].

To check the coagulation-flocculation behavior at the most effective dose of coagulant aid, new tests were carried out at the polyacrylamide doses of 50 mg/L and 175 mg/L for RB and RO 12, respectively. The dose of alum was varied from 100 mg/L to 1000 mg/L while the initial dye concentration and pH were kept constant at 100 mg/L and 5.5, respectively.

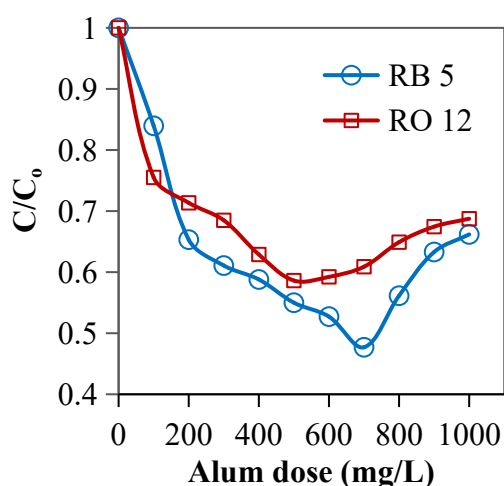


Figure 3. Effect of alum dose on the removal of dyes in the CF process at the most effective dose of polyacrylamide (50 mg/L for RB 5 and 175 mg/L for RO 12)

Figure 3 shows the removal of dyes as a function of coagulant concentration in the CF process carried out at the most effective dose of coagulant aid. It was found that removal of dye initially increased with the increase of alum dose up to a certain limit and then dye removal decreased with the application of higher doses of alum. The best performance in terms of color removal (52.30% and 41.38% for RB 5 and RO 12, respectively) was achieved at the coagulant dose of 700 mg/L and 500 mg/L for RB 5 and RO 12, respectively. The remaining concentrations of RB 5 and RO 12 were 47.70 mg/L (final solution pH 6.3) and 58.62 mg/L (final solution pH 5.9), respectively. Daud et al. ^[54] reported that waste removal increased with an increase in coagulant dose until it reached an optimum value, then the removal started to decrease. This could be attributed to the restabilization of colloidal particulates when coagulants were used at doses above the optimum value.

3.1.2 Effect pH on dye removal in the coagulation-flocculation process

Figure 4 shows the effect of initial dye solution pH (2 to 9) on the dye removal in the CF process. The conditions used were: initial dye concentration of 100 mg/L; dose of alum of 700 mg/L for RB 5 and 500 mg/L for RO 12 and dose of polyacrylamide of 50 mg/L for RB 5 and 175 mg/L for RO 12. The CF process was strongly influenced by the pH of initial dye solution. For both dyes, the best performance was achieved at the natural pH (5.5) of dye solution and the dye removals at this pH were 52.30% and 41.38% for RB 5 and RO 12, respectively. When alum is added to the aqueous solution, there is an interrelation between pH and the type of aluminum hydroxide formed. This in turn determines the charge on the hydrous oxide complex. At pH 5.5, positively charged $\text{Al}(\text{OH})^{2+}$ and $\text{Al}(\text{OH})^{2+}$, and insoluble $\text{Al}(\text{OH})_3$ species prevailed. The dye removal could be explained by the fact that at the optimum pH, dye particles retain net negative charges which enhance the performance of cationic coagulant. The anionic charges on RB 5 and RO 12 dyes in aqueous solution are neutralized by positively charged species of aluminum while insoluble aluminum species favor coagulation by sweep precipitation ^[49]. Apart from a narrow pH region approximately 5-6, the dominant soluble species are Al^{3+} and $\text{Al}(\text{OH})^{4-}$ at low and high pH, respectively ^[55]. It is also observed from Figure 4 that decolorization is very poor at low and high pH where soluble species of aluminum ions become predominant ^[48].

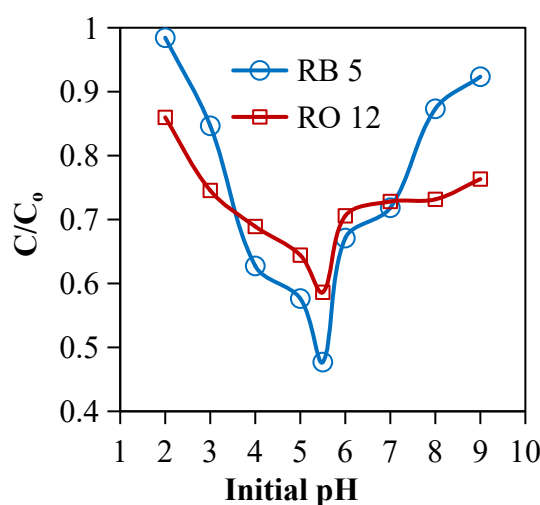


Figure 4. Effect of initial dye solution pH on the removal of dyes in the CF process

The best operational conditions of different parameters (coagulant dose, coagulant aid dose and pH) for the CF process and the corresponding dye removal percentages were presented in Table 2. As shown in Table 2, the maximum percentage removals by the CF method were 52.30% and 41.38% for the dyes RB 5 and RO 12, respectively.

Table 2. The best conditions for coagulation-flocculation process and the corresponding dye removal performance

Dye	Alum dose (mg/L)	Polyacrylamide dose (mg/L)	Polyacrylamide dose (mg/L)	Removal (%)
RB 5	700	50	5.5	52.30
RO 12	500	175	5.5	41.38

Selcuk^[56] reported 60% color removal from real textile water at 1500 mg/L and 5 mg/L aluminum sulfate and anionic polyelectrolyte, respectively. About 48% removal of trihalomethane was achieved at the alum coagulant dose of 100 mg/L^[57]. Wong et al.^[58] achieved 78% decolorization of CibacronYellow FN-2R reactive dye solution ($C_0 = 1000$ mg/L) at the alum dose of 6000 mg/L. Mohamed et al.^[59] reported 49% color removal from mixed reactive dye solution ($C_0 = 12424$, pH = 5) at the alum dose of 3000 mg/L. About 23% removal of color from real textile water was obtained at the alum dose of 400 mg/L^[60]. Kim et al.^[38] reported that the maximum dye removal percentages for reactive blue 49 and reactive yellow 84 dyes were 60.9% and 71.3%, respectively, at coagulant concentrations of 2.78 and 1.85 mM ferric chloride.

3.2 Photochemical Oxidation (PCO) of dyes using H_2O_2 and UV irradiation

In this case, the CF step was first carried out at the best conditions of process parameters and the conditions used were: initial dye concentration of 100 mg/L; initial dye solution pH value of 5.5; dose of alum of 700 and 500 mg/L for RB 5 and RO 12, respectively; and dose of polyacrylamide of 50 and 175 mg/L for RB 5 and RO 12, respectively. The residual dye solutions (with concentrations of 47.70 mg/L (pH 6.3) for RB 5 and 58.62 mg/L (pH 5.9) for RO 12) obtained from the CF processes were the raw solutions for the second step of the coupling process, i.e. PCO (UV/ H_2O_2). The CF treated dye solutions were treated with different doses of H_2O_2 (20-124 mL/L) under UV irradiation for 60 minutes and the dye removal efficiency as a function of H_2O_2 dose was represented in Figure 5a. As shown in Figure 5a, the best doses of H_2O_2 for color removal were 60 mL/L and 100 mL/L for RB 5 and RO 12, respectively.

The PCO process using UV/ H_2O_2 is based on the generation of highly reactive oxidants, primarily hydroxyl radical ($\bullet OH$). This radical is the second most powerful oxidizing agent (after fluorine) with a redox potential of $E^\circ (\bullet OH/H_2O) = 2.8$ V/SHE and can non-selectively react with most organics and inorganics via hydroxylation or dehydrogenation^[61, 62]. Hydrogen peroxide (oxidation potential ~ 1.78 V) alone is ineffective in the treatment of textile wastewater at both alkaline and acidic pH. Under UV irradiation, hydroxyl radicals ($\bullet OH$) are produced by the decomposition of H_2O_2 as shown in Eq.(1)^[63, 64].



Hydrogen peroxide (H_2O_2) itself acts as an effective hydroxyl radical ($\bullet OH$) scavenger as shown in Eq.(2) and Eq.(3)^[36, 65].



Although HO_2^\bullet promotes radical chain reactions and it is an oxidant itself, its oxidation potential is much lower than that of hydroxyl radical ($\bullet\text{OH}$). Further, it is also reported that light energy delivered to the target site promotes the photosensitizer to an electronically excited state from which a number of reactive oxygen species, including singlet oxygen, are generated via electron or energy transfer processes^[66]. The generated oxidizing agents ($\bullet\text{OH}$, HO_2^\bullet , $\text{O}_2^{\bullet-}$...) oxidize the organic dye molecules leading to intermediate compounds. Finally, complete mineralization is achieved through the further breakdown of these intermediates by the oxidizing agents^[63]. Therefore, it is assumed that the cumulative generation of oxidizing species from photo-excited H_2O_2 during photochemical oxidation was the prime cause of decolorization of tested dye solutions. It is also apparent from Figure 5a that the removal of dye increased with the increase in the dose of H_2O_2 up to a certain value. This enhancement in color removal by the addition of H_2O_2 is due to enhance of hydroxyl radical formation. Hydrogen peroxide, at low doses, cannot generate enough hydroxyl radical and the treatment will be limited reasonably^[67]. The addition of more H_2O_2 above the best amount reduced the dye removal performance. This may be because an increase of H_2O_2 dose beyond the best dose causes the formation of low active hydroxyl radicals (HO_2^\bullet), and reduces the efficiency of the oxidation process^[36]. This phenomenon was also reported in the literature and was referred to as a scavenging effect^[63].

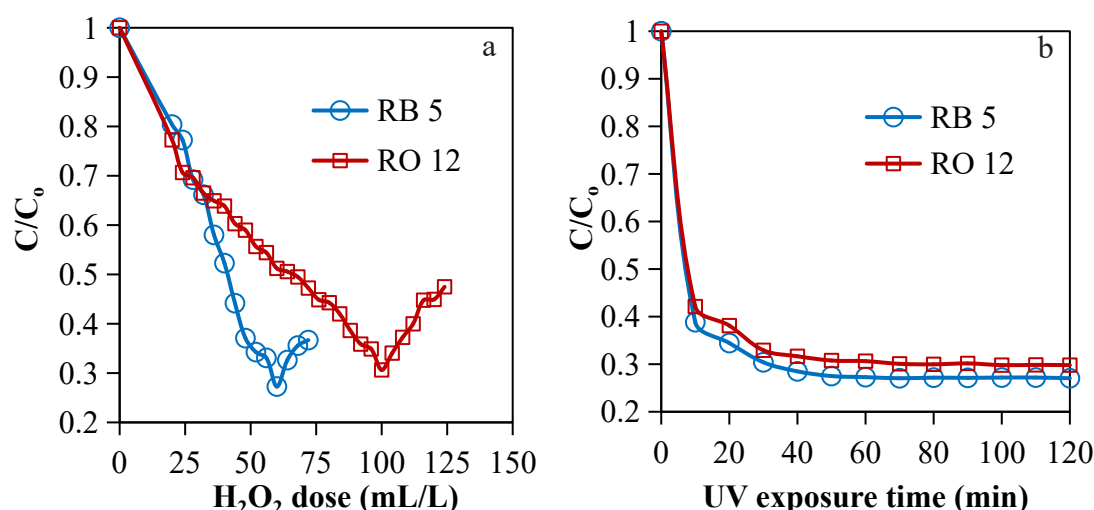


Figure 5. Effects of (a) dose of H_2O_2 and (b) UV exposure time (10-120) on the removal of dyes in case of CF treated dye solution

Further, the effect of the UV exposure time (10-120 min) on dye removal was also checked at the best doses of H_2O_2 (i.e., 60 mL/L and 100 mL/L for RB 5 and RO 12, respectively) and the obtained result was presented in Figure 5b. It was found that there was no appreciable change in the dye removal performance after 60 min of UV irradiation. After 120 min of UV/ H_2O_2 treatment, the remaining dye solution concentrations were 12.9 mg/L and 17.47 mg/L for RB 5 and RO 12, respectively. The dye removal percentages by this step were found to be 72.95% and 70.19% for RB 5 and RO 12, respectively. Mousavi et al.^[68] achieved 38% removal of Rhodamine B dye ($C_0 = 100$ mg/L) by UV/ H_2O_2 method at the UV irradiation time of 80 minutes and H_2O_2 concentration of 100 (mg/L).

4. Overall dye removal efficiency using combined CF and PCO (UV/ H_2O_2) methods

The overall removal percentages achieved by the combined CF and PCO treatment system were 87.10 % and 82.53 % for RB 5 and RO 12, respectively. Almost similar results were observed from some other combined treatment techniques for reactive dye removal from water. Furlan et al.^[69] employed a combined treatment process consisting of CF and adsorption that allowed average color removals of 90% and 84%, for the dyes RB 5 and reactive Orange 16, respectively. Riera-Torres et al.^[6] used the CF process in combination with the nanofiltration technique and observed that the combined process could remove 90% of RB 5 dye from aqueous solution. Harrelkas et al.^[70] studied CF coupled with membrane

processes or adsorption for the treatment of reactive dye-containing wastewater and showed that the performances of CF/microfiltration, CF/ultrafiltration and CF/adsorption combinations in terms of color removal were 65%, 74%, and 50%, respectively.

As reported by Yonar^[36], the UV/H₂O₂ method is less expensive compared to some other advanced oxidation methods (such as UV/O₃, UV/O₃/H₂O₂, and ozonation), but is ~18-22 fold costlier than coagulation process. Despite the fact that the CF process is cheap, as observed in the present study this technique can remove only 52.30% and 41.38% of RB 5 and RO 12, respectively. On the other hand, the UV/H₂O₂ method uses expensive reagent (H₂O₂) and consumes large amounts of electrical energy (UV). As the CF process is much cheaper and can remove a significant percentage of dye, the pretreatment of dye solution with this technique will reduce the consumption of costly reagent and electricity in the subsequent UV/H₂O₂ step. Therefore the combination of CF and UV/H₂O₂ methods could be economically/energetically a more viable choice for the treatment of reactive dye-containing wastewater.

5. Conclusions

In this study, the performance of CF and PCO (UV/H₂O₂) processes in terms of color removal from reactive dye-containing wastewater was investigated. Our experiments showed that decolorization efficiency was affected by the process parameters such as dye solution pH, coagulant and coagulant aid dose, hydrogen peroxide dose and UV exposure time. The best conditions of these parameters will contribute to minimizing the reactor size, reagent consumption and the costs associated with the treatment. The color removal percentage was different for the two dyes both in CF and PCO processes. We could not obtain complete color removal by a single process. The coupling of CF and PCO methods was more effective than the individual process. The best conditions for the combined treatment method yielded color removals of 87.10% and 82.53%, for the dyes RB 5 and RO 12, respectively. According to our observations, this combined process can be applied for the treatment of reactive dye-containing wastewater.

Acknowledgements

This work has been funded by the Department of Chemical Engineering and Polymer Science, Shahjalal University of Science and Technology, Bangladesh. We are thankful to Universiti Malaysia Pahang for collaboration in this project.

Conflicts of interest

The authors declare no conflicts of interest in this research.

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