Coagulation/flocculation of dye-containing solutions using polyaluminium chloride and alum

M. Hasani Zonoozi, M. R. Alavi Moghaddam and M. Arami

ABSTRACT

This study aims to compare the performance of Polyaluminium Chloride (PAC) and alum as coagulants to remove a specific type of dye (Acid Blue 292 (AB292)) from dye-containing solution. For this purpose, the influence of pH, coagulant dosage, coagulant aids (kaolinite and bentonite), and initial dye concentration on dye removal efficiency were examined. According to the results, removal of AB292 was absolutely dependent on the pH variations. The maximum dye removal occurred when pH was 7 and 5 for PAC and alum, respectively. Both coagulants efficiently removed the dye (about 85%) with a relatively low dosage (40 mg/l) in their optimum pH range. By adding kaolinite as a coagulant aid, the removal efficiencies tended to increase, especially for lower dosages of PAC and alum. With the increase of initial dye concentration, PAC and alum represented different behaviors. In the case of PAC, Q (the amount of the removed dye per unit mass of coagulant) increased at first and reached to a maximum value, 2.1 mg dye/mg PAC, and then decreased rapidly. While for alum, Q steadily increased with the increase of dye concentration and reached to 2.8 mg dye/mg alum. No reduction of Q occurred for alum with the increase of dye concentration in the range of 25–250 mg/l.

Key words | Alum, coagulation/flocculation, dye removal, polyaluminium chloride

INTRODUCTION

Dye compounds are some of the most important chemicals which are used in various industries such as textile, papermaking, printing, and plastics. Discharge of high colored wastes impedes light penetration, reduces dissolved oxygen and disturbs aquatic life. In addition, it has been found that some dyes are able to produce carcinogenic aromatic amines in the process of reductive degradation (Sponza & Isik 2005; Lee et al. 2006; Shi et al. 2007). On the other hand, without adequate treatment, these compounds are stable and can remain in the environment for an extended period of time (Dos Santos et al. 2007). Therefore they must be removed from wastewaters prior to discharge, in order to comply with the environmental protection laws for the receiving waters (Gao et al. 2007).

The widely used methods which effectively remove dyes and color materials are coagulation/flocculation, adsorption using activated carbon, membrane filtration and advanced chemical oxidation such as H₂O₂/UV and O₃. Each has its advantages and limitations in application. A common problem with most of them is their relatively high cost in large-scale utilization (Kim et al. 2004; Liu & Jiang 2005; Wen et al. 2005; Yuan et al. 2006).

Coagulation/flocculation is one of the most popular unit operations in water and wastewater treatment trains. Also it is one of the most effective chemical treatment methods for dye removal from industrial wastewaters (Golob et al. 2005; Gao et al. 2007). The main advantage of this method is removal of dye due to the removal of dye molecules from the effluents, and not due to a partial decomposition of dyes, which can lead to production of harmful and toxic aromatic compound (Golob et al. 2005). Moreover, this process can be used in large-scale operation.
with relatively high operability and cost effectiveness. A limitation of this technique is that some high-soluble, low molecular and cationic dyes might not be effectively removed. Another restriction associated with this technique is the disposal of sludge produced during the coagulation process (Golob et al. 2005; Gao et al. 2007; Shi et al. 2007).

The most common coagulants which have been used for water and wastewater treatment are aluminium and ferric-based salts, such as alum, ferric chloride and ferric sulfate. Recently, based on conventional iron and aluminium salts, inorganic polymer floculants (IPFs) have been developed rapidly and become applied widely, for treatment of water and wastewater. Among them, polyaluminium chloride (PAC) is one of the typical kinds and has become most widely applied (Wang et al. 2004; Ye et al. 2007).

The main objective of this study is to compare the performance of Polyaluminium Chloride and alum as coagulants to remove a specific type of dye (Acid Blue 292) which is used widely in textile industry in Iran. The study focuses on the effects of pH, coagulant dosage, coagulant aids (kaolinite and bentonite), and initial dye concentration on dye removal efficiency.

MATERIALS AND METHODS

Reagents and stock solutions

Experiments were performed at laboratory scale. Commercial grades of PAC (30% w/w Al₂O₃) and alum (17% w/w Al₂O₃) were used as coagulating agents. The dye used in this study—Acid Blue 292 (AB292, trade name: Erionyl Blue 5GL, provided by Ciba (Iran))—is a commercial dye and used widely in textile industry in Iran. The study focuses on the effects of pH, coagulant dosage, coagulant aids (kaolinite and bentonite), and initial dye concentration on dye removal efficiency.

Experimental apparatus and procedure

In this study, the effects of various parameters on dye removal efficiency were determined by a six beaker jar-test apparatus from Zag-Chemi Co. (Iran). Each beaker contained 250 ml of the dye solution. A period of 2 min was allowed for the rapid mixing of the dye containing solutions at 200 r/min followed by a 10 min period of slow mixing at 30 r/min. Then the solutions were allowed to settle for 45 min. After settling, samples for measurement of dye concentration were withdrawn using a pipette from a height of 2–3 cm below the surface in each jar. The maximum absorbance (λmax) of the dye with the background of deionized water was 632 nm, which was determined according to scanning pattern performed on Hach spectrophotometer DR/4000 (USA). During the experiments, λmax was used for all the absorbance readings. Percentage of dye removal was calculated by the following equation:

\[
\text{dye removal (\%)} = \frac{C_r - C_t}{C_r} \times 100
\]

where \(C_r\) and \(C_t\) are the dye concentration in raw and treated solutions, respectively.

pH measurement was carried out using a 340i/SET pH meter (WTW-Germany). Each series of the experiments were done separately for both coagulants (PAC and alum).

RESULTS AND DISCUSSION

Effect of pH on dye removal

pH is an important variable in dye removal studies. Coagulant chemicals have an optimum pH range in which good coagulation/flocculation occurs in the shortest time with a given dosage of coagulant. Trial and error testing is the only sure method to determine the most efficient pH range (Sanghi et al. 2006). To study the effect of pH on dye removal efficiency, the dosages of PAC and alum were kept constant at 100 mg/l, while varying pH of the samples using H₂SO₄ (0.1 N and 1 N) and NaOH (0.1 N and 1 N) solutions. Kaolinite and bentonite were sieved by 75 μm sieve and particles under 75 μm were used in further experiments.
dye removal efficiencies were obtained when pH was 7 for PAC and 5 for alum. Also, the pH range, in which the efficiency of the process was relatively high, was broader for PAC in compare with alum. This is probably due to the presence of preformed Al species in PAC, which are formed by partially neutralization. This feature is in consistent with the findings reported by Jiang (2001) and Ye et al. (2007). In the optimum pH ranges (6–8 for PAC and 5–7 for alum), larger flocs with more rapid settling velocity were formed. However, different optimum pH ranges for dye removal using PAC and alum have been reported by other researchers, which are compared with the results of the present study in Table 1.

**Effect of PAC and alum dosage on dye removal**

In this step, to study the effect of coagulant dosage on dye removal efficiency, different amounts of PAC and alum were dosed into the dye-containing solutions. Dye concentration was kept constant at 100 mg/l and pH was adjusted to 7 and 5 for PAC and alum, respectively. The variations of dye removal with coagulants dosage are presented in Figure 2.

The obtained results showed that with the increase of coagulant dosage, the removal efficiency increased for both of the coagulants. The curves exhibited similar changing trends: relatively slow increase at low dosages, then followed by a rapid increase with increase in dosage, and finally the increase became slow again and the curves approached plateau. When the coagulants dosage was 20 mg/l, removal efficiency was only about 20% for both coagulants. While, it dramatically increased to about 85% (for 40 mg/l of both coagulants), and then slowly increased to more than 96% at the coagulants dosage of 100 mg/l. Similar trend were reported by Shi et al. (2007), for removal of some dyes with PAC.

With the increase of dosage, no re-stabilization phenomenon or removal reduction was observed even at the dosage of 200 mg/l for both coagulants. This result is also similarly reported by Shi et al. (2007), concerning the application of PAC in removal of some dyes.

**Dye removal mechanism**

As the functional groups of acid dyes are anionic, they release negative charges when dissolve in water. So it seems that the main mechanism dealing with removal of these dyes from the solution is charge neutralization mechanism in which the hydrolysis products of the coagulant chemicals can neutralize the negative charges on dye molecules. On the other hand, in charge neutralization mechanism, with
the decrease of pH, dye protonation processes could lead to reduction of charge density and induce self-aggregation of dye molecules (Shi et al. 2007). Therefore, higher efficiencies are expected for lower pH conditions. While, in the case of AB292, the maximum efficiencies were obtained at pH of 7 for PAC and 5 for alum, and when pH was less than those values, the efficiencies declined for both coagulants (Figure 1). Furthermore, in charge neutralization

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**Table 1 | Optimum pH ranges reported for PAC and alum applied in dye removal**

<table>
<thead>
<tr>
<th>Coagulant</th>
<th>Dye—containing solutions</th>
<th>Optimum pH</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyaluminium chloride (PAC)</td>
<td>Reactive Red DB-8</td>
<td>3.5–5.5</td>
<td>Klimiuk et al. (1999)</td>
</tr>
<tr>
<td></td>
<td>Reactive Orange OGR</td>
<td>4.5–5.5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Reactive Black DN</td>
<td>4–5</td>
<td>Shi et al. (2007)</td>
</tr>
<tr>
<td></td>
<td>Direct Black 19</td>
<td>Less than 6.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Direct Red 28</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Direct Blue 86</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Direct Orange S</td>
<td>9–9.5</td>
<td>Sanghi et al. (2006)</td>
</tr>
<tr>
<td></td>
<td>Sandolan Red RSNI</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Procion Brilliant blue Rs</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Real wastewater including dye, food, electronic, and other manufacturing</td>
<td>6</td>
<td>Liu &amp; Liang (2004)</td>
</tr>
<tr>
<td></td>
<td>AB292</td>
<td>6–8</td>
<td>Present study</td>
</tr>
<tr>
<td>Alum</td>
<td>Acrylic water base color</td>
<td>10</td>
<td>Asilian et al. (2006)</td>
</tr>
<tr>
<td></td>
<td>Real wastewater including dye, food, electronic, and other manufacturing</td>
<td>6</td>
<td>Liu &amp; Liang (2004)</td>
</tr>
<tr>
<td></td>
<td>Textile finishing industry effluents</td>
<td>8.2</td>
<td>Nabi Bidhendi et al. (2007)</td>
</tr>
<tr>
<td></td>
<td>AB292</td>
<td>5–7</td>
<td>Present study</td>
</tr>
</tbody>
</table>

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**Figure 2 | Effect of the coagulant dosage on dye removal efficiency.**
mechanism there is a critical coagulant concentration at which the removal efficiency reaches a maximum and then with further increase of the coagulant dosage, re-stabilization of the suspension and removal reduction occurs. While, according to the results illustrated in section 3.2, no re-stabilization of the dye molecules was observed with the increase of the coagulants’ dosage.

Hence, it can be found that charge neutralization was not the only mechanism by which removal of the dye particles occurred. In other words, there are also other coagulation mechanism/mechanisms which enhance the dye removal efficiency in different conditions. These mechanism/mechanisms could be one or both of bridging mechanism and sweep Flocculation (Enmeshment in Precipitate). However, the bridging mechanism is more probably for PAC because of its polymeric properties.

Effect of kaolinite and bentonite as coagulant aids on dye removal

Coagulant aids such as activated silica, clay and poly-electrolytes are used in coagulation/flocculation process, usually to obtain higher efficiency, to reduce the amount of required coagulant, and to form stronger and more settle-able flocs (AWWA 2003). In this study, the effect of kaolinite and bentonite as coagulant aids were investigated. The experiments were conducted under two dosage levels of PAC and alum (30 mg/l and 40 mg/l), with different concentrations of the coagulant aids. The results are shown in Figures 3 and 4.

By adding kaolinite to the coagulation/flocculation process, the efficiencies tended to increase for both coagulants. With the aid of 40 mg/l of kaolinite, the dye removal efficiency increased from 35% to 66% for PAC and from 54% to 78% for alum, when the concentration of both coagulants was 30 mg/L (Figure 3). Bentonite had a negative effect on the coagulation/flocculation performance of both coagulants. By adding 40 mg/l of bentonite, the dye removal efficiency decreased by about 15% and 30% for PAC and alum, respectively (Figure 4). This can be explained by the difference in surface charge of kaolinite and bentonite, as it affects the coagulation behavior of colloidal and suspended particles. Bentonite particles have very large negative surface charge comparing with kaolinite particles (Zhang et al. 2002). Hence, by adding bentonite to the coagulation/flocculation process, the dye removal efficiencies decreased (Figure 4).

The data of other researchers regarding the effect of different coagulants and coagulant aids for dye removal are compared with our results in Table 2.
Effect of initial dye concentration on dye removal efficiency

In the last step of the study, experiments were performed to determine the influence of initial dye concentration on dye removal efficiency, using a constant coagulant dosage (60 mg/l for both coagulants). pH was adjusted to 7 and 5 for PAC and alum, respectively. The results are illustrated in Figure 5.

For PAC, as the initial dye concentration increased, dye removal efficiency decreased, so that the efficiency for dye concentrations of 25 and 250 mg/l was 95% and 21%, respectively. In the case of alum, at the first, the removal efficiency increased slightly with the increase of dye concentration from 25 mg/l to 50 mg/l. After that, the efficiency decreased slowly with the increase of dye concentration. Also it is considerable that the rate of the efficiency reduction versus dye concentration was more

![Graph showing the effect of bentonite on dye removal efficiency.](Figure 4)

Table 2 | Effect of different coagulants and coagulant aids on treatment performance of dye-containing solutions

<table>
<thead>
<tr>
<th>Coagulant</th>
<th>Coagulant aid</th>
<th>Effect</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alum</td>
<td>Polyelectrolyte</td>
<td>No positive effect on dye or COD removal</td>
<td>Nabi Bidhendi et al. (2007)</td>
</tr>
<tr>
<td>FeSO₄</td>
<td>Polyelectrolyte</td>
<td>Increase in turbidity and the volume of settled sludge, but for concentrations more than 2 mg/l it reduced TSS</td>
<td>Nabi Bidhendi et al. (2007)</td>
</tr>
<tr>
<td>MgCl₂</td>
<td>Polyelectrolyte</td>
<td>No positive effect on dye removal, but adding 1 mg/l, reduced TSS by 27%, and adding 3 mg/l, reduced the volume of settled sludge by 10%</td>
<td>Nabi Bidhendi et al. (2007)</td>
</tr>
<tr>
<td>FeCl₃</td>
<td>Polyelectrolyte</td>
<td>Increase in TSS, turbidity, and the volume of settled sludge</td>
<td>Nabi Bidhendi et al. (2007)</td>
</tr>
<tr>
<td>Alum</td>
<td>Synthetic Polymer</td>
<td>Increase in dye removal up to 60%, no significant effect on turbidity removal</td>
<td>Joo et al. (2007)</td>
</tr>
<tr>
<td>MgCl₂</td>
<td>CaOH₂</td>
<td>Increase in dye removal</td>
<td>Gao et al. (2007)</td>
</tr>
<tr>
<td>PAC</td>
<td>Kaolinite</td>
<td>Adding 40 mg/l, increased dye removal efficiency by 31%</td>
<td>Present study</td>
</tr>
<tr>
<td>Alum</td>
<td>Kaolinite</td>
<td>Adding 40 mg/l, increased dye removal efficiency by 24%</td>
<td>Present study</td>
</tr>
<tr>
<td>PAC</td>
<td>Bentonite</td>
<td>Adding 40 mg/l, reduced dye removal efficiency by 15%</td>
<td>Present study</td>
</tr>
<tr>
<td>Alum</td>
<td>Bentonite</td>
<td>Adding 40 mg/l, reduced dye removal efficiency by 30%</td>
<td>Present study</td>
</tr>
</tbody>
</table>
rapid for PAC compared with alum, especially for higher concentrations of dye (more than 150 mg/l).

In addition, the variations of the amount of the removed dye per unit mass of coagulant ($Q$), versus the initial dye concentration are presented in Figure 6. In the case of PAC, $Q$ increased at first and reached to its highest value, 2.1 mg dye/mg PAC, when the dye concentration was 150 mg/l, and then it decreased rapidly to 0.9 mg dye/mg PAC. While, in the case of alum, $Q$ increased steadily with the increase of dye concentration and reached to 2.8 mg dye/mg alum, so that no reduction of $Q$ occurred with the increase of dye concentration in the range of

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**Figure 5** | Effect of initial dye concentration on dye removal efficiency.

**Figure 6** | Effect of initial dye concentration on the amount of the removed dye per unit mass of coagulant ($Q$).
25–250 mg/l. It could be concluded that alum performed better than PAC when the initial concentration of the dye was high (more than 150 mg/l).

Little data was found in literature to compare the influence of dye concentration on coagulation efficiency. According to Klimiuk et al. (1999), at the optimum coagulant (polyaluminium chloride) dosages, the removal degree (the amount of the removed dye per unit mass of Al) was associated with the initial concentration of the selected dyes. Also, the smallest removal degree was obtained for smallest concentrations of the dyes (Klimiuk et al. 1999). This result is in consistent with the results obtained for PAC and alum in this study, which showed the smallest value of Q for dye concentrations of 25 and 50 mg/l.

**CONCLUSIONS**

In this study, the performance of PAC and alum was investigated for removal of AB292 under the effect of different parameters and conditions. The dye removal efficiency of both coagulants was severely influenced by pH variations. Also, the pH range, in which the efficiency of the process was relatively high, was broader for PAC in compare with alum. Both of the coagulants removed the dye efficiently, with a relatively low dosage. As the decrease of pH was not always beneficial for enhancing the dye removal, and also as no re-stabilization or removal reduction was observed for both coagulants, it was concluded that in addition of charge neutralization mechanism, sweep flocculation and bridging mechanisms were as well involved in removal of AB292 using PAC and alum. With the increase of initial dye concentration, PAC and alum represented different behaviors. In the case of PAC, Q (the amount of the removed dye per unit mass of coagulant) increased at first and reached to a peak value (2.1 mg dye/mg PAC), and then decreased rapidly. While, in the case of alum, Q increased steadily with the increase of dye concentration and reached to 2.8 mg dye/mg alum. No reduction of Q occurred for alum with the increase of dye concentration in the range of 25–250 mg/l. In other words, alum performed better when initial concentration of the dye was high.

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