Removal of Disperse Dye and Reactive Dye by Coagulation - Flocculation Method

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ABSTRACT

Two types of commercially used dyes, reactive dye Cibacron Yellow FN - 2R and disperse dye Terasil Blue BGE - 01 have been used to investigate the effectiveness of coagulation - flocculation process in the removal of colouring matters in wastewater. Aluminium sulfate (alum), polyaluminium chloride (PAC) and magnesium chloride ($MgCl_2$) were used as coagulant together with polyelectrolyte, Koaret PA 3230 as the coagulant aid. The coagulants' dosage between 100ppm to 5000 ppm has been studied. The initial concentration of the synthetic dye wastewater is 1.0 g/L. Jar test was conducted to determine the effects of solution pH, type and dosage of coagulant and the addition of coagulant aid on the percentage of removal of colouring matters in wastewater. The treated dye wastewater was determined in terms of percentage colour removal and the concentration of the dyes was determined through colour point. The results show that the percentage colour removal of reactive dye can achieve up to 90.40 % using alum of concentration 6000 ppm at a pH of 3.50. $MgCl_2$ of concentration 4000 ppm can achieve up to 99.58 % colour removal at a pH of 9.70 and for PAC of concentration 800 ppm, 100 % colour removal can be achieved in a pH range of 3.98 – 4.60. Up to 99.90 % of disperse dye can be removed with alum of concentration 200 ppm in a pH range of 4.00 - 4.50 and $MgCl_2$ of concentration 4000ppm at a pH of 9.81 respectively. With 200ppm PAC at a pH of 4.61 the percentage removal of disperse dye is 100 %. Furthermore, removal of dye mixture which contains 50% reactive dye and 50% disperse dye can reach 99.69 % using PAC of concentration 600ppm at a pH of 4.31 and 99.26 % using $MgCl_2$ of concentration 3000ppm at a pH of 10.27. By using alum of concentration 3000 ppm, 99.71% colour removal can be achieved at a pH of 4.00.

Keywords
Reactive dye, disperse dye, coagulation, flocculation, alum, PAC, $MgCl_2$.

INTRODUCTION

In recent years, the textile industries grow rapidly, particularly in Asia. Hence, the use of synthetic complex organic dyes as a colouring materials in dyeing and finishing processes which are integral parts of textile manufacturing process also show a significant increment (Talarposhti et al., 2001). The synthetic dyes can be classified as disperse dyes, reactive dyes, sulfur dyes, vat dyes, direct dyes, acid dyes, and basic dye. They are commonly used in the textile industries. Reactive dyes are now important in colouring cellulosic and wool fibres. During the colouration process, reactive dyes combine covalently with the fibres through nucleophilic displacement (Nunn, 1979). Disperse dyes are nonionic dyes and widely used for dyeing of synthetic fibres, such as cellulose acetate, polyamide, polyesters, polyacrylonitries, and etc (Sunthankar, 1962). The disperse dye which have low solubility in water can be treated as colloidal particles. This insoluble dyes, can be effectively decolorized by coagulation method (Kuo, 1992).

Reactive dyes are considered unique and a different class of dyes because of its low removal rate in textile wastewater treatment plants. Although there are some existing technologies that are more efficient in the removal of reactive dyes but their initial and operational costs make it not practical and economical to the textile industry (Morais et. al., 1999).

In dyeing and finishing processes in the textile industries, considerable amount of wastewater is generated and its composition varies in characteristics. The composition of textile industrial wastewater depends on technological operations, types of dyes and raw materials being used (Anielak, 1996a). In the textile industries, different types of dyes are used in a single day in dyeing process. Therefore, the wastewater generated also contains a mixture of different type of dyes in unknown and complexity in their chemical composition, which makes the textile waste effluents, is difficult to treat satisfactorily. When there is more than one dye in a solution, it can't be foreseen the result of the treatment of dyes. Being chemical substances dissociating in water, the dyes can react chemically between themselves and giving a new dye (Anielak, 1996b). The decolorization is affected by different type of dye structure (Kuo, 1992). Changes of the pH of wastewater due to dyes changes also make the wastewater difficult to treat as the pH tolerance of conventional biological and chemical treatment systems is very limited (Lin & Lin, 1993).

The wastewater treatment is a very important subject in pollution control because the dyestuffs are not only highly structured polymer that are difficult to decompose biologically, it also consists combination of strong colour and high dissolved solid contents which lead to high turbidity of waste effluent. The high turbidity of the waste effluent also seriously affects the photosynthetic activity of aquatic plants and causes disturbance to the ecological system (Lin & Lin 1993).

Major pollutants of textile industrial wastewater include high suspended solids (SS), chemical oxygen demand (COD), biochemical oxygen demand (BOD), heat, colour, acidity, basicity and other soluble substances (Kuo, 1992). All pollutants except colour can be reduced effectively by general chemical and physical methods. Therefore, the main problem of textile industries wastewater is the colour which is produced by the residual dyes during the dyeing and finishing processes. Futhermore, the chemical structure of synthetic organic pigments in dyes makes them resistant to breakdown. Colour removal of textile effluents has been giving great attention recently because of its toxicity and visibility (Morais, et al., 1999).

Various wastewater treatment methods such as mechanical, chemical, biological and physicochemical methods are being used for the treatment of post dyeing wastewater in textile industries. Biological methods are not effective in decolorization of the commercial dyes because most commercial dyes are toxic to the organism used in the process (Anielak, 1996c).

Physicochemical methods included coagulation, flocculation, co precipitation, electrodialysis, flotation, ultrafiltration, sorption and others. Among physicochemical methods applied, coagulation - flocculation methods, which can be used in a simple technological system, is mostly applied in textile industries. Coagulation is a process that brings colloidal particles and very find solid suspensions initially present in a wastewater into contact to form large agglomerates that can be separated via sedimentation, flocculation, filtration, centrifugation or other separation methods (Ching et. al., 1994). Flocculation is a process that makes the destabilized particle to form a larger agglomeration of floc by physical mixing or addition of chemical aid of both.

Coagulation method is effective in removing BOD, dry residue, dissolved substances, suspended matters and ether extractable substances (Kuo, 1992). The coagulating agent, coagulant dosage, the solution pH, ionic strength, the concentration and nature of the organic compounds influenced the coagulation method's effectiveness (Stephenson and Duff, 1996). The large variation in textile effluent wastewater characteristic made it difficult in the determination of optimal dosage of coagulants (Lin & Liu, 1994).

The treatment alternatives applicable for the colour removal vary, depending upon the type of dyes wastewater. Tan et al. (2000) had carried out a research on the removal of reactive dye via coagulation method by using $MgCl_2$ as the coagulant whereas Ooi (2000) did a research on removal of reactive dye via coagulation method using alum, $MgCl_2$, mixture of alum and $MgCl_2$, and mixture of PAC and $MgCl_2$.

The present study is to investigate the effectiveness of coagulation - flocculation method in the removal of colouring matters in wastewater containing the mixture of reactive dye Cibacron Yellow FN - 2R and disperse dye Terasil Blue BGE - 01. Up to date, only research on the treatment of mixture of the same type of dyes had been carried out but the treatment of the different type of dyes is not given enough attention (Mahdavi et al, 2000; Al Degs et al., 2000; Arslan et al., 2000).

EXPERIMENTAL

The reactive dye Cibacron Yellow FN - 2R and disperse dye Terasil Blue BGE - 01 were supplied by Callaway Enterprise and used to prepare dye solutions of concentration 1.0 g/L as synthetic dye wastewater. In this study, aluminium sulfate (alum), polyaluminium chloride (PAC) and magnesium chloride ($MgCl_2$) were used as coagulants. Alum of industrial grade and PAC 30% in powdeer form of ana[illegible]l grade was supplied by T.C. Chem. Technology and M[illegible]2 of analytical grade was supplied by Fluka Biochemika. The coagulant aid used is Polyelectrolyte, Koaret PA 3230 of commercial grade from Giulini Chemie. Distilled water have been used to prepare all the dye solutions, coagulants and coagulant aid solutions. The dye mixture contained 50 % of reactive dye Cibacron Yellow FN - 2R and 50% of disperse dye Terasil Blue BGE - 01 with the final concentration of 1.0 g/L.

The dye solutions' concentrations were measured at a wavelength corresponding to the maximum absorbance, λ_{max}, by means of a UV-visible spectrophotometer (Shimadzu UV - 160 A). The percentage of colour removal was calculated by comparing the absorbance value of the supernatant to the standard curve obtained by a known dye concentration. The dye solutions' pH were measured by the pH meter (Hach Sension 3). The dye concentrations were determined through colour point (Pt/Co) measurement by Hach DR/2000 Spectrophotometer.

Jar test was conducted to determine the effec[illegible] solution pH, type of coagulant, coagulant dosage and coagulant aid dosage on colour removal. A six paddle stirrer with six beaker apparatus and each beaker contained 150ml of the prepared dye solution was used in this study. The jar test procedure began with the mixing of dye solution with sodium hydroxide (NaOH) for pH adjustment for a period of 1 minute at 60 - 65 rpm. The initial pH of the dye solutions were measured by the pH meter. After adding coagulant, dye solution was stirred for 3 minutes. It was followed for a further mixing for 1 minute after the addition of polyelectrolyte. The formed flocs were allowed to settle and the settling times (to reach half of the dye solution height) were recorded. The supernatant of the treated dye solution was taken for the determination of the colour remained.

RESULTS AND DISCUSSION

The light absorbance at the peak wavelength, λ_{max} of the reactive dye, disperse dye and the dye mixture were measured by the UV - visible spectrophotometer and shown in Table 1. It is found that the light absorbance at the corresponding wavelength is proportional to the concentration of the colour in the solution. Thus, the dye solutions that were used in this study obey the Beer's law which can be expressed as:

$A = abc$, where A = absorbance of the dye solution
a = absorptivity of the dye solution
b = the cell path length
c = concentration of the dye solution

Table 1. λ_{max} of the different dyes.

Dye solution	λ_{max} (nm)
Cibacron Yellow FN - 2R	501.0
Terasil Blue BGE - 01	748.5
Dye mixture	748.0

The effect of coagulant dosage on colour removal

The effect of coagulant dosage was investigated by varying the dosage of a coagulant but keeping other conditions constant. Figures 1, 2 and 3 clearly show that the % of colour removal increases with the coagulant dosage.

Figure 1 shows that 200 ppm of alum is required for disperse dye to achieve 99 % of colour removal but reactive dye needs 6000 ppm of alum in order to achieve 90 % of colour removal. The percentage of colour removal of the reactive dye decreased when the alum dosage increased to 7000 ppm. 3000 ppm of alum can only give 49 % of colour removal but an increase to 99 % of colour removal is observed in the dye mixture with the same alum dosage.

Treatment of PAC on the disperse dye also shows the similar trend in the percentage of colour removal as in alum. Figure 2 shows that total removal was achieved when 200, 300 and 400 ppm of PAC were used in the treatment of disperse dye. Further increase in the coagulant dosage after the optimal dosage does not increase the percentage of colour removal because all the dyes have been removed at this stage. Excessive coagulant will result in forming of too much flocs which in turn will prolong the floc settling time.

For reactive dye, the same phenomenon occurred in the treatment with PAC and alum. After the highest percentage of colour removal achieved when 800 ppm of PAC was used, further increase in the PAC dosage decreased the percentage removal of colour. This may be due to the restabilization of the dye particle (Chu, 2001; Ahmad & Syafie, 2002). Figure 2 shows that 500, 600 and 700 ppm of PAC show higher percentage of colour removal (98.62 %, 99.69 % and 99.83 %) in dye mixture as compared to the treatment in reactive dye with the same PAC dosage.

The three dye solutions need 3000 ppm of $MgCl_2$ in order to achieve 99 % of colour removal. An increase of 44 % of colour removal occurred in the dye mixture as compared to the reactive dye at 1000 ppm of $MgCl_2$ while the disperse dye gives a removal of 62 % at the same dosage of $MgCl_2$.

Figures 1 and 2 show that when 50% reactive dye is mixed with 50% disperse dye, the coagulant dosage needed to achieve a satisfactory colour removal rate is between the dosage of coagulants needed for both individual dyes. Figure 3 shows that for $MgCl_2$ the colour removal rate reaches 99 % for both the single dyes and the dye mixture at the same dosage of $MgCl_2$ that is 3000 ppm. The results show that the alum and PAC dosage needed for the disperse dye increased in the presence of the reactive dye and vice versa.

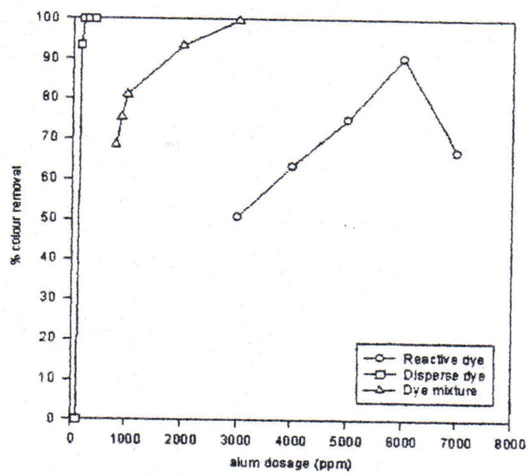

Fig. 1. Colour removal rate of different dyes by different alum dosage.

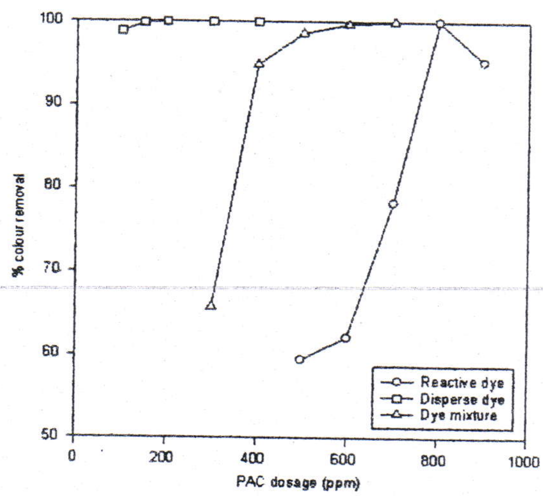

Fig. 2. Colour removal rate of different dye by different PAC dosage.

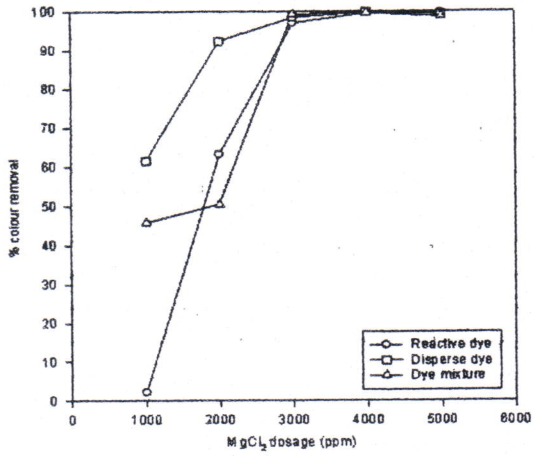

Fig. 3. Colour removal rate of different dyes by different $MgCl_2$ dosage.

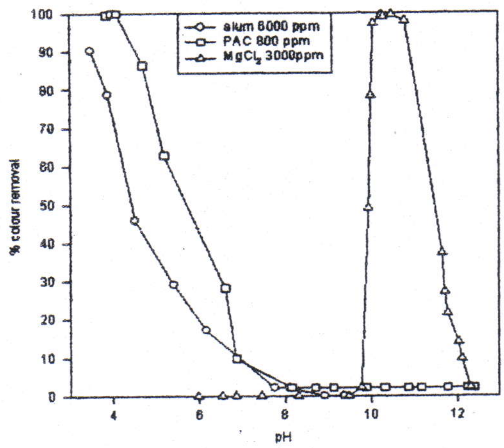

Fig. 4. Colour removal rate of reactive dye as function of pH.

The effect of the pH on colour removal

The percentages of colour removal for reactive dye, disperse dye and the dye mixture are greatly affected by the pH of the dye solution as shown in Figures 4, 5 and 6. The results are summarized in Table 2.

Table 2. Optimal pH range for the different coagulant.

Coagulant	Coagulant dosage(ppm)	Dye solution	Optimal pH range
	6000	Reactive dye	3.5-4.0
Alum	300	Disperse dye	4.0-4.5
	3000	Dye mixture	4.0-5.0
	800	Reactive dye	3.5-4.5
PAC	200	Disperse dye	4.0-5.0
	600	Dye mixture	4.0-5.0
	3000	Reactive dye	10.0-11.0
$MgCl_2$	3000	Disperse dye	10.0-12.0
	3000	Dye mixture	10.0-11.0

Alum and PAC are more effective in a lower pH range but $MgCl_2$ is more effective in a higher pH range. The optimal pH range of the different coagulant for the reactive dye, disperse dye and dye mixture is almost the same.

The effect of coagulant aid dosage on flocs settling time

Polyelectrolyte, Koaret PA 3230 was used as coagulant aid to interconnect and enmesh the colloidal particles into larger flocs and easier settled. Figures 7, 8 and 9 show the effect of the amount of coagulant aid on the flocs settling time. The optimal pH and the optimal dosage of coagulant are kept constant for each dye solution. The result shows that the increase of coagulant aid dosage reduces the flocs settling time.

A significant increase in flocs settling time of about 590 s and 645 s when 4.0 ml of coagulant aid was used for 600 ppm of alum and 800 ppm of PAC for the

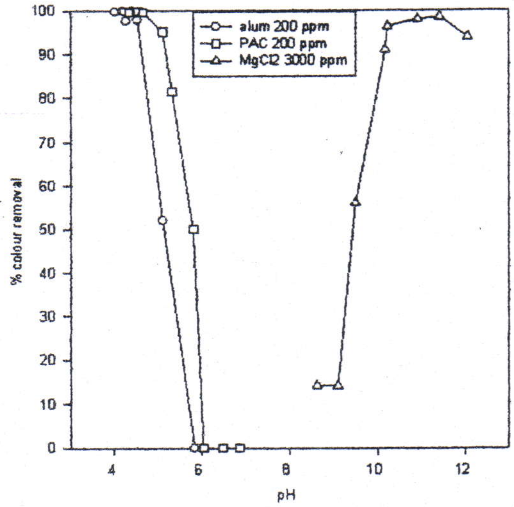

Fig. 5 Colour removal rate of disperse dye as function of pH.

reactive dye. For $MgCl_2$, 3.0 ml of polyelectrolyte can reduce the flocs settling time to less than 100 s and further increase of the dosage of coagulant aid doesn't give significant improvement in flocs settling time for the reactive dye.

Figure 8 shows that the flocs formed without coagulant aid give a settling time of about 390 s. The addition of 1.0 ml of coagulant aid reduces the settling time to about 100 s by using the $MgCl_2$. In the case of 200 ppm alum, the flocs settling time decreases with the coagulant aid dosage. There is no significant reduction in flocs settling time when 1.0 ml of coagulant aid was added to the dye solution when the solution is treated by 150 ppm PAC. However, the flocs

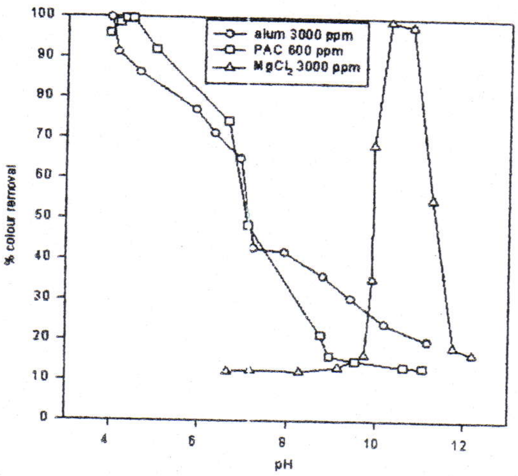

Fig. 6. Colour removal rate of dye mixture as function of pH.

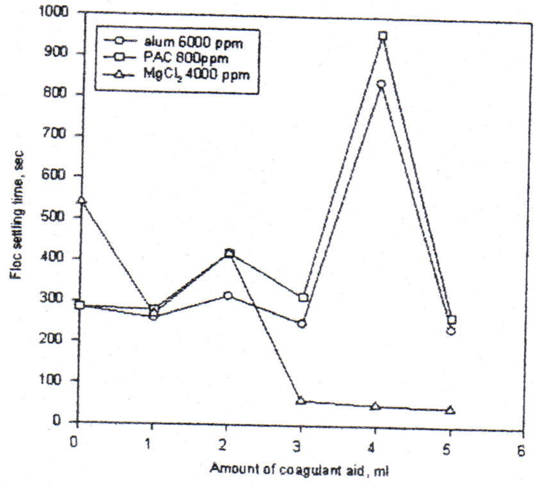

Fig. 7. Effect of amount of coagulant aid on floc settling time of reactive dye.

settling time drops from 265 s to 130 s when 2.0 ml of coagulant aid is added. When 5.0 ml of coagulant aid is added, the settling time increases. This may be due to the over dosage of the coagulant aid. Over dosage of coagulant aid may increase the volume of sludge for disposal and it is not merely uneconomic but may inhibit the flocculation process by coating the particles completely with the subsequent re- stabilization of the suspension. Reduction in settling time has an implication of reduction in the retention time in the settling tanks with the corresponding savings in capital investment and producing cleaner water for the subsequent processes. (Tan et al., 2000)

Figure 9 shows that the flocs settling time of the dye mixture treated with alum and PAC are about the same. The dye mixture solution treated with $MgCl_2$ requires less time for the flocs to settle. This phenomenon could be due to the excessive $Mg(OH)_2$ in the treated dye solution (Tan et al., 2000).

Using different amounts of coagulant aid (0 - 3.0 ml) with alum and PAC didn't have a profound impact on the flocs settling time but for $MgCl_2$ as the amount of coagulant aid was increased, the flocs settling time decreased sharply. When 4.0 ml of coagulant aid is used, 3000 ppm of alum and 600 ppm of PAC have the flocs settling time of 430 s and 840 s respectively. The flocs settling time by using $MgCl_2$ is reduced with the increasing amount of coagulant aid. The size of the flocs formed by using $MgCl_2$ seen to be much bigger than those formed by using alum and PAC.

The effect of different coagulants on colour removal

Among the coagulants used, PAC is the most effective coagulant in treating each dye with the colour removal rate of up to 100 % at 800 ppm for reactive dye, 200 ppm for disperse dye and 600 ppm for the dye mixture.

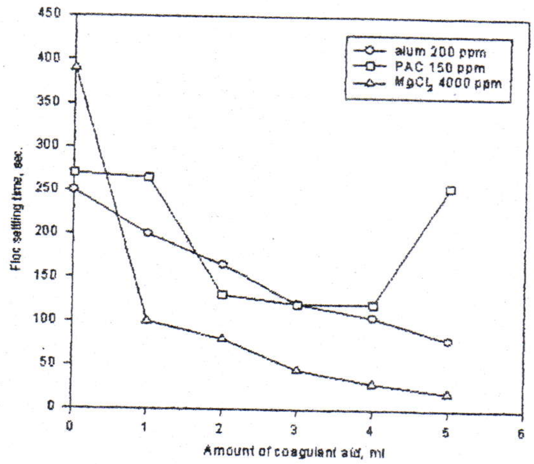

Fig. 8. Effect of amount of coagulant aid on floc settling time of disperse dye.

Dosages of alum and PAC needed to achieve a satisfactory colour removal rate are far less compared to the dosage of $MgCl_2$ required. The flocs settling time of different coagulants are investigated and are shown in Figures 7, 8 and 9. The figures above indicate that by using $MgCl_2$, shorter flocs settling time is required as compared to alum and PAC due to the larger size and weight of the flocs formed.

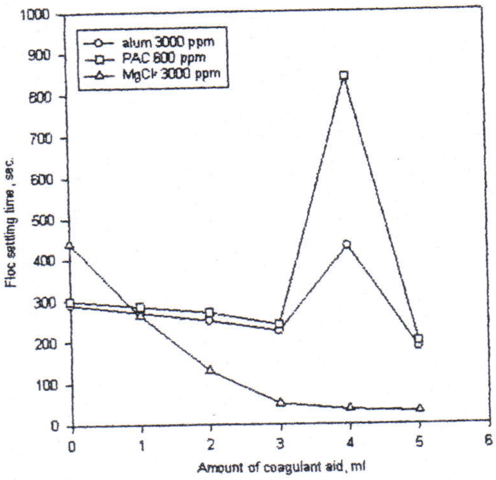

Fig. 9. Effect of amount of coagulant aid on floc settling time of dye mixture.

CONCLUSION

The percentage colour removal of reactive dye can achieve up to 90.40 % using alum of concentration 6000 ppm at a pH of 3.50. $MgCl_2$ of concentration 4000 ppm can achieve up to 99.58 % colour removal at a pH of 9.70 and for PAC of concentration 800 ppm, 100 % colour removal can be achieved in a pH range of 3.98 – 4.60. Up to 99.90 % of disperse dye can be removed with alum of concentration 200 ppm in a pH range of 4.00 - .4.50 and $MgCl_2$ of concentration 4000ppm at a pH of 9.81 respectively. With 200ppm PAC at a pH of 4.61 the percentage removal of disperse dye is 100 %. The removal of dye mixture containing 50% reactive dye and 50% disperse dye can reach 99.69 % using PAC of concentration 600ppm at a pH of 4.31 and 99.26 % using $MgCl_2$ of concentration 3000ppm at a pH of 10.27. By using alum of concentration 3000 ppm, 99.71% colour removal can be achieved at a pH of 4.00.

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