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EVALUATION OF INDUSTRIAL DYEING WASTEWATER TREATMENT WITH COAGULANTS AND POLYELECTROLYTE AS A COAGULANT AID

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ABSTRACT
Textile industry is the major source of water consumption and wastewater pollution. There are various treatment techniques to remove textile wastewater pollution. Coagulation-flocculation is a widely used process to remove pollution due to suspended particles. In this research, different coagulants like Alum, Lime, $FeCl_3$, $FeSO_4$ and $MgCl_2$ were applied to select the suitable ones with optimum removal efficiency. Settling characteristics of flocs formed in the coagulation process were studied in a laboratory scale settling column unit. Parameters such as color, COD, TSS, turbidity and settled sludge volume have been evaluated. The optimum coagulant dose and pH value were determined by comparing the effectiveness of these coagulants. Results showed other coagulants except lime could eliminate color and COD successfully. In this case, $FeSO_4$ was chosen as an optimum coagulant for color removal because of the lowest required coagulant dose, minimum settled sludge volume and maximum decolorization.

Key words: Dye, color removal, coagulation, coagulants, textile wastewater, alum, lime

INTRODUCTION
Wastewater is the major environmental issue of the textile industries besides other minor issues like solid waste, resource wastage and occupational, health and safety. Textile and dyeing mills use many kinds of artificial composite dyes and discharge large amounts of highly colored wastewater. Pretreatment, coloration and after treatment of fibers, usually require large amounts of water and variety of chemicals. Variations in the fabric quality and treatment process results into large fluctuation in daily flow rates and pollutants concentrations. Textile wastewater pollutants are generally caustic soda, detergents, starch, wax, urea, ammonia, pigments and dyes that increase its BOD, COD, solids contents and toxicity. These wastes must be treated prior to discharge in order to comply with the environmental protection laws for the receiving waters. Biological treatment processes are frequently used to treat textile effluents. These processes are generally efficient for biochemical oxygen demand (BOD) and suspended solids (SS) removal, but they are largely ineffective for removing color from the wastewater (McKay,1979; Taebi Harandi,1986) because dyes have slow biodegradation rate (Bennett and Reeser,1988). Now, the treatment technologies recommended meeting color removal requirements are physicochemical treatment operations, including adsorption (Ahmad and Ram,1992; McKay ,1979), ozonation (Lin's, 1993), oxidation (Boon and Tjoon, 2000), chemical precipitation (Dziubek and Kowal,1983), etc. Each has its merits and limitations in applied decolorization treatment operations. But Coagulation-flocculation is the most common chemical treatment method for decolorization (Beulker and Jekel,1993 ; Bennett and Reeser, 1988).

Review of the studies on chemical treatment of textile industry and dyeing wastewater in Iran
Shirazi and *et al.*, investigated textile factories wastewater decolorization by ferric chloride in 1977 .They found it removes 51% COD and 68% dye. Torabian and *et al.*, investigated textile

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industry wastewater decolorization by magnesium carbonate (Torabian, 1996). They reported magnesium carbonate is appropriate for some dyes such as *khomi* dyes and showed by adding 40 mg/L magnesium carbonate; decolorization effectiveness of 250 mg/L lime could increase from 57% to 86.9%. All test results in Iran and other countries show chemical treatment is effective enough to treat textile wastewater and decrease considerable COD and dye (Yaghmaee, 1996).

Case study position

Hengame Goya factory is located in Eshtehard industrial town. In this factory, sulfuric colorants and 522 black color made in Shanghai China commercially named *sulfur black 522 BR 200%* are usually used for dyeing process.

MATERIALS AND METHODS

Chemical coagulation

Both suspended and colloidal particles do not settle under gravity so they can not be removed by physical processes. Reason of this event is that some suspended solid have trifle weight and the charges present on colloid surfaces result into repulsion and do not allow them to agglomerate and form flocs. Coagulation process neutralizes the charge present on the particles surfaces with the help of coagulants whereas flocculation makes them to come close to each other to make flocs by slow agitation. Settling follows coagulation and flocculation to remove resultant flocs from the wastewater. Designing of coagulation, flocculation and settling tank requires study regarding optimum dose of coagulants at suitable pH to give maximum removal and settling characteristics of resultant flocs (Cooper, 1993; Jorgenson, 1974).

Coagulants

A) Inorganic coagulants

There are various inorganic coagulants which can be used as coagulants such as ferric sulfate II, ferric chloride and sulfate III, lime and inorganic polymer flocculers. In this research, different coagulants like Alum, Lime, $FeCl_3$, $FeSO_4$ and $MgCl_2$ were applied to select the suitable ones with optimum removal efficiency.

B) Organic coagulants

Organic coagulants including poly electrolytes, synthetic polymers and natural polymers can also be used for coagulation process (Beulker and Jekel , 1993). Polymers with initial monomers such as carboxyl or amino are called poly electrolytes. Different types of poly electrolyte are used as coagulant aids recently. Poly electrolyte has huge molecules with a high molecular weight which has a high ionization power. It produces a large amount of ions in water and shows the properties of both polymers and electrolytes. Polyamphotypes, anionic and cationic poly electrolytes are some types of poly electrolytes. The most practical benefit of poly electrolytes is the formation of massive flocs. These massive flocs speed up the flocs settling velocity, reduce the expenses of decolorization and also decrease settled sludge volume. However, the use of poly electrolytes may have some problems.

Dyeing wastewater sampling and test conditions

Factory wastewater samples were averagely taken weekly and then conveyed to the laboratory of Environment Faculty in Tehran University per month. Parameters such as pH, COD, dye concentration and TSS were determined. Then, COD and dye removal efficiencies were calculated. Experimental conditions of all tests are:

- All tests have been performed in (25 ºC$\pm$ 2). Because temperature is one of the effective parameters on density, viscosity and thus retained volume of coagulant.
- The volume of studied wastewater was 500 cc.

Physicochemical analysis

Method No.522 in Standard Method was used to determine COD (chemical oxygen demand). COD concentration of the samples was measured by potassium dichromate method using HACH spectrophotometer. Color was determined by comparative methods using HACH spectrophotometer DR/2000. The color measurement unit is Pt/Co. TSS was determined in conformity with Standard Method using HACH Spectrophotometer RD/2000. PH was measured using digital SCHOTT pH meter model CG824 (accuracy pH$\pm$0.1) .Turbidity was determined using ANNA turbidity meter and the measurement unit is NTU (Rinker and Starent, 1974).

Jar test

All experiments were conducted using the jar testing method to determine the optimum pH value and coagulant dose. Six beakers positioned on magnetic stirrers were dosed with 0.5 L dye solution and a specified dosage of coagulant. The samples were stirred rapidly for 90 seconds, followed by 20 minute slow stirring for flocculation. The generation of flocs can be watched during this period. Flocs were allowed to settle for one hour before withdrawing samples for analysis. These procedures are performed for several times so that the optimum pH and dose of coagulant can be calculated (Hosseinian, 1991; Metcalf and Eddy, 1979). In the next series of the experiment the influence of polyelectrolyte on the effectiveness of dye removal was examined. The same test was run but before precipitation stage, different polyelectrolyte concentration was added to the samples.

RESULTS

In this study, coagulation-flocculation processes are used to decolorize and biodegrade textile finishing industry effluents. The optimum coagulant dose and pH value are determined by comparing the effectiveness of alum, $FeSO_4$, $FeCl_3$, lime, $MgCl_2$ for obtaining maximum color, TSS and COD removal. For each case, the optimum pH is primarily determined for 400 mg/L coagulant concentration based on more color and COD removal and also less settled sludge. Then the optimum effective dose of coagulant is calculated at the optimum pH. Finally at constant optimum pH and coagulant dose, the effect of coagulant aids such as polyelectrolyte has been evaluated. Following figures show the final results of all experiments. Fig. 1 shows the percent removal of color , COD and also TSS and turbidity of using alum and Ferric Sulfate for different pHs.

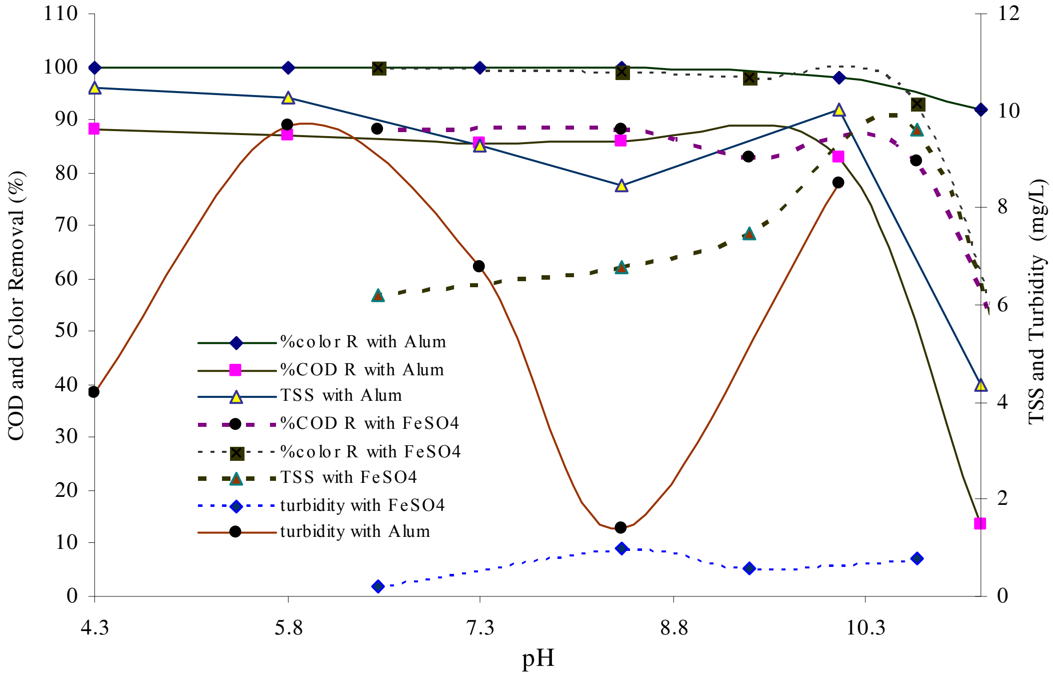

Fig. 1: Percentage removal of color , COD and TSS and turbidity for different pH; (for 400 mg/L alum or 400 mg/L of $FeSO_4$)

Fig. 2 shows the volume of settled sludge for 400 mg/L of each coagulant versus different pHs. And Fig.4 shows the volume of settled sludge of each coagulant in its optimum pH. Using a better coagulant generates less amount of settled sludge. Optimum pH of the coagulant is calculated using Figs. 1, 2 and 8. Fig. 3 and 9 show the percent removal of color and COD and also TSS and turbidity of the coagulants in their optimum pH , so that the optimum dose of coagulant can be calculated.

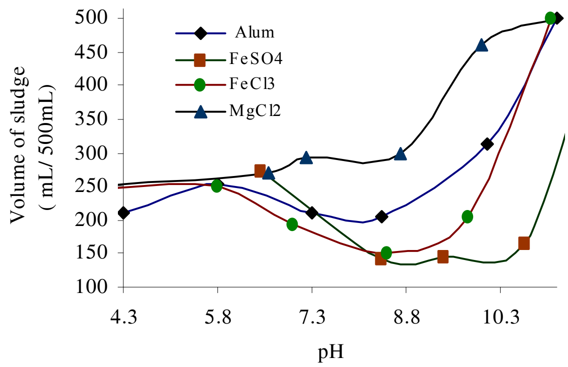

Fig. 2: Settled sludge volume for 400 mg/L of coagulants

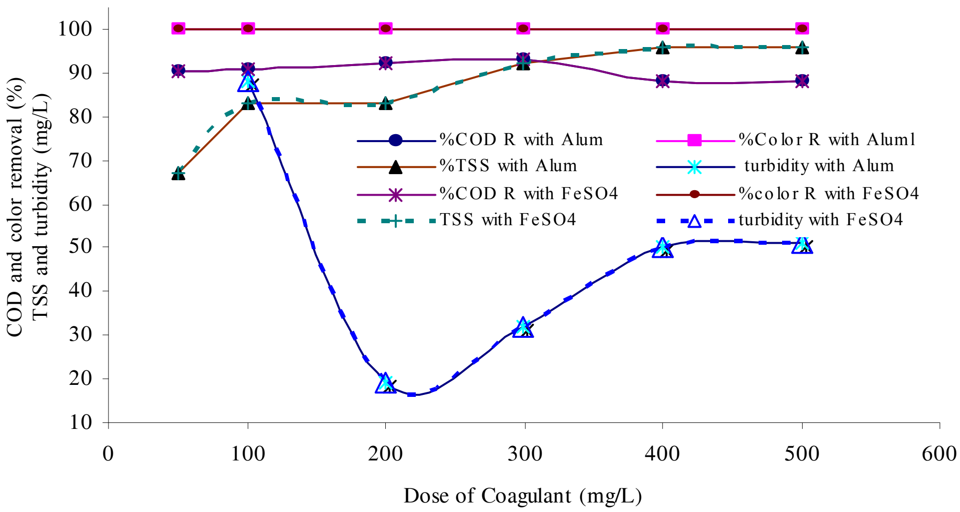

Fig. 3: Percentage removal of color, COD and TSS and turbidity for different doses of coagulant (At optimum pH=8.2 for Alum or at pH=9.4 for $FeSO_4$)

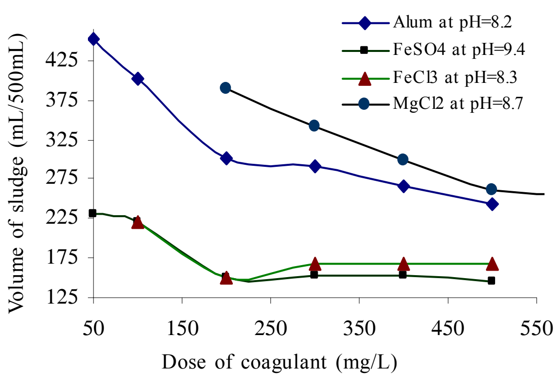

Fig. 4: Settled sludge volume for different coagulants at their optimum pH

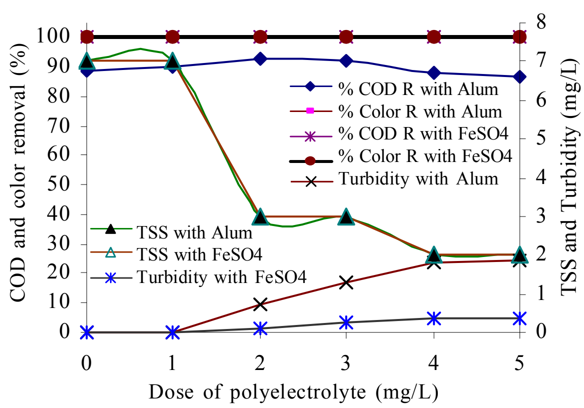

Fig. 5: Percentage removal of color and COD And TSS and turbidity for different doses of polyelectrolyte. (For 200 mg/L Alum or 200 mg/L of $FeSO_4$)

Fig. 5 and 10 show the percent removal of color and COD and also TSS and turbidity for different doses of polyelectrolytes as coagulant aid. Fig.7 also shows the volume of settled sludge for different doses of polyelectrolyte. Fig. 6 show the results of lime tests which shows that lime has a little color removal effect , so it is not recommended for dye removal from textile wastewater at all.

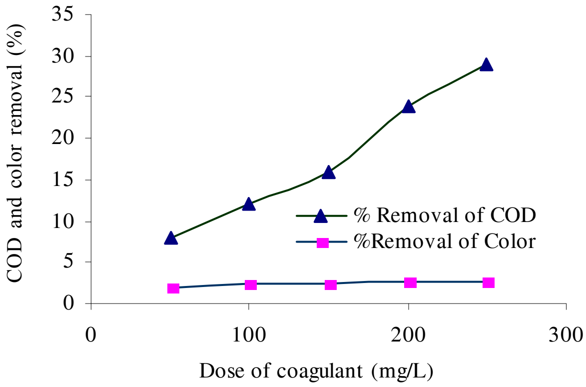

Fig. 6: Percentage removal of color and COD for different doses of lime (At pH= 10.3)

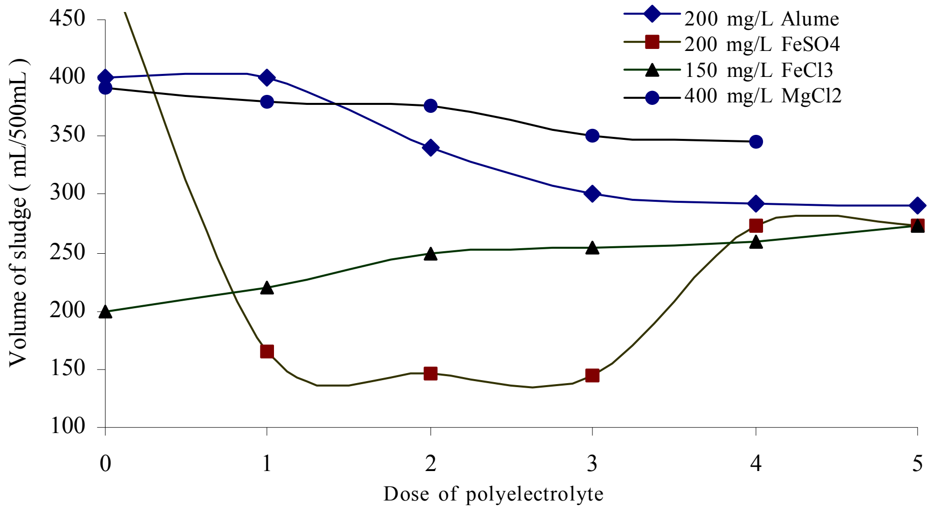

Fig.7: Settled sludge volume Vs. dose of polyelectrolyte with different doses of coagulants

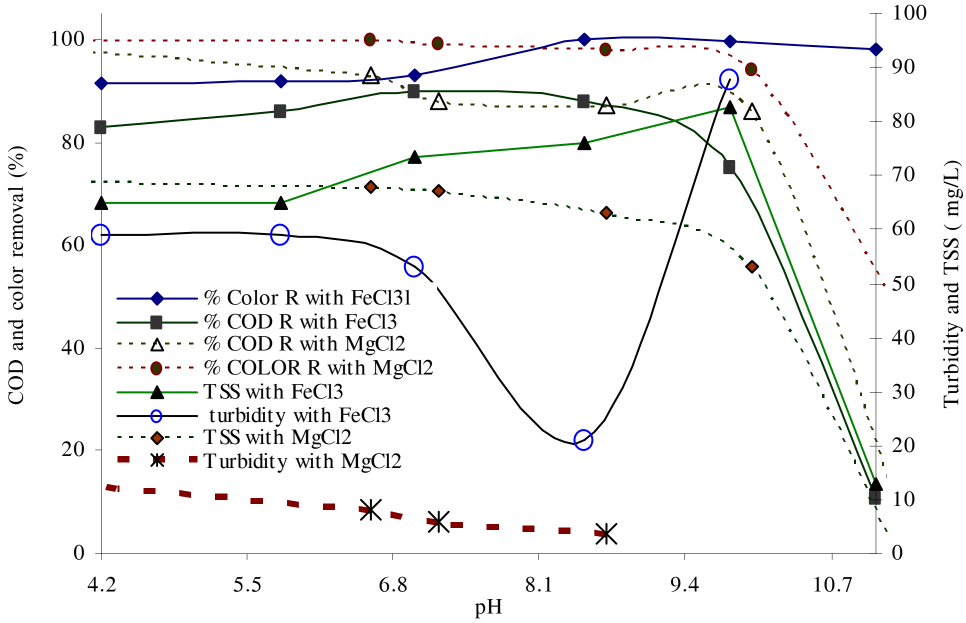

Fig. 8: Percentage removal of color , COD and TSS and turbidity for different pH; (for 400 mg/L $FeCl_3$ or 400 mg/L of $MgCl_2$)

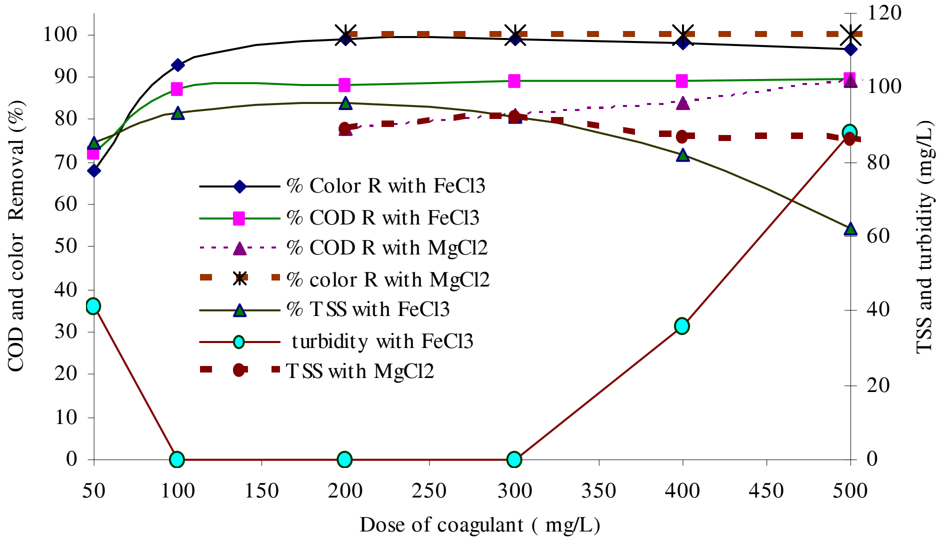

Fig. 9: Percentage removal of color, COD or TSS and turbidity for different doses of coagulant (at optimum pH=8.3 for $FeCl_3$ or pH=8.7 for $MgCl_2$)

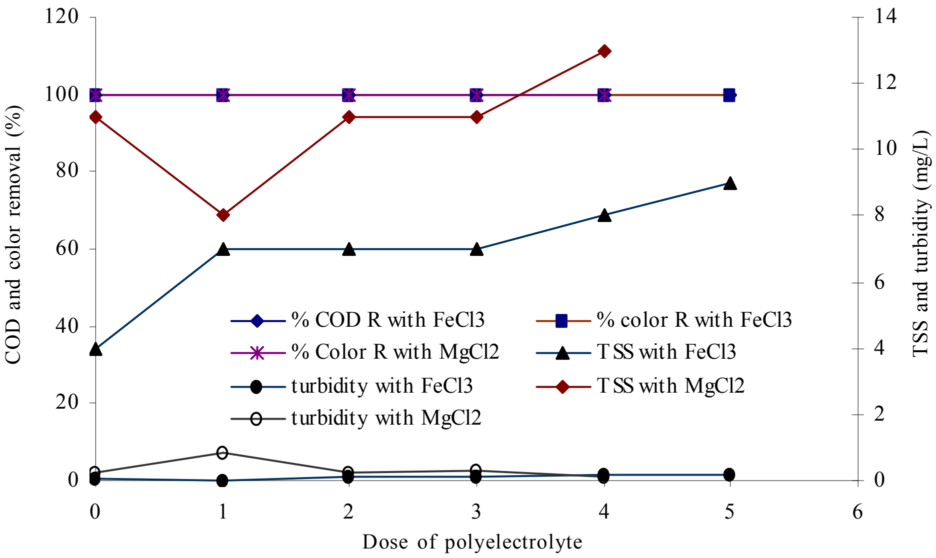

Fig.10: Percentage removal of COD, color and TSS and turbidity for different doses of Polyelectrolyte. (for 150 mg/L $FeCl_3$ or 400 mg/L of $MgCl_2$)

DISCUSSION

Alum effect

According to Figs. 1 and 2 the optimum pH for 400 mg/L alum is 8.2 due to higher color and COD removal and lower volume of settled sludge. Figs. 3 and 4 shows that the optimum dose of alum for color and COD removal is 200 mg/L Fig. 5 shows that polyelectrolyte does not have any special positive effect on color or COD removal.

Lime effect

To evaluate lime effect on color and COD removal of dyeing wastewater, first its effect at a constant pH for different doses of lime has been evaluated. Fig. 6 shows that 250 mg/L lime eliminates only 29 % COD and just 2.5 % colors. After 3 hours no settled sludge has been found. Thus lime is not recommended for color removal of dyeing wastewater. Therefore the effect of poly electrolytes won't be evaluated.

$FeSO_4$ effect

According to Fig. 1 and 2 the optimum pH for 400 mg/L $FeSO_4$ is 9.4 due to higher color and COD removal and lower volume of settled sludge. Figs. 3 and 4 shows that the optimum dose of $FeSO_4$ for color and COD removal is 200 mg/L The effects of polyelectrolyte have been showed in Figs. 5 and 7. It is clear that poly electrolytes not only have any positive effect on color or COD removal but also it increases turbidity and the volume of settled sludge but for concentration more than 2 mg/L it reduces TSS.

$FeCl_3$ effect

According to Figs. 2 and 8 the optimum pH for 400 mg/L $FeCl_3$ is 8.3 due to higher color and COD removal and lower volume of settled sludge. Figs. 4 and 9 shows that the optimum dose of $FeCl_3$ for color and COD removal is 200 mg/L The effect of poly electrolyte has been showed in Figs. 7 and 10. It is clear considering figures that using poly electrolyte has a negative effect on $FeCl_3$ as a coagulant because it increases TSS, turbidity and the volume of settled sludge. And the appropriate setting time is 15 minutes.

$MgCl_2$ effect

According to Figs. 2 and 8 the optimum pH for 400 mg/L $MgCl_2$ is 8.7 due to higher color and COD removal and lower volume of settled sludge. Figs. 4 and 9 shows that the optimum dose of $MgCl_2$ for color and COD removal is 500 mg/L Figs. 7 and 10 show that Polyelectrolyte does not have a positive effect on color removal and also on turbidity. But adding 1 mg/L of poly electrolyte reduces TSS by 27 %. And adding 3 mg/L of poly electrolyte reduces settled sludge volume by 10 % in the first 15 minutes of setting time. By the way using of poly electrolytes by $MgCl_2$ is not recommended. Shirazi and *et al*., investigated textile factories wastewater decolorization by ferric chloride in 1977 .They found it removes 51% COD and 68% dye. Torabian and *et al*., investigated textile industry wastewater decolorization by magnesium carbonate (Torabian, 1996). They reported magnesium carbonate is appropriate for some dyes such as *khomi* dyes and showed by adding 40 mg/L magnesium carbonate; decolorization effectiveness of 250 mg/L lime could increase from 57% to 86.9%. The results of the tests in this research showing all coagulants except lime removed color. Both ferric sulfate and alum removed color at low concentration with roughly high efficiency whereas low concentration ferric chloride removed less dye. It was observed that magnesium chloride started to remove color in concentration higher than 200 mg/L and Lime did not have any effect on COD removal. Magnesium chloride started to remove COD with concentration higher than 200 mg/L Ferric chloride, alum and ferric sulfate had same COD removal with concentration higher than 100 mg/L Magnesium chloride and alum generated large amount of sludge it can cause sludge disposal problem and involve extra costs. To select the best coagulant, in addition to above parameters, it should be considered parameters such as required coagulant dose, coagulant cost and optimum pH after reaction for discharging into environment. Therefore alum because of large amount of generated sludge, ferric chloride and ferric sulfate because of their high cost are not appropriate for dye removal. In this study, ferric sulfate ($FeSO_4$) is recommended as the best coagulant to remove sulfuric dyes.

By the way adding polyelectrolytes as coagulant aids showed good results for decolorization. Before industrial wastewater treatment, it would be better considering other aspects to decrease wastewater volume and mitigate its contamination. Following considerations are recommended increasing industrial wastewater treatment efficiency and also mitigating wastewater contamination of this industry:

Process control properly to save water consumption in industrial units; Recovery and recycle; Chemicals substitutions for example substitution of soaps with lower BOD detergents or dye oxidation steam with acetic acid bath; Separation of dyeing wastewater from other units due to its different components; Investigation of used coagulant fluctuation on effluent wastewater; Investigation of rate and time effect in rapid and slow mixing on effluent wastewater, mixing condition reach to optimum energy consumption and time; The ability of various dyeing process wastewater reuse for using in other processes;

The ability of dye bath reuse and Use premanent systems especialy for dye removal.

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