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Dye Removal from Wastewater Using Iron Salts

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Abstract

This investigation was carried out to study the treatment and recycling of wastewater in the cotton textile industry for an effluent containing three dyes: direct blue, sulphur black and vat yellow. The reuse of such effluent can only be made possible by appropriate treatment method such as chemical coagulation. Ferrous and ferric sulphate with and without calcium hydroxide were employed in this study as the chemical coagulants.

The results showed that the percentage removal of direct blue ranged between 91.4 and 94 , for sulphur black ranged between 98.7 and 99.5 while for vat yellow it was between 97 and 99.

Key words: dye removal by iron salts, dye removal from wastewater.

Introduction

The urgent need to conserve, recycle and reuse the limited water sources of the earth has forced mankind to research and develop new methods and technologies for treating and managing used waters from process, cooling and/or rinse facilities of industrial applications. This is especially important in textile finishing and dyeing industries, where huge amounts of water are consumed in dyeing and washing/rinsing of the fabrics [1].

Textile mill operations consist of weaving, dying, printing, and finishing. Many processes involve several steps, each contributing a particular type of waste, e.g. sizing of the fibers, queering (alkaline cooking at elevated temperature), desizing the woven cloth, bleaching, mercerizing, dyeing, and printing.

Textile wastes are generally, colored, highly alkaline, high in BOD and suspended solids, and high in temperature. Wastes from synthetic-fiber manufacture resemble chemical-manufacturing wastes and their treatment depends on the chemical process employed in the fiber manufacture. Equalization and holding are generally preliminary steps to the treatment of those wastes because of their variable composition. Additional methods are chemical precipitation, trickling filtration, and, more recently, biological treatment and aeration. The textile industry has long been one of the largest of water users and polluters and there has been little success in developing low-cost treatment methods, which the industry urgently needs to lessen the pollution loads it discharges to streams [2].

Coagulation is the method in which certain chemicals are rapidly dispersed in wastewater to change the characteristics of the suspended particles so that they coalesce and form flocs that sink rapidly. Coagulation is employed to improve or make possible the removal of negatively charged colloidal suspensions, which do not normally settle out and cannot be removed by conventional physical treatment. Coagulation is done by the addition of positive ions, e.g., Al3+, which reduce the electrokinetic repulsion between the particles [3].

In industrial wastewater treatment, coagulation is frequently used for oily emulsions, and finely divided and nonsettleable solids such as pigments, paper fiber, meat and tannery effluents, and mineral benefaction slimes. The most widely used coagulants for wastewater treatment are aluminum and iron salts such as aluminum sulphate (alum), ferric sulphate, and ferric chloride. At high (alkaline) pH prevalent in the water these salts produce insoluble aluminum hydroxide or ferric hydroxide flocs [4]. The overall reaction may be represented as:

$$Al_2(SO_4)_3 + 3Ca(HCO_3)_2 \rightarrow 2Al(OH)_3 + 3CaSO_4 + 6CO_2$$

As they form and grow, the aluminum hydroxide flocs entrap the solid particles. The precipitate is then flocculated to produce large, dense settleable solids. Sometimes, with very low concentration of colloidal matter, floc formation is difficult; therefore, coagulant aids like polyelectrolytes are added to promote the coagulation-flocculation process [5].

If properly performed, the addition of chemicals for promoting coagulation and flocculation can remove both suspended and colloidal solids. After the flocs are formed, the solution is led to settling tank where the flocs are allowed to settle, while most of the flocculated material is removed in the settling basin. These flocs are removed by the process [6].

Ince and Tezcanli (1999) investigated the treatability of textile dye-bath effluents by advanced oxidation with Fenton and Fenton-like reagents (Fe II / H2O2 and Fe III / H2O2), in the presence and absence of UV light, using a reactive azo-dye (Procion Red HE7B), and typical dye bath constiuents. Under the experimental conditions employed, it was found that with 20 minutes UV irradiation, complete colour removal and 79% total organic carbon degradation is possible, when the system is operated at pH = 3, and with a H2O2 / Fe II molar ratio of 20:1. The individual effects of H2O2 and Fe II injections to the UV-irradiated dye solution were tested by running the advanced oxidation respectively with Fe II, H2O2 and both (at molar H2O2/ Fe II ratios of 20:1). The data is plotted in Fig. (2.10). Total colour removal with UV / Fe II, UV / H2O2 and UV / Fe II: H2O2 were found to be 30%, 90% and 97% respectively. Furthermore, the rate of colour degradation was unaffected by the variations in the ratio (H2O2 / Fe II) under dark conditions, whereas the degradation was found to be 0.75 times faster at a ratio of 20:1 than at 10:1, when the solution was irradiate

A survey was made to study the industrial wastewater problem in ten different factories in and around Baghdad. The survey included the amount of feed water to the factory, the amount of industrial wastewater leaving the factory, the amount of treated water, and major physical and chemical properties of industrial wastewater before and after the treatment unit.

It was concluded from this survey that the textile-finishing industry uses large quantities of water (150 m3/hr) and produces large volumes of aqueous effluent (125 m3/hr). The provision of water and disposal of effluents cannot be viewed as two separate problems as the viability of the industry in the future may well depend on the extent to which water can be reused.

Experimental Work

Chemicals used: Ferrous sulphate, Ferric sulphate, Ferric chloride and Calcium hydroxide all of technical grade.

Procedure and Equipment: Preliminary experiments were carried out to find the effect of the rate of agitation and the agitation time. These were fixed at their best value of 350 rpm and 30 minutes respectively.

Analysis of the waste water from the cotton textile treatment showed that the maximum concentrations of each dye were 6,10 and 16 ppm for direct blue, sulfure black and vat yellow respectively. Thus a model dye solutions were prepared by dissolving a weighed amount of the powder dye in distilled water.

Each dye solution was mixed with the above mentioned coagulants in a one-liter vessel at a constant speed (350 rpm) and a temperature of 27°C for about 30 minutes. It was then filtered using slow medium filter paper. The filtered solution was analyzed using UV-spectophotometer to find the dye concentration.

DISCUSSION

Addition of ferrous sulphate $FeSO_4$

Figure (1) indicates that increasing the amount of ferrous sulphate added will increase the removal of dye. A complete decolorization has been achieved for Sulphur Black dye solution at 0.2 gm/l ferrous sulphate dose, while the Direct Blue dye solution had a moderate decolorization (91%). Further observations showed that the Vat Yellow dye solution can not meet the required percent dye removal for the purpose of industrial wastewater recycling.

Figure (2) shows the effect of ferrous sulphate dose to mixture of dyes in water. The behaviour of Vat Yellow dye controls the overall behavior of mixture dyes solution especially the Sulphur Black dye.

This behaviour is probably due to the interaction between the molecules of dye-ferrous sulphate products in the mixture solution, which decreases the ability of formation of the coagulant.

For this reason the use of ferrous sulphate as a coagulant is not recommended unless using another material with it, for example calcium hydroxide

Addition of ferrous sulphate and calcium hydroxide

Figures (3) to (6) show the effect of adding calcium hydroxide as well as ferrous sulphate for dye removal. Calcium hydroxide improved the decolorization even with small doses. This is probably due to the neutralization of the colloidal charge by flooding the medium with an excess of oppositely charged ions. Usually hydrous oxide colloids are formed by reaction of the coagulant with ions in the water. The coagulant colloid also becomes destabilized by the reaction with foreign, oppositely charged colloids and produce hydrous oxide, which is a floc-forming material.

The same behaviour can be achieved for Direct Blue dye removal with 0.05 gm calcium hydroxide dose if the dye was in water alone or with the mixture of dyes. For Sulphur black and Vat Yellow, the removal of dye increase slightly. Figure (4) clearly demonstrates that increasing the amount of $FeSO_4$ added had no effect in the dye removal of Direct Blue and Sulphur Black dyes, while for Vat Yellow dye removal increases up to 92% using 0.05 gm ferrous sulphate dose then the same behavior can take place.

Furthermore Figure (6) shows that the concentration of Sulphur Black and Vat Yellow dyes dose not change when adding 0.02 gm of ferrous sulphate while the concentration of Direct Blue dye will reduce with a moderate percent. This may be due to the faster interaction between the Direct Blue with the coagulant ($FeSO_4$ + $Ca(OH)_2$) compared to other dyes.

After that, increasing the amount of ferrous sulphate will cause a step change to reach ultimate removal of all dyes.

The best coagulant dose is (0.15 gm/l $FeSO_4$ and 0.05 gm/l $Ca(OH)_2$) to achieve 93%, 99% and 98% for the removal of Direct Blue, Sulphur Black and Vat Yellow respectively.

Addition of ferric sulphate Fe2(SO4)3

Figure (7) indicates that Sulphur Black dye reaches nearly a complete dye removal even at 0.02 gm/l of ferric sulphate dose, then any increase of ferric sulphate added had no effect. For the Direct Blue, dye removal increase gradually with increasing ferric sulphate dose. Furthermore, Vat Yellow dye removal has a sharp increase up to 0.02 gm/l of ferric sulphate added. Increasing the ferric sulphte added will cause a gradual decrease in the dye removal. Iron oxides can acquire both positive and negative charges. Excess Fe^{3+} makes the colloids positively charged.

Figure (8) clearly demonstrates that all dyes in the mixture behave like Vat Yellow dye in water alone as noted in Figure (7). This means that Vat Yellow dye may control the behaviour of the dyes mixture in water. The best ferric sulphate dose to achieve 94%, 99% and 98% dye removal for Direct Blue, Sulphur Black and Vat Yellow respectively is 0.02 gm/l.

Addition of ferric sulphate and calcium hydroxide

Sulphur Black dye had been completely removed on adding 0.02 gm of ferric sulphate, then addition of any other compound had no significant effect as shown in Figures (9) and (10).

Direct Blue dye removal increases by adding 0.1 gm/l of calcium hydroxide to reach 94% removal with 0.02 gm ferric sulphate added. Then the addition of more calcium hydroxide (0.5 gm) will reduce the dye removal slightly (91%) as noted in Figures (10) and (11) . The addition of calcium hydroxide has a negative effect in Vat Yellow dye removal. Addition of 0.1 gm calcium hydroxide will decrease the removal from 99% to 0.1% , where the 99% removal, being achieved by only 0.02 gm/l ferric sulphate dose. Increasing the amount of ferric sulphate up to 0.15 gm will increase the dye removal to 97%.

This behaviour is probably due to the difference in structure of each dye and the reaction products of each dye with the coagulant in the aqueous solution.

Each dye in the solution mixture had nearly the same behaviour of the other dyes, while each dye solution had its own behaviour as noted previously. This is probably due to the interaction between molecules of the dye and its coagulation products with each other. Addition of calcium hydroxide even with small amount will prevent the decreasing of dye removal with the increase in the ferric sulphate dose. Furthermore, addition of 0.1 gm/l or 0.5 gm/L of calcium hydroxide had no effect on the dye removal of Direct Blue and Sulphur Black dyes, Figures (8), (12) and (13).

The best coagulant dose is (0.15 gm/l $Fe_2(SO_4)_3$ + 0.1 gm/l $Ca(OH)_2$) to achieve 93%, 99.5% and 97% removal for Direct Blue, Sulphur Black and Vat Yellow respectively.

Addition of ferric chloride, FeCl3

Figure (14) shows the effect of adding ferric chloride to Direct Blue dye in water solution. 70% dye removal can be achieved on adding 0.02 gm/L of ferric chloride. Increasing this amount up to 0.2 gm/L will decrease the dye removal to 50%. Thus, using this coagulant is not recommended, because it can not meet the dye removal requirements for recycling processes.

Addition of calcium hydroxide alone

Figure (15) indicats that calcium hydroxide is ineffective for dye removal of Sulphur Black solution in water. Even large amounts of calcium hydroxide added did not improve the dye removal, but rather causing an increase in the turbidity of the solution. While, the addition of calcium hydroxide with ferrous sulphate improves its ability for dye removal, as mentioned before.

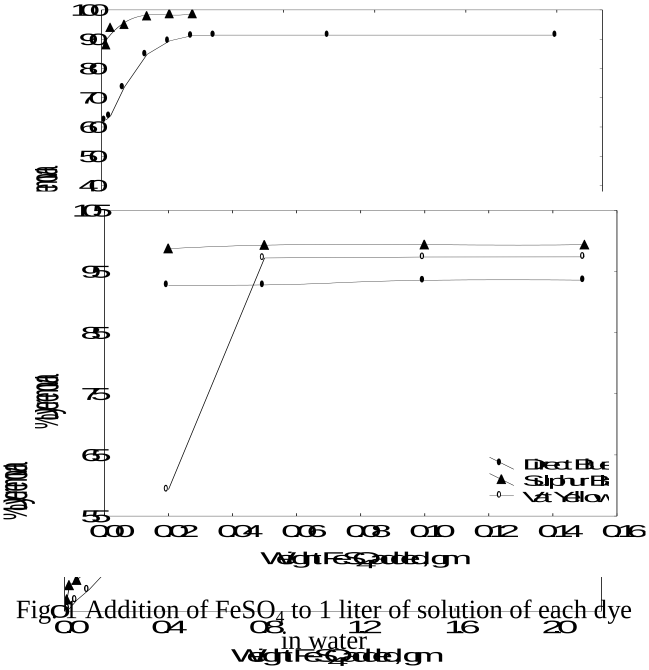


Fig. 1 Addition of $FeSO_4$ to 1 liter of solution of each dye in water

Fig. 2 Addition of $FeSO_4$ to 1 liter of solution mixture of dyes in water

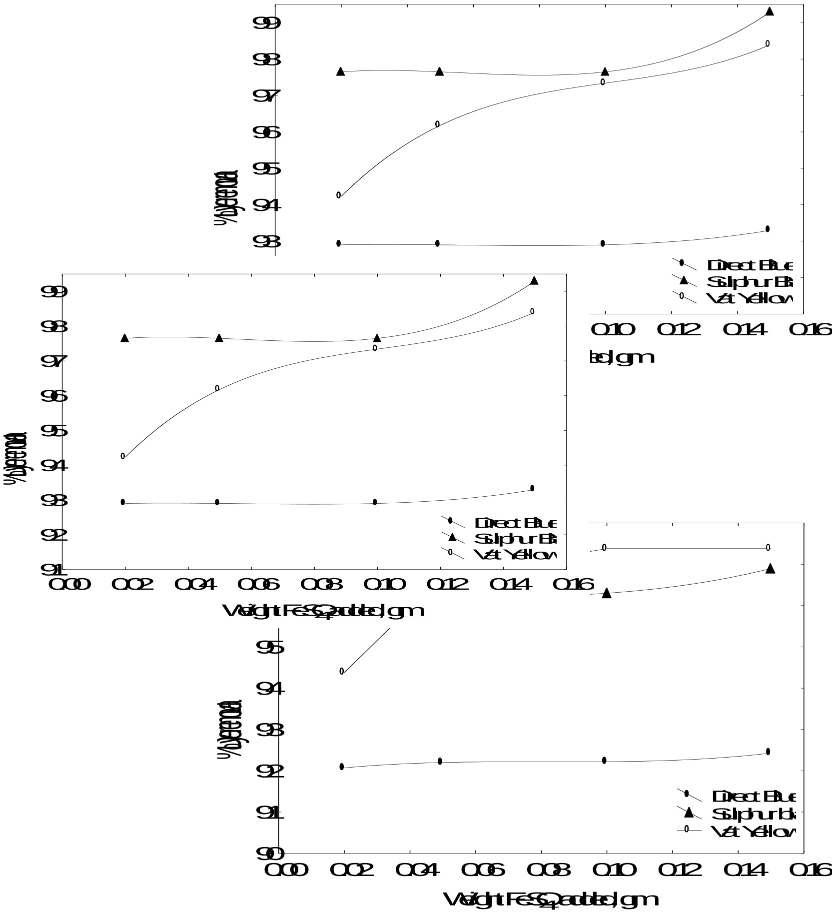


Fig. 3 Addition of $FeSO_4$ + (0.05 gm) $Ca(OH)_2$ to 1 liter of solution of each dye in Water

Fig. 4 Addition of $FeSO_4$ + (0.1 gm) $Ca(OH)_2$ to 1 liter of solution of each dye in water

Fig. 5 Addition of $FeSO_4$ + (0.05 gm) $Ca(OH)_2$ to 1 liter of solution mixture of dyes in water

Fig. 6 Addition of $FeSO_4$ + (0.1 gm) $Ca(OH)_2$ to 1 liter of solution mixture of dyes in water

Fig. 9 Addition of $Fe_2(SO_4)_3$ + (0.05 gm) $Ca(OH)_2$ to 1 liter of Sulphur Black dye solution

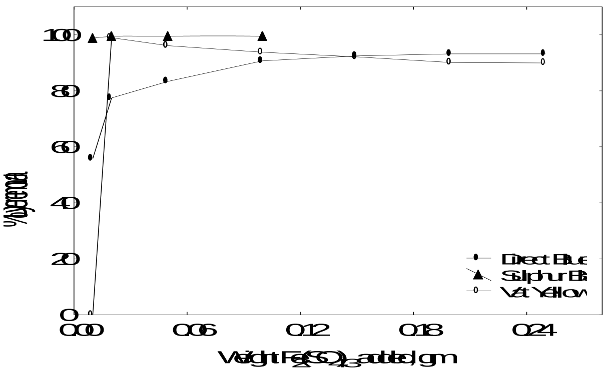
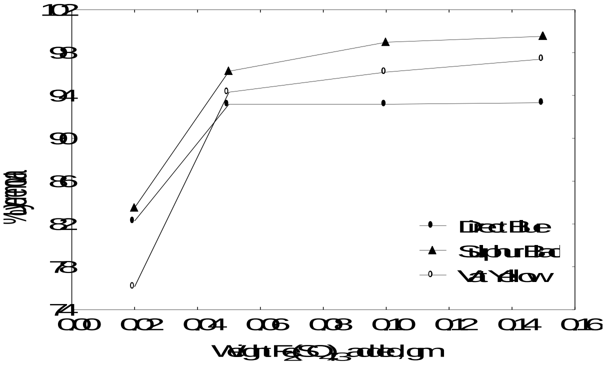


Fig. 10 Addition of $Fe_2(SO_4)_3$ + (0.1 gm) $Ca(OH)_2$ to 1 liter of solution of each dye in water

Fig. 11 Addition of $Fe_2(SO_4)_3$ + (0.5 gm) $Ca(OH)_2$ to 1



liter of solution of each dye in water

Fig. 7 Addition of $Fe_2(SO_4)_3$ to 1 liter of solution of each dye in water

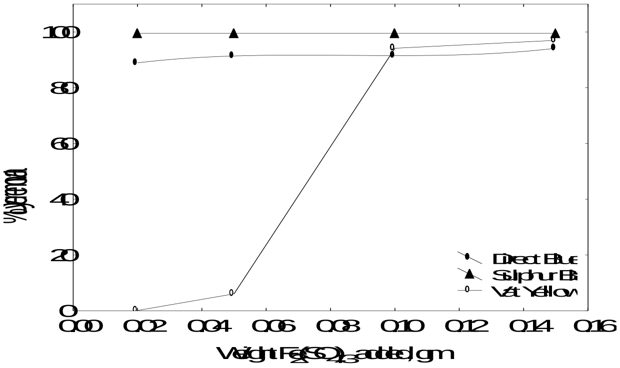


Fig. 8 Addition of $Fe_2(SO_4)_3$ to 1 liter of solution mixture of dyes in water

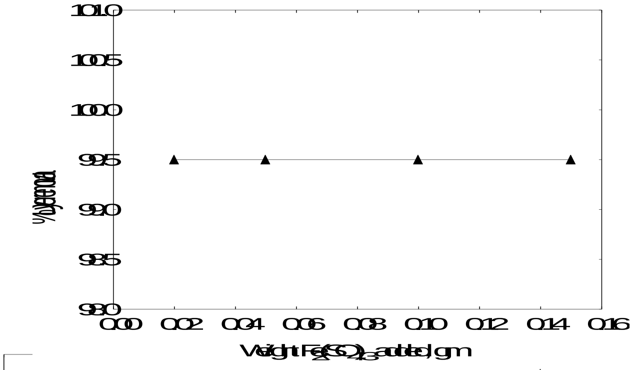
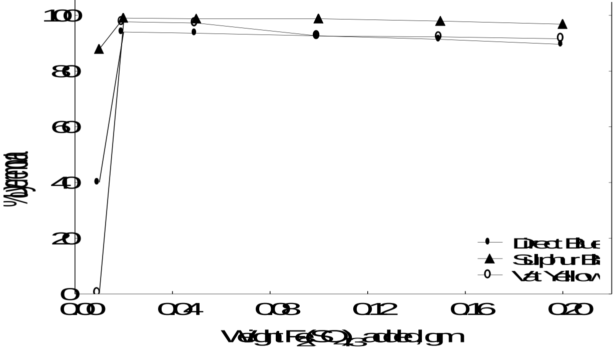
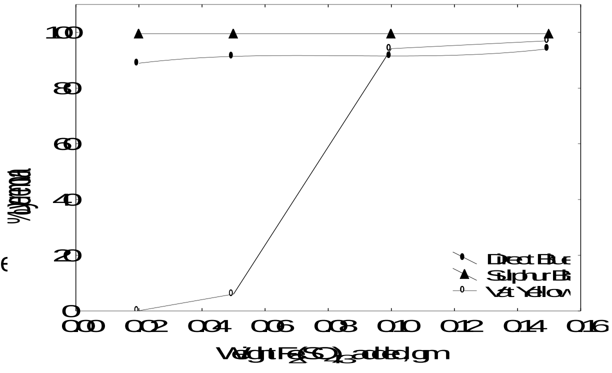


Fig. 12 Addition of $Fe_2(SO_4)_3$ + (0.1 gm) $Ca(OH)_2$ to 1 liter of solution mixture water of dyes in





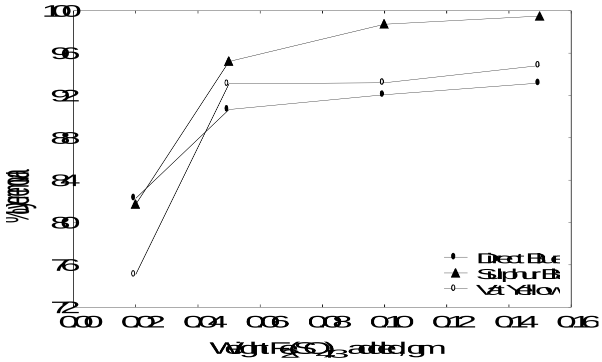


Fig. 13 Addition of $Fe_2(SO_4)_3$ + (0.5 gm) $Ca(OH)_2$ to 1 liter of solution mixture of Dye in water

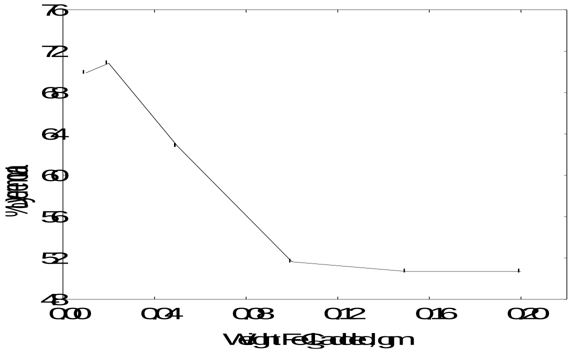


Fig. 14 Addition of $FeCl_3$ to Direct Blue Dye in Water

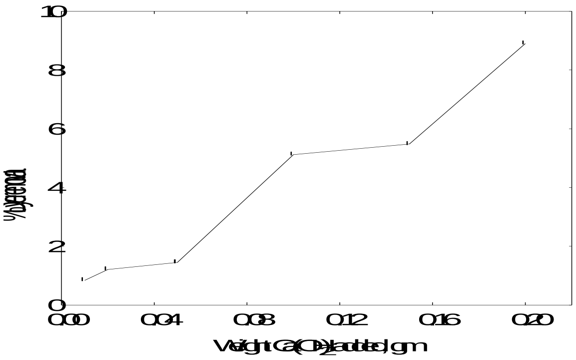


Fig. 15 Addition of $Ca(OH)_3$ to Sulpher Black dye in solution

CONCLUSIONS

1. Nearly complete dye removal can be achieved by the addition of ferrous sulphate to individual aqueous solutions of direct blue and sulphur black, while vat yellow is hardly affected. Thus ferrous sulphate is not recommended for treatment of a mixture of the three dyes considered.
2. The best coagulant dose for treating a solution of the three dyes considered, here, is 0.15 gm/l $FeSO_4$ and 0.05 gm/l $Ca(OH)_2$ to a colour removal of 93%, 99% and 98% for direct blue, sulphur black and vat yellow respectively .
3. The best dose of ferric sulphate to achieve 94%, 99% and 98% dye removal for direct blue, sulphure black and vat yellow respectively is 0.02 gm/l.
4. Ferric chloride is not recommended for the concentration reduction of these dyes.

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