



Efficient Coupling Optimization of Coagulants with the Adsorbent for Depollution of Dyes Manufacturing Effluent

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Abstract: Dyes manufacturing plant effluent was treated via coagulation as well as combined process of coagulation and adsorption to investigate the depollution potential of the coagulants used (FeCl_3 , FeSO_4 and lime) with and without the application of adsorbent Powdered Activated Carbon (PAC). The efficiency of the process was checked via effluent quality parameters such as Color, COD, Turbidity and TSS. The experimental results showed that single coagulation process did not prove to be effective treatment option as indicated by lower removal of the given parameters. Whereas during coupled process of coagulation and adsorption, combination of FeCl_3 -lime and FeCl_3 -PAC were found to be more effective for the effluent treatment than those of FeSO_4 -lime and FeSO_4 -PAC. In the coupled processes, induction of FeCl_3 -PAC resulted in overall reduction of 65%, 52%, 50% and 72% for color, COD, turbidity and TSS respectively, as against 56% and 36%, 49% and 27%, 47% and 23% and 50% and 20% obtained with FeCl_3 -lime and FeSO_4 - FeCl_3 -lime-PAC severally. These results suggested that the given coupled process could be a good match for the treatment of dyes manufacturing effluent.

Keywords: Coupling, Coagulation, Adsorption, Powdered Activated Carbon, Dyes effluent

1. INTRODUCTION

The disposal of dyes and pigments' effluents particularly without the required treatment is a major problem for such industries. These industries utilize high amount of water for processing and cleaning operations and discharge highly toxic and polluted effluent to rivers and sea (Namsivayam. *et al.* 2001). It has been reported that such effluents contain high concentration of leftover toxic dyes, metals, organic materials, toxic chemicals and acids making them typical oxygen-consuming wastewaters (Hsu, *et al.*, 1997). However, the effluent characteristics vary according to the nature of the product being manufactured. Direct disposal of these untreated effluents creates serious problems for marine life in particular and the environment in general (Gupta *et al.*, 2002). Various methods have been employed for wastewater treatment in order to reduce their harmful effects, which include Coagulation, Flocculation, Adsorption, Fenton reaction, Ultra filtration, Nano filtration, Reverse osmosis, Oxidation and Bioremediation. Since dyes' effluents contain high range of toxic dyes and suspended solids, the filtration technology might not be suitable as processing of these effluents could damage the membranes as well as filtration media, which will probably lead to problems of fouling and blockage. Fenton reaction is the advanced technology for dyes wastewater treatment, but it can be a costly choice due to higher cost as well as consumption of hydrogen peroxide used during the process (Gogate *et al.*, 2004). Coagulation is perhaps

the most suitable and economical treatment process for such wastewaters. The efficiency of coagulation varies with regard to the nature of effluent being dealt with, nature and dosage of coagulants being used as well as process operating conditions. In addition, coagulation process has been reported as being effective for the removal of organic compounds from the effluents thus causing parallel decrease in the effluent COD or BOD, color and suspended solids (Verna *et al.*, 2012). Adsorption is also an effective technique foreffluent treatment particularly for reduction of dyes, color, COD, BOD and other organic substances. Adsorption capacity depends upon adsorbent porosity, chemical structure, surface area, density and particle size. At commercial level, powdered activated carbon (PAC) is widely reported as an effective adsorbent for effluent treatment; however, it can yield still better results when used with an efficient coagulant during the treatment process, (Jiuhui , *et al.*, 2008). The aim of this research work was to optimize the coupling of experimentally efficient coagulant with the adsorbent PAC for the possible enhancement of effluent depollution efficiency.

2. MATERIALS AND METHODS

Raw effluent samples were collected from the discharge points of dyes manufacturing plant that included dyes manufacturing effluent as well as complex-nature effluent, which was the mixture of dyes, pigments, pharmaceutical chemicals, textile chemicals and emulsion plant products residue. Analytical grade coagulants such as Ferric Chloride (FeCl_3), Ferrous

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Sulfate (FeSO_4), lime and the adsorbent powdered activated carbon (PAC) were purchased from Al- Mehran Chemicals Limited, Karachi.

Dyes manufacturing and complex nature effluents treatment by simultaneous-coagulation-adsorption process

Dyes and complex nature effluents were treated via simultaneous coagulation-adsorption process in jar test system using FeCl_3 -PAC and FeSO_4 -PAC and mixed coagulants-PAC with a fixed dosing of 1.2-0.8 g respectively. The process was carried out under similar conditions as observed earlier. After the treatment process was over, the effluent samples were first filtered and then analyzed for quality characteristics as per the standard protocols. The treatment of effluent samples was carried out at varied pH in between 6.5 and 10.5 and was adjusted by either 1N NaOH or 1N HCl prepared solution.

Equipment

The effluent quality parameters such as pH, COD, color, turbidity and TSS were analyzed prior and after the treatment as per the standard laboratory protocols, (Singh, *et al.*, 2005). pH of effluent samples was directly measured using pH meter (Hach, USA). COD was determined via dichromate COD method using standard COD vials in DR-2000 Spectrophotometer (Hach, USA). The Effluent samples were diluted for 10 times with double distilled water before 2 ml of the diluted sample were poured into COD vial, inverted for 30 seconds and placed in COD Reactor (TR-320, Merck, USA) at 148°C for 2 hr for digestion of the prepared sample. COD, Color, turbidity and TSS of effluent samples were measured through absorptometric method using DR-2000 Spectrophotometer at their specific wavelengths such as 620nm, 455nm, 450nm and 810 nm respectively. In addition, metals analysis of the effluent samples was also carried out using EPA mild digestion method comprising of sample acidification, evaporation, pH maintenance and digestion. After the sample digestion process, concentration of metals such as iron, copper zinc were measured via DR-2000 Spectrophotometer using analytical grade reagents viz Iron Phenanthroline, Copper Form 1 bicinchoninat and Zincon at their specific wavelengths such as 510nm, 560nm and 620nm respectively. (Georgious, *et al.*, 2003).

3. RESULTS AND DISCUSSIONS

The effluent samples of various processing plants of Clariant Pakistan Limited were analyzed after their treatment via single and coupled processes of coagulation and coagulation-adsorption using mixed combination of selected coagulants and the adsorbent. In simple coagulation process, the induction of FeSO_4 -lime combination with the effluent samples yielded that

effluents of Dyes, Binder and Disposal (complex nature) were probably too toxic and strong for these coagulants to reduce their pollutant loading to be at par with the NEQS. The results obtained via this process showed that parametric values for COD, TSS, Color and turbidity were still higher than the NEQS after the end of the single coagulation process suggesting that the simple coagulation with the given pair of coagulants for the specified time period was not enough to treat such highly polluted effluents probably due to the non-separation of elementary bonding of the pollutants in the samples. However, concentration of metals such as copper, zinc and chromium showed decrease except iron, which was expected to show a little increase due to the addition of ferrous compounds as coagulants. Overall, single coagulation process yielded treatment efficiency in the range of 40-80% for plants effluent. From laboratory analysis of industrial untreated and treated effluents, it was concluded that TDS, Electrical conductivity, COD, Color, turbidity and TSS values were found higher in dyes, binder and disposal (complex nature) effluents (Tables 1 and 2). For the treatment of pigments and Textile chemical plant effluent, single coagulation process was found best.

Table 1. Analysis of Raw Effluent Samples of Processing Plants of Clariant Pakistan Limited

Parameters	Dyes Chemicals	Binder Disposal	Emulsion	Pigments	Textile
pH	6.7	10.2	6.9	8.5	8.0
COD	123	1385	129	1030	994
Color	1350	43900	744	4180	4760
Turbidity	8000		780		265
	128		860		
TSS	320	1340	115	215	330

Table 2. Treatment of Plant Effluents through Industrial Coagulation Technique Using FeSO_4 -Lime

Parameters	Dyes Chemicals	Binder Disposal	Emulsion	Pigments	Textile
pH	5.8	7.9	7.3	7.6	6.5
COD	47	839	44	550	555
Color	820	14200	632	1060	1428
Turbidity	2700		40		150
	90		490		
TSS	70	610	68	80	45

From the earlier results it was concluded that dyes and complex nature effluents were probably refractory type of effluents to allow the removal of pollutants from them by the given treatment. Therefore, further experimental study was conducted to attempt an increase in the efficiency of effluent treatment. Dyes effluent samples were now treated via mixed coagulation process using combined coagulant pairs of

FeCl_3 -lime and FeSO_4 -lime separately. From this treatment analysis it was found that TDS, Salinity and EC values were increased in both the processes, with maximum increase was registered via FeSO_4 -lime treatment. pH was observed to decrease during the course of both processes indicating the occurrence of chemical reaction between the coagulants and the sample contents. The coagulant pair of FeCl_3 -lime and FeSO_4 -lime influenced removal of COD by 49% and 27%, color by 56% and 36%, turbidity by 47% and 23% and TSS by 50% and 20% respectively (**Fig.1**).

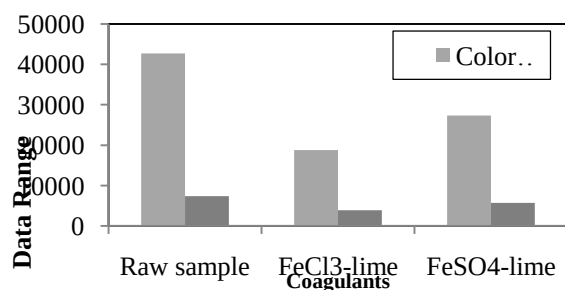


Fig.1 Treatment of dyes effluent via coagulation process for reduction of effluent pollutants

These results are comparable with those obtained by Georgious D *et al*, (2003), Selcuk H, *et al*, (2005) and Joo D.J *et al*, (2007) who reported in their work COD and color removal of around 60% and 60% from cotton textile industry wastewater with coagulant dosing of 0.8 g/l.

Similar treatment was accorded to the complex nature effluent samples, which were treated via coagulation process using coagulant pairs of FeCl_3 -lime and FeSO_4 -lime at dosing rate of 1.2-0.80g/l. The results obtained were slightly different than the earlier ones with TDS, salinity and EC showing increase during the course of effluent treatment with coagulant pair of FeCl_3 -lime as compared to the treatment with FeSO_4 -lime in which slightly lower values for these parameters were recorded. The induction of coagulant pairs of FeCl_3 -lime and FeSO_4 -lime caused reduction in the effluent COD by 40% and 26%, color by 54% and 40%, turbidity by 31% and 29% and TSS by 64% and 56% severally (**Fig.2**).

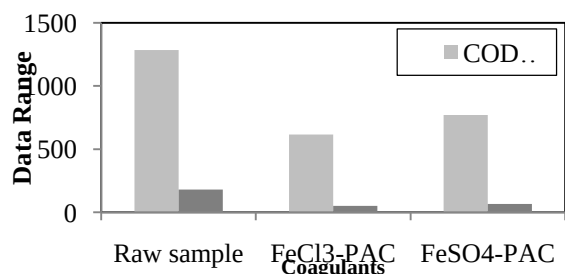


Fig.2 Treatment of complex nature effluent via coagulation process for reduction of effluent pollutants

These results implied that coagulant pair of FeCl_3 -lime was the better coagulant pairing than FeSO_4 -

lime likely due to the highly reactive nature of FeCl_3 coagulant, which readily forms oxide compounds. The increase observed during the course of effluent coagulation in the concentration of TDS, salinity and EC could be associated with the increase in the concentration of iron salts, the chemical reaction of which with reactive contents contained in the dyes effluents was probably the basic reason behind the reduction of COD and color. Due to complex nature of the disposal effluent, application of the coagulation processes transpired in lesser reduction of the concentration of organic pollutants.

In order to improve the treatment efficiency, dyes effluent was further investigated when it was treated via simultaneous coagulation and adsorption (SCA) process using the coagulants used earlier with the adsorbent powdered activated carbon (PAC). Two combinations of FeCl_3 -PAC and FeSO_4 -PAC were applied with a dosing 1.2-1.0 g/l. The results obtained with this treatment suggested that combination of FeCl_3 -PAC yielded better results in terms of effluent depollution than FeSO_4 -PAC when COD, color, turbidity, TSS, copper and zinc concentrations were reduced by 52%, 65%, 50%, 72%, 30% and 57% as against 40%, 60%, 42%, 65%, 20% and 13% respectively. The 75% increase in the concentration of iron was recorded as higher during the process with FeCl_3 -PAC combination as compared to 55% observed during the process run with FeSO_4 -PAC combination (**Fig.3**).

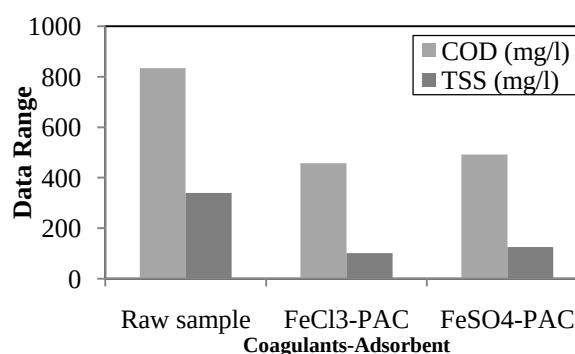


Fig.3 Treatment of dyes effluent via simultaneous coagulation-adsorption process for reduction of effluent pollutants

These results implied that combination of the selected coagulants with PAC enhanced the treatment efficiency due to the synergistic nature and higher reactivity profile of this treatment protocol.

Complex nature effluent samples were also treated by SCA process using the same pairing of FeCl_3 -PAC and FeSO_4 -PAC. The results of this treatment transpired that FeCl_3 -PAC yielded higher values of TDS (42% / 8%), salinity (46% / 8%) and EC (40% / 7%) than that obtained with the combination of FeSO_4 -PAC (**Fig. 6**). The pH decrease (65%) was also lower by around 13% during SCA process run with FeCl_3 -PAC as

compared to that observed during coagulation process with no adsorbent. As for other parameters, the effluent treatment with FeCl_3 -PAC and FeSO_4 -PAC resulted in the removal of COD by 45% and 41%, color by 58% and 46%, turbidity by 40% and 37%, TSS by 70% and 63%, copper by 89% and 91% and zinc 50% and 88% respectively. Increase in the iron concentration in both treatment processes of FeCl_3 -PAC and FeSO_4 -PAC was around 63% and 50% respectively (**Fig.4**). The multivalent Fe^{3+} cations of FeCl_3 compound possibly coordinated with the anions present in the effluent resulting in complexation of the effluent, since complex nature effluent already contains high concentration of dye compounds and toxic chemicals making it almost non-responsive to any given treatment.

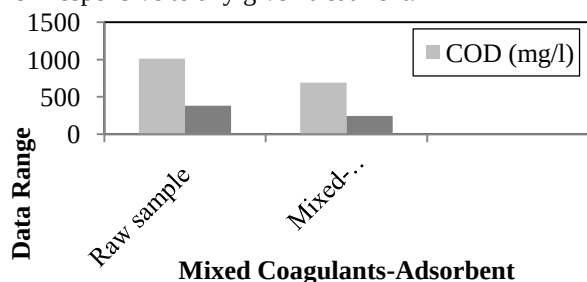


Fig4 Treatment of complex nature effluent via simultaneous coagulation-adsorption process for reduction of effluent pollutants

Dyes effluent sample was also treated with all the selected coagulants FeCl_3 , FeSO_4 and lime to evaluate their combined effect on the effluent treatment. The results showed that TDS, Salinity, EC and pH were decreased by 17%, 17%, 16% and 14% respectively. The concentration of copper and zinc was reduced by 94% and 53%. The concentration of iron was increased by 22%. This treatment reduced the concentration of COD, color, turbidity and TSS by 40%, 52%, 33% and 42% severally, which meant that this treatment enhanced the removal efficiency for organic pollutants by 53% (**Fig.5**). This was likely caused by the induction of all the selected coagulants, which perhaps prompted in the formation of solid metal hydroxide precipitates resulting in the effective removal of pollutants from the effluent.

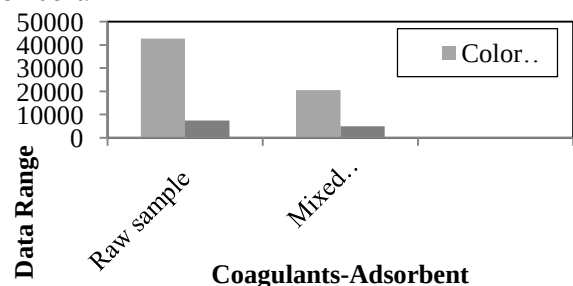


Fig.5 Treatment of dyes effluent via simultaneous coagulation-adsorption process for reduction of effluent pollutants

4.

CONCLUSION

The analytical results of this study revealed that dyes, complex nature and binder effluents were a

major problem in terms of their treatment. Simple coagulation process was not effective for the treatment of dyes and complex nature effluents. It was found that FeCl_3 -lime and FeCl_3 -PAC were more effective in effluent treatment than FeSO_4 -lime and FeSO_4 -PAC. In dyes effluent treatment, FeCl_3 -lime, FeCl_3 -PAC and mixed coagulants-PAC reduced COD by 49%, 52% and 40%, color by 56%, 65% and 52%, turbidity by 47%, 50% and 33%, and TSS by 50%, 72% and 42% respectively. In complex nature effluent treatment, FeCl_3 -lime, FeCl_3 -PAC and mixed Coagulants-PAC reduced COD by 40%, 45% and 32%, color by 54%, 58% and 46%, turbidity by 31%, 40% and 20%, TSS by 64%, 70% and 35% severally. When complex nature effluent was treated through FeCl_3 -PAC at different pH variations, best results were found at pH 10.5 by reducing COD (60%), color (88%), turbidity (88%) and TSS (98%). These results suggested that effluent treatment process efficiency varied according to the effluent nature. Combined processes of coagulation-adsorption were more suitable to reducing concentration of copper and zinc metals. It is therefore recommended that for the effective treatment of dyes and complex nature effluent, combined process of coagulation-adsorption should be implemented. In addition, FeCl_3 coagulant should be coagulation phenomenon.

5.

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