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REMOVAL OF COLOR FROM SYNTHETIC TEXTILE DYE STUFF BY ADSORPTION ONTO PREFORMED FLOCS

N. MUNILAKSHMI, M. SRIMURALI & J. KARTHIKEYAN

Department of Civil Engineering, S.V.U. College of Engineering, S.V. University, Tirupati, India

ABSTRACT

This paper presents the results of colour removal from aqueous solutions of textile dye namely C.I.Acid blue 45 by adsorption onto preformed flocs of Alum, Ferric Chloride and Ferrous Sulphate. Agitated non-flow batch kinetic and isothermal equilibrium experiments were conducted and the experimental results revealed the potential of preformed flocs in the removal of colour of dye. Dye responded favourably and exhibited good to excellent colour removal at pH=4 with respective to dosage and at pH=10 with respective to contact time. Isothermal equilibrium adsorption data fitted well to Langmuir model representing formation of a unimolecular monolayer of dyes over a homogeneous surface of uniform energy.

KEYWORDS: Adsorption, Alum, Colour Removal, Ferric Chloride, Ferrous Sulphate, Preformed Flocs

INTRODUCTION

Dyes are synthetic organic aromatic compounds that are molecularly dispersed and bound to the substrates by intermolecular forces and have high application potential in the industrial sector as colouring material. The textile industry ranks first in the consumption of the dyes and effluents released from textile dyeing are intensely coloured and pose serious problems to various segments of the environment. Presence of colouring matter in significant quantities in receiving water would not only reduce light penetration and photosynthetic activity, but would also render their appearance unaesthetic (Karthikeyan 1988).

Therefore; it becomes imperative that colour be removed from dye effluents before disposal of the effluent. Treatment processes such as physical, physicochemical, chemical and biological methods have been investigated and proved to be effective but to varying degree of success. Adsorption and chemical treatment processes have shown promise as a practical and economic process for treatment of textile waste, especially for colour removal.

Among several methods investigated for colour removal from textile dyestuffs, coagulation and adsorption appears to be better suited; however each method has its own merits and demerits. Combining the merits of both these methods, the present investigation was conducted to remove colour of synthetic textile dyestuff employing preformed flocs of Aluminium Sulphate, Ferric Chloride and Ferrous Sulphate .

MATERIALS

All the glass ware used in this study was of 'Pyrex' quality and analytical grade (AR) chemicals were used throughout the study.

EXPERIMENTATION

Adsorbent

Preformed flocs of Alum, Ferric Chloride and Ferrous Sulphate.

Adsorbate

Stock solution of C.I.Acid blue 45 (Anthraquinone) was prepared by dissolving 50mg in 1000ml distilled water.

Adsorption Experiment

Varying doses of coagulants were dissolved in distilled water and was maintained at different pH conditions varying from 2 to 13 and observed for floc density. Floc density of preformed flocs was measured in terms of turbidity, and the dose and pH in both acidic and basic medium which produced highest turbidity were adopted as favourable dose and favourable pH. Agitated, non-flow batch sorption studies were conducted by bottle point method using reagent bottles of 250ml capacity. To a 100ml of test dye solution of 50mg/l concentration taken in the reagent bottle, premeasured quantity of preformed floc was added and the resultant mixture was agitated in a horizontal shaker at a rate of 125 rpm for varying time intervals of 1,3,5,7,9,12,15,30,45 and 60 minutes. The bottles were withdrawn from the shaker at designated time intervals and the reagent bottles were kept undisturbed for 4 hours for sedimentation at the end of which, samples were withdrawn by carefully pipetting out 10ml portion and analyzed for colour content remaining in the test dye solution. The time at which maximum removal of colour takes place and no further significant difference in colour removal occurs from that time was taken as the equilibrium contact time and used in all further studies. Equilibrium Isothermal studies were conducted by adding varying doses of preformed flocs such as 100,200,300,400,500,600,700,800,900 and 1000mg/l to the test dye solution and contacted for equilibrium time. The residual colour was analyzed with a Spectrophotometer (Systronics spectrophotometer 106) by measuring OD/% T at respective maximum wavelength of dye solution and computing concentrations from the calibration curve. To evaluate colour removal, concentrations were measured before and after the experiment.

RESULTS AND DISCUSSIONS

Favourable dose of coagulants and favourable pH of the solution, where floc density is more were determined in terms of solution turbidity and the results are presented in Table 1. All subsequent experiments were performed employing favourable dose and at favourable pH.

Table 1: Favourable pH and Favourable Dose of Coagulants

Coagulant	Favourable pH		Favourable Dose, mg/100ml
	Acidic Medium	Basic Medium	
Alum($Al_2(SO_4)_3.18\ H_2O$)	4.0	10.0	1000
Ferric chloride($FeCl_3$)	4.0	10.0	1000
Ferrous sulphate($FeSO_4$)	4.0	10.0	500

Kinetics of Colour Removal by Preformed Flocs

The length of the time required to reach equilibrium of sorption reaction is important to determine the capacity of the sorbent with respect to solute removal. Thus, the results of the kinetic studies are the basis for all additional batch studies. Sorption kinetics also influence the shape of the adsorption profile, fast kinetics will result in a steep profile (Venkata Mohan,1997).

Effect of Contact Time

The influence of contact time vis-à-vis kinetics of colour removal by preformed flocs is presented in Fig.1 and Fig.2 for pH of 4 and pH of 10. It may be observed from figures that the rate of colour removal was rapid initially. The rate leveled off gradually and then attained a more or less constant value (equilibrium) beyond which there was no significant increase in colour removal. The time required to attain equilibrium was 15 minutes.

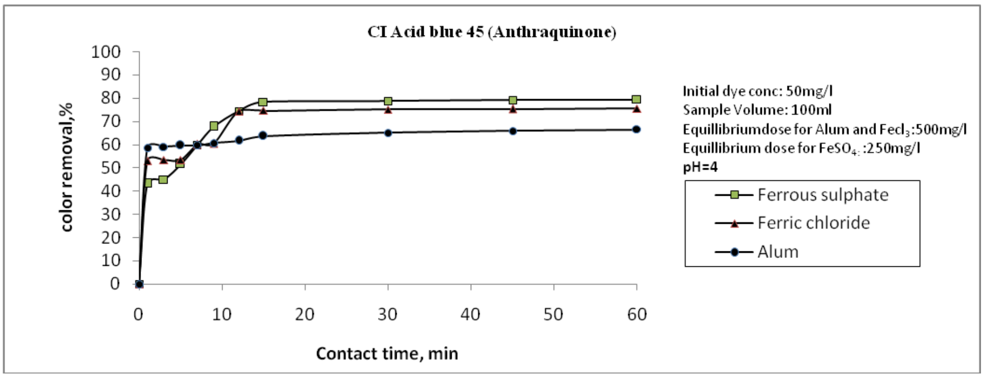

Figure 1: Kinetics of Removal of Colour (C. I. Acid Blue 45) onto Preformed Flocs at Different Contact Times

From fig.1, it was observed that among all the preformed flocs, Ferrous sulphate accomplished high removal and this is followed by Ferric chloride and Alum at pH=4.

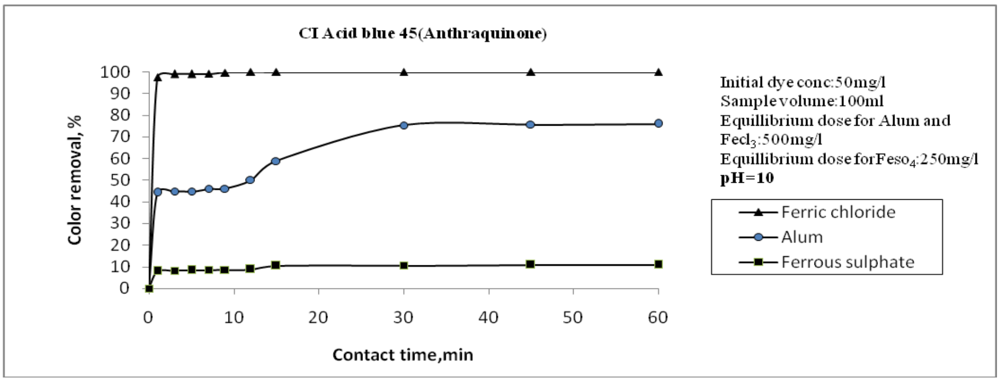

Figure 2: Kinetics of Removal of Colour (C. I. Acid Blue 45) onto Preformed Flocs at Different Contact Times

From fig.2, it was observed that among all the preformed flocs, Ferric chloride accomplished high colour removal (100%)and this is followed by Alum and Ferrous sulphate at pH=10.

Equilibrium Isothermal Adsorption by Preformed Flocs

Equilibrium isothermal adsorption studies were conducted by varying the amount of floc dose from 100 to 1000 mg/l and the results are presented graphically as % color removal at different doses of flocs for C.I.Acid blue 45 at pH=4 and pH=10 , as shown in fig.3 and fig.4.

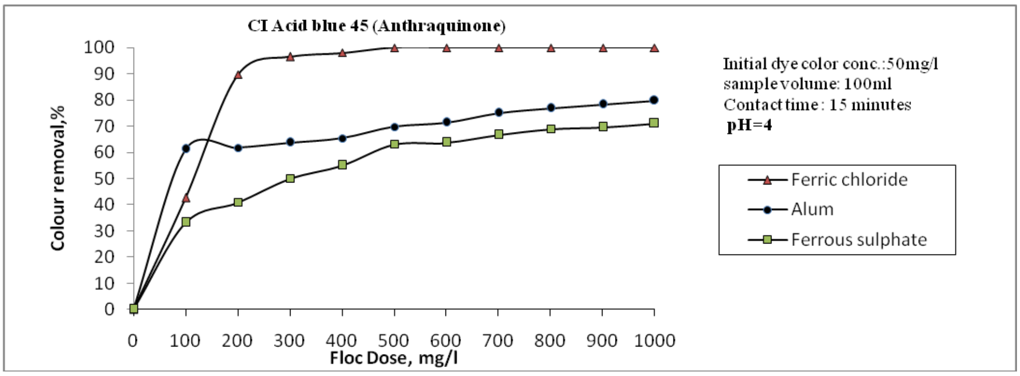

Figure 3: Response of C. I. Acid Blue 45 to Preformed Flocs at Different Dose

From fig.3 it shows that C.I. Acid blue 45 responded favorably to preformed flocs of all coagulants and the removal range increases in the order of coagulant Ferrous sulphate, Alum and Ferric chloride at pH of 4**.**

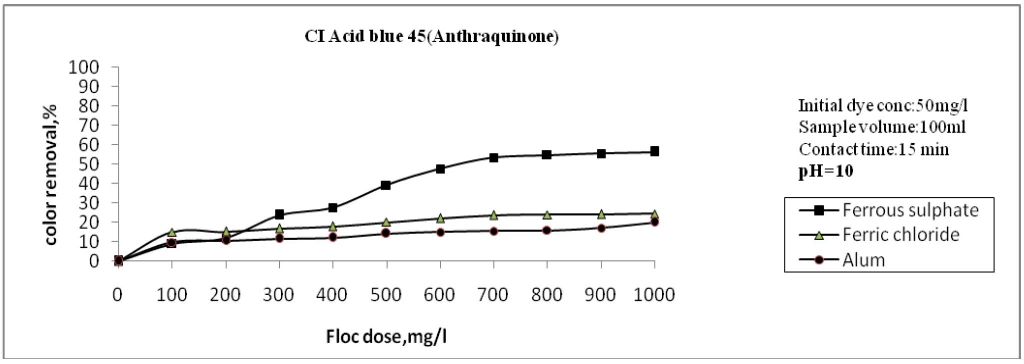

Figure 4: Response of C. I. Acid Blue 45 to Preformed Flocs at Different Dose

From fig.4, it shows that C.I. Acid blue 45 responded to preformed flocs of all coagulants and the removal range increases in the order of coagulant Alum, Ferric chloride and Ferrous sulphate at pH of 10**.**

Equillibrium Study

Adsorption isotherms are mathematical models that describe the distribution of the adsorbate species among liquid and adsorbent, based on a set of assumptions that are mainly related to the homogeneity/ heterogeneity of adsorbents, the type of coverage and possibility of interaction between the adsorbate species. Adsorption data are usually described by adsorption isotherms, such as Langmuir, Freundlich and Temkin isotherms. These isotherms relate dye uptake per unit mass of adsorbent, qe, to the equilibrium adsorbate concentration in the bulk fluid phase C_e.

The Langmuir Isotherm

The Langmuir model (Senthil and kirthika 2009) is based on the assumption that the maximum adsorption occurs when a saturated monolayer of solute molecules is present on the adsorbent surface, the energy of adsorption is constant and there is no migration of adsorbate molecules in the surface plane. The linear form of Langmuir isotherm is given by

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{q_m K_L}\frac{1}{C_e}$$

Where q_m and K_L are the Langmuir constants, representing the maximum adsorption capacity for the solid phase loading and the energy constant related to the heat of adsorption respectively. The plot between $1/q_e$ and $1/C_e$ is as shown in the fig.5.

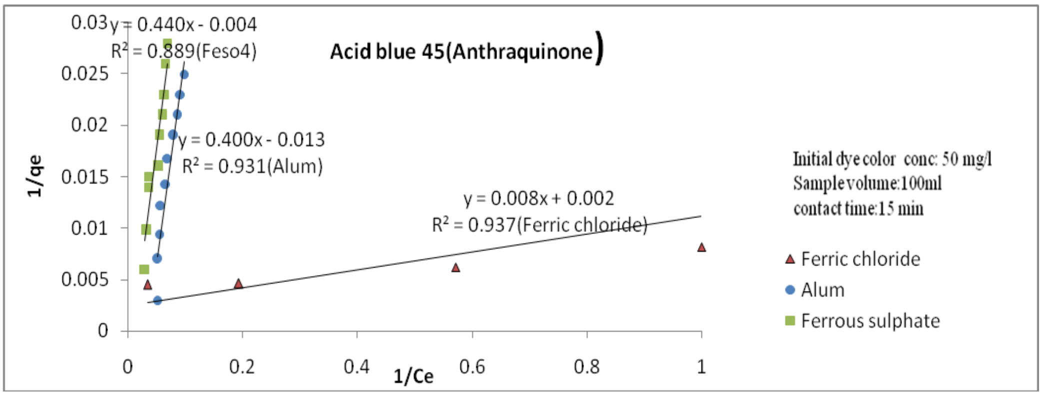

Figure 5: Langmuir Adsorption Isotherm

From the figure.5, it states that the isotherm data fits the Langmuir equation well, as it is straight line. (Sridhar,2006).

The Freundlich Isotherm

The Freundlich isotherm model (Senthil and kirthika 2009) is an empirical relationship describing the adsorption of solutes from a liquid to a solid surface and assumes that different sites with several adsorption energies are involved. Freundlich adsorption isotherm is the relationship between the amounts of dye adsorbed per unit mass of adsorbent, qe, and the concentration of the dye at equilibrium, C_e.

$$q_e = K_f \, Ce^{1/n}$$

The logarithmic form of the equation becomes

$$\text{Log } q_e = \log K_f + \frac{1}{n} \log C_e$$

Where k_f and n are the Freundlich constants, the characteristics of the system. K_f and n are the indicators of the adsorption capacity and adsorption intensity, respectively. The ability of Freundlich model to fit the experimental data was examined. Plot between $\log C_e$ and $\log q_e$ was drawn to generate the intercept value of k_f and the slope of n as shown in the Fig.6. .

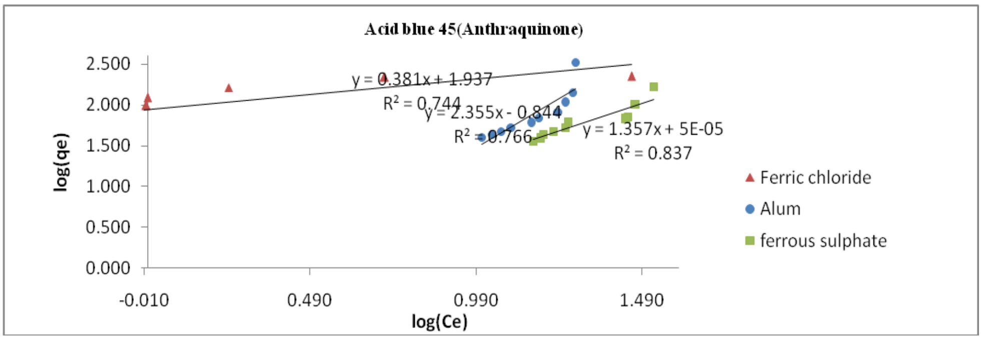

Figure 6: Freundlich Adsorption Isotherm

The values of sorption capacities and coefficient of correlation (R^2) for various sorbents and equilibrium models are as shown in the Table.2.

Table 2: Isotherm Models Constants and Correlation Coefficients for Adsorption of Dye from Aqueous Solution

Adsorbent	Langmuir Isotherm			Freundlich Isotherm		
	$q_{m,}$ (mg/g)	K_L (L/mg)	R^2	K_f	n	R^2
Alum	76.92	0.0325	0.931	6.98	0.425	0.766
Ferric chloride	500	0.25	0.937	86.49	2.62	0.744
Ferrous sulphate	250	0.009	0.889	1.00	0.737	0.837

From Table.2 above, The values of coefficient of correlation (R^2) was obtained as 0.931,0.937 and 0.889 for Alum, Ferric chloride and Ferrous sulphate giving a best fit for Langmuir equation compared to Freundlich Isotherm. The monolayer capacity (q_m) and adsorption energy K_L calculated from the linear plot are given the in the same table.

It follows from the data the equilibrium adsorption of dye onto Alum, Ferric chloride and Ferrous sulphate preformed flocs follows Langmuir isotherm model, which reflects the formation of a monolayer of sorbate over a homogeneous surface of uniform energy and that the adsorbed layer is unimolecular (Sridhar,2006)). It may also be observed that the isotherm fits of Alum and Ferrous sulphate have negative intercepts which indicates that the removal is good at lower concentrations, but not as good, at higher concentrations(Sridhar,2006).

KINETIC STUDY

In order to investigate the controlling mechanism of adsorption processes such as mass transfer and chemical reaction, the pseudo-first-order and pseudo-second-order equations are applied to model the kinetics of dye adsorption onto preformed flocs. The pseudo-first-order rate equation is given as (Senthil and Kirthika,2009):

$$\text{Log}\ (q_e - q_t) = \log q_e - \frac{K_{ad}}{2.303} t$$

Where qt and qe are the amount adsorbed (mg/g) at time t, and at equilibrium respectively and k_{ad} is the rate constant of the pseudo-first-order adsorption process (min^{-1}). To determine the correlation coefficients graph was drawn between log (q_e-q_t) and time as shown in the fig.7.

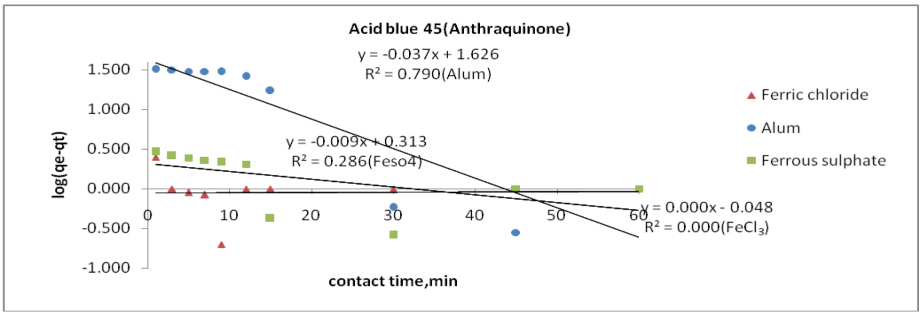

Figure 7: Pseudo-First-Order Reaction for Dye Adsorption onto Preformed Flocs

The pseudo-second order equation is expressed as:

$$\frac{t}{q_t} = \frac{1}{h} + \frac{1}{q_e} t$$

Where $h = kqe^2$ (mg g^{-1} min^{-1}) can be regarded as initial adsorption rate as $t \rightarrow 0$ and k is the rate constant of pseudo-second-order adsorption (g mg^{-1} min^{-1}). The graph between t/qt versus t was drawn as shown in the fig.8, to determine the values of qe, k and h from the slope and intercept of the plot.

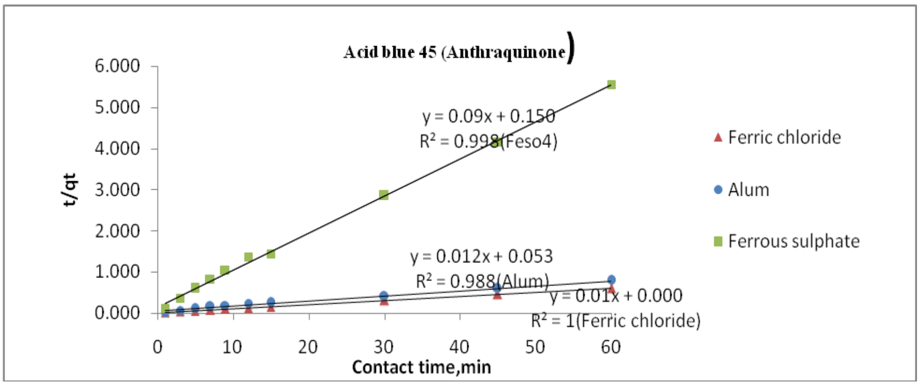

Figure 8: Pseudo-Second-Order Reaction for Dye Adsorption onto Preformed Flocs

Adsorption rate constants qe and correlation coefficients from pseudo-first-order and pseudo-second-order plots are as shown in the table.3 below.

Table 3: Comparision between the Adsorption Rate Constants, qe, Estimated and Correlation Co-Efficents Associated with Pseudo-First-Order and Pseudo-Second-Order Equations

Coagulant	Pseudo-First-Order Equation			Pseudo –Second-Order Rate Equation			
	K_{ad}	qe	R^2	K	q_e	R^2	h
	Min-1	Mg/g		gmg^{-1}	mg/g		$mgg^{-1}min^{-1}$
Alum	0.085	42.26	0.790	0.0027	83.33	0.988	18.86
Ferric chloride	0.0	0.895	0.0	0.00001	100	1.0	0.1
Ferrous sulphate	0.020	2.055	0.286	0.054	11.11	0.998	6.66

From the figures and table.3, it was observed that pseudo-second-order model yields very good straight lines (R^2>0.98) for all coagulants as compared to the plot of pseudo-first order. It is clear that adsorption of dye onto preformed flocs follows second order kinetic model, which relies on the assumption that chemisorptions may be the rate-limiting step (Sridhar rao, 2006).

CONCLUSIONS

The present investigation shows that Ferric chloride is an effective adsorbent for the C.I.Acid blue 45 dye color removal. From kinetic studies, it is observed that the adsorption of dye is very rapid in the initial stage and constant while approaching equilibrium. The percentage removal increases with the increase in adsorbent dosage. Langmuir isotherm model was well fitted to the data showing that the monolayer characteristics and of homogeneous nature.

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