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Adsorptive Removal of Aqeous Disperse Dye by using Flocs

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Abstract: ***Ferric chloride, Aluminium sulphate, and Ferrous sulphate flocs were used as an adsorbent in the decolourisation of aqueous dye C.I. Disperse yellow 3. To evaluate the potentiality of adsorbents, non-flow agitated experiments were carried out to find the equilibrium contact time, optimum equilibrium adsorbent dose. Preformed flocs at pH:: 4 rather than pH:: 10 produced excellent colour removal. Adsorption capacity of flocs of Ferric chloride, Aluminium sulphate and Ferrous sulphate was obtained as 500 mg/g, 333mg/g and 23.3mg/g at pH:4. The equilibrium data sorption follows Langmuir Isotherm and kinetic data follows pseudo second order stating that chemisorptions is the rate limiting step.***

Keywords : Kinetic adsorption studies, equilibrium studies, aqueous solution, preformed flocs of Aluminium Sulphate.

I. INTRODUCTION

Synthetic dyes are widely used in the textile industry in various applications such as dyeing and printing process and is one of the largest consumer of synthetic dyes of about 56% of the total world dyes production per annum (7x 10^5 T) [3]. Dyes even with low concentration causes effect to water ecosystem, further affecting food web. When dye wastewater is discharged into water body, esthetic nature of water body will get affected and also it reduces the passage of sunlight through it which affects the photosynthesis process in aquatic plants [4]. It is necessary to decolourize the wastewater. Dye colour removal by physical treatment, physico chemical process, chemical treatment and biological process seems to be less effective in the decolourization of textile dye effluents; adsorption and chemical treatment had proved to be very effective one. Adsorption treatment is one of the effective processes in the removal of dye from an aqueous solution when compared to other process because of its low cost and reusability [1],[8], [9], [10]. From different methods of investigations for the removal of Colour of textile dyes, coagulation and adsorption methods are effective; with the advantages of these methods, the present investigation were carried out by using flocs of Aluminium sulphate, Ferric chloride and Ferrous sulphate as adsorbents for decolourizing Disperse Yellow 3.

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II. MATERIALS

A. Adsorbent

Flocs of Aluminium Sulphate, Ferric chloride and Ferrous Sulphate were used as adsorbent.

B. Adsorbate

C.I. Disperse Yellow 3 was used as adsorbate solution with concentration of 50 mg/L.

C. Glass ware and chemicals

Pyrex quality glass ware and AR grade chemicals are used in the present study. Thermo UV-VIS -Spectrophotometer was used in this study for the measurement of absorbance readings.

D. Analyses

All the analyses were carried out as per the standard procedures (APPHA).

III. EXPERIMENTAL PROCEDURE

Optimum dose of a coagulant and optimum pH was determined by measuring the turbidity of different coagulant concentration at different pH. Non-flow method of agitated batch sorption studies were conducted with a 100mL of test dye solution of 50 mg/L concentration with an equilibrium dose of preformed floc for varying time intervals of 1min, 3min, 5min, 7min, 9min, 12min, 15min, 30min, 45 and 60 minutes. The bottles were allowed for sedimentation for about 4 hours and then analyzed for absorbance value so as to get percentage removal of colour from that aqueous solution.

IV. RESULTS AND DISCUSSION

Favorable coagulant dose at optimum pH of coagulants are given in Table I.

Table-I: Optimum pH--optimum dose of coagulant

Coagulant	**Optimum pH**		**Optimum dose, mg/100 mL**
	Acidic Medium	**Basic Medium**	
Aluminium Sulphate ($Al_2(SO_4)_3.16 H_2O$)	4	10	1000
Ferric Chloride ($FeCl_3$)	4	10	1000
Ferrous Sulphate ($FeSO_4.7H_2O$)	4	10	500

A. Kinetics of colour adsorption

Efficiency of sorbent can be obtained by conducting sorption reaction experiments at different contact time interval.

A.1. Influence of contact time

The influence of kinetic contact time on the removal of colour by preformed flocs with respect to pH::4 and pH::10 are presented in Fig. 1 and Fig. 2.

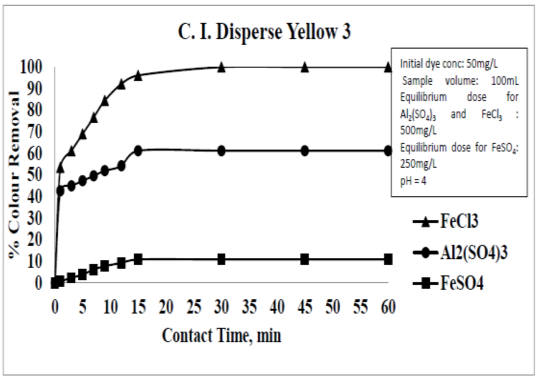

Fig.1 Kinetics of colour removal from aqueous C. I. Disperse Yellow3 solution at pH::4

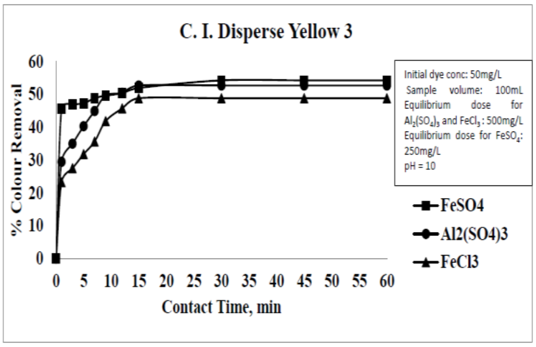

Fig. 2 Dye colour removal from aqueous C.I. Disperse Yellow 3 solution at pH::10 at different contact time

Fig.1 states that the rate of sorptive potential of preformed flocs of Ferric Chloride, Aluminium Sulphate was higher than the preformed flocs of Ferrous Sulphate at pH:: 4. From the Fig. 2, the rate of sorptive uptake by the preformed flocs of Ferrous Sulphate, Aluminium Sulphate was higher than the preformed flocs of Ferric Chloride at pH: 10. From the figures equilibrium contact time is 15 min.

A.2. Equilibrium Isothermal studies by preformed flocs

The percentage of colour removal of C.I. Disperse Yellow3 at different doses of flocs at pH:: 4 and pH::10 are presented in Fig.3 and Fig.4.

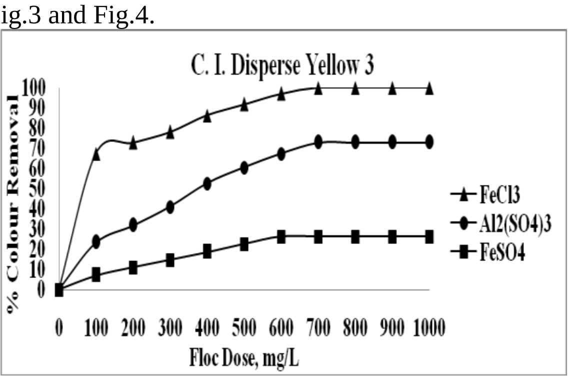

Fig.3. Removal of colour of C.I. Disperse Yellow3 at different doses of flocs at pH::4

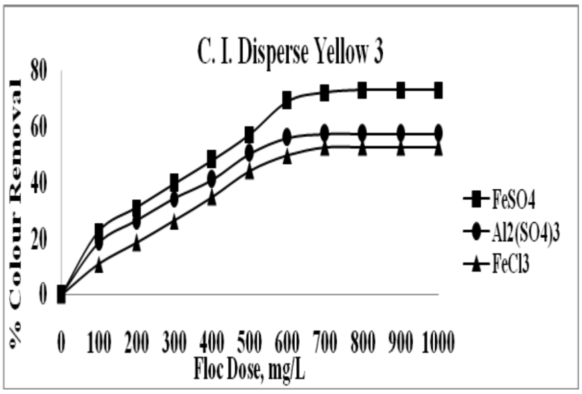

Fig. 3 Removal of colour of C. I. Disperse Yellow3 at different doses of flocs at pH::10

From Fig. 3 and Fig. 4, It was observed that excellent colour removal was obtained at pH : 4 than pH:10 .The adsorption capacity of Ferric chloride flocs is more than Aluminium sulphate. The colour removal capacity of Aluminium sulphate flocs is more than Ferrous sulphate.

A.3. Equilibrium study

Langmuir, Freundlich and Temkin isotherms are applied for the adsorption data. The isotherms gives relationship between the amount of dye adsorbed per unit mass of adsorbent, qe, and the equilibrium concentration of adsorbate.

A.3.1. Langmuir Isotherm

Langmuir Isotherm [6] assumes that the inter molecular forces decrease rapidly with distance.

The Langmuir isotherm is represents as:

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

Where q_m and K_L represents Langmuir Constants. Graph between $1/q_e$ and $1/C_e$ is as given in the Fig.5.

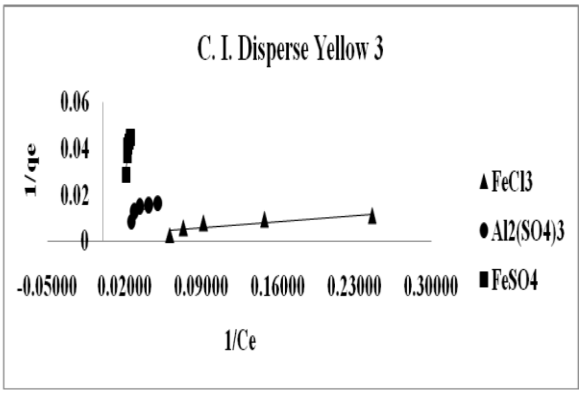

Fig.5 Langmuir Isotherm

From Fig. 5, it follows that data of the isotherm follows the Langmuir isotherm, as the graph is of straight line.

A.3.2. The Freundlich isotherm

Freundlich adsorption isotherm [2] gives the relation between the amount of dye adsorbed per unit mass of adsorbent, qe, and concentration of the dye at equilibrium, C_e.

$$q_e = K_F C_e^{1/n}$$

The Freundlich equation in terms of log is given by

$$\log qe = logK_F + \frac{1}{n}\log Ce$$

Where k_F and n are Freundlich constants. The Plot between $\log C_e$ and $\log q_e$ is as given in Fig. 6.

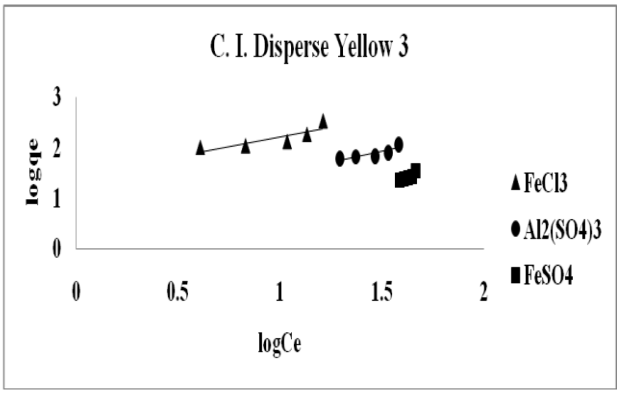

Fig. 6 Freundlich Isotherm

The value of correlation coefficient (R^2) and maximum sorption concentration of different sorbents are presented in Table 2.

From Table II, it was observed that R^2 values of Langmuir isotherm is nearer to 1.0 than freundlich isotherm, it implies that sorption fits well for Langmuir isotherm.

Table-II: Langmuir and Freundlich Isotherm Constants

Adsorbent	Langmuir isotherm			Freundlich isotherm		
	$q_{m,}$ (mg/g)	K_L (L/mg)	R^2	K_F (mg of color/g of flocs)	n	R^2
Aluminium Sulphate flocs	333	0.011	0.758	4.71	1.2	0.753
Ferric Chloride flocs	500	0.05	0.77	29	1.3	0.722
Ferrous Sulphate flocs	23.8	0.012	0.857	$5.8\text{x}10^{-3}$	0.45	0.835

B. Kinetic Study

The nature of adsorption reaction involved in the Sorption process can be known by applying adsorption data to Lagergren Pseudo- First-Order equation [6] given by

$$\text{Log}(q_e - q_t) = \text{Log}(q_e) - \left(\frac{k_1}{2.303}\right)t$$

Where q_t is the quantity of color adsorbed (mg/g) at time t, and q_e is the amount of color sorbed at equilibrium time t and k_1 is the rate constant of the pseudo – first - order adsorption process (min^{-1}).

In order to get correlation coefficients, graph was plotted between log (q_e-q_t) and time as shown in the Fig.7.

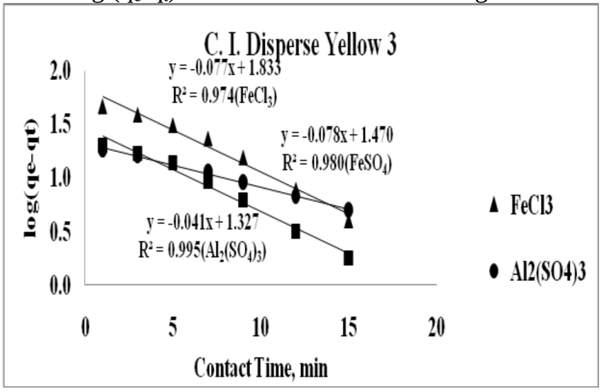

Fig.7. Pseudo-First-Order kinetics of dye – sorbent interaction

Where $h = k_2 q_e^2$ (mg g^{-1} min^{-1}) and k_2 is reaction constant (g mg^{-1} min^{-1}).

The graph was plotted with t/qt on x-axis and t on y-axis was drawn as presented in Fig. 8. The value of correlation coefficient of pseudo – first -. order and pseudo-second-order plots are presented in Table III

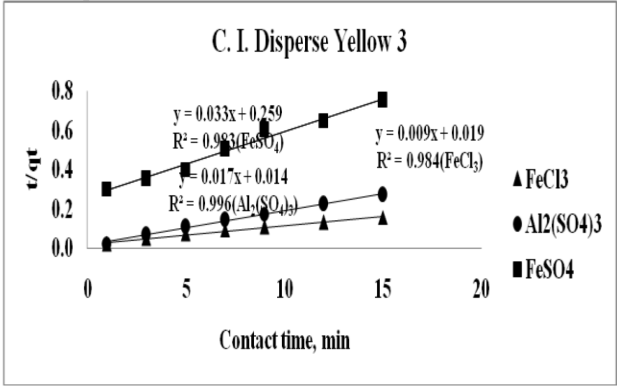

Fig. 8 Pseudo – Second - Order Kinetics of Dye - sorbent interaction

From the Table III, it states that chemi sorption may be the rate-limiting step as R^2 value of Pseudo-second-order is nearer to 1.0 than Pseudo-first-order.

Table-III: The values of correlation co-efficient from Pseudo-first - order and Pseudo – second order kinetic reactions

floc	Pseudo First Order			Pseudo Second			
	K_1	q_e	R^2	K_2	q_e	R^2	h
	min-1	mg/g		$gmg^{-1}min^{-1}$	mg/g		$mgg^{-1}min^{-1}$
Aluminium Sulphate	0.09	21.23	0.995	0.02	59	0.996	71
Ferric Chloride	0.177	68	0.974	0.0043	111	0.984	53
Ferrous Sulphate	0.179	29.5	0.98	$4.2x10^{-3}$	30	0.983	3.86

C. Sorption Mechanism

To know the sorption mechanism involved in the adsorption process, obtained kinetic data were applied to Webber's Intra particle Diffusion equation [11]. The graph obtained was used to know the diffusion mechanism, which states that

$$q_t = k_{id} t^{1/2} + C$$

Where q_t indicates the amount of dye color that is adsorbed on gram of adsorbent surface, t reflects uptake time, C denotes intercept and k_{id} denotes the intra particle diffusion rate constant. The intra particle diffusion plot of C.I. Disperse Yellow 3 is as shown in Fig.9. Initial portion of curved nature reflects the boundary layer diffusion effects and the final portion of curve represents the Intra particle diffusion effects. From Fig.9, it was observed that Intra particle diffusion was the rate limiting step because straight line is not passing through the origin.

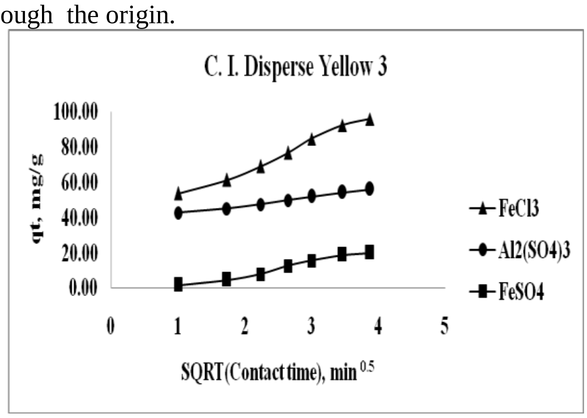

Fig. 9 Intra particle Diffusion - C. I. Disperse Yellow 3

V. CONCLUSIONS

It was observed that the preformed flocs of Aluminium Sulphate, Ferrous Sulphate and Ferric Chloride produced excellent colour removal. preformed flocs of Aluminium Sulphate and Ferric Chloride are more effective at pH:4 whereas Ferrous sulphate was more effective at pH:10. Equilibrium data fitted well to Langmuir isotherm, which indicated that monolayer formation involved in the sorption process. Kinetic data fitted well to Pseudo-Second-order reaction indicating that chemisorption is the rate limiting step.

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