

Adsorptive Removal of Acid blue 45, from Aqueous Solutions by Preformed Floccs

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Abstract: This paper presents the results of colour removal from aqueous solutions of textile dye namely C.I. Acid Blue 45, Azo group by adsorption onto preformed floccs of Ferric Sulphate, Manganese Sulphate and Manganese Chloride. Agitated non-flow batch kinetic and isothermal equilibrium experiments were conducted and the experimental results revealed the potential of preformed floccs in the removal of colour of dye. Dye responded favorably and exhibited good to excellent colour removal of Ferric sulphate at pH of 4 and Manganese chloride, Manganese sulphate at pH of 10. The maximum colour removal of Ferric Sulphate, Manganese Sulphate and Manganese chloride floccs was 90%, 85% and 65% respectively. 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, preformed floccs, Ferric Sulphate, Manganese Chloride, Manganese Sulphate

I. INTRODUCTION

Global industrialization has resulted in the release of large amounts of potentially toxic, mutagenic and xenobiotic compounds into the biosphere. Cleaning up of the environment by the removal of hazardous contaminants is a crucial and challenging problem needing numerous approaches to reach long-lasting suitable solutions. The textile industries are using synthetic dyes with ease of production, fastness and variety in colour compared to natural dyes and daily discharging millions of liters of untreated effluent containing harmful dye wash into receiving water bodies posing serious health problems. The estimated total wastewater discharge from textile plants engaged in wet finishing is 625 million gallons per day (Kerry M. Lanza et.al, 2007). Synthetic dyes are known to cause immediate visible pollution in effluent water aside from contamination by inferring with light which may retard photosynthesis and biota growth (Benadjema et.al, 2011). Thus the removal of these colored compounds from wastewater is an important target from the environmental point of view (Lara abramian et.al, 2009). Treatment processes such as physical, physicochemical, chemical and biological methods have been investigated and proved to be effective but to varying degree of success. Colour removal by physical process is negligible while the ability of biological processes for decolourization of dye effluents is ambiguous, differing and divergent, perhaps due to toxic nature of dye chemicals. Adsorption and chemical treatment processes have shown promise as a practical and economic process for treatment of textile waste; especially for colour removal.

Adsorption has been reported as an efficient method for the removal of different toxic pollutants in dye waste effluents. Activated carbons are widely used as powerful adsorbents for most pollutants in waste water. Even though colour removal by adsorption onto activated carbon is highly efficient, the overlying cost of the activated carbon and associated problems of regeneration and reuse warrants search for alternative low cost adsorbents. Low cost adsorbents like materials derived from industrial waste materials, agricultural wastes, minerals, coal, soil, etc. have been widely investigated for textile dye colour removal (Gupta et.al. 2003). Treatment with chemicals like Ferric Sulphate, Manganese Sulphate, Manganese Chloride, Calcium chloride, Copper Sulphate, Sulphuric and hydrochloric acid etc., either alone or in combination for removal of colour from individual dye wastes, as well as composite mill waste were investigated (Venkatamohan et.al., 1999). 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 C.I. Acid Blue 45 dye colour employing preformed floccs of Ferric Sulphate, Manganese Chloride and Manganese Sulphate. Scope of the study includes kinetics and isothermal equilibrium studies, effect of adsorption process parameters such as pH and adsorbent dose on colour removal, also chemical groups that are involved in the adsorption process. This study will be useful for further applications in designing the batch adsorption process for the decolourization of dye wastewaters.

II. MATERIALS AND METHODS

2.1. Glass ware and chemicals

All the glass ware used in this study is of 'Pyrex' quality and analytical grade (AR) chemicals were used throughout the study. Thermo UV VIS Spectrophotometer of Evolution 201 Model was used for taking transmittance and absorbance readings.

2.2. Adsorbent

Preformed floccs of Ferric Sulphate, Manganese Chloride and Manganese Sulphate were used as adsorbent.

2.3. Adsorbate

Acid Blue 45 was used as adsorbate. Stock solution of C.I. Acid Blue 45 (Anthraquinones) was prepared by dissolving 50mg in 1000ml distilled water.

2.4. Analysis and Characterization

The maximum wavelength of Acid Blue 45 (595nm) was observed using Thermo make UV VIS Spectrometer of Evolution 201 Model. The spectra were recorded from 4000 to 400 cm⁻¹. All analyses were done in accordance with standard methods (Clescerl et.al., 1998).

III. EXPERIMENTAL PROCEDURE

Varying doses of adsorbents 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 floccs was measured in terms of turbidity, and the dose and pH at which highest turbidity was recorded, were adopted as favorable dose and favorable 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 (pH adjusted to respective pH of preformed floc) 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 are 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 floccs 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 by measuring OD/% T at respective maximum wavelength (595nm) of dye solution and computing concentrations from the calibration curve.

IV. RESULTS AND DISCUSSION

Favorable dose and Favorable pH of adsorbents are presented in Table 1. All subsequent experiments were performed by employing favorable dose at favorable pH.

Table.1 Favourable pH and Favorable dose of coagulants

Adsorbents	Favorable pH		Favorable dose, mg/100ml
	Acidic Medium	Basic Medium	
Ferric Sulphate (Fe ₂ S ₃ O ₁₂)	4	10	1000
Manganese Chloride (MnCl ₂ .4H ₂ O)	4	10	1000
Manganese Sulphate (Mnso ₄ .H ₂ O)	4	10	1000

4.1. Kinetics of colour adsorption

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 (Venkatamohan et.al., 1997).

4.1.1. Effect of contact time

The influences of contact time vis-à-vis kinetics of colour removal by preformed floccs are presented in Fig. 1 and Fig.2 at 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.

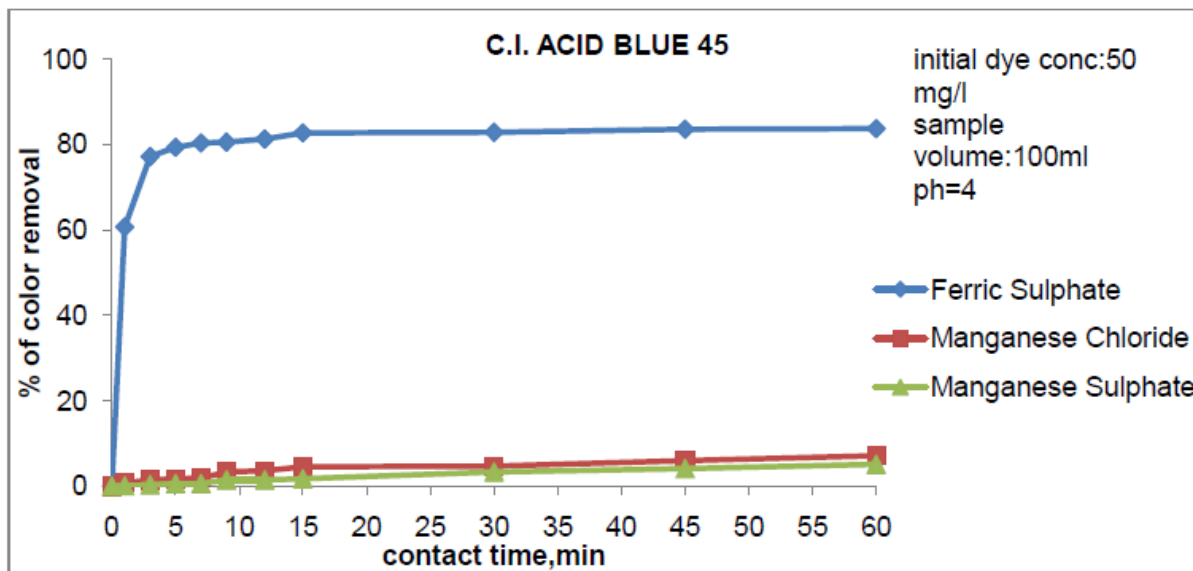


Fig.1. Effect of contact time on colour removal from acid blue45 aqueous solution at pH=4.

As per Fig.1, Excellent colour removal of 85 % was observed with Ferric sulphate preformed flocs, Low colour removal of 8% was observed with Manganese Chloride preformed flocs and low colour removal of 6% was observed with Manganese Sulphate preformed flocs at pH of 4.

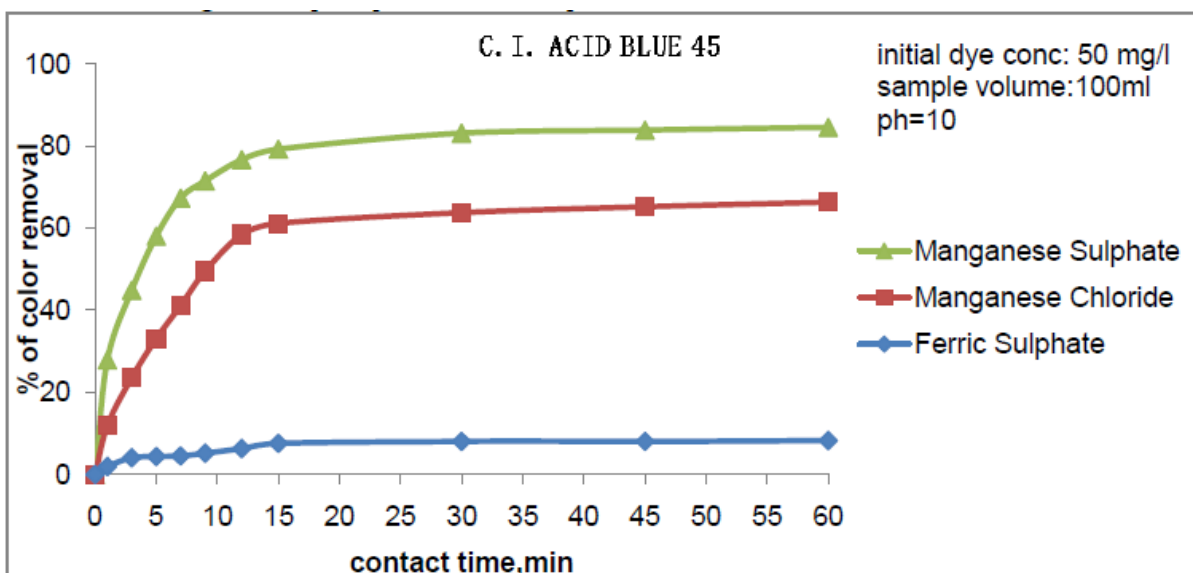


Fig.2. Effect of contact time on colour removal from acid blue 45 aqueous solution at pH=10.

As per Fig.2, Excellent colour removal of 85% was observed with Manganese Sulphate preformed flocs, good colour removal of 65% with Manganese Chloride preformed flocs and low colour removal of 9% with Ferric Sulphate preformed flocs at pH of 10.

4.2. 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 Blue45, at pH=4 and pH=10 , as shown in Fig.3 and Fig. 4.

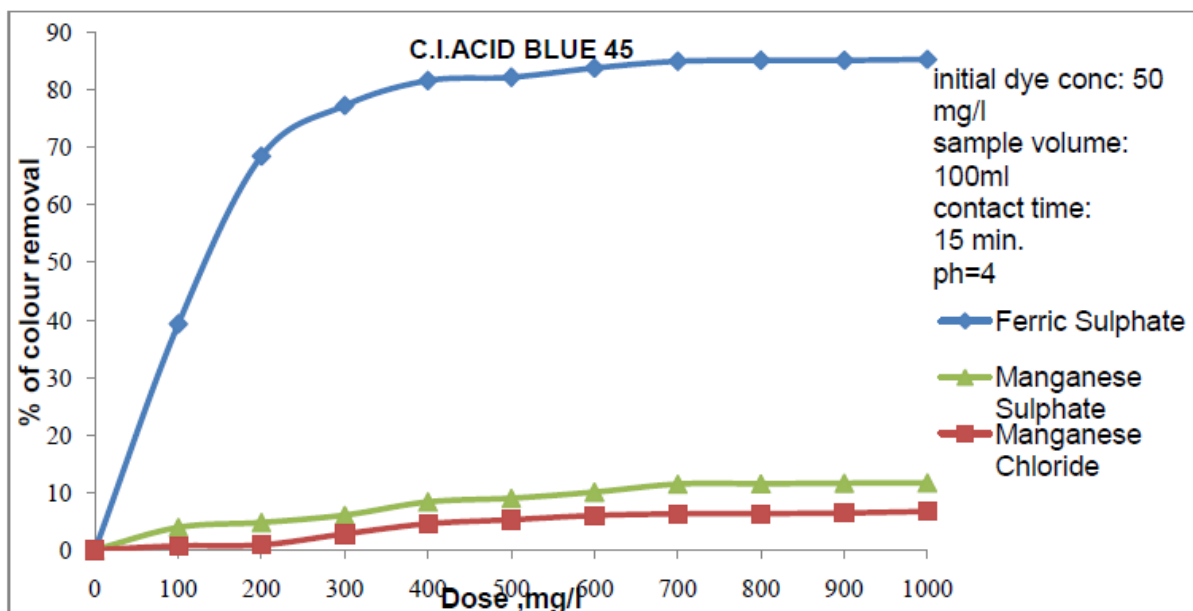


Fig.3. Response of C.I. Acid Blue 45 to preformed floccs at different dosages (pH=4)

From Fig.3, it was observed that C.I. Acid Blue 45 dye, Anthraquinones, responded favorably to preformed floccs of all adsorbents and the colour removal range is decreasing in the order of coagulant Ferric Sulphate, Manganese Sulphate and Manganese chloride at pH of 4. Excellent colour removal of 90 % was observed with Ferric Sulphate preformed floccs, Low colour removal of 12% was observed with Manganese Sulphate preformed floccs and Low colour removal of 10% was observed with Manganese Chloride preformed floccs at pH of 4.

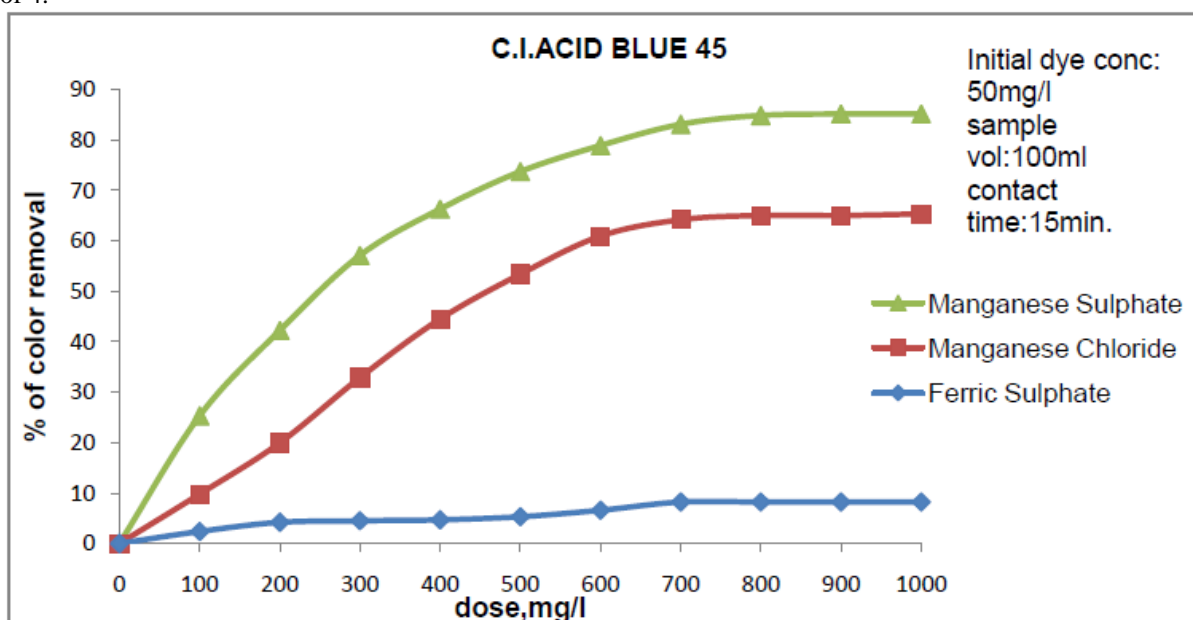


Fig.4. Response of C.I. Acid Blue 45 to preformed floccs at different dosages (pH=10)

From Fig.4, it shows that C.I. Acid Blue 45, responded favorably to preformed floccs of all floccs and the colour removal range is decreasing in the order of adsorbent Manganese Sulphate, Manganese Chloride and Ferric Sulphate at pH of 10. Excellent colour removal of 85% was observed with Manganese Sulphate preformed floccs, good colour removal of 65% with Manganese Chloride preformed floccs and low colour removal of 32% with Ferric Sulphate preformed floccs at pH of 10

4.3. Equilibrium 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 and Freundlich isotherms. These isotherms relate dye uptake per unit mass of adsorbent, q_e , to the equilibrium adsorbate concentration in the bulk fluid phase C_e .

4.3.1. The Langmuir isotherm

The Langmuir model (Weihuaet.al, 2013) 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 as;

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

Table.2. Isotherm Model constants and Correlation Coefficients for Adsorption of Dye from Aqueous Solution

Adsorbent	Langmuir isotherms			Freundlich isotherms		
	q_m (mg/g)	K_L (L/mg)	R^2	K_F (mg of colour/g of floccs)	n	R^2
Ferric Sulphate	0.3395	0.02	0.901	2.2181×10^{-30}	0.0537	0.7546
Manganese Chloride	72.9927	0.0734	0.9414	14.0896	2.6816	0.8679
Manganese Sulphate	172.4137	0.0562	0.932	35.3183	3.2615	0.7069

Table.3. Comparison between the Adsorption Rate constants, q_e , and correlation co-efficient associated with Pseudo-first order and Pseudo-second order equations

Adsorbent	Pseudo-first order equation			pseudo-second order rate equation			
	K_1 (min^{-1})	q_e (mg/g)	R^2	K_2 ($\text{gmg}^{-1}\text{min}^{-1}$)	q_e (mg/g)	R^2	h ($\text{mgg}^{-1}\text{min}^{-1}$)
Ferric Sulphate	0.0014	37.93	0.5059	8.28×10^{-03}	15.87	0.9173	2.086
Manganese Chloride	0.0165	1.3677	0.8605	0.013	32.36	0.9965	13.613
Manganese Sulphate	0.0143	1.4763	0.3963	7.714×10^{-03}	42.91	0.9933	14.198

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.

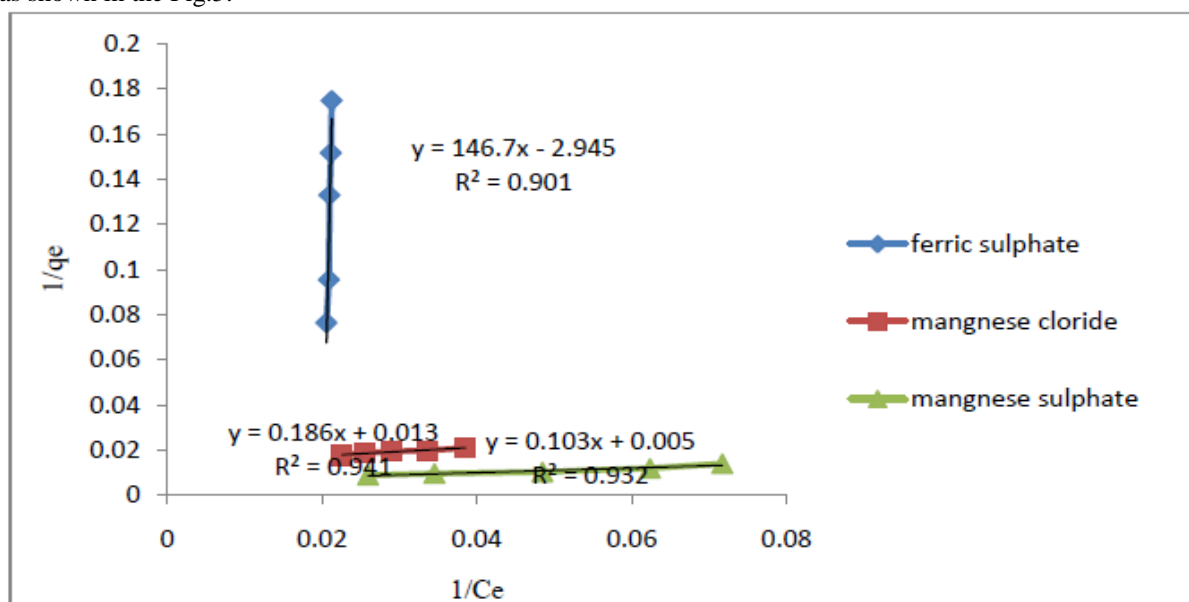


Fig.5. Langmuir Adsorption Isotherm

From Fig.5, it can be concluded that the isotherm data fits the Langmuir equation well, as it is straight line.

4.3.2. The Freundlich isotherm

The Freundlich isotherm model (Srichandana et.al, 2012) 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, q_e , and the concentration of the dye at equilibrium, C_e .

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

The logarithmic form of the equation is

$$\log q_e = \log K_F + \frac{1}{n} \log C_e$$

Where K_F and n are the Freundlich constants. 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.

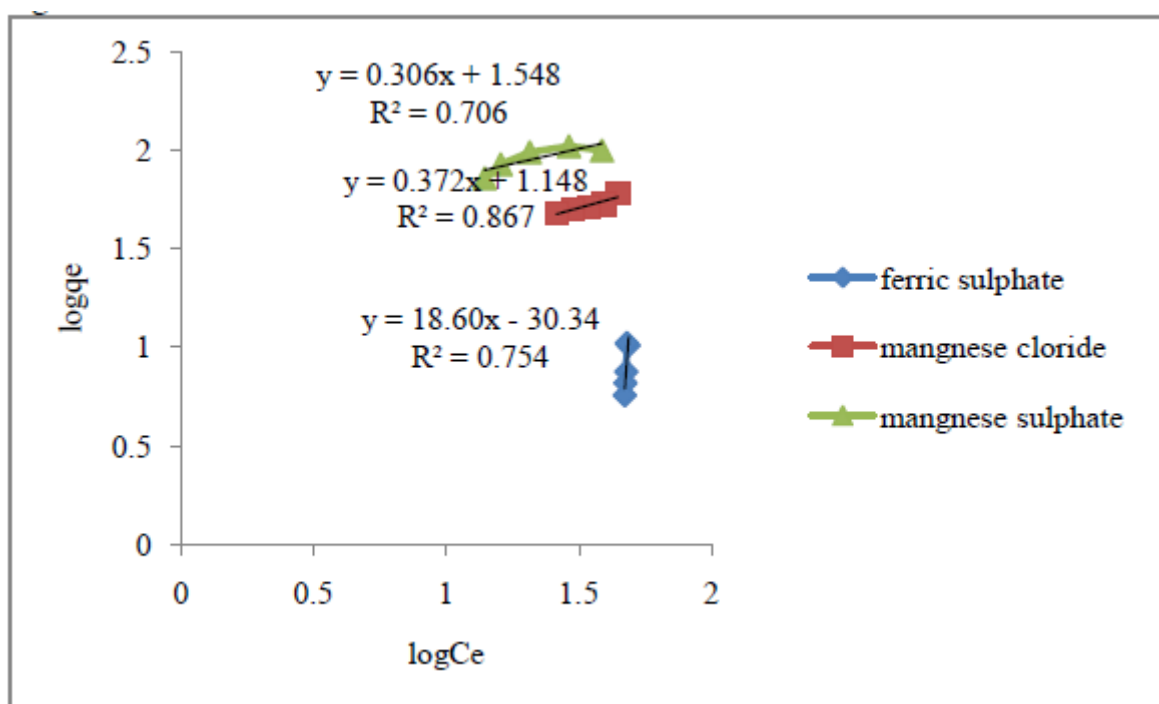


Fig.6. Freundlich Adsorption Isotherm

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

From Table 2 above, The values of coefficient of correlation (R^2) was obtained as 0.9414, 0.932 and 0.901 for Manganese Chloride, Manganese Sulphate and Ferric 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 in the same table.

It follows from the data that the equilibrium adsorption of dye onto Manganese sulphate, Manganese Chloride and Ferric Sulphate preformed floccs 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 (Hameedet.al. 2008).

4.4. 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 floccs (Senthilet.al. 2009). The pseudo-first-order rate equation is given as

$$\log(q_e - q_t) = \log q_e - (K_1/2.303)t$$

Where q_t and q_e are the amount of color adsorbed (mg/g) at time t , and at equilibrium respectively and k_1 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.

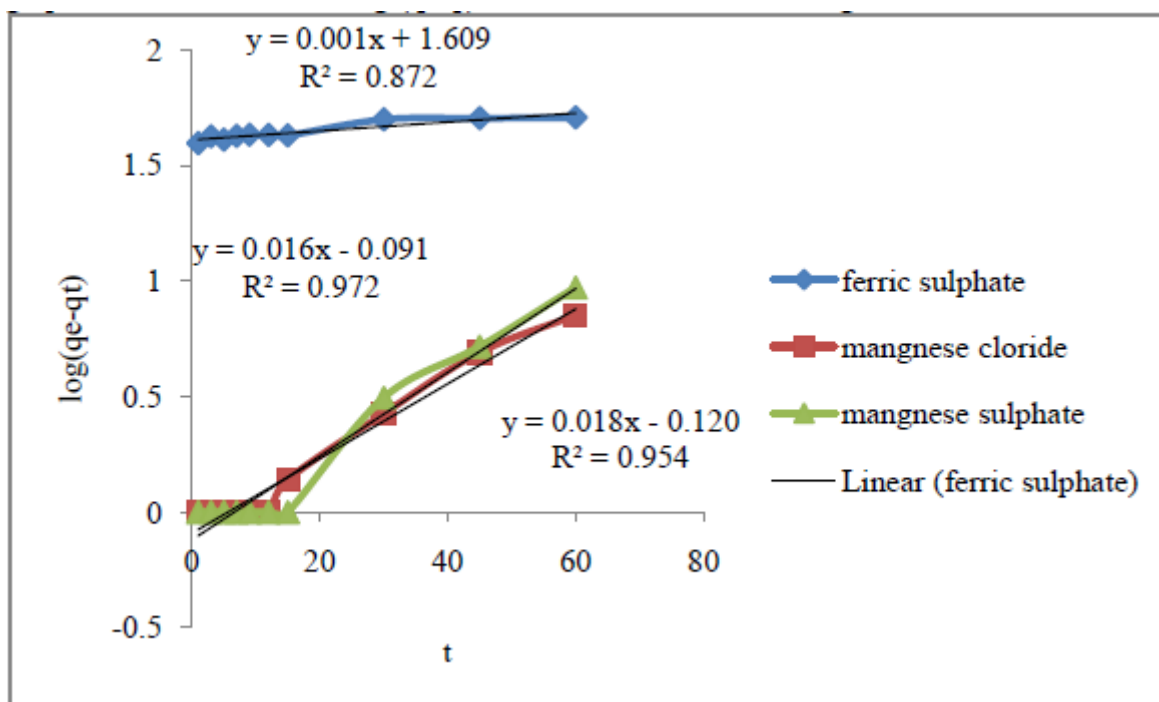


Fig.7. Pseudo-first-order Reaction for dye Adsorption onto preformed floccs

The pseudo-second order Kinetics is expressed as:

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

Where $h = k_2 q_e^2$ (mg g⁻¹ min⁻¹) can be regarded as initial adsorption rate as $t \rightarrow 0$ and K_2 is the rate constant of pseudo-second-order adsorption (g mg⁻¹ min⁻¹).

The graph between t/q_t versus t was drawn as shown in the Fig.8, to determine the values of q_e , k and h from the slope and intercept of the plot.

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

From the Table.3, it was observed that pseudo-second order model yields very good straight lines ($R^2=1$) for all adsorbents as compared to the plot of pseudo-first order. It is clear that adsorption of dye onto preformed floccs follows second order kinetic model, which relies on the assumption that chemisorptions may be the rate-limiting step.

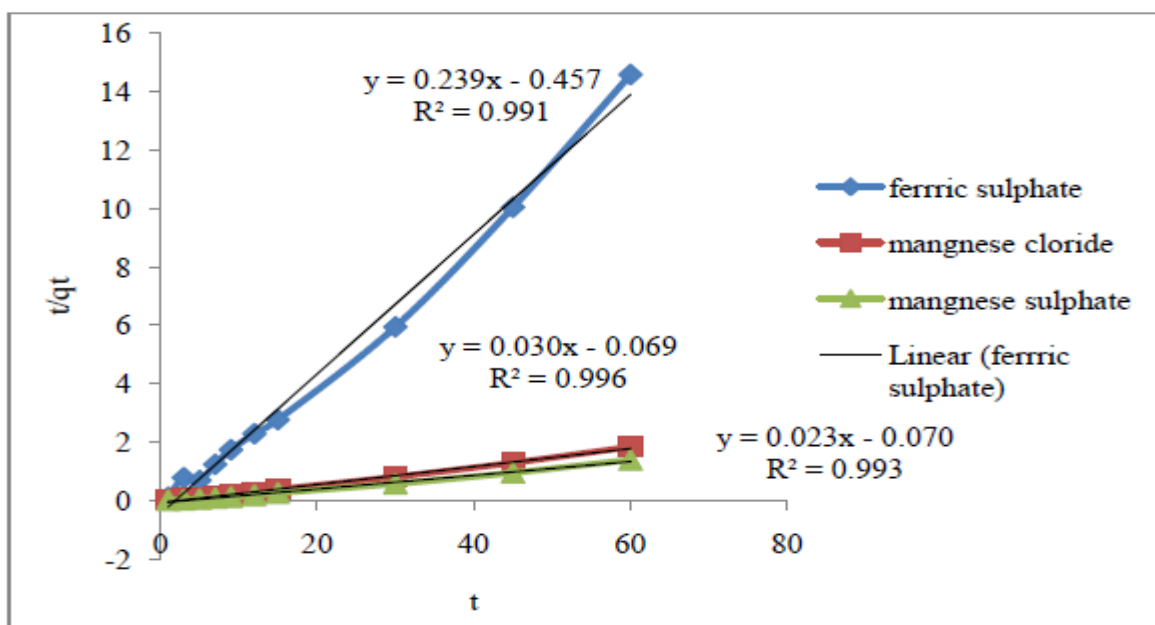


Fig.8 Pseudo-second-order Reaction for Dye Adsorption onto preformed flocc

V. CONCLUSIONS

As evidenced in this study, C.I. Acid Blue45 dye aqueous solution can be decolorized by adsorption onto preformed floccs. Excellent colour removal can be achieved with preformed floccs of Ferric Sulphate, Manganese Sulphate and Manganese Chloride at pH of 10 than 4. Colour removal decreased in the order of adsorbents Manganese Sulphate, Manganese Chloride and Ferric Sulphate at pH of 10. The data fitted well with Langmuir isotherm and Pseudo second order equation stating monolayer formation and chemisorptions is involved in the colour removal.

List of symbols

q_e - Solid phase concentration at equilibrium (mg/g).

q_t -average solid phase concentration at time t in min (mg/g)

k_1 - pseudo-first order rate constant

k_2 - pseudo-second order rate constant

k_{id} -intraparticle diffusion rate coefficient

C_e and $1/n$ -empirical constant related to the magnitude and driving force of adsorption

K_L -Langmuir constant

q_m -Maximum amount of adsorption corresponding to complete monolayer coverage.

REFERENCES

- [1] M.Benadjema, L.Milliere, L. Reinert, N. Benderdouche, L.Duclaux (2011), preparation, characterization and Methylene blue adsorption of phosphoric acid activated carbons from globe artichoke leaves, *Fuel Processing Technology*, 92, 1203-1212.
- [2] Lara Abramian and Houssam EI-Rassy(2009), Adsorption kinetics and thermodynamics of azo-dye orange II onto highly porous titania aerogel, *Chemical Engineering Journal* 150, 403-410. E.A.EI-Sharkawy, Afaf Y.Soliman and Kawthar M.Al-Amer (2007), Comparative study for the removal of Methylene blue via adsorption and photocatalytic degradation, *Journal of colloid and interface science* 310, 498-508.
- [3] V.K.Gupta, I.Ali, Suhas and Dinesh Mohan (2003), Equilibrium uptake and sorption dynamics for the removal of a basic dye using low-cost adsorbents, *Journal of colloid and Interface Science* 265, 257-264.
- [4] S.Venkatamohan, P.Sailaja, M.Srimurali and J.Karthikeyan (1999), Colour removal of monoazo acid dye from aqueous solution by adsorption and chemical coagulation, *Journal of Environmental Engineering and policy*, 1(3):149. L.S.Clescerl, N.Munilakshmi(2013)
- [5] Removal of colour from Reactive blue 82 dye by adsorption onto preformed floccs, *International Journal of Emerging Technologies in Computational and Applied Sciences*. A.E. Greenberg, A.D. Eaton (1998),
- [6] APHA, Standard Methods for the Examination of Water and Wastewater. 20th ed., American Public Health Association/American water works Association/Water Environment Federation, Washington, DC. S. Venkata Mohan and J.Karthikeyan (1997),
- [7] Removal of lignin and tannin colour from aqueous solution by adsorption and activated carbon, *Journal of Environ poll.*, 97(1-2), 183-187.
- [8] Weihua Zou, Hongjuan Bai, Shuai peng Gao and Ke Li (2013), Characterization of modified sawdust - kinetic and equilibrium study about Methylene blue adsorption in batch mode, *Korean J. Chem. Eng.*, 30(1), 111-122
- [9] P.Sri Chandana and J.Karthikeyan, (2012), Sorptive removal of color from aqueous coffee and tea infusions, *Journal of Desalination and Water Treatment*, 50, 338-347.
- [10] B.H. Hameed Mahmoud and A.L. Ahmad (2008), Equilibrium modeling and kinetic studies on the adsorption of basic dye by a low-cost adsorbent: Coconut (Cocos nucifera) bunch waste, *Journal of Hazardous Materials*, Science direct, 158, 65-72.
- [11] P. Senthil Kumar and K.Kirthika (2009), Equilibrium and kinetic study of adsorption of nickel from aqueous solution onto bael tree leaf powder, *Journal of Engineering Science and Technology*, Vol.4. No.4, 351-363.
- [12] Julidyener, Turkankopac, Gulsen Dogu and Timur Dogu (2006), Adsorption of Basic yellow 28 from aqueous solutions with clinoptilolite and amberlite, *Journal of colloid and interface science*, 294, 255-264.
- [13] Laila Al-Khatib, Feras Fraige, Mohammad Al-Hwaiti and Omar Al-Khashman (2012), Adsorption from aqueous solution onto natural and acid activated bentonite, *American Journal of Environmental Science*, 8 (5), 510522.