

Adsorptive Removal of Acid Blue 113 Dye over Alkali Activated Fly Ash

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ABSTRACT: Dyes used in various industries has eco-toxic hazardous effects and is a major cause of pollution in waste water system. Assessing and minimizing the risk of dyes is a need for today. Water soluble Acid blue 113 dye, which is used in many industries is a major cause of pollution.

In this study fly ash from coal burning power plant was activated chemically, used as a low cost adsorbent for the removal of Acid blue 113 dye. The activated fly ash was characterized by XRD, SEM. Results showed that activated fly ash due to increased amorphous property possesses more activity over surface to act as a suitable adsorbent for the removal of dye waste from industrial effluents. The adsorption kinetics is well represented by first order kinetic model.

KEYWORDS: Chemical activation, fly ash, Acid blue 113, adsorption.

I. INTRODUCTION

Acid blue 113 an azo dye, is extensively used in textile industries^[1] which leads to formation of aromatic amines and these aromatic amines are known as mutagens and carcinogens to human beings^[2]. It has been reported earlier that dyes precipitate in aquatic organisms leading to haematological and histopathological alterations in vital organs^[3]. Biochemical changes in blood and tissue of fish under exposure to toxicant may be used to predict the toxic effects^[4]. Various reports are available on the toxic effects of acid blue dyes such as acute toxicity bioassay in fish^[5], allergen susceptibility and skin irritation in fish, rat and rabbit^[6,7]. Internal organ colour change in fish and rat^[8], changes in mineral constituents in the liver and kidney of fish has also been reported^[9]. This biochemical effect of acid blue 113 in various organs of fish and aquatic animals need attention.

Fly-ash, a finely divided powdered byproduct^[10] from coal fired plant or biomass combustion facilities required ultimate disposal. The major constituents of fly-ash are silica, alumina, iron oxide, lime, magnesia and alkali in varying amount with some unburnt activated carbon. Besides these, some minor elements such as Hg, As, Ge, Ga and traces of heavy metals (Cr, Co, Cu, Pb, Mn, Ni, Zn)^[15] and rare earths may also be present in fly ash. The glassy (amorphous) siliceous spherical particulates are the active portion of fly ash. Typically, fly ash is 30-50% glass and higher glass content in the form of quartz is also present in it^[11]. Other metal oxides such as Mn₂O₃, TiO₂ etc^[12] and minerals like mullite, hematite, ferrite and rutile in fly ash^[13] are desirable from the point of view of reactivity.

Fly-ash has been employed as a low cost adsorbent for flue gas and water cleaning^[14-17] and many efforts have been made focused on heavy metals^[18,19] and dye adsorption^[20,21] on fly-ash particles. In this paper we report use of fly-ash as an adsorbent by activating it, for the complete removal of acid blue 113 dye from aqueous waste. Batch adsorption studies were carried out systematically and attempts have also been made to understand the adsorption equilibrium and kinetics.

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II. EXPERIMENTAL

2.1 Materials

Class F fly ash, collected from KSTPS (Kota super thermal power plant), Rajasthan, was dried and sieved to obtain uniform particle size sample. Stock solution of acid blue 113 dye of BDH make was prepared by doubly distilled water. Phenolphthalein was used as an indicator in this study.

2.2 Types of catalysts and their synthesis

1. Fly ash (FA)
2. Activated fly ash (AFA)

FA was used directly for the study. To prepare activated fly ash (AFA) alkaline treatment was given to the pure fly ash by adding NaOH concentration 50 wt%. The chemical activation was carried out in a stirred reactor taking the mixtures of fly ash and NaOH, heated at 110 °C under stirring and aged for 2 days maintaining the temperature. After ageing, the pulp obtained was washed with distilled water to remove leached compounds and excess NaOH. The pulp thus obtained was dried at 110 °C for 24 h. The chemically activated fly ash was thermally stabilized after calcination at 450 °C for 4 h in static conditions.

2.3 Characterisation

Both the initial i.e. pure fly-ash (F.A) and the residue obtained after alkaline treatment i.e. activated fly-ash (AFA) were characterized mineralogically and microstructurally. Philips Expert XRD used for determining crystallite size were scanned at 2θ range of 0 - 80°C at a scanning rate of 0.04 s⁻¹ [22]. FT-IR spectra of both the samples (Fig. 3 a,b) were recorded in the range 400- 4000 cm⁻¹ with a resolution of 4 cm⁻¹. Specific surface area, pore volume and pore size in the sample were determined from N₂ adsorption-desorption isotherms using NOVA 1000E surface area at 77 K. Thermogravimetric analysis (TGA) was investigated in the temperature range 50 °C to 1000 °C using model Mettler Toledo. To determine the morphology, external surface structures and external elemental distribution of individual FA particle, scanning electron microscope (Philips XL 30 ESEM TMP) has been used.

2.4 Adsorption Kinetics

In the batch method, 50 mL of adsorbate solution was taken into an Erlenmeyer flask and allowed to attain the desired temperature by circulating thermostated water around the reaction vessel. To initiate the reaction, a fixed amount of adsorbent (2 g dm⁻³) was added and stirred continuously at about 1400 ± 1 rpm. The kinetics was followed by withdrawing 0.05 dm³ aliquot sample at different intervals.

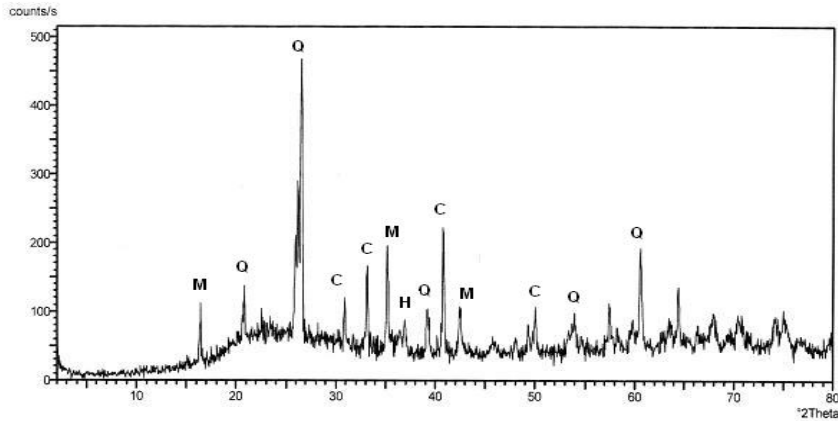
Temperature was varied for estimating activation energy. Experimental runs were observed with initial rapid adsorption trends for a period of 0.5- 2.5 min.

III. RESULTS AND DISCUSSION

3.1 Characterization of adsorbent

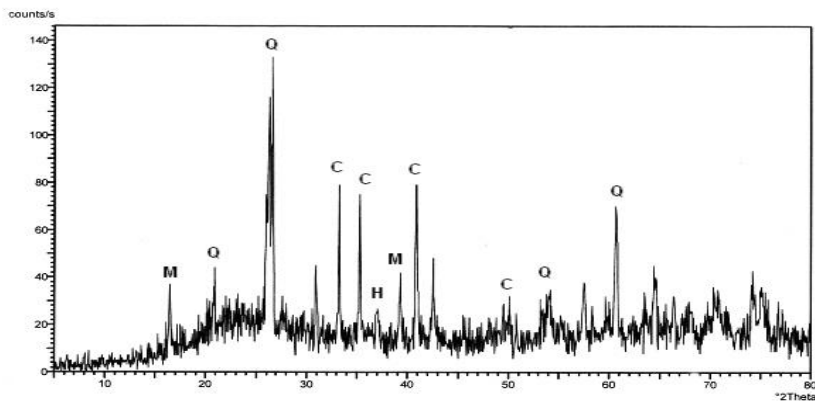
3.1.1 XRD Analysis

The presence of quartz, mullite and calcite is witnessed in both FA and AFA (Fig 1 a, b). Crystallite size was decreased from 33 nm to 11 nm on NaOH treatment. It is evident from XRD study that chemical activation has removed most of the crystalline component present in the pure fly-ash thus lowering of crystallinity of the sample and increasing amorphous nature showed the presence of nanocrystalline phase in the sample.



Q – Quartz, C- Calcite, M – Mullite, H- Haematite

Fig. 1(a) - XRD of Pure Fly ash



Q – Quartz, C- Calcite, M – Mullite, H- Haematite

Fig. 1 (b) - XRD of Alkali Activated Fly ash

Fig. 1(a, b) - XRD of Pure FA and alkali activated FA (calcined at 450 °C).

3.1.2 SEM Analysis

Fig 2 (a) and (b) shows the scanning electron microscope picture of pure and activated FA respectively. In addition to the general physical characteristics the elemental composition of random population of fly-ash, the SEM data clearly indicate intermixing of silica and alumina phases and predominance of Ca and other nonsilicate minerals. These results supported the data obtained from XRD.

Fig 2(a) reveals that in the FA, the size of particles range from 840 nm to 10 µm and the majority of particles ranged in 1 µm to 100 µm, consisted of solid sphere, hollow cenosphere, irregularly shaped unburnt carbon particles and mineral aggregates and agglomerated particles which after alkali treatment (Fig 2b) resulted into scattered agglomerated particles conferring the increase in amorphous property. These results supported data obtained from previous studies and were consistent with XRD data^[23].

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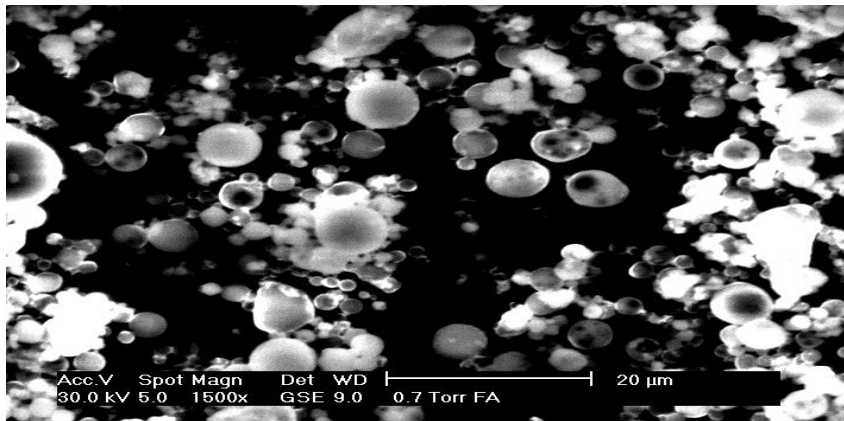


Fig. 2(a) : SEM Photograph of Pure Fly Ash

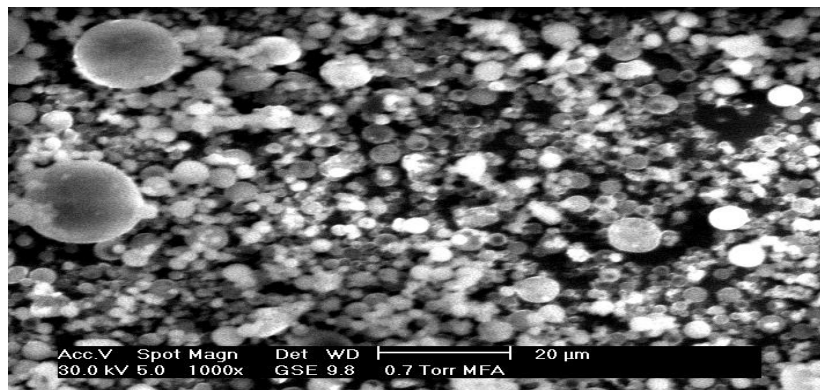


Fig. 2(b) :SEM Photograph of alkali activated Fly Ash

3.1.3 FT-IR Analysis

In alkali activation process higher concentration of $-OH$ group favours the breaking of $Si-O-Si$, $Al-O-Al$ and $Si-O-Al$ bonds and formation of $Si-OH$ and $Al-OH$ groups occurs which confirms by a broad band between $3400-3000\text{ cm}^{-1}$ (Fig. 3b) attributes the presence of surfacial hydroxyl group of $-OH$ and adsorbed molecules on the surface. The broadening of a band is due to the strong hydrogen bonding. Signals at 996 cm^{-1} , 1081 cm^{-1} , 1185 cm^{-1} is attributed respectively to the vitreous phase of unreacted fly-ash, quartz and mullite while a new component appearing at around $1025-1006\text{ cm}^{-1}$ is attributed to the sodium alumino silicate^[24] which is also confirmed by some previous studied^[25].

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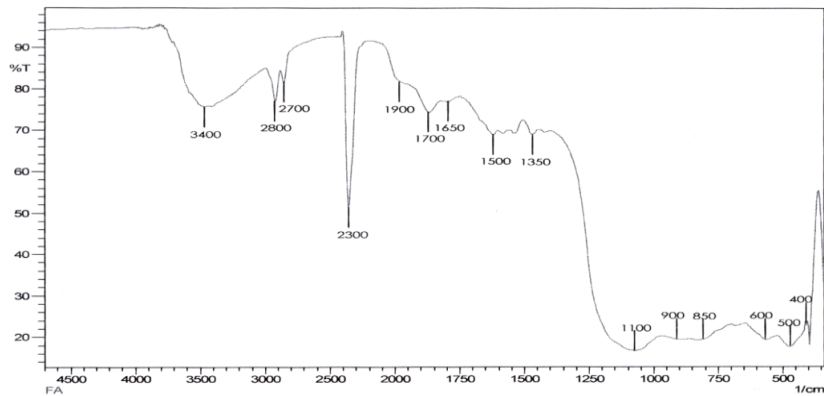


Fig. 3(a) – FT-IR spectra of pure Fly Ash.

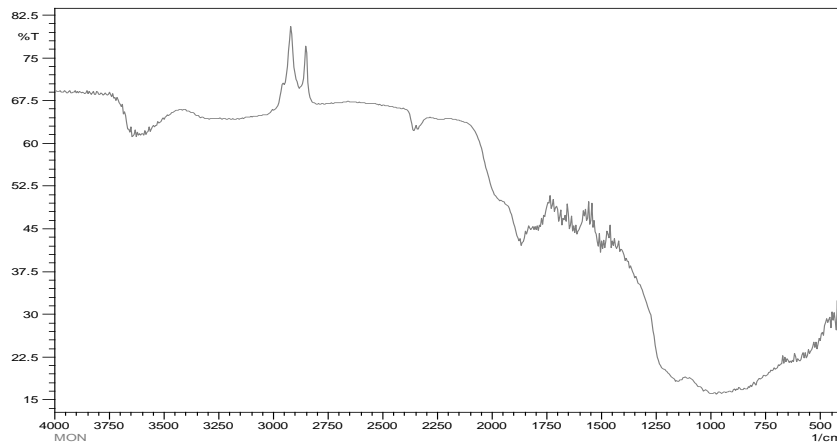


Fig. 3(b) – FT-IR spectra of alkali activated FA

3.2 Adsorption Isotherms

To optimize the design of an adsorption system for the adsorption of adsorbate, the most appropriate correlation for the equilibrium curve is Langmuir and Freundlich.

The Langmuir isotherm is valid for monolayer adsorption onto a surface containing a finite number of identical sites.

$$Q_e = \frac{Q_0 b C_e}{1 + b C_0} \text{Eq. (A.1)}$$

$$\text{or } \frac{m}{x} = \frac{1}{Q_0} + \frac{1}{Q_0 b C_e} \text{Eq. (A.2)}$$

Where C_e is the equilibrium concentration in mg/L and Q_0 is the solid phase concentration corresponding to complete coverage of adsorption sites, b is the Langmuir constant, which indicates the nature of adsorption and indicates the shape of the isotherm accordingly. The essential characteristics of a Langmuir isotherm can be expressed in terms of a dimensionless separation factor (r), which describes the type of isotherm and is defined by equation (3)

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$$r = \frac{1}{1 + bC_0} \quad \text{Eq. (A.3)}$$

Linearized Freundlich adsorption isotherm equation is given by equation (3)

$$\lg q_e = \lg K_f + 1/n \lg C_e \quad \text{Eq. (A.4)}$$

Where q_e is the amount of acid adsorbed per unit weight of adsorbent (mg/g), K_f and $1/n$ are the Freundlich constants related to adsorption capacity and intensity respectively.

Table 1: Values of Langmuir and Freundlich constants for Acid Blue 113 adsorption over AFA at different [acid] at 30°C

10 ⁻³ [acid] mol dm ⁻³	Langmuir constants				Freundlich constant	
	b	r	Q ₀	R ²	K _f	1/n
5	1.045	0.18	39.37	1.0	117.5	0.3984
10	0.528	0.18	76.92	1.0	151.5	0.3992
50	0.100	0.19	169.4	1.0	1893.6	0.4921

The Langmuir plots are linear, shown in fig (4a). The plots of Freundlich isotherm yield a straight line of slope $1/n$ and intercept $\log K_f$. It is clear from table 1 that the r values for the present experimental plot favors the adsorption of adipic acid on alkali activated fly ash.

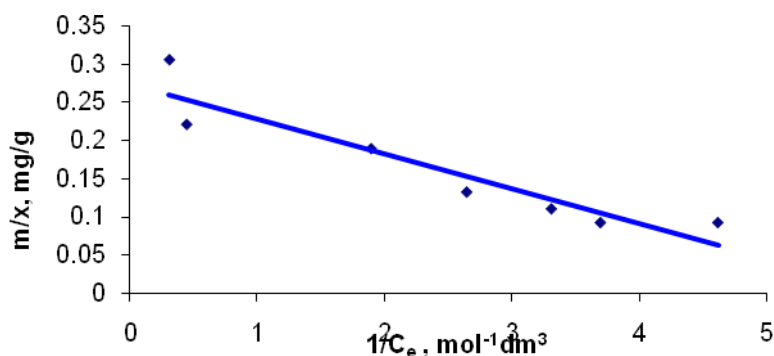


Fig 4.(a) : Langmuir plot

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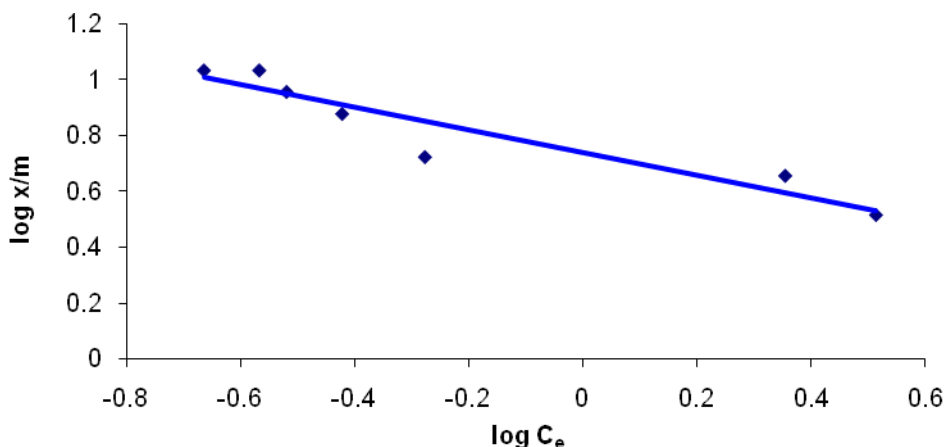


Fig 4.(b) : Freundlich plots

3.3 Kinetics of adsorption

Kinetics of adipic acid removal over AFA is studied by varying concentration of adipic acid, AFA and temperature.

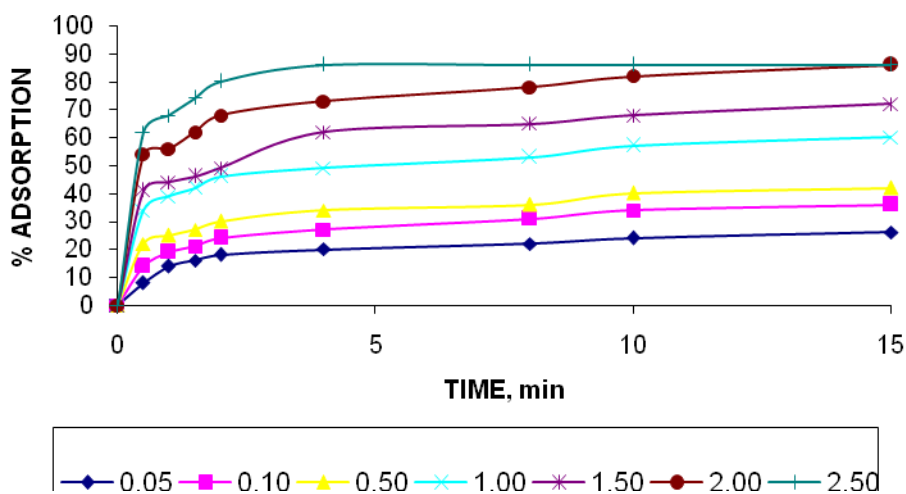


Fig. 5: Change in % adsorption of Acid Blue 113 with time at different [AFA] at 30°C

Time v/s percentage adsorption graph shows (fig 5) initial rapid adsorption. Initial slope is used for determining initial rate (R_{obs}). From the log-log plot of R_{obs} v/s Acid Blue 113 and R_{obs} v/s AFA, an order of 1.0 and 0.7 ± 0.05 is achieved respectively.

The functional dependence of rate on [acid] and [AFA], the final rate law is

$$R_{obs} = K [(I) [AFA]^{0.7}] \quad \text{Eq. (B.1)}$$

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value of K is calculated $0.3875 \pm 0.15 \text{ g dm}^{-1.9} \text{ s}^{-1}$ from the plot of R_{obs} with $[AFA]^{0.7}$.

Temperature was varied from 25 °C to 35 °C. The values of k determined at different temperature were used in Arrhenius equation. From the plot of log k against 1/T, the value of activation energy was calculated to be $59.54 \pm 3.15 \text{ kJ mol}^{-1}$.

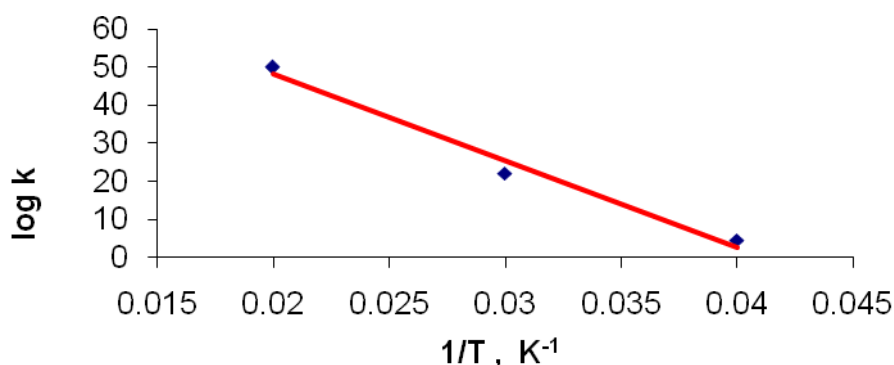


Fig. 6: Arrhenius equation plot for Acid Blue 113 adsorption

The above adsorption kinetics was modeled on five different models. All models were tested with least square regression analysis; values of statistical parameters for different examples are given in table 2. On the basis of high values of R^2 and low SEE the most favorable model is first order kinetic model.

Table 2: Coefficient of determination (R^2), standard error of estimate (SEE), and slope for graphical equation of different kinetic models applied on Acid Blue 113 adsorption on [AFA] at 30 °C.

[ACID]= $5 \times 10^{-3} \text{ mol dm}^{-3}$, [AFA]= 2 g dm^{-3}			
Kinetic models	R^2	SEE	Slope
Zero order	0.574 0	0.21569	-0.06
First order	0.995 7	0.00934	- 0.238 2
Elovich equation	0.617 3	0.11509	- 0.098 6
Parabolic diffusion	0.452 2	0.44016	- 0.399 9
Two rate constant	0.545 8	0.13133	- 0.026

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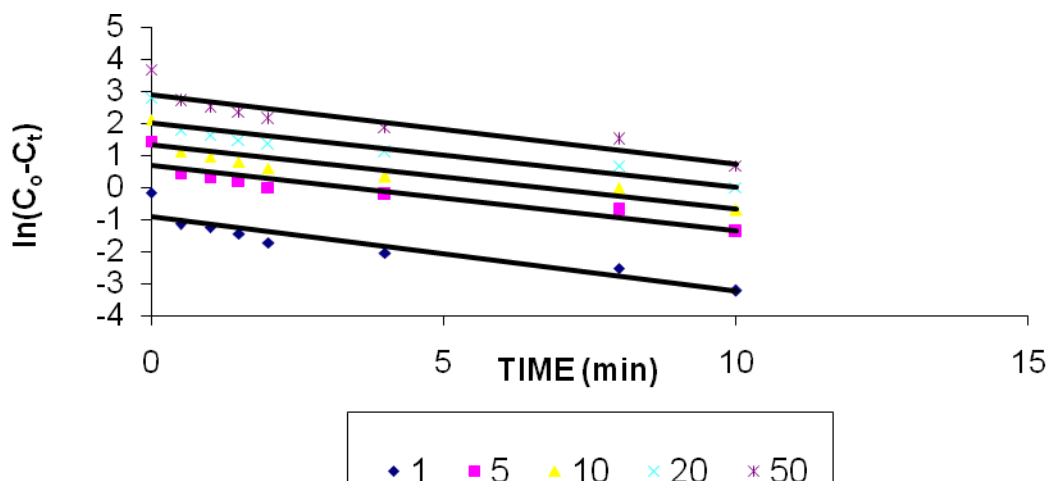


Fig. 7 : First order equation plots for Acid Blue 113 adsorption at different [Acid]. [AFA]= 2.0 g dm⁻³ Temp.= 30°C.

IV. CONCLUSION

The adsorption catalyst AFA synthesized during this work is found to have sufficient activity to remove Acid Blue 113. Kinetic rate law has given first order with respect to initial concentration and a fractional order of 0.7 ± 0.05 for [AFA] at 30 °C. A high value of activation energy indicates, chemisorption is to be important in case of using AFA than physisorption. The study generates fly-ash catalyst for waste water treatment in lubricants, plasticizer, pharmaceutical industries etc. where Acid Blue 113 remains as waste in the effluent.

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REFERENCES

1. Tae – Kung Kim, Mee – Kyung Kim, Yong – Jim Lim and Young A S., Dyes & Pigments. **67**, 127 – 132, (2005).
2. Brown, M.A., De Vito, S.C., Cri. Rev. Env. Sci. Tec., **23**, 249 –324, (1993).
3. Afaq, S. and Rana, K.S., Asian J. Exp. Sci., **23**, 299-302, (2009).
4. Ramesh, M. and Saravanan, M., Inter. J. Integra. Biol., **3**, 113 – 83, (2008).
5. Linda, W. L., and James, C. L. III., Department of Environmental Sciences and Engineering, School of Public Health, University of North Carolina 27514 for Ecology Committee American Dye Manufacturers Institute, INC. (1972).
6. Anonymous, Orange textile dye. National Industrial Chemical notification and assessment scheme (NICNAS). File No: STD/1008, In: National Occupational Health and Safety Commission, Australia.(2003).
7. Anonymous, Acid blue113.21cclab.com. (2008).
8. SCCP(Scientific Committee of Consumer Products), Acid Blue 62 (COLIPA1 n° C 67). European Commission, Health & Consumer Protection Directorate General, Directorate C – Public Health & Risk Assessment. (2005). <http://pharmacos.eudra.org/F3/cosmetic/doc/HairDyeStrategyInternet.pdf>.

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9. Karthikeyan, S., Jambulingam, M., Sivakumar, P., Shekhar, A.P. and Krithika,J., E – Journal of Chemistry, **3**, 303 – 306, (2006).
- 10.Kumar K., Kumar S., Mehrotra SP., Resour. Conserve. Recycl., 52, 157, (2007).
- 11.Mallik D., Khanra S., Chaudhury S.K., J. Chem. Technol. Biotechnol., ,70, 231, (1997).
- 12.Karapanagioti H.K., AtalayA.S.,Laboratory, G Nest: Int. J., 3, 11, (2001).
13. KastenerJ.R, Melear N.D, Das K.C, J.Hazar.Mater., 95, 81, (2002).
14. Lu G.Q., Do D.D, Fuel Process Technol., 27, 95, (1991).
15. Carry T.R, Richardson C.F., Chang R., F.B Meserole, Rostam M. Abadi, Chen S., Environ. Prog., 19, 167, (2000).
16. Malerius O., Werther J., Chem. Eng. J., 96, 197, (2003).
17. Peloso A., Rovatti M., Ferraiolo G., Resour. Conserv., 10, 211, (1983).
18. Panday K.K., Prasad G., Singh V.N., Water Res., 19, 869, (1985).
19. Sen A.K., De A.K, Water Res., 21, 885, (1987).
20. Mohan D., Singh K.P., Singh G., Kumar K., Ind. Eng. Chem. Res. 41, 3688, (2002).
21. Janos P., Buchtova H., Ryznarova M., Water Res., 37, 4938, (2003).
22. M.T. Postek, K.S. Howard, A.H.Johnson, K.L. Mc. Michael, A students Handbook Burlington: Ladd Research Industries (19113).
- 23.B.G. Kutchko, A.G. Kim, Fuel, 85, 2537, (2006).
- 24.A. Fernandez -Jimenez, A. Palomo, Microporous and Mesoporous Material, 86(1-30) 207, (2005).
25. A.Fernandez-Jimnez, M. Monzo, M. Vincent, A.Barba, A.Palomo, Microporous and Mesoporous Mater. 108, 41, (2008).