Adsorptive Removal of Tartrazine (E 102) Over Alkali Activated Fly Ash

Monika Dakshene* and Renuka Jain

Department of Chemistry, Government Post Graduate College, Kota-324 002, India
Tel: (91)(744)2460531; E-mail: monika.dakshene@gmail.com

In this study, fly ash from coal burning power plant was activated chemically, used as a low cost adsorbent for the removal of tartrazine dye. The activated fly ash was characterized by XRD. 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.

Key Words: Tartrazine, Dye, Fly ash, Activation, Adsorption.

INTRODUCTION

Among the different pollutants of aquatic ecosystem, dyes are a large and important group of industrial chemicals[1]. The organic effluents produced in industries such as textile, paper, plastic, cosmetic, rubber, *etc*., impart intense colour to the water bodies[2]. Tartrazine is a synthetic lemon yellow azo dye known as E102, which is used as food colouring agent[3] and also commonly used in pharmaceutical, cosmetic and other industries[4]. Discharging of this dye into water resources even in small amount can affect the aquatic life and the food web. It can also cause allergic dermatitis[5], skin irritation and may have carcinogenic and other disorders. Literature survey has shown that tartrazine has clear immunosuppressive effects[6]. Cases of skin eruptions in children have been reported. One published case report in a 5 year girl showed that she suffered from recurrent reactions to this colourant, with associated conditions such as urticaria, angioedema, headaches, dyspnea, loss of consciousness and abdominal pain[7]. Tartrazine has a noticeable effect on the behaviour of young mice[8,9]. It also inflamed the stomach lining (increasing number of lymphocytes and eosinophils) of rats[10]. Some existing technologies (oxidative destruction *via* UV/ozone treatment, photocatalytic degradation, electrochemical reduction *etc*.) may have certain efficiency in the removal of dyes but their initial operation cost is so high that they constitute an inhibition to dying and finishing industries[11-13]. Therefore this necessitates to find low cost treatment technologies and adsorption[14] to remove the dye.

Fly-ash, a finely divided powdered byproduct from coal fired plant or biomass combustion facilities required ultimate disposal. The major constituents of fly ash are silica, alumina and iron oxide. In this paper we report use of fly-ash as an

adsorbent by activating it for the effective removal of tartrazine from aqueous waste. Batch adsorption studies were carried out systematically and attempts have also been made to understand the adsorption equilibrium and kinetics.

EXPERIMENTAL

Class F fly-ash was collected from Kota super thermal power plant (KSTPS), Rajasthan for the present study.

Catalyst synthesis: The catalyst has been synthesized by adding 0.05 N NaOH to the pure fly-ash sample in a fixed ratio. Chemical activation was carried out by continuous stirring of a mixture (NaOH and fly ash) for 3 h at 90 °C then washed to a neutral pH and dried in an oven.

Characterization: Both the initial *i.e.*, pure fly-ash (FA) and the residue obtained after alkaline treatment *i.e.*, activated fly-ash (AFA) were characterized mineralogically and microstructurally. Philips Expert XRD was used for determining crystallite size. Samples were scanned at 2θ range of 0-80 °C at a scanning rate of 0.04 s^{-1}.

Adsorption kinetics: In the batch method, 50 mL of adsorbate solution was taken into an Erlenmayer 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 *ca.* 1400 ± 1 rpm. The kinetics was followed by withdrawing 0.05 dm^3 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.

RESULTS AND DISCUSSION

XRD Analysis: The presence of quartz, mullite and calcite is witnessed in both fly ash and activated fly ash [Fig. 1(a-b)]. Crystallite size was decreased from 33 nm to 11 nm on NaOH treatment. It is evident from XRD study that the 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. Previous studies have shown that fly ash after alkali treatment gives sharp diffraction peaks which are different from those present in untreated one. The diffractogrames show the original crystalline phases of fly ash, quartz and mullite are mostly absent in zeolite material after reaction[15].

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

$$Q_e = \frac{Q_0 b C_e}{(1 + b C_0)} \tag{1}$$
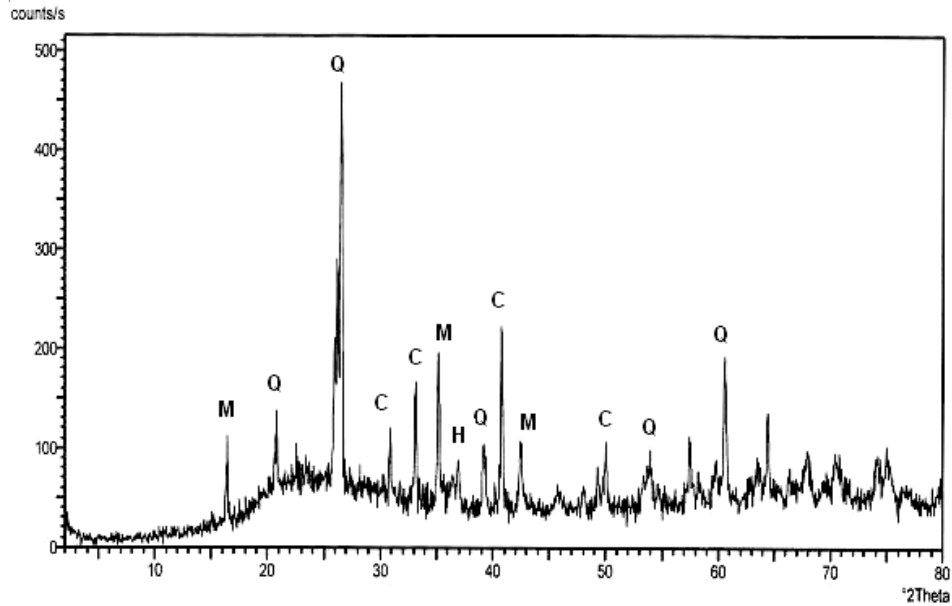
(a)
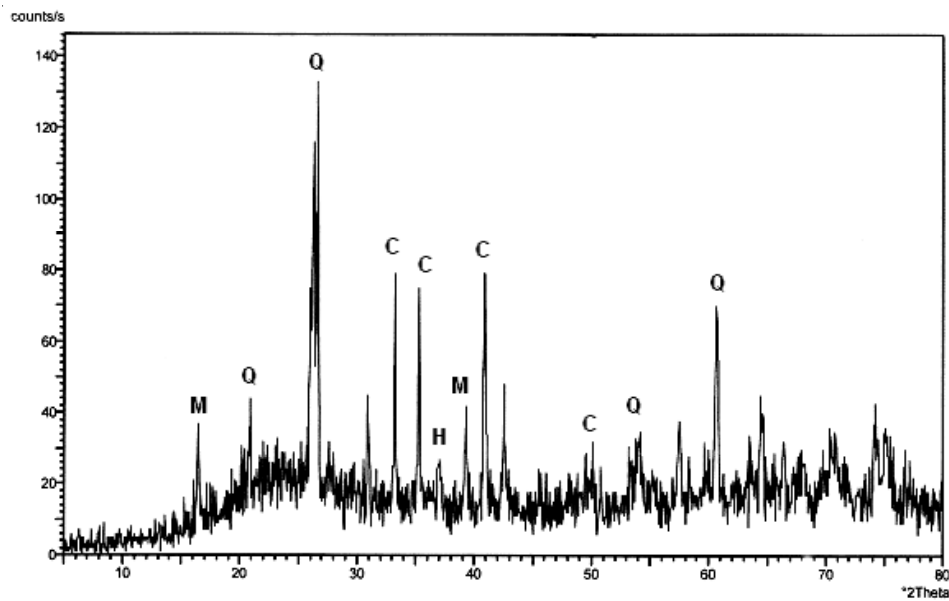
(b)

Fig. 1.   (a) XRD of pure fly ash (b) XRD of alkali activated fly ash (calcined at 400 °C).
          Q: Quartz, C: Calcite, M: Mullite, H: Hematite

or

$$\frac{m}{x} = \frac{1}{Q_0} + \frac{1}{Q_0 b C_e} \qquad (2)$$

where C_e = equilibrium concentration in mg/L and Q_0 = solid phase concentration corresponding to complete coverage of adsorption sites, b = 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)[16,17] which describes the type of isotherm and is defined by eqn. 3

$$r = \frac{1}{(1 + bC_0)} \tag{3}$$

Linearized Freundlich adsorption isotherm equation is given by eqn. 4

$$\log q_e = \log K_f + 1/n \log C_e \tag{4}$$

where q_e = amount of dye 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).
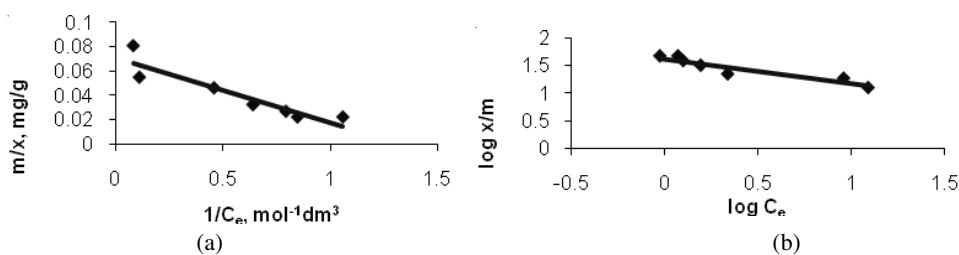

Fig. 2. (a) Langmuir plot (b) Freundlich plot

TABLE-1
VALUES OF LANGMUIR AND FREUNDLICH CONSTANTS FOR DYE ADSORPTION OVER ACTIVATED FLY ASH AT DIFFERENT CONCENTRATION [DYE] AT 30 °C

10^{-3} [dye] mol dm^3	Langmuir constants				Freundlich constant	
	b	r	Q_0	R^2	K_f	1/n
5	1.105	0.18	42.37	1.0	127.5	0.3554
10	0.624	0.18	83.92	1.0	162.5	0.3522
50	0.110	0.19	174.40	1.0	1980.6	0.4121

The above adsorption kinetics was modeled on five different models. All models were tested with least square regression analysis. The values of statistical parameters for different examples are given in Table-2. On the basis of high values of R^2 and low standard error of estimation the most favourable model is first order kinetic model (Fig. 3).

Kinetics of adsorption: Kinetics of tartrazine dye removal over activated fly ash is studied by varying concentration of dye, activated fly ash and temperature.

Time *versus* percentage adsorption graph shows initial rapid adsorption in both cases *i.e.*, dye variation and activated fly ash variation. Initial slope is used for determining initial rate (R_{obs}). From the log-log plot of R_{obs} *versus* tartrazine and R_{obs} *versus* activated fly ash, an order of 1.0 and 0.5 ± 0.04 is achieved, respectively.

TABLE-2
COEFFICIENT OF DETERMINATION (R^2), STANDARD ERROR OF ESTIMATION
(SEE) AND SLOPE FOR GRAPHICAL EQUATION OF DIFFERENT KINETIC
MODELS APPLIED ON DYE ADSORPTION ON [AFA] AT 30 °C

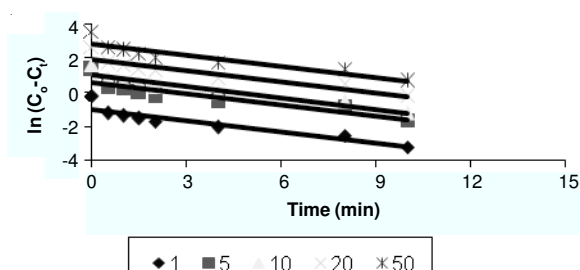| [dye] = 5 × 10 mol dm^{-3}		[AFA] = 2 g dm^{-3}	
Kinetic models	R^2	SEE	Slope
Zero order	0.6280	0.3327	-0.1180
First order	0.9825	0.1863	-0.1481
Elovich equation	0.7682	0.4522	-0.2215
Parabolic diffusion	0.4132	0.6125	-0.3236
Two rate constant	0.5303	0.0234	-0.0149

Fig. 3.   First order plot of dye with time at different concentration of activated fly ash [AFA] at 30 °C

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

$$R_{obs} = K[dye] [AFA]^{0.5} \qquad (5)$$

The value of K is calculated 0.42 ± 0.18 g $dm^{-1.8}$ s^{-1} from the plot of R_{obs} with $[AFA]^{0.5}$. Temperature was varied from 25-35 °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 42.16 ± 1.56 kJ mol^{-1}.
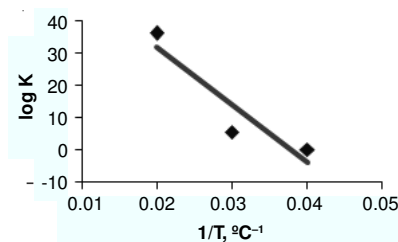

Fig. 4. Arrhenius equation plot for dye adsorption

Conclusion

It is concluded that adsorption catalyst activated fly ash synthesized during this work is found to have sufficient activity to remove tartrazine. Kinetic rate law has given first order with respect to initial concentration and a fractional order of 0.5 ± 0.04

for [AFA] at 30 °C. High values of activation energy indicates, chemisorption is to be important in case of using activated fly ash than physiosorption. The study generates fly-ash catalyst for waste water treatment in lubricants, plasticizer, pharmaceutical industries *etc*., where tartrazine remains as waste in the effluent.

REFERENCES

1. E. Voudrias, K. Fytianos and E. Bozani, *Global Nest: the Int. J*., **4**, 75 (2002).
2. Sumanjeet, T.P.S. Walia and I. Kansal, *J. Surface Sci. Tech*., **24**, 179 (2008).
3. Food Standards Australia New Zealand, Food Additives-Numerical List. Retrieved Dec (2009).
4. Business News for the Food Industry http://www.flexnews.com/console/PageViewer.aspx?page =10868&str.
5. K. Hatch and H. Maibach, *J. Am. Acad. Dermatol*., **12**, 1079 (1985).
6. N. Inomata, H. Osuna, H. Fujita, T. Ogawa and Z. Ikezawa, *Allergol Int*., **55**, 203 (2006).
7. K.S. Rowe and K.J. Rowe, *J. Pediatrics*, **125**, 691 (1994).
8. T. Tanaka, O. Takahashi, S. Oishi and A. Ogata, *Reprod. Toxicol*., **26**, 156 (2008).
9. T. Tanaka, *Food Chem. Toxicol*., **44**, 179 (2006).
10. I.L. Moutinho, L.C. Bertges and R.V. Assis, *Brazil. J. Biol.*, **67**, 141 (2007).
11. J. Churchley, *Ozone Sci. Eng*., **20**, 111 (1998).
12. S. Kang, C. Liao and S. Po, *Chemosphere*, **41**, 1287 (2000).
13. U. Ogutveren and S. Kaparal, *J. Environ. Sci. Health*, **29**, 1 (1994).
14. S. Pura and G. Atun, *Sep. Sci. Tech*., **44**, 75 (2009).
15. K. Ojha, N.C. Pradhan and A. Samanta, *Bull. Mater. Sci*., **27**, 555 (2004).
16. T.W. Weber and R.K. Chakravorti, *J. Am. Inst. Chem. Eng*., **2**, 228 (1974).
17. N. Kanan and M.M. Sundaram, *Ind. J. Environ. Protect*., **22**, 9 (2002).