

Adsorption of Glutaric Acid on Alkali Activated Fly Ash: A Kinetic Study

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ABSTRACT: Glutaric acid is a chemical that is commonly used in the production of different polymers such as polyester polyols, polyamides component, pharmaceutical and various other industries. Effluent emitted from these industries contain this chemical is a major cause of pollution in water system and is hazardous to the living beings. Fly ash from coal burning power plant was activated chemically, used as a low cost adsorbent for the removal of glutaric acid, which is a major cause of pollution in water system. The activated fly ash was characterized for mineralogical, physiochemical and morphological properties by XRD, FT-IR and 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 acidic waste from individual effluents. The adsorption kinetics is well represented by first order kinetic model.

KEYWORDS: Chemical activation, fly ash, glutaric acid, adsorption.

I. INTRODUCTION

Glutaric acid is one of the most widely used chemical in the world. A green house gas data shows that nearly 1.8 million metric tonnes of glutaric acid produced all over the world annually. It is mainly used to manufacture nylon fiber and plastic grease and as softener in rubber industries, wet strength resin, as a buffer in flue gas desulphurization treatment in power plants, plasticizers and pharmaceutical industries. This chemical is reported to affect individuals to difficulty in moving and may experience spasms, jerking, rigidity, or decreased muscle tone. Some individuals with glutaric acidemia (1,2) have developed bleeding in the brain or eyes that could be mistaken for the effects of child abuse pain, tearing in eyes, skin irritation etc., mucous membrane irritation, and possibility of asthma due to glutaric acid exposure, which is a major challenge for the environmentalists today.

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, 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) [3] 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 [4]. Other metal oxides such as Mn₂O₃, TiO₂ etc [5] and minerals like mullite, hematite, ferrite and rutile in fly ash [6] 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 [7-12] and many efforts have been made focused on heavy metals [13,14] and dye adsorption [15,16] on fly-ash particles. However no investigations have been reported on organic acids. In this paper we report use of fly-ash as an adsorbent by activating it, for the complete removal of glutaric acid from aqueous waste. Batch adsorption studies were carried out systematically and attempts have also been made to understand the adsorption equilibrium and kinetics.

II. EXPERIMENTAL

2.1 Materials and Methods

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 glutaric acid of BDH make was prepared by doubly distilled water. Phenolphthalein was used as an indicator in this study.

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Vol. 6, Issue 9, September 2017

2.2 Catalyst synthesis

The catalyst has been synthesized by adding 60 mL of 0.05 N NaOH to 40 g of pure fly-ash sample. Chemical activation was carried out by continuous stirring of a mixture (NaOH and F.A) for 3 h at 90 °C then washed to a neutral pH and dried in an oven.

2.3 Characterization

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. Samples were scanned at 2θ range of 0 - 80° at a scanning rate of 0.04 s⁻¹ [17]. FT-IR spectra of both the samples 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 30 s to 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 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 the 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 that are different from those present in untreated one. The diffractograms show the original crystalline phases of fly ash, quartz and mullite are mostly absent in zeolite material after reaction [18].

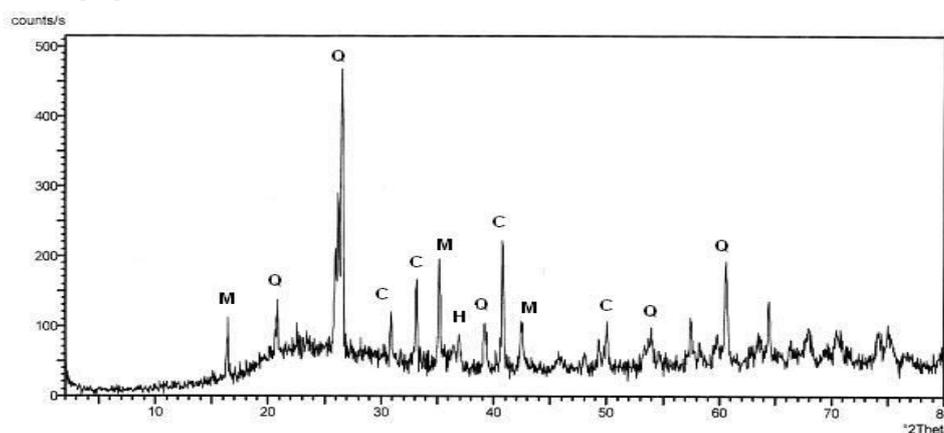


Fig. 1(a) - XRD of Pure Fly ash

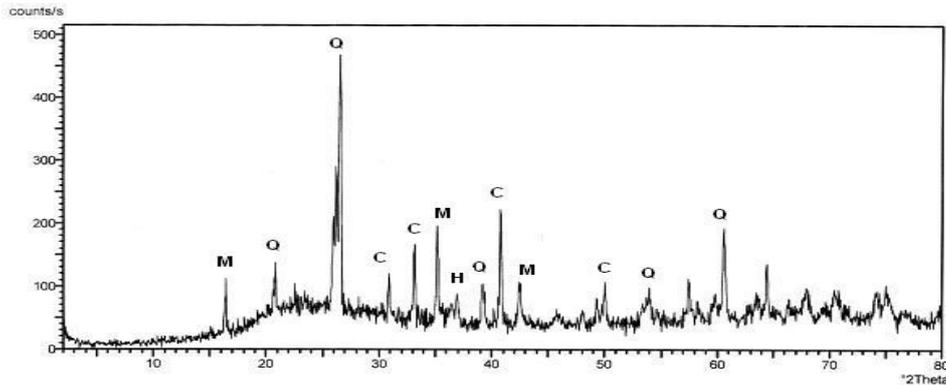


Fig. 1(b) - XRD of alkali activated Fly ash

3.1.2 SEM Analysis

Fig 2 (a) and (b) show 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 [19].

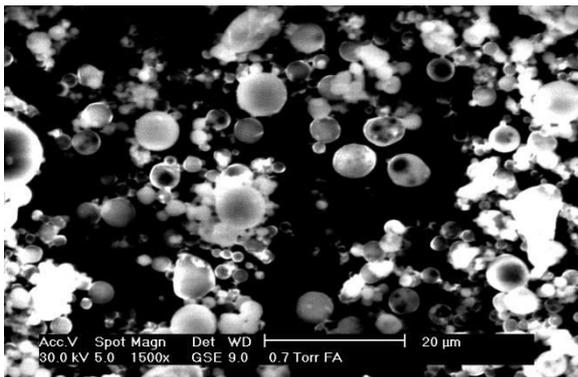


Fig. 2(a): SEM Photograph of Pure Fly Ash

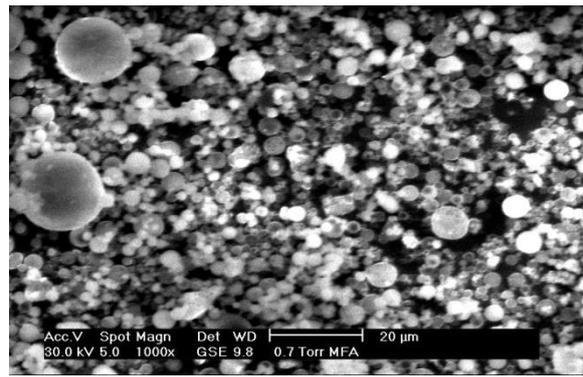


Fig. 2(b): SEM Photograph of alkali activated Fly Ash

3.1.3 FT-IR Analysis

In alkali activation process higher concentration of -OH groups favor the breaking of Si-O-Si, Al-O-Al and Si-O-Al bonds and formation of Si-OH and Al-OH groups occur which is confirmed by a broad band between 3400 - 3000 cm⁻¹ 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 cm⁻¹ is attributed to the sodium aluminosilicate [20] which is also confirmed by some previous studied [21].

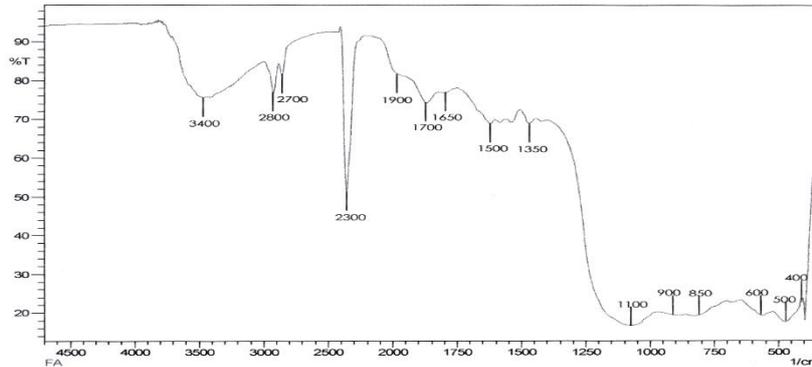


Fig. 3(a): FT-IR spectra of pure Fly Ash.

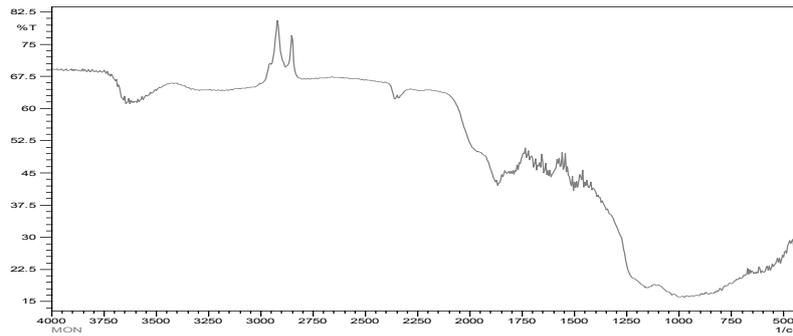


Fig. 3(b): FT-IR spectra of alkali activated Fly Ash.

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.

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

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

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) [22,23], which describes the type of isotherm and is defined by equation (3)

$$r = \frac{1}{1 + b C_0} \quad \text{Eq. (A.3)}$$

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.

International Journal of Innovative Research in Science, Engineering and Technology

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Vol. 6, Issue 9, September 2017

10 ³ [acid] mol dm ⁻³	Langmuir constants				Freundlich constant	
	b	r	Q ₀	R ²	K _f	1/n
5	1.035	0.18	39.39	1.0	117.8	0.3982
10	0.548	0.18	76.98	1.0	153.6	0.3989
50	0.103	0.19	169.7	1.0	1889.6	0.4932

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

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 glutaric acid on alkali activated fly ash.

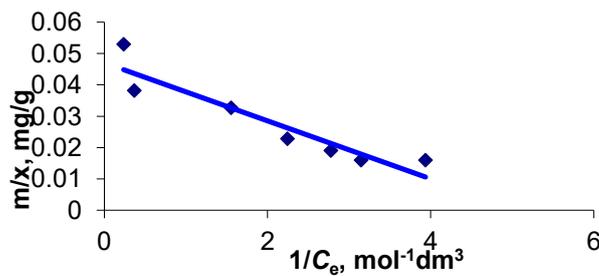


Fig 4(a): Langmuir plot

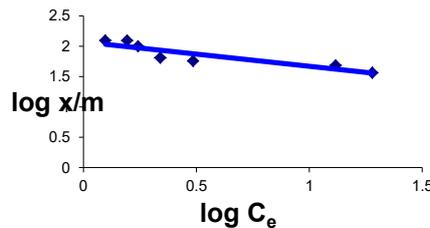


Fig 4(b): Freundlich plots

3.3 Kinetics of adsorption

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

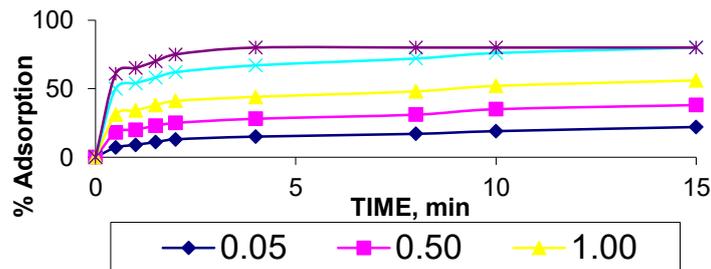


Fig. 5: Change in % adsorption of glutaric acid with time at different [AFA] at 30°C

International Journal of Innovative Research in Science, Engineering and Technology

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Vol. 6, Issue 9, September 2017

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 glutaric acid and R_{obs} v/s AFA, an order of 1.0 and 0.5 ± 0.03 is achieved respectively.

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

$$R_{obs} = K [GA] [AFA]^{0.5}$$

Eq. (B.1) The value of K is calculated $0.46 \pm 0.23 \text{ g}^{-0.5} \text{ dm}^{1.5} \text{ s}^{-1}$ from the plot of R_{obs} with $[AFA]^{0.5}$.

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 $39.15 \pm 1.95 \text{ kJ mol}^{-1}$.

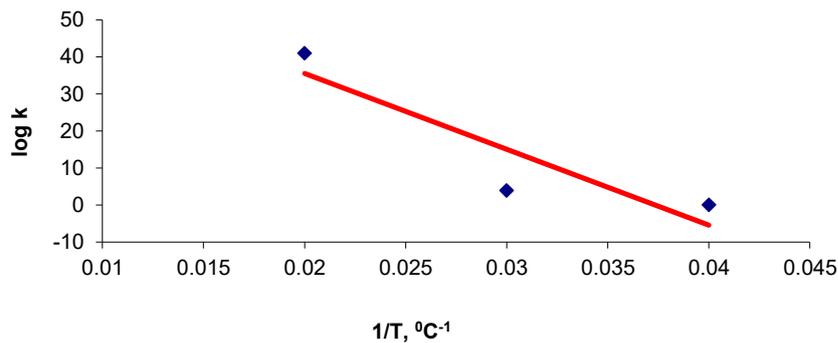


Fig. 6: Arrhenius equation plot for glutaric acid adsorption

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.

[ACID]= $5 \times 10^{-3} \text{ mol dm}^{-3}$, [AFA]= 2 g dm^{-3}			
Kinetic models	R^2	SEE	Slope
Zero order	0.7450	0.23559	-0.07
First order	0.9449	0.21044	-0.2182
Elovich equation	0.6078	0.12519	-0.0886
Parabolic diffusion	0.5919	0.41046	-0.4199
Two rate constant	0.7318	0.03103	-0.021

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

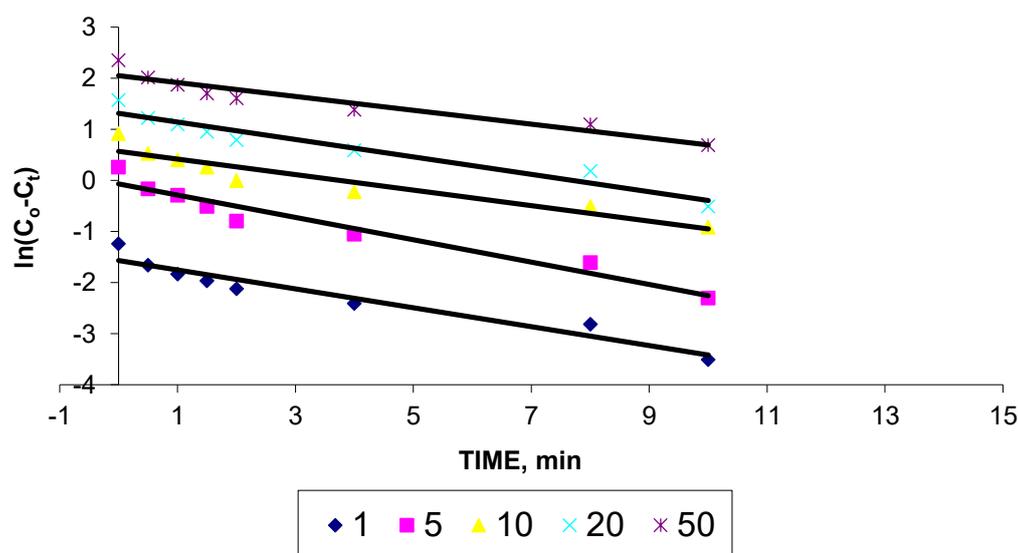


Fig. 7: First order equation plots for glutaric acid adsorption at different [Acid]. [AFA]= 2.0 g dm⁻³ Temp. = 30°C.

IV. CONCLUSION

The adsorption catalyst AFA synthesized during this work is found to have sufficient activity to remove glutaric acid. Kinetic rate law has given first order with respect to initial concentration and a fractional order of 0.5 ± 0.03 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 glutaric acid remains as waste in the effluent.

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Vol. 6, Issue 9, September 2017

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