Removal and Kinetics of Oxalic Acid Adsorption from Aqueous Waste over Alkali Activated Power Plant Fly Ash

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Oxalic acid is a chemical that is commonly used in the production of lubricant component, plasticizers, pharmaceutical, and rubber 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. This chemical is reported to cause pain, tearing in eyes, skin irritation etc. Fly ash from coal burning power plant was activated chemically, used as a low cost adsorbent for the removal of oxalic 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.

Keyword: Chemical activation, fly ash, oxalic acid, adsorption.

1. Introduction
Oxalic acid, a predominant organic acid present in urban aerosol and in the effluent of several industries. oxalic acid is widely used as a bleaching agent in pharmaceuticals and fiber sectors, as cleaning agent for pig iron, as precipitating agent for rare earth metals in film processing of aluminium alloys, as plasticizers for polymers, in leather tanning, as an auto radiator cleaner, as a disinfectant to control bacteria and in film processing of aluminium alloys, as plasticizers for polymers, in leather tanning, as an auto radiator cleaner, as a disinfectant to control bacteria and germs, and also as a grinding agent in marble polishing industries etc. [1].

In addition, oxalic acid is also used in waste water treatment, as a reducing agent for photography and ink removal, removal of rust stains from kitchen counter tops, plumbing fixtures and fabrics. It is a good substitute of acetic acid as colouring moderant for dye stuffs. In organic synthetic uses, oxalic acid is used in producing resins, urea-formaldehyde moulding powder, butadiene catalyst, in producing bacteriophage, preparation of raw material for porcelain capacitor and electronic equipment detergents and in photocatalytic effluent treatment [2]. It is also used in oil and gas industries [3] and sugar mills [4].

Oxalic acid as a dust or in solution irritates the eyes [5], mucous membranes and skin [6]. There is little reported information on industrial scale exposures [7, 8], although chronic inflammation of the upper respiratory tract [9] has been described due to exposure to hot vapours arising from oxalic acid [10]. Solutions are irritating to skin after prolonged exposure and may cause localized pain with cyanosis [11] of the fingers and even gangrenous changes. Splashes in the eye produce epithelial damage. Fatalities have been reported [12, 13] following ingestion of as little as 5 gm of acid; the onset symptoms are rapid including those of shock, collapse.
and convulsions. There may be marked renal damage, with the deposition of calcium oxalate in the lumen of the renal tubules. The potassium and calcium salts of oxalic acid are found naturally in few vegetables i.e. in cabbage, spinach and rhubarb leaves and also in the bark of some species of eucalyptus tree. Oxalic acid is most abundant in the Ali mountain region \[14\] followed by oxalic and malonic acid which are the photochemical products from natural emission. Concentrations of oxalic acid in summers are 2 to 3 times higher. The soil from the agriculture waste burning contains large quantities of oxalic acid which is a major challenge for the environmentalists today. So the removal of oxalic acid from the waste water is therefore quite essential and important.

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) \[15\] 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. Other metal oxides such as Mn\(_2\)O\(_3\), TiO\(_2\) etc. \[16\] and minerals like mullite, hematite, ferrite and rutile in fly ash \[17\] 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 \[18 -23\] and many efforts have been made focused on heavy metals \[24, 25\] and dye adsorption \[26, 27\] 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 oxalic acid from aqueous waste. Batch adsorption studies were carried out systematically and attempts have also been made to understand the adsorption equilibrium and kinetics.

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

2.2 Catalyst synthesis
The catalyst has been synthesized by adding 60 mL of 0.05 N NaOH to 40 gm of pure fly-ash sample. Chemical activation was carried out by continuous stirring of a mixture (NaOH and F.A) for 3 hr 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 micro structurally. Philips Expert XRD used for determining crystallite size. Samples were scanned at 2 \(\theta\) range of 0 - 80° at a scanning rate of 0.04 s\(^{-1}\) \[28\]. 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 N\(_2\) adsorption-desorption isotherms using NOVA 1000 E 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 gm dm\(^{-3}\)) was added and stirred continuously at about 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 30s to 2.5 min.

3. 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 1a, 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 \[29\].

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 non-silicate 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 \(\mu\)m and the majority of particles ranged in 1 \(\mu\)m to 100 \(\mu\)m, 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 \[30\].

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 \[31\] which is also confirmed by some previous studied \[32\].
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.

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

Or

\[
m/x = \frac{1}{Q_0} + \frac{1}{Q_0 b C_e}
\]  
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 \((r)\) \[^{33, 34}\] which describes the type of isotherm and is defined by equation (3)

\[
r = \frac{1}{1 + b C_0}
\]  
Eq. (A.3)

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

\[
\lg q_e = \lg K_f + \frac{1}{n} \lg C_e
\]  
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 oxalic acid adsorption over AFA at different [acid] at 30 °C

<table>
<thead>
<tr>
<th>10(^{-3}) [acid] mol dm(^{-3})</th>
<th>Langmuir constants</th>
<th>Freundlich constant</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>1.045</td>
<td>0.18</td>
</tr>
<tr>
<td>10</td>
<td>0.528</td>
<td>0.18</td>
</tr>
<tr>
<td>50</td>
<td>0.100</td>
<td>0.19</td>
</tr>
</tbody>
</table>

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.
3.3 Kinetics of adsorption
Kinetics of oxalic acid removal over AFA is studied by varying concentration of oxalic acid, AFA and temperature.

Fig 5: Change in % adsorption of oxalic acid 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 oxalic acid and $R_{obs}$ v/s AFA, an order of 1.0 and 0.6±0.03 is achieved respectively. The functional dependence of rate on [acid] and [AFA], the final rate law is

$$R_{obs} = K[(CH_2)_4(COOH)_2][AFA]^{0.6} \quad \text{Eq. (B.1)}$$

The value of $K$ is calculated 0.3475±0.13 g dm$^{-1.9}$ s$^{-1}$ from the plot of $R_{obs}$ with [AFA]$^{0.6}$.

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 43.54±2.15 kJ mol$^{-1}$.

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 oxalic acid adsorption on [AFA] at 30 °C.

<table>
<thead>
<tr>
<th>Kinetic models</th>
<th>$R^2$</th>
<th>SEE</th>
<th>Slope</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zero order</td>
<td>0.5540</td>
<td>0.23569</td>
<td>-0.07</td>
</tr>
<tr>
<td>First order</td>
<td>0.9953</td>
<td>0.01034</td>
<td>-0.2182</td>
</tr>
<tr>
<td>Elovich equation</td>
<td>0.6073</td>
<td>0.12509</td>
<td>-0.0886</td>
</tr>
<tr>
<td>Parabolic diffusion</td>
<td>0.4922</td>
<td>0.41016</td>
<td>-0.4199</td>
</tr>
<tr>
<td>Two rate constant</td>
<td>0.5419</td>
<td>0.13100</td>
<td>-0.021</td>
</tr>
</tbody>
</table>

4. Conclusion
The adsorption catalyst AFA synthesized during this work is found to have sufficient activity to remove oxalic acid. Kinetic rate law has given first order with respect to initial concentration and a fractional order of 0.6±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 oxalic acid remains as waste in the effluent.

Fig 7: First order equation plots for oxalic acid adsorption at different [Acid]. [AFA]= 2.0 g dm$^{-3}$ Temp. = 30 °C.

5. Acknowledgement
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6. References
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