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Removal and Kinetics of Phthalic Acid from Aqueous Waste over Activated Fly-Ash, Carbon and Their Blends

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ABSTRACT: Phthalic acid and its derivatives like phthalates and ester are important pollutants in surface and waste water system. In an attempt to investigate the most suitable cost effective adsorbent for the removal of phthalic acid, a comparative study was carried out on five different adsorbents- CAC, FA, AFA, CAC-AFA blends. XRD, SEM, FT-IR, TGA techniques were used to characterize mineralogical, morphological and physicochemical properties of pure and activated fly ash. Results showed that activated fly ash due to increased amorphous property possesses more activity over the surface to act as a suitable adsorbent for the removal of acid in waste; it can be taken as a replacement of costly treatment technologies.

KEYWORDS: Phthalic acid, activated fly ash, adsorption

I. INTRODUCTION

Phthalic acid and its derivatives are produced in large amount and being used in industries for making phthalate² plasticizer, unsaturated polyester^{1,3} and in various consumer products including building materials, clothing, pharmaceuticals⁴ etc. which seriously contaminate ground water, aquifers and surface water through leaching⁵⁻⁹. The acute toxicity of various phthalic acid esters and anhydrides has been determined in mammals and birds^{10, 11}. It is found to generate teratogenic effects in rats¹². Several biomonitoring studies have revealed a widespread exposure of the nonoccupational human population via food from plastic containers and via inhalation of dust in domestic environment^{13, 14}. Endocrinal disrupting effects¹⁵ are suspected by phthalate diester and phthalic acid ester¹⁶. Damage of reproductive system¹⁷, alteration of thyroid hormone levels in men¹⁸ were also identified by some researchers. It also causes apoptotic cell death in murine macrophage after short term exposure.

Methods are available for separation of phthalic acid from aqueous slurry of the industrial waste. The coal generated fly ash is also reported to act as a decomposer and adsorbent for the removal of industrial waste from water. 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) [10] 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 [10]. Other metal oxides such as Mn₂O₃, TiO₂ etc [11] and minerals like mullite, hematite, ferrite and rutile in fly ash [12] 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 [13-18] and many efforts have been made focused on heavy metals [19,20] and dye adsorption [21,22] on fly-ash particles. However no investigations have been reported on organic acids.

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This paper reports the adsorptive removal of phthalic acid over fly ash (FA), commercially activated carbon (CAC), chemically activated fly ash (AFA) and their mixed blends. Batch adsorption studies were carried out systematically to understand the adsorption equilibrium and kinetics.

In the present study the effort has been made to prepare cost effective fly ash catalyst having higher adsorption capacity to replace CAC. A comparative study of different adsorbents has also been done on the basis of their adsorption capacities.

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. CAC of BDH make, AR grade was used directly as an adsorbent. Stock solution of phthalic acid 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)
3. Commercially activated carbon (CAC)
4. AFA-CAC mixed blends

CAC and FA were used directly for the study. To prepare activated fly ash (AFA) alkaline treatment was given to the pure fly ash by adding 60 mL of 0.05N NaOH to 40 g of pure fly ash sample. Continuous stirring of mixture was carried out for 3 h at 90°C, then washed to a neutral pH and dried in an oven. This indigenously prepared alkali activated fly ash (AFA) was blended with CAC in a fixed ratio to prepare AFA-CAC mixed blends.

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 (18). 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 77K. 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 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 gdm⁻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.

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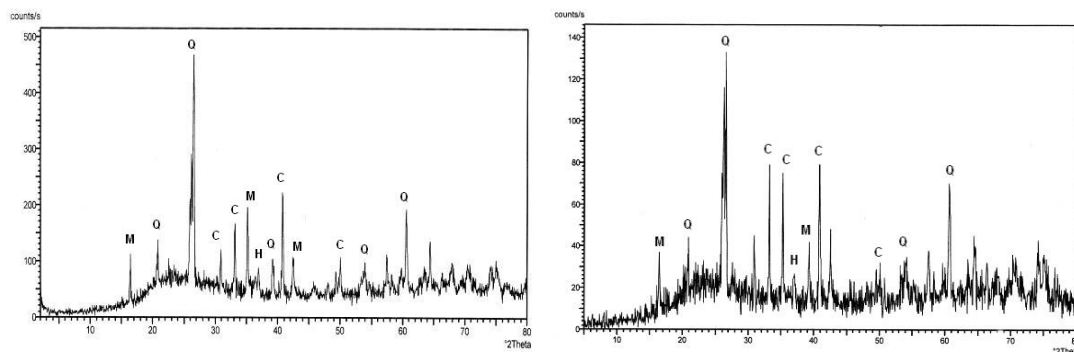
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III. RESULTS AND DISCUSSION

Characterization of adsorbent

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 33nm to 11nm 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. Previous studies have shown that fly ash after alkali treatment gives sharp diffraction peaks which 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 reaction¹⁹.



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

Fig. 1(a, b) - XRD of Pure FA and alkali activated FA (calcined at 400^o)

SEM Analysis

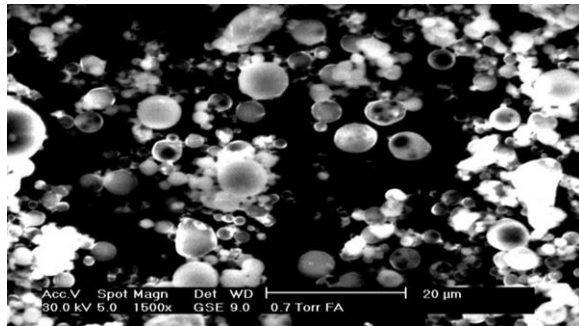
Fig 2 (a) and (b) shows the scanning electron microscope picture of pure and activated FA respectively. In addition to the general physical characteristics the elemental composition of random population of fly-ash, the SEM data clearly indicate intermixing of silica and alumina phases and predominance 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 840nm to 10µm and the majority of particles ranged in 1µm to 100µm, 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 data²⁰.

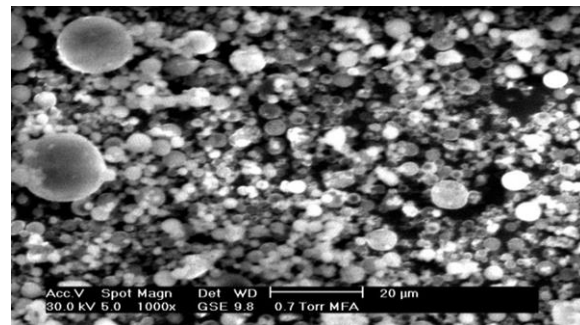
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(a)



(b)

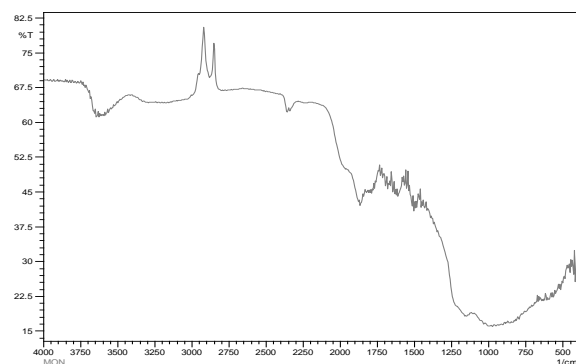
Fig. 2(a, b): SEM Photograph of Pure and alkali activated FA

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 $3400-3000\text{ cm}^{-1}$ 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 aluminosilicate²¹ which is also confirmed by some previous studied²².



(a)



(b)

Fig. 3(a, b) – FT-IR spectra of pure and alkali activated FA.

Kinetics of adsorption

In order to compare the adsorption capacity of indigenously prepared activated fly ash with FA, CAC and AFA-CAC mixed blends, % adsorption was determined with time for five different acid concentration for various adsorbents at amount of 2 gdm^{-3} .

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| TYPE OF ASORBENT, amount = 2 g dm ⁻³ | CONCENTRATION OF ACID, mol dm ⁻³ | | | | |
|--|---|--------------------|--------------------|--------------------|--------------------|
| | 1×10 ⁻³ | 5×10 ⁻³ | 1×10 ⁻² | 2×10 ⁻² | 5×10 ⁻² |
| 100% CAC | 98 | 97 | 96 | 95 | 94 |
| 100% F.A | 49 | 47 | 45 | 43 | 40 |
| 100% A.F.A | 90 | 88 | 87 | 86 | 85 |
| 75% CAC + 25% A.F.A | 99 | 97 | 96 | 95 | 94 |
| 50% CAC + 50% A.F.A | 97 | 95 | 94 | 93 | 92 |
| 25% CAC + 75% A.F.A | 95 | 93 | 92 | 91 | 90 |

Table1: Comparison of maximum % adsorption of phthalic acid at various [acid] and [adsorbents] at 30°C

It is clear from the table that activation of pure fly ash has increased its adsorption capacity remarkably and activated carbon can be replaced by AFA with a comparable removal capacity

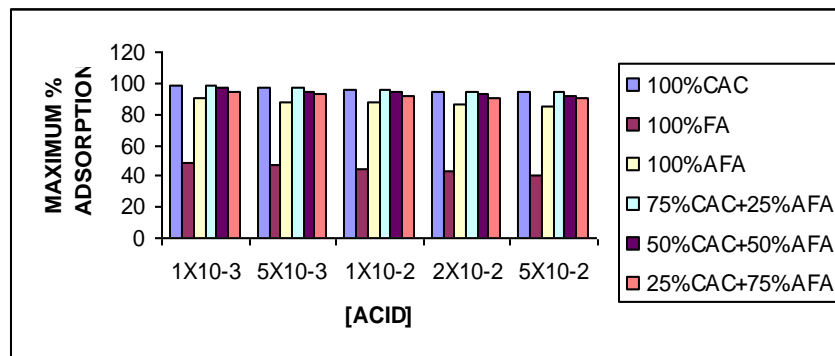


Fig 4: Comparison of maximum % adsorption of various adsorbents

Detailed kinetic study for activated fly ash is described here

Time v/s percentage adsorption graph shows (fig) initial rapid adsorption in both cases i.e. acid variation and AFA variation. Initial slope is used for determining initial rate (R_{obs}). From the log-log plot of R_{obs} v/s phthalic acid and R_{obs} v/s AFA, an order of 1.0 and 0.5 ± 0.03 is achieved respectively.

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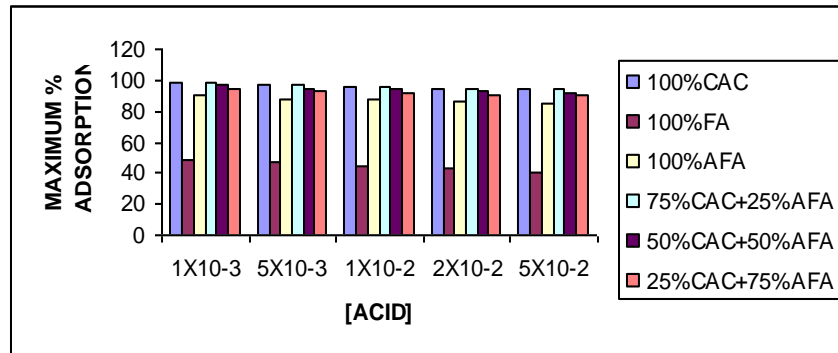


Fig. 5: Change in % adsorption of phthalic acid with time at different [AFA] at 30°C

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

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

The value of K is calculated $0.8044 \pm 0.2 \text{ gdm}^{-1.39} \text{ s}^{-1}$ 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 $61.24 \pm 3.06 \text{ kJ mol}^{-1}$.

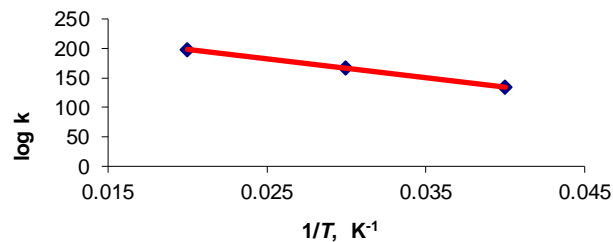


Fig. 6: Arrhenius equation plot for phthalic acid adsorption

Adsorption Isotherms

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

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

$$Q_e = \frac{Q_0 b C_e}{1 + b C_0}$$

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or

$$m/x = \frac{1}{Q_0} + \frac{1}{Q_0 b C_e}$$

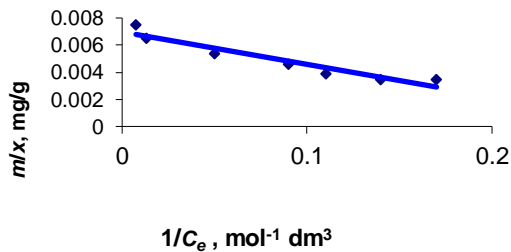
Where C_e is the equilibrium concentration in mg/L and Q_0 is the solid phase concentration corresponding to complete coverage of adsorption sites, b is the Langmuir constant which indicates the nature of adsorption and indicates the shape of the isotherm accordingly. The essential characteristics of 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)

$$r = \frac{1}{1 + bC_0}$$

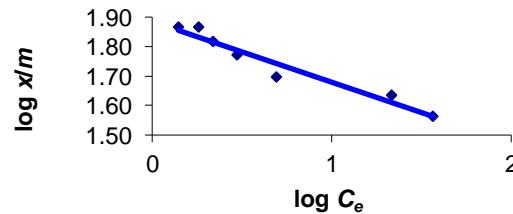
Linearized Freundlich adsorption isotherm equation is given by equation (3)

$$\log q_e = \log K_f + 1/n \log C_e \quad (4)$$

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.



Langmuir plot



Freundlich plot

The above adsorption kinetics was modelled 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.

| Kinetic models | R^2 | SEE | Slope |
|----------------|-------|--------|-------|
| Zero order | 0.708 | 0.3887 | - |
| First order | 0.927 | 0.2223 | - |
| | 5 | 1 | 1 |

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| | | | |
|---------------------|------------|--------|-----------------|
| Elovich equation | 0.769 2 | 0.4402 | 0.200 5 |
| Parabolic diffusion | 0.383 2 | 0.5755 | 0.323 6 |
| Two constant rate | 0.690 3 | 0.0234 | - 0.014 9 |

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

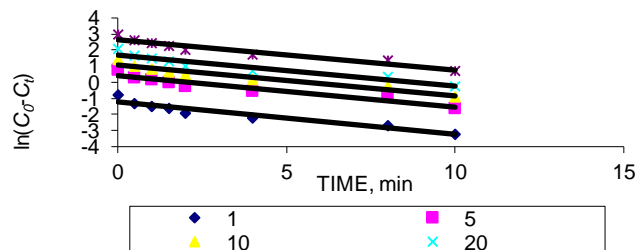


Fig. 7: First order equation plots for phthalic acid adsorption at different [Acid]. [AFA] = 2.0g dm⁻³ Temp.= 30°C.

IV. CONCLUSION

Removal efficiency and adsorption capacity was found to be highest for CAC. Experimental results have shown a comparable removal capacity of activated fly ash with CAC. These experiments indicate that AFA is a promising adsorbent for the removal of phthalic acid from aqueous waste, since it is easily available in large quantity and its treatment method is very economical. The isothermal data of adsorption followed both Langmuir and Freundlich isotherm.

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