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Removal of Tannic Acid from Aqueous Waste Over NaOH Treated Power Plant Fly-Ash

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Waste water containing tannic acid pose grave problems to the environment. As organic molecules are recalcitrant to bio degradation and difficult to treat by conventional methods, their effective removal from pollution generating sites is essential to prevent environmental hazards. In this study, fly ash from coal burning power plant was activated chemically and used as a low cost adsorbent for the removal of tannic acid from their aqueous waste. The activated fly ash was characterized for mineralogical, physiochemical and morphological properties by XRD, FT-IR and SEM analysis. 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 industrial effluents.

Key Words: Chemical activation, Fly ash, Tannic acid, Adsorption.

INTRODUCTION

Tannic acid belongs to the category of tannins, a toxic component present dominantly in plants and vegetables[1] were in commercial use long before there was any clue about their natural function. It has astringent, antibacterial and anti enzymatic properties. It is used in industrial process to convert animal skin to leather. Researchers have reported an interesting background regarding the use of tannic acid in leather industry and also demonstrated the toxicity of tannery effluent to the larvae of mosquito[2,3]. Negative effect of these effluents was also observed in fish. They altered the biochemical composition of fish tissue[4,5]. These effluents significantly decreased the food transportation capabilities in Channa Straitus and Ciprinus Carpio[6]. They are also used as a clarifying agent in wine fining industries[7], used for removing adhesiveness and for fungus control in common carp eggs[8]. Tannic acid and their byproducts are well known in degrading aquatic habitat and are problem for sick fish and inflict mortalities in aquatic organisms[9]. Toxicity of tannic acid was tested in Sea Urchin[10] both inhibitory and hormetic effects were detected. High dose of tannic acid can cause oxidative injury in mice[11] and definitely toxic when rats and mice injected intraperitoneally[12]. It shows mutagenic effects by damaging DNA in human lymphocytes[13]. Due to its wide applications in various industries, tannic acid is present in waste as toxic effluents emerging out of such industries and influences the properties of soil and aquatic environment receiving industrial waste.

Fly-ash, a finely divided powdered byproduct[14] 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[15]. Other metal oxides such as Mn_2O_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[18-21] and many efforts have been made focused on heavy metals[22,23] and dye adsorption[24,25] 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 tannic acid 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, collected from KSTPS (Kota super thermal power plant), Rajasthan, was dried and sieved to obtain uniform particle size sample. Stock solution of tannic acid of BDH make was prepared by doubly distilled water. Phenolphthalein was used as an indicator in this study.

Two types of fly ash *i.e.*, pure fly ash (FA) and activated fly ash (AFA) are used in this study. Fly ash was used directly for the study. To prepare activated fly ash 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 ℃ under stirring and kept 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 ℃ for 24 h. The chemically activated fly ash was thermally stabilized after calcination at 450 ℃ for 4 h in static conditions.

Characterization: Both the initial *i.e.*, pure fly-ash and the residue obtained after alkaline treatment *i.e.*, activated fly-ash were characterized mineralogically and microstructurally. Philips expert XRD used for determining crystallite size were scanned at 2θ range of 0-80 ℃ at a scanning rate of 0.04 s^{-1} [26]. FT-IR spectra of both the samples (Fig. 3a-b) were recorded in the range 4000-400 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 1000E surface area at 77 K. Thermogravimetric analysis was investigated in the temperature range 50-1000 ℃ 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.

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 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 0.5-2.5 min.

RESULTS AND DISCUSSION

Characterization of adsorbent

XRD Analysis: The presence of quartz, mullite and calcite is witnessed in both pure fly ash and activated fly ash (Fig. 1a-b). Crystallite size was decreased from 33-11 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 nano-crystalline phase in the sample.

SEM Analysis: Fig. 2(a-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.

(a)

(b)

Q: Quartz, C: Calcite, M: Mullite, H: Haematite
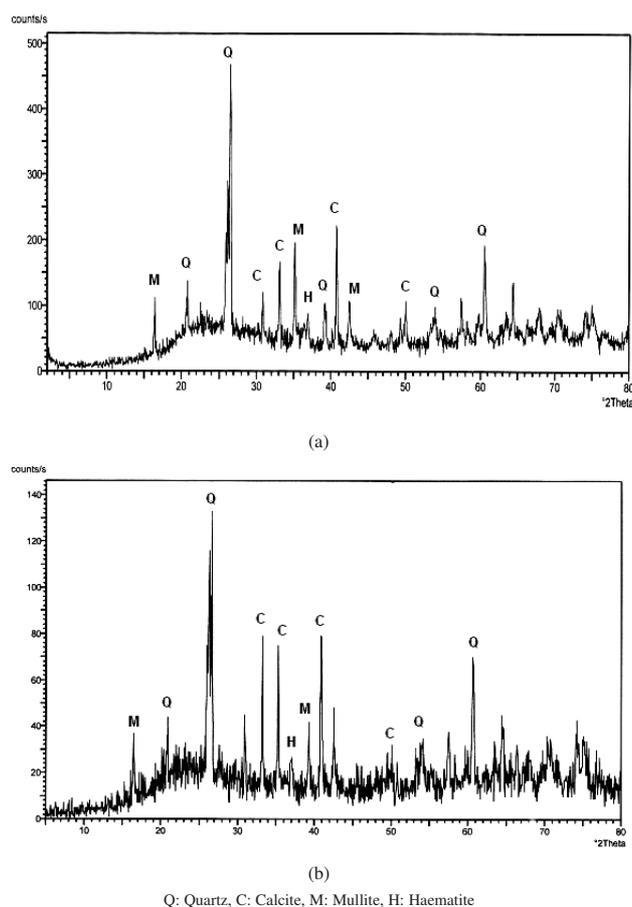
Fig. 1(a-b). XRD of pure fly ash and alkali activated fly ash (calcined at 450 ℃)
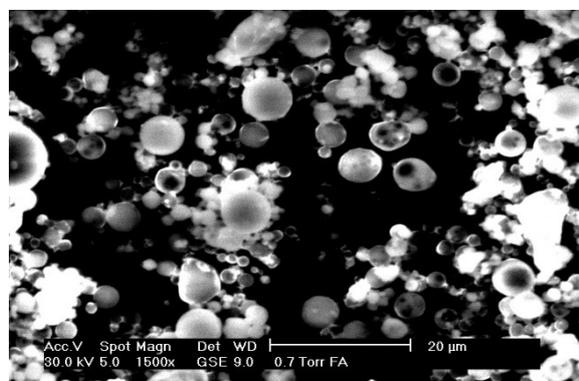
(a)
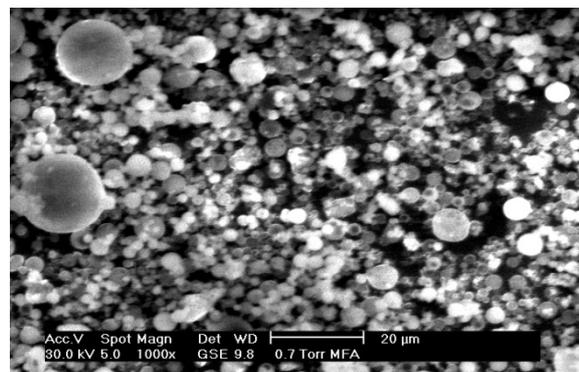
(b)

Fig. 2. (a-b): SEM Photograph of pure and alkali activated FA

Fig. 2(a) reveals that in the pure fly ash, the size of particles range from 840 nm to 10 μm and the majority of particles ranged in 1-100 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[27].

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 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, 1081 and 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 alumino silicate[28] which is also confirmed by some previous studied[29].

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

Time *versus* percentage adsorption graph shows initial rapid adsorption in both cases *i.e.*, acid 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* tannic acid (Fig. 3) and R_{obs} *versus* activated fly ash, an order of 1.0 and 0.65 ± 0.03 is achieved for dependence of rate on tannic acid and activated fly ash, respectively.
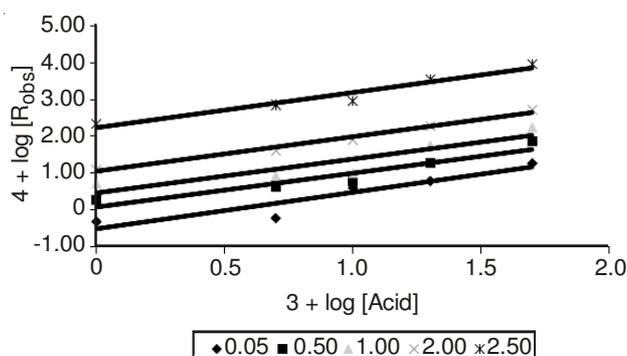
Fig. 3. log-log plots of R_{obs} against tannic acid for at 30 ℃

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

$$R_{obs} = k[C_{76}H_{52}O_{46}] [AFA]^{0.65} \qquad (1)$$

The value of k is calculated (0.46 ± 0.23) g$^{-0.5}$ dm$^{-1.5}$ s^{-1} from the plot of R_{obs} with [AFA]$^{0.65}$. Temperature was varied from 25-35 ℃. 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 (53.42 ± 1.05) kJ mol^{-1}.

Conclusion

The adsorption catalyst activated fly ash synthesized during this work is found to have sufficient activity to remove tannic acid. Kinetic rate law has given first order with respect to initial concentration and a fractional order of 0.65 ± 0.03 for [AFA] at 30 ℃. A high value of activation energy indicates, chemisorption is to be important in case of using activated fly ash than physisorption. The study generates fly-ash catalyst for waste water treatment in lubricants, plasticizer, pharmaceutical industries *etc.*, where tannic acid remains as waste in the effluent.

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