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ScienceDirect
Journal of Colloid and Interface Science 315 (2007) 41–46
JOURNAL OF Colloid and Interface Science
www.elsevier.com/locate/jcis

Humic acid adsorption on fly ash and its derived unburned carbon

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Received 3 April 2007; accepted 19 June 2007
Available online 23 June 2007

Abstract

Fly ash is solid waste from combustion process, containing oxide minerals and unburned carbon. In this investigation, fly ash has been separated into metal oxide mineral section and unburned carbon. The fly ash with different contents of unburned carbon was employed for humic acid adsorption to investigate the influence of unburned carbon on adsorption. It is found that metal oxides and unburned carbon in fly ash exhibit significant difference in humic acid adsorption. The unburned carbon plays the major role in adsorption. Higher content of unburned carbon in fly ash results in higher surface area and thus higher humic acid adsorption. Fly ash and unburned carbon exhibit adsorption capacity of humic acid of 11 and 72 mg/g, respectively, at 30 °C, pH 7. Humic acid adsorption is also affected by ion strength, pH, and temperature. The thermodynamic calculations indicate that the adsorption is endothermic nature with ΔH^0 and ΔS^0 as 5.79 kJ/mol and 16.0 J/K mol, respectively.

Keywords: Fly ash; Unburned carbon; Humic acid adsorption; Isotherm

1. Introduction

Humic acid (HA) is one of the major components of humic substances which arise by the microbial degradation of biomolecules. The presence of humic substance in water introduces a yellowish to brown colour. Moreover, high affinity of humic substance for complexation with various pollutants including heavy metals and pesticides causes contamination of ground and surface water. In addition, HA will form very toxic disinfection (chlorinated organic compounds including trihalomethanes) by-products which exhibit mutagenic properties during chlorination step in drinking water treatment [1–4]. Thus, removal of HA from surface water or wastewater is very important.

Adsorption is one of the efficient methods in humic acid removal. In the past years, several adsorbents have been employed for humic acid adsorption including activated carbon [5–8], clays [9,10], zeolite [11–13], chitosan [14,15], and metal oxides [16]. However, those adsorbents are expensive. In recent years, using low-cost adsorbent for adsorption has been much interested.

Fly ash is solid waste from coal and biomass combustion. In fly ash, unburned carbon is an important component, whose content changes with the combustion conditions. Disposal of fly ash has been an environmental burden. In the past a few years, a lot of investigations have been conducted using fly ash for adsorption in aqueous solution such as heavy metal ions and organics [17]. However, no study has been reported on HA adsorption using fly ash and its derivatives.

It has been found that fly ash exhibited a significant variation in adsorption capacity, which was always ascribed to fly ash sources. Little work has been done to identify the role of unburned carbon in fly ash for adsorption. Our recent work has shown that the unburned carbon plays a significant role in fly ash for cationic dye adsorption [18].

Unburned carbon in fly ash is a partially developed porous material due to high-temperature activation during combustion processes. Unburned carbon can be a precursor of activated carbon. Utilisation of unburned carbon replacing activated carbon as adsorbent will provide an economic method. In the past years, some investigations have been reported in utilisation of unburned carbon for mercury removal [19,20], surfactant [21],

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0021-9797/$ – see front matter
doi:10.1016/j.jcis.2007.06.034

and dyes [22–24]. In this paper, we report an investigation of humic acid adsorption on fly ash and its derived unburned carbon. We separated fly ash into several samples with varying contents of unburned carbon so as to investigate the effect of unburned carbon on adsorption and further to investigate adsorption characteristics of humic acid on fly ash and unburned carbon.

2. Experimental

2.1. Materials and chemicals

A raw fly ash sample (FA) was collected using electrostatic precipitators from Western Power, Australia. The raw fly ash sample has a content of unburned carbon at 5.2 wt%. The raw fly ash has been separated into a carbon-lean sample (FA-CL) and a carbon-riched sample (FA-CR) by dry sieving method. After that the FA-CR samples was further separated using water floating method to obtain unburned carbon (UC). Another carbon-free sample (FA-CF) was prepared by heat treatment of the raw fly ash at 800 °C for 16 h to remove all unburned carbon.

HA in sodium form was supplied by Aldrich. Other chemicals, sodium chloride, sodium sulfate, and potassium nitrate are of analytic grade and obtained from Chem-Supply, Australia.

2.2. Sample characterisation

The carbon content of the tested samples was determined using combustion method. The samples were put into an oven and heated to 800 °C for 16 h. The surface area and total pore volume of all samples were determined by N_2 adsorption under −196 °C using Autosorb (Quantachrome Corp.). All samples were degassed at 200 °C for 4 h, prior to the adsorption experiments. The BET surface area and pore volume were obtained by applying the BET equation and $p/p_0 = 0.95$ to the adsorption data, respectively.

The phases of all samples were determined by X-ray diffraction (XRD) analyses from a Rigaku Miniflex diffractometer with Co$K\alpha$ radiations generated at 30 kV, 15 mA. Scattering angles were ranged from 5° to 80°, with a scanning speed at 2° per minute.

The pH of samples was measured as follows: 0.1 g of various fly ash samples was mixed with 10 ml of distilled water and shaken for 24 h at 30 °C. After filtration, the pH of solution was determined by a pH meter (Radiometer PHM250 Ion Analyser). In addition, the point of zero charge of raw fly ash and unburned carbon was measured using the potentiometric mass titrations developed by Lycourghiotis and his colleagues [25,26].

2.3. Adsorption tests

The tests of HA adsorption onto various fly ash and unburned carbon samples were conducted in batch mode. In these experiments, 50 mg adsorbents, along with 100 ml HA solutions of concentrations 10–100 ppm, were put into 250 ml bottles. The temperature of all solutions was controlled at 30 °C, otherwise indicated, and pH 7 was maintained using 0.1 M HNO_3 and NaOH solution. The tests were conducted in an orbital-shaker at 100 rpm. The samples were taken out for centrifugation separation and then analysed. A UV–vis spectrophotometer (Metertech UV–vis SP-8001) was used for the determination of HA concentration at 258 nm.

The pH effect on HA adsorption was studied similarly as described above. In batch experiments, 50 mg adsorbents mixed with 100 ml HA solution at 50 ppm with different initial pH was set at 30 °C in the orbital-shaker at 100 rpm. The samples were taken out at different time interval for analysis.

The effect of different salts on HA adsorption on unburned carbon was also investigated. Solutions of sodium chloride, potassium chloride, potassium nitrate, sodium sulfate, and potassium sulfate at a concentration of 0.010 or 0.020 N were used. For each run, 50 mg solid with 100 ml of HA solution at 50 ppm at solution pH 7 was put in the orbital-shaker with set shaken rate of 100 rpm and 30 °C. The samples were then taken out for analysis at varying time interval using the spectrophotometer.

3. Results and discussion

3.1. Characteristics of various fly ash samples

The textural properties of the fly ash samples were determined by N_2 adsorption and the results are presented in Table 1. The raw fly ash shows BET surface area and total pore volume of 15.6 m^2/g and 0.016 cm^3/g, respectively. After sieving, carbon-lean sample presents smaller surface area and pore volume than the raw fly ash while carbon-riched sample produces much higher surface area and pore volume due to higher content of unburned carbon. After combustion, the carbon-free sample gives the lowest values of surface area and pore volume. The unburned carbon with carbon content of 84.5% has the highest surface area and pore volume.

The pH of slurry solution with different solid samples indicates that solid surface is acidic. The raw fly ash shows the strongest acidity while FA-CF exhibits the weakest acidity. UC has the same acidity as FA-CR and FA-CL around 5.3. This suggests that FA samples present positive charge on the surface. Potentiometric mass titrations of FA and UC give the PZC values (Table 1) and it is seen that they are close to the pH values of solid slurry solution. Some investigations have demonstrated that the pH values of suspensions may not differ substantially from the PZC of solid [26,27].

The XRD analysis (Fig. 1) shows that the mineral phases of FA, FA-CF, FA-CL, and FA-CR are much similar includ-

Table 1
Some properties of fly ash adsorbents

Sample	Carbon content (%)	S_{BET} (m^2/g)	V (cm^3/g)	pH	PZC
FA	5.2	15.6	0.016	4.4	5.0
FA-CF	0.3	2.5	0.005	6.0	–
FA-CL	2.7	8.3	0.010	5.4	–
FA-CR	36.7	169	0.14	5.3	–
UC	84.5	224	0.16	5.3	5.6