Journal of Hazardous Materials B126 (2005) 91–95

Journal of Hazardous Materials

www.elsevier.com/locate/jhazmat

# Sonochemical treatment of fly ash for dye removal from wastewater

Shaobin Wang *, Z.H. Zhu

*Department of Chemical Engineering, Curtin University of Technology, G.P.O. Box U1987, Perth, WA 6845, Australia*

Received 7 February 2005; received in revised form 23 May 2005; accepted 7 June 2005
Available online 19 July 2005

**Abstract**

Fly ash samples modified by NaOH solution and sonochemical treatment were tested for a basic dye (methylene blue) adsorption in aqueous solution. It is found that sonochemical treatment of fly ash can significantly increase the adsorption capacity depending on the concentration of NaOH and treatment time. The untreated FA and the sonochemically treated sample exhibits adsorption capacity at $6 \times 10^{-6}$ mol/g and $1.2 \times 10^{-5}$ mol/g at 30 °C, respectively. The adsorption tests show that solution pH and adsorption temperature also influence the adsorption behaviour. The adsorption isotherms can be fitted by Langmuir and Freudlich models, while the two-site Langmuir heterogeneous model will present the best result.


*Keywords:* Fly ash; Basic dyes; Wastewater; Adsorption; Ultrasonic treatment

## 1. Introduction

Many industries such as textile and printing use dyes and pigments and thus produce highly coloured waste effluents. Disposal of these wastes into waters causes environmental problems. Adsorption techniques employing solid sorbents are widely used for removal of certain chemical pollutants from waters and the adsorption process provides an attractive alternative for dye removal from wastewater if the sorbent is inexpensive.

Coal combustion produces a huge amount of by-product, fly ash, whose disposal requires large quantities of land and water. At present, most of fly ash is used as a fine aggregate for Portland cement. Resource recovery from coal fly ash is one of the most important issues in waste management all over the world. Since the major chemical compounds contained in fly ash are aluminosilicate, intensive efforts have been recently made to recycle fly ash by zeolitization [1]. In addition, fly ash is also used as low cost adsorbent for flue gas desulfurization (FGD) [2,3], adsorption of organics [4–6], dyes [7–9] and metal ions [10] from water. Our recent work has shown that modification of fly ash by chemical treatment could significant change the adsorption capacity of fly ash for dye removal [11].

In the last a few years, sonochemical method has been utilised for materials synthesis [12–15] and chemical processing [14,16]. It has been found that ultrasonics will provide an efficient method for synthesis and treatment. However, no investigation has been reported using sonochemical technique for fly ash treatment and application. In this paper, we report an investigation of sonochemical treatment of fly ash and the application for dye adsorption in aqueous solution. The effects of several parameters for treatment on adsorption capacity were investigated.

## 2. Materials and methods

### 2.1. Adsorption materials

The fly ash (FA) sample was obtained by separation of unburned carbon from the mineral section in a raw fly ash received from Western Power, Australia. The chemical compositions of the raw fly ash are $SiO_2$ (55%), $A1_2O_3$

* Corresponding author.
*E-mail address:* wangshao@vesta.curtin.edu.au (S. Wang).

0304-3894/$ – see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.jhazmat.2005.06.009

(29%), $Fe_2O_3$ (8.8%), CaO (1.6%) and MgO (1.0%). The chemical treated samples were obtained using NaOH at different concentrations and different methods. One sample was obtained at room temperature by mixing 5 g fly ash with 5 M NaOH solution at 10 mL for 24 h. After treatment, the samples will be filtered, washed and dried at 100 °C overnight. The sonochemical treated fly ash samples were obtained by mixing 5 g fly ash with 10 mL NaOH at different concentrations in an ultrasonic bath (40 Hz, 300 W, FXP14M, Unisonics, Australia). After a varying period of time, the samples were filtrated, washed and dried in oven at 100 °C overnight.

Methylene blue (MB), a typical dye widely used in medicine, textile and printing industry, was employed as dye pollutant and obtained from Unilab, AJAX Chemicals. A stock solution ($3.5 \times 10^{-4}$ M) of the dye was made by dissolving the dye in doubly distilled water. Further solutions of different concentrations were made by using the same stock solution.

### 2.2. Characterisation of adsorbents

X-ray diffraction (XRD) patterns of all samples were obtained with an automated Siemens D500 Bragg-Brentano instrument using Cu Kα radiation at 40 kV and 40 mA over the range ($2\theta$) of 5–70 °.

The BET surface area was obtained by applying the BET equation to the $N_2$ adsorption data, which were carried out manometrically at −196 °C using an Autosorb (Quantachrome Corp.). Before adsorption, all samples were degassed at 200 °C for 4 h.

The pH of solid samples was measured as follows: 0.5 g of the raw or treated fly ash 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).

### 2.3. Sorption method

Batch adsorption experiments were performed at varying temperatures in this investigation. The adsorption of dyes was performed by shaking 0.02–0.1 g of solids in 100 mL of dye solution with varying concentrations at 100 rpm for 72 h (Certomat R shaker from B. Braun). The determination of dyes was done spectrophotometrically on a Spectronic 20 Genesis Spectrophotometer (USA) by measuring absorbance at $\lambda_{max}$ of 665 nm for methylene blue. The contact time and other conditions were selected on the basis of preliminary experiments. It is found that the equilibrium can be established in 70–80 h and thus the contact period was determined to be 72 h for all equilibrium tests [11].

The effect of solution pH on adsorption was also investigated. A series of dye solution was prepared by adjusting initial pH of solution over a range of 2–11 using 1 M $HNO_3$ or NaOH solution. The pH of solutions was measured with a pH meter (Radiometer PHM250 ion Analyser).

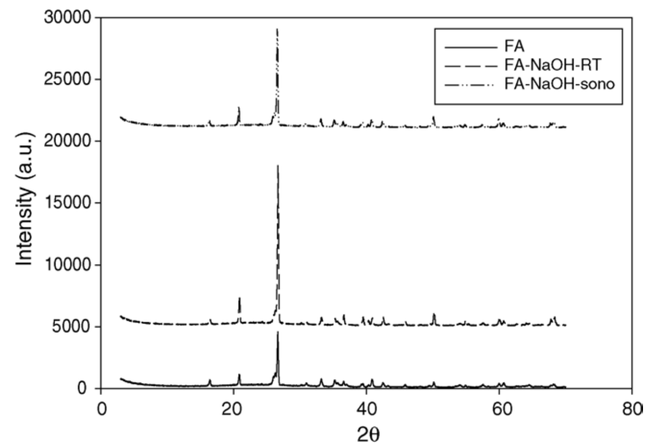


Fig. 1. XRD patterns of fly ash and treated fly ash samples.

## 3. Results and discussion

### 3.1. Characteristics of adsorbents

The XRD patterns of the fly ash and treated samples are shown in Fig. 1. As seen that there is no significant profile change for all samples, suggesting that NaOH treatment at room temperature will not induce the conversion of fly ash into other new phases. Major phases for all samples are quartz and mullite. Minor phases such as hematite and magnetite are also existed. However, other surface properties of fly ash are changed due to NaOH treatment (Table 1). The surface areas of treated fly ash samples are increased and the acid-basicity of solid slurry is also changed from acidity to basicity. Sonochemical treatment produced higher surface area and basicity than conventional chemical treatment. This is probably due to the strong interaction between solid and solution during sonochemical treatment process. The chemical effect of ultrasound is produced through the phenomenon of cavitation, which is caused by the expansion and contraction of cavitation nuclei due to the compression and rarefaction cycles of the ultrasonic waves. Cavitation causes the formation, rapid growth and finally implosive collapse of the bubbles, resulting in unusual reaction environment in the vicinity of the bubbles [17].

Table 1
Physico-chemical properties of fly ash

| Sample | $S_{BET}$ ($m^2$/g) | pH | Chemical phases |
|---|---|---|---|
| FA | 5.6 | 5.4 | Quartz, mullite with minor hematite and magnetite |
| FA-NaOH | 20.2 | 8.8 | Quartz, mullite with minor hematite and magnetite |
| FA-NaOH-sono | 35.4 | 9.7 | Quartz, mullite with minor hematite and magnetite |