

Sonochemical treatment of fly ash for dye removal from wastewater

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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 6×10^{-6} mol/g and 1.2×10^{-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 Freundlich models, while the two-site Langmuir heterogeneous model will present the best result.

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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 significantly 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 SiO₂ (55%), Al₂O₃

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(29%), Fe₂O₃ (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 (3.5×10^{-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 K α radiation at 40 kV and 40 mA over the range (2θ) of 5–70 °.

The BET surface area was obtained by applying the BET equation to the N₂ 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 λ_{\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 HNO₃ or NaOH solution. The pH of solutions was

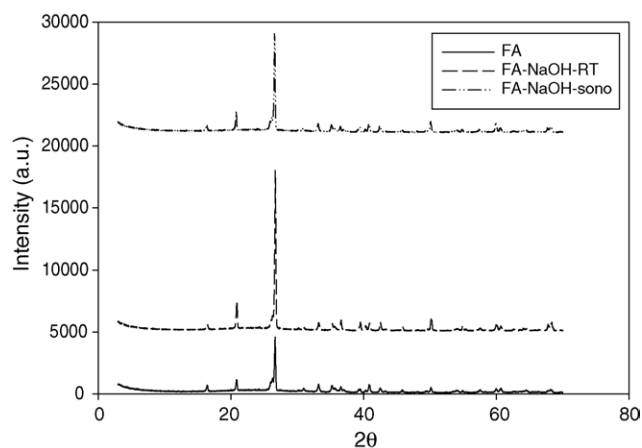


Fig. 1. XRD patterns of fly ash and treated fly ash samples.

measured with a pH meter (Radiometer PHM250 ion Analyser).

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

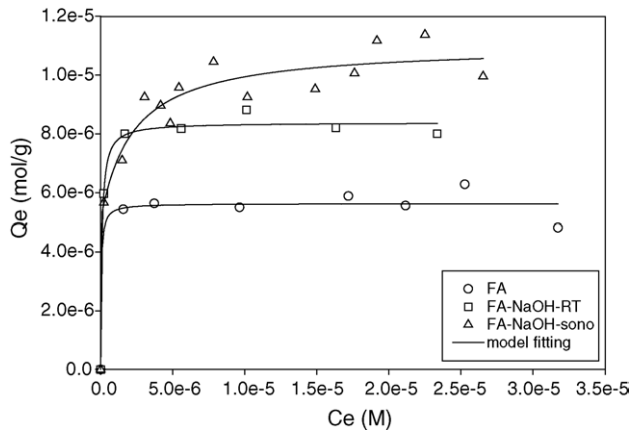


Fig. 2. Adsorption isotherms of various fly ash samples at 30 °C for MB.

3.2. Effects of chemical and sonochemical treatment

Fig. 2 presents a comparison of adsorption behaviour of fly ash, conventionally chemical-treated sample and sonochemically treated fly ash. As shown that the raw fly ash exhibits low adsorption at capacity around 6×10^{-6} mol/g. After chemical treatment by NaOH, the adsorption capacity can increase to 8×10^{-6} mol/g. The sonochemically treated sample shows much higher adsorption, reaching 1.2×10^{-5} mol/g, almost doubling the capacity value of the untreated fly ash. From the table, it is found that the adsorption capacity is in the order similar to the variation of surface area and pH of solid slurry, suggesting that higher surface area and basicity of solid surface will produce higher adsorption capacity.

3.3. Effect of treatment time

Fig. 3 shows the effect of sonochemical treatment time on adsorption of methylene blue. It is seen that the increased treatment time can also result in the enhancement of adsorption capacity. The adsorption capacity can be enhanced from 6×10^{-6} mol/g to 9×10^{-6} mol/g at the treatment of 2 h.

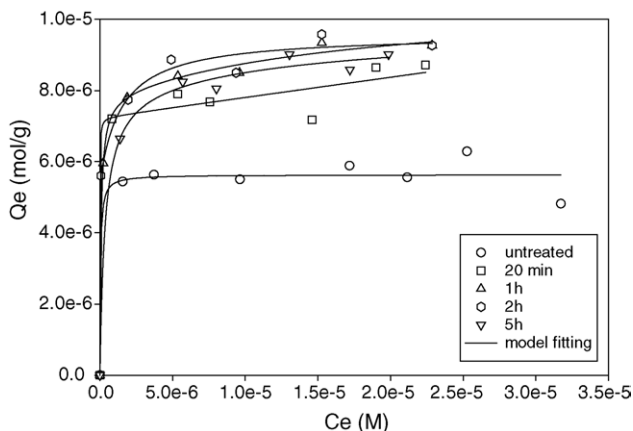


Fig. 3. Effect of treatment time on adsorption capacity.

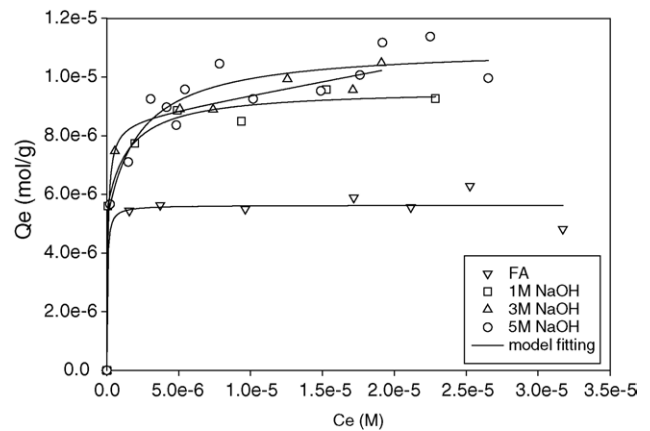


Fig. 4. Effect of NaOH concentration on adsorption capacity.

When the treatment time is longer than 2 h, the adsorption shows a bit of decreased values, suggesting that longer treatment may not have further effect to change the properties of adsorbents.

3.4. Effect of NaOH concentration

Fig. 4 displays the adsorption isotherms of fly ash treated at different NaOH concentrations. One can see that an increased NaOH concentration will bring about a positive effect on adsorption capacity. The higher of the concentration, the higher the adsorption capacity is. The adsorption capacity can change from 9.0×10^{-6} mol/g to 1.2×10^{-5} mol/g when the NaOH solution concentration increases from 1 M to 5 M.

3.5. Adsorption isotherms

The successful representation of the dynamic adsorptive separation of solute from solution onto an adsorbent depends upon a good description of the equilibrium separation between the two phases. There are many theories relating to adsorption equilibrium [18]. The important adsorption isotherms are the Langmuir isotherm and Freundlich isotherm.

The Langmuir isotherm theory assumes monolayer coverage of adsorbate over a homogenous adsorbent surface. Once a dye molecule occupies a site, no further adsorption can take place at that site. The generalised Langmuir isotherm can be written in the form:

$$Q_e = \sum_{i=1}^n \frac{A_i B_i C_e}{1 + B_i C_e} \quad (1)$$

Q_e is the adsorbed amount of the dye, C_e the equilibrium concentration of the dye in solution and A_i and B_i are the parameters on the Langmuir isotherm. A_i is the monolayer adsorption capacity and B_i is the constant related to the free energy of adsorption. In most cases, the single- or two-site models give a satisfactory fit to experimental data.

Table 2
Comparison of adsorption models

Model	Parameters	R^2
Single-site Langmuir isotherm	$A_1 = 9.18 \times 10^{-6}$ (mol/g); $B_1 = 4.22 \times 10^6$ (L/mol)	0.9620
Two-site Langmuir isotherm	$A_1 = 7.84 \times 10^{-6}$ (mol/g); $B_1 = 1.31 \times 10^7$ (L/mol); $A_2 = 2.87 \times 10^{-6}$ (mol/g); $B_2 = 5.20 \times 10^4$ (L/mol)	0.9978
Freundlich isotherm	$K = 2.57 \times 10^{-5}$ (mol/g); $1/n = 0.0934$	0.9954

The Freundlich expression Eq. (2) is an exponential equation and therefore, assumes that as the adsorbate concentration increases so too does the concentration of adsorbate on the adsorbent surface. In this equation K and n are the Freundlich constants. This expression is characterised by the extent of the adsorption (K) and the heterogeneity factor (n), and so the Freundlich isotherm may be used to describe heterogeneous systems.

$$Q_e = KC_e^{1/n} \quad (2)$$

Fig. 5 shows a comparison of adsorption isotherms for curve fitting of the experimental results. The model parameters from all isotherms obtained from nonlinear regression to the above equations are presented in Table 2. From correlation coefficients, it is evident that the Freundlich model is better than single-site Langmuir model, and the two-site Langmuir model will be the best for simulation of the adsorption isotherm. This suggests that some heterogeneity in the surface or pores of the fly ash will play a key role in dye adsorption and that the heterogeneous adsorption model will be better for isotherm simulation.

3.6. Effect of pH

The pH of the dye solution is an important factor influencing the adsorption capacity. The variation of adsorption on FA and the sonochemical treated FA samples with the pH is displayed in Fig. 6. One can see that the adsorption is quite low at low pH values. When the pH is greater than 10, adsorption will be significantly increased. The adsorption of these charged dye groups onto the adsorbent surface is primarily

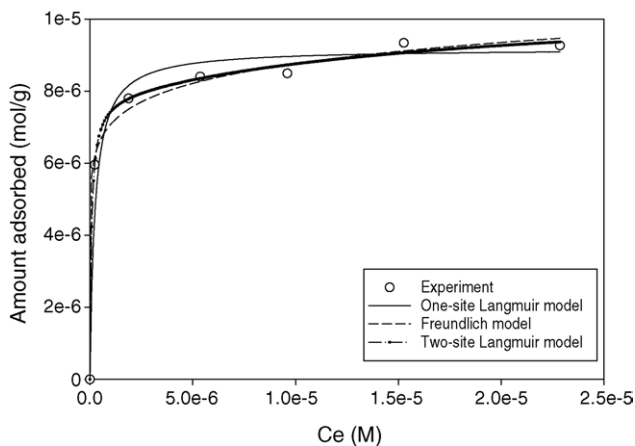


Fig. 5. Comparison of adsorption isotherms.

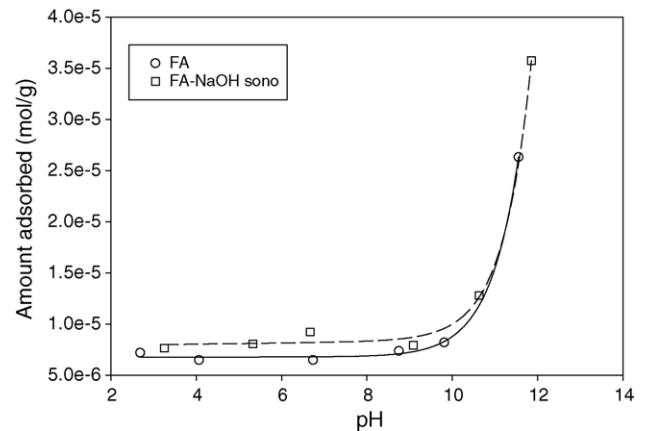


Fig. 6. Effect of solution pH on adsorption at 30 °C.

influenced by the surface charge on the adsorbent which is in turn influenced by the solution pH. Methylene blue is a basic dye. In water, it produces cation (C^+) and reduced ions (CH^+). As the pH of the dye solution becomes higher, the association of dye cations on solid will take place more easily.

3.7. Effect of adsorption temperature

The adsorption isotherms of FA-NaOH-sono at different temperatures are illustrated in Fig. 7. As shown that adsorption at 30 °C is higher than that at 20 °C while the adsorption isotherm at 40 °C is similar to that at 30 °C, which suggests that temperature will have a remarkable effect at lower temperatures. Table 3 presents the parameters of Freundlich isotherm fitting to the above adsorption isotherms. It is seen

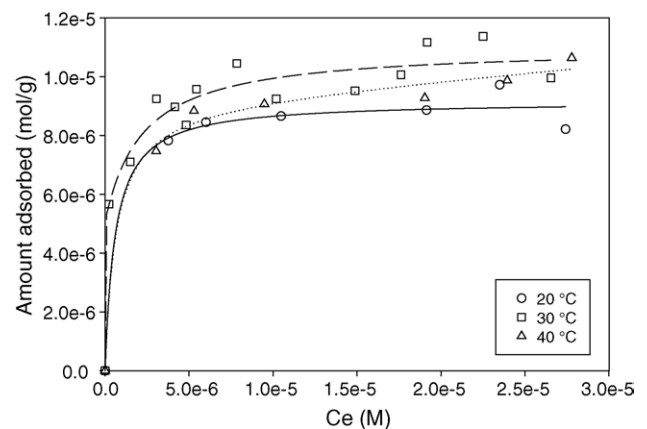


Fig. 7. Effect of temperature on adsorption capacity.

Table 3
Freundlich parameters at different temperatures for FA-NaOH-sono

Temperature (°C)	K (mol/g)	$1/n$	R^2
20	1.62×10^{-5}	0.0559	0.979
30	4.02×10^{-5}	0.124	0.949
40	3.72×10^{-5}	0.123	0.990

Table 4
Comparison of adsorption capacity for various adsorbents

Adsorbent	Adsorption capacity (mmol/g)	Reference
FA	0.0189	[19]
FA	0.0046	[19]
FA	0.0144	[20]
FA	0.0035	[21]
FA	0.0202	[8]
Fly ash derived zeolite	0.0338	[21]
Coconut shell derived activated carbon	0.0524	[22]
FA	0.014	[23]
FA-HNO ₃	0.025	[23]
Red mud	0.0078	[23]
FA	0.006	This work
FA-NaOH	0.008	This work
FA-NaOH-sono	0.016–0.040	This work

that adsorption capacity (K) and $1/n$ is close at 30 and 40 °C but both are much higher than that at 20 °C.

Table 4 presents a comparison of adsorption capacity obtained from other investigations on fly ash with the data in this work. As shown that fly ash in this work has similar adsorption capacity to others. After sonochemical treatment, the adsorption capacity can be comparative to the zeolite derived from fly ash and activated carbon from agricultural waste.

4. Conclusion

Fly ash could be utilised as a low cost adsorbent for dye removal after sonochemical treatment with NaOH. Sonochemical treatment with NaOH can significantly increase the surface area and surface basicity of the solid. The adsorption capacity can reach as high as 1.2×10^{-5} mol/g, while the adsorption capacity depends on treatment conditions such as NaOH concentration and treatment time. Solution pH and adsorption temperature also influence the adsorption capacity. Adsorption isotherm could be fitted using Langmuir and Freundlich models and the two-site Langmuir model showed the best results.

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