



Synthesis of zeolite/hydrous metal oxide composites from coal fly ash as efficient adsorbents for removal of methylene blue from water



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ARTICLE INFO

Article history:

Received 1 August 2015

Received in revised form 25 December 2015

Accepted 15 January 2016

Available online 22 January 2016

Keywords:

adsorption
hydrous metal oxide
methylene blue
variable charge
zeolite

ABSTRACT

Zeolites are useful crystalline aluminosilicate minerals, and zeolite synthesis from coal fly ash (ZFA) has been investigated widely to recycle solid waste. This synthesis process produces waste alkaline solution as a by-product. To date, research has focused mainly on ZFA synthesis and use; the problematic waste alkaline solution has rarely been addressed. In this study, we developed two composites of zeolite/hydrous iron oxide (ZFA/HIO) and zeolite/hydrous zirconia (ZFA/HZ) by adding, after zeolite synthesis, a step in which waste alkaline solutions are neutralized with an iron or zirconium salt. The composites were characterized by X-ray fluorescence, X-ray diffractometry, scanning electron microscopy, acid–base neutralizing ability, specific surface area and pore size distribution, and their performance as adsorbents for the removal of methylene blue (MB) from water was investigated. MB adsorption by ZFA/HIO and ZFA/HZ was much higher than that by ZFA, and increased with increasing pH. This behavior was explained by the increased variable charge on the metal oxides. The adsorption was rapid, and nearly complete removal could be achieved at a sufficiently high dose. Material heating resulted in a decrease in pH and adsorption, but heating with pH adjustment could regenerate adsorbents for repeated use in MB removal. Zeolite/hydrous metal oxide synthesis from coal fly ash was environmentally friendly and products exhibit a high potential as reusable adsorbents for MB removal from water.

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1. Introduction

Product coloring with dye is an important manufacturing process in, amongst others, textile, paper, plastics, tannery, and paint industries. Large amounts of dye wastewater are generated annually worldwide. Dye release into the environment can reduce water quality by reducing water clarity and aesthetic value and influencing photosynthetic activity, and may even pose a health risk for aquatic organisms and human beings because many dyes are toxic and carcinogenic (Crini, 2006; Gupta and Suhas, 2009; Mustafa et al., 2014). Therefore, decontamination of dyes from wastewater is critical before discharge.

Biological treatment is used widely, but it does not yield satisfactory color elimination because of its complex structure, artificial origin, and xenobiotic nature of dyes (Robinson et al., 2001; Khraisheh et al., 2005). Thus, further treatment is often needed to remove dyes efficiently. Adsorption can produce a high-quality treated effluent without sludge and secondary harmful substance production (Mustafa et al., 2014; Robinson et al., 2001). Most commercial systems currently use activated carbon as adsorbent to remove dyes from wastewater because of its excellent adsorption ability. However, the drawback of activated carbon is its high cost. In recent years, numerous materials have been studied as inexpensive and effective alternative adsorbents; these

include mineral materials, biosorbents, waste materials from industry and agriculture, and artificially synthesized materials (Crini, 2006; Gupta and Suhas, 2009; Mustafa et al., 2014; Robinson et al., 2001).

Basic dye is one of the main classes of dyes and is used widely. This water-soluble product exists as a cation in water. Methylene blue (MB) is a representative basic dye that has been investigated extensively for its adsorptive removal from water/waste water (Khraisheh et al., 2005; Ghosh and Bhattacharyya, 2002; Dogan et al., 2007; Almeida et al., 2009; Yao et al., 2015; Chen et al., 2014; Kannan et al., 2013; Han et al., 2007, 2009; Wang et al., 2006a, 2006b; Wang and Zhu, 2006; Tsai et al., 2009; Jin et al., 2008; Rida et al., 2013; Sapawe et al., 2013; Shirani et al., 2014; Li et al., 2015). Zeolite has received much attention amongst the numerous adsorbent materials investigated for MB removal (Han et al., 2007, 2009; Wang et al., 2006a, 2006b; Wang and Zhu, 2006; Tsai et al., 2009; Jin et al., 2008; Rida et al., 2013; Sapawe et al., 2013; Shirani et al., 2014; Li et al., 2015). Zeolites are aluminosilicate minerals with permanent negative charges in their porous crystal structures, which makes them suitable to adsorb cationic dyes.

A method to produce zeolite from coal fly ash (ZFA) has been developed to recycle global coal fly ash (CFA), which is a solid waste generated in large amounts worldwide (Querol et al., 2002; Murayama et al., 2008; Majchrzak-Kuceba and Nowak, 2011; Sommerville et al., 2013; Itskos et al., 2015; Bukhari et al., 2015; Sun et al., 2010; Koukouzas et al., 2010). Zeolite manufacture of this nature is appealing because of its low- or zero raw material cost and the possibility of reusing solid

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waste. Our previous study has shown that the capacity of ZFA to adsorb MB is comparable to or higher than other natural, commercial or chemically synthesized pure zeolites (Sun et al., 2010).

Although ZFA preparation and application has been investigated widely to recycle solid waste, large amounts of problematic waste alkaline solution remain after the synthesis process. We have recently initiated a novel method to synthesize ZFA/hydrous metal oxide hybrid material by introducing a reaction step into the traditional ZFA synthesis route that involves neutralizing waste alkaline solution with soluble metal salts (Xie et al., 2013, 2014). We also found that the newly developed material had a higher cation exchange capacity and specific surface area than the corresponding ZFA (Xie et al., 2013, 2014). Our new composite material may be an alternative to remove cationic dyes from wastewater. The aim of this study was to synthesize two hybrid materials, i.e., ZFA/hydrous iron oxide (ZFA/HIO) and ZFA/hydrous zirconia (ZFA/HZ), from CFA using our new method and to investigate their performance for the first time as efficient materials in MB removal. Hydrous oxides of iron and zirconium were selected to represent the trivalent and tetravalent metal oxides. Iron and zirconium are affordable, non-toxic and environmentally friendly (U.S. Department of the Interior and US Geological Survey, 2008; Nielsen and Wilfing, 2005; Schroeder and Balassa, 1966). The obtained materials were characterized and MB adsorption was tested under different solution conditions. Finally, material regeneration was tested to establish its behavior in repeated usage.

2. Materials and methods

2.1. Materials

A CFA sample with chemical composition as given in Table 1 was collected from Minhang thermal power plant, Shanghai, China and was used as raw material to synthesize ZFA/HIO and ZFA/HZ. Approximately 150 g of fly ash sample and 900 mL of 2 mol/L NaOH solution were placed in a continuously stirred reactor. The mixture was heated with stirring for 24 h at 98 °C. After being cooled to room temperature, the mixture was titrated, with stirring, using 1 mol/L FeCl₃ or ZrOCl₂·7H₂O solution until the pH reached ~7.1. The mixture was aged for 24 h in an oven at 20 °C, without stirring. The solid phase was recovered by centrifugation and washed with ethanol three times and acetone once. Finally, the ZFA/HIO or ZFA/HZ product was dried in an oven at 24 °C (a higher temperature such as 120 °C was not used to facilitate metal oxide preparation in order to obtain a poorly crystallized material of higher specific surface area, which has a greater adsorptive performance) for 24 h, ground to pass through an 80-mesh sieve and stored in a sealed polyethylene sample bottle. For comparison, ZFA was also synthesized by the same method but without titration whereas hydrous

oxides of iron and zirconium were prepared separately by titration of waste alkaline solution with corresponding metal salts.

2.2. Material characterization

The material chemical composition was determined by X-ray fluorescence (PW2404, Philips Company). Crystalline material phases were identified by powder X-ray diffraction (XRD) analysis (D/max 2550VL/PC) with Cu-Kα filtered radiation (30 kV, 15 mA). Particle morphology was observed by scanning electron microscopy (SEM, OVA NanoSEM 230, FEI, USA). The Brunauer–Emmett–Teller (BET) specific surface area and pore size distribution were measured using the nitrogen adsorption method (ASAP 2010 M + C, Micromeritics Inc., USA). The pore size distribution curve was obtained by the Barrett–Joyner–Halenda (BJH) method.

2.3. Acid and base neutralizing capacity

A batch titration procedure was used to examine the neutralizing capacity of the materials. Approximately 0.2 g of each material and 40 mL of deionized water were placed into 50 mL centrifuge tubes. Appropriate volumes of 0.1 mol/L HCl or NaOH were added to the tubes to achieve amounts of H⁺ or OH⁻ ranging from 0 to 6 mmol H⁺/g. The tubes were sealed and placed in an orbital shaker. After being shaken continuously for 24 h at 25 °C and 200 rpm, the suspension pH was determined using a HACH sension + pH meter. The amount of H⁺ or OH⁻ required to achieve a certain pH, i.e., the acid neutralizing capacity (ANC) and base neutralizing capacity (BNC), respectively, can be estimated by subtracting the amount of H⁺ or OH⁻ required to achieve the same pH using deionized water in the blank experiment. The pH as a function of the amount of H⁺ or OH⁻ added was drawn as the neutralizing curve.

2.4. Batch adsorption experiments

To determine the adsorption isotherms, approximately 0.2 g of adsorbent was placed into 50 mL centrifuge tubes to which was added 40 mL aqueous solution with MB concentrations of ~0–2000 mg/L. The pH was adjusted to 5.0, 8.0, and 11.0, according to the material neutralizing capacity. Tubes were sealed and agitated continuously in an orbital shaker (25 °C, 200 rpm) for 4 h. This reaction time was sufficient to achieve MB equilibrium in the kinetic studies. Tubes were centrifuged at 4000 rpm for 10 min. The concentrations of MB in the supernatants were determined using a visible Unico spectrophotometer at 668 nm. The supernatant was diluted with deionized water before determining when the absorbance was out of the range of the calibration curve. The amount of MB adsorbed per unit mass of adsorbent was calculated from:

$$Q_e = \frac{(C_0 - C_e)V}{m} \quad (1)$$

where Q_e is the amount of MB adsorbed per unit mass of adsorbent (mg/g), C_0 is the initial MB concentration (mg/L), C_e is the MB concentration (mg/L) at equilibrium, m is the mass of adsorbent on a dry basis (g), and V is the solution volume (L).

The effect of pH on MB adsorption was studied from pH 4.0 to 12.0. Approximately 0.2 g of adsorbent was placed into a 50 mL centrifuge tube to which was added 40 mL of MB aqueous solution with an initial MB concentration of 250 mg/L. Appropriate amounts of 0.1 or 1 mol/L HCl or 0.1 mol/L NaOH were added to the mixture to achieve a specified final pH according to the neutralizing capacity measurements. After 4 h, MB concentrations in the supernatants were measured and the amount of MB adsorbed was calculated. The final suspension pH was detected using a Hach Sension + pH meter.

Table 1
Chemical composition of materials (%).

Item	CFA	ZFA	ZFA/HIO	ZFA/HZ
SiO ₂	48.00	38.67	24.24	26.34
Al ₂ O ₃	38.05	34.19	16.18	20.89
Fe ₂ O ₃	2.90	2.77	17.60	1.58
CaO	2.32	2.42	1.12	1.32
MgO	0.67	0.75	0.38	0.47
Na ₂ O	0.47	8.41	8.80	7.02
K ₂ O	1.55	0.66	0.42	0.34
TiO ₂	1.64	1.34	0.73	0.86
ZrO ₂	N.D. ^{a)}	N.D.	0.08	25.54
HfO	N.D.	N.D.	0.00	0.49
SO ₃	0.58	0.04	0.13	0.09
Cl	0.08	N.D.	4.70	2.72
LOI ^{b)}	3.18	10.49	25.53	12.26
Others	0.56	0.29	0.09	0.08

^a not determined.

^b Loss on ignition at 1000 °C.

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