



Full Length Article

Performance of surfactant modified zeolite/hydrous zirconium oxide as a multi-functional adsorbent

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HIGHLIGHTS

- The composite of zeolite and hydrous zirconia was prepared from coal fly ash.
- Surfactant was successfully loaded onto the composite creating a patchy bilayer.
- The surfactant modified composite (SMZFA/HZ) was investigated as a new adsorbent.
- SMZFA/HZ was able to adsorb cationic, anionic, and organic pollutants from water.
- SMZFA/HZ was a better versatile adsorbent than previously developed SMZFA.

ARTICLE INFO

Article history:

Received 10 March 2017
 Received in revised form 26 April 2017
 Accepted 29 April 2017
 Available online 5 May 2017

Keywords:

Adsorption
 Coal fly ash
 Surfactant
 Zeolite
 Zirconium

ABSTRACT

Surfactant modified zeolite from coal fly ash (SMZFA) was previously developed as a multi-functional adsorbent. But its ability to capture anionic pollutants depends on the type and composition of coal fly ash and the synthesis process of zeolite (ZFA), the precursor of SMZFA, produces waste alkaline solution. To tackle these problems, the composite of zeolite and hydrous zirconia (ZFA/HZ) was synthesized by neutralizing waste alkaline solution with zirconium salt and was then modified with the surfactant of hexadecyltrimethylammonium to develop a new type of multi-functional adsorbent, SMZFA/HZ. The obtained materials were evaluated for their performances to sequester multiple classes of pollutants from water. The target pollutants include cationic pollutant (ammonium), anionic pollutant (phosphate) and organic pollutants (humic acid and bisphenol A). Results showed that, when compared with ZFA, ZFA/HZ had 3 times higher adsorption capacity for phosphate, and more negative charges on both external (by 16.9%) and internal surfaces (by 12.3%). For both ZFA and ZFA/HZ, modification with surfactant reduced the capacity for uptake of ammonium by less than 10% and the reduction was trivial for phosphate. However, surfactant modification greatly augmented the adsorption performances for humic acid and bisphenol A. Compared with SMZFA, SMZFA/HZ was found to have higher potential for the retention of each pollutant and is thus a more excellent versatile adsorbent.

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1. Introduction

Coal fly ash (CFA) is a solid waste generated in great amounts every year as a by-product, due to the worldwide use of coal in electricity/heat generation processes. It was estimated that 349 Mt of CFA was produced worldwide in 2000 [1] and was over 750 Mt in 2012 [2]. With a coal-dominated energy source structure and a great consumption of electricity/heat, China produces the greatest amount of CFA [3]. Internationally, only a part of CFA is reused. For instance, the reutilization rate is 39% for the United

States [2], 47% for Europe [2], and 68% for China [3]. As a result, a huge amount of CFA is impounded or land filled.

Zeolites are a family of porous aluminosilicate minerals which are useful materials in industry as they contain large specific surface area and cation exchange capacity (CEC) [4,5]. In recent years, synthesis of zeolites (ZFAs) from CFAs has been intensively investigated [6–13]. ZFAs are attractive in water/wastewater treatment as their raw material is a solid waste generated in great amounts worldwide and hence they are cost-effective with the possibility of reusing solid waste. Our previous studies revealed that ZFA could simultaneously remove ammonium (a cation) and phosphate (an anion) from wastewater [14–17]. We have shown that the negative charge in the zeolite fraction is responsible for the retention

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of cationic pollutants, while the oxides of CaO, Al₂O₃ and Fe₂O₃ in the non-zeolite fraction, which originated from coal fly ash but received modification during zeolite synthesis, account for the removal of oxyanions [14–17]. By loading cationic surfactants with a long hydrophobic alkyl chain onto the external surface, additional function to capture organic pollutants could be developed, making surfactant modified ZFAs (SMZFAs) unique versatile adsorbents to simultaneously remove different pollutants from water [18–21]. Modification of the external surface of ZFA with another organic polycation, chitosan, was also reported as an efficient multi-functional adsorbent [22].

Nevertheless, the capability of SMZFAs to fix oxyanionic species, such as phosphate, might be limited as the type and content of the oxides depend on the origin of CFA. On the other hand, preparation of zeolite from CFA using traditional synthesis process produces not only useful ZFA product but also leaves behind large amounts of problematic waste alkaline solution. We have recently initiated a novel method to synthesize zeolite/hydrous metal oxide hybrid material (ZFA/hydrous metal oxide) by introducing a reaction step into the traditional zeolite synthesis route that involves neutralizing waste alkaline solution with soluble metal salts [23,24]. The phosphate-immobilization capacity and the BET surface area of ZFA/hydrous metal oxide increased by 2–3 times and by 2–6 times, respectively, when compared with ZFA, while the cation exchange capacity remained roughly unchanged or increased to some extent [23,24]. It could thus be assumed that modifying ZFA/hydrous metal oxide using surfactant may be a method to develop multi-functional material which might be superior to SMZFA though related studies have not been done to date. The purpose of our present study was to investigate the possibility to prepare surfactant modified ZFA/hydrous zirconia (SMZFA/HZ) and to examine its versatility to sequester cationic (ammonium), anionic (phosphate) and organic (humic acid and bisphenol A) pollutants from water. Because high affinity of zirconium for phosphate was widely documented [25–30], the soluble zirconium salt (ZrOCl₂·7H₂O) solution was used in the neutralization process to obtain ZFA/HZ before surfactant modification. As CFA is easily available with low or no cost, and the method of SMZFA/HZ production is a facile one pot process, production of large amount of SMZFA/HZ would be viable.

2. Materials and methods

2.1. Materials

The CFA sample used in this study was obtained from the Wenzhou Power Plant, Zhejiang Province, China. The synthesis of ZFA, ZFA/HZ and surfactant modification of ZFA and ZFA/HZ were performed as follows. (i) Step 1: for zeolite preparation, approximately 150 g of CFA was placed in a bench-scale reaction vessel and mixed with 900 mL of 2.0 M NaOH solution. The slurry was boiled with reflux for 24 h with stirring at 95 °C. After the mixture was allowed to cool to room temperature, zeolite was recovered by centrifugation and washed with doubly distilled water three times and with ethanol twice. Finally, zeolite product was dried in an oven at 45 °C, ground to pass through an 80-mesh sieve, and stored in airtight containers for later experiments. (ii) Step 2: to synthesize ZFA/HZ, after the mixture of zeolite and waste alkaline solution was allowed to cool to room temperature, it was neutralized with ZrOCl₂, that is, 900 mL of 1.0 M ZrOCl₂ solution was added dropwise (10 mL/min) to the mixture with continuous stirring. To guarantee a sufficient reaction of ZrOCl₂ with the waste alkaline solution, stirring was maintained for another 4 h after the addition of ZrOCl₂ solution was completed. The ZFA/HZ was then recovered, washed, dried, and ground in a manner similar to that used for ZFA.

(iii) Step 3: for surfactant modification, 500 ml of the solution of the surfactant, hexadecyltrimethylammonium bromide, with a concentration of 55 mM was vigorously mixed with 10g of ZFA or ZFA/HZ at 50 °C for 4 h. After being cooled to room temperature, the product was centrifuged, washed with doubly distilled water, dried in an oven at 60 °C and ground to pass through an 80-mesh sieve.

2.2. Characterization of materials

The elemental compositions of the materials were determined by X-ray fluorescence (Axios X, PANalytical Company). The FTIR spectra were recorded with an FT-IR spectrophotometer (SHIMAZU IR Prestige-21) using the KBr method. The crystalline phase(s) in the materials were identified by powder X-ray diffraction analysis on a D8 ADVANCE instrument (Bruker-AXS Company) with Cu K α filtered radiation (30 kV, 15 mA). Particle morphology was observed by a NOVA NanoSEM 230 SEM (FEI Company). The specific surface area was determined on an ASAP 2460 Version 2.01 from Micromeritics by fitting the amount of N₂ adsorbed at -196 °C for the BET equation after preliminary heating at 200 °C. The surfactant content in the SMZFA and SMZFA/HZ was measured by the content of nitrogen in the materials on a Foss Kjeltec™ 2100 (Tecator Company).

2.3. Batch adsorption studies

Ammonium (inorganic cation), phosphate (inorganic anion), the sodium salt of humic acid and bisphenol A (organic pollutants) were selected to assess the versatility in decontamination performance of materials. The humic acid used in the experiments was supplied by Aldrich Chemical, in the form of sodium salt. It was extracted from waters draining an open pit mine in Oberhessen, Germany. Other chemicals with analytical grade were purchased from the Shanghai Reagent Company, China.

As adsorption of cationic pollutants by materials is essentially an ion exchange process, the adsorption capacity for cationic pollutants was evaluated in terms of the number of negative charges, i.e., the cation exchange capacity (CEC) possessed by the materials. The total CEC (TCEC), which involves negative charges on both external surface and internal surface in pores, was determined from the amount of retained ammonium by the ammonium acetate method [31]. The external cation exchange capacity (ECEC) was determined by adsorption of methylene blue from aqueous solution [32].

The ability of materials for the uptake of pollutants, except ammonium, was evaluated by the determination of adsorption isotherms. For this purpose, the materials were mixed with aqueous solutions containing the pollutants and then shaken continuously in an orbital shaker (25 °C, 200 rpm) for a given period. The suspensions were then separated by centrifugation for analysis of the equilibrium concentrations of solutes and pH. The amount of solutes adsorbed per unit mass of adsorbent was calculated from the difference between initial and equilibrium concentrations in solution. pH was measured using a Hach Sension + pH meter. Analysis of the concentrations of phosphate and ammonium in solution were conducted using an INESA spectrophotometer (model UV-759) by the molybdenum-blue ascorbic acid method and the salicylic acid spectrophotometry method [33], respectively. The concentrations of methylene blue, humic acid, and bisphenol A were measured directly using the INESA spectrophotometer. Due to the widely varied properties (including water solubility) and adsorbability of the pollutants, different initial concentration ranges, liquid/solid ratios, and wavelengths used for determination were adopted, as listed in Table 1.

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