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A comparative study on fly ash, geopolymer and faujasite block for Pb removal from aqueous solution

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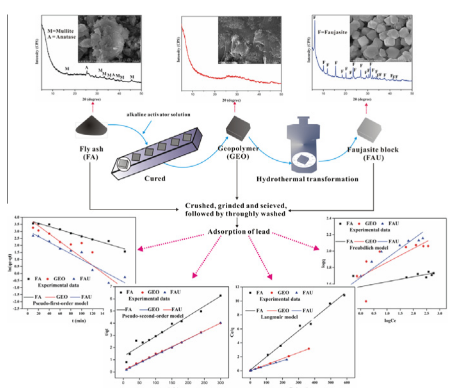
HIGHLIGHTS

- Geopolymer and its deriving zeolite–faujasite–was prepared from fly ash.
- Both geopolymer and its deriving faujasite can effectively remove Pb.
- Geopolymer has the same adsorption mechanisms as faujasite or zeolite materials.
- Shows geopolymer technology is a feasible process in adsorbent manufacturing.

GRAPHICAL ABSTRACT



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ABSTRACT

This work aims to evaluate the efficiencies of fly ash, fly ash-based geopolymer and faujasite block, which is transformed from geopolymer, as sorbents for lead (Pb) from aqueous solutions. Comparative experiments were performed to examine the mineralogical features of the fly ash, geopolymer and faujasite block and their adsorption capacities. Equilibrium isotherms and thermodynamic parameters were obtained through systematic investigation of parameters including pH, initial Pb concentration, temperature and contact time. The adsorption kinetics of geopolymer and faujasite block fit well to the pseudo-second-order kinetic model, while the adsorption of fly ash fit to the pseudo-first-order kinetic model. The adsorption equilibrium data of fly ash, geopolymer and faujasite can be expressed using Langmuir model. The maximum adsorption capacities of fly ash, geopolymer and faujasite block at pH = 3 were determined to be 49.8, 118.6 and 143.3 mg/g, respectively. Through this study we demonstrate that both geopolymer and faujasite can effectively remove Pb from wastewater. Most importantly, we prove that geopolymer has the same adsorption mechanisms as faujasite or similar zeolite materials. This finding suggests geopolymer technology being an energy-saving, low cost and environmentally friendly process in adsorbent manufacturing.

1. Introduction

Lead (Pb) is one of the most toxic heavy metal pollutants discharged into environment (soil, groundwater and air) through industrial wastes [1]. The sources include petroleum refining industry, lead-containing pesticides, discarded batteries and

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painting materials [2,3]. Lead is nondegradable and persistent, and is detrimental to humans and other living beings [1,4]. A large number of techniques have been applied to remove such heavy metals (particularly from aqueous solution), such as chemical precipitation followed by coagulation and ion exchange, solvent extraction, ultrafiltration, reverse osmosis, electro-dialysis, evaporative recovery and adsorption [4–6]. Among these techniques adsorption is particularly effective by using a variety of adsorbents. In industrial application the selection of a 'suitable' adsorbent is critical because it deals with the cost and efficiency. Adsorbents with low-cost and high pollutant-removal efficiency, such as activated carbon [7,8], and gasified granulated scrap tires [9] recommended in the literature, are always favored.

Fly ash has been found to be a potential and versatile adsorbent for removal of toxic metals from aqueous solutions [10] and capture metals in gas phase [11]. Fly ash is collected from coal combustion at power station and petroleum industry, and is cheap and ready available in large quantities (world generation is over 500 Mt annually) [12]. However, the problem of raw fly ash is the low adsorption capacity [13], which usually needs proper physical and/or chemical treatments [14,15]. The conversion of fly ash into crystalline zeolites has gained significant interests in the last 30 years [16,17].

Zeolites are crystalline aluminosilicates with three-dimensional frameworks of SiO_4 and AlO_4 tetrahedral units. The negative charge is balanced by the interchangeable positive ions such as: Na^+, K^+, Ca^{2+} and Mg^{2+}. A particular zeolite usually has fixed-sized pores and paths that allow certain heavy metals to pass through, which means selective separation. Faujasite is such a type of zeolite which can be used for the adsorption of Pb^{2+} heavy metals from wastewaters [6]. Nevertheless, synthesize zeolites from fly ash normally cause alkaline pollution [18]. Moreover, the conversion procedures have problems of low yields and high costs [19].

Recently a new process of converting fly ash into geopolymers is attracting more and more interests because of the effective absorption [15,20–22] and immobilization [23,24] of heavy metals. Geopolymers are a class of amorphous materials formed by reaction of aluminosilicate source with alkaline solution at ambient or higher temperatures [25]. They consist of SiO_4 and AlO_4 tetrahedral units linked alternatively in three directions by sharing all oxygen atoms between two tetrahedral units, and positive ions, such as Na^+ and K^+, in the frame work cavities balance the negative charge of Al [26]. The formation of geopolymer follows almost the same way as that for most zeolites, and the difference between zeolites and geopolymers is that geopolymer gel has no sufficient time and space to grow into a well crystallized structure. The mixture of geopolymer usually contains a much lower water content than the reaction system of zeolite synthesis. However, many geopolymers can also be further transformed into zeolites through hydrothermal curing and ageing [27–29]. Hence, geopolymers are regarded as the precursor of zeolites with almost the same structure at atomic scale, and are paid great attention as an emerging group of sorbents. Studies on fly ash-based geopolymers as adsorbents for the removal of Cu^{2+} [20], Pb^{2+} [22], Cd^{2+} [23] have been reported, which have clearly shown the advantage ofgeopolymer technique in improving the adsorption capacity offly ash. However, comparative study of the difference between geopolymer and its deriving zeolite or the same type of commercial zeolite in adsorption of heavy metal ions and relevant mechanisms is rarely reported. Wang et al. [15] investigated the adsorption capacity of fly ash, geopolymer and natural zeolite, and they found the synthetized geopolymer adsorption capacity outclass the natural zeolite and raw ash for Cu^{2+} removal. However, their study did not clarify the relation between zeolite and its analogue - geopolymer. This is a widely concerned question in industry: is it necessary or cost-effective to further convert geopolymer into well crystalline zeolite to increase the adsorption efficiency?

In this work, raw fly ash, a geopolymer manufactured from the fly ash and a faujasite block material derived from the geopolymer were comparatively evaluated by scanning electron microscopy (SEM), X-ray diffractometry (XRD) and Fourier Transform Infrared Spectroscopy (FTIR). Their adsorption behavior of Pb under different conditions was investigated to understand the adsorption model and relevant thermodynamic parameters of adsorption process.

2. Materials and methods

2.1. Materials

Fly ash was obtained from Shenhua Junggar Energy Corporation in Junggar, Inner Mongolia, China. Analytical grade sodium hydroxide and hydrochloric acid were supplied by Sinopharm Chemical Reagent Co., Ltd. Commercial sodium water glass was obtained from Shenghuai Chemical Technology Co. Ltd., Foshan, with original modulus of 3.25. The Pb^{2+} solutions with different concentrations were prepared by dissolving analytical grade $Pb(NO_3)_2$ (Sinopharm Chemical Reagent Co., Ltd) in distilled water.

2.2. Characterization of materials

The chemical compositions of fly ash, geopolymer and faujasite block were determined by X-ray fluorescence (AXIOSmAX, PANalytical Netherlands). X-ray diffractions of these materials were recorded on a D8-Focus type X-ray powder diffractometer (BrokerAXS Germany). The scanning range was from 5° to 50° 2θ at a scanning rate of 0.5°/min using Cu Kα radiation (generator voltage of 40 kV and current of 40 mA). The morphologies of the sample fracture surfaces were analyzed using a scanning electron microscopy (SU8010, Hitachi Japan) at an acceleration voltage of 10 kV. The FTIR spectra of the samples were obtained using Nicolet iS50 spectrometer (Thermo Scientific America) in the range of 450–4000 cm^{-1} using the KBr pellet technique [30]. Pore size distribution is obtained from N_2 adsorption branch of nitrogen isotherms by BJH method by using an automatic ASAP2020 surface area and porosimetry system (Micromeritics, America), and the specific surface area was calculated by the Brunauer–Emmet–Teller (BET) method.

2.3. Synthesis of geopolymer and faujasite block

A mixture of sodium hydroxide and the commercial sodium water glass mixed at a mass ratio of 1:4.15 was used as alkaline activator. Fly ash was then mixed with the alkaline activator solution at a mass ratio of 1:1.12 to make geopolymer paste. After thoroughly mixed for 3–5 min, the paste was cast into a 20 mm × 20 mm × 20 mm mold, followed by air curing for 12 h and sealed curing at 80 °C in an oven for another 12 h. Thin geopolymer specimens (20 mm × 20 mm × 2.0 mm; an average mass of 2.5 g) were made by the steps described above.

Faujasite blocks were fabricated from geopolymer via in-situ hydrothermal method. Geopolymer specimens were placed into a 100 ml Teflon bottle containing 20 ml 1.0 mol/L NaOH solution, under the hydrothermal condition of 70 °C for 24 h. The effects of various factors, such as the SiO_2/Al_2O_3 molar ratio of the geopolymer, the alkalinity, crystallization time and crystallization