Adsorption of Pb(II) from aqueous solution by a poly-elemental mesoporous adsorbent

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ABSTRACT

A poly-elemental mesoporous adsorbent was hydrothermally prepared from microcline in an alkaline condition with cetyltrimethylammonium bromide as synthesis directing agent. The properties of the mesoporous adsorbent were determined by X-ray powder diffraction, high-resolution transmission electron microscope, N_2 adsorption, and solid-state Magic Angle Spinning Nuclear Magnetic Resonance. The pore size distribution was detected by small angle X-ray scattering. The particles size was observed by Scanning electron microscope imagine. The chemical content of SiO_2 in the mesoporous adsorbent was determined by spectrometry of the silicone molybdenum and sulfosalicylic acid complexes, and Al_2O_3 determined by complexometry with ethylene diamine tetraacetic acid in the presence of KF–Zn(Ac)2 tests. The adsorption properties of the mesoporous adsorbent to Pb(II) were studied, and three main factors, the adsorption time, solution pH, and initial concentration of Pb(II), were considered in the adsorption experiments.

1. Introduction

The contamination of wastewater by toxic metal ions is a worldwide environmental problem. Heavy metal ions are of great concern, due to their mobility in natural water ecosystems and that, unlike organic pollutant, heavy metal ions do not undergo biological degradation and tend to accumulate in the organisms, thereby eventually entering the food chains. Pb(II) is among the most toxic heavy metal ions, affecting the environment. Main sources of lead are the manufacture of storage batteries, pigments, leaded glass, mining, metal electroplating, painting, coating, smelting, petrochemical, plumbing fuels, photographic materials, matches and explosives. Apart from this, lead is also used in insecticides, plastic water pipes, food, beverages, ointments and medicinal concoctions for flavoring and sweetening.

High levels of Pb(II) are harmful if inhaled or swallowed, and may cause long-term health risks to humans and ecosystems. It is therefore mandatory that the levels in drinking water, waste water and water used for agricultural and recreational purposes must be reduced to be less than the maximum allowable concentrations recommended by World Health Organization (WHO). According to Chinese hygienic standard for drinking water (GB5749), the level of Pb(II) for drinking water is $0.05 \, \text{mg L}^{-1}$, but a level of $0.02 \, \text{mg L}^{-1}$ has been proposed, and for discharge waste water to surface water $0.1 \, \text{mg L}^{-1}$.

The accustomed methods for treatment of Pb(II) in wastewater include chemical precipitation [1,2], adsorption [3,4], ion exchange [5], biosorption [6,7], filtration, membrane processes [8–10] or photocatalysis [11,12]. Among these methods, adsorption is the most simple, so it is easy to be operated by laypeople. Many kinds of adsorbents have been studied for removing heavy metal ions, and the general adsorbent was activated carbon [3,13,14]. However, the predominantly non-polar surface of activated carbon often limits its effectiveness for removal of metal ions. Many studies were used mesoporous materials as catalyst in organic reactions [15], limited researches have been reported on their use as adsorbents [16].

The mesoporous material applied here for adsorbing Pb(II) is poly-element, was prepared from microcline, and with cetyltrimethylammonium bromide (C_{16}TMABr) as synthesis directing agent. Three adsorption parameters, the adsorption equilibrium time, pH values and initial concentrations of Pb(II), were studied in batch experiments.

2. Materials and methods

2.1. Materials

The microcline was from the Song County, Henan province in China, with an average molar mass 68, and its main components

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are silica (65.0 mass%) and alumina (16.4 mass%), with a small amount of other metal oxide, such as Fe_2O_3, FeO, CaO, Na_2O, and K_2O. Other compounds used in the synthesis process (Na_2CO_3, Cetyltrimethylammonium bromide (C_{16}TMABr), hydrochloric acid, silica, $Pb(NO_3)_2$, NaOH and deionized water) were supplied by Beijing Chemical Reagents Company (China).

2.2. Preparation of mesoporous adsorbent

A mesoporous adsorbent, named AH-1, was prepared the same as previously reported [4,17]. The preparation of Si and Al sources: the mixture of microcline (its size ≤77 μm) and Na_2CO_3 (molar ratio 1:1.05) was calcined at 1103 K for 2.5 h, and named the calcined mixture SOX-2. The main components of SOX-2 were silica (38.7 mass%), alumina (9.8 mass%), and sodium monoxide (41.9 mass%). The preparation of mesoporous adsorbent: The molar ratio of $(SiO_2 + Al_2O_3):C_{16}$TMABr$:H_2O$ was 1:0.2:25, and the molar ratio of Si:Al was 20:1. Exactly as follows, an aqueous solution (60 mL) of C_{16}TMABr (9.71 g) was mixed with SOX-2 (3.4 g) and silica (6.5 g, for adjusting the Si and Al molar ratio). The mixture solution with an initial pH value about 9.2 was during stirred about 2 h, and its pH value (measured by an acidometer PHS-3C) was adjusted to 10.5 with hydrochloric acid (5 mol L^{-1}) to form a gel. The gel solution was transferred into a 70-mL Teflon-lined stainless autoclave and crystallized at 378 K for 72 h. After crystallization, the autoclave was cooled to 293 K automatically, and the solid product was filtered and dried at 378 K for 24 h. Finally, the powder was calcined in air at 823 K for 6 h to remove the directing agent, using a ramping rate of 2 K min^{-1} before 573 K, and fast heating from 573 K to 823 K.

2.3. Characterization of the mesoporous aluminosilicate

X-ray diffraction (XRD) patterns were measured at a scanning rate of 1°/min by the reflectance method on a Siemens D5005 using Cu Kα radiation. Transmission electron microscope (TEM) images were taken with a JEOL JEM-2011 microscope operated at an acceleration voltage 200 kV. Scanning electron microscope (SEM) image was obtained with a LEO435VP microscope operated at an accelerating voltage of 20 kV. The surface area of the sample was measured by nitrogen isotherms at 77.4 K using AUTOSORB-1 system. The pore size distribution was detected by small angle X-ray scattering (SAXS), with a long-slit collimation system on 4B9A beam line at the Beijing Synchrotron Radiation Facility, China. The incident X-ray wavelength λ was 0.154 nm, the scattering angle 2θ approximately 0–3°, and the scattering vector denoted as q, and $q = 4\pi \sin \theta/\lambda$. The detail explanation about SAXS can refer to a previous report [18]. The solid states ^{29}Si and ^{27}Al Magic Angle Spinning Nuclear Magnetic Resonance (MAS NMR) spectra were recorded on a Varian Unity Inova 300M spectrometer at 59.584 MHz and 78.155 MHz, using 1.5 μs and 0.3 μs pulse length, 3 s and 1 s recycle delays, and a spinning rate of 5 kHz and 7 kHz, respectively. ^{27}Al chemical shifts were measured relative to $Al(H_2O)_6^{+3}$.

The compositions of SiO_2 and $T(Fe_2O_3 + FeO)$ were determined by spectrometry of the silicone molybdenum and sulfosalicylic acid complexes. The contents of Al_2O_3 and CaO were determined by complexometry with ethylene diamine tetraacetic acid in the presence of KF–$Zn(Ac)_2$ tests. The contents of Na_2O and K_2O were measured by the flame atomic absorption spectrometry.

2.4. Adsorption experiment

A solution of 500 mg L^{-1} Pb(II) was prepared by dissolving required amount of $Pb(NO_3)_2$. Solutions of lower concentrations were prepared by dilution. Deionized water was used in all the experimental runs. The concentration of Pb(II) was determined by

an X-ray atomic fluorescence spectrophotometer (AF-610A). In a typical sorption process, 0.01 g sorbent was dispersed in 20 mL aqueous solution of Pb(II) (Pb(II) concentration: 10–270 mg L^{-1}, pH 3–8). The dispersion was shaken in a water oscillator (200 rpm) at 293 K for 10–60 min. The pH values of aqueous solutions were adjusted with HCl or NaOH at the beginning of experiments and not controlled afterwards. The Pb(II) uptake was calculated by the following equation,

$$q_e = \frac{[(C_o - C_e)V]}{m} \tag{1}$$

where C_o (mg L^{-1}) and C_e (mg L^{-1}): the initial and final concentrations of Pb(II) in the aqueous solution, V (L): the total volume of the aqueous solution, and m (g): the mass of the adsorbent.

The adsorption percentage R was calculated by the difference between the initial and final concentration of adsorption solution given as

$$R = \frac{C_o - C_e}{C_o} \times 100\% \tag{2}$$

2.5. Isotherm models

The sorption data obtained for variation of metal ion concentrations were treated using Langmuir and Freundlich isotherm models as given by Eqs. (3) and (4).

Langmuir isotherm $\quad \dfrac{C_e}{q_e} = \dfrac{1}{bq_m} + \dfrac{C_e}{q_m} \tag{3}$

Freundlich isotherm $\quad \ln q_e = \ln K_F + \dfrac{1}{n} \ln C_e \tag{4}$

where q_e (mg g^{-1}) and C_e (g L^{-1}) are the amount of Pb(II) adsorbed on AH-1 and the concentration of Pb(II) in the adsorption solution at equilibrium, b (L g^{-1}) is the Langmuir constant termed as apparent energy of adsorption and q_m (mg g^{-1}) is an adsorption uptake. K_F and $1/n$ are constants indicating the adsorption uptake and the adsorption intensity, respectively. The Freundlich constant, 'n' indicates the degree of favorability of adsorption [28]. The Langmuir isotherm theory assumes monolayer coverage of adsorbate over a homogeneous adsorbent surface [29]. Langmuir isotherm can be characterized by a plateau graphically. A saturation point reaches at equilibrium where no further adsorption occurs. Adsorption is assumed to take place at specific homogeneous sites within the adsorbent. Once a sorbate molecule occupies a site, no further adsorption takes place at that site. The Freundlich isotherm gives an expression encompassing the surface heterogeneity and the exponential distribution of active sites and their energies.

3. Results and discussion

3.1. Textural properties

The XRD pattern of AH-1 (not shown) gave the (1 0 0) and (1 1 0) reflection at 2.3° and 3.8°. The basal spacing d_{100} and the unit cell $a_0 = (2/3^{1/2})d_{100}$ were 3.84 nm and 4.43 nm respectively. Fig. 1 showed the HRTEM images of AH-1. The image in Fig. 1a revealed the wormlike pore structure, and the image in Fig. 1b displayed a roughly hexagonal pore mouth. The pore diameter was about 2–3 nm. Some pores were straight, and some were tortuous.

The BET specific surface area was 835 $m^2 g^{-1}$ given by N_2 adsorption–desorption isotherms. The pore size distribution curve of AH-1 was given by SAXS (Fig. 2). Shull–Roess method [19] was used to calculate the pore size distribution. The mesopore diameter was centered at around 2.5 nm, and mainly distributed from 1.5 nm to 7.0 nm. The particle sizes of AH-1 are observed by SEM image,