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Adsorptive removal of phosphate by a nanostructured Fe–Al–Mn trimetal oxide adsorbent

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A B S T R A C T

A nanostructured Fe–Al–Mn trimetal oxide adsorbent for phosphate removal with a Fe:Al:Mn molar ratio of 3:3:1 was prepared using simultaneous oxidation and coprecipitation method. The adsorbent was characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM) and scanning electron microscope (SEM) with an EDAX (energy dispersive analysis of X-ray). The results indicated that the Fe–Al–Mn trimetal oxide was amorphous and nanostructured. Zeta potential measurements showed that it possessed a high isoelectric point (around 9). The phosphate removal gradually decreased with the increasing of pH (4–10.5). The adsorption isotherms on the adsorbent were described by Langmuir, Freundlich and Temkin models at pH 6.8 and followed the fitting order: Freundlich > Temkin > Langmuir. At 25 °C, the maximum adsorption capacity for the adsorbent was about 48.3 mg/g, which was higher than their reported single component oxide. The kinetic data were described better by the pseudo-second-order adsorption kinetic rate model. Thermodynamic analyses indicated that the phosphate adsorption on the Fe–Al–Mn trimetal oxide was endothermic and spontaneous in nature. The sequence of coexisting anions studied competing with phosphate was $SiO_3^{2-} > HCO_3^- > SO_4^{2-}$. The results of zeta potential, Fourier transform infrared spectroscopy (FTIR) and X-ray photoelectron spectroscopy (XPS) analyses indicated that electrostatic attraction and replacement of surface hydroxyl groups (M–OH) by phosphate via the formation of inner-sphere complex were the main adsorption mechanism. The Fe–Al–Mn trimetal oxide with good specific affinity towards phosphate was a promising adsorbent for phosphate removal from natural waters and municipal wastewaters.

1. Introduction

As a primary nutrient, phosphate is essential for growth of organisms in most ecosystems. However, excessive discharge of phosphate into water bodies may cause detrimental eutrophication and deteriorate water quality subsequently [1]. Therefore, it is necessary to develop effective methods to remove excessive phosphate from water and wastewater, especially at low concentrations in order to satisfy increasingly stringent environmental need. Typical methods for phosphate removal consist of biological treatments [2], chemical precipitation (with aluminum, iron and calcium salts) [3], adsorption [4], and reverse osmosis [5]. Among these treatment methods, biological treatments and chemical precipitation are generally not suitable for phosphate removal of low concentrations, and reverse osmosis has a high capital cost. However, adsorption is comparatively more economical and highly effective even at low phosphate concentrations [6]. Recently, the development of novel adsorbents for phosphate removal has been most widely investigated, such as fly ash [7], red mud [8], iron oxide tailing [9], iron based compounds [10], aluminum based compounds [11], and layered double hydroxides [12].

It is well known that iron, aluminum and manganese (hydr) oxides exist ubiquitously in natural aquatic system and play a great role in the geochemical cycling of nutrients and contaminants. In water treatment engineering system, these oxides are also widely-used important adsorbents for removing contaminants because of their low cost and environmental friendliness. Moreover, in above-mentioned environmental systems, these metal (hydr) oxides are often found in combination with each other to form composite oxides [4]. Thus, it has been presumed that the physic-chemical properties of multimetal oxide differ from those of their single component oxides [10], and may be a promising material for phosphate removal by adsorption reaction from contaminated water in engineering systems.

In our previous study [13], a Fe–Mn binary oxide was prepared by oxidation and coprecipitation using iron and manganese oxides, and gained good efficiency for phosphate removal. The pH_{ZPC} (the pH value of zero point of charge) of Fe–Mn binary oxide was found to be only about 6.6. But when the Fe–Mn binary oxide was used for phosphate adsorption in natural water and municipal wastewater treatments whose pH values usually ranged between 6 and 9, its surface tended to be negatively charged and yielded electrostatic

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repulsion for phosphate ions. If the pH_{ZPC} of oxides was increased, it might be advantageous for the adsorption of anions such as phosphate from aqueous solutions from the viewpoint of electrostatic attraction. Aluminum oxide was usually considered to have a higher pH_{ZPC} [14,15]. Valdivieso et al. pointed out that aluminum oxide had a pH_{ZPC} as high as above 8.0 [15]. The pH_{ZPC} of δ-Al_2O_3 was also reported to be above 9.0 [16]. Furthermore, low crystalline aluminum oxides might have more surface active sites [17]. Therefore, if the aluminum oxide was incorporated into the Fe–Mn binary oxide and a Fe–Al–Mn trimetal oxide was synthesized, its pH_{ZPC} and amounts of surface active sites could be expected to increase and accordingly its phosphate adsorption capacity could be enhanced. However, up to the present, no information is available on the phosphate adsorption on Fe–Al–Mn trimetal oxide and its removal mechanism.

In this study, a nanostructured Fe–Al–Mn trimetal oxide synthesized by oxidation and coprecipitation method was reported. The effects of various parameters on the phosphate adsorption, adsorption isotherms, kinetics and thermodynamics were investigated in batch experiments. The surface characteristics, FTIR and XPS of this adsorbent were also analyzed to elucidate the mechanisms for phosphate adsorption.

2. Materials and methods

2.1. Materials

All chemicals such as potassium dihydrogen orthophosphate, potassium permanganate, aluminum chloride, ferrous sulfate, sodium hydroxide, sodium chloride, sodium sulfate, sodium bicarbonate and sodium silicate were of analytical reagent grade and purchased from Sinopharm Chemical Reagent Company (China). The phosphate stock solution was prepared from anhydrous potassium dihydrogen orthophosphate. All solutions were prepared using deionized water.

Fe–Al–Mn trimetal oxide was prepared with a Fe (II):Al (III):Mn (VII) molar ratio of 3:3:1 using oxidation and coprecipitation method. The main preparation procedure was briefed as follows: potassium permanganate ($KMnO_4$, 2.37 g) was dissolved in a 200 mL of deionized water; aluminum chloride ($AlCl_3 \cdot 6H_2O$, 10.86 g) and ferrous sulfate heptahydrate ($FeSO_4 \cdot 7H_2O$, 12.51 g) were dissolved in another 200 mL of deionized water. Under vigorous magnetic stirring, the mixture solution of $AlCl_3$ and $FeSO_4$ was added into the $KMnO_4$ solution, and simultaneously 5 M NaOH solution was added dropwisely to keep the solution pH in the range of 7–8. After addition, the formed suspension was continuously stirred for 1 h, aged at room temperature for 12 h, and then washed repeatedly with deionized water. The suspension was freeze dried. The obtained dry material was stored in a desiccator for further use.

2.2. Adsorbent characterization

XRD analysis was carried out on an X-ray powder diffractometer (X'Pert PRO MPD, PANalytical, Netherlands) using copper Kα radiation. The specific surface area of Fe–Al–Mn adsorbent was measured by nitrogen adsorption using the BET method with a Micromeritics ASAP 2000 (Micromeritics Co., USA) surface area analyzer. Particle size of the adsorbent was determined by a laser particle size analyzer (Mastersizer 2000, Malvern Co., UK). The morphology and surface element composition of the Fe–Al–Mn trimetal oxide were obtained using a scanning electron microscope with an EDAX KEVEX level 4 (Hitachi U3010, Japan). The Fe–Al–Mn trimetal oxide was also observed using a transmission electron microscopy (TEM, Hitachi H-7500, Japan). Before TEM observation, samples were placed into ethanol and dispersed for 1.5 h by ultrasonic, and then a droplet was placed onto a copper net and dried at room temperature.

FTIR spectra were collected on a Nicolet 5700 FTIR spectrophotometer (Thermal electron Co., USA) using transmission model. Samples for FTIR determination were ground together with spectral grade KBr in an agate mortar. IR spectra of the original adsorbent and phosphate-loaded adsorbent were obtained as dry samples in KBr pellets corresponding to 1 mg of sample in approximately 100 mg of spectral grade dehydrated KBr. All IR measurements were carried out at room temperature.

A Zetasizer 2000 analyzer (Malvern Co., UK) was used to measure the zeta potential of adsorbent suspension before and after phosphate adsorption. The content of the adsorbent in the suspension was about 100 mg/L and phosphate concentration was separately 5 and 10 mg/L. NaCl was used as background electrolyte to maintain a constant ionic strength of 0.01 M. Under rapid magnetic agitation, 10 mL of adsorbent suspension was transferred to a sample tube. Zeta potential of the suspensions was then measured by the Zetasizer 2000 analyzer and the average of triplicate measurements was used for data analysis.

XPS analyses of the original and phosphate loaded Fe–Al–Mn adsorbents were performed by an X-ray photoelectron spectroscopy (Kratos AXIS Ultra, UK) with the monochromatic Al Kα X-ray radiation (1486.7 eV). The wide scans were conducted from 0 to 1200 eV with pass energy of 160 eV. The high resolution scans were conducted according to the peak being examined with pass energy of 40 eV. The energy scale of the XPS spectra was calibrated with graphitic carbon as the reference at a binding energy of 284.8 eV due to the surface contamination. The XPS spectra peaks of O 1s were fitted using the XPSpeak software and the percentage of different surface species of O atom was obtained in terms of the relative ratio of area.

2.3. Adsorption studies

Phosphate ions (PO_4^{3-}) stock solution was prepared by dissolving 4.394 g anhydrous KH_2PO_4 in 1 L deionized water. The initial pH of all solutions was adjusted by adding HCl and/or NaOH solutions. Measurements of solutions pH were carried out using an Orion pH meter (Model 420). All water samples containing phosphate were filtrated through 0.45 μm membrane filters and then phosphate concentrations were determined by the molybdate blue method using a UV–vis spectrophotometer (Hitachi S-3500N, Japan).

The variation of equilibrium pH as a function of initial pH was investigated. Experiments were conducted using solutions of 50 mL and an ionic strength of 0.01 M NaCl and the initial pH was adjusted by adding HCl and/or NaOH solutions. Then a certain amount of adsorbent was added and agitated at 150 rpm for 24 h at 25 °C. After membrane filtration of water samples, the pH of filtrates was measured and the concentrations of metal ions such as Fe, Al and Mn were also determined using an inductively coupled plasma-optical emission spectrometer (ICP-OES 700, Agilent Technologies, USA) to check the solubility of Fe–Al–Mn adsorbent at different pH values.

The adsorption kinetic experiment was performed at 25 °C. A 1000 mL solution containing initial phosphate concentration of 4.7 mg/L and 8.6 mg/L was added into a beaker, respectively. The initial pH of solutions was adjusted to 6.8 and 0.2 g adsorbent was added to obtain a 0.2 g/L suspension. The solutions with an ionic strength of 0.01 M NaCl were equilibrated for 32 h under gently magnetic stirring. Approximately 10 mL aliquots were taken from the suspensions at different intervals for the analysis of phosphate concentrations.

The kinetic data were fitted using the pseudo-first-order model and pseudo-second-order model. The kinetic rate equations can be written as follows:

Pseudo-first-order model:

$$^{dq_t}/_{dt} = k_1(q_e - q_t). \tag{1}$$

Pseudo-second-order model:

$$^{dq_t}/_{dt} = k_2(q_e - q_t)^2. \tag{2}$$