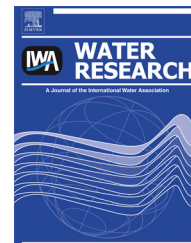


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Strong adsorption of phosphate by amorphous zirconium oxide nanoparticles

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ABSTRACT

Phosphate removal is important in the control of eutrophication of water bodies. Adsorption is one of the promising approaches for the removal of phosphate, which could serve as a supplement for the biological phosphate removal process commonly used in the wastewater treatment industry to meet the discharge requirement when the biological performance is deteriorated from changes of operation conditions. Amorphous zirconium oxide nanoparticles were synthesized by a simple and low-cost hydrothermal process, and their phosphate removal performance was explored in aqueous environment under various conditions. A fast adsorption of phosphate was observed in the kinetics study, and their adsorption capacity was determined at about 99.01 mg/g at pH 6.2 in the equilibrium adsorption isotherm study. Commonly coexisting anions showed no or minimum effect on their phosphate adsorption performance. The phosphate adsorption showed little pH dependence in the range from pH 2 to 6, while it decreased sharply with the pH increase above pH 7. After adsorption, phosphate on these am-ZrO₂ nanoparticles could be easily desorbed by NaOH solution washing. Both the macroscopic and microscopic techniques demonstrated that the phosphate adsorption mechanism of am-ZrO₂ nanoparticles followed the inner-sphere complexing mechanism, and the surface hydroxyl groups played a key role in the phosphate adsorption.

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1. Introduction

With the rapid development of modern agriculture and industry, more and more wastewater is being produced every day. If wastewater is discharged into rivers, lakes and oceans without proper treatment, it could do harm to the environment and subsequently on the human health (Shannon et al., 2008). Many nutrients, such as nitrogen and phosphorus, exist in wastewater, which are needed for aquatic organisms to grow. The excessive presence of nitrogen and phosphorus in

water bodies could cause eutrophication and subsequently stimulate blue-green algae blooms when proper temperature conditions are present (Boujelben et al., 2008). It had been found that blue-green algae have the ability of biological fixation of nitrogen, and planktonic N₂-fixing cyanobacteria bloom in freshwaters when phosphorus is abundant while nitrogen availability is low (Schindler et al., 2008; Conley et al., 2009). Consequently, the removal of phosphorus is essential to preventing eutrophication of natural water bodies, especially for freshwaters. The World Health Organization (WHO)

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suggested a maximum discharge limit of phosphorus of 0.5–1.0 mg/L (Galalgorchev, 1992), which is now being adopted in many countries and regions. For example, the emission standard for the newly-built urban sewage treatment plant in China will be upgraded to GB 1A (Total P at 0.5 mg/L) from GB 1B (Total P at 1.0 mg/L) (Ren et al., 2012). In aqueous environment, phosphorus exists in the pentavalent form as orthophosphate, pyrophosphate, longer-chain polyphosphates, organic phosphate esters and phosphodiesteres, and organic phosphonates, and these various phosphorus compounds could be hydrolyzed to orthophosphate, the only form of phosphorus that could be utilized by bacteria, algae, and plants (Correll, 1998).

Various techniques, such as chemical precipitation, adsorption, biological removal, reverse osmosis, membrane, ion exchange, and constructed wetlands, have been studied for the removal of phosphate from wastewater (Choi et al., 2012; de-Bashan and Bashan, 2004; Morse et al., 1998; van Voorthuizen et al., 2005; Zhang et al., 2012a, b). Among these approaches, the biological process is considered a cost-effective and environmentally sound alternative to the chemical precipitation treatment, and is now widely used for the removal of phosphate at industrial level (Gebremariam et al., 2011). However, its effectiveness could be affected by many factors, such as volatile fatty acids, cations, temperature, sludge quality and settlement, and pH (Mulkerrins et al., 2004). So the biological process is usually supplemented by an additional treatment to meet the discharge requirement, when its performance is deteriorated from the fluctuations in operating conditions. The adsorption process requires simple operating conditions, possesses stable phosphate removal effect, and produces little sludge compared with other methods. Thus, it is promising as a supplement to the biological process for the phosphate removal, and it also could be easily applied for phosphate removal on small-scale treatment facilities or wastewater with relatively low phosphate concentrations. For this purpose, various adsorbents have been examined, including zero-valent iron (Almeelbi and Bezbaruah, 2012), activated carbon (Wang et al., 2012), aluminum oxide/hydroxide (Li and Guan, 2011), goethite (Gu et al., 2011), calcite (Liu et al., 2012), zeolite (Schick et al., 2012), red mud (Castaldi et al., 2012), and fly ash (Lu et al., 2009). Because of their large surface areas and preferred surface properties, synthesized metal oxides at nano-size have demonstrated effective phosphate adsorption (Lu et al., 2013; Yang et al., 2007; Yu et al., 2012).

Zirconium based oxides could be an attractive adsorbent choice for water treatment because of their non-toxicity, good resistance to oxidant agents and acids/bases, high thermal stability, and very low solubility in water (Bergamaschi et al., 2005; Blaney et al., 2007; Suzuki et al., 2000). The use of zirconium based oxides for phosphate adsorption had been reported in literature (Awual et al., 2011). Most of the studies were focused either on fibers (Awual et al., 2011) or activated carbon (Okumura et al., 1999, 1998) loaded with zirconium hydroxide, or binary oxides of zirconium with other metals (for example, Fe–Zr binary oxides) (Ren et al., 2012). No report is available on the study of the phosphate adsorption by more stable amorphous ZrO₂ nanoparticles, while amorphous adsorbents may have high adsorption capacity because of their

porous and highly hydrated structure. In our recent study, amorphous zirconium oxide nanoparticles were synthesized by a simple and low-cost hydrothermal process and were found to have very strong adsorption on arsenic species from water (Cui et al., 2012). Phosphorus and arsenic belong to the same element group (main group V) and have similar electronic structures. They form similar components in water (phosphate and arsenate), and our recent study indicated that a strong adsorption competition existed between arsenate and phosphate (Cui et al., 2012). Thus, amorphous zirconium oxide nanoparticles may be a good choice for the removal of phosphate from water.

In this study, the phosphate removal performance of amorphous zirconium oxide nanoparticles was examined in details by both the kinetics study and equilibrium adsorption isotherm study. The influences of various experimental parameters, such as solution pH, ionic strength, and competitive anions on phosphate removal were investigated. The phosphate desorption from these am-ZrO₂ nanoparticles and their reuse for phosphate adsorption were explored. Moreover, the phosphate adsorption mechanism of am-ZrO₂ nanoparticles was investigated by both the macroscopic and microscopic techniques.

2. Experimental section

2.1. Chemicals and material

Zirconium oxychloride octahydrate (ZrOCl₂•8H₂O, 99.0%, Sinopharm Chemical Reagent Co., Ltd., Shanghai, P.R. China) was used as the raw material, deionized water was used as the solvent, and aqueous ammonia (25 wt%, Tianjin Kermel Chemical Reagents Development Center, Tianjin, P.R. China) was used as the solvent, and aqueous ammonia (25 wt%, Tianjin Kermel Chemical Reagents Development Center, Tianjin, P.R. China) was used as the precipitation agent in the hydrothermal process. Sodium dihydrogen phosphate anhydrous (NaH₂PO₄, AR, Sinopharm Chemical Reagent Co. Ltd, Shanghai, P.R. China) was used to prepare phosphate stock solution. Concentrated hydrochloric acid (HCl, 32–38%, Tianda Chemical Reagents Factory, Tianjin, P.R. China) and sodium hydroxide (NaOH, 98%, Tianda Chemical Reagents Factory, Tianjin, P.R. China) were used to adjust solution pH. Sodium chloride (NaCl, 99.5%, Shenyang Chemical Reagents Factory, Shenyang, P.R. China), sodium sulfate anhydrous (Na₂SO₄, 99%, Tianjin Da Mao Chemical Reagents Factory, Tianjin, P.R. China), and sodium bicarbonate (NaHCO₃, AR, Sinopharm Chemical Reagent Co. Ltd, Shanghai, P.R. China) were used in the competing ion effect experiment. Sodium chloride was also used in the ionic strength effect experiment.

2.2. am-ZrO₂ nanoparticle synthesis and characterization

am-ZrO₂ nanoparticles were prepared by a hydrothermal process as detailed in our previous report (Cui et al., 2012). The Fourier transform infrared (FTIR) spectra of am-ZrO₂ nanoparticles before and after phosphate adsorption were measured on a Nicolet 6700 FT-IR spectrometer (Thermo Fisher Scientific Inc., Waltham, MA, U.S.A.), and their zeta

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