



Research article

Effect of pre-treatment of bentonite with sodium and calcium ions on phosphate adsorption onto zirconium-modified bentonite

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ABSTRACT

To understand the influence of the pre-treatment of bentonite with Na^+ and Ca^{2+} on the adsorption of phosphate on zirconium-modified bentonite, three kinds of adsorbent materials including zirconium-modified raw, Na^+ -pretreated and Ca^{2+} -pretreated bentonites were synthesized and characterized firstly, and afterward their adsorption performance and mechanism for phosphate were studied comparatively. The phosphate adsorption ability for zirconium-modified bentonite decreased after the pre-treatment of bentonite with Na^+ , but it increased after the pre-treatment of bentonite with Ca^{2+} . The maximum phosphate adsorption capacity calculated from the Langmuir isotherm model for zirconium-modified Ca^{2+} -pretreated bentonites (13.4 mg P/g) was much higher than that for the zirconium-modified raw bentonite (9.06 mg P/g). The pre-treatment of bentonite with Na^+ and Ca^{2+} did not change the interaction type between zirconium-modified bentonite and phosphate, i.e., the coordination of phosphate to zirconium. The decreased phosphate adsorption capacity for zirconium-modified bentonite induced by the Na^+ pre-treatment could be mainly attributed to the decrease of the specific surface area and the content of exchangeable Ca. The increased phosphate adsorption capacity for zirconium-modified bentonite induced by the Ca^{2+} pre-treatment could be mainly due to the increase in the amount of exchangeable Ca. Results of this work suggest that the zirconium-modified Ca^{2+} -pretreated bentonite is more suitably used as an adsorbent for the removal of phosphate from wastewater than the zirconium-modified raw and Na^+ -pretreated bentonites.

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1. Introduction

Removal of phosphate (PO_4^{3-}) from wastewater is of great importance to prevent surface water bodies such as lakes and rivers from eutrophication, because phosphorus (P) is generally considered as one of the key nutrient elements for algae production and the release of excess P from wastewater to water bodies can cause algal bloom/eutrophication (Gu et al., 2017; Lin et al., 2017b; Smith et al., 1999). For the removal of phosphate from wastewater, various technologies have been developed, including biological removal process, chemical precipitation of phosphate with aluminum or ferrous salt, crystallization, ion exchange and adsorption (Zhang et al., 2017). Among them, adsorption is commonly considered to

be a very promising method for phosphate removal from wastewater, due to its low cost, high and stable P removal efficiency, simple design, easy operation, and great potential for P recovery from wastewater at low P concentration (Fang et al., 2017; Gu et al., 2017; Lin et al., 2017a, 2017c; Rashid et al., 2017; Rashidi Nodeh et al., 2017; Xie et al., 2014; Zhang et al., 2016).

Bentonite is a kind of clay minerals with high content of montmorillonite. Structurally, montmorillonite consists of an octahedral alumina layer between two tetrahedral silica sheets. Due to the isomorphous replacement of Mg^{2+} for Al^{3+} in the octahedral layer and Al^{3+} for Si^{4+} in the tetrahedral layer, montmorillonite possesses permanent negative charges on its structure surface (Chinoune et al., 2016). These permanent negative charges are neutralized by the exchangeable cations such as Na^+ and Ca^{2+} , resulting in that montmorillonite has cation exchange capacity (Chinoune et al., 2016; Kalantari et al., 2015). As a low cost clay, bentonite has been widely used as an adsorbent for dye and heavy metal removal in recent years (Glatstein and Francisca, 2015; Roulia and Vassiliadis, 2008; Taha et al., 2016; Tahir and Rauf, 2006).

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Although bentonite has an excellent affinity towards cations due to its high cation exchange capacity (CEC), it has a low adsorption performance for anions such as phosphate (El Bouraie and Masoud, 2017). Thus, modification of raw bentonite is necessary to increase its phosphate adsorption capability.

To enhance its affinity towards aqueous phosphate, metals like lanthanum, aluminum, iron, magnesium and zirconium are commonly used to modify the surface of bentonite. As a result, various metal-modified bentonites including lanthanum-modified bentonite clay (LMB) (Kuroki et al., 2014; Kurzbaum and Bar Shalom, 2016), Al-intercalated acid activated bentonite beads (Pawar et al., 2016), lanthanum/aluminum pillared bentonite (Tian et al., 2009), Fe(III)-modified montmorillonite (Borgnino et al., 2009), hydroxy-iron-aluminum pillared bentonite (Yan et al., 2010), magnesium hydroxide-modified bentonite (El Bouraie and Masoud, 2017), zirconium/aluminum-pillared montmorillonite (Zr/Al-Mt) (Huang et al., 2015), zirconium-pillared montmorillonite (Zr-Mt) (Huang et al., 2015) and zirconium-modified bentonite (ZrBT) (Lin et al., 2016) have been prepared and used as adsorbents to remove phosphate from aqueous solution. In recent years, using zirconium-containing materials as adsorbents to remove phosphate from aqueous solution has gained a great of attention among researchers, because hydrous zirconium oxide (HZO) is non-toxic, environment-friendly, not dissolvable in water and shows high adsorption capacity towards phosphate through ligand exchange and inner-sphere complex formation mechanism (Chen et al., 2015; Luo et al., 2017; Qiu et al., 2015; Shang et al., 2017; Su et al., 2013). Therefore, ZrBT is expected to be a very promising adsorbent for phosphate removal from wastewater, and great efforts should be made to strength the study of the ZrBT preparation and its phosphate adsorption.

Generally, bentonites are classified as Na-dominated bentonite, Ca-dominated bentonite and Na/Ca-dominated bentonite according to their exchangeable cation type (Şans et al., 2017). Different types of bentonites may have different physicochemical properties (Karakaya et al., 2011). Therefore, different ZrBTs prepared by modifying different bentonites with zirconium under the same preparation condition may have different physicochemical characteristics and thus may have different adsorption performances for phosphate. Treatment of bentonite with sodium salt is a feasible method to increase its Na content, while treatment of bentonite with calcium salt is a feasible method to increase its Ca content (Ait-Akbour et al., 2015; Boussen et al., 2015). Thus, the zirconium-modified Na⁺-pretreated and Ca²⁺-pretreated bentonites may have different affinities towards phosphate than the zirconium-modified raw bentonite.

Previous literature have found that coexisting Ca²⁺ can enhance the adsorption of phosphate on hydrous zirconium oxide (Lin et al., 2017c) and the release of Ca²⁺ from zirconium oxide-based adsorbent materials such as zirconium-modified zeolite can promote the phosphate adsorption (Zhan et al., 2017). Based on these findings, it is expected that the release of Ca²⁺ from ZrBT can facilitate the adsorption of phosphate. Furthermore, the zirconium-modified Na⁺-pretreated and Ca²⁺-pretreated bentonites may have different Ca²⁺ releasing abilities than the zirconium-modified raw bentonite due to their different exchangeable Ca amounts. Therefore, the release of Ca²⁺ from the zirconium-modified Na⁺-pretreated and Ca²⁺-pretreated bentonites may have different promoting effect on the phosphate adsorption than that from the zirconium-modified raw bentonite. Understanding the effect of the pre-treatment of bentonite with Na⁺ and Ca²⁺ on phosphate adsorption onto ZrBT is helpful for preparing better Zr-based adsorbent for phosphate removal from aqueous solution as well as helpful for understanding the adsorption mechanism of phosphate on ZrBT. Although the adsorption performance and

mechanism of phosphate on a kind of ZrBT, i.e., zirconium-modified raw bentonite (Lin et al., 2016), there are no published studies about the role of the pre-treatment of bentonite with Na⁺ and Ca²⁺ in the adsorption of phosphate on ZrBT.

The objective of this research was to investigate the influence of Na⁺ and Ca²⁺ pre-treatment on phosphate adsorption onto ZrBT. For this purpose, three kinds of ZrBTs, including zirconium-modified raw bentonite (ZrRBT), zirconium-modified Na⁺-pretreated bentonite (ZrNaBT), and zirconium-modified Ca²⁺-pretreated bentonite (ZrCaBT) were prepared and characterized firstly, and then the adsorption performances and mechanisms of phosphate on ZrRBT, ZrNaBT and ZrCaBT were comparatively studied.

2. Materials and methods

2.1. Materials

The raw bentonite used in this study was purchased from Sinopharm Chemical Reagent Co. Ltd., China (Shanghai). ZrOCl₂·8H₂O, NaOH, HCl, H₂SO₄, KH₂PO₄, NaCl, KCl, MgCl₂, CaCl₂, Na₂SO₄, NaHCO₃, ammonium molybdate and ascorbic acid were analytical grade and purchased from Sinopharm Chemical Reagent Co. Ltd., China (Shanghai). Deionized water was used to prepare all solutions throughout the experiments.

2.2. Preparation of ZrBTs

The samples of ZrNaBT and ZrCaBT were prepared by a two-step method. Firstly, the pre-treatment of raw bentonite was performed by mixing of raw bentonite and 1 mol/L NaCl (or CaCl₂) solution at a solid/liquid ratio of 100 g/L. After 24 h of shaking at 150 rpm and 298 K, the mixtures were centrifuged and the supernatants were poured out. Then, the NaCl-pretreated or CaCl₂-pretreated bentonite was mixed with ZrOCl₂·8H₂O solution with a concentration of 100 g/L at a solid/liquid ratio of 200 g/L. After 30 min of shaking at 150 rpm and 298 K, the pH value of the solution was adjusted to 10.0 using 1 mol/L NaOH solution. After that, the mixtures were shaken at 150 rpm and 298 K for 24 h. After that, the solid was separated by centrifugation and washed with deionized water. At last, the products were dried in an oven at 378 K and stored in seal plastic bags until their use in adsorbent characterization and adsorption experiments. For comparison, the ZrRBT sample was prepared through the same procedure but without the pre-treatment of raw bentonite with NaCl or CaCl₂ solution.

2.3. Material characterization

The surface morphologies of ZrRBT, ZrNaBT and ZrCaBT were studied using field-emission scanning electron microscopy (FE-SEM, Mira 3, Tescan, Czech) operated at 5 kV. The surface element compositions of ZrRBT, ZrNaBT and ZrCaBT were determined by energy-dispersive X-ray spectroscopy (EDS, Oxford Aztec, Oxford Instruments, UK). The phase structure of ZrRBT, ZrNaBT and ZrCaBT was characterized by X-ray diffraction (XRD, D8 ADVANCE Da Vinci, Bruker, Germany) with Cu-K α radiation ($\lambda = 0.15418$ nm) as a source operating at 40kV/30 mA for 2θ values between 5° and 90°. The N₂ adsorption/desorption isotherms of ZrRBT, ZrNaBT and ZrCaBT were obtained on a QuadraSorb SI surface area and porosity analyzer (Quantachrome Instruments, USA) at 77 K. According to the N₂ adsorption isotherm data, the specific surface area (SSA) was calculated by using the Brunauer-Emmett-Teller (BET) method, and the pore size distribution was determined by using the Barrett-Joyner-Hallenda (BJH) method. The pHPZC (pH at the point of zero charge) values of ZrRBT, ZrNaBT and ZrCaBT were measured using the pH shift method as described in the previous literature (Lin et al.,

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