Sequential removal of phosphate and cesium by using zirconium oxide: A demonstration of designing sustainable adsorbents for green water treatment

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HIGHLIGHTS

- Life cycle extension of adsorbents is desirable for sustainable water treatment.
- The life cycle of ZrO_2 is extended to sequentially remove phosphate and cesium.
- Surface adsorbed phosphate can be converted to a zirconium phosphate overlayer.

GRAPHICAL ABSTRACT
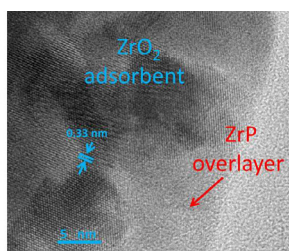
Green Water Treatment by Extending the Life Cycle of Adsorbents

ARTICLE INFO

ABSTRACT

Adsorption is one of the most cost-effectiveness methods to effectively remove pollutants particularly in the low concentration region. Extending life cycle of adsorbents is hence highly desirable for the perspective of green water treatment as it would ultimately reduce environmental impacts and associated cost in the waste disposal and adsorbent synthesis. In this study, we demonstrate the extension of the life cycle of zirconium oxide (ZrO_2) adsorbent for sequentially removing phosphate and cesium. High affinity of ZrO_2 to phosphate allows surface adsorbed phosphate to be converted to a zirconium phosphate over-layer in the following thermal treatment. By this manner, waste zirconium oxide adsorbent in the end of phosphate removal can be functionalized as a new cation exchange material for following Cs removal application. Importantly, our demonstrated strategy provides a valuable example in arranging and designing a sustainable adsorbent for green water treatment in the future.

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1. Introduction

A healthy ecosystem is strongly relied on minimizing the discharge of anthropogenic materials such as hazardous metals ions and excess nutrients into it. Phosphorus, for instance, is an essential nutrient but once its concentration exceeds 0.05 mg/L in the

ecosystem eutrophication and algae bloom will be spurred. Controlling phosphate concentration to meet this level with currently available engineering methods is not a challenge. Alternatively, the cost of these treatments is actually the major issue of concern. Based on the cost-effectiveness consideration, utilization of adsorbents would be a rational choice to further reduce phosphate concentration in the discharge from the water/wastewater treatment plants. Several cost-effectiveness adsorbents such as zero valent iron [1], porous silica [2] and waste cements [3] have been

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demonstrated good candidates for phosphate removal. Their performances can be further enhanced by impregnating with alkaline earth elements such as calcium and magnesium [4,5]. Despite efficient phosphate removal can be achieved by using these high performance adsorbents and these adsorbents can be regenerated for several times, a follow-up question emerges that how to appropriately dispose of these waste adsorbents without introducing any secondary pollution.

Based on the consideration of pursuing sustainable water treatment technology, converting wastes to other functionalized materials always stands at the top priority in the respect of waste management [6,7]. By expanding the life cycle of adsorbents, waste production and raw material exploit can be effectively minimized. To achieve this goal, knowledge regarding the chemistry of adsorbent and the surface engineering plays the crucial role in designing and managing a practical life-cycle-extension reaction route. In this study, we demonstrate to expend the life cycle of zirconium oxide adsorbent to sequentially remove phosphate and cesium. Zirconium oxide was selected as the model material as its high affinity to phosphate results in approximately 40% of adsorbed phosphate remaining on its surface even after the regeneration in a harsh alkaline environment (0.5 M NaOH) [8]. This means the strong interactions between the adsorbed phosphate and the sorptive sites on the surface of ZrO_2 will gradually deteriorate its performance in a few regeneration cycles. This high affinity, on the other hand, provides an opportunity to convert waste zirconium oxide adsorbents to zirconium phosphate (ZrP), which is an interesting layered material with many potentials in the industrial application [9–12]. Our results showed that with a simple thermal treatment (at 250 °C), surface bound phosphate can be effectively converted to a ZrP overlayer. The presence of ZrP overlayer further changed the surface chemistry of ZrO_2 to behave as a cation exchange material. Although the cation exchange capacity of obtained materials is lower than other conventional ion exchange counterparts due to the limited amount of ZrP overlayer, our results are still significant in the respect of sustainable water treatment technology. First, we demonstrate that the cost of utilization of ZrO_2 adsorbent would likely be comparable with other low-cost adsorbents when the cost of waste disposal is taken into account. Second, knowledge regarding the surface chemistry of the adsorbent is important as it is the basis for designing a practical waste reutilization/functionalization process in response to the development of a sustainable water treatment technology.

2. Materials and methods

2.1. Chemicals and adsorption experiment procedures

All chemicals were ACS grade purchased from Sigma-Aldrich and used as-received without any further purification, including ZrO_2 powders. Milli-Q water (18.2 MΩ) was used for preparing all solutions. All adsorption experiments including isotherm adsorption and adsorption at different pH were carried out in 50 mL conical flasks with a fixed solid/liquid ratio of 0.1 g adsorbent in 10 mL solutions. The background electrolyte was 0.01 M NaCl and the pH adjustment was by using 0.1 N hydrochloric acid (HCl) and sodium hydroxide (NaOH) solutions. For isotherm adsorption experiments, the initial phosphate concentrations (Na_3-PO_4 salt) were designed ranging from 0.1 mg/L to 50 mg/L at pH 6.3 ± 0.2, while the initial phosphate concentration was fixed at 10 mg/L for adsorption experiments at different pH. All adsorption experiments were conducted at room temperature (28 ± 1.0 °C) in a thermostatic-controlled shaker and the mixtures were allowed to equilibrate for 24 h. In the end of adsorption, the mixtures were separated by centrifugation (13,000 rpm for 20 min). The equili-

brated pH was recorded using a pH meter (Mettler Toledo) and the phosphate concentration remaining in supernatant was analyzed using ICP-MS (Agilent 7500A). The difference in phosphate concentration was assumed to be the amount of phosphate adsorbed on the surface of zirconium oxide. For cesium adsorption experiments, aliquot amount of ZrO_2 and ZrP@ZrO_2 powders were dispersed in 0.01 M NaCl solutions containing 0.1 mg/L CsCl (solid/liquid ratio was fixed at 1/100 as well). The adsorption procedure was identical to that of phosphate adsorption experiments and remained Cs concentration in solution was determined using ICP-MS (Agilent 7500A).

2.2. Converting adsorbed phosphate to surface ZrP overlayer

To convert surface adsorbed phosphate to zirconium phosphate (ZrP) overlayer, 10 g of ZrO_2 powders were dispersed in the solution containing 100 mg/L phosphate (100 mL) at pH 6.5. In the end of adsorption, phosphate adsorbed ZrO_2 powders were separated by centrifuge and dried at 60 °C overnight. Dried samples were then calcined at 250 °C 2 h in a box furnace with a heating ramp of 10 °C/min. As-obtained samples were then pulverized using a mortar and pestle for additional Cs adsorption experiments and characterization.

2.3. Characterization

The scanning electron microscopy (SEM) images of ZrO_2 and ZrP@ZrO_2 nanostructures were obtained using JSM700F, JEOL scanning electron microscope with acceleration voltage of 10 kV. High-Resolution transmission electron microscopy (HRTEM) images and energy dispersive X-ray analysis (EDX) were recorded using JEOL JEM-2100 HRTEM. X-ray Diffractometer (XRD, D2 Phaser diffractometer, Brucker) was utilized for the structure characterization with Cu Kα1 radiation (0.154056 nm). Collection of FTIR spectra was carried out using a Bruker Vertex 80v spectrometer with a resolution of 4 cm^{-1} in the range of 650–3850 cm^{-1} for 1024 scans. The zeta potential of ZrO_2 and ZrP@ZrO_2 samples were determined using a zeta potential analyzer (Zetasizer NanoZ, Malvern) with a mixture of 0.1 g sample dispersed in 100 mL 10 mM NaCl solution. The specific surface area and porous property of ZrO_2 and ZrP@ZrO_2 samples were characterized using N_2-BET method (Micromeritics ASAP 2020).

3. Results and discussion

3.1. Phosphate adsorption to zirconium oxides

Characteristic behaviors of phosphate adsorption to ZrO_2 are shown in Fig. 1. As indicated in Fig. 1a, phosphate adsorption to ZrO_2 is strongly pH-dependent. While no significant drops in adsorption are observed from pH 2 to pH 6, it decreases profoundly when the pH is above pH 7. Similar pH-dependent adsorption behaviors are reported in the literature [8,13]. The dominant phosphate species in the studied pH range are $H_2PO_4^-$, HPO_4^{-2}, and PO_4^{3-}, respectively. In the acidic environment, ZrO_2 is positively charged as a result of protonation of surface Zr-OH groups, which could enhance the electrostatic attraction between the adsorbent surface and the phosphate anions and hence facilitate the phosphate adsorption. When the solution pH exceeds pH 6, deprotonation of surface Zr-OH groups leads the formation of negatively charged. The coulomb repulsive between the negatively charged ZrO_2 surface and the negatively charged phosphate species therefore accounts for the observed decrement in phosphate adsorption in the neutral and alkaline environment. This interpretation is clearly supported by the following zeta potential study (Fig. 2b), where