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Role of zeolite's exchangeable cations in phosphate adsorption onto zirconium-modified zeolite

Yanhui Zhan [a,1], Honghua Zhang [b,1], Jianwei Lin [a,*], Zhe Zhang [a], Jian Gao [a]

[a] College of Marine Ecology and Environment, Shanghai Ocean University, Shanghai 201306, China
[b] College of Environment, Zhejiang University of Technology, Hangzhou 310032, China

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ABSTRACT

To determine the role of zeolite's exchangeable cations such as Ca^{2+} and Na^{+} in the adsorption of phosphate on zirconium-modified zeolite (ZrMZ), the adsorption behaviors and mechanisms of phosphate on ZrMZ, NaCl-treated ZrMZ and $CaCl_2$-treated ZrMZ in the absence and presence of ammonium were comparatively investigated in this study. Results showed that coexisting ammonium promoted the adsorption of phosphate on the raw, NaCl-treated and $CaCl_2$-treated ZrMZs. In the absence of ammonium, the treatment of ZrMZ with NaCl inhibited the phosphate adsorption, but the treatment of ZrMZ with $CaCl_2$ enhanced the adsorption of phosphate. In the presence of ammonium, the treatment of ZrMZ with NaCl suppressed the adsorption of phosphate, but the effect of $CaCl_2$ treatment on the phosphate adsorption depended upon coexisting ammonium amount. In the presence of a certain amount of ammonium (5–30 mg N/L), the treatment of ZrMZ with $CaCl_2$ improved the phosphate adsorption efficiency. The mechanism for phosphate adsorption onto ZrMZ was the exchange of surface hydroxyl groups with phosphate ions and the formation of phosphate inner-sphere coordination complexes, and the enhancement of phosphate adsorption onto ZrMZ by coexisting Ca^{2+} could be attributed to the formation of $CaHPO_4^0$ species in the calcium/phosphate solution and the formation of phosphate-bridged ternary complex ($\equiv$Zr)(OPO_3H)Ca on the adsorbent surface. The increased phosphate adsorption induced by $CaCl_2$ treatment could be attributed to the increase in the amount of released Ca^{2+} from ZrMZ, and the decreased phosphate adsorption induced by NaCl treatment could be attributed to the decrease in the amount of released Ca^{2+} from ZrMZ. This work suggests that the exchangeable Ca^{2+} in ZrMZ plays an important role in the phosphate adsorption, and its release enhances the adsorption of phosphate.

1. Introduction

Phosphorus (P) is an essential nutrient for the growth of biological organisms in surface water bodies such as lakes, reservoirs and rivers. However, excessive input of P from municipal, industrial and agricultural sources into surface water bodies can cause eutrophication problems resulting in harmful algal blooms [1–4]. Therefore, it is important to remove phosphate (PO_4^{3-}), the main species of P, from wastewater prior to its emission in order to protect surface water bodies from eutrophication. Various techniques, such as enhanced biological phosphorus removal process (EBPR) [5], chemical precipitation [6] and adsorption [2], have been developed to remove phosphate from wastewater. Of these methods, adsorption has attracted broad attention recently, due to its simple operation and design, steady and high P removal efficiency, low cost, and easy recovery of phosphate at low concentration from wastewater [2,7,8].

Many adsorbents have been considered for phosphate removal from aqueous solution [9,10]. Among them, hydrous zirconium oxide (HZO) has been found to exhibit a specific affinity towards phosphate in aqueous solution because zirconium has hard Lewis acid property and phosphate can behave as a Lewis base [8,11–18]. Furthermore, HZO is nontoxic and has very low solubility in water [13]. Therefore, HZO could be a highly attractive adsorbent choice for phosphate removal from wastewater. However, the use of pure HZO is generally not cost-effective. In order to reduce its cost, HZO can be loaded onto a low-cost porous supporter to prepare a HZO-based composite.

Natural zeolites are porous crystalline aluminosilicate minerals whose framework structure is negatively charged and can adsorb exchangeable cations such as Na^{+}, K^{+}, Ca^{2+} and Mg^{2+} [19–22]. Considering their high specific surface area, high cation exchange capacity, high chemical and mechanical stability, abundant reserves and low cost, natural zeolites have been widely used as adsorbents to remove ammonium from aqueous solution [23–26], and they are also indicated to be ideal supports for metals [27,28]. However, natural zeolites generally

* Corresponding author at: College of Marine Ecology and Environment, Shanghai Ocean University, No. 999 Hucheng Huan Road, Pudong District, Shanghai 201306, China.
E-mail address: jwlin@shou.edu.cn (J. Lin).

[1] These authors contributed equally to this work.

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have a very low affinity for phosphate in aqueous solution owing to the constant negative charges on their framework structure surface [19,29,30]. When HZO is laden on the surface of natural zeolite, the resulting zirconium-modified zeolite (ZrMZ) could be a promising adsorbent for phosphate removal from aqueous solution because of its high adsorption capacity and relatively low cost [31].

In municipal wastewater, phosphate generally coexists with ammonium (NH_4^+). When ZrMZ is contacted with this wastewater, it can remove not only phosphate but also ammonium [32]. Besides, the cation-exchange mechanism is expected to play an important role in the adsorption of ammonium on ZrMZ, because the adsorption of ammonium on zeolite mainly relies on the cation-exchange mechanism [21,33–36] and the crystalline structure of zeolite does not change after the loading of HZO [31]. Assuming that the exchangeable cations in zeolite are mainly Na^+ and Ca^{2+}, these exchangeable cations are expected to be released from ZrMZ after the adsorption of ammonium through Na^+/NH_4^+ and Ca^{2+}/NH_4^+ exchange mechanisms [33,36]. Since coexisting Na^+ can slightly enhance the adsorption of phosphate on HZO while coexisting Ca^{2+} can greatly enhance the phosphate adsorption [8], the adsorption of phosphate on ZrMZ is expected to be enhanced by the presence of Na^+ and Ca^{2+}. Therefore, the release of Na^+ and Ca^{2+} from ZrMZ after the adsorption of ammonium may enhance the phosphate adsorption. However, there are few studies on the role of zeolite's exchangeable cations such as Na^+ and Ca^{2+} in the adsorption of phosphate on ZrMZ in the presence of ammonium.

Owing to the presence of the permanent negative charges on the crystal structures of zeolites, many cations such as cationic surfactant, Na^+ and Ca^{2+} can be loaded onto the zeolite surface through cation exchange mechanism when these cations are contacted with zeolites. It is worth mentioning that small cations can occupy both internal and surface ion exchange sites of zeolites, while bulky cationic surfactant can only occupy the surface ion exchange sites of zeolites. When the active sites of zeolites are occupied by cationic surfactant, the obtained surfactant-modified zeolites (SMZs) can be used as good adsorbents to remove organic pollutants and anions [37–39]. NaCl treatment is widely used to enhance the ammonium adsorption capacity for zeolites [33,40], while $CaCl_2$ treatment can be used to increase the phosphate immobilization capacity for zeolites [41]. The treatment of zeolites with NaCl solution decreases the amount of exchangeable Ca^{2+} but increases the amount of exchangeable Na^+, while the treatment of natural zoelite with $CaCl_2$ solution increases the amount of exchangeable Ca^{2+} but decreases the amount of exchangeable Na^+ [33,34]. Therefore, it is expected that the treatment of ZrMZ with NaCl or $CaCl_2$ solution will influence the content of exchangeable Na^+ or Ca^{2+}, and thus will change the amount of Na^+ or Ca^{2+} released from ZrMZ after the adsorption of ammonium. Since the change in the amount of released Na^+ or Ca^{2+} after the ammonium adsorption may influence the adsorption of phosphate on ZrMZ, the treatment of ZrMZ with NaCl or $CaCl_2$ may influence the phosphate adsorption in the presence of ammonium. Knowing the effect of NaCl and $CaCl_2$ treatment on phosphate adsorption onto ZrMZ in the absence and presence of ammonium is helpful not only for preparing a better adsorbent for phosphate removal, but also for determining the role of zeolite's exchangeable cations such as Na^+ and Ca^{2+} in phosphate adsorption onto ZrMZ. However, there are few studies on the effect of NaCl and $CaCl_2$ treatment on the adsorption of phosphate on ZrMZ in the absence and presence of ammonium.

The main objectives of this study were: (1) to investigate the effect of NaCl and $CaCl_2$ treatment on the adsorption of phosphate on ZrMZ in the absence and presence of ammonium; and (2) to determine the role of zeolite's exchangeable cations such as Na^+ and Ca^{2+} in the adsorption of phosphate on ZrMZ. For these purposes, three kinds of ZrMZs, i.e., raw, NaCl-treated and $CaCl_2$-treated ZrMZs were prepared and characterized firstly, and then the adsorption characteristics and mechanisms of phosphate on the raw, NaCl-treated and $CaCl_2$-treated ZrMZs in the absence and presence of ammonium were comparatively investigated.

2. Materials and methods

2.1. Materials

The natural zeolite (NZ) with a particle size of less than 0.075 mm was acquired from Jinyun County in Zhejiang Province, China. The natural zeolite was composed of 52% clinoptilolite, 32% silicon oxide and 16% mordenite as indicated by X-ray diffraction (XRD) analysis [31]. $ZrOCl_2 \cdot 8H_2O$, NH_4Cl, KH_2PO_4, KCl, NaCl, $CaCl_2$, NaOH and HCl were all obtained from Sinopharm Chemical Reagent Co., Ltd., China, and all these chemicals were of analytical grade. Phosphate stock solution was prepared by dissolving KH_2PO_4 in deionized water, and its phosphate concentration was expressed in element P. The phosphate/ammonium stock solutions were prepared by dissolving KH_2PO_4 and NH_4Cl in deionized water, and their phosphate and ammonium concentration were expressed in element P and N, respectively. The stock solutions were further diluted with deionized water to prepare working solutions.

2.2. Preparation of ZrMZs

The raw ZrMZ was synthesized by a one-step method as follows. In brief, $ZrOCl_2 \cdot 8H_2O$ (10 g) and NZ (20 g) were added together into a conical flask containing 200 mL of deionized water. After that, the resulting suspension was violently stirred at room temperature for 2 h. Subsequently, the solution of NaOH (1.0 mol/L) was added dropwisely into the suspension with vigorous stirring until the pH value reached 10.0. The mixture was then stirred for 2 h continuously. After completion of the reaction, the solid products were collected from the suspension by centrifugation, followed by washing with deionized water. At last, the solid products were dried at 105 °C in an oven, grounded and stored in airtight container for later experiments. For comparison purpose, the hydrous zirconium oxide (HZO) was prepared by the same synthesis procedure but without adding NZ.

The NaCl-treated ZrMZ (Na-ZrMZ) was prepared by shaking 8 g of raw ZrMZ in 100 mL of 1.6 mol/L NaCl solution at 25 °C and 150 rpm for 24 h. The $CaCl_2$-treated ZrMZ (Ca-ZrMZ) was prepared by shaking 8 g of raw ZrMZ in 100 mL of 1.6 mol/L $CaCl_2$ solution at 25 °C and 150 rpm for 24 h. After finishing, the solid products were recovered from the mixtures by centrifugation, and then were washed with deionized water repeatedly until the Cl^- in the supernatant was not detected by $AgNO_3$ solution. Finally, the solid products were dried in a 105 °C oven, grounded and stored in airtight container for later experiments.

2.3. Material characterization

The chemical compositions of adsorbents were determined by an XRF-1800 X-ray Fluorescence (XRF) spectrometer (Shimadzu Corporation, Japan). The elemental spectra and chemical composition on the surfaces of adsorbents were measured on an INCA X-Act energy-dispersive X-ray spectroscopy (EDS) analyzer (Oxford Instruments, UK). The X-ray photoelectron spectroscopy (XPS) spectra of adsorbents were measured by a Kratos Axis Ultra^{DLD} spectrometer (Kratos Analytical-A Shimadzu Group Company) equipped with a monochromatic Al K_α source (1486.6 eV). The composition of adsorbent surface was determine based on the areas of O 1 s, Zr 3d, Al 2p, Si 2p, Na 1 s, K 2p, Fe 2p, P 2p and N 1 s photoelectron peaks. The high resolution spectra of O 1 s and Zr 3d were fitted by a Gaussian/Lorentzian (70/30) peak model after Shirley background correction. The solid state ^{31}P magnetic angle spinning (MAS) nuclear magnetic resonance (NMR) spectra of adsorbents were gotten by an Avance III 400 MHz NMR spectrometer (Bruker Corporation, Germany) equipped with a 4.0 mm broadband solid MAS probe at a spinning rate of 8 kHz. The ^{31}P chemical shifts were reported using external KH_2PO_4 as reference. The values of pH_{PZC} (pH at the point of zero charge) for adsorbents were determined using the known method of pH drift described elsewhere [19,42].