Development of polymeric iron/zirconium-pillared clinoptilolite for simultaneous removal of multiple inorganic contaminants from wastewater

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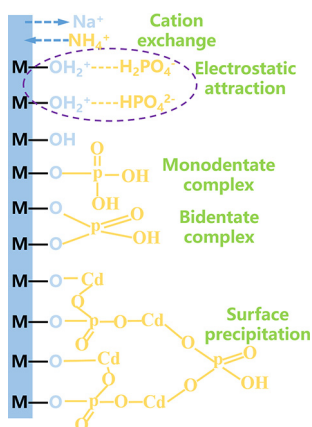[c] Shanghai Institute of Pollution Control and Ecological Security, Shanghai 200092, China

HIGHLIGHTS

- Simple synthesis of nano Fe/Zr-PC with multiple functionary mechanism.
- Excellent simultaneous removal of multiple inorganic contaminants was achieved.
- Selective sorption mechanism was probed and discussed.

GRAPHICAL ABSTRACT

ARTICLE INFO

ABSTRACT

Excessive levels of ammonium, phosphate, and heavy metals in surface water are serious environmental concerns that could potentially cause eutrophication and health issues. In this study, a novel iron/zirconium-pillared clinoptilolite (nano Fe/Zr-PC) was developed by intercalating Fe^{3+}/Zr^{4+} polyhydroxy-cations into clinoptilolite for the simultaneous removal of ammonium, phosphate, and cadmium (Cd (II)). The obtained material was characterized using a transmission electron microscope (TEM), BET analysis, X-ray diffraction (XRD), and Fourier transform infrared spectroscopy (FT-IR), which indicated that nanoscale Fe or Zr particles were successfully formed on the surface and pore structures of clinoptilolite. Batch experiments were conducted to investigate the effects of varied operation parameters on the adsorption behavior. The results show that nano Fe/Zr-PC achieved high removal efficiencies for ammonium, phosphate, and Cd (II) over a wide pH range (4–8), indicating higher adaptability towards varying environmental conditions. In addition, kinetic analysis suggested that the adsorption process was best represented by the pseudo-second-order kinetic model, suggesting the rate-limiting step for removing ammonium, phosphate, and Cd (II) on nano Fe/Zr-PC may be the chemical adsorption stage. The underlying mechanism was also assessed using X-ray photoelectron spectroscopy (XPS) analysis. Ammonium, phosphate, and Cd (II) were captured *via* a cation exchange reaction, electrostatic attraction and ligand exchange, and surface precipitation, respectively. Overall, the analysis and the characterization results

revealed that nano Fe/Zr-PC is a highly efficient adsorbent for the simultaneous removal of ammonium, phosphate, and Cd (II) with an excellent adaptability to varying and undesirable environmental conditions.

1. Introduction

Nutrients (e.g., ammonium and phosphate) and heavy metal cations (e.g., Cd) are typical inorganic contaminants in the environment. Although essential elements to support the growth of most biological organisms, excessive amounts of ammonium and phosphate in water cause environmental issues. An example of their adverse consequences is accelerated eutrophication in lakes and seas [1–3]. Being carcinogenic contaminants, various heavy metals are released in excess from industrial sites and ultimately find their way into the water and soil, where they are more likely to become potential threats to human health *via* the food chain [4]. Therefore, coexisting nutrients and heavy metals from domestic and industrial sources are commonly identified in environmental media. The simultaneous removal of multiple inorganic contaminants for wastewater from mixed collection system of municipal sewage, industrial wastewater, and rainwater is urgently required.

Numerous approaches have been developed to treat nutrient-rich and Cd (II)-rich effluents before their discharge into natural water bodies, including chemical precipitation, ion exchange, reverse osmosis, and biological methods [5–8]. However, the complex operation and relatively high costs are major limitations of these conventional techniques. Among the alternative methods, adsorption is generally recommended as one of the most effective and efficient techniques for nutrient and heavy metal removal, owing to its suitability for technologically economical and highly efficient removal [9].

Currently, different kinds of adsorbents have been developed, such as natural zeolites for ammonium removal [10], blast furnace slag for phosphate removal [11], and carbon nanotubes for Cd (II) removal [12]. The key to the adsorption technique lies in the perfect characteristic of the adsorbent; thus, adsorbents with high surface areas and more binding sites are required. Notably, among these materials, natural zeolites are the most promising material for removing nutrients and heavy metals. As the most abundant natural zeolite, clinoptilolite – a silicate mineral composed of tetrahedral silicon oxide [SiO_4] and tetrahedral aluminum-oxide [AlO_4] – has ideal adsorption abilities [13] and the perfect ion-exchange properties for many cations [14]. The porous structure of clinoptilolite, with its many channels and cavities, makes it a potential adsorbent material, with a high surface area [15]. Other important properties such as its non-toxic nature, abundance, and cost-effectiveness and environmental acceptability have enabled clinoptilolite to garner more attention to be developed as a material with outstanding adsorbent properties for use in a wide range of applications [16]. Nevertheless, owing to the present limitation of its negative surface charge, clinoptilolite needs to be modified to enable it to adsorb phosphate. Conversely, metal oxides/hydroxides, such as zirconium oxide [17], zirconium hydroxide [18], aluminum hydroxide [19], and Fe-Mn binary oxide [20] have been reported as highly efficient adsorbents of phosphate. However, it is not cost-effective to utilize pure metal oxides/hydroxides for practical phosphate removal.

Recently, much research has been focused on the modification of clay minerals by using inorganic metal polyhydroxy cations to replace the original cations [21]. The prepared materials, namely pillared clay minerals, can achieve a high adsorption capacity and are cost effective. Many metal-pillared clay minerals have proven to be promising adsorbents of nutrients or heavy metals. For instance, Yan et al. [22] reported that the phosphate removal capacity of Al-pillared bentonite was 12.7 mg P/g in contrast to that of un-pillared bentonite, which was undetectable. Moreover, the mixed metal-pillared clay minerals have been reported to possess superior adsorption capacities compared to the single metal-pillared ones [23]. Tian et al. [23] discovered that Al/La-

pillared montmorillonite performed better than Al-pillared montmorillonite in removing phosphate.

Nutrients and heavy metals often coexist in wastewater; thus, their transport and destination may be significantly influenced by each other [24]. According to our literature survey, no studies report the application of Fe/Zr-pillared clinoptilolite as an adsorbent in the simultaneous adsorption of ammonium, phosphate, and heavy metals. In the present study, Cd, a commonly identified pollutant of priority in the environment was selected as the study objective. A novel nanocomposite, Fe/Zr-pillared clinoptilolite (nano Fe/Zr-PC) was developed and used for the simultaneous removal of ammonium, phosphate, and Cd (II) to evaluate its feasibility as an adsorbent in environmental remediation. The basic micro-morphology and physicochemical properties of the adsorbent were characterized through a combined analysis using TEM-EDS, XRD, FT-IR and XPS. The experimental conditions including the solution pH and adsorbent dosage were examined. In addition, the underlying mechanism of the simultaneous adsorption of ammonium, phosphate, and Cd (II) was also investigated to assess the role of Fe/Zr pillars in the adsorption.

2. Materials and methods

2.1. Materials

Natural clinoptilolite obtained from Gongyi Mines Co., Henan, China, was first sliced and sieved so that it was within a size range of 0.5–1.5 mm. Prior to the modification process, the clinoptilolite was washed with deionized water to remove any impurities such as salinity, ash, and sand, and then dried at 60 °C for 12 h. The sodium-saturated clinoptilolite (Na-clinoptilolite) was prepared *via* an ion-exchange reaction between natural clinoptilolite and NaCl, following a common procedure, as previously described in the previous study [19]. Unless otherwise stated, all chemicals were of analytical reagent grade and were used without further purification. Further, if not specially stated, all the reagents used in this study were analytically pure (Sinopharm Chemical Reagent Co. Ltd., China). Stock solutions (100 mg/L) of N, P, and Cd (II) were prepared by dissolving NH_4Cl, $NaH_2PO_4·2H_2O$, and Cd $(NO_3)_2·4H_2O$ in deionized water, respectively.

2.2. Preparation of adsorbent

The Fe-Zr pillaring solution prepared was based on the method of Zhou et al. [25]. 200 mL of NaOH (1 M) solution was added drop wise to a mixing solution of 0.5 M $FeCl_3$ (100 mL) and 0.5 M $ZrOCl_2·8H_2O$ (100 mL) under vigorous magnetic stirring through a separating funnel at a constant dropping rate of ~ 5 mL/min. After continuous stirring for 2 h, the resultant solution was aged for 24 h. A constant temperature of 60 °C in the water bath was maintained during the entire preparation process. Subsequently, 20 g of Na-clinoptilolite was added to the above Fe-Zr pillaring solution under vigorous stirring to obtain a ratio of total metal/clay = 5 mmol/g. Then, the resulting dispersion was kept stirred for 5 h and aged for 24 h. Finally, the solid was separated using centrifugation at 4000 rpm for 10 min, washed several times with deionized water to remove the excess pillaring agent on the surface until free of chlorides, as indicated by the $AgNO_3$ test, and then dried at 60 °C and stored in a sealed bottle before use.