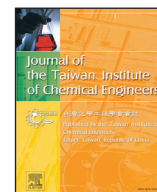




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# Amine-crosslinked Shaddock Peel embedded with hydrous zirconium oxide nano-particles for selective phosphate removal in competitive condition

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## ABSTRACT

In this paper, we prepared a novel biomass-based adsorbent, amine-crosslinked Shaddock Peel embedded with nano hydrous zirconium oxide (ACSP-HZO), to capture the phosphate ions in competitive adsorption systems. The ACSP-HZO was characterized by SEM, EDS, FTIR, XRD, TEM, XPS and Zeta potential analysis. Zeta potential indicated that the pure HZO nanoparticles were negatively charged. Element mapping showed that Zr distribution is closely related to P distribution, which indicated that the phosphate adsorption was dominated by the negatively charged HZO nanoparticles in ACSP-HZO. Results indicated that the ACSP-HZO exerted higher absorption capacity for phosphate than amine-crosslinked Shaddock Peel (ACSP). The maximum adsorption capacity of phosphate declined as temperature arose, which indicated the exothermal nature of phosphate adsorption by ACSP-HZO. Results in kinetics study indicated that the adsorption equilibrium data was fitted better with pseudo-second-order rate model. Phosphate adsorption by ACSP-HZO decreased as the increase of humic acid (HA), but effect of HA on phosphate adsorption by ACSP was negligible. In desorption experiment, spent ACSP-HZO still showed great capacity for phosphate after two cycles of adsorption–desorption.

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## 1. Introduction

In the past 50 years, the quantity of phosphorus discharged to underground and surface water, from non-renewable phosphoric rock, attach to almost  $5 \times 10^8$  t. The non-renewable phosphorus was required for modern agriculture to meet the need of fertilizer industry [1–3]. However, excessive supply of phosphorus discharged from chemical fertilizer, municipal wastewaters and industrial wastewaters always resulted in undesirable eutrophication in aquatic ecosystem [4].

Ordinary techniques for the phosphorus recover and phosphorus removal include chemical precipitation with metal salts, activated sludge systems for enhancing biological phosphorus removal, adsorption and some innovative engineering solutions [5]. Because of its low cost, environmentally friend as well as the potential possibility to regain from the wastewater, adsorption has been considered as one of the most preferred methods, especially for effluents with moderate or low levels of phosphate [5,6]. Recently, many metal (hydro) adsorbents with high selectivity towards phosphate

have been fabricated for capturing the phosphate from wastewater. These metal(hydro) oxide-based hybrid adsorbents, such as hydrated ferric oxide (HFO) [7], hydrated La(III) oxide [8], Fe–Al–Mg trimetal oxide [9], hydrated zirconium oxide (HZO) [10,11] and so on, are attractive due to their commendable adsorptivity and fantastic hydraulic capacity. It is worth noting that the hydrous zirconium oxide (HZO) with high surface area ( $404 \text{ m}^2/\text{g}$ ) always has great resistance to oxidant agents and low solubility in water [12,13]. However, these zirconium oxides always existed in forms of nanoparticles and could not be used as the emergent adsorbents in flow-through systems. Therefore, these high selective zirconium oxides should be supported on the available carriers for adsorption. Results indicated that many agriculture by-products as well as other biomass materials could be used a carrier for HZO because of their low cost, easy operation, bio-degradability, biocompatibility as well as enough porous structures [14,15]. Shaddock is the maximum local citrus fruit of Rutaceae family and it is diffusely planted in China and Southeast Asia. Its peels account for 15% of shaddock and can be modified into some new bio-resin/adsorbents that replaced the commercial anion exchangers, which means enormous economic values [16].

In this work, an eco-friendly and low-cost biomass based adsorbent was prepared using the Shaddock Peels as starting

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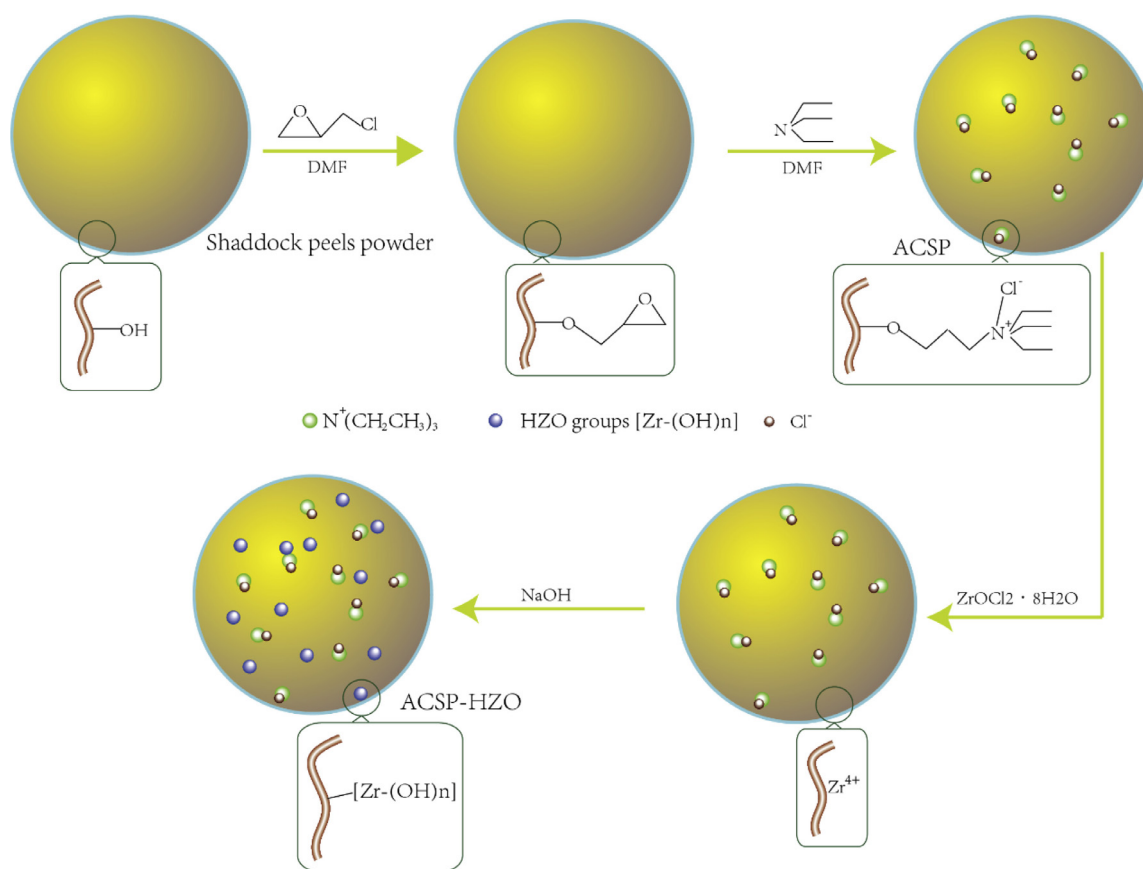


Fig. 1. Schematic diagram of the preparation process for ACSP-HZO.

material for supporting the HZO [16]. In addition, bio-sorbents loaded with quaternary ammonium also showed high adsorption capacity for phosphate [17,18]. As a result, adsorption properties of Shaddock Peels containing both nano-HZO and quaternary ammonium groups would be considered. In addition, characteristics properties of amine-crosslinked Shaddock Peel embedded with nano hydrous zirconium oxide (ACSP-HZO) would also be evaluated.

## 2. Materials and methods

### 2.1. Materials

In this study, all chemical agents were analytically pure. The Shaddock Peels were first dried at 343 K for 24 h, and then they were sieved into powders with size ranging from 250 to 500  $\mu\text{m}$ . Zirconium oxychloride ( $ZrOCl_2 \cdot 8H_2O$ ), epichlorohydrin, N,N-Dimethylformamide, ethylenediamine, and triethylamine are purchased from Tianjin Kemiou chemical Co., Ltd. All sodium salts ( $NaCl$ ,  $NaNO_3$ ,  $Na_2SO_4$ , sodium Humic acid (HA) and  $NaH_2PO_4$ ) are purchased from Sinopharm Chemical Reagent Co.Ltd in China.

### 2.2. Preparation for ACSP-HZO

The preparation of ACSP-HZO was comprised of two stages, including amine-crosslinked reaction and HZO immobilization. In the first stage, ten grams of Shaddock Peel powders were reacted with 30 ml of epichlorohydrin and 30 ml of N,N-dimethylformamide in a three-necked flask for 2 h (85  $^{\circ}\text{C}$ ). It was then slowly added with 7.5 ml of ethylenediamine and stirred for 0.5 h (75  $^{\circ}\text{C}$ ). Thereafter, 30 ml of trimethylamine was added into the mixture for grafting and stirring at 85  $^{\circ}\text{C}$  (2 h). After amine cross-linked process, the

intermediate product (amine-crosslinked Shaddock Peel, ACSP) was washed with deionized water and dried at 75  $^{\circ}\text{C}$  for 12 h [15,19].

In the second stage, 30 g of  $ZrOCl_2 \cdot 8H_2O$ , 130 ml of  $H_2O$ , 10 ml of fuming hydrochloric acid and 60 ml of ethanol were mixed with ACSP in 500 ml beaker for 24 h (50  $^{\circ}\text{C}$ ). During this process, the Zr would enter into the inner surface of ACSP in the form of  $[Zr_4(OH)_8(OH_2)_{16}]^{18+}$ . Thereafter, the solid was filtrated and added into 200 ml solution (0.25 mol NaOH/L, 0.25 mol NaCl/L) at 35  $^{\circ}\text{C}$  for 6 h. The preloaded Zr[IV] was then gradually precipitated and the HZO nanoparticles were successfully embedded inside the pore of ACSP, forming the ACSP-HZO. The ACSP-HZO were filtrated with suction filter and rinsed with deionized water until pH neutral. Finally, the products were dried at 60  $^{\circ}\text{C}$  for 12 h [20]. The preparing procedure for the ACSP-HZO was given in Fig. 1.

In addition, The ASP-HZO laden with low (15 g), moderate (30 g) and high (60 g) amounts of  $ZrOCl_2 \cdot 8H_2O$  were also prepared. They were named as ASP-HZO (L), ASP-HZO (M) and ASP-HZO (H).

### 2.3. Batch static adsorption experiments

The batch static adsorption experiments focused on the phosphate adsorption (1 mmol P/L) under constant competitive conditions (1.0 mmol  $Cl^-$ /L, 0.5 mmol  $NO_3^-$ /L, 0.5 mmol  $SO_4^{2-}$ /L, 0.1 mmol HA/L). In the static adsorption experiment, 0.1 g of ACSP-HZO or ACSP was mixed with 100 ml of phosphate solution (1 mmol P/L) in 250 ml conical flask (298 K). In the HA test, the concentration of additional HA was increased from 0.05 mmol/l to 1.0 mmol/l. Phosphate concentrations in isotherm experiment were set in the range of 30–300 mg P/L and temperatures were set at 298 and 323 K. In the pH test, HCl and NaOH (1 mol/l) were applied to adjust the pH in ranges from 2.0 to 12.0. Kinetic

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