

Preparation of a Hybrid Zirconium Phytate and Its Application for the Removal of Fluorine in Metal-Precoating Effluent

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Abstract A hybrid zirconium phytate (Zr_xIP_6) with porous surface was synthesized via the direct precipitation method. The as-prepared Zr_xIP_6 was characterized by SEM, EDS, FT-IR. The sample obtained from P/Zr=3:1(mol/mol) indicated that a hybrid material might be formed through coordination of the zirconium ions with the $-COPO_3$ groups in phytic acid molecules. An attempt to employ the hybrid Zr_xIP_6 as a sorbent in the removal of fluoride ions in metal-precoating wastewater was performed. The adsorption capacity q_e and the residual F^- ions concentration C_e using the Zr_xIP_6 (P/Zr=3:1) as an adsorbent, were $1.21 \text{ mg}\cdot\text{g}^{-1}$ and $1.47 \text{ mg}\cdot\text{L}^{-1}$, respectively.

Keywords: zirconium phytate; metal-precoating wastewater; hybrid material; adsorption

1 Introduction

In the past decade, one acceptable and well-developed metal-precoating method has been the application of zirconium oxide on metal surfaces by immersion in or rinsing with hexafluorozirconic acid solution or by the sol-gel method[1]. The treatment is free of heavy metals, such as chromates, zinc and nickel, which are subject to restrictions due to worker's safety or waste disposal and is now widely adopted by metal coating factories in many countries. However, Fluoride is present in the wastewater after this industrial pretreatment activity, and the discharge of such industrial wastewater leads to fluoride contamination. Thus, fluoride elimination has to be addressed in the event that the fluorine concentration is above the established wastewater disposal standards in metal pre-coating process.

Several methods have been developed to remove fluoride from wastewater. These methods are based on the principles of ion exchange[2], chemical precipitation[3], adsorption[4], electrodialysis and reverse osmosis[5]. Generally, selective adsorption is a more attractive method. Recently, considerable works have been conducted in developing new adsorbents loaded for the purpose of the adsorptive removal of fluoride. Among such adsorbents, trivalent and tetravalent metal fixed onto porous adsorbents or carrier materials have shown promising results[6]. adsorptive resin based adsorbents that use rare earth elements or Zr(IV) ions are receiving increased attention because of their selective affinity

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to F⁻, high adsorption capacity, and ease of operation. However, there are some trivial deflections, especially complicated preparation for these assembled resins. Therefore, developing new adsorbents for selective separation of fluoride from aqueous solutions is still of great significance.

Phytic acid (IP₆H₁₂ or IP₆) is safely used in many industrial fields and regarded as a nontoxic and “green” reagent for the environment. Each IP₆ molecule contained 6 -O₃PO²⁻ groups with 12 acidic protons and this feature made IP₆ a strong chelating agent, as a result of intermolecular hydrogen bonding between phosphate groups. Complex compounds or hybrid materials prepared from IP₆ often show attractive properties. For example, conducting polymer hydrogels had been synthesized by polymerizing conductive polymer monomers with IP₆. The excellent electrode performance of this hydrogel made it a possible candidate for bioelectronics and future-generation energy storage electrodes[7]. The nanoporous film of zirconium phytate could be employed as a substrate for making biosensors and displayed good bioelectrocatalytic ability toward the reduction of H₂O₂[8].

Whereas stoichiometric zirconium phytate has been prepared and is recognized as a potential substrate for sensor assembly, there is still a lack in knowledge concerning the relationship between the morphology and the initial molar ratio of zirconium ions to IP₆ in solution. We proposed that the tendency of cross-linked Zr_xIP₆ particles (Zr_xIP₆, the subscript x means that Zr coordinated by IP₆ is not the theoretical stoichiometric ratio), as reported, should lead to the possible preparation of promising coordinated hybrid materials for anion adsorption,, similar to the reported higher fluorine ions removal capacity of ZrP [9]. In this study, hybrid Zr_xIP₆ particles with porous surfaces were prepared and characterized at low molar ratios of Zr⁴⁺ and IP₆¹²⁻ (higher P/Zr ratio) in the initial solution .The probability of Zr_xIP₆ material as adsorbents for removing F⁻ from metal-precoating effluent is also investigated.

2 Experimental

2.1 Reagents and apparatus

All chemicals were of analytical grade and were used without further purification. Industrial grade phytic acid (60% wt.) was obtained from Ruifeng biochemicals reagent Co. Buffer solutions with different pH values were prepared using HCl or CH₃COONa purchased from Shenyang 2nd chemical reagent Co.

Fourier transform infrared (FT-IR) spectrometer analysis was recorded in the region of 4000-500 cm⁻¹ (PerkinElmer®;USA) using a KBr wafer. The microstructure, morphological and elemental composition of the Zr_xIP₆ sample was characterized with a JSM-6460 LV scanning electron microscope (SEM) along with Energy dispersive X-ray spectroscopy (EDS) . N₂ adsorption-desorption measurement (NOVA-2200E Quantachrome®;USA) of the dried powders was performed at the temperature of liquid nitrogen (77 K).

2.2 Synthesis of hybrid ZrxIP6

The hybrid Zr_xIP₆ particles were prepared by the reaction of ZrOCl₂·8H₂O with phytic acid. The concentration of the ZrOCl₂·8H₂O solution was kept constant at 0.1 mol.L⁻¹. The introduced phytic acid varied from 0.05 mol.L⁻¹ to 0.15 mol.L⁻¹ to prepare hybrid Zr_xIP₆ material. After stirring for 30 min, the white precipitated products were collected from the solution by centrifuging at 7000 rpm for 15 min, rinsing with deionized water several times and then drying at 70 °C for 24 h .

2.3 Fluoride adsorption experiments

The adsorption abilities of fluoride onto sorbents were performed by shaking 1 g Zr_xIP_6 with 100 mL collected wastewater sample in a polyethylene beaker with at 200 rpm at 25°C. The specific amount of fluoride adsorbed was calculated from the usual mass balance [10]. Equation (1):

$$q_t = \frac{(C_0 - C_t) \times V}{m_b} \quad (1)$$

With q_t being the sorbate loading ($mg \cdot g^{-1}$) at time t , C_0 and C_t ($mg \cdot L^{-1}$) are the liquid phase concentrations of fluoride at initial and time t , V the volume of liquid in the experiment (L) and m_b the mass of the sorbent (g). Moreover, the subscript of e preceded by q and C used in this article, q_e and C_e , indexes the corresponding quantities at adsorption equilibrium.

3 Results and Discussion

3.1 SEM images morphology of Zr_xIP_6 compounds

Zr_xIP_6 ($x < 3$) porous particles were obtained in a wide concentration range of phytic acid to $Zr(OCl)_4 \cdot 8H_2O$. An increasing molar ratio of P/Zr from 2:1 to 3:1 gave similarly porous Zr_xIP_6 . However, the higher P/Zr (>3:1) led to the agglomerated porous particles were shown in Figure 1(a) and Figure 1(b) due to insufficient electrostatic stabilization and oligo-clusters assembly by adjacent IP_6 or Zr_xIP_6 molecules. The BET surface area of the hybrid Zr_xIP_6 was $112.3 m^2 \cdot g^{-1}$, similar to reported cited reference. EDS spectra recorded shown that the P/Zr molar ratio of sample was 2.25:1 (figure.S1), a little higher than the theoretical stoichiometry of Zr_3IP_6 (P/Zr=2:1), but lower than that of initial stoichiometry of the solution (P/Zr=3:1). Thus, we proposed that a Zr^{4+} ion coordinates with four -OH in two or more separate -COPO₃ groups in one or more IP_6 molecules, rather than with four -OH in one single IP_6 molecule. This ratio of P in Zr_xIP_6 could be partly explained by the integer of IP_6 molecules in this oligo-cluster structure. It can be supposed that when the amount of IP_6 introduced is sufficiently high, the growth of Zr_xIP_6 should result in a deeply interlinked network. As shown in Figure 1(c) and Figure 1(d).

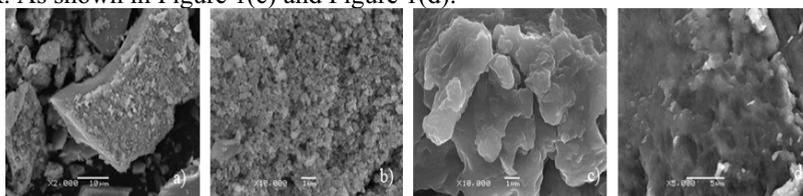


Figure 1. SEM images of prepared Zr_xIP_6 : a) P/Zr=3:1; b) enlarged image P/Zr=3:1 c) P/Zr=6:1; d) P/Zr=9:1.

3.2 Infrared characteristic of hybrid Zr_xIP_6

The FT-IR spectra of the Zr_xIP_6 compounds with different initial P/Zr ratios were presented in figure 2. Whereas all of the prepared Zr_xIP_6 compounds shown a weak absorption band approximately $1630 cm^{-1}$ and a broad absorption band at $3400 cm^{-1}$, these bands were not shown. Both of the adsorption bands could be due to the unbounded P-O-H bonds, and crystalline H_2O .

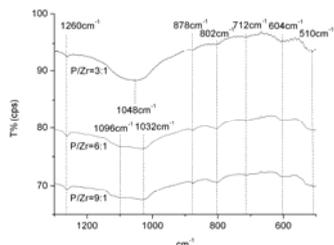
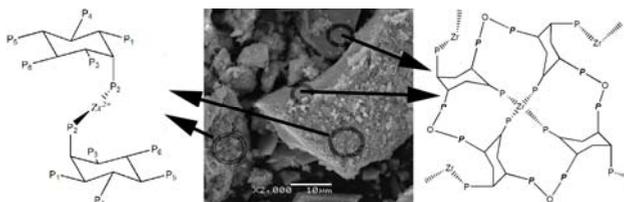


Figure 2. FT-IR spectra of the as-prepared Zr_xIP_6 compounds.

The bands of the phosphate group presenting at 962 cm^{-1} and 1060 cm^{-1} in the FT-IR spectrum of IP_6 disappeared and was replaced with a broad one at 1048 cm^{-1} with less trailing character ($P/Zr=3:1$). The 510 cm^{-1} and 1260 cm^{-1} adsorption bands for PO_4^{3-} and the $P=O$ double bond stretching are still present in all samples [11]. In the spectra of the higher molar ratio of P/Zr (6:1 and 9:1), the broad band gradually split into two overlapped but distinguishable bands at 1032 cm^{-1} and 1096 cm^{-1} . Similar to the spectral characteristics of trivalent metal compounds (Fe or Al phytate), there was a strong band at 1092 cm^{-1} , and the adsorption bands at 1096 cm^{-1} of hybrid. The minor absorption bands in the $880\text{--}700\text{ cm}^{-1}$ region were more similar to doublet bands and were also shifted upward $10\text{--}30\text{ cm}^{-1}$ compared to the reported FT-IR spectra of trivalent, divalent or monovalent metal phytate compounds[12].



Scheme.1 Schematic view of the structure of the hybrid Zr_xIP_6 coordinated on the surface and internally. (P) represented the $-COPO_3H$ group

The tentative mechanism was depicted in Scheme.1. Stable hybrid material with a nanoporous surface were obtained in a wide range of phytic acid to $Zr(OCl)_4$. A molar ratio of P/Zr between 3:1 and 6:1 gave the best results. If the ratio of Zr^{4+} ions to IP_6 was lower, only an interlinked oligomer-like Zr_xIP_6 with a regular surface was found, most likely due to coating of the polymerized IP_6 molecules on the hybrid Zr_xIP_6 particles. In the optimal range, the excess IP_6 molecules could be interlinked with the same Zr^{4+} ions by the di-, tri-, and tetra- coordination method. We proposed that tetra-coordination occurred at the internal of the hybrid Zr_xIP_6 , whereas unsaturated coordination occurred at the surface of hybrid material.

3.3 Fluoride adsorption experiment results

Zr_xIP_6 as F^- ions adsorbents in metal-precoating wastewater is attractive because of two advantages. If dissociation of hybrid Zr_xIP_6 solids happened: i) a small amount of introduced IP_6 anions in recycled wastewater could act as a corrosion inhibitor for Zr -based nanofilms coated on a metal surface [13] ii) free $Zr(IV)$ cations could be used as one supplementary component of diluted hexafluorozirconic acid metal-precoating agents.

Table.1 Anions Analysis Of Wastewater From Metal-Coating Enterprises

Analysis items	unit	colected metal-coating wastewater	water sample
pH	-	4-5	6.92
Sulfate	mg.L ⁻¹	28.0-38.0	38.6
Fluoride	mg.L ⁻¹	9.38-28.21	0.347
Nitrate	mg.L ⁻¹	2.94-3.17	2.85
Phosphate	mg.L ⁻¹	0.027-0.029	< 0.1

Note: All wastewater and underground water samples were collected from Yingkou, Liaoning PR, China. A concentration range is listed here for repeat tests of samples from different enterprises.

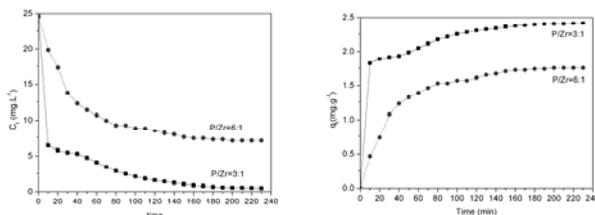


Figure 3. The removal of fluoride ions in metal pre-treatment wastewater by the Zr_xIP₆ oligome. left: variations of residual concentration *C_t* vs time; right: variations of adsorption capacity *q_t* vs time.

To investigate the feasible application of Zr_xIP₆ in the treatment of metal pre-coating wastewater, a comparison of the adsorption capacity of hybrid Zr_xIP₆ was conducted in a solution and an initial concentration of F⁻ ions was 25.6 mg.L⁻¹(Figure 3). The *q_e* and *C_e* by taking Zr_xIP₆ (P/Zr=3:1) as adsorbent were 1.21 mg.g⁻¹ and 1.47 mg.L⁻¹. For oligomer-like Zr_xIP₆ (P/Zr=6:1) hybrid materials, *q_e* was decreased to 1.754 mg.g⁻¹ and *C_e* was increased to 7.06mg.L⁻¹. The variation could be ascribed to the decreased chelating Zr(IV) ions exposed to surrounding environmental due to small specific surface area of Zr_xIP₆ (P/Zr=6:1).The influence of other anions on the fluoride ion removal efficiency has been researched previously for complicated practical water recycling systems. Thus, the presence of other anions in pre-treatment wastewater might have a negative interference to fluoride adsorption process.

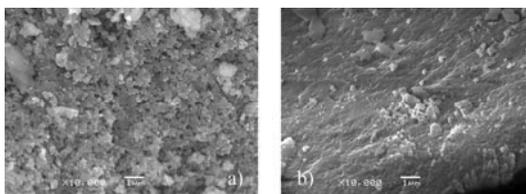


Figure 4. SEM images of hybrid Zr_xIP₆ powder after fluoride removal experiments: a) P/Zr=3:1; b) P/Zr=6:1.

Zr_xIP₆ powder with adsorbed F⁻ ions was separated, filter-collected and dried at 70°C for 24h. SEM images shown that there was no morphology change of the hybrid Zr_xIP₆ (Figure 4). It was supported by the results of the EDS analysis of the recollected Zr_xIP₆ (P/Zr=3:1). The quantitative ratio of P/Zr was 2.30:1 (figure.S2), similar to that of fresh Zr_xIP₆ (2.25:1). Thus, the high adsorption capacity of the Zr_xIP₆ clusters for fluoride ions cannot be interpreted simply by an ion exchange mechanism, which was based on the electrostatic attraction force.

4 Conclusions

A novel, adsorbent hybrid Zr_xIP₆ material with porous surface was synthesized. The

results revealed that Zr^{4+} ions might interact with the $-OH$ of the same or another phosphate groups in various IP_6 molecules. The external-linked interaction meant that many phytic acid molecules were either covalently bonded to the phytate complexes or were polymerized, forming oligophytate clusters through P-O-P bands in higher P/Zr ratio Zr_xIP_6 . A schematic view of the mechanism of coordination was suggested according to the FT-IR, SEM and EDS data. Fluoride removal experiments revealed that the adsorption capacity q_e and residual F^- ions concentration C_e using hybrid Zr_xIP_6 (P/Zr=3:1) as adsorbent were $1.21 \text{ mg}\cdot\text{g}^{-1}$ and $1.47 \text{ mg}\cdot\text{L}^{-1}$, respectively. The experimental results confirmed that the as-prepared Zr_xIP_6 was an attractive adsorbent for hexafluorozirconic acid metal-precoating wastewater treatment.

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