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 mg.g$^{-1}$ and 1.47 mg.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
defections, 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 ZrxIP₆ particles (ZrxIP₆, 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 ZrxIP₆ particles with porous surfaces were prepared and
characterized at low molar ratios of Zr⁴⁺ and IP₆⁻¹²⁻ (higher P/Zr ratio ) in the initial
solution. The probability of ZrxIP₆ 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 ZrxIP₆ 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 powers was performed at the temperature of liquid nitrogen (77 K).

2.2 Synthesis of hybrid ZrxIP₆

The hybrid ZrxIP₆ 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 ZrxIP₆
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 Zr₆IP₆ 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):

\[
q_t = \frac{(C_0 - C_t) \times V}{m_b}
\]  

With \(q_t\) being the sorbate loading (mg.g⁻¹) at time t, \(C_0\) and \(C_t\) (mg.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 ZrXIP6 compounds

Zr₆IP₆ (x < 3) porous particles were obtained in a wide concentration range of phytic acid to Zr(OCl)₄·8H₂O. An increasing molar ratio of P/Zr from 2:1 to 3:1 gave similarly porous Zr₆IP₆. 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 IP₆ or Zr₆IP₆ molecules. The BET surface area of the hybrid Zr₆IP₆ was 112.3 m²·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 Zr₃IP₆ (P/Zr=2:1), but lower than that of initial stoichiometry of the solution (P/Zr=3:1). Thus, we proposed that a Zr⁴⁺ ion coordinates with four –OH in two or more separate –COPO₃ groups in one or more IP₆ molecules, rather than with four –OH in one single IP₆ molecule. This ratio of P in Zr₆IP₆ could be partly explained by the integer of IP₆ molecules in this oligo-cluster structure. It can be supposed that when the amount of IP₆ introduced is sufficiently high, the growth of Zr₆IP₆ should result in a deeply interlinked network. As shown in Figure 1(c) and Figure 1(d).

![Figure 1. SEM images of prepared Zr₆IP₆: a) P/Zr=3:1; b) enlarged image P/Zr=3:1 c) P/Zr=6:1; d) P/Zr=9:1.](image)

3.2 Infrared characteristic of hybrid ZrₓIP₆

The FT-IR spectra of the ZrₓIP₆ compounds with different initial P/Zr ratios were presented in figure 2. Whereas all of the prepared ZrₓIP₆ 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 H₂O.
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 880-700 cm$^{-1}$ region were more similar to doublet bands and were also shifted upward 10-30 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$_x$IP$_6$ coordinated on the surface and internally. (P) represented the –COPO$_3$H$^-$ 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$_x$IP$_6$ with a regular surface was found, most likely due to coating of the polymerized IP$_6$ molecules on the hybrid Zr$_x$IP$_6$ 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$_x$IP$_6$, whereas unsaturated coordination occurred at the surface of hybrid material.

3.3 Fluoride adsorption experiment results

Zr$_x$IP$_6$ as F$^-$ ions adsorbents in metal-precoating wastewater is attractive because of two advantages. If dissociation of hybrid Zr$_x$IP$_6$ 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 | Collected 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 ZrxIP6 oligomer. Left: variations of residual concentration Ct vs time; right: variations of adsorption capacity qt vs time.

To investigate the feasible application of ZrxIP6 in the treatment of metal pre-coating wastewater, a comparison of the adsorption capacity of hybrid ZrxIP6 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 ZrxIP6 (P/Zr=3:1) as adsorbent were 1.21 mg.g⁻¹ and 1.47 mg.L⁻¹. For oligomer-like ZrxIP6 (P/Zr=6:1) hybrid materials, $q_e$ was decreased to 1.754 mg.g⁻¹ and $C_e$ was increased to 7.06 mg.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 ZrxIP6 (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 ZrxIP6 powder after fluoride removal experiments: a) P/Zr=3:1; b) P/Zr=6:1.

ZrxIP6 powder with adsorbed F⁻ ions was separated, filter-collected and dried at 70ºC for 24h. SEM images shown that there was no morphology change of the hybrid ZrxIP6 (Figure 4). It was supported by the results of the EDS analysis of the recollected ZrxIP6 (P/Zr=3:1). The quantitative ratio of P/Zr was 2.30:1 (figure S2), similar to that of fresh ZrxIP6 (2.25:1). Thus, the high adsorption capacity of the ZrxIP6 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 ZrxIP6 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\(_x\)IP\(_6\). 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\(_x\)IP\(_6\) (P/Zr=3:1) as adsorbent were 1.21 mg.g\(^{-1}\) and 1.47 mg.L\(^{-1}\), respectively. The experimental results confirmed that the as-prepared Zr\(_x\)IP\(_6\) was an attractive adsorbent for hexafluorozirconic acid metal-precoating wastewater treatment.

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