



Selective removal of Pb(II), Cd(II), and Zn(II) ions from waters by an inorganic exchanger Zr(HPO₃S)₂

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ABSTRACT

The present study reported synthesis of a new inorganic exchanger, i.e., zirconium hydrogen monothio-phosphate [Zr(HPO₃S)₂, denoted ZrPS] and its selective sorption toward Pb(II), Cd(II) and Zn(II) ions. ZrPS sorption toward all the three metals is dependent upon solution pH due to the ion-exchange nature. As compared to another inorganic exchanger zirconium phosphate [Zr(HPO₄)₂, denoted ZrP], ZrPS exhibits highly selective sorption toward these toxic metals from the background of calcium ions at great levels. Such sorption preference is mainly attributed to the presence of –SH group in ZrPS, as further demonstrated by FT-IR analysis and XPS study. Moreover, ZrPS particles preloaded with heavy metals could be efficiently regenerated with 6 M HCl for multiple use without any noticeable capacity loss. All the experimental results indicated that ZrPS is a promising sorbent for enhanced heavy metals removal from contaminated water.

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1. Introduction

Heavy metal ions present in water are non-biological, toxic, and carcinogenic even at a very low level [1], and thus still remain a serious threat to environmental and public health [2]. Up to now various techniques including chemical precipitation, coagulation–flocculation, membrane separation, and sorption have been developed for effective removal of heavy metals from contaminated water. Among the available techniques, ion exchange by polymeric cation exchange resins is one of the most efficient and widely used approaches for metal decontamination from water media [3–5]. Such ion-exchange process is essentially driven by electrostatic or Columbic interaction and is non-specific for uptake of heavy metal ions. Consequently, alkali or alkaline earth ions such as Na(I), Ca(II), and Mg(II), which are frequently encountered in the contaminated water laden with heavy metals, strongly compete against heavy metals sorption and thus, result in a dramatic decrease in working capacity of a cation exchange resin [3,6].

In the past decades, more and more inorganic ion exchangers have been exploited for heavy metals removal from aqueous media, namely, zeolite [7,8], clay [9,10], and M(HPO₄)₂ (M = Zr, Ti, Hf) [11,12]. As a widely used inorganic exchanger, zirconium phos-

phate (denoted ZrP) has been extensively studied for sorption of alkali and alkaline earth metal ions from aqueous solution [13–15] because of its high capacity, fast kinetics, and remarkable thermal and radiolytic stabilities [16–19]. Nevertheless, insufficient efforts were made concerning heavy metal ions sorption onto zirconium phosphates [20].

In our earlier study [11], we found that ZrP exhibits preferable sorption toward Pb(II), Cd(II) and Zn(II) over Ca(II), as compared to a commercial cation exchange resin D-001. Unfortunately, ZrP is present as fine or ultrafine particles and cannot be employed for direct use in fixed-bed or any other flow-through systems due to the excessive pressure drop and poor mechanical strength. To overcome the technical difficulties, we impregnated ZrP particles within different porous polymeric supports and obtained hybrid sorbents to facilitate its potential application [15,21,22]. However, the sorption selectivity of ZrP toward some of the heavy metals, e.g., Cd(II) and Zn(II), is still not satisfied and needs further improvement [6,11].

In the current study, we synthesized another inorganic exchanger, i.e., zirconium hydrogen monothio-phosphate (ZrPS), and compared its selective heavy metals sorption with ZrP. Note that the main structure difference between ZrP and ZrPS is that, the hydroxyl group of ZrP is replaced by thiol group within ZrPS. Thiol modification is an effective approach to improving sorption selectivity of a given sorbent toward heavy metals, as implied by the HSAB (Hard and Soft Acids and Bases) principles [23–27]. Selective sorption of ZrPS toward Pb(II), Zn(II) and Cd(II) ions was

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evaluated as compared to ZrP particles, and its sorption mechanism was primarily explored by FT-IR and XPS analysis.

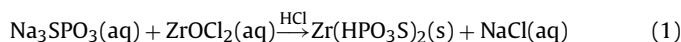
2. Experimental methods

2.1. Materials

Lead nitrate, zinc nitrate, and cadmium nitrate were used in this study as the heavy metal sources by dissolving them into the double-deionized water. All the chemicals including $ZrOCl_2$, H_3PO_4 , and Na_3PO_3S are of analytical grade and were purchased from Nanjing Chemical Reagent Station (Nanjing, China).

2.2. Preparation and characterization of inorganic exchanger particles

ZrP particles were readily synthesized according to the reference [13] and ZrPS particles were prepared by modifying a simple method for amorphous ZrP synthesis [28,29]. In brief, 25-g $ZrOCl_2$ was dissolved in 100-mL 2 M HCl at the room temperature. Then the above solution was gradually added into a flask containing 250 mL Na_3PO_3S solution (160 g/L), and the ZrPS particles were formed immediately as follows.



The white mixture of ZrPS particles was stirred at 160 rpm for 24 h and centrifuged to decant the aqueous portion. The residual ZrPS particles were then rinsed by double-deionized water till the neutral pH and vacuum desiccated at 323 K for 24 h for further study.

ZrPS samples were characterized by X-ray diffraction (XRD) using an XTRA X-ray diffractometer (Switzerland), X-ray photoelectron spectroscopy (XPS) analysis with a spectrometer (ESCALAB-2, Great British) equipped with an MgK α X-ray source (1253.6 eV protons) [30], and FT-IR spectrometer (Nexus 870, USA) with a pellet of powered potassium bromide and sorbent in 500–4000 cm^{-1} . Their size distributions were determined using dynamic light scattering technique (DLS, 90 Plus, Brookhaven Instrument Corp.) [31]

2.3. pH titration

Portions (500 mg) of ZrPS or ZrP were mixed with 100 mL of 0.10 M NaCl respectively. Each mixture solution was kept for 2 h and titrated against 0.17 M NaOH solution. The pH of the solution was recorded after each addition of 1.0 mL of the titrant till the pH became constant. Based on the pH values before and after the exchange process, the milliequivalents of OH^- consumed were determined. Milliequivalents of OH^- ions consumed by ZrPS or ZrP particles were then plotted against the corresponding pH values to obtain the pH-titration curves [32].

2.4. Batch sorption experiments

Batch sorption tests were carried out by the traditional bottle-point method in 250-mL Erlenmeyer flasks. To start the experiments, a desired amount of sorbent particles was added to a 100-mL solution containing known heavy metal ions. Ca(II) was introduced as a competing cation by dissolving its nitrate in water. The flasks were then transferred to a G-25 model incubator shaker with thermostat (New Brunswick Scientific Co. Inc.). Then they were shaken under 200 rpm for 24 h at desired temperature to ensure equilibrium of the sorption process. Preliminary kinetic study indicated that 3 h is enough to reach sorption equilibrium onto both ZrP and ZrPS particles. A HNO_3 solution (10%) was used to adjust the solution pH throughout the experiments.

A 0.5-mL solution at various time intervals was sampled from the flasks to determine sorption kinetics. To examine the continuous sorption–regeneration performance of ZrPS particles, they were filtered from the sorption systems and then subjected to regeneration by using 6 M HCl solution. Prior to next sorption run the regenerated ZrPS particles were rinsed to neutral pH by double deionized water. The amount of metal ions loaded on the sorbent particles was calculated by conducting a mass balance on the solute before and after sorption tests.

2.5. Analysis

The contents of all the heavy metals were usually determined by atomic adsorption spectroscope (AAS) (Thermal Co., USA). When lead content was less than 1 mg/L and the contents of zinc and cadmium were less than 0.1 mg/L, they were determined by an atomic fluorescence spectrophotometer (AFS) equipped with an online reducing unit (AF-610A, China) by using $NaBH_4$ and HCl solution.

3. Results and discussion

3.1. Characterization of ZrPS particles

As shown in Fig. 1a, ZrPS particle sizes range from 400 to 560 nm mostly. The Zr/P ratio in the particles is obtained as 1:2 by XPS data, which further indicates its structure as $Zr(HPO_3S)_2$. FT-IR spectra of the fresh ZrPS sample further demonstrates the presence of –SH group, as discussed below. XRD pattern of ZrP (Fig. 1b) suggests that ZrPS particles are amorphous in nature [11,33].

To elucidate the presence of ion-exchangeable sites of ZrPS, pH titration of ZrPS was performed and the results are depicted in Fig. 2. Similarly to ZrP, hydrogen ions within amorphous ZrPS are also released in a continuous and stepwise manner. This is mainly

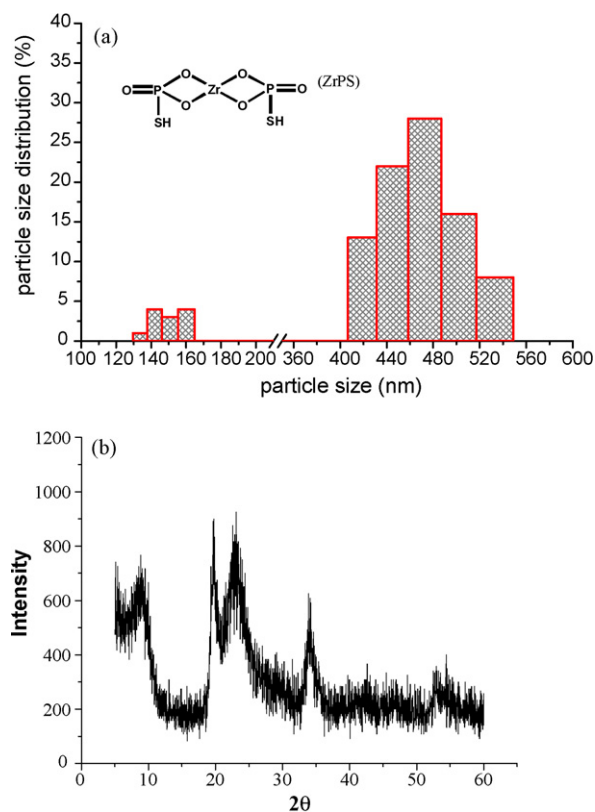


Fig. 1. Size distribution (a) and XRD spectra (b) of ZrPS particles prepared in the current study.

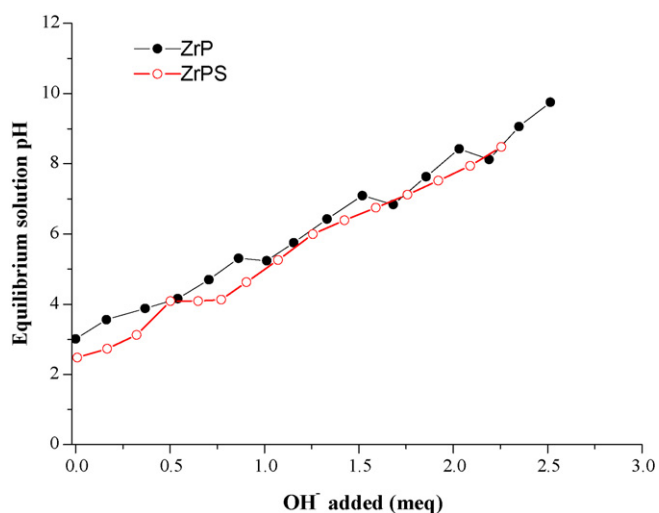
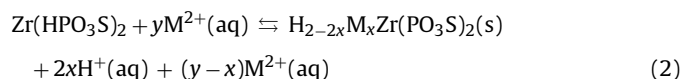


Fig. 2. pH-titration curves of ZrPS and ZrP particles using 0.170 M NaOH solution at 303 K (0.5 g of each sorbent was used for titration test).

because of the presence of the weakly acidic –SH for ZrPS or –OH groups for ZrP, which are reluctant to exchange H^+ for Na^+ [11,12,16]. Of noteworthy observation is that only half of the exchangeable hydrogen ions (~ 2.3 mmol/g) within ZrPS undertake ion exchange under neutral or weakly acidic conditions, and the rest can only be released under alkaline condition. Thus, uptake of heavy metals from acidic or neutral solution to ZrPS particles could be described as follows [33].



3.2. Effect of solution pH on sorption

Effects of solution pH on Pb(II), Cd(II), and Zn(II) sorption by ZrPS particles were examined and the results are depicted in Fig. 3. Obviously, pH-dependent sorption was observed for all these metals, i.e., higher pH values (under acidic or neutral conditions) are more favorable for heavy metals sorption onto ZrPS. It is consistent with the ion-exchange process mentioned in Eq. (2). Lower

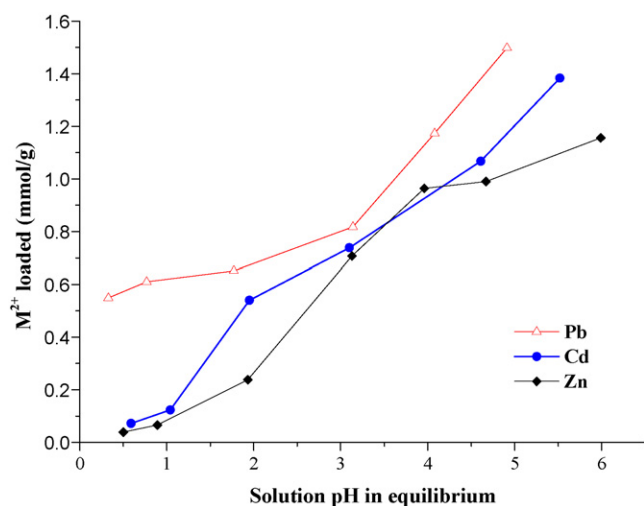


Fig. 3. Effect of solution pH on the uptake of heavy metal ions onto ZrPS at 303 K (0.05 g ZrPS was added into 100 mL solution with 0.93 mmol/L of each ions, $M^{2+} = Pb^{2+}$, Zn^{2+} and Cd^{2+}).

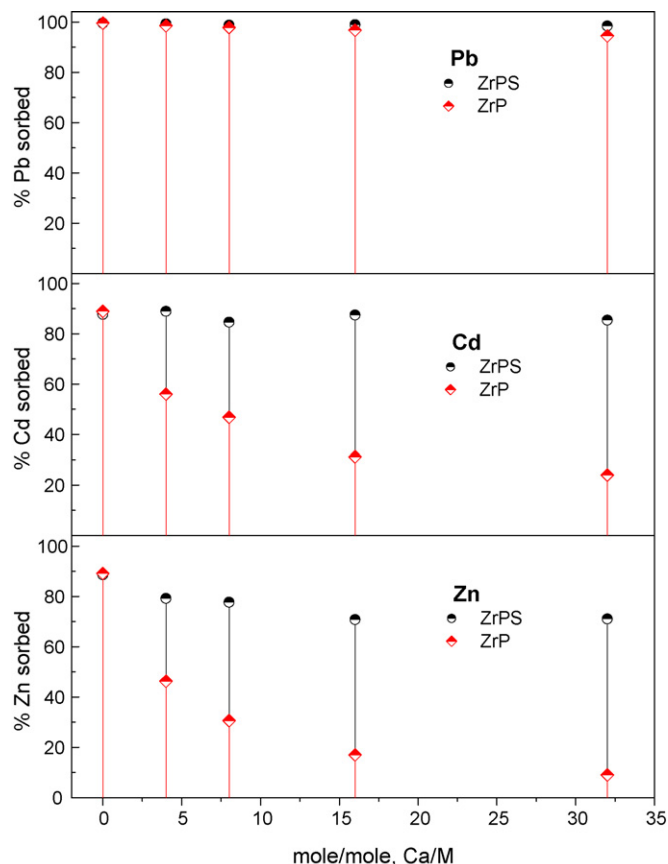


Fig. 4. Effect of Ca(II) on uptake of heavy metal ions onto ZrPS and ZrP at 303 K (0.1 g ZrPS or ZrP particles were introduced into 100-mL solution containing 0.5 mmol/L of each metal ion respectively).

uptake at more acidic pH also implies that a solution of high acidity will be favorable for regeneration of the exhausted ZrPS particles if the sorption is reversible. It was further demonstrated below.

3.3. Effect of Ca(II) on heavy metals sorption

Alkali or alkaline earth cations such as Na(I), Ca(II), and Mg(II) ions are ubiquitous in natural waters or industrial effluents and thus, sorption selectivity of a given sorbent toward target toxic metals is an important factor to ensure its technical applicability. In the current study, calcium ion was chosen as a representative competing cation because of its ubiquity and relatively high competitive capacity [11,34], and effect of Ca(II) ion on ZrPS sorption toward heavy metals was examined. To elucidate specific sorption of ZrPS, ZrP was also involved here for comparison.

As shown in Fig. 4, Pb(II), Cd(II), and Zn(II) uptake onto both sorbents decrease as the Ca(II)/M(II) ratios increase. It seems reasonable due to the competitive effect exerted by the added calcium ions. However, ZrPS displays more preferable sorption toward three toxic metals, particularly Cd(II) and Zn(II), over calcium ions than ZrP.

To quantify sorption selectivity of both sorbents, the distribution ratios K_d (in L/g) were determined as [8]:

$$K_d = \frac{\text{mmol of heavy metals/g sorbent}}{\text{mmol of heavy metals/Lsolution}} \quad (3)$$

The K_d values thus defined provide a measure of the sorptive ability for three metals per gram of sorbent. Table 1 lists the calculated K_d values of three metals onto both sorbents. Substantially

Table 1Effect of calcium ion on the distribution coefficients (K_d) of three heavy metal ions onto ZrPS and ZrP at 303 K.

| Heavy metals (M^{2+}) | Sorbent | K_d (L/g) at different initial Ca^{2+}/M^{2+} ratios (mol/mol) | | | |
|---------------------------|---------|--|------|------|------|
| | | 0 | 4 | 16 | 32 |
| Pb^{2+} | ZrPS | 181 | 137 | 93.6 | 62.8 |
| | ZrP | 209 | 68.5 | 29.4 | 17.0 |
| Cd^{2+} | ZrPS | 7.14 | 8.02 | 6.97 | 5.84 |
| | ZrP | 8.03 | 1.27 | 0.46 | 0.32 |
| Zn^{2+} | ZrPS | 7.75 | 3.81 | 2.42 | 2.46 |
| | ZrP | 8.18 | 0.86 | 0.21 | 0.10 |

larger K_d values of ZrPS indicated that ZrPS would offer more selective removal of heavy metals from waters than ZrP.

3.4. Selective sorption mechanism

As inferred from different structure of ZrPS and ZrP, selective sorption of ZrPS toward heavy metals may be attributed to the presence of thiol group ($-SH$) within ZrPS particles. The thiol group ($-SH$) can exhibit specific affinity with heavy metals ions through the formation of metal–sulfur complexes [24]. One can get similar conclusions based on the principle of hard and soft acids and bases (HSAB) [23] because soft Lewis base such as $-SH$ would be more favorable to undergo interaction with soft Lewis acids (e.g., $Pb(II)$, $Zn(II)$, and $Cd(II)$ ions) rather than hard Lewis acids (e.g., alkali and alkaline earth metal ions). On the contrary, ZrP of oxygen-rich compounds would be more preferably to adsorb $Ca(II)$, $Na(I)$, and $Mg(II)$ ions than ZrPS. The underlying mechanism of ZrP sorption toward heavy metal ions was revealed in our earlier study [11].

To gain insight into sorption mechanism of heavy metals onto ZrPS, FT-IR and XPS study of ZrPS samples before and after metal loadings were performed. The IR spectra (Fig. 5) confirm the presence of external water in addition to the strongly hydrogen-bonded OH or extremely strongly coordinated H_2O by the sharp peaks at ~ 3500 and ~ 1650 cm^{-1} [30,35,36]. The presence of $-SH$ group within ZrPS was further confirmed by the absorption peak at ~ 2540 cm^{-1} .

It is noteworthy that heavy metals uptake onto ZrPS resulted in a dramatic intensity decrease in $-SH$ absorption peak, while the added calcium ions did not change the peak intensity significantly. Such observation may be attributed to the fact that heavy metal ions are intercalated into ZrPS particles and undergo ion exchange with the protons present on the S atoms of PO_3S^{3-} groups [28], which further demonstrated the ion-exchange nature of heavy metals sorption. Negligible effect of $Ca(II)$ may result from its unfavorable sorption by ZrPS, as indicated by the HASB principle [23,27]. Addi-

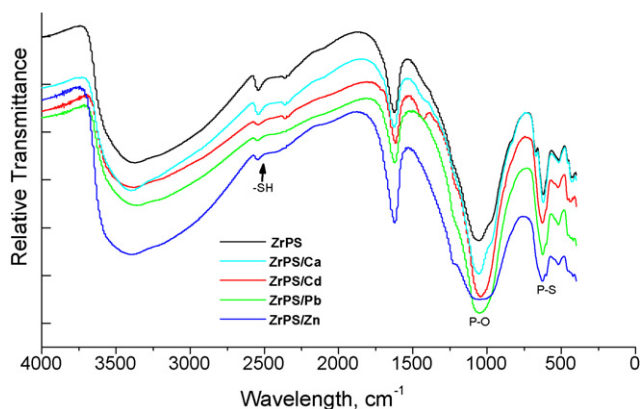


Fig. 5. FT-IR spectra of ZrPS samples before and after being loaded with different metal cations.

Table 2Absorption peak values of ZrPS samples loaded with different metal ions (cm^{-1}).

| Samples | ZrPS | ZrPS/Ca | ZrPS/Cd | ZrPS/Zn | ZrPS/Pb |
|-------------|--------|---------|---------------|---------------|--------------|
| ν (P–S) | 621.7 | 621.0 | 627.9 | 625.1 | 625.7 |
| ν (P–O) | 1058.7 | 1055.8 | 1045.3 | 1050.9 | 1055.0 |

Table 3

Electron binding energy shifts of Zr(3d), S(2p), P(2p) and O(1s) regions of ZrPS samples loaded with different metal ions by comparing with fresh ZrPS.

| Samples | ZrPS/Ca | ZrPS/Cd | ZrPS/Pb | ZrPS/Zn |
|--------------|---------|---------|---------|---------|
| Zr (3d) (eV) | 0.15 | 0.80 | 0.45 | 0.40 |
| S (2p) (eV) | 0.05 | 0.50 | 0.45 | 0.00 |
| P (2p) (eV) | 0.05 | 0.85 | 0.20 | 0.20 |
| O (1s) (eV) | 0.10 | 0.80 | 0.35 | 0.10 |

tionally, we also observed the variation in ν (P–O) and ν (P–S) peaks around 1050 and 620 cm^{-1} [35,37], and the results are presented in Table 2. More significant shifts of both absorption peaks after heavy metals uptake than calcium sorption also implied the specific role of the thiol group in heavy metals binding.

Similar conclusions can also be available from XPS data analysis. Table 3 shows that heavy metal loadings onto ZrPS result in more electron binding energy shifts of Zr(3d), S(2p), P(2p) and O(1s) regions than $Ca(II)$ loadings, indicating the specific affinity between ZrPS and heavy metal ions. Our earlier study demonstrated non-specific sorption of $Cd(II)$ and $Zn(II)$ by ZrP particles, though specific $Pb(II)$ sorption can occur onto ZrP [11]. It is quite different from ZrPS, which exhibits specific affinity toward all these toxic metal ions.

3.5. Regeneration and environmental implications

Sorption–regeneration cycle tests were carried out on ZrPS particles toward three toxic metals in batch runs, and the results are presented in Table 4. 6 M HCl was employed as regenerant as indicated by the pH-dependent sorption onto ZrPS. Regeneration efficiency was obtained by dividing the metal amount regenerated by HCl solution with that preloaded on the sorbent particles. The results indicate that ZrPS is an effective and recyclable sorbent for removal of all these toxic metals.

Table 4Batch sorption–regeneration cycles of heavy metals from a mixed solution by ZrPS at 303 K (For sorption tests: 0.50 g ZrPS + 100 mL solution containing $Pb(II)$ (150 mg/L), $Cd(II)$ (80 mg/L), $Zn(II)$ (30 mg/L); for regeneration test 20 mL 6 M HCl was used as regenerant).

| Cycles | Removal efficiency (%) | | | Regeneration efficiency (%) | | |
|--------|------------------------|-----------|-----------|-----------------------------|-----------|-----------|
| | Pb^{2+} | Cd^{2+} | Zn^{2+} | Pb^{2+} | Cd^{2+} | Zn^{2+} |
| 1 | 99.8 | 99.8 | 71.9 | 93.2 | 83.0 | 99.9 |
| 2 | 99.9 | 99.8 | 76.9 | 97.1 | 93.2 | 100 |
| 3 | 99.9 | 99.8 | 70.0 | 97.7 | 99.8 | 100 |
| 4 | 99.9 | 99.8 | 74.8 | 100 | 92.3 | 100 |
| 5 | 99.8 | 99.6 | 72.8 | 100 | 99.8 | 100 |

However, it is still noteworthy that, like other inorganic sorbents such as ZrP and hydrated ferric oxides [38,39], ZrPS cannot be directly employed for heavy metals removal in fixed-bed and any other flow-through systems due to the excessive pressure drop resulting from its fine particle sizes. However, these fine particles can be impregnated onto porous supporting materials, namely activated carbon [40], polymeric adsorbents [21,41], and alginate [42], to fabricate hybrid sorbents for potential application.

4. Conclusions

Zirconium hydrogen monothio-phosphate (ZrPS) was synthesized as a highly selective sorbent for Pb(II), Cd(II) and Zn(II) from waters. Heavy metals removal by ZrPS is an ion-exchange process in nature. As compared to a widely used inorganic exchanger zirconium phosphate (ZrP), ZrPS exhibits more selective sorption toward heavy these targeted metal ions in the presence of calcium ion at greater levels, which is mainly because of the presence of thiol group on ZrPS. In addition, the exhausted ZrPS are amenable to an efficient regeneration by 6 M HCl solution for repeated use without any significant capacity loss. All the results indicated that ZrPS is a promising sorbent for enhanced removal of heavy metals from contaminated waters.

Acknowledgments

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