Modification of polyacrylamide–β-zeolite composite by phytic acid for the removal of lead from aqueous solutions

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Polyacrylamide–zeolite composite was prepared by direct polymerization of polyacrylamide in suspensions of β-zeolite. Phytic acid was then immobilized on the composite surface. Fourier transform infrared spectrometry (FT-IR), X-Ray Diffraction (XRD) and Thermal gravimetry (TG) techniques were employed to characterize the synthesized adsorbent. The adsorptive features of the composite and the modified composite were investigated for the removal of Pb^{2+} from aqueous solution in view of dependency on pH, time, ion concentration, temperature, selectivity, kinetics and reusability. The adsorption isotherms were evaluated with reference to the Langmuir and Freundlich models. Thermodynamic of the system was calculated. ΔG<0 indicated that the adsorption process was spontaneous. Good compatibility of the adsorption kinetics to the pseudo-second-order model predicted that the rate-controlling step was a chemical sorption. The selectivity experiments showed that the adsorbents were selective toward Pb^{2+} in the presence of Zn^{2+} and Cd^{2+}. The reusability of the adsorbent was tested for four regeneration cycles.

Keywords: adsorption, lead, composite, polyacrylamide, phytic acid.

INTRODUCTION

Lead is potentially a very toxic cation. Its presence in the environment occurred as a result of extensive and wide applications of mining, chemical, electroplating, petroleum refining, paper and pulp industries. Through the food chain system Pb^{2+} is transferred into animals and human beings, causing severe contamination. For the protection and restoration of the environment adsorption of the contaminants by suitable adsorbents is considered as the most attractive method, because of its efficacy, practicality, and economical feasibility. Among the different materials that have been used for the adsorption of the metal ions from solutions are clays and zeolites. Zeolites are infinitely tetrahedral network of aluminosilicates linked together by corner-sharing oxygen. The tetrahedra are arranged in interconnecting channels and apertures to form crystalline structure. Beta zeolite is a high-silica zeolite possessing a three-dimensional system of large rings (rings of 12 oxygen atoms as the minimum constricting apertures). Although the aluminosilicate based materials are desirable compounds for adsorption processes, aggregation and coagulation in aquatic environments are undesired features limiting their practical usage.

This limitation can be minimized by the use of mineral-polymer composites. Polymers have attracted great interest because they are easily and effectively produced in a wide variety of compositions, and exhibit specific sorption properties after modification with various functional groups. Polyacrylamide (PAA) is a hydrogel, which being a crosslinked polymer consists of acrylamide monomers and N,N'-methylenebisacrylamid (crosslinking agent). PAA imbibes a considerable quantity of water, up to swelling equilibrium and can be practically used in adsorption investigations with appropriate structural modifications. The adsorption properties of the composites made by aluminosilicates and PAA can be enhanced by further modification. The practical applicability of this approach has been reported for the composite of bentonite and zeolite with polyacrylamide for Fe^{3+}, Zn^{2+}, UO_{2}^{2+} and Pb^{2+} adsorption. Phytic acid 1,2,3,4,5,6 hexakis (di-hydrogen phosphate) myo-inositol, is a very important molecule from a biological, environmental and technological point of view. Phytic acid, a hexaphosphate-substituted inositol ring compound is a renewable resource. It is the cyclic alcohol (cycitol) derivative of glucose, water soluble and ubiquitous plant product readily available in large quantities. Phytic acid has 12 replaceable protons, of these 6 are strongly dissociable. Therefore, it exists as a negatively charged molecule over a wide pH range. With this feature, it has a high affinity to form phytate complexes with positively charged multivalent metal cations. Phytic acid can be used to modify the surface properties of many adsorbents. The molecular structure of phytic acid is shown in (Fig. 1).

The aim of this investigation was to modify polyacrylamide–β-zeolite composite with phytic acid
(PAA–Z–Phy) and to study the modified composite for adsorption of Pb\(^{2+}\) from aqueous solution. The adsorptive features of the composite with reference to the dependency on pH, concentration, temperature and time were also investigated.

**EXPERIMENTAL**

**Reagents and chemicals**

TEAOH (tetaethyl ammonium hydroxide) from Aldrich, NaAlO\(_2\), KCl, NaOH, aerosil-200 silica, N,N',-methylenebisacrylamid, N,N,N',N'-tetramethylethylene-diamine and Na-phytate (inositol hexaphosphoric acid in the form of dodecasodium salt; C\(_{6}\)H\(_{6}\)O\(_{24}\)P\(_{6}\)Na\(_{12}\)) were purchased from Sigma (USA); AA (Acrylamid monomer), Pb(NO\(_3\))\(_2\), NaOH and HNO\(_3\) were obtained from Merck (Germany). All chemicals used were of analytical reagent grade. Distilled water was used in all the investigations.

**Apparatus**

Zeoite, PAA-Z and PAA-Z-Phy samples were characterized by a series of complementary analytical techniques. Infrared Fourier transform spectroscopy was carried out using a (Nicolet 400D Impact spectrum single FT-IR machine) at wavenumbers 400–4000 cm\(^{-1}\) by using KBr pellets. The structural studies were performed by X-Ray diffractometry (Bruker, Diffractometer D8 ADVANCE, Germany) using Cu K\(\alpha\) as radiation source and Ni as filter. The thermal curves were obtained using a Seta-rAm TG-DSC thermobalance (range 25–700°C). The atmosphere was pure nitrogen and the heating rate of 10°C min\(^{-1}\) was used.

**Synthesis of Beta Zeolite**

A mixture containing 120.0 g of 20 wt % TEAOH solution, 2.22 g of NaAlO\(_2\), 0.90 g of KCl, and 0.15 g of NaOH was stirred until it became a transparent solution. Then 32.59 g of aerosil-200 silica was added. The resulting homogeneous sol was transferred into a Teflon-lined stainless-steel autoclave and heated to 170°C statically. After 40 h, the autoclave was quenched, the content filtered, and the solid was washed with deionized water. After drying at 96°C overnight, it was calcined at 540°C for 2 h. The product was characterized by different characterization techniques.

**Preparation of polycrylamide-zeolite composite**

A mixture of 1.0 g of zeolite in 20 ml of distilled water was stirred for 30 minutes to obtain a homogeneously dispersed suspension. 2.0 g of acrylamide monomer, 0.20 g of N,N'-methylenebisacrylamid and 5.0 mg ammonium-persulphate were dissolved in 10 ml of distilled water. The solution was then added to the zeolite suspension. The mixture was stirred for additional 10 minutes. 100 \(\mu\)l of N,N,N',N'-tetramethylethylene-diamine was then added to propagate the polymerization. After the completion of polymerization, the polycrylamide–zeolite (PAA-Z) gel was washed with distilled water until the effluent attained neutral pH. The final composition of the composite had a 2 : 1 mass ratio of PAA to zeolite. The gel was dried at ambient temperature, ground and sieved to particle size of 1 mm, and stored in a container.

**Modification of composite by phytic acid**

Solution of \(4.5 \times 10^{-3}\)M of phytate was prepared by dissolving the required amount of sodium phytate in distilled water. 10 ml portions of the phytate solution were added to 0.1 g of PAA-Z in polypropylene bottles. The pH of the solutions was adjusted within the range of 9–11. The absorbent–solution systems were then equilibrated for 24 hours by occasional shaking at 25°C. The suspensions were centrifuged at 3000 rpm for 10 minutes and the supernatants were separated. The solid (PAA-Z-Phy) in the form of gel was washed by distilled water until the water conductivity was attained. Phytate adsorption onto the PAA-Z was confirmed by comparing the FT-IR spectra and thermal analysis curves of PAA-Z with PAA-Z-Phy.

**Adsorption studies**

Batch adsorption experiments were conducted in 100 ml stoppered reagent bottles. A measured amount (0.2 g) of PAA-Z and PAA-Z-Phy composites were placed into the 100 ml reagent bottles, which containing 25 ml of various concentrations of Pb\(^{2+}\) solution. The solution pH was adjusted to the desired value by adding HNO\(_3\) or NaOH solution and the bottles were shaken at 200 rpm at room temperature using a mechanical shaker for a prescribed length of time to attain equilibrium. The effect of the initial metal ion concentration (100–2500 ppm), contact time (30–1440 min) and solution pH (2.0–5.0) on the adsorption of Pb\(^{2+}\) was studied. After centrifugation at 3000 rpm for 10 min the concentration of Pb\(^{2+}\) was measured by Atomic Absorption Spectroscopy method (Perkin Elmer A Analyst 300).

**Time dependence Pb\(^{2+}\) adsorption**

To study the adsorption kinetic, 0.20 g of sample was equilibrated with 25 ml of Pb\(^{2+}\) solution (400 ppm) and the pH of the solution was adjusted to p\(\text{H}=4\). The adsorbent–solution systems were then equilibrated by occasional shaking at 25°C for contacting time within the range of 0.5–24 h. The suspensions were centrifuged and the Pb\(^{2+}\) concentration was measured.

**Concentration dependence of Pb\(^{2+}\) adsorption**

The concentration dependence of adsorption was investigated for PAA-Z and PAA-Z-Phy samples. 0.20 g of sample was equilibrated with 25 ml of Pb\(^{2+}\) solution within the range of 100–2500 mgL\(^{-1}\) at pH=4. The adsorbent–solution system was then equilibrated for 2 hours by occasional shaking at 25°C. The suspension was centrifuged and the Pb\(^{2+}\) concentration was measured.

**Temperature dependence of Pb\(^{2+}\) adsorption**

For the determination of thermodynamic parameters the effect of temperature on adsorption was studied at four temperatures of 298, 308, 318 and 328 K. 0.20 g fractions of the samples were equilibrated with 25 ml solution (1500 mgL\(^{-1}\)) of Pb\(^{2+}\) at pH=4 for 2 h. After equilibration, the mixture was centrifuged and the Pb\(^{2+}\) concentration was measured in aqueous phase.

**Reusability of the adsorbent**

0.20 g of the PAA-Z-Phy loaded with Pb in a column with a glass-wool cover was eluted with 25 ml of
0.5 mol/L HNO₃ with flow rate of 2 ml min⁻¹. The recovery of Pb²⁺ with HNO₃ was determined. The column was then reconditioned with distilled water until the effluents had a neutral pH. The regeneration step was repeated for four regeneration cycles.

**RESULTS AND DISCUSSION**

**Characterization of the adsorbents**

The FT-IR spectra of β-zeolite, PAA-Z, Phytic acid and PAA-Z-Phy are given in (Fig. 2). The bands within the range 1000–1300 cm⁻¹ and 400–700 cm⁻¹ attributed to the zeolite structure (Fig. 2a). The peaks at 3200 cm⁻¹ of N–H and 1700 cm⁻¹ of C=O of amide are observed in the spectrum of PAA-Z (Fig. 2b). The peaks at 1322 cm⁻¹ of C–O, 1755 cm⁻¹ of P=O and 3527 cm⁻¹ O–H of acid are observed in the spectrum of phytic acid (Fig. 2c).

**Effect of pH**

The effect of pH on the adsorption of Pb²⁺ by the adsorbents at initial lead concentration of 400 mg L⁻¹ and samples dose of 0.2 g is shown in (Fig. 5). It is conceivable that at low pH values, where there is an excess of H₃O⁺ ions in the solution, a competition exists between the positively charged hydrogen ions and metal ions for the available adsorption sites on the adsorbents surface.
As the pH increases and the balance between H_3O^+ and OH^- are more equal, more positively charged metal ions are adsorbed and the amount of adsorbed Pb^{2+} increased with increasing pH and reached a plateau around pH=4. It is assumed that the surface of aluminosilicates had amphoteric SiOH sites in aquatic solutions and they were either protonated to form SiOH_2^+ or deprotonated to form SiO^-.

The SiO^- concentration increased with increasing pH whereas SiOH concentration decreased with increasing pH according to the following equations:

\[ \text{SiOH} + \text{H}^+ \rightleftharpoons \text{SiOH}_2^+ \]  

\[ 2(\text{SiO}^-) + \text{Pb}^{2+} \rightleftharpoons (\text{SiO})_2\text{Pb} \]

\[ 2(\text{SiOH}) + \text{Pb}^{2+} \rightleftharpoons (\text{SiO})_2\text{Pb} + 2\text{H}^+ \]

Adsortion isotherms

Two adsorption isotherms, namely the Langmuir and the Freundlich were used to analyze the adsorption data. The Langmuir isotherm is based on monolayer adsorption on the active sites of the adsorbent. The Freundlich isotherm explains the adsorption on a heterogeneous surface with adsorption energy. The Langmuir \( q=(K_LX_LC_e)/(1+K_LC_e) \) and Freundlich \( (q= X_F C_e^{1/\beta}) \) models were fit to the isotherms experimentally obtained, where \( X_L \) is the monolayer sorption capacity (mg g\(^{-1}\)), \( K_L \) is the adsorption equilibrium constant (L mg\(^{-1}\)), \( X_F \) and ‘1/β’ are empirical Freundlich constants associated with the capacity and intensity of adsorption. These constants can be calculated from the slope and intercept of the linear plot, with log \( q_e \) versus log \( C_e \). The fitted constants for the Langmuir and Freundlich isotherm models along with regression coefficients (\( R^2 \)) are summarized in (Table 1).

The experimentally attained adsorption isotherms and their compatibility to Langmuir and Freundlich models were provided in the values of the adsorption capacities (\( X_L \), \( X_F \)) for PAA–Z and PAA–Z-Phy for Pb\(^{2+}\). It is obvious that the introduction of phytic acid into PAA–Z remarkably improved its adsorption capacity (Table 1). This should be ascribed to the fine distribution of phytic acid in PAA–Z causing the increase in adsorptive surface and numbers of active sites available for adsorption.

Thermodynamics of Pb\(^{2+}\) adsorption

The thermodynamic parameters such as change in free energy (\( \Delta G \)), enthalpy (\( \Delta H \)) and entropy (\( \Delta S \)) were calculated from the following equations and listed in (Table 2). The distribution coefficients (\( K_d \)) were derived from \( K_d=[(C_i-C_e)/C_i]V/W \) for each temperature and ln\( K_d \) was depicted against 1/T to provide adsorption enthalpy (\( \Delta H \), J mol\(^{-1}\)) and entropy (\( \Delta S \), J mol\(^{-1}\) K\(^{-1}\)) from the slopes (\( \Delta H/R \)) and intercepts (\( \Delta S/R \)) of the depictions with reference to ln\( K_d=(\Delta S/R - \Delta H/RT) \) shown in (Fig. 6). Where R is ideal gas constant, 8.314 (J mol\(^{-1}\) K\(^{-1}\)) and T is the absolute temperature, 298K. The enthalpy changes were negative for the studied adsorbents, showing that the overall process was exothermic and the entropy change was positive for PAA–Z.

Table 1. Langmuir and Freundlich parameters obtained for Pb\(^{2+}\) onto PAA–Z and PAA–Z-Phy

<table>
<thead>
<tr>
<th></th>
<th>Langmuir</th>
<th>Freundlich</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( X_L ) (mg g(^{-1}))</td>
<td>( K_L ) (L mg(^{-1}))</td>
</tr>
<tr>
<td>PAA–Z</td>
<td>116.3</td>
<td>0.0034</td>
</tr>
<tr>
<td>PAA–Z-Phy</td>
<td>142.8</td>
<td>0.0046</td>
</tr>
</tbody>
</table>

Table 2. Thermodynamic parameters for adsorption of Pb\(^{2+}\)

<table>
<thead>
<tr>
<th></th>
<th>( \Delta H/\text{kJ mol}^{-1} )</th>
<th>( \Delta S/\text{J mol}^{-1} \text{K}^{-1} )</th>
<th>( \Delta G/\text{kJ mol}^{-1} )</th>
<th>( R^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>PAA–Z</td>
<td>-7.78</td>
<td>12.92</td>
<td>-11.63</td>
<td>0.9911</td>
</tr>
<tr>
<td>PAA–Z-Phy</td>
<td>-11.51</td>
<td>3.77</td>
<td>-12.63</td>
<td>0.9911</td>
</tr>
</tbody>
</table>
This was attributed to blockage of adsorption centers or washing of some active sites during the regeneration procedure. Regeneration is assumed to follow according to the equations:

\[
\begin{align*}
\text{(SiO)}_2\text{Pb} + 2\text{H}^+ & \rightleftharpoons 2(\text{SiOH}) + \text{Pb}^{2+} \quad (5) \\
\text{SiOH} + \text{H}^+ & \rightleftharpoons \text{SiOH}^2+ \quad (6) \\
\text{SiOH}^2+ + \text{H}_2\text{O} & \rightleftharpoons \text{SiOH} + \text{H}_3\text{O}^+ \quad (7)
\end{align*}
\]

Table 3. Kinetic parameters for Pb\(^{2+}\) adsorption onto PAA-Z, PAA-Z-Phy

<table>
<thead>
<tr>
<th></th>
<th>Pseudo first order</th>
<th>Pseudo second order</th>
<th>Intraparticle diffusion</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(K_1) q R^2</td>
<td>(K_2) q R^2</td>
<td>(K) R^2</td>
</tr>
<tr>
<td>PAA-Z</td>
<td>0.109 2.11 0.9851</td>
<td>0.25 29.65 29.67</td>
<td>0.9999 0.49 0.9788</td>
</tr>
<tr>
<td>PAA-Z-Phy</td>
<td>0.099 1.56 0.9404</td>
<td>0.57 34.22 34.24</td>
<td>1 0.39 0.8932</td>
</tr>
</tbody>
</table>

This was attributed to blockage of adsorption centers or washing of some active sites during the regeneration procedure. Regeneration is assumed to follow according to the equations:

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\text{SiOH} + \text{H}^+ & \rightleftharpoons \text{SiOH}^2+ \quad (6) \\
\text{SiOH}^2+ + \text{H}_2\text{O} & \rightleftharpoons \text{SiOH} + \text{H}_3\text{O}^+ \quad (7)
\end{align*}
\]

Table 4. Tolerance limit of PAA–Z, PAA–Z–Phy from solutions containing possible combination of studied ions at equivalent concentration (500ppm) of Pb\(^{2+}\)

<table>
<thead>
<tr>
<th>Ion</th>
<th>PAA-Z(ppm)</th>
<th>PAA-Z-Phy(ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cd(II)</td>
<td>2500</td>
<td>2500</td>
</tr>
<tr>
<td>Zn(II)</td>
<td>2500</td>
<td>2500</td>
</tr>
</tbody>
</table>

This was attributed to blockage of adsorption centers or washing of some active sites during the regeneration procedure. Regeneration is assumed to follow according to the equations:

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\text{SiOH} + \text{H}^+ & \rightleftharpoons \text{SiOH}^2+ \quad (6) \\
\text{SiOH}^2+ + \text{H}_2\text{O} & \rightleftharpoons \text{SiOH} + \text{H}_3\text{O}^+ \quad (7)
\end{align*}
\]

Selectivity of the adsorbents

The selectivity of PAA–Z and PAA-Z-Phy sample for Pb\(^{2+}\) in the solutions containing combinations of ions at equivalent concentrations (500 mg L\(^{-1}\)) was studied. 25 ml fraction of solution containing the studied ions was contacted with 0.20 g of the adsorbents. After equilibrium (24 h), the concentration of the studied cations was measured in the filtrate. The reported tolerance limit is defined as the ion concentration causing a relative error < ± 5% (Table 4). Adsorbents showed the highest affinity for Pb\(^{2+}\) in the presence of Zn\(^{2+}\) and Cd\(^{2+}\). This can also be explained by the effects of the affective ionic charge and the parameters related to the affinity of Pb\(^{2+}\) to the adsorbents together with the ion strength of the medium.

Reusability

The reusability feature of PAA–Z–Phy was tested for Pb\(^{2+}\) for four regeneration cycles (Table 5). The recovery percentage declined with the number of regenerations.

Figure 7. Compatibility of Pb adsorption kinetics for PAA-Z and PAA-Z-Phy to (a) pseudo-one order log (q_e – qt) vs.t (b) pseudo-second order (t/qt vs. t) and (c) intraparticle diffusion (qt vs.t^{0.5})

This was attributed to blockage of adsorption centers or washing of some active sites during the regeneration procedure. Regeneration is assumed to follow according to the equations:

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(\text{SiO})_2\text{Pb} + 2\text{H}^+ \rightleftharpoons 2(\text{SiOH}) + \text{Pb}^{2+} \quad (5) \\
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\text{SiOH}^2+ + \text{H}_2\text{O} \rightleftharpoons \text{SiOH} + \text{H}_3\text{O}^+ \quad (7)
\]
**Table 5. Reusability of PAA–Z–Phy for Pb**

<table>
<thead>
<tr>
<th>Recycle</th>
<th>% regeneration</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>96.8</td>
</tr>
<tr>
<td>2</td>
<td>94.8</td>
</tr>
<tr>
<td>3</td>
<td>92.4</td>
</tr>
<tr>
<td>4</td>
<td>90.5</td>
</tr>
</tbody>
</table>

**CONCLUSION**

In this study, adsorptive features of PAA-Z and PAA-Z-Phy were investigated for Pb\(^{2+}\) adsorption. It was concluded that the amount of adsorbed Pb\(^{2+}\) was further increased by the modification of the composite PAA-Z with phytic acid. Thermodynamic studies showed that the adsorption process was endothermic and spontaneous. The experimental data were analyzed in terms of the Langmuir and Freundlich isotherm models and the data was well fitted by the Langmuir isotherm. Compatibility of adsorption kinetics to the pseudo second-order model indicated that the rate-controlling step is a chemical sorption. The kinetics of adsorption were fast, allowing its application in column operation. The adsorbent was regenerated for 4 cycles and showed that acceptable capacity remained after the last regeneration step.

**LITERATURE CITED**


