Lead removal by polyacrylamide-bentonite and zeolite composites: Effect of phytic acid immobilization

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Abstract

Polyacrylamide (PAA)-bentonite (B) and zeolite (Z) composites were prepared by direct polymerization of PAA in suspensions of B and Z. Phytate (Phy) immobilized onto the composites to obtain their Phy modifications. FT-IR and XRD were employed to characterize their structures. The sorption of Pb^{2+} from various adsorption media onto the composites was then investigated. The reusability and storage characteristics of the adsorbents with and without Phy were also considered for Pb^{2+} adsorption.

All isotherms were L and H type of the Giles classification. The Phy adsorption capacities (X_M) of PAA-B and Z lower than those of bare B and Z due to their surface coverage by PAA. The Phy modification decreased the Pb^{2+} adsorption capacities of B and PAA-B but ascended those of Z and PAA-Z. However, Phy significantly increased the Langmuir equilibrium constants (K_L) for all adsorbents. Ionic strength of the adsorption media was favorable for the adsorption capacity of PAA-B while not for that of PAA-Z. The chemical structure of the composites was not changed after five reuses and the storage foregoing.

It is foreseen that the use of PAA-B and PAA-Z and their Phy modifications will provide practicality and effectiveness for Pb^{2+} separation and removal procedures. The X_M ($mol\,kg^{-1}$) and K_L ($L\,mol^{-1}$) values for Pb^{2+} adsorption from a model solution were 0.16 and 3625 for PAA-B, 0.18 and 5.1×10^5 for PAA-B-Phy, 0.28 and 13210 for PAA-Z and 1.65 and 2.0×10^5 for PAA-Z-Phy.
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1. Introduction

Lead is potentially very toxic to mammals and aquatic lives by its presence in the environment as a result of extensive and wide applications of mining, chemical, electroplating, petroleum refining, paper and pulp industries. For this reason, the remediation treatment and removal of lead in waste and contaminated water have been a major concern of process industries [1–3].

The adsorption processes are generally known to be one of the most effective techniques for removal of environmentally hazardous metals. Adsorbents with strong affinity and high loading capacity for targeted metal ions have been developed by modifications of the surface of various substrates, such as polymers and clays with metal complexing groups [4–6]. Whilst synthetic ion-exchange resins are expensive to use on a large scale, natural materials such as clay and zeolite are classified amongst the low-cost adsorbents [7–9]. The mineralogical and physicochemical features of clay and zeolite are considered to be the basis for their immense importance in separation, ion exchange and catalysis.

Zeolite minerals are infinitely extending tetrahedral network of aluminium oxide and silicon silicates (aluminosilicates) linked together by corner-sharing oxygens. The tetrahedra are arranged in interconnecting channels and apertures permeate the crystalline structure. Montmorillonite (bentonite), as the interest of this investigation is a member of the smectite type clay, which is 2:1 type of aluminosilicate. Its crystalline structure presents an alumina octahedral layer between two tetrahedral layers of silica. The substitution of

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the Al^{3+} for the Si^{4+} in the tetrahedral structures of zeolite and montmorillonite, and that of divalent cation for Al^{3+} in the octahedral sheet of montmorillonite causes residual negative charges. These are neutralized by the electrostatic adsorption of alkali and alkali earth cations. These are free to exchange with other cationic ions, as a measure of cation exchange capacity (CEC) of a given clay or zeolite mineral [10,11].

The aggregation and coagulation of zeolite and clay particles under varying conditions of temperature and electrolytes lead variations in flow properties of these minerals. This is an undesired feature for their practical use as adsorbents [10–12]. Having a composite of a mineral and a polymer, in which the mineral dispersed in the polymer network may enable the use of mineral itself as an adsorbent confined in an isolated and practically usable medium in aquatic solutions. Beside this, the particles embedded in a network strengthen the gel and prevent its collapse in bad solvents. The enhancement in adsorptive features of the mineral can also be possible with additional surface modifications.

Phytic acid, a hexaphosphate-substituted inositol ring compound is a renewable resource. It is a water soluble, 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 [13–15]. For this reason, phytic acid should be used as an adsorbent with its immobilized form on a solid support. The immobilized phytic acid should be stable and have a good adsorption capacity within a reasonable pH range [16,17].

By considering the features mentioned above, preparation of a composite of bentonite (B) or zeolite (Z) with a polymer should provide a useful material for adsorption studies. Additionally, phytic acid (Phy) modifications should enhance the adsorptive features of the composites. However, the practical applicability of this approach was shown for the composite of B with polyacrylamide (PAA), PAA-B, for adsorption of Fe^{3+}, Zn^{2+} and UO_2^{2+} [18]. The application was also confirmed for adsorption of naturally occurring radionuclides at pmol L^{-1} levels, including ^{212}Pb [19,20]. The results of both study suggested that the composites of B and Z with PAA should be effectively used in studies of Pb^{2+} adsorption.

The concerns of this investigation are divided into three parts: first, to introduce preparation and characterization of PAA-B/Z composites. Second, to investigate the adsorption of Phy onto the B, Z, PAA-B and PAA-Z prior to obtain the Phy modified composites. Third, due to the specific interest of phytic acid and its relevance to divalent cations, and also environmental importance of Pb^{2+}, to inspect the practical usability of these composites and their Phy modifications in adsorption of Pb^{2+} in various aquatic media. Additional considerations were also given to the reusability and storage capability of the composites in Pb^{2+} adsorption. The adsorptive features of the studied adsorbents were evaluated on the base of adsorption parameters derived from the compatibility of adsorption isotherms to the Langmuir and Freundlich models.

2. Experimental

2.1. Reagents

Na-montmorillonite (bentonite) in 98% purity (with a univalent CEC of 0.8 mol kg^{-1}), N,N'-methylenebisacrylamide, N,N,N',N'-tetramethylethylenediamine and Na-Phytate (Inositol hexaphosphoric acid, as dodecasodium salt; $C_6H_6O_{24}P_6Na_{12}$) and 4-(2-pyridylazo) resorcinol (PAR) were purchased from Sigma. Amersham and Fluka were the suppliers of AA monomer and $YCl_3 \cdot 6H_2O$. All chemicals used were of analytical reagent grade.

Zeolite was obtained from Central North Anatolian occurrences associated with Eocene submarine volcanism [21]. The certified chemical composition of zeolite is provided in Table 1. The mineral is composed of ∼90% zeolite, as clinoptilolite $\{(Na,K)_6 \cdot [Al_6Si_{30}O_{72}] \cdot 24H_2O\}$ and mordenite $\{Na_3KCa_2 \cdot [Al_8Si_{40}O_{96}] \cdot 28H_2O\}$, 5% kuartz, 5% feldspar and smectite in trace level. The ratio of SiO_2/Al_2O_3 is 4.7, which suggests that the zeolite is clinoptilolite with reference to the classification of International Mineralogical Association [11]. The univalent CEC of zeolite was 1.64 mol kg^{-1} [22]. The total univalent charge exchange capacity and (Na + K)/Ca of Z were calculated to be 3.68 mol kg^{-1} and 0.4 [23].

The zeolite rocks were crashed, ground and sieved to 100 mesh size. No pre-treatment was applied to the chemicals, clay and zeolite. All experiments were always performed in duplicates.

2.2. Preparation of composites

PAA-B or PAA-Z was prepared by direct polymerization of AA monomer in the clay and zeolite suspensions [18]. The final composition of the composites had 2:1 mass ratio of PAA to the clay and zeolite. The gels were dried at ambient temperature, ground and sieved to a particle size 1 mm, and stored in a container. One batch for each of PAA-B or PAA-Z was prepared at once to conduct the overall investigation.

FT-IR (Mattson 1000, UK) was employed to estimate chemical structure of B, Z and their composites while XRD (Philips, Type PW 1140/00, using Cu Kα radiation, a pro-

Table 1
Chemical composition of the studied zeolite, % (certified by IMO GmbH)

SiO$_2$	71.89	K$_2$O	0.57
Al$_2$O$_3$	15.16	TiO$_2$	0.36
CaO	6.51	BaO	0.13
Fe$_2$O$_3$	1.80	P$_2$O$_5$	0.08
MgO	1.80	MnO	0.05
Na$_2$O	1.06		
SrO	0.59	Total	100.00

portional counter, 2θ/min scan rate) was used for powder diffraction.

The swelling features of B, Z, PAA, PAA-B and PAA-Z were compared. Dry samples (0.1 g) were let to swell in water and the swelling ratio was calculated with reference to the dry weights.

2.3. Phytate adsorption

In studies of Phy adsorption, 0.1 g of B, Z, PAA-B and PAA-Z were added on 10 mL of phytate solutions at concentrations within the range from 1.0×10^{-3} to 2.0×10^{-3} mol L^{-1}. The pH values of solutions were at 9–11. The adsorbent–solution systems were equilibrated for 24 h at 298 K in a thermostatic water bath, the suspensions were then centrifuged at 3000 rpm for 10 min. The metal-dye detection method described by Laussmann et al. [24] was used for Phy determination in the supernatants. The required amount for 0.7 mol L^{-1} of Tris was dissolved in water and the pH was adjusted to 8–9 with addition of HCl. The complexing reagent was prepared to provide 3.5×10^{-3} mol L^{-1} of PAR and 6×10^{-5} mol L^{-1} of Y^{3+} in the Tris–HCl solution. A 50 µL fraction of supernatant was added on to 3 mL of the PAR reagent. Absorbance of the formed complex was measured at 510 nm by means of a UV–vis spectrophotometer (Shimadzu-160A, Japan).

In preparation of Phy immobilized B, Z, PAA-B and PAA-Z composites prior to Pb^{2+} adsorption studies, the adsorption procedure was repeated for replicates of 0.1 g of each sample with 10 mL of Phy solution at a constant concentration (4.5×10^{-3} mol L^{-1}). The Phy immobilized samples were then washed by distilled water until the water conductivity was attained and kept for further use in Pb^{2+} adsorption studies. The washing treatment did not cause de-sorption of Phy. The chemical structure of B, Z, PAA-B, PAA-Z and their Phy modifications was characterized by means of the FT-IR.

2.4. Pb^{2+} adsorption

Adsorptive features of the adsorbents was investigated for Pb^{2+} in three different solution environments: a model solution (water containing Pb^{2+} as single cation), a 0.01 mol L^{-1} CaCl$_2$ and a solution containing leachate with 10 mg mL^{-1} of dissolved solid (equivalence amount to the solid content of 0.01 M CaCl$_2$). The leaching solution was obtained from a regional fluorite sample containing naturally occurring radioactive ^{212}Pb at secular equilibrium with ^{232}Th, which was used as the tracer for measurement of Pb^{2+} adsorption. The adsorption onto bare B and Z and their Phy modifications was only considered for the leachate added solution.

Adsorbents (0.1 g) in the studied solutions were equilibrated with 10 mL of Pb^{2+} at concentrations within the range from 0.1×10^{-3} to 10×10^{-3} mol L^{-1}. The adsorbent–solution systems were subjected to the procedures described for the Phy adsorption study. The initial and final pH values of Pb^{2+} solutions were always within the range

of 4–5, which was well below the precipitation pH level of Pb^{2+}, pH > 6.5 [4].

The metal-dye detection procedure provided by Laussmann et al. [24] was modified for Pb^{2+} determination in supernatants from the model and CaCl$_2$ solutions. Pb^{2+} was utilized as the complexing metal instead of Y^{3+} used in the Laussmann's procedure. A solution of 3.5×10^{-3} mol L^{-1} of PAR in 0.7 mol L^{-1} of Tris–HCl at pH 8–9 was prepared. A 50 µL fraction of supernatant was added onto 3 mL of the reagent and the absorbance of the formed metal complex was measured at 550 nm.

A gamma spectrometer [NAI(Tl) detector combined with a EG&G ORTEC multi-channel analyzer and software, MAESTRO 32, MCA Emulator, USA] was employed for determination Pb^{2+} in supernatants obtained from the study with leachate. The adsorbed amounts were calculated by comparing the specific activity at 238.6 keV of ^{212}Pb (tracer) in supernatants with that in the leachate not interacted with the adsorbents.

2.5. Reusability and storage capability

The reusability and storage capability of PAA-Z and PAA-Z-Phy were tested for adsorption of Pb^{2+} from the model and leachate added solutions. The B composites were not studied, since their features were previously considered for adsorption of Fe^{3+} [18].

To test of reusability, five duplicates of 0.1 g samples in polypropylene columns ($H = 10$ cm, $\Phi = 1$ cm) were equilibrated with 10 mL of 5×10^{-3} mol L^{-1} Pb^{2+} for 24 h and the supernatants were discharged. The contents of columns were eluted with 5 mL fractions of 20 mL of 1 mol L^{-1} HCl and the columns were then washed with distilled water until the effluents had a neutral pH. The Pb^{2+} contents of the effluents (HCl) were determined. Each column was subjected to the same procedure for five sequential times.

For the storage ability, duplicates of the samples were subjected to the Pb^{2+} adsorption procedure for one use for 1 month with a week interval.

2.6. Data evaluation

The amount of adsorption of Phy and Pb^{2+} (Q, mol kg^{-1}) were calculated from $Q = [(C_i - C_e)V/w]$, where C_i and C_e are the initial and equilibrium concentrations of the studied ions (mol L^{-1}), w is the mass of adsorbent (kg) and V is the solution volume (L). The Langmuir [$Q = (K_L X_L C_e)/(1 + K_L C_e)$] and Freundlich ($Q = aC_e^{\beta}$) models were fit to the isotherms experimentally obtained, where X_L is the monolayer sorption capacity (mol kg^{-1}), K_L is the adsorption equilibrium constant (L mol^{-1}) related to the Gibbs free energy change, $\Delta G = -RT \ln K_L$ (R is ideal gas constant, 8.314 J mol^{-1} K^{-1} and T is the absolute temperature, 298 K). 'a' and 'β' are empirical Freundlich constants.

A t-test was applied to obtain the significance of regression coefficients (r) calculated from the compatibility of experi-
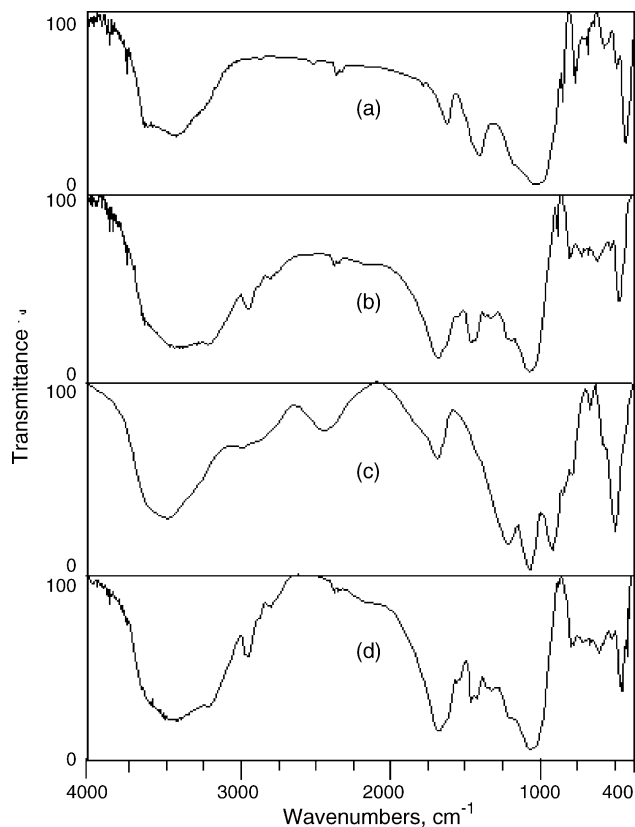
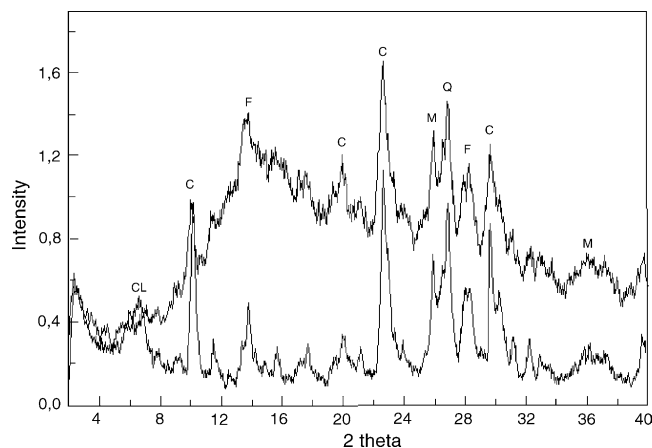Fig. 1. FT-IR spectra of Z (a), PAA-Z (b), Phy (c) and PAA-Z-Phy (d).

Fig. 2. XRD spectra of Z (lower spectrum) and PAA-Z [Clinoptilolite (C), Mordenite (M), Clay (CL), Kuartz (Q) and Feldspar (F) are the main composition of Z].

mental data to the Langmuir and Freundlich models; $p < 0.01$ was considered as the threshold for the significance [25].

3. Results and discussion

3.1. Structural evaluation

The IR spectra of Z, PAA-Z and PAA-Z-Phy with same amount Z contents and of Phy are provided in Fig. 1a–d. The broad appearance at $3500\,cm^{-1}$ in all spectra was of O–H stretches. The counters within the range $1000–1700\,cm^{-1}$ and $400–700\,cm^{-1}$ were of silicates in Z. The peaks at 3200 and $1700\,cm^{-1}$ of C=O of amide and $2900\,cm^{-1}$ of C–H were of PAA and PAA of PAA-Z (Fig. 1a and b). From the comparison of Fig. 1b and c with d, it can be postulated that

the inclusion of Phy to the composite is as hydrogen bond formations between P–OH of Phy and Si–OH and Al–OH of Z for which the declines at $2500\,cm^{-1}$ for Si–OH and $800\,cm^{-1}$ of Al–OH and the absence of the broad band around $2350–2400\,cm^{-1}$ of P–OH were evidences [26–29].

Fig. 2 shows the XRD pattern of Z and PAA-Z. There was no shift in any of diffraction peaks. The intense increase in background of PAA-Z was due to the amorphous nature of PAA. In consequent, the IR spectra and XRD patterns of Z and PAA-Z defined that the zeolite particles were uniformly dispersed in polymer. The interfacial interaction between PAA and Z was the binding formation between PAA and the siloxane oxygen atoms or hydroxylated edge sites of zeolite. Polymer sorption into channels and holes of zeolite should also be possible [5,30,31]. The structural evaluation of B and its composite were provided in the early communication [18] in which where the similar features were reported also for B and PAA-B with the difference of intercalation of clay layers by PAA.

The magnitude of swelling was 1400% for PAA and PAA-Z, 200% for Z, 1700% for PAA-B and 1150% for B. The swelling of PAA-B was higher than that of PAA-Z despite the fact that B or Z contents of the composites were the same (1/3 of dry weights). The tendency to adsorb water of PAA-B increased due to de-lamination and surface modification of its clay component [12]. There was no such effect for PAA-Z, since the swelling of Z is associated with its Si/Al, the higher

Table 2
Langmuir and Freundlich parameters obtained for Phy adsorption onto B, PAA-B, Z and PAA-Z

Composite	Langmuir				Freundlich		
	X_L (mol kg^{-1})	K_L (L mol^{-1})	ΔG (kJ mol^{-1})	R^{2a}	a	β	R^{2a}
B[b]	0.04	29800	−25.5	0.966	0.08	0.12	0.941
PAA-B[b]	0.03	1440	−18.0	0.978	1.02	0.60	0.939
Z	0.12	1818	−18.6	0.994	2.95	0.54	0.964
PAA-Z	0.05	3282	−20.1	0.912	0.62	0.42	0.998

[a] All coefficients of variations calculated for the Langmuir and Freundlich fits are significant at $p < 0.01$.

[b] Data obtained from previous study [18].

ratio provides a higher degree of hydrophobicity [27]. The ratio for Z was 4/1 so that its swelling was low.

3.2. Phytate adsorption

The results for Phy adsorption onto Z and PAA-Z and their compatibility to the Langmuir and Freundlich models are compared with the previous results of B and PAA-B [18] in Fig. 3. Table 2 provides the parameters derived from the model fits. The shape of isotherms corresponds to the high affinity class (L and H type) of the Giles classification, i.e. the adsorption has a chemical character. The adsorption hyperbolically increases with increasing concentration. The steep rise at the beginning lowers gradually and reaches a plateau defining the completion of filling the monolayer adsorption capacity (X_L).

The values of X_L of B, Z and PAA-B/Z were in the order of Z > B > PAA-Z > PAA-B. The adsorbed amounts declined for the composites. Despite the fact that both composites had the same mass fraction of B or Z, the degree of decline was more effective on Z's. This asserts that the Phy adsorption occurred only on active sites of Z surface because of the molecule size of Phy is large to insert in the channels of zeolite with size up to ca. 1 nm [32]. Number of active adsorption sites in Z surface decreased by the surface coverage of PAA, whilst such residential hindrance was compensated by the expansion of plane layers with strong hydration of interlayer Na$^+$ ions in B of PAA-B.

Fig. 4. Isotherms with Langmuir and Freundlich fits for adsorption of Pb^{2+} from Pb(CH$_3$COO)$_2$ in the model solution onto PAA-B, PAA-Z and their Phy modifications.

The ΔG values as the measure of spontaneity of Phy adsorption declined in the order of B > PAA-B and PAA-Z > Z as the same sequence with K_L, as expected. As inversely related to the water affinity of Z, the adsorption preference of Phy onto Z was higher than that onto B. Water molecules at contact with the solid surface declined the kinetics of molecular Phy transfer to Z surface, this transfer was catalyzed by PAA in PAA-Z, in contrast to the case in B, since both B and PAA had highly hydrophilic characters so that Phy suffered competition with water molecules. There was not any systematic relation between the Langmuir and Freundlich parameters.

From the preparation of Phy modified adsorbents, the immobilized amounts of Phy were found to be 40×10^{-3} mol kg^{-1} for B, 15×10^{-3} mol kg^{-1} for PAA-B, 80×10^{-3} mol kg^{-1} for Z and 30×10^{-3} mol kg^{-1} for PAA-Z.

3.3. Pb^{2+} adsorption

The isotherms for adsorption of Pb^{2+} from the model and CaCl$_2$ solutions onto the composites and their Phy modifications are depicted in Figs. 4 and 5. The adsorptions from the leachate added solution onto bare B, Z and the composites with and without Phy are compared in Fig. 6. All isotherms were in L and H types of Giles classification signifying that the adsorbents were high affinity class of materials for Pb^{2+}
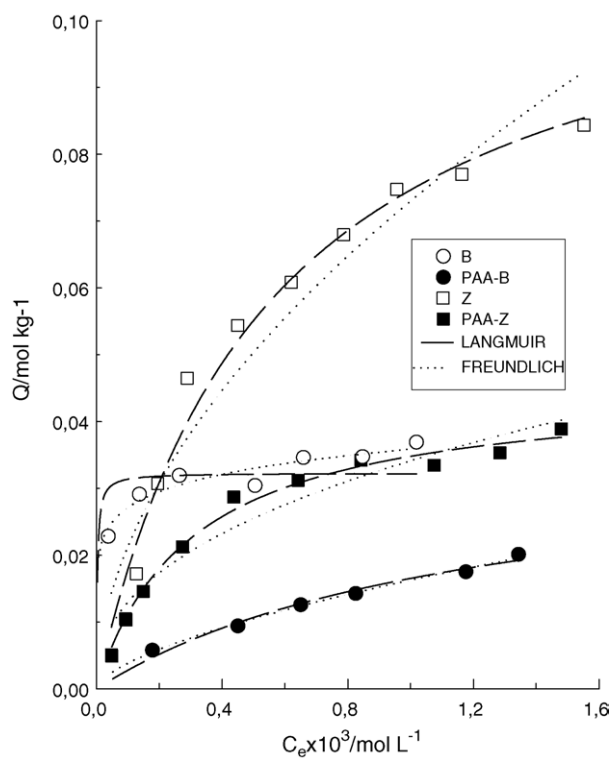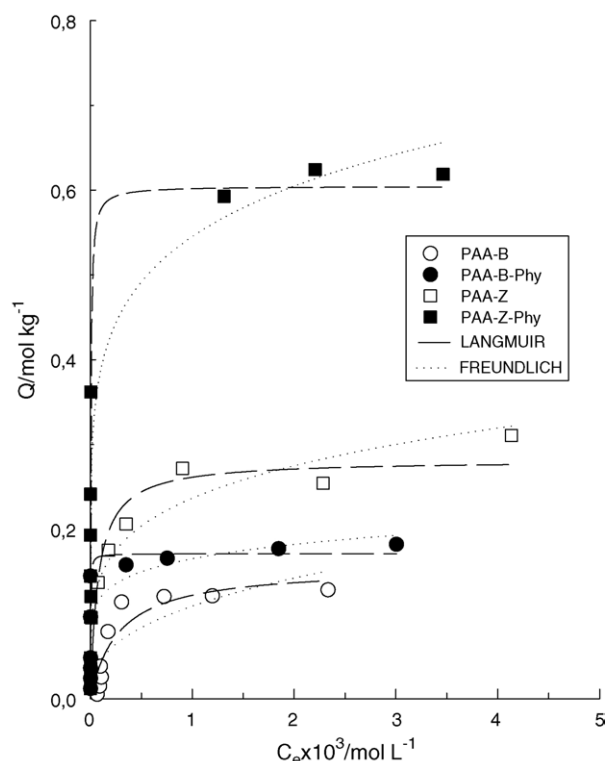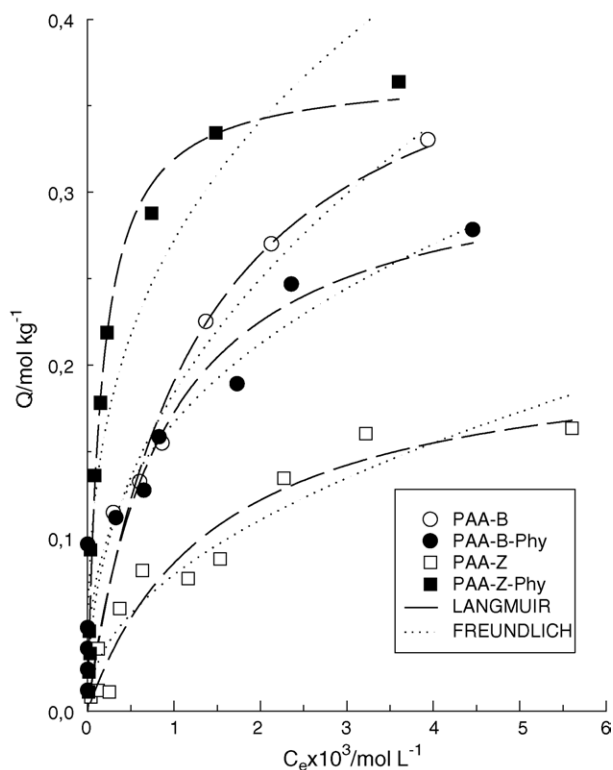

Fig. 3. Isotherms with Langmuir and Freundlich fits for adsorption of phytate onto B, PAA-B (obtained from ref. [18]), Z and PAA-Z.

Fig. 5. Isotherms with Langmuir and Freundlich fits for adsorption of Pb^{2+} from $Pb(CH_3COO)_2$ in 0.01 mol L^{-1} of $CaCl_2$ onto PAA-B, PAA-Z and their Phy modifications.

adsorption. The parameters derived from the compatibility of the Langmuir and Freundlich models to the data are provided in Table 3.

Pb^{2+} adsorption was dependent to CEC of B and Z, and the adsorption environments. The X_L values of the composites was in the sequence of PAA-Z > PAA-B in the model solution as accordant with the univalent CEC values of Z and B. The sequence turned in favor of PAA-B in both $CaCl_2$ and leachate added solutions, and that was also of bare B compared to Z in the leachate. The change was attributable to the increase in the ionic strength of adsorption media; in fact, PAA-B in the $CaCl_2$ solution had the highest X_L value. PAA-B in the leachate had a lower capacity compared to that in the $CaCl_2$ solution, but the value was still about the same with that in the model solution, despite the fact that the leachate contained many competing ions with Pb^{2+}. Similar trend was also observed for PAA-B-Phy along with the adsorptive media. The increase of the counter ions had inverse effect on adsorption onto Z and its composite with and without Phy; the sequence of X_L values for the composites with and without Phy was Model > $CaCl_2$ > leachate. This shows that the affinity of Z to the competing ions such as Ca^{2+} was higher than that to Pb^{2+}, i.e. the trend of Pb^{2+} selectivity of B and its composite without Phy is higher than that of Z and its composite. In the absence of Phy, the K_L values obtained for Z and PAA-Z for each adsorption media were higher than those of B and its composite. As discussed in the Phy adsorp-
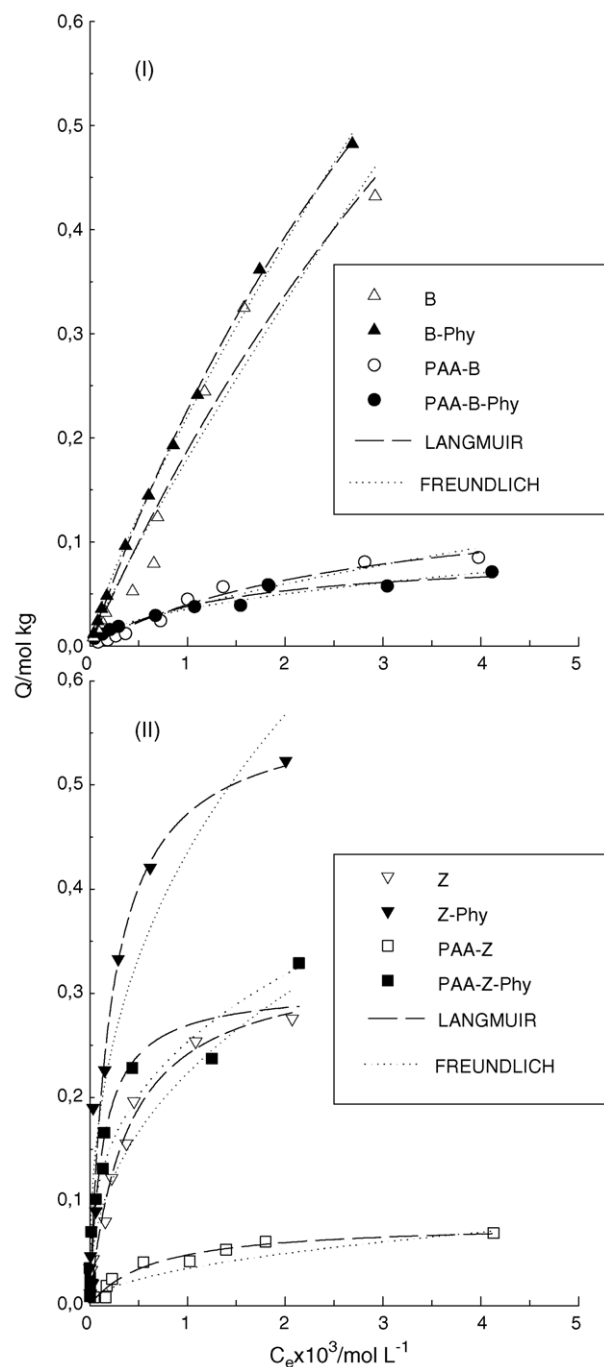

Fig. 6. Isotherms with Langmuir and Freundlich fits for adsorption of Pb^{2+} from $Pb(CH_3COO)_2$ in the leachate added solution onto B (I) and Z (II) and their PAA composites with and without Phy modifications.

tion section, this should also be explained by the fact that the affinity difference between B and Z to water molecules.

The Phy modification lowered or not much changed the adsorption capacities of B and PAA-B, but significantly enhanced those of Z and PAA-Z. Samba-Fouala et al. [29] postulated that the insertion of phytic acid into clay layers caused cross-linking at the silicon atoms and condensation reactions between silicon and phosphorus atoms of clay and

Table 3

Langmuir and Freundlich parameters obtained for adsorption of Pb^{2+} in various solutions onto B, B-Phy, Z, Z-Phy PAA-B, PAA-B-Phy, PAA-Z and PAA-Z-Phy

Composite	Langmuir			Freundlich			
	X_L (mol kg^{-1})	K_L (L mol^{-1})	ΔG (kJ mol^{-1})	R^{2a}	a	β	R^{2a}
Pb^{2+} adsorption onto bentonite composites							
B_{leach}	1.64	129	−12.0	0.964	76.4	0.88	0.914
B-Phy$_{leachate}$	1.48	181	−12.9	0.998	60.3	0.81	0.998
PAA-B$_{Model}$	0.16	3625	−20.3	0.850	1.52	0.38	0.709
PAA-B-Phy$_{Model}$	0.18	5.1×10^5	−32.6	0.728	0.43	0.14	0.741
PAA − B$_{CaCl_2}$	0.43	790	−16.5	0.865	3.92	0.44	0.870
PAA − B − Phy$_{CaCl_2}$	0.32	1141	−17.4	0.814	1.83	0.35	0.826
PAA-B$_{leachate}$	0.15	348	−14.5	0.974	3.84	0.67	0.947
PAA-B-Phy$_{leachate}$	0.09	767	−16.5	0.976	1.08	0.49	0.966
Pb^{2+} adsorption onto zeolite composites							
$Z_{leachate}$	0.33	2646	−19.5	0.986	4.10	0.42	0.924
Z-Phy$_{leachate}$	0.57	4626	−20.9	0.939	6.12	0.38	0.899
PAA-Z$_{Model}$	0.28	13210	−23.5	0.916	1.14	0.23	0.937
PAA-Z-Phy$_{Model}$	1.65	2.0×10^5	−30.2	0.812	1.14	0.10	0.935
PAA-Z$_{CaCl2}$	0.21	673	−16.1	0.929	2.30	0.49	0.912
PAA-Z-Phy$_{CaCl2}$	0.37	6343	−21.7	0.988	2.57	0.33	0.899
PAA-Z$_{leachate}$	0.08	1440	−18.0	0.966	0.52	0.36	0.918
PAA-Z Phy$_{leachate}$	0.31	7397	−22.1	0.941	2.44	0.33	0.951

[a] All coefficients of variations calculated for the Langmuir and Freundlich fits are significant at $p < 0.01$.

phytic acid. The lowering effect of Phy on X_L values in B and PAA-B can also be explained by the same approach. Such hindrance should not be possible for Z since the immobilized Phy was at the surface in fact the highest X_L value (1.65 mol kg^{-1}) was obtained for PAA-Z-Phy in the model solution. This fact and the high affinity of Pb^{2+} to Phy eventually made PAA-Z-Phy more selective for Pb^{2+} than PAA-B-Phy.

The Phy modification resulted in a significant increase in the K_L values for all studied adsorbents i.e. that increased the spontaneity of forming complex (ΔG) between phosphate terminals of Phy and Pb^{2+}. This effect was much apparent for Z and PAA-Z in all studied solutions. The enormous increase in K_L values obtained for the adsorption from the model solution by both composites with Phy was worth nothing.

There was a systematic relation between the Freundlich and Langmuir parameters obtained for each composite couples (PAA-B and PAA-B-Phy, PAA-Z and PAA-Z-Phy) in the same adsorption media; the one with the higher X_L had the higher 'a' and that with the higher K_L had the lower 'β'.

This relation might be interpreted as the 'a' is a measure of the adsorption intensity and 'β' is of the heterogeneity of adsorbents for the ion of interest.

3.4. Reusability and storage ability

After five sequential reuses, the mean of Pb^{2+} adsorption from the model solution was constantly about 50% for PAA-Z and 95% for PAA-Z-Phy, whilst that from the leachate added solution was $16.7 \pm 1.0\%$ (range 18.7–14.4%) for PAA-Z and $31.6 \pm 2.6\%$ (range 37.5–24.7%) for PAA-Z-Phy (Table 4). The amounts adsorbed declined with the number of reuse because of the matrix effect of ions in the leachate; the used stripping reagent could not remove the adsorbed competing ions onto the active sites. The storage ability tests for one use of PAA-Z-Phy performed in the leachate solution for 4 weeks with 1-week interval indicated that the fractional Pb^{2+} adsorption remained unchanged (Table 4). The mean of the four trials was $38.2 \pm 1.0\%$ (range 37.8–42.2%). The storage

Table 4

Reusability of PAA-Z and PAA-Z-Phy, and storagability of PAA-Z-Phy for adsorption of Pb^{2+} (5×10^{-3} mol L^{-1}) from the leachate solution

Reusabilty			Storagability of PAA-Z-Phy	
Reusage No.[a]	Adsorption (%)		Time elapsed (week)	Adsorption (%)
	PAA-Z	PAA-Z-Phy		
1	18.7	37.5	Initial	39.0
2	18.5	36.1	1	35.8
3	17.2	33.3	2	37.8
4	14.5	26.5	3	42.2
5	14.4	24.7	4	36.1
Mean ± S.E.M.	16.7 ± 1.0	31.6 ± 2.6		38.2 ± 1.0

[a] Number of sequential usage of the adsorbents.

ability investigation was not performed for PAA-Z, since it was used throughout the investigation and remained stable for months.

The results obtained from this and previous one for Fe^{3+} adsorption [18] suggested that the both composites and their Phy forms were reusable and could be stored. For this, the obtained unchanged IR spectra for both adsorbents before and after the investigation and the long half-life of hydrolysis of Phy (100–150 years) in ground waters at 298 K [33] should be evidences.

4. Conclusion

The major disadvantages of zeolite and clay like natural inorganic ion-exchangers are their unsuitable aggregative, granule and mechanical properties, which limit their use in practical applications. In this study, PAA was used as a binding material for preparation of composites materials of Z and B to enable their practical use. The adsorptive features of B, Z and their composites were investigated for Pb^{2+} removal from various solution environments with increasing ionic strength. The effect of Phy immobilization onto the adsorbents was also of specific interest. The reusability and storage ability features of the composites were tested.

Based on the parameters derived from the Langmuir model, the modification procedures caused substantial changes in Pb^{2+} sorption capability of B and Z. The PAA involvement decreased the sorption capacity and spontaneity of B, whilst significantly improved both features of Z. The increasing ionic strength of the adsorption media increased the capacity of PAA-B but reduced that of PAA-Z. The Phy modification caused significant enhancement in Pb^{2+} sorption capacity of PAA-Z but not that of PAA-B. For both composites, the spontaneity of Pb^{2+} adsorption significantly ascended with the Phy modification. The X_M (mol kg^{-1}) and K_L (L mol^{-1}) values for Pb^{2+} adsorption from the model solution (containing Pb^{2+} as single cation) were 0.16 and 3625 for PAA-B, 0.18 and 5.1×10^5 for PAA-B-Phy, 0.28 and 13210 for PAA-Z and 1.65 and 2.0×10^5 for PAA-Z-Phy. The chemical structure of the composites was not changed after five reuses and the storage foregoing.

The studied features of the composites suggest that these materials, preferentially their use with Phy should be considered amongst the favorable adsorbents. It is envisaged that the use of PAA-B and PAA-Z composites and their Phy modifications will provide practicality and effectiveness for Pb^{2+} separation and removal procedures and they have potential research materials in studies of adsorption involving di/trivalent cations.

Acknowledgements

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