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Investigations for Modification of Polyacrylamide-Bentonite by Phytic Acid and its Usability in Fe^{3+}, Zn^{2+} and UO_2^{2+} Adsorption

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Abstract. Composite of polyacrylamide-bentonite (PAA-B) was prepared by direct polymerisation of PAA in a suspension of bentonite (B). Adsorption and thermodynamic features of phytic acid (Phy) adsorption onto B, PAA and PAA-B, and those of Fe^{3+}, Zn^{2+}, UO_2^{2+} adsorption onto PAA-B and its modification by Phy (PAA-B-Phy) have been investigated. The reusability, storagability, ion selectivity and recoverability of sorbed ions with 1 M HCl have also been considered.

The chemical and physical structure of adsorbents has been characterised by means of FT-IR and XRD. All adsorption isotherms for Phy and the ions were L-type of the Giles classification except, the one which is S type for adsorption of Phy onto PAA. The maximum adsorption capacities for the ions adsorbed were in order of $UO_2^{2+} > Fe^{3+} > Zn^{2+}$ for PAA-B and $Zn^{2+} > Fe^{3+} > UO_2^{2+}$ for PAA-B-Phy. Langmuir equilibrium constants for the adsorption of ions onto PAA-B-Phy were significantly higher than those found for PAA-B; the magnitude of increase for UO_2^{2+} was about 100. The thermodynamic parameters indicated that adsorption reactions are spontaneous in terms of adsorption free enthalpy.

The chemical structure of PAA-B-Phy was not changed at the end of the studies of reusability and storagability. The composite was selective for UO_2^{2+} of the ions of interest.

The composite of PAA-B and its modification by Phy have been used for the first time in this investigation. It is proposed that the composites can be practically used in the investigations and applications of adsorption.

Keywords: metal adsorption, uranium, composite, bentonite, polyacrylamide, phytic acid

Introduction

Clay minerals possess a layered structure and are typically suspended in aqueous solutions as fine particles having average diameter of about 2 μm. Generally they have potential for ion-exchange, being able to accommodate ionic and even nonionic foreign organic molecules (Grim, 1968; Theng, 1974). Bentonite (B) as a representative clay mineral is a clay mainly composed of montmorillonite, a 2:1 type of aluminosilicate. Its crystalline structure presents an alumina octahedral layer between two tetrahedral layers of silica which by isomorphous substitutions, require cations, denominated exchange cations (Na, Ca, Mg etc.), to compensate the negative layer charge. Cause of cation adsorption of clay minerals is that the presence of broken bands around the edges of silica-alumina units would give rise to unsatisfied charges, which would be balanced by adsorbate cations. Clay minerals may also adsorb anions due to existence of exchange spots with unbalanced charges within the lattice, e.g., an excess of aluminium in the octahedral positions (Grim, 1968).

Bentonite has Na counterions, high swelling capacity (not less than ten times its weight of water) due to strong hydration of Na ions, high cation exchange capacity (1 mol of univalent charge per kg of clay),

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specific surface areas associated with their small particle size, the ability to adsorb many ions on its surface, modifiable surface properties and low cost (Luckham and Rossi, 1999). Bentonites have been used as adsorbents in studies of adsorption of organics (pesticides, phenols etc.) and surfactants (Haderlein et al., 1996; Ceyhan et al., 1999; Celis et al., 2000; Lagadic et al., 2001) with or without surface modification. The specific affinity of some metals such as uranyl ions to bentonite is also of special interest of adsorption applications (Borovec, 1981; Chisholm-Brause et al., 1994).

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 (Domb et al., 1988; Güven and Akkas, 2000).

An important characteristic that clay minerals are able to provide adequate particle dispersion, which is necessary to obtain a uniform and stable system. This is important for many industrial applications of clay minerals (e.g., ceramic, cement, drilling fluids, paints an paper). Under certain conditions the clay particles may become aggregated, which leads to the variations of important properties required for a particular function. The aggregation of the clay particles under varying conditions of e.g., temperature and electrolytes leads to strong variations of the flow properties, which cause difficulties in its practical usage, as in some procedures in the applications of adsorption. It becomes necessary therefore to add certain additives, or polymers, to stabilize clay particles and prevent this behaviour (Luckham and Rossi, 1999). Synthesis of nano composites by direct polymer intercalation, the spatial confinement of the polymer between the dense bentonite layers, interlamellar polymerization (Lagaly, 1999), provide materials with impressive conductivity and barrier like features, beside its potential usage as ion exchange chromatography after surface modification with surfactants. However it is relatively difficult to achieve complete exfoliation of bentonite clays into a continuous polymer matrix, because of the strong electrostatic attraction between the silicate layers and the intergallery cations (Shi et al., 1996; Carrado and Xu, 1998). Having a hydrogel plated bentonite in which bentonite particles dispersed in the polymer network, a composite, without or with the intercalation should provide opportunity to use bentonite itself as an adsorbent, confined in an isolated and practically usable medium in aqua solutions. Beside this, such composites may display more properties of an effective adsorbent than polymer and bentonite individually. Metal adsorption properties of the composite could be enhanced by additional modifications.

Phytic acid is a hexaphosphate-substituted inositol ring compound which constitutes 1–6% by weight of most cereals, legumes, and oilseeds. It has a high affinity to di or trivalent minerals such as Ca, Mg, Zn, Fe and Co, in the deprotonated form. With this property, phytic acid binds minerals in the gastrointestinal tract, potentially making them biologically unavailable (Vohra et al., 1965; O'Neill et al., 1980; Brooks and Lampi, 2001). Biosynthesis, metabolism and importance in bioavailibilty of phytic acid are well documented by Loewus and Loewus (1983) and Frossard et al. (2000).

Phytic acid due to its attraction to di and trivalent cations can be used to modify the surface properties of clay or polymers. By today there is only one publication reported by Tsao et al. (1997), in which phytic acid has been used to adsorb heavy metal ions onto phytic acid immobilised on polyvinylpyridine.

The concerns of this investigation are divided into two parts: First, to synthesize of PAA as hydrogel and PAA-B as hydrogel plated/intercalated bentonite, and its characterisation by comparing the structures of each composing materials (B and PAA), and to investigate the adsorption mechanism and its thermodynamic of the adsorption of Phy onto the B, PAA, and PAA-B. Second, because of the specific interest of phytic acid and its relevance to Zn and Fe as of essential minerals (also as di and trivalent cations), to investigate the adsorption mechanism with its thermodynamic features of the adsorption of Fe^{3+} and Zn^{2+} onto PAA-B and PAA-B-Phy. Adsorption of UO_2^{2+}, as a hard lewis acid and its high affinity to bentonite, was also considered by expecting a wider applicability of the composites in sorption processes. Additional considerations were also given to the reusability and storagability, and the ion selectivity and recoverability with 1 M HCl for Fe^{3+}, Zn^{2+} and UO_2^{2+}.

Materials and Methods

Reagents

Na-montmorillonite (bentonite) in 98% purity (with a cation exchange capacity, CEC of 0.8 mol kg^{-1}),

N,N′-methylenebisacrylamid, N,N,N′,N′-tetramethylethylenediamine and Na-Phytate (Inositol hexaphosphoric acid, as dodecasodium salt; $C_6H_6O_{24}P_6Na_{12}$ with a weight composition of 30.2% Na, 20.7% Ca and 16.3% H_2O) were purchased from Sigma (USA); AA monomer, metallic Zn and Fe, $UO_2(NO_3)_2.6H_2O$ and all other chemicals were obtained from Merck (Germany). Radioactive ^{59}Fe (as $FeCl_3$ in 0.5 M HCl, 315 μg Fe/0.045 mL, 200 μC_i) was purchased from Amersham (USA). All chemicals used were of analytical reagent grade. Distilled water was used in overall investigation. No pre-treatment was applied to the reagents.

All experiments were always performed in duplicates. ±5% was the limit of experimental error of each duplicates, any experiment resulted in higher than this limit was repeated.

Preparation of PAA and PAA-B Composites

For preparation of a total of 2 g of PAA, 2 g of AA monomer, 0.2 g of N,N′-methylenebisacrylamid and 5 mg ammoniumpersulphate were dissolved in 10 mL distilled water. 100 μL of N,N,N′,N′-tetramethylethylenediamine was then added to propagate the polymerization at 25°C (Domb et al., 1988). PAA gel was washed after completion of the polymerization with distilled water until the effluent attained neutral pH. The gel was dried at ambient temperature, ground and sieved to a particle size smaller than 1 mm, and stored in polypropylene container.

1 g of bentonite in 20 mL of distilled water was stirred for 30 min by using a magnetic stirrer to obtain a homogeneous suspension. 10 mL of solution containing 2 g of AA monomer to provide a mass ratio 2:1 (an optimum plating of bentonite by the polymer was obtained in preliminary experiments) was added to the suspension and stirred additional 30 min. Finally, PAA-B composite was obtained by addition of the propagating reagent . The PAA-B granules were prepared as described for PAA. To avoid the variations in characteristics of the adsorbents as depending on their preparation, 10 g lots of PAA and PAA-B was prepared to conduct the overall investigation.

FT-IR spectrometric (Mattson 1000, UK) analysis was used to characterise the chemical structure of B, PAA and PAA-B. Pellets of samples were prepared by mixing with KBr and spectra were obtained at a resolution of 4 cm^{-1}. XRD analysis were carried out on a Regaku DMAX IIIC using Cu K_α radiation, a NAI detector, 2θ/min scan rate.

The change in swelling feature of PAA-B was compared to that of PAA and B. Dried samples were weighed 0.1 g of each and let to swell in tubes for the equilibrium with water, the swollen samples were then weighed to find swelling ratio as percentage with reference to the dry weights.

Phytate Adsorption onto B, PAA and PAA-B

A stock solution of phytate in concentration of 5.4×10^{-3} mol L^{-1} was prepared by dissolving the required amount of sodium phytate in distilled water. 0.1 g of B, PAA or PAA-B were weighed in polypropylene tubes. 10 mL of phytate solutions at concentrations ranging from 1.0×10^{-3} to 2.0×10^{-3} mol L^{-1} prepared from the stock solution with appropriate dilution were added to each of the samples. The pH of the solutions were in a range of 9–11. The adsorbent-solution systems were then equilibrated for 24 h by occasionally shaking at 25°C in a thermostatic water bath. The suspensions were centrifuged at 3000 g for 10 min and the supernatants at equilibrium were transferred into polypropylene tubes. Phytate concentrations in supernatants were then determined with the precipitation method modified from de De Boland (1975). A constant amount of Fe^{3+} solution labelled with ^{59}Fe in 0.6% HCl containing 5% Na_2SO_4 was added to each supernatant. After completion of the precipitation, ^{59}Fe activity at equilibrium was counted. The activity values transformed into phytate concentrations by the use of a calibration curve (activity versus phytate concentration) derived from activity in equilibrium solutions obtained from the precipitation of phytate at known concentrations. Chemical structure of PAA-B-Phy was also evaluated by its FT-IR spectrum.

Phytate adsorbed PAA-B (PAA-B-Phy) samples were prepared at a constant phytate concentration (4.5×10^{-3} mol L^{-1}) for 0.1 g of PAA-B samples for the investigations of metal adsorption, reusability, storagabilty and ion selectivity.

Iron, Zinc and Uranyl Adsorption onto PAA-B and PAA-B-Phy

The investigation for metal adsorption onto PAA-B and PAA-B-Phy was performed for each of Fe^{3+}, Zn^{2+} and UO_2^{2+} ions. 0.1 g of adsorbents were interacted with 10 mL solutions of the ions at concentrations ranging

from 0.7×10^{-3} to 8.9×10^{-3} mol L^{-1} for Fe^{3+} labelled with ^{59}Fe, $0.2\times10^{-3}-5.4\times10^{-3}$ mol L^{-1} for Zn^{2+} and $0.9\times10^{-3}-3.0\times10^{-3}$ mol L^{-1} for UO_2^{2+} ions. The adsorbent-solution systems were equilibrated for 2 and 24 h by occasionally shaking at 25°C in a thermostatic water bath. A fraction of 0.5 mL solution was taken at the end of each equilibrium period for determination of the ion concentration.

Ion concentrations were determined by flame atomic absorption spectrophotometer, FAAS (Unicam-929, UK) for Zn^{2+}, UV-VIS spectrophotometer (Shimadzu-160A, Japan) after complexation with sodium salicylate (Lurie, 1975) for UO_2^{2+}, and gamma spectrometer [NAI(Tl) detector combined with a ND-65 multichannel analyzer, USA] for activity of ^{59}Fe tracer used for Fe^{3+}.

Reusability, Storagability and Selectivity Properties of PAA-B and PAA-B-Phy

0.1 g of PAA-B and PAA-B-Phy (prepared at constant Phy concentration) samples, as being three for reusability and five for storagability investigations were weighed in polypropylene tubes. The reusability and storagability was tested only for Fe^{3+} since the principle concern of this investigation was not to developed separation procedures for the elements of interest.

10 mL of 3.1×10^{-3} mol L^{-1} Fe^{3+} solution (at pH = 3.5) containing ^{59}Fe tracer was added onto the adsorbents and equilibrated for 24 h. Fe^{3+} adsorbed samples were transferred in to polypropylene columns (H = 10 cm, Φ = 1 cm). On the basis of preliminary studies, 10 mL of 1 mol L^{-1} HCl was sufficient to elute whole Fe^{3+} adsorbed, the contents of the columns were eluted with the HCl. The columns were washed with distilled water until the effluent had a neutral pH. The columns were treated for five times with the same adsorption and recovery procedures described above. Each of the five samples prepared for the storagabilty was treated with the Fe^{3+} adsorption procedure with an interval of one week.

The adsorption from solutions containing the pairs and all the ions were investigated for the ion selectivity of the adsorbents. 10 mL of the solutions of ions at equivalent concentrations of 500 ppm for each (8.9×10^{-3} mol L^{-1} for Fe^{3+}, 7.7×10^{-3} mol L^{-1} for Zn^{2+} and 1.8×10^{-3} mol L^{-1} for UO_2^{2+}) were added onto 0.1 g of the adsorbents in columns and the concentrations at equilibrium after 24 h for PAA-B and 2 h for PAA-B-Phy (since 2 h was sufficient to attain equilibrium) were determined.

Temperature Effect on Adsorption of Phytate and Metal Ions

Temperature effect on adsorption for determination of thermodynamic parameters was studied for two temperatures chosen in a wide range (5 and 40°C) to well differentiate the dependence of the adsorption to the temperature.

0.1 g of adsorbents were interacted with 10 mL of the solutions of 4.5×10^{-3} mol L^{-1} phytate for PAA-B, 2.7×10^{-3} mol L^{-1} Fe^{3+}, 2.5×10^{-3} mol L^{-1} Zn^{2+}, and 0.4×10^{-3} mol L^{-1} UO_2^{2+} for PAA-B and PAA-B-Phy at 5 and 40°C.

Data Evaluation

The amount of adsorption (Q, mol kg^{-1}) were calculated from

$$Q = [(C_i - C_e)/w]\,V \tag{1}$$

where C_i and C_e are the initial and equilibrium concentrations of the adsorbates (mol L^{-1}), w is the amount of adsorbent (kg) and V is the volume of solution (L) interacted with the adsorbents.

The adsorption isotherms were fit to the Langmuir and Freundlich equations (Altın et al., 1998),

$$C_e/Q = C_e/X_M + 1/(KX_M) \tag{2}$$

$$\ln Q = \ln a + \beta \ln C_e \tag{3}$$

where X_M and K are maximum adsorption capacity (mol kg^{-1}) and adsorption equilibrium constant (L mol^{-1}) in Eq. (2) (Jin and Zu, 2000). a and β are positive valued empirical Freundlich constants parameters with $0 < \beta < 1$ in Eq. (3). X_M and K, or a and β can be calculated from the linear plot of C_e/Q vs. C_e, or ln Q vs. ln C_e correspondingly.

A t-test was applied to test the significance of the regression coefficients (r) obtained from the compatibility of experimental data to the equations of the isotherms; $p < 0.01$ was considered for the significancy (Miller and Miller, 1989).

To calculate thermodynamic parameters, the following equations were used (Eligwe et al., 1999; Rauf and

Tahir, 2000).

$$\Delta G^\circ = -\mathrm{RT}\ln \mathrm{K} \quad (4)$$

$$\ln(K_{e2}/K_{e1}) = -\Delta H^\circ/R(1/T_2 - 1/T_1) \quad (5)$$

$$\Delta S^\circ = (\Delta H^\circ - \Delta G^\circ)/T \quad (6)$$

where R is the gas constant, K (from Langmuir), K_{e1} and K_{e2} are the equilibrium constans at temperature T (25°C), T_1 (5°C) and T_2 (40°C) respectively which, were calculated from

$$K_{e1,2} = C_{e1,2}/C_{a1,2} \quad (7)$$

where C_e and C_a are the equilibrium concentrations of the adsorbate in solution and on the adsorbent correspondingly (Singh and Tiwari, 1997; Panayotova, 2000).

Results and Discussion

Phytate Adsorption onto B, PAA and PAA-B

The magnitude of swelling were 1700% for PAA-B, 1400% for PAA and 1150% for B. By considering the PAA contents of the PAA-B (0.07 of 0.1 g), it is obvious that the swelling property of the PAA-B increased. The reason should be increasing tendency of the composite to adsorb water due to delamination and surface modification of the clay (Starodoubtsev et al., 2000).

The FT-IR spectra of B, PAA-B, Phy and PAA-B-Phy are provided in Fig. 1. When the FT-IR spectra of B and PAA-B (Figs. 1(a) and (b)) were compared, the clear decrease in intensities at 425 and 1089 cm^{-1} of the Si─O, near 3700 cm^{-1} of the O─H stretching bands of the surface silanol, and 808 and 3642 cm^{-1} of Al─O─H of B were observed. This might signify that there is interfacial interactions between the siloxane oxygen atoms or hydroxylated edges on the basal surface of the silicate layers of B with PAA (Shi et al., 1996). This interaction is explained as the establishment of hydrogen bonds between the ─Si─OH and ═Al─OH surface groups and the neutral polyacrylamide, $-CH_2-CH-C=O-NH_2$ (Pefferkorn, 1999).

Beside this possible chemical binding, there should also be physical interaction between B and PAA resulting in plating B by PAA (Shi et al., 1996; Carrado and Xu, 1998). Obvious increase in basal spacing from 1.18 nm (11.8 Å) of B to 1.41 nm (14.1 Å) of PAA-B should be evident for the presence of AA in the interlayers of B (Fig. 2) but, intercalated nanocomposite had a more or less regular basal spacing (1.41 nm) equivalent to a gallery height only 0.23 nm larger than that of B. This should indicate the presence of monolayer molecules between the silicate layers (Shi et al., 1996; Lagaly, 1999).

The bands in spectrum of PAA-B obtained before and after Phy adsorption (Figs. 1(b) and (d)) implied that Phy adsorption on the composite is chemical as in Phy adsorption onto B for which the L-type isotherms (see below) were evident (Giles et al., 1960). In fact the difference between the FT-IR spectra of PAA-B

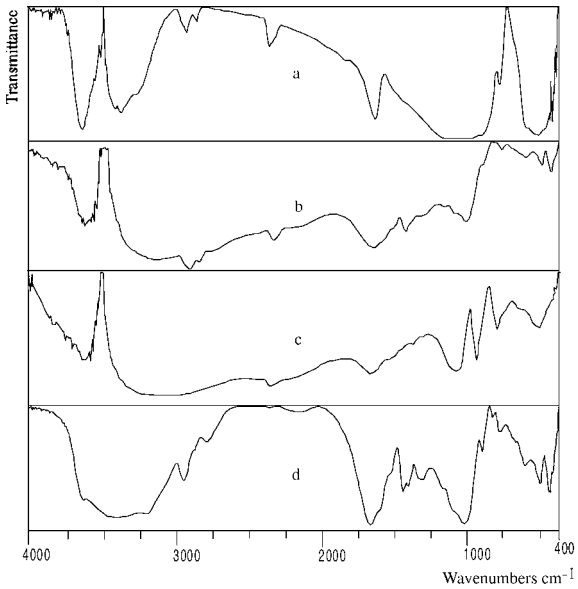

Figure 1. FT-IR spectra of B (a), PAA-B (b), Phy (c) and PAA-B-Phy (d).

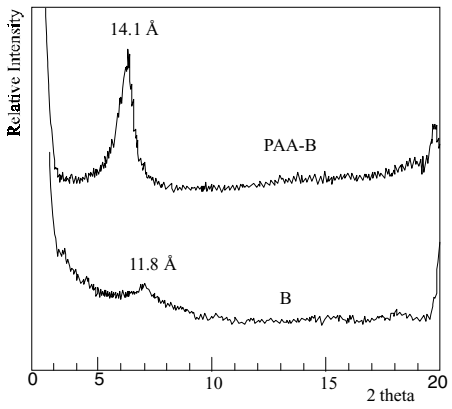

Figure 2. XRD basal diffraction of B and PAA-B.

and PAA-B-Phy (Figs. 1(b) and (c)) should support this approach. The disappearance at 2560–2700 cm^{-1} of the P─OH of Phy explained the binding between PAA-B and Phy over the oxygen of P─OH and OH of B in PAA-B. The intense increase at 3640 cm^{-1} and 1089 cm^{-1} should be due to the interaction between the (Mg─Al)..OH and P─OH, and Si─O and P─OH respectively (Van der Maas, 1972).

The shape of adsorption is important characteristic because it provides information about adsorption mechanisms. The isotherms obtained for the adsorption of phytate onto B, PAA and PAA-B are provided in Fig. 3.

Adsorption isotherms for Phy onto PAA, B and PAA-B are the S, H and L-types (Fig. 3) according to the Giles classification (Giles et al., 1960). S-type isotherm suggests the solid has a higher affinity for the solvent than for the solid at low concentrations. Phytate adsorption onto B provides the H-type showing a high affinity of the adsorbent surface for the adsorbate, where the adsorbed species are often large units (i.e. ionic micelles or polymeric molecules) but sometimes they are apparently single ions exchanging with others of much lower affinity for the surface. The amount of adsorption rises hyperbolically with rising concentration of adsorbate. The isotherms of S and H-types are transformed into L-type for the PAA-B composite. This indicates that adsorbates do not suffer competition with the solvent molecules and the adsorption increases with increasing solute concentration hyperbolically (Giles et al., 1960). The transformation into L-type may also imply that the adsorbent B is dominant to the PAA in PAA-B composite in terms of the adsorption of Phy, so Phy is adsorbed preferentially onto B rather than PAA, but the degree of adsorption to PAA-B is less than that of B. This could be explained by the decrease in efficient adsorption surface due to coverage of B by PAA. This change can be seen from the adsorption parameters (Table 1) derived from Langmuir equation (Eqs. (2) and (3)) where $(X_M)_B > (X_M)_{PAA\text{-}B}$.

The thermodynamic parameters (Table 2) derived from Eqs. (4)–(6) for adsorption of Phy onto B and PAA-B also indicate that the adsorption for B is more spontaneous than that for the PAA-B in terms of the apparent change in free adsorption enthalpy and entropy as being $(\Delta G^\circ)_B < (\Delta G^\circ)_{PAA\text{-}B}$ and $(\Delta S^\circ)_B > (\Delta S^\circ)_{PAA\text{-}B}$. The positive values for the adsorption entropy indicates that the adsorption process is irreversible (Eligwe et al., 1999). The positive values of enthalpy change, ΔH°, show the adsorption of Phy is endothermic and $(\Delta H^\circ)_B > (\Delta H^\circ)_{PAA\text{-}B}$, which is an indication of the existence of a strong interaction between the adsorbate and adsorbent (Rauf and Tahir, 2000).

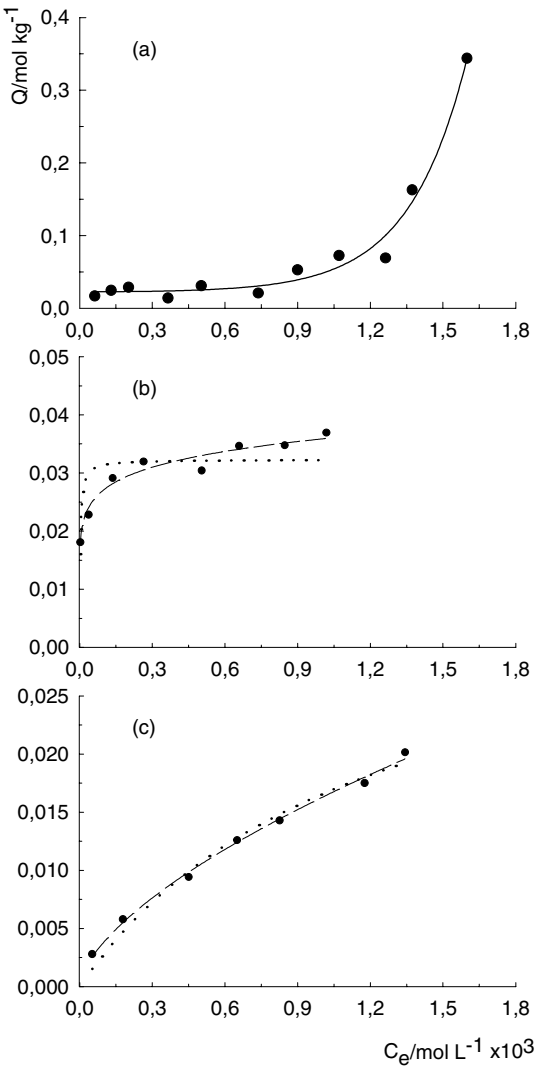

Figure 3. Adsorption isotherms of phytate onto PAA (a), B (b) and PAA-B (c) [•, experimental; . . . . . , Langmuir; - - -, Freundlich].

Iron, Zinc and Uranyl Adsorption onto PAA-B and PAA-B-Phy

The isotherms obtained for the adsorption of Fe^{3+} onto PAA-B and PAA-B-Phy are provided in Fig. 4.

In upper panel of the figure, adsorption of Fe^{3+} onto PAA-B was shown for 2 and 24 h since adsorption of

Table 1. Langmuir and Freundlich parameters calculated for phytate adsorption onto B and PAA-B.

	Langmuir			Freundlich		
Adsorbent	X_M/mol · kg^{-1} × 10^3	K/Lmol^{-1}	r^*	$a \times 10^3$	β	r^*
B	36	29800	0.997	0.08	0.12	0.982
PAA-B	28	1440	0.955	1.02	0.60	0.999

*Significant at $p < 0.01$ for coefficient of correlation, r, found for the Langmuir or Freundlich plots.

Table 2. Thermodynamic parameters calculated for phytate adsorption onto B and PAA-B.

	ΔG°/kJmol^{-1}	ΔH°/kJmol^{-1}	ΔS°/Jmol^{-1} K^{-1}
B	−25.5	11.5	124.3
PAA-B	−18.0	5.2	78.0

Fe^{3+} was completed in 24 h unlike of Zn^{2+} and UO_2^{2+} for which the time of completion was 2 h. The isotherms of Fe^{3+} onto both PAA-B and PAA-B-Phy (Fig. 4) are in L-type according to the Giles classification (Giles et al., 1960). The parameters derived from Langmuir and Freundlich equations and compatibility of the isotherms to these equations are shown in Table 3.

When the parameters found for Fe^{3+} were compared in terms of their magnitude and change by the time and adsorbents; The X_M, is time dependent for Fe^{3+} and $(X_M)^{24\,h}_{PAA\text{-}B} > (X_M)^{2\,h}_{PAA\text{-}B}$, as expected because of incomplete adsorption in 2 h. The change of the X_M with adsorbent is in order of $(X_M)_{PAA\text{-}B\text{-}Phy} > (X_M)_{PAA\text{-}B}$ as both being for 2 h equilibrium (completion of adsorption to PAA-B-Phy), which shows the increase in adsorption of Fe^{3+} onto PAA-B-Phy. The value of K (equilibrium constant), as being related to adsorption surface energy and measurement of affinity to the adsorbate (Bajpai and Sachdeva, 2000), for Fe^{3+} to PAA-B-Phy is twice the higher than that of PAA-B for 2 h equilibrium time. As being confirming each other, the a and β values for Fe^{3+} (2 h) decreased with the Phy modification. No such evaluation was possible for Zn^{2+} and UO_2^{2+} since Freundlich equation were not fit to experimental data.

The isotherms obtained for Zn^{2+} were L and H-type for PAA-B and PAA-B-Phy according to the Giles classification (Giles et al., 1960) (Fig. 5).

The parameters found from Langmuir indicate that the values are in order of $(X_M)_{PAA\text{-}B\text{-}Phy} > (X_M)_{PAA\text{-}B}$ and $(K)_{PAA\text{-}B\text{-}Phy} > (K)_{PAA\text{-}B}$. This supports that Zn^{2+} has a higher affinity to PAA-B-Phy than PAA-B.

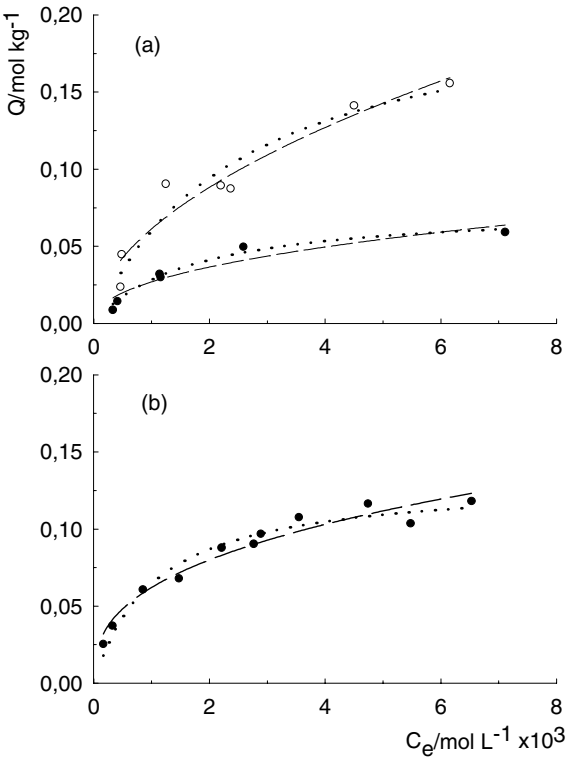

Figure 4. Adsorption isotherms of Fe^{3+} onto PAA-B (a) for 2 and 24 h, and PAA-B-Phy (b) for 2 h equilibrium [● and ○, experimental for 2 and 24 h; . . . ., Langmuir; - - -, Freundlich].

For UO_2^{2+}, the shape of the isotherms were in L and H-type for PAA-B and PAA-B-Phy respectively (Fig. 6).

For the values of the Langmuir parameters of UO_2^{2+}, X_M for PAA-B-Phy was lower than that for PAA-B but, there was not much change as in Fe^{3+} and Zn^{2+}. There was an enormous change in K values in favour of PAA-B-Phy when compared those found for Fe^{3+} and Zn^{2+}. This indicates that the PAA-B-Phy is selective adsorbent for UO_2^{2+} in comparison to Fe^{3+} and Zn^{2+}.

Table 3. Langmuir and Freundlich parameters calculated for metal adsorption onto PAA-B and PAA-B-Phy.

	Langmuir			Freundlich		
Metal	X_M/mol kg^{-1} × 10^3	K/Lmol^{-1}	r^1	$a \times 10^3$	β	r^1
Fe^{3+} (2 h)$^3_{PAA\text{-}B}$	76	540	0.988	1.55	0.606	0.947
Fe^{3+} (24 h)$_{PAA\text{-}B}$	226	340	0.934	3.76	0.609	0.935
Fe^{3+} (2 h)$_{PAA\text{-}B\text{-}Phy}$	131	1030	0.991	1.02	0.410	0.988
Zn^{2+}(2 h)$_{PAA\text{-}B}$	47	12100	0.997	0.14	0.180	0.957
Zn^{2+}(2 h)$_{PAA\text{-}B\text{-}Phy}$	165	23300	0.997	na^2	na	na
UO_2^{2+}(2 h)$_{PAA\text{-}B}$	193	7970	0.935	0.13	0.57	0.895
UO_2^{2+}(2 h)$_{PAA\text{-}B\text{-}Phy}$	114	663000	0.999	na^2	na	na

[1]Significant at $p < 0.01$ for coefficient of correlation, r, found for the Langmuir or Freundlich plots.
[2]Not applicable, or the r is insignificant at $p > 0.01$.
[3]Time elapsed for equilibrium from which the isotherms derived.

The selectivity sequence was $UO_2^{2+} \approx Zn^{2+} > Fe^{3+}$ for PAA-B and $UO_2^{2+} > Zn^{2+} > Fe^{3+}$ PAA-B-Phy in terms of K comparison.

Thermodynamic parameters derived from Eqs. (4)–(6) are provided in Table 4.

The ΔG° values as a measure of the spontaneity of adsorption are in the same sequence with K, as expected. The ΔS° values for PAA-B-Phy also support the spontaneity as in order of $UO_2^{2+} > Zn^{2+} > Fe^{3+}$, so the process is controlled by the entropy (Atun et al.,

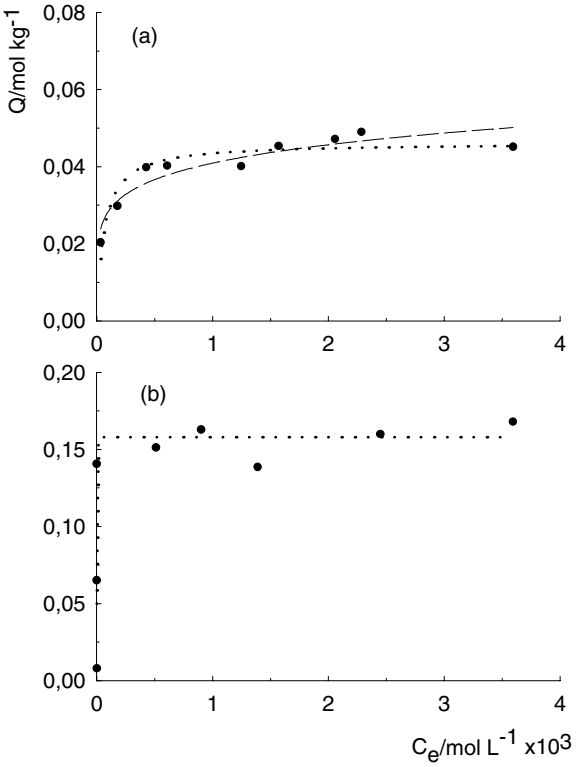

Figure 5. Adsorption isotherms of Zn^{2+} onto PAA-B (a) and PAA-B-Phy (b) [•, experimental; . . . . . , Langmuir; - - -, Freundlich] (data for PAA-B-Phy is unfitting to the Freundlich equation).

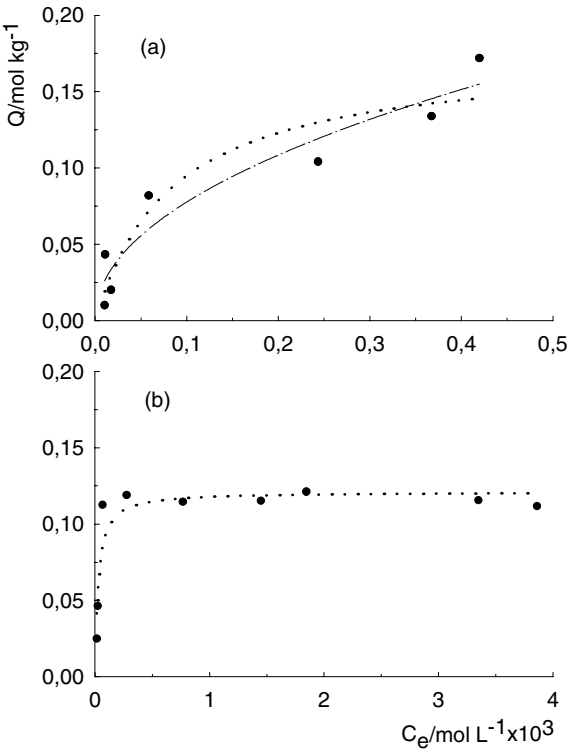

Figure 6. Adsorption isotherms of UO_2^{2+} onto PAA-B (a) and PAA-B-Phy (b) [•, experimental; . . . . . , Langmuir; - - -, Freundlich] (data for PAA-B-Phy is unfitting to the Freundlich equation).

Table 4. Thermodynamic parameters for metal adsorption onto PAA-B and PAA-B-Phy.

	PAA-B			PAA-B-Phy		
	ΔG°/kJ mol^{-1}	ΔH°/kJ mol^{-1}	ΔS°/J mol^{-1} K^{-1}	ΔG°/kJ mol^{-1}	ΔH°/kJ mol^{-1}	ΔS°/J mol^{-1} K^{-1}
Fe^{3+}	−15.6	−21.8	−20.8	−17.2	−63.8	−156.4
Zn^{2+}	−23.3	−3.4	66.9	−24.9	−39.9	−50.3
UO_2^{2+}	−22.3	−47.1	−83.3	−33.2	70.5	347.9

Table 5. Reusability of PAA-B and PAA-B-Phy, and storagability of PAA-B-Phy for adsorption of Fe^{3+}.

	Reusabilty			
	Adsorption/%		Storagability of PAA-B-Phy	
Reusage no*	PAA-B	PAA-B-Phy	Time elapsed (wk)	Adsorption/%
1	25.3	35.2	Initial	35.2
2	27.6	31.3	1	31.1
3	30.2	26.8	2	24.6
4	35.7	31.5	3	25.1
5	29.8	29.7	4	33.9
Mean ± SDM	29.7 ± 3.9	30.1 ± 3.0		30.0 ± 4.9

*Number of sequential usage of the adsorbent.

1998), whilst the ΔH° values were in the reverse order. No such conclusion was possible from the ΔS° and ΔH° values obtained for PAA-B. Changes for all ΔS° values suggest the existence of some structural changes at the solid–liquid interface (Rauf and Tahir, 2000).

Reusabilty, Storagability and Selectivity Properties of PAA-B and PAA-B-Phy

As seen from the results obtained for reusability in Table 5, the difference between adsorption percentage of Fe^{3+} onto PAA-B and PAA-B-Phy were not significant ($p < 0.01$) i.e. the maximum adsorption capacity was not influenced by the Phy modification of PAA-B. On the base of the FT-IR spectra obtained for the both adsorbents before and after the investigation, finding no structural change was worthy to note.

Repeatable adsorption values were also obtained from the storagability investigation ($p < 0.05$, when a Q test was applied for outlier, Miller and Miller, 1989) for PAA-B-Phy (Table 5). There was no need to perform such investigation for PAA-B because of its use in overall investigation. The unchanged FT-IR spectra of PAA-B-Phy taken 4 weeks after its synthesis and usability foregoing were evident for the structural stability of the composites.

The selectivity features of the adsorbents for the pairs of ions and for all are shown in Table 6. Whilst the both adsorbent sorbed Zn^{2+} from solution containing only Zn^{2+} ions, there were no considerable amount of Zn^{2+} (none for PAA-B in any case) adsorption in the presence of any other studied ions. The preference of Fe^{3+} to Zn^{2+} from solution containing this pairs could be explained by the difference in ionic radius of these ions, 0.74 and 0.64 Å Zn^{2+} to Fe^{3+} respectively (Greenwood and Earnshaw, 1995). Fe^{3+} was adsorbed from solutions containing the pairs or all ions of interest. There was a considerable increase in adsorption of Fe^{3+} in favour of PAA-B-Phy.

The most adsorbable or preferable ion was UO_2^{2+} in any case despite the fact that its radius is the biggest, ≈5 Å (Dai et al., 1997). The preference of the adsorbents for this ion is due to the high stability of complexes formed by UO_2^{2+} and the active sites of bentonite, Si─O and Mg─O, in PAA-B and additionally phosphate groups of PAA-B-Phy. However, it is known that UO_2^{2+} is a strong Lewis acid so the complexation with hard bases such as oxygen containing ligands is expected to be strong (Dai et al., 1997). It was noteworthy that the

Table 6. Metal selectivity of PAA-B and PAA-B-Phy from solutions containing ion pairs and all ions of interest.

	Adsorption/%	
Metal ions	PAA-B	PAA-B-Phy
Fe^{3+}	24.1[1] (100)[2]	33.8 (93.3)
Zn^{2+}	0.0	2.4 (6.6)
Fe^{3+}	26.4 (22.2)	35.0 (27.8)
UO_2^{2+}	92.5 (77.8)	91.1 (72.2)
Zn^{2+}	0.0	13.0 (12.1)
UO_2^{2+}	93.1 (100)	94.7 (87.9)
Fe^{3+}	17.6 (17.4)	26.3 (22.7)
Zn^{2+}	0.0	0.0
UO_2^{2+}	83.8 (82.6)	89.5 (77.3)

[1]As percentage adsorption of the amount of ion added into the solution.
[2]As percentage adsorption of total ion adsorption onto the adsorbent.

amounts of adsorption of UO_2^{2+} was not significantly changed by the Phy modification, but the equilibrium constant, K, was about 100 times higher than that for PAA-B.

In conclusion, this investigation suggests that the PAA-B composite and its modification by Phy have potential as research materials in studies of adsorption. It is proposed that using such composites provides practicality and effectiveness for studies of adsorption and separation procedures.

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