

Adsorption of Lead on to Poly(acrylamide-maleic acid)-Based Hydrogel Composites

Poli(Akrilamid-Maleik Asit) Temelli Hidrojel Kompozitlere Kurşun Adsorpsiyonu

Research Article

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ABSTRACT

In this study, adsorptive features of the hydrogel (PAA-MA) and composites (PAA-MA-B and PAA-MA-Z) were investigated for lead (Pb^{2+}). Adsorption of lead on hydrogels and composites is studied by batch adsorption technique at 25°C. In the experiments of the adsorption, the classical Langmuir, Freundlich and Dubinin-Radushkevich (DR) models sorption models were fitted to the results. Isotherms were L and H type of Giles classification and evaluated with reference to Langmuir, Freundlich and Dubinin-Radushkevich (DR) models. PAA-MA-B had higher adsorption capacity than PAA-MA-Z for lead ion. To increase the adsorption capacity of Pb^{2+} ion preparing the PAA-MA hydrogel. It has also been observed with increasing B and Z content Pb^{2+} ion adsorption. The values of enthalpy and entropy changed were positive for lead ions for PAA-MA, PAA-MA-B and PAA-MA-Z. The negative free enthalpy change value indicated that the adsorption process is spontaneous in the sequence of PAA-MA > PAA-MA-B > PAA-MA-Z. Free energy values derived from DR model implied that the sorption process is the ion exchange. The reusability tests for Pb^{2+} for five uses proved that the composites were reusable after complete recovery of the loaded.

Key Words

Polyacrylamide-maleic acid (PAA-MA), polyacrylamide-maleic acid-bentonite (PAA-MA-B), polyacrylamide-maleic acid-zeolite (PAA-MA-Z), lead, adsorption, hydrogel, composites.

ÖZET

Bu çalışmada, poliakrilamid-maleik asit hidrojel (PAA-MA) ve kompozitlerine (PAA-MA-B ve PAA-MA-Z) kurşun adsorpsiyonu araştırıldı. Adsorpsiyon 25°C'lik kesikli sistemde çalışıldı. Deneysel izotermelerin Langmuir, Freundlich ve Dubinin-Radushkevich modellerine uyumundan türetilen parametreler bu ilgiyi kanıtlamıştır. Adsorpsiyonun derişimle deęişiminin incelenmesi sonucu elde edilen izotermelerin tümünün Giles sınıflandırmasındaki L veya H tipte olduęu görülmüştür. PAA-MA-B kompoziti PAA-MA-Z kompozitinden daha iyi adsorpsiyon kapasitesine sahip olduęu görülmüştür. Adsorpsiyon kapasitesi hidrojeldeki B ve Z bileşenlerinin artması ile artış göstermektedir. Adsorpsiyon entalpi ve entropi deęişim deęerleri, adsorpsiyonun, araştırması yapılan tüm adsorbanlar için pozitif deęerlidir. Serbest entalpi (ΔG) deęerleri ise adsorpsiyon sürecinin beklenildięi gibi kendiliğinden yürüdüęünü göstermiştir (PAA-MA > PAA-MA-B > PAA-MA-Z). DR modelinden türetilen serbest enerji açısından da tüm adsorbanlar için kimyasal olduęunu kanıtlamıştır. Kompozitlerin yeniden kullanılabilirlikleri ile ilgili sonuçlar tekrar kullanılabilir olduęunu göstermiştir.

Anahtar Kelimeler

Poliakrilamid-maleikasit (PAA-MA), poliakrilamid-maleikasit-bentonite (PAA-MA-B), poliakrilamid-maleikasit-zeolite (PAA-MA-Z), kurşun, adsorpsiyon, hidrojel, kompozit.

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INTRODUCTION

Given the growing use of a large variety (wide applications of mining, chemical, electroplating, petroleum refining, paper and pulp industries) of lead, pollution from lead in wastewater is one of the major environmental problems of world [1]. For this reason, the remediation treatment and removal of lead in waste and contaminated water have been a major concern of process industries [2,3].

Hydrogels can be non-toxic, chemically stable and they exhibit a low interfacial tension with aqueous environments [4,5]. The hydrogels based polyelectrolyte structures are crosslinked hydrophilic polymers capable of swelling retain water without dissolving. PAA-MA hydrogels are highly hydrophilic and neutral but are not reusable materials [6]. The swelling of PAA-MA is important problem about the studying of column techniques and metal adsorption.

In recent studies, hydrogels-clay and zeolite nanocomposites have attracted much attention in many fields of polymer industry due to improved mechanical, thermal, barrier and fire retardant properties, dimensional stability compared with the pure polymer or conventional composites [7].

The adsorption processes are generally known to be one of the most effective techniques for removal of environmentally hazardous metals [2]. Adsorbents should have strong affinity and high loading capacity for targeted metal ions. 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 adsorbent [2,8,9]. The aggregation and coagulation of these minerals under varying conditions of temperature and electrolytes which lead variations in flow properties of these minerals are undesired features for their practical use as adsorbents [2,10,11].

Due to their suitable features, polymer-based composites, composites in particular has been the scope of considerable number of adsorption investigations. Amongst these, poly(*N*-isopropylacrylamide) (PNIPAM) hydrogel was

used for Pb^{2+} in view of kinetics and diffusion [12]. The hybrid material features of cellulose-manganese for removal of Pb^{2+} of interest in studies performed by Maliyekkal et al., 2010 [13]. For the purpose of lead ion adsorption from aqueous solutions, we have synthesized different functional groups containing acrylamide-based hydrogels [14,15].

The aim of the work is increase the adsorption capacity of Pb^{2+} on the novel nanocomposites. In this study, the preparation of the acrylamide-maleic acid based composites (PAA-MA-B and PAA-MA-Z) and their adsorptive features with reference to the dependency on concentration were investigated for lead (Pb^{2+}). Additional considerations were also given to the reusability and thermodynamic properties of the adsorption.

EXPERIMENTAL

Reagents

Na-montmorillonite (bentonite) in 98% purity (with a cation exchange capacity, CEC of 0.8 mol kg^{-1}), $Pb(NO_3)_2$, was purchased from SigmaAldrich. The Zeolite mineral is composed of ~90% zeolite, as clinoptilolite $\{(Na,K)_6[Al_6Si_{30}O_{72}].24H_2O\}$ and mordenite $\{Na_3KCa_2[Al_8Si_{40}O_{96}].28H_2O\}$, 5% quartz, 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. The univalent cation exchange capacity (CEC) zeolite was 1.64 meq g^{-1} [16]. The zeolite rocks were crashed, ground and sieved to 100 mesh size. No pre-treatment was applied to the chemicals, clay and zeolite.

Acrylamide (AA) and maleic acid (MA), monomers, the activator *N,N'*-methylene-bisacrylamide, *N,N,N',N'*-tetramethylethylene diamine (TEMED), the initiator, ammonium peroxydisulfate APS ($H_8N_2O_8S_2$), 4-(2-pyridylazo) resorcinol (PAR), Arsenazo III (disodium salt), 4-(2'-pyridylazo)-resorcinol (PAR) were purchased from Sigma. All chemicals used were of analytical reagent grade.

All experiments were always performed in duplicates. $\pm 5\%$ was the limit of experimental

error of each duplicates, any experiment resulted in higher than this limit was repeated.

Preparation of PAA-MA, PAA-MA/B and PAA-MA/Z

Preparation of hydrogels (PAA-MA)

In the first part of this study, PAA-MA hydrogels were synthesized by bulk copolymerization of AA and MA using N,N,N',N'-tetramethylethylenediamine as the crosslinker. APS and TEMED were used as an initiator and an activator, respectively. The solution containing AA (4 g), MA (0.36 g), N,N,N,N (1.2 g), APS (4 mL) and TEMED (800 μ L) were prepared in 40 mL water mixture [17].

Preparation of modified PAA-MA hydrogels (PAA-MA/B and PAA-MA/Z)

For preparation of 6 g of PAA-MA/B; 4 g of B or Z in 20 mL of water was stirred 15 min to obtain a homogeneous suspension. 10 mL of solution containing 0.135 g maleic acid, 20 mL of solution containing 1.5 g of acrylamide monomer to provide a mass ratio 2:1 was added to the suspension and stirred additional 4 hours. 2 mL of N,N'-methylenebisacrylamide as cross linking agent and 50 mg ammonium persulphate dissolved in 10 mL distilled water was contained on to the suspension. Finally, 200 μ L of N,N,N',N'-tetramethylethylenediamine was added to propagate the polymerization at 25°C. PAA-MA/B or PAA-MA/Z composites were washed after completion of the polymerization with distilled water until the effluent attained neutral pH. The composites were dried at ambient temperature, ground and sieved to a particle -25 mesh size, and stored in polypropylene container [14].

Concentration dependence of Pb²⁺ adsorption

The concentration dependence of adsorption was investigated for PAA-MA, PAA-MA-B and PAA-MA-Z. 0.1 g fractions of PAA-MA, PAA-MA-B and PAA-MA-Z were equilibrated with 10 mL of 10⁻⁵ - 10⁻² mol L⁻¹ (2-2000 mg L⁻¹) Pb²⁺ solutions. The adsorbent-solution systems were equilibrated for 24 hours at 298 K in a thermostatic water bath and the suspensions were then centrifuged at 2500 rpm for 3 min.

PAR was used as complex forming reagent for determination of Pb²⁺ in the supernatants [2]. A solution of 3.5 x 10⁻³ mol L⁻¹ of PAR in 0.7 mol L⁻¹ of Tris/HCl at pH 8-9 was prepared. A 50 μ L fraction of supernatant was added onto 3 mL of the reagent and the absorbance of the formed metal complex was measured at 510 nm (Shimadzu-160A, Japan).

Temperature dependence of adsorption

Temperature effect on adsorption for determination of thermodynamic parameters was studied for five temperatures; 278, 288, 298, 308 and 313 K. Duplicates (0.1 g) of PAA-MA, PAA-MA-B and PAA-MA-Z were equilibrated with solutions of Pb²⁺ at 4.8 x 10⁻³ mol L⁻¹ (1000 mg L⁻¹), at the chosen temperatures for 24 h. The samples were subjected to the same procedure described above, equilibrium concentrations and adsorbed amounts were then determined.

Reusability

0.1 g of the composites in polypropylene columns (100 mm height x 10 mm i.d., with a glass-wool over its stopcock) was equilibrated with 10 mL of 4.8 x 10⁻³ mol L⁻¹ Pb²⁺ solutions for 4 h (adequate time for completion of the adsorption after kinetic studies). The adsorbed amounts were derived from the contents of solutions at equilibrium. The contents of columns was eluted with 15 mL of 1 mol L⁻¹ HCl with a flow rate of 0.5 mL min⁻¹. The complete recovery of the adsorbed for Pb²⁺ was justified by Pb²⁺ determination in the eluents. The columns was then reconditioned with distilled water until the effluents had a neutral pH. Each sample was subjected to the same procedure for 4 sequential times to provide 5 uses in total.

Data evaluation

The amounts of adsorption of the Pb²⁺ (Q, mol kg⁻¹) was calculated from $Q = [(C_i - C_e)V/w]$, where C_i and C_e are the initial and equilibrium concentrations (mol L⁻¹), w is the mass of adsorbent (kg) and V was the solution volume (L).

Experimentally obtained isotherms (Q vs C_e) were elucidated with their compatibility to the Langmuir, Freundlich and Dubinin-Radushkevich (DR) models.

The Langmuir [$Q=(K_L X_L C_e)/(1+K_L C_e)$] and Freundlich ($Q=X_F C_e^\beta$) models were fit to the isotherms experimentally obtained, where X_L is the monolayer sorption capacity (mol kg^{-1}), K_L was the adsorption equilibrium constant (L mol^{-1}) related to the adsorption energy. X_F and β were empirical Freundlich constants associated with the capacity and intensity of adsorption (β represents the heterogeneity of the adsorptive surface). The isotherms were also evaluated with reference to Dubinin-Radushkevich (DR) model to find out the constant (K_{DR} ; $\text{mol}^2 \text{K J}^{-2}$) related to the sorption energy from $Q=X_{DR} \exp.-(K_{DR} \varepsilon^2)$, where X_{DR} was adsorption capacity (mol kg^{-1}) and $\varepsilon=RT \ln(1+1/C_e)$ in which R and T represented the ideal gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$) and absolute temperature (298 K), was Polanyi potential. Free energy change (E ; J mol^{-1}) required to transfer one mole of ion from the infinity in the solution to the solid surface was derived from $E=(-2K_{DR})^{1/2}$ [15-19].

Langmuir isotherms were further considered to predict if the composites were 'favorable' in view of dimensionless factor (R_L) and to calculate the weight of composites (W ; kg) for removing half of Lead from a hypothetical solution (100 mg L^{-1} of Pb^{2+}) with 'V'(L) volume: $R=1/(1+K_L C_e)$ and $W/V=(C_i-C_e)/[K_L X_L C_e/(1+K_L C_e)]$ as suggested by Doğan and Alkan [19]. Where C_e is the initial metal concentration (mg/L) and K_L is the Langmuir constant. The value of R_L indicates the shape of the isotherms to be un favorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$), irreversible ($R_L = 0$) [19].

In obtaining thermodynamic parameters, the distribution coefficients (K_d) were derived from

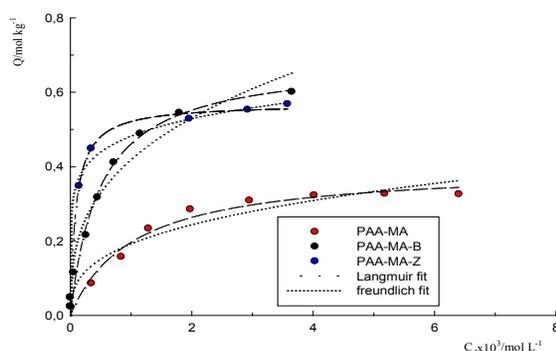


Figure 1. Adsorption isotherms of Pb^{2+} onto PAA-MA, PAA-MA-B and PAA-MA-Z and their compatibility to Langmuir and Freundlich models

$K_d=Q/C_e$ for each temperature and $\ln K_d$ was depicted against $1/T$ to provide adsorption enthalpy ($\Delta H, \text{J mol}^{-1}$) and entropy ($\Delta S, \text{J mol}^{-1} \text{ K}^{-1}$) from the slopes ($\Delta H/R$) and intercepts ($\Delta S/R$) of the depictions with reference to the VanHoff equation $\ln K_d=[(\Delta S/R)-(\Delta H/R1/T)]$, where R is ideal gas constant, $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ and T is the absolute temperature. Having had ΔH and ΔS , ΔG values were calculated from $\Delta G= \Delta H-T \Delta S$ for 298 K.

A t-test was applied to obtain the significance of regression coefficients (R^2) for the compatibility of experimental data to the Langmuir, Freundlich and DR models, and for those to the linearity of kinetic equations; $p < 0.01$ was considered as the threshold for the significance [20].

RESULTS AND DISCUSSION

Concentration dependence of adsorption

Experimentally attained adsorption isotherms and their compatibility to Langmuir and Freundlich, and DR models of Pb^{2+} was provided in Figures 1-2. The parameters derived from the models were contained in Table 1. The profiles of isotherms were L or H types of Giles classification implying that all adsorbents had comparatively high affinity to Pb^{2+} ions. Langmuir, Freundlich and Dubinin-Radushkevich (D-R) adsorption isotherms fits the experimental data over a wide range of concentration.

Each curve was obtained by varying the initial concentration of lead in solution between 1.2×10^{-4} and $9.6 \times 10^{-3} \text{ mol L}^{-1}$ (25-2000 ppm) concentrations of Pb^{2+} .

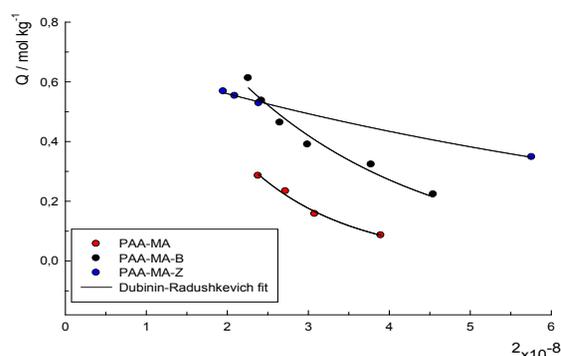


Figure 2. Adsorption isotherms of Pb^{2+} onto PAA-MA, PAA-MA-B and PAA-MA-Z and their compatibility to Dubinin-Radushkevich model

Table 1. Experimentally obtained isotherms and their compatibility to Langmuir, Freundlich and Dubinin-Radushkevich models for adsorption of Pb²⁺ onto the studied PAA-MA, PAA-MA-B and PAA-MA-Z materials.

	Langmuir			Freundlich			Dubinin-Radushkevich		
	¹ X _L	² K _L × 10 ³	³ R ²	a	b	*R ²	X _{DR}	-K _{DR} × 10 ⁹	*R ²
PAA-MA	0.40	965.4	0.964	2.04	0.34	0.921	1.97	0.80	0.989
PAA-MA-B	0.69	2033	0.984	4.42	0.34	0.963	1.55	0.44	0.967
PAA-MA-Z	0.57	10780	0.988	1.21	0.13	0.954	0.72	0.13	0.999

¹: mol kg⁻¹; ²: L mol⁻¹; * Statistically significant correlation (p < 0.05).

The isotherm for the lead adsorption onto the PAA-MA/B, PAA-MA/Z and PAA-MA respectively, indicates that this composites have a affinity towards lead. The increase of the adsorption capacity of the composites (PAA-MA/B and PAA-MA/Z) when compared with the component (B, Z and PAA-MA) may be explained by the changes, the changes in values in favor of the composites were evidence for the enhancing contribution of the encapsulation of minerals in PAA-MA, that occurred on the surface of the composites adsorbents treated B and Z. As can be seen from Table 1, the monolayer sorption capacities (X_L) of Pb²⁺ ion adsorbed on the PAA-MA/B, PAA-MA/Z and PAA-MA were 0.69, 0.57 and 0.40 mol kg⁻¹, respectively. Figure 2 shows adsorption isotherms. The amount of Pb²⁺ ion adsorbed per unit mass of the composites increasing rapidly the initial concentration of Pb²⁺ ions and then reach a plateau value (adsorption equilibrium), which represents saturation of the active regions on the composites. As can be seen from Table 1, the K_L value of PAA-MA/B and PAA-MA/Z were bigger than PAA-MA, which indicates the favorable interaction of accessible functional group sites on the surface of the composites.

The Langmuir constant K_L, increased with temperature showing that intensity of adsorption was enhanced at higher temperatures indicating the endothermic nature of adsorption [21]. The increase in adsorption intensity and adsorption capacity may be due to the change in pore size and enhanced rate of intraparticle diffusion of solute as diffusion is an andothermic process [21-24]. The adsorption coefficient "K_L", which is related to energy of adsorption of Pb²⁺ ions was greater for PAA-MA/B and PAA-MA/Z adsorbents and lesser for PAA-MA adsorbent. The high value of "K_L" for Pb²⁺ ions adsorption onto PAA-MA/B and PAA-MA/Z, indicates that the energy of

Table 2. R_L values from sorption isotherm for Pb²⁺ sorption onto PAA-MA, PAA-MA-B and PAA-MA-Z.

C _{Pb²⁺ ions} (ppm)	PAA-MA	PAA-MA/B	PAA-MA/Z
100	0.682	0.001	0.11
250	0.462	0.001	0.01
500	0.300	0.01	0.05
750	0.222	0.010	0.04
1000	0.177	0.028	0.03
1250	0.146	0.034	0.03
1500	0.125	0.039	0.02
1750	0.109	0.045	0.02
2000	0.097	0.051	0.02

adsorption is more favourable than that of PAA-MA hydrogel.

The effect of isotherms curve can be used to estimate whether a adsorption balance is "favorable" or "unfavorable". The feasibility of the on-going adsorption processes was also evaluated by the method suggested by Weber and Chakraborti [25]. The values of "R_L" could be expressed by a dimensionless constant or seperation factor. The value of R_L indicates of isotherm to be irreversible (R_L = 0), favorable (0 < R_L < 1), linear (R_L = 1) or unfavorable (R_L > 1). Table 2 shows that in all the composites the values of R_L were positive and always 0 < R_L < 1, indicating suggesting that the adsorbents were favorable for Pb²⁺ adsorption.

The amounts of adsorbents for removal of 50% of Pb²⁺ from a hypothetical solution containing 100 mg L⁻¹ Pb²⁺ were 3 and 8 g L⁻¹ for PAA-MA, 1 and 4 g L⁻¹ for PAA-MA-B and 1 and 4 g L⁻¹ for PAA-MA-Z. The sufficiency of such low amounts for Pb removal/recovery procedures should ascertain the cost effectiveness of PAA-MA-B, PAA-MA-Z in comparison to PAA-MA.

The calculated correlation coefficients, “R²” for each model (Table 1) indicated that best fits were achieved for Langmuir model. The results of Langmuir analysis indicated that the maximum adsorption for all four adsorbent follow the order; PAA-MA-B > PAA-MA-Z > PAA-MA. PAA-MA-B had a more developed porosity and a higher surface area.

The sufficiency of such low amounts for Pb²⁺ ions removal procedures should ascertain the cost effectiveness of the studied composites especially for PAA-MA-B and PAA-MA-Z in comparison to PAA-MA in which B and Z were naturally occurring highly abundant minerals, resistant to acidic and basic solutions and reusable. The found values for ‘R_L’ were always 0 < R_L < 1 suggesting that the all adsorbents was favorable for Pb²⁺ ions adsorption.

The results of the PAA-MA, PAA-MA/B and PAA-MA/Z adsorbents suggested for the Pb²⁺ ions.

Temperature dependence of Pb²⁺ adsorption

1/T as a function of ‘ln K_d’ was depicted in Figure 3 to obtain temperature dependence of the adsorption of the studied ions. The thermodynamic parameters derived from the depictions and free energy change (E_{DR}) derived from DR model were introduced in Table 3.

The negative values of ΔG were due to the fact that the adsorption process was spontaneous with high affinity of meta ions onto adsorbent.

The positive value of ΔH confirms the endothermic nature of the adsorption process [21]. Increased temperature will cause a decreasing hydrated diameter, framework channels expansion, increasing diffusion force by supplying partial ion-exchange activation energy, increasing diffusion into the inner sections of the adsorbent and subsequently, an increase in the degree of adsorption/exchange [21-24].

The enthalpy and entropy changes were ΔH>0 and ΔS>0 for all studied adsorbents, showing that the overall process was endothermic and the randomness in the solid-solution interface increased throughout the adsorption process.

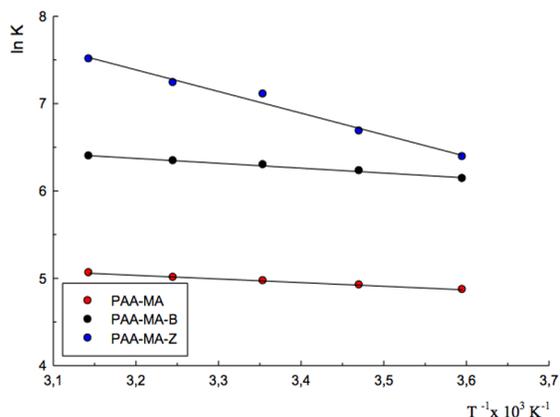


Figure 3. Temperature dependence of the adsorption for studied Pb²⁺

Table 3. Thermodynamic parameters for Pb²⁺ adsorption onto PAA-MA, PAA-MA-B and PAA-MA-Z.

	Van't Hoff (Thermodynamic parameters)				Free energy (ΔR)	
	ΔH ¹	ΔS ²	-ΔG ¹	*R ²	E ¹	*R ²
PAA-MA	3.47	52.9	12.3	0.997	8.89	0.989
PAA-MA-B	4.64	67.8	15.6	0.990	10.7	0.978
PAA-MA-Z	20.61	127.3	17.4	0.983	19.8	0.999

1. kJ mol⁻¹, 2. J mol⁻¹K⁻¹, *Statistically significant correlation (p<0.05)

One possible interpretation of endothermic of the enthalpy (ΔH) of adsorption was that metal ions with high hydration energies were strong solvated in water. The decomposition of the hydration shell will increase the entropy (ΔS) of the solvent [23]. Gibbs free enthalpy change was ΔG<0, i.e., the adsorption process was spontaneous. The E_{DR} values were higher than 8 kJ mol⁻¹ also indicated that the nature of adsorption was chemical [22-25].

Reusability

The reusability feature of PAA-MA-B and PAA-MA-Z was tested for TI⁺ for four regenerations in a total of five uses (Table 4). The IR spectra obtained before and after reuses provided no evidence signifying any changes in the structures.

The reusability efficiency was consistent for PAA-MA-B (90%) and PAA-MA-Z (98%) but not for PAA-MA for which structure of hydrogel were decomposition for effluents 15 m L⁻¹ of 1 mol HCl. The values of means were not significantly different from the values of their first use and 100% (p < 0.05). The drastically decrease

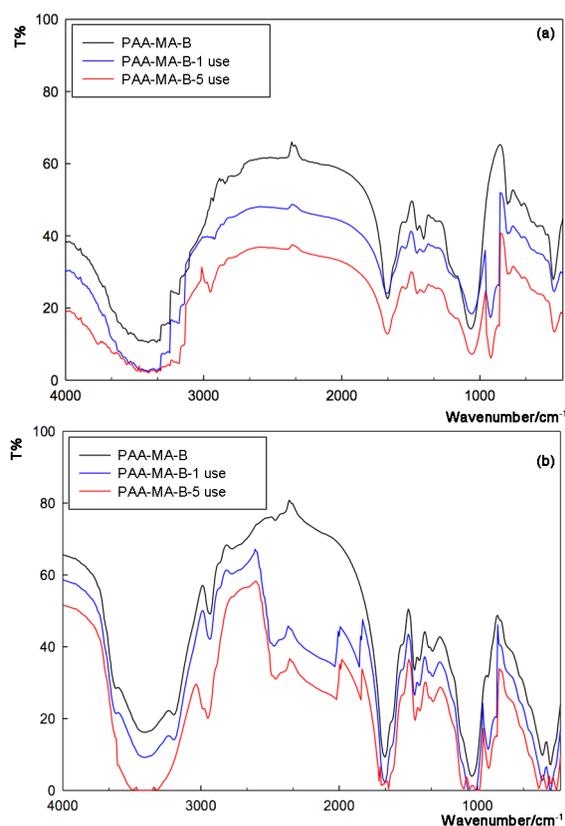


Figure 4. The FT-IR spectra of PAA-MA-B (a) and PAA-MA-Z (b): before unloaded, after one use and after five uses Pb^{2+} adsorption

observed for the PAA-MA was obvious evidence for the decomposition of PAA-MA structure beside which the hydrolysis of PAA-MA- Pb^{2+} complex formed after the adsorption should be responsible from the decomposition (Figure 4).

CONCLUSION

In this study, adsorptive features of the PAA-MA, PAA-MA-B and PAA-MA-Z hydrogel and composites were investigated for Pb^{2+} .

Experimentally obtained isotherms were well compatible to the Langmuir, Freundlich and DR models. The results obtained for the adsorption capacities indicated that the capacities of B and Z could be significantly improved by using their composites with PAA-MA. All isotherms obtained from the adsorption dependency on concentration were of L and H type of Giles classification. These results qualified that all adsorbents had high affinity to the lead ions of interest. The found monolayer adsorption capacities (X_L) for PAA-MA,

Table 4. Reusability of the PAA-MA, PAA-MA-B and PAA-MA-Z composites for adsorption of Pb^{2+} from solution.

Reuse no	PAA-MA	Adsorption%	
		PAA-MA-B	PAA-MA-Z
1	58.4	81.5 (100) ¹	92.8 (100) ¹
2	-	78.7 (96.5)	91.9 (99.0)
3	-	77.3 (94.8)	91.4 (98.5)
4	-	72.0 (88.3)	89.5 (96.4)
5	-	65.8 (80.6)	89.6 (96.6)
Mean \pm SEM	-	75.05 \pm 1.1 ² (90.1 \pm 1.2)	91.04 \pm 0.3 ² (97.6 \pm 0.4)

1. Values of % adsorption with reference to the first use assumed to be 100%

PAA-MA-B and PAA-MA-Z were 0.69, 0.57 and 0.40 mol kg^{-1} for Pb^{2+} .

The values of enthalpy and entropy changes were positive for all composites and lead ions. The reusability tests for five uses proved that the PAA-MA-B and PAA-MA-Z were reusable and complete recovery of the adsorbed Pb^{2+} was possible, but the PAA-MA due to its chemical instability and the adsorbed fractions onto PAA-MA-B and PAA-MA-Z were effectively recovered with HCl solution (15 mL, 0.1 mol L^{-1}).

In consequence, the studied features of PAA-MA-B and PAA-MA-Z suggest that the materials should be considered as a new adsorbent. It is envisaged that the use of B and Z in PAA-MA will enhance practicality and effectiveness of B and Z in separation and removal procedure.

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