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Removal of lead (II) ions from aqueous solution by using crosslinked chitosan-clay beads

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ABSTRACT

A simple and effective biodegradable material known as chitosan-clay composite beads were prepared to remove Pb(II) ions from aqueous solution. For this purpose, various important parameters such as contact time, pH and temperature were examined on the adsorption of Pb(II) ions onto crosslinked chitosan-clay composite beads. Maximum adsorption capacity of Pb(II) was observed at pH 4.5 and 25°C and calculated as 7.93 mg/g according to Langmuir isotherm model. Thermodynamic parameters namely $\Delta G°$, $\Delta H°$ and $\Delta S°$ of the Pb(II) adsorption process have been calculated as 7.889 kJ/mol, −15.131 kJ/mol and −0.0785 kJ/molK respectively. EDTA was the best eluent for the desorption of Pb(II) ions from the crosslinked chitosan-clay beads. Scanning electron microscope (SEM) was used to characterize the surface morphology of the crosslinked chitosan-clay beads.

Keywords: Adsorption; Chitosan-clay composite beads; Atomic absorption spectrophotometer; Heavy metal; Pb removal; Langmuir isotherm

1. Introduction

Heavy metal ions such as Pb(II) is toxic and carcinogenic at relatively low concentrations. Lead has many functions, ranging from sheets for roofing, to pipes and blocks for screening from radioactive emissions [1]. Moreover, Pb is widely used in industrial applications, such as battery, printing, pigments, fuels, photographic materials, and explosives manufacturing [2,3]. However, lead has the most damaging effects on human health [4]. Many methods such as ion exchange, precipitation, adsorption, and membrane processes have been used for the removal of toxic metal ions [5–10]. In particular, adsorption is recognized as an effective and economic method for the removal of pollutants from wastewaters and low cost adsorbents are becoming the focus of many investigations on the removal of heavy metals from aqueous solutions [11–15]. Biopolymers are potential adsorbents due to their biodegradability, non-toxicity, efficiency. These are inexpensive and thus are competitive with ion-exchange resins and activated carbon. They contain chemically active functional groups that serve as efficient sites to bind metal ions [16]. Both chitin and chitosan are becoming increasingly important natural polymers because of their unique combination of properties like biodegradability, biocompatibility and bioactivity, non-toxicity in addition to attractive physical and mechanical properties [17]. Chitosan is obtained from the deacetylation of the natural biopolymer chitin, found in crustaceous shells, insects, and fungal cell walls [16,18]. It has been used widely as an adsorbent for transition metal ions and organic species because the amino ($-NH_2$) and hydroxy (–OH) groups on chitosan chains can serve as the coordination and reaction sites [19–23]. It is also reported that

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chitosan has the highest chelating ability in comparison to other natural polymers obtained from seafood wastes and natural substances like bark, activated sludge and the synthetic polymer poly(4-aminostyrene) which is used in commercial chelating ion-exchange resins [23–26]. The use of chitosan alone would be costly, because construction of filters along the stream requires large quantities of adsorbents. Immobilizing chitosan on a low-cost material such as activated carbon, silica, sand and clay would result in lower amounts of chitosan being used but the overall metal adsorption capacity may not be affected [27]. Clay materials possess a layered structure and are considered as host materials [28]. Natural clay minerals are well known and familiar to mankind from the earliest days of civilization. Because of their low cost, abundance in most continents of the world, high adsorption properties and potential for ion-exchange, clay materials are strong candidates as adsorbents. Abollino et al. have observed that Na-montmorillonite adsorbs Cd, Cr, Cu, Mn, Ni, Pb or Zn even when organic substances (bonds) are present [29]. In Covelo et al. Cd, Cr, Cu, Ni, Pb and Zn were adsorbed in mineral clays simultaneously from solutions with several concentrations [30].

In this paper, crosslinked chitosan-clay composite beads were prepared, characterized and used to remove the toxic metal ions such as Pb(II) from aqueous solution in batch adsorption system. The Pb(II) adsorption of the crosslinked chitosan-clay beads was examined in an aqueous solution. Surface morphology of the crosslinked chitosan-clay beads were characterized by Scanning Electron Microscope SEM and the effects of contact time, pH and temperature on the adsorption capacity were carried out. Desorption studies were performed using EDTA solution on adsorbed metal ions. Adsorption isotherms of Pb(II) on the composite was in good agreement with the Langmuir model.

2. Experimental

2.1. Reagent

All reagents were analytical grade. The working standard solutions of Pb(II) was prepared using appropriate dilutions of stock solutions (1000 mg/l), which were obtained from Merck. The following buffer solutions were used at a concentration of 0.1 mol/l to adjust the pH: citric acid/sodium citrate buffer (pH 3.0), acetic acid/sodium acetate (pH 4.0–6.0). Chitosan, sodium triphosphate pentabasic (TPP) and nanoclay were obtained from Sigma.

2.2. Preparation of crosslinked chitosan-clay beads

Fifty grams of nanoclay (hydrophilic bentonite) were activated by refluxing with 250 ml of 1 mol/l H_2SO_4 at 80°C in around-bottom flask for 2 h. The slurry was air-cooled and filtered with a glass fiber. The filter was repeatedly washed with deionized water and dried [31]. The solution of chitosan (1% w/v), prepared with 1 g of chitosan was dissolved into 100 ml 2% (v/v) of CH_3COOH. Then 1 g of activated nanoclay was added. Chitosan-clay suspension solution was dropped slowly into tripolyphosphate (pH 8.2) by syringe needle. Beads were stirred 4 h for hardening and then the beads were filtered and washed with distilled water. The beads were incubated for 2 h in 1% (v/v) of glutaraldehyde solution at 30°C. The crosslinked beads were filtered and rinsed with distilled water and stored at 4°C for further use.

2.3. Instruments

Lead (II) concentration measurements were carried out using Varian 220 FS AAS. The pH of solution was measured with a Hanna P211 microprocessor pH-meter using a combined glass electrode. The shaking was carried out in a thermostated electronic shaker Labart SH-5. Surface morphology of samples was determined by Philips (FEI) XL30-SFEG Scanning Electron Microscope.

2.4. Method

Stock solutions (1000 mg/l) of Pb(II) were prepared by dissolving 0.80 ± 0.02 g $Pb(NO_3)_2$ diluted to 500 ml with ultra pure deionized water. Standard solutions of lead at required concentrations were prepared by appropriate dilution. The pH of the solutions was adjusted by using citric acid/sodium citrate, acetic acid/sodium acetate.

2.5. Batch adsorption experiments

Adsorption experiments were carried out batch technique. 0.50 ± 0.02 g of each adsorbent (crosslinked chitosan-clay beads) was put into beaker containing 50 ml of 50 mg/l Pb(II) solution and the suspension was stirred. After decantation, the concentration of Pb(II) was analyzed by Atomic Absorption Spectrometer at 193.7 nm by acetylene/air flame method. The effect of contact time was studied 30−100 min. The effect of pH on Pb(II) adsorption was studied by using pH 3.0 (0.1 M citric acid −0.1 M sodium citrate) and pH 4.0–6.0 (0.1 M CH_3COOH −0.1 M $NaCH_3COO$) buffer systems. Isotherm studies were conducted with a constant crosslinked chitosan-clay composite beads weight (0.50 ± 0.02 g) and varying initial concentrations of Pb(II) in the range of 25–800 mg/l. All the experiments were carried out twice.

The percentage adsorption of lead on adsorbate from aqueous solution was computed as follows:

$$\text{Adsorption}\,(\%) = \frac{C_{\text{int}} - C_{\text{fin}}}{C_{\text{int}}} \times 100 \tag{1}$$

C_{int} is the initial Pb(II) concentration (mg/l), C_{fin} is the final Pb(II) concentration (mg/l), V is the volume of the Pb(II) solution (ml) and W is the weight of the chitosan and crosslinked chitosan beads (g).

3. Results and discussion

3.1. Effect of contact time on sorption of lead(II)

The optimum period for the adsorption of Pb(II) on crosslinked chitosan-clay beads can be observed by looking at the difference in absorbance of Pb(II) solution before and after adsorption. Fig. 1 shows the effect of contact time on the adsorption of Pb(II) by crosslinked chitosan-clay beads. Equilibrium was reached around 80 min, and beyond this time no change in adsorption was occurred. Thus, the equilibrium time was maintained 80 min in subsequent adsorption studies. Wan et al. were reported the equilibrium period for adsorption of Pb(II) on the chitosan-coated sand as 4 h [16]. However, there are several parameters which determine sorption rate, like structural properties of the adsorbent (size, surface area, porosity), metal ion properties, initial concentration of metal ions, pH or chelate formation rate. Therefore, it is difficult to make a comparison between adsorbents [32].

3.2. Effect of pH on sorption of lead (II)

The pH of the aqueous solution is an important parameter in adsorption processes. To prevent precipitation, experiments were carried out at pH < 6.0 to ensure to solubility of metal ions [2,33,34]. At high pH, precipitation usually occurred with the metallic ions attached to hydroxide ions forming metal hydroxides [16]. The adsorption of Pb(II) ions was highly dependent on the pH of the metal solution because pH can affect the solubility of the metal ions and at the same time influence the ionization state of the functional groups existing on the adsorbent [35].

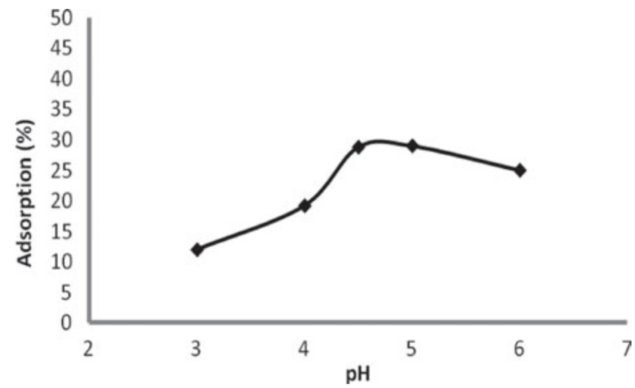


Fig. 2. Effect of pH on the adsorption capacity of crosslinked chitosan-clay beads for Pb(II) ions (25 ml 100 mg/l Pb^{2+}, 0.5 g adsorbent, contact time 80 min).

The effect of pH on the adsorption of lead (II) ions were studied at different pH values (3.0–6.0) using crosslinked chitosan-clay beads (100 mg) at constant metal ion concentration (100 mg/l). pH selection in the range of 4.0–6.0 was rationalized by the fact that chitosan could be dissolved with pH < 3.0; while pH > 7.0 could result in the formation of metal hydroxide precipitates. The results indicate that the maximum uptake of Pb(II) ions takes place at pH 4.5. Effect of pH on sorption of Pb(II) ions was shown in Fig. 2. Similar trend was observed with the adsorption of lead from aqueous solution by chitosan [4–6].

3.3. Effect of temperature on sorption of Pb(II) ions

In this study, the adsorption process was assessed at different temperatures between 20 and 45°C. Fig. 3 shows the effect of temperature on the adsorption of Pb(II).

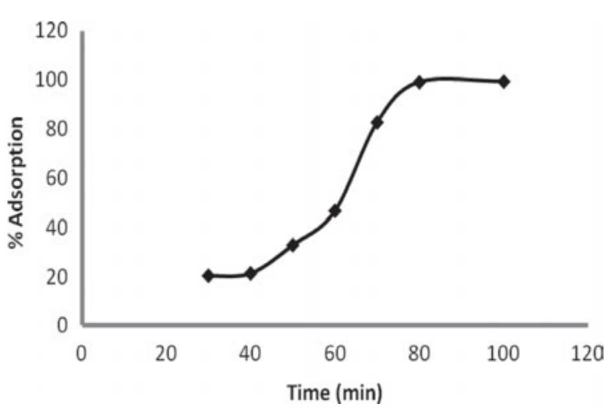


Fig. 1. Effect of the adsorption time on the adsorption capacity of crosslinked chitosan-clay beads for Pb(II) ions (25 ml 100 mg/l Pb^{2+}, 0.5 g adsorbent).

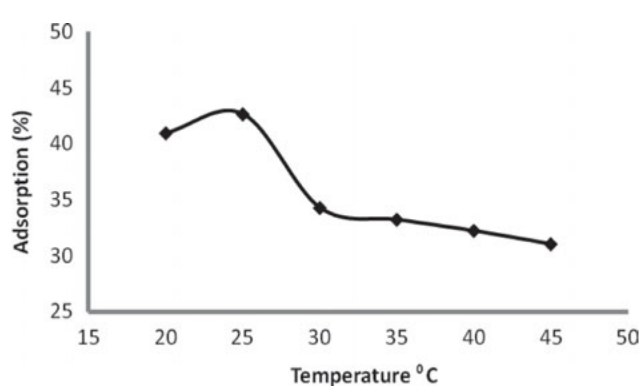


Fig. 3. Effect of temperature on the adsorption capacity of crosslinked chitosan-clay beads for Pb(II) ions (25 ml 100 mg/l Pb^{2+}, 0.5 g adsorbent, contact time 80 min pH: 4.5).

Maximum adsorption was observed at 25°C. It can be seen in Fig. 3 that over 25°C adsorption decreased. As seen in Fig. 3, with an increase in temperature, adsorption capacity decreases. This is mainly because of decreased surface activity suggesting that adsorption between Pb^{2+} metal ion and chitosan-clay composite beads was an exothermic process. With increasing temperature, the attractive forces between the chitosan-clay composite beads' surface and metal ion are weakened and then sorption decreases. In contrast, in endothermic adsorption studies, the increase in temperature not only increases the rate of diffusion of the metal ions present in the bulk solution to the adsorbent surface but also increases the rate of complexation with the functional groups present in the adsorbent [36].

3.4. Thermodynamics parameters

Temperature dependent distribution coefficient for adsorption of Pb(II) was computed as follows:

$$K_d = \frac{C_{\text{int}} - C_r}{C_r} \times \frac{V}{m} \tag{2}$$

C_{int} and C_r are the initial and residual lead concentrations (mg), respectively. V is volume of the solution (L) and m is the amount of the adsorbent (g).

Thermodynamic parameters such as free energy change ($\Delta G°$), enthalpy change ($\Delta H°$) and entropy change ($\Delta S°$) were calculated by using the following Eq. (3):

$$\Delta G° = -RT \ln K_d \tag{3}$$

The change of enthalpy ($\Delta H°$) and entropy ($\Delta S°$) can be obtained from the intercept and slope of van't Hoff equation of $\Delta G°$ versus T:

$$\Delta G° = \Delta H° - T\Delta S° \tag{4}$$

where $\Delta G°$ is standard Gibbs free energy change (J), R is universal gas constant (8.314 J/molK) and T is absolute temperature (K).

Values of the standard Gibbs free energy change for the adsorption process obtained from Eq. (4) were listed in Table 1. The negative value of $\Delta H°$ (–15.131 kJ/mol) and $\Delta G°$ (7.889 kJ/mol) indicates that the adsorption processes are spontaneous and exothermic in nature. The negative value of $\Delta S°$ (–0.078 kJ/molK) suggests decreased randomness during adsorption and reflects the affinity of the chitosan-clay composite beads for Pb(II) ions. Similar results for thermodynamic parameters were also reported by the earlier workers for the adsorption of Pb^{2+} as well as other heavy metals from aqueous solution [36–38].

3.5. Adsorption isotherms

Adsorption isotherm is a functional expression that correlates the amount of solute adsorbed per unit weight of the adsorbent and the concentration of an adsorbate in bulk solution at a given temperature under equilibrium conditions. The adsorption isotherms are one of the most useful data to understand the mechanism of the adsorption and the characteristics of isotherms are needed before the interpretation of the kinetics of the adsorption process. Langmuir and Freundlich isotherms were most used to describe the equilibrium sorption of metal ions [4].

Fig. 4 shows the experimental equilibrium isotherms for adsorption of Pb(II) on crosslinked chitosan-clay beads. Their adsorption behaviors can be described with the Langmuir adsorption equation as:

$$\frac{C_e}{q_e} = \frac{1}{Qb} + \frac{C_e}{Q} \tag{5}$$

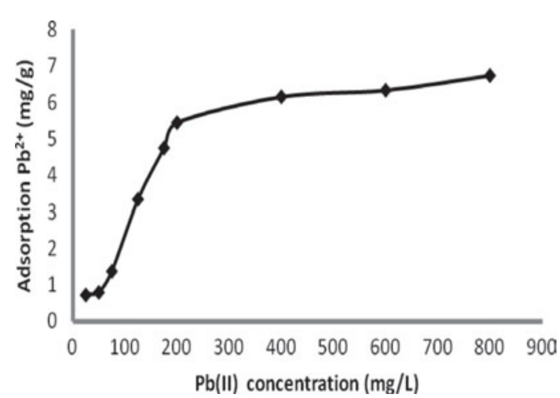


Fig. 4. Effect of Pb(II) concentration on the adsorption capacity of crosslinked chitosan-clay beads (0.5 g adsorbent, contact time 80 min pH: 4.5, temperature 25°C).

Table 1

Isotherm constants and thermodynamic parameters for adsorption of Pb(II) ions on crosslinked chitosan-clay beads

Adsorbent	Langmuir isotherm constants			Thermodynamic parameters		
	R^2	Q (mg/g)	b(mg/l)	$\Delta G°$(kJ/mol)	$\Delta H°$ (kJ/mol)	$\Delta S°$ (kJ/molK)
Crosslinked chitosan-clay beads	0.983	7.930	0.009	7.889	–15.131	–0.078

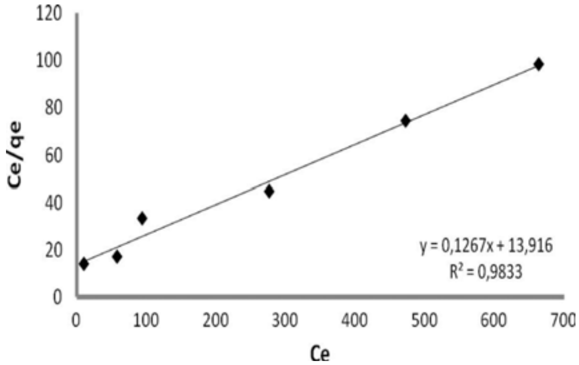


Fig. 5. Langmuir isotherm of the Pb(II) ions (0.5 g adsorbent, contact time 80 min pH: 4.5, temperature 25°C).

C_e is equilibrium concentration of the metal (mg/l) and q_e is the amount of the metal adsorbed (mg) by per unit of the adsorbent. When C_e/q_e is plotted against C_e, a straight line with a slope of $1/Q$ and intercept was obtained (Fig. 5), which shows that the adsorption of Pb(II) follow Langmuir isotherm model. The Langmuir parameters Q (mg/g) and b (l/mg) were calculated from the slope and intercept and were given in Table 1.

According to the results, Langmuir model was found to describe adsorption successfully than Freundlich model isotherm in respect to linearity coefficients obtained for both model (R^2= 0.983 and 0.923) (Fig. 6). In this study the maximum adsorption capacity of crosslinked chitosan-clay beads for Pb(II) was determined as 7.93 mg/g. Table 2 shows the reported adsorption data of Pb(II) ions on the various adsorbents. The maximum reported value for Pb(II) ions was 18.00 mg/g.

3.6. Desorption studies

Desorption studies will help to regenerate the crosslinked chitosan-clay beads so it can be used again to adsorb metal ions. For this purpose, 0.1 M HCl, 0.5 M HCl, 0.1 M HNO_3, 0.5 M HNO_3 and 0.02 M EDTA (prepared in distilled water, pH 10.9) solutions were used for the desorption studies. Desorption experiments were carried out using batch technique. 0.50 ± 0.02 g of adsorbent (crosslinked chitosan-clay beads) was put into beaker containing 50 ml of each desorbent solutions and the suspension was stirred for 60 min at 25°C. After decantation, the concentration of Pb(II) was analyzed by Atomic Absorption Spectrometer. Maximum desorption of Pb(II) (94.9%) from crosslinked chitosan-clay beads was obtained by using 0.02 M EDTA solution. Results were listed in Table 3. Laus et al. studied the desorption of Pb(II) ions adsorbed on chitosan (CTS) crosslinked with both epichlorohydrin (ECH) and Sodium triphosphate pentabasic (TPP) covalent and ionic crosslinking, respectively, using different eluents [5]. 79.2% desorption was obtained when 1 mol/l HCl was used. Wan et al. was found 55.88% desorption of Pb(II) ions, adsorbed on chitosan-coated sand (CCS) bioadsorbent using the dilute HCl [16].

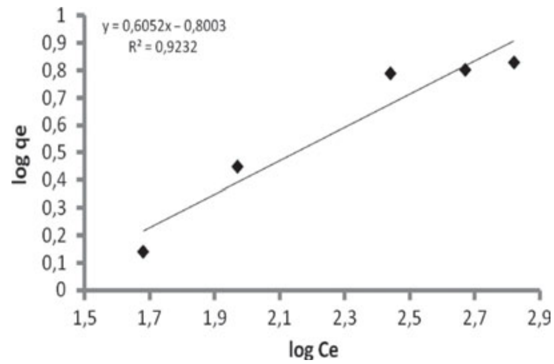


Fig. 6. Freundlich isotherm of the Pb(II) ions (0.5 g adsorbent, contact time 80 min pH: 4.5, temperature 25°C).

Table 2
Comparative adsorption of Pb(II) ion onto various types of adsorbents; q_m, is the adsorption capacity of the metals ions adsorbed onto the adsorbents

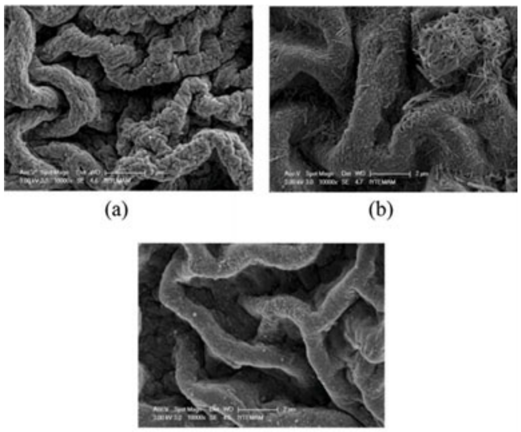
Type of adsorbent	Pb(II) q_m (mg/g)
pHEMA/chitosan membranes [39]	18.73
Kaolin clay [40]	3.93
Chitosan–pectin pellets [6]	11.20
Chitosan-GLA beads [9]	14.24
Tobacco stem [5]	5.54
Chitosan-coated sand (CCS) bioadsorbent [16]	12.32
Crosslinked chitosan-clay beads (This study)	7.93

3.7. SEM analysis

Scanning electron microscopy (SEM) is an extremely useful method for visual confirmation of surface morphology and the physical state of the surface. SEM

Table 3
Desorption (%) results of Pb(II) ions from crosslinked chitosan-clay beads by using different eluents

Eluent	Concentration (M)	Desorption (%)
HCl	0.10	72.17
HCl	0.50	79.43
HNO_3	0.10	88.26
HNO_3	0.50	90.48
EDTA	0.02	94.89



(c)

Fig. 7. a) SEM micrographs of crosslinked chitosan-clay beads, b) SEM micrographs of Pb(II) adsorbed crosslinked chitosan-clay bead, c) SEM micrographs of Pb(II) desorbed crosslinked chitosan-clay beads with EDTA.

analysis of samples was determined by Philips (FEI) XL30-SFEG Scanning Electron Microscope. SEM micrographs of crosslinked chitosan-clay beads before, after their exposure to metal ion solutions and after desorption with EDTA were shown at Fig. 7 (a–c). The general morphology of the beads before adsorption can be characterized as rough and folded (Fig. 7a). After adsorption of metal ions, needle crystals were observed on the surface of the beads (Fig. 7b) and it may be due to $Pb(CH_3COO)_2$. After desorption, needle crystals were not observed (Fig. 7c) and surface morphology of the beads seems smoother than before adsorption of Pb(II) ions.

4. Conclusions

Crosslinked chitosan-clay beads have been proven to be an effective adsorbent for removal of toxic metal ion such as Pb(II). The maximum adsorption capacity of crosslinked chitosan-clay beads was obtained at pH 4.5 and 25°C. Based on a linearized correlation coefficient the Langmuir isotherm model gives better fit than the Freundlich isotherm model. The maximum adsorption capacity of crosslinked chitosan-clay beads for Pb(II) was determined as 7.93 mg/g. Pb(II) ion adsorption on surface of crosslinked chitosan-clay beads was observed via SEM analysis. Desorption study were done to evaluate the possible metal recovery from cross linked chitosan-clay beads. In conclusion, these results indicate the possibility of using crosslinked chitosan-clay beads for metal removal in aqueous solution.

Symbols

$\Delta G°$ — Energy change
$\Delta H°$ — Enthalpy change
$\Delta S°$ — Entropy change
C_e — Equilibrium concentration
C_r — Residual lead concentrations
C_{int} — Initial Pb(II) concentration
C_{fin} — The final Pb(II) concentration
q_e — The amount of the metal adsorbed
Q — Capacity of the adsorbent calculated from the slope of Langmuir isotherm
b — Capacity of the adsorbent calculated from the intercept of Langmuir isotherm
V — Volume of the solution
m — Amount of the adsorbent
R — Universal gas constant
K — Temperature
K_d — Distribution coefficient
W — Weight of the adsorbent

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