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Evaluation of Cu^{2+}, Co^{2+} and Ni^{2+} ions removal from aqueous solution using a novel chitosan/clinoptilolite composite: Kinetics and isotherms

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ABSTRACT

A novel chitosan/clinoptilolite composite, as beads with an average size of 800 μm in diameter, in dry state, was used for comparative studies on the removal of toxic metal ions like: Cu^{2+}, Co^{2+} and Ni^{2+} from aqueous solutions. The effects of the initial pH value of the solution, contact time, the initial metal ion concentration and temperature on the adsorption capacity of the composite were investigated. The kinetics data were analysed by pseudo-first order, pseudo-second order, and intra-particle diffusion equations. The adsorption kinetics were well described by the pseudo-second order equation, and the adsorption isotherms were better fitted by the Langmuir equation. The maximum theoretical adsorption capacities of the chitosan/clinoptilolite composite for Cu^{2+}, Co^{2+} and Ni^{2+} were found to be 11.32, 7.94 and 4.209 mmol/g, respectively. The negative values of Gibbs free energy of adsorption (ΔG°_{ads}) indicated the spontaneity of the adsorption of all metal ions on the novel composite. Desorption of the metal ions from the composite was achieved by using 0.1 M HCl in about 20 min.

1. Introduction

In recent years, special attention has been given to the environmental contamination with heavy metals because of their high toxicity and non-biodegradability. Conventional methods that have been used to remove heavy metal ions from various industrial effluents usually include chemical precipitation, membrane separation, ion exchange, evaporation, and electrolysis, etc. and are often costly or ineffective, especially in removing heavy metal ions from dilute solutions.

Among the conventional techniques commonly used in the removal of heavy metals from wastewaters the adsorption process is mainly preferred especially when the enrichment of trace metal amounts or a high selectivity for a certain metal are required [1–4]. However, the benefits of this technique are offset by the rising cost of adsorbents like activated carbon and synthetic ion exchangers. The hunt for a cheap and widely available adsorbent has motivated researchers to focus on naturally available adsorbents like natural zeolites [5–8]. Clinoptilolite (CPL), one of the most common natural zeolites, is a hydrated alumina–silicate member of the heulandite group, occurring in the zeolitic volcanic tuffs, being widespread in many countries in the world. CPL is characterized by infinite three-dimensional frameworks of $[AlO_4]^{5-}$ and $[SiO_4]^{4-}$ tetrahedra linked to each other by sharing all of the oxygens, and the negative charge being balanced by metal cations, like Na^+, K^+, Ca^{2+} and Mg^{2+} [7].

Chitosan (CS) and its derivatives have been also extensively investigated as biosorbent for removal of heavy metals [9–11]. To improve the mechanical properties, adsorption capacity, or even to prevent dissolution in acidic medium of the CS, numerous studies have been devoted to the chemical modification of the CS surface by homogeneous or heterogeneous cross-linking with di- or polyfunctional agents, such as sodium tripolyphosphate, glutaraldehyde, ethyleneglycol diglycidyl ether and epichlorhydrin [11–13]. On the other hand, CS-based composite materials have also been reported to exhibit enhanced mechanical, thermal or adsorption properties comparative with any of its components used alone. Novel CS-based composite materials with enhanced adsorption properties for removal of heavy metal ions like Cu^{2+}, As^{3+} and As^{5+} have been designed by loading attapulgite into chitosan-*g*-poly(acrylic acid) polymeric network [14] or by coating ceramic alumina with chitosan [15]. Other CS-based composites were obtained by coating with CS the iron hydroxide [16], or perlite, an inorganic porous aluminosilicate [17].

In our recent studies, we reported on the synthesis of some novel CS/CPL composites by embedding zeolite microparticles in a matrix of cross-linked chitosan [18,19]. A comparative evaluation of the adsorption capacities of the CS/CPL composite containing 20 wt.% of zeolite against three environmentally problematic divalent metal ions, namely, Cu^{2+}, Co^{2+} and Ni^{2+}, from aqueous solutions, was developed in this paper. The factors influencing the adsorption capacity of the composite such as the initial pH value of the metal

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ions solutions, contact time, the initial concentration of metal ions solutions and temperature were investigated. In order to examine the controlling mechanism of the adsorption process, the kinetics, adsorption isotherms and thermodynamics parameters were evaluated.

2. Materials and methods

2.1. Materials

CS as powder was purchased from Fluka, ash content less than 1%, and was used without further purification. The viscometric average molar mass and the deacetylation degree of CS used in this study were 334 kDa and 82.4%, respectively. These values were estimated according to the methods presented elsewhere [19]. The natural CPL sample used in the preparation of the composite comes from volcanic tuffs containing 60–70% CPL, cropped out in Măcicaş area (Cluj County, Romania), and has the following elemental composition: $(NaKCa_{0.5})_{5.4}(Al_{5.4}Si_{30.6}O_{72})\cdot 20H_2O$ (Si/Al = 5.7) [7]. The zeolitic volcanic tuff was used as collected. $CuSO_4\cdot 5H_2O$, $CoCl_2\cdot 6H_2O$, $NiCl_2\cdot 6H_2O$ (all from Aldrich) were used as metal ion source for the adsorption experiments. All the reagents were of analytical grade or highest purity available, and used without further purification.

2.2. Preparation and characterization of CS/CPL composite

Ionic composite based on chitosan (CS) and clinoptilolite (CPL) were prepared as microspheres by a “tandem” ionic/covalent cross-linking, according to the method previously presented [19]. Typically, 0.15 g CPL powder was mixed with distilled water, the volume of water being 1/2 volume of CS solution used for the synthesis of the composite, and kept under vigorous magnetic stirring for 1 h at least. Two volumes of CS solution were mixed with one volume of water containing the dispersed zeolite, and after a vigorous magnetic stirring, the epichlorohydrin as cross-linker was added step-by-step. The mixture thus prepared was added by a syringe into an aqueous solution of sodium tripolyphosphate with a concentrantion of 0.05 M, under mild magnetic stirring. The mass ratio between CS and CPL was 4:1, the sample name being CS_4CPL_1. The composite microspheres were kept under stirring 5 h at 37 °C, and then were separated from the dispersion medium and intensively washed with distilled water to remove the excess of small ions. For characterization in dried state, the composite microspheres were filtered off, dried at room temperature for 24 h and under vacuum at 40 °C, for 48 h. The average size of the microspheres in dry state was 800 μm, measured by environmental scanning electron microscopy (ESEM) type Quanta 200, operating at 15 kV with secondary electrons, in high vacuum mode. The average size of the composite microspheres in hydrated state was 1200 μm.

2.3. Adsorption studies

Study of the metal ion retention properties of the composites was carried out using a batch equilibrium procedure. Thus, 0.25 g of dried CS_4CPL_1 composite was placed in a flask and contacted with 25 mL of the aqueous solution of each metal ion (Cu^{2+}, Co^{2+} and Ni^{2+}) at different temperatures and pH. The kinetics of the metal ion retention was studied by placing 0.25 g of dried CS_4CPL_1 composite in 25 mL of aqueous solution of metal ion with a concentration of 0.07 mol/L, at 25 °C, the equilibrium concentration of the metal being measured at different contact durations. The contact time ranged between 2 and 36 h. The effect of medium pH on the adsorption capacity of the CS_4CPL_1 composite was investigated in the pH range 2.0–6.0 for each metal ion at 25 °C. To determine the effect of initial concentrations of the metal ion on the adsorption rate and capacity on the CS_4CPL_1 composite, the initial concentration of the Cu^{2+}, Co^{2+} and Ni^{2+} metal ion solutions was varied between 0.0025 and 0.1 mol/L in the adsorption medium at pH 5.0. The CS_4CPL_1 composite was filtered off, and the residual concentration of the metal cation remained in the filtrate was measured by the UV–vis spectroscopy at 510 nm for Co^{2+}, 720 nm for Ni^{2+} and 775 nm for Cu^{2+} (these were the maximum absorption wavelengths of $CoCl_2\cdot 6H_2O$, $NiCl_2\cdot 6H_2O$ and $CuSO_4\cdot 5H_2O$). UV–vis spectroscopy was performed on a UV–vis SPECORD M42 Carl Zeiss Jena, Germany.

The amount of metal ion bound on the CS_4CPL_1 composite was calculated with Eq. (1):

$$\text{Adsorption capacity} = \frac{(S_0 - S)V}{W \times A_M \times 1000},\ \text{mmol/g} \qquad (1)$$

where S_0 and S are the concentrations of the metal ion in aqueous solution (mg/L) before and after the interaction with dried CS_4CPL_1 composite, respectively, V is the volume of the aqueous phase (L), W is the amount of the dried CS_4CPL_1 composite (g) and A_M is the atomic mass of the metal ion.

For each adsorption experiments, the average of three replicates was reported.

2.4. Desorption and regeneration studies

Desorption studies were performed in 25 mL 0.1 M HCl solution by contacting with maximum amount of metal ion absorbed CS_4CPL_1 composite for 1 h. After removing the CS_4CPL_1 composite from the desorption medium, the metal ion concentrations were determined by UV–vis spectroscopy.

The regeneration of the CS_4CPL_1 composite was performed with 0.1 M NaOH, followed by washing to neutral pH.

3. Results and discussion

From the previous study on the influence of zeolite content on the adsorption capacity of the CS/CPL composite for Cu^{2+} ions [19] it was observed an abrupt increase of the adsorption capacity of CS/CPL composites compared with cross-linked chitosan, starting with the lowest content of CPL loaded in the composite ($CS_{10}CPL_1$), up to about 20% of CPL (CS_4CPL_1). The increase of the adsorption capacity of the CS/CPL composites compared with cross-linked chitosan was explained by a synergy of both components, the presence of CPL microparticles leading to the increase of the accessibility at the functional groups of CS network. Therefore, for the present study, the CS_4CPL_1 composite has been selected to perform a comparative evaluation of the metal ion removal to examine the controlling mechanism of the adsorption process the kinetics, adsorption isotherms and thermodynamic parameters.

3.1. Effect of pH

The pH of the metal ion solution plays an important role in the whole adsorption process and particularly on the adsorption capacity by the modification of the level of ionization of CS. Fig. 1 showed the effect of solution pH on the adsorption capacity of CS_4CPL_1 composite for Cu^{2+}, Co^{2+} and Ni^{2+}.

It can be seen from Fig. 1 that the amount of M^{2+} adsorbed by CS_4CPL_1 composite slowly increased when pH of M^{2+} solution increased from 2 to 5, the optimum adsorption pH being located at 5. At low pH, most of the amino groups of CS in the composite were ionized and presented in the form of NH_3^+, electrostatic repulsion between M^{2+} and NH_3^+ ions may prevent the adsorption of M^{2+} ions onto the composite. At pH > 5 the M^{2+} retention decreased because small amount of M^{2+} started to deposit as $M(OH)_2$. This also supports the chelation of M^{2+} on the CS_4CPL_1 composite. Considering

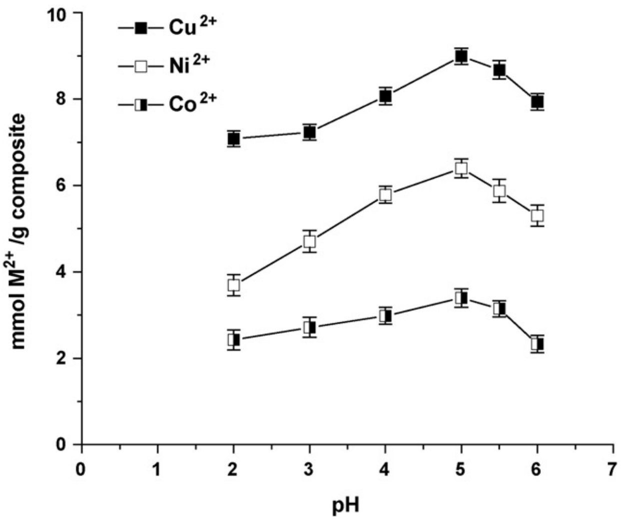

Fig. 1. Metal ions retention on CS_4CPL_1 composite as a function of pH; 25 °C, contact time 24 h, and initial metal concentration of 0.07 mol/L.

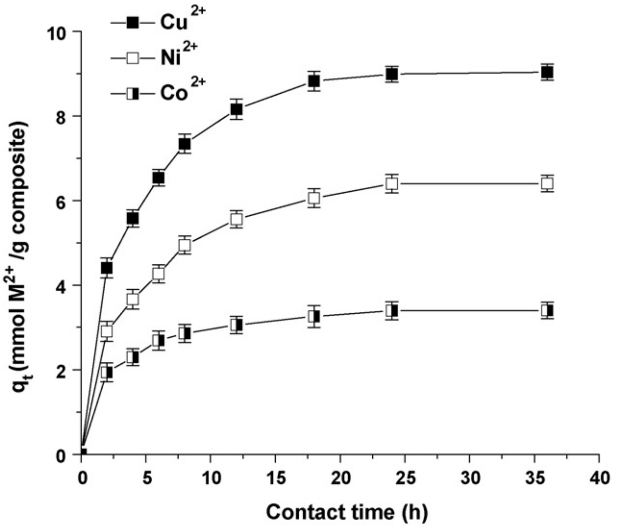

Fig. 2. Metal ions retention on CS_4CPL_1 composite as a function of contact time; 25 °C, pH 5 and initial metal concentration of 0.07 mol/L.

the formation of $M(OH)_2$ when the pH value of M^{2+} solution exceeds 5, the pH of 5 was selected as the initial pH value of M^{2+} solution for the following adsorption experiments.

3.2. Effect of contact time

3.2.1. Kinetic parameters

The effect of the contact time on the metal ions (i.e., Cu^{2+}, Co^{2+} and Ni^{2+}) retention capacity of the CS_4CPL_1 composite is shown in Fig. 2. The contact time varied in the range 0–36 h, and the initial metal concentration was fixed at 0.07 mol/L, the composite being used after the regeneration with 0.1 M NaOH. As Fig. 2 shows, the time required to achieve the equilibrium at pH 5 was about 24 h.

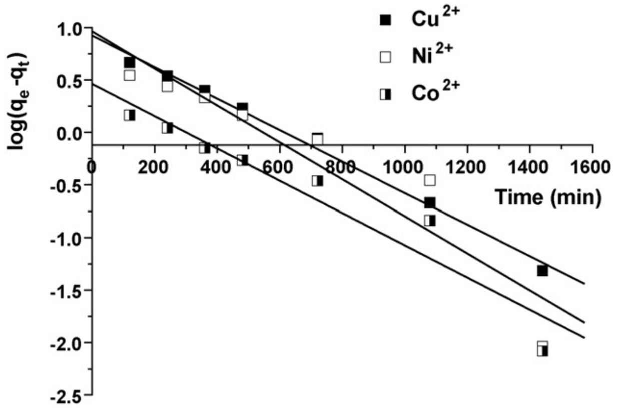

Fig. 3. Pseudo-first order model fitted for the adsorption of metal ions on CS_4CPL_1 composite.

In order to examine the controlling mechanism of the adsorption process such as mass transfer and chemical reaction, kinetic models were used to test the experimental data. The kinetics of metal ion adsorption on the CS_4CPL_1 composite was determined with three different kinetic models, i.e., the pseudo-first and pseudo-second order and the intra-particle diffusion model. The pseudo-first order equation of Lagergren (Eq. (2)) is one of the most widely used equation, being the first rate equation developed for sorption in liquid/solid systems [20].

$$\log(q_e - q_t) = \log(q_e) - \frac{k_1}{2.303}t \tag{2}$$

where q_e and q_t are the amounts of ion metalic adsorbed at equilibrium (mmol/g) and at time t, respectively, and k_1 is the rate constant of pseudo-first order sorption (g/mmol min).

The slopes and intercepts of plots of $\log(q_e - q_t)$ versus t (Fig. 3) were used to determine the pseudo-first order rate constant k_1 and q_e, the values obtained were presented in Table 1. The theoretical q_e values estimated from the pseudo-first order kinetic model gave significantly different values compared to experimental values, and the correlation coefficients were also found to be lower (Table 1). These results showed that the pseudo-first order kinetic model did not describe these sorption systems.

The adsorption data were also treated according to the pseudo-second order kinetics (Eq. (3)) because it was shown to be more likely to predict the behavior over the whole range of adsorption being based on the assumption that the rate-determining step may be a chemical sorption involving valence forces through sharing or exchange of electrons between adsorbent and sorbate [5,9,21]:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}t \tag{3}$$

where k_2 is the rate constant of pseudo-second order sorption (g/mmol min).

The values of q_e and k_2 were obtained from the slope and intercept of the straight line obtained by plotting t/q_t against t (Fig. 4)

Table 1
Kinetic data for the adsorption of Cu^{2+}, Co^{2+} and Ni^{2+} on CS_4CPL_1 composite.

M^{2+}	$q_{e,exp}$ (mmol/g)	Pseudo-first order constants			Pseudo-second order constants			Weber and Morris intra-particle diffusion constants	
		$q_{e,calc}$ (mmol/g)	k_1 (g/mmol min)	R^2	k_2 (g/mmol min)	$q_{e,calc}$ (mmol/g)	R^2	k_{id} (mmol/g min$^{0.5}$)	R^2
Cu^{2+}	9.038	8.356	3.45×10^{-3}	0.996	0.64×10^{-3}	9.832	0.999	0.132	0.920
Ni^{2+}	6.405	9.147	4.05×10^{-3}	0.940	0.69×10^{-3}	7.102	0.999	0.103	0.942
Co^{2+}	3.401	2.893	3.54×10^{-3}	0.958	2.27×10^{-3}	3.615	0.999	0.040	0.926

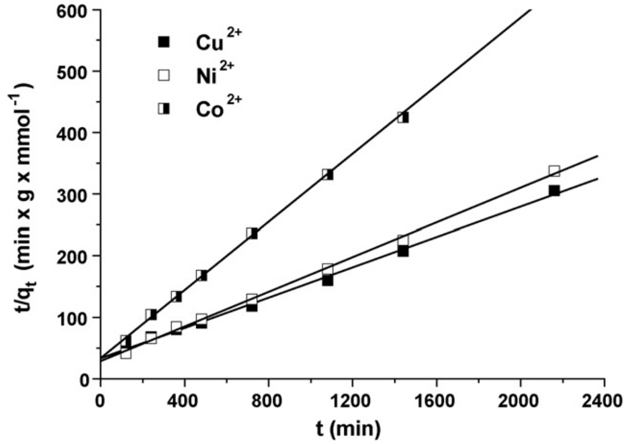

Fig. 4. Pseudo-second order model fitted for the adsorption of metal ions on CS_4CPL_1 composite.

and were collected in Table 1. As Table 1 shows, the correlation factors are high for the CS_4CPL_1 composite, this indicates the validity of the pseudo-second order model for metal ion adsorption on CS_4CPL_1 composite. The pseudo-second order kinetics supports the chemisorption would be the rate-determining step controlling the adsorption process of metal ion, in agreement with the results reported by other groups [9,14].

In order to assess the nature of the diffusion process reasonable for the adsorption of metal ions onto the composite attempts were made to calculate the pore diffusion coefficients. The intra-particle diffusion model was proposed by Weber and Morris [22], the intra-particle diffusion rate constant (k_{id}, mmol/g min$^{0.5}$) has been determined by linearization of the curve $q_t = f(t^{0.5})$ (Eq. (4), Fig. 5):

$$q_t = k_{id} t^{0.5} \tag{4}$$

All the plots have the similar general features, initial linear portion followed by a plateau. The initial linear portion was attributed to the intra-particle diffusion. However, such a deviation of the straight line from the origin could likely be due to the difference in the rate of boundary layer diffusion in the initial stage of adsorption [22]. Generally, the intercept of the plot of q_t versus $t^{0.5}$ gives an idea about boundary layer thickness, the larger the value of the intercept, the greater the boundary layer diffusion effect is [22,23]. The values of intra-particle diffusion rate constant, k_{id}, are presented in Table 1. These results indicate that the metal ion molecules diffused quickly among the sorbents at the beginning of the adsorption process, and then intra-particle diffusion slowed down and stabilized. If the regression of q_t versus $t^{0.5}$ is linear and passes through the origin, then intra-particle diffusion is the sole rate-limiting step. The deviation of straight lines from the origin indicates that intra-particle transport is not the rate-limiting step, in the adsorption process of Cu^{2+}, Co^{2+} and Ni^{2+} on the CS_4CPL_1 composite.

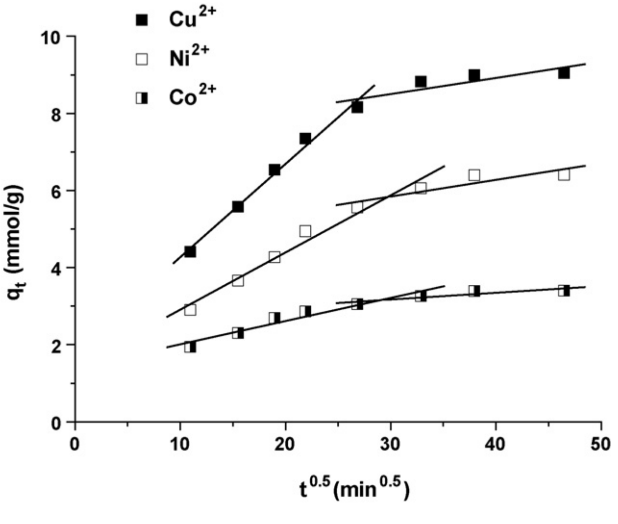

Fig. 5. Weber and Morris intra-particle diffusion model fitted for the adsorption of metal ions on CS_4CPL_1 composite.

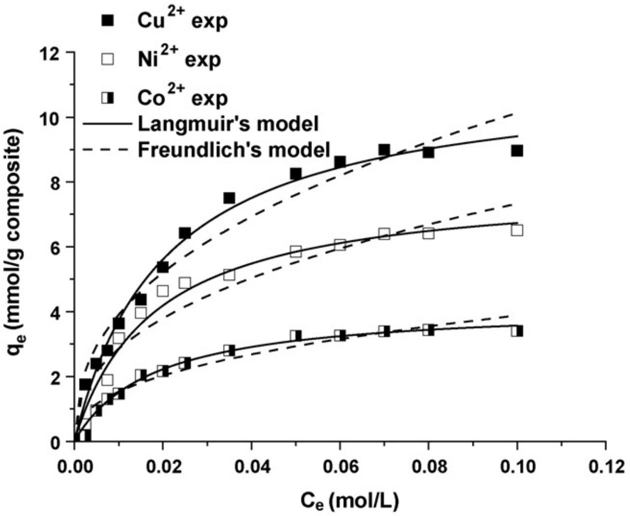

Fig. 6. Comparison of experimental and calculated data for two models for the adsorption of Cu^{2+}, Ni^{2+} and Co^{2+} on CS_4CPL_1 composite. The calculated data were obtained with an Origin 7.5 program by applying Eq. (5) for the Freundlich model and Eq. (6) for the Langmuir model.

3.3. Effect of initial concentrations of metal ion on the adsorption efficiency

In the adsorption process of a solute from solution onto a solid surface, the solute adsorbed on the solid surface is in a dynamic equilibrium with the solute remained in solution. A plot of the solute concentration adsorbed on the solid surface (mg/g) as a function of the solute concentration in the solution at equilibrium (mg/L), at constant temperature, gives an adsorption isotherm, which can be described by some adsorption models. Fig. 6 shows that the retention capacity of CS_4CPL_1 composite for Cu^{2+}, Co^{2+} and Ni^{2+} ions increased with the increase of the equilibrium metal concentration resulting in a concave curve, i.e., a type L isotherm according to the classification of Limousin et al. [24].

Analysis of equilibrium data is important for developing an equation that can be used to compare different sorbents under different operational conditions and to design and optimize an operating procedure [23]. Some isotherm equations have been tested in the present study, namely the Freundlich (Eq. (5)) and Langmuir (Eq. (6)) isotherm models (Fig. 6):

$$q_e = K_F C_e^N \tag{5}$$

$$q_e = \frac{K_L b C_e}{1 + K_L C_e} \tag{6}$$

where q_e is the amount of metal ion adsorbed in mg/g, C_e is the concentration (mg/L) of metal ion in the solution at equilibrium; K_F, Freundlich constant which predicts the quantity of metal ion per gram of resin at the unit equilibrium concentration; N, a measure of the nature and strength of the adsorption process and of the distribution of active sites. If $N < 1$, bond energies increase with the surface density; if $N > 1$, bond energies decrease with the surface

Table 2
Adsorption isotherm constants of Freundlich and Langmuir models for the adsorption of Cu^{2+}, Ni^{2+} and Co^{2+} on CS_4CPL_1 composite.

Adsorption model	Cu^{2+}	Ni^{2+}	Co^{2+}
Freundlich			
K_F (mmol/g)	26.27	18.82	9.841
N	0.414	0.409	0.404
R^2	0.962	0.918	0.943
Langmuir			
K_L (L/mmol)	49.08	55.68	55.77
b (mmol/g)	11.32	7.94	4.209
R^2	0.991	0.977	0.989
R_L	0.225	0.204	0.203

density, and when $N = 1$, all surface sites are equivalent; The Langmuir constants K_L and b represent adsorption equilibrium constant and saturated monolayer adsorption capacity, respectively.

The constants corresponding to the adsorption models were calculated with an Origin 7.5 program by applying Eq. (5) for the Freundlich model and Eq. (6) for the Langmuir model and were collected in Table 2.

As Table 2 shows the experimental data obtained for the adsorption of all metal ions onto CS_4CPL_1 composite well fitted in the Langmuir model with a maximum theoretical adsorption capacity of 11.32 mmol Cu^{2+}/g composite, 7.94 mmol Ni^{2+}/g composite and 4.209 mmol Co^{2+}/g composite, respectively. The CS_4CPL_1 composite showed good retention ability for the metal ions in the following order: $Cu^{2+} > Ni^{2+} > Co^{2+}$, i.e., increased with the decrease of the hydrated cation radius, at pH 5 and 0.07 mol/L metal ions.

The essential features of a Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor or equilibrium parameter, R_L (Eq. (7)), which is used to predict if an adsorption system is favourable "or "unfavorable" [23].

$$R_L = \frac{1}{1 + K_L C_i} \tag{7}$$

where C_i is the initial metal concentration. The value of R_L indicates the shape of isotherm to be either unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$) or irreversible ($R_L = 0$). Herein, R_L values obtained for Cu^{2+}, Co^{2+} and Ni^{2+} ions are listed in Table 2. The fact that all the R_L values for the adsorption of Cu^{2+}, Co^{2+} and Ni^{2+} ions onto CS_4CPL_1 composite are in the ranges of 0–1 for 0.07 mol/L initial metal ion concentration, confirmed that the CS_4CPL_1 composite is favorable for adsorption of Cu^{2+}, Co^{2+} and Ni^{2+} ions under the selected conditions (Table 2).

3.4. Temperature effect on the metal retention capacity of composite

To evaluate the thermodynamic parameters of the metal cation adsorption on the composite under study, the adsorption experiments were performed at three different temperatures (298, 308 and 318 K). 25 mL of the cation metal solution with a concentration of 0.07 mol/L was allowed to equilibrate with 0.25 g of composite. The equilibrium constant for the adsorption process, K_C, calculated with Eq. (8) [1,2], was evaluated at 298, 308 and 318 K for each metal cation (Table 3):

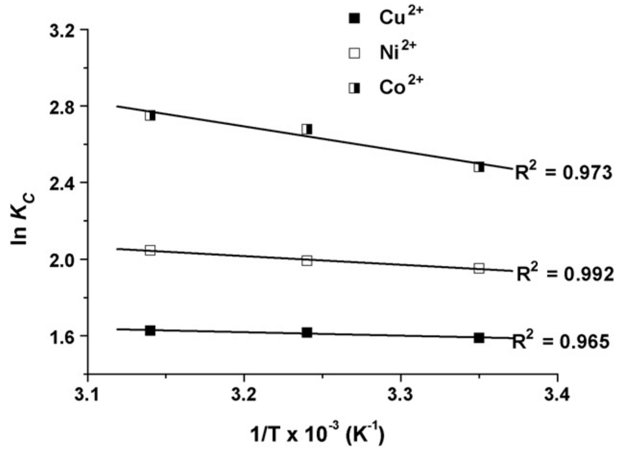

Fig. 7. Plot of ln K_C as a function of reciprocal of temperature ($1/T$) for the adsorption of Cu^{2+}, Ni^{2+} and Co^{2+} by CS_4CPL_1 composite.

$$K_C = \frac{X_e}{C_i - X_e} \tag{8}$$

where X_e is the concentration of solute adsorbed on the resin at equilibrium, mmol/L; C_i is the initial ion concentration, mmol/L.

To calculate the free energy of the adsorption (ΔG°_{ads}), the following equation was employed:

$$\Delta G^\circ_{ads} = -RT \ln K_C \tag{9}$$

The Eq. (10), allows to evaluate the standard enthalpy (ΔH°_{ads}) and enthropy (ΔS°_{ads}) of the adsorption by plotting ln K_C versus $1/T$.

$$\ln K_C = \frac{\Delta S^\circ_{ads}}{R} - \frac{\Delta H^\circ_{ads}}{RT} \tag{10}$$

where R (8.314 J/mol K) is the gas constant.

The values of the slope $-\Delta H^\circ_{ads}/R$ and the intercept $\Delta S^\circ_{ads}/R$ from Fig. 7 give ΔH°_{ads} and ΔS°_{ads} for the adsorption of Cu^{2+}, Co^{2+} and Ni^{2+} ions on the composite.

The values of the thermodynamic parameters (ΔG°_{ads}, ΔH°_{ads}, ΔS°_{ads}) were collected in Table 3.

As presented in Table 3, the negative values of ΔG°_{ads} for all ions under all conditions indicates the spontaneous nature of the adsorption. The negative ΔH°_{ads} means a chemical exothermic process and support the chemisorption is the rate-determining step. The positive values of ΔS°_{ads} show an irregular increase of the randomness at the composite-solution interface during adsorption [23].

3.5. Desorption of metal ions and composite regeneration

An important characteristic of the composite sorbents is the rate of desorption of the metal adsorbed. The results obtained at the desorption of metal ions from CS_4CPL_1 composite as a function of time were plotted in Fig. 8.

The optimal desorption condition for all metal ions was 0.1 M HCl, and a complete desorption was achieved under this condi-

Table 3
Thermodynamic parameters for the adsorption of Cu^{2+}, Ni^{2+} and Co^{2+} on CS_4CPL_1 composite.

M^{2+}	K_C			$-\Delta G^\circ_{ads}$(kJ/mol)			$-\Delta H^\circ_{ads}$(kJ/mol)	ΔS°_{ads}(J/mol K)
	298 K	308 K	318 K	298 K	308 K	318 K		
Cu^{2+}	5.087	5.041	4.898	4.03	4.142	4.2	1.508	18.282
Ni^{2+}	7.75	7.333	7.046	5.073	5.102	5.162	3.76	28.799
Co^{2+}	15.666	14.555	11.96	6.817	6.857	6.56	10.758	56.817

Table 4
Comparison of adsorption capacities (q_{max}, mmol/g) for Cu^{2+}, Co^{2+} and Ni^{2+} of different sorbents.

Sorbent	pH	q_{max} (mmol/g)			Ref.
		Cu^{2+}	Co^{2+}	Ni^{2+}	
CS beads	6	0.59	–	–	[9]
Cross-linked CS beads (epichlorohydrin)		0.55	–	–	
CS-g-poly(acrylic acid) attapulgite composite	5.5	4.772	–	–	[14]
Cross-linked CS	5	5.744	–	–	[19]
CS_2CPL_1 composite		8.183			
Cross-linked CS beads (glutaraldehyde)	5–6	2.58	1.68	2.34	[25]
Alumina/CS composite	5–6	3.2	–	–	[26]
Magnetic CS nanoparticles	5.5	–	0.465	–	[27]
Poly(amidoxime)/SiO_2 composite	4.5	1.575	–	–	[28]
CS_4CPL_1 composite	5	11.32	4.209	7.94	This study

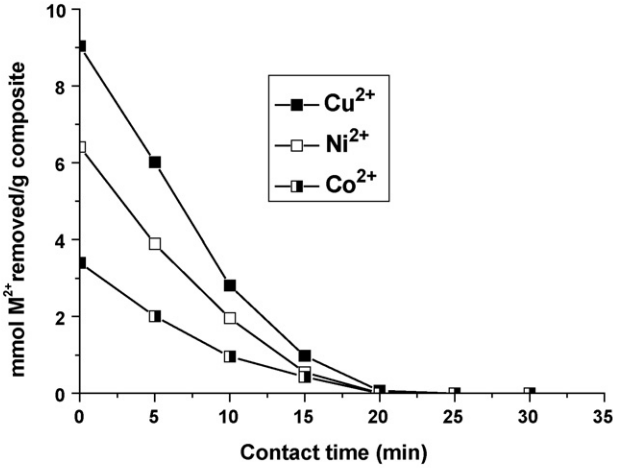

Fig. 8. Metal ions removal from CS_4CPL_1 composite with HCl 0.1 M as a function of contact time.

tion in about 20 min (Fig. 8). The eluent used for the regeneration of the spent sorbent was 0.1 M NaOH. The regenerated composite was reused again for the retention of metal ions at least four times (results not shown here).

Table 4 summarizes some comparative adsorption capacities for Cu^{2+}, Co^{2+}, and Ni^{2+} based on results reported in literature and own results obtained by the adsorption of these metal ions on CS/CPL composites. As Table 4 shows, the adsorption capacities for the metal ions reported in this work are higher than those found in literature, and recommend this novel composite as an alternative for the sorption of heavy metal ions.

4. Conclusions

A novel composite based on CS and CPL, CS_4CPL_1, was used for the removal of Cu^{2+}, Co^{2+} and Ni^{2+}, as a function of different parameters like: pH, contact time, metal ion concentration and temperature. The optimum adsorption pH of all metal ions was located at 5 and the contact time required to achieve the equilibrium was 24 h.

The adsorption process of metal ions obeyed of the pseudo-second order kinetics, supporting the chemisorption would be the rate-determining step. The equilibrium data obtained for the adsorption of all metal ions onto CS_4CPL_1 composite well fitted in the Langmuir model with a maximum theoretical adsorption capacity of 11.32 mmol Cu^{2+}/g composite, 7.94 mmol Ni^{2+}/g composite and 4.209 mmol Co^{2+}/g composite, respectively. The adsorption process was spontaneous ($\Delta G^{\circ}_{ads} < 0$) and exothermic ($\Delta H^{\circ}_{ads} < 0$), supporting also the chemisorption is the rate-determining step.

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References

[1] A. Baraka, P.J. Hall, M.J. Heslop, Preparation and characterization of melamine–formaldehyde–DTPA chelating resin and its use as an adsorbent for heavy metals removal from wastewater, React. Funct. Polym. 67 (2007) 585–600.
[2] M.V. Dinu, E.S. Dragan, Heavy metals adsorption on some iminodiacetate chelating resins as a function of the adsorption parameters, React. Funct. Polym. 68 (2008) 1346–1354.
[3] M.V. Dinu, E.S. Dragan, A.W. Trochimczuk, Sorption of Pb(II), Cd(II) and Zn(II) by iminodiacetate chelating resins in non-competitive and competitive conditions, Desalination 249 (2009) 374–379.
[4] C. Liu, R. Bai, Q. San Ly, Selective removal of copper and lead ions by diethylenetriamine-functionalized adsorbent: Behaviors and mechanisms, Water Res. 42 (2008) 1511–1522.
[5] M.E. Argun, Use of clinoptilolite for the removal of nickel ions from water: Kinetics and thermodynamics, J. Hazard. Mater. 150 (2008) 587–595.
[6] W. Qiu, Y. Zheng, Removal of lead, copper, nickel, cobalt, and zinc from water by a cancrinite-type zeolite synthesized from fly ash, Chem. Eng. J. 145 (2009) 483–488.
[7] H. Bedelean, M. Stanca, A. Măicăneanu, S. Burcam, Zeolitic volcanic tuffs from Măcicaş (Cluj County), natural raw materials used for NH^{4+} removal from wastewaters. Studia Universitatis Babes-Bolyai, Geologia 52 (2006) 43–49.
[8] P.R. Shukla, S. Wang, H.M. Ang, M.O. Tadé, Synthesis, characterisation, and adsorption evaluation of carbon–natural-zeolite composites, Adv. Powder Technol. 20 (2009) 245–250.
[9] A.-H. Chen, S.-C. Liu, C.-Y. Chen, Comparative adsorption of Cu(II), Zn(II), and Pb(II) ions in aqueous solution on the crosslinked chitosan with epichlorohydrin, J. Hazard. Mater. 154 (2008) 184–191.
[10] G. Crini, Recent developments in polysaccharide-based materials used as adsorbents in wastewater treatment, Prog. Polym. Sci. 30 (2005) 38–70.
[11] E. Guibal, Interactions of metal ions with chitosan-based sorbents: a review, Sep. Purif. Technol. 38 (2004) 43–74.
[12] P.O. Osifo, A. Webster, H. van der Merve, H.W.J.P. Neomagus, M.A. van der Gun, D.M. Grant, The influence of the degree of cross-linking on the adsorption properties of chitosan beads, Bioresour. Technol. 99 (2008) 7377–7382.
[13] W.S. Wan Ngah, C.S. Endud, R. Mayanar, Removal of copper(II) ions from aqueous solution onto chitosan and cross-linked chitosan beads, React. Funct. Polym. 50 (2002) 181–190.
[14] X. Wang, Y. Zheng, A. Wang, Fast removal of copper ions from aqueous solution by chitosan-g-poly(acrylic acid)/attapulgite composites, J. Hazard. Mater. 168 (2009) 970–977.
[15] V.M. Boddu, K. Abburi, J.L. Talbott, E.D. Smith, R. Haasch, Removal of arsenic (III) and arsenic (V) from aqueous medium using chitosan-coated biosorbent, Water Res. 42 (2008) 633–642.
[16] A. Gupta, V.S. Chauhan, N. Sankararamakrishnan, Preparation and evaluation of iron–chitosan composites for removal of As(III) and As(V) from arsenic contaminated real life groundwater, Water Res. 43 (2009) 3862–3870.
[17] K. Swayampakula, V.M. Boddu, S.K. Nadavala, K. Abburi, Competitive adsorption of Cu (II), Co (II) and Ni (II) from their binary and tertiary aqueous solutions using chitosan-coated perlite beads as biosorbent, J. Hazard. Mater. 170 (2009) 680–689.
[18] E.S. Dragan, M.V. Dinu, Removal of copper ions from aqueous solution by adsorption on ionic hybrids based on chitosan and clinoptilolite, Ion Exchange Lett. 2 (2009) 15–18.
[19] E.S. Dragan, M.V. Dinu, D. Timpu, Preparation and characterization of novel composites based on chitosan and clinoptilolite with enhanced adsorption properties for Cu^{2+}, Bioresour. Technol. 101 (2010) 812–817.

[20] K.V. Kumar, S. Sivanesan, Selection of optimum sorption kinetics: comparison of linear and non-linear method, J. Hazard. Mater. 134 (2006) 277–279.

[21] Y.S. Ho, Second-order kinetic model for the sorption of cadmium onto tree fern: a comparison of linear and non-linear methods, Water Res. 40 (2006) 119–125.

[22] J.W.J. Weber, J.C. Morriss, Kinetics of adsorption on carbon from solution, J. Sanit. Eng. Div., Proc. Am. Soc. Civil Eng. 89 (1963) 31–60.

[23] G. Bayramoglu, B. Altintas, M.Y. Arica, Adsorption kinetics and thermodynamic parameters of cationic dyes from aqueous solutions by using a new strong cation exchange resin, Chem. Eng. J. 152 (2009) 339–346.

[24] G. Limousin, J.-P. Gaudet, L. Charlet, S. Szenknect, V. Barthes, M. Krimissa, Sorption isotherms: a review on physical bases, modeling and measurement, Appl. Geochem. 22 (2007) 249–275.

[25] Z. Cao, H. Ge, S. Lai, Studies on synthesis and adsorption properties of chitosan cross-linked by glutaraldehyde and Cu(II) as template under microwave irradiation, Eur. Polym. J. 37 (2001) 2141–2143.

[26] G.C. Steenkamp, K. Keizer, H.W.J.P. Noeomagus, H.M. Krieg, Copper(II) removal from polluted water with alumina/chitosan composite membranes, J. Membr. Sci. 197 (2002) 147–156.

[27] Y.-C. Chang, S.-W. Chang, D.-H. Chen, Magnetic chitosan nanoparticles: Studies on chitosan binding and adsorption of Co(II) ions, React. Funct. Polym. 66 (2006) 335–341.

[28] B. Gao, Y. Gao, Y. Li, Preparation and chelation adsorption property of composite chelating material poly(amidoxime)/SiO_2 towards heavy metal ions, Chem. Eng. J. 158 (2010) 542–549.