

COMPARATIVE SORPTION OF Co^{2+} , Ni^{2+} AND Cr^{3+} ONTO CHITOSAN/POLY(VINYL AMINE) COMPOSITE BEADS

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The aim of the present study was to investigate the adsorption properties of chitosan (CS)/poly(vinyl amine) (PVAm) composites in aqueous solutions containing Co^{2+} , Ni^{2+} or Cr^{3+} ions. Adsorption of metal ions onto the CS/PVAm composite beads was investigated in batch mode. The effects of initial pH, and of the initial metal ion solution concentration were studied. The equilibrium data obtained for the adsorption of all metal ions onto CS/PVAm composite fitted well the Langmuir model with a maximum theoretical adsorption capacity of 153.35 mg Cr^{3+} /g composite, 143.73 mg Ni^{2+} /g composite, and 67.89 mg Co^{2+} /g composite, respectively.

Keywords: composite, chitosan, poly(vinyl amine), metal uptake

INTRODUCTION

Heavy metal pollution is spreading throughout the world with the expansion of industrial activities, trace metals being widely present in the environment. Heavy metal ions are persistent, bio-accumulative and toxic substances, their presence in the environment being harmful to a variety of living species, including human beings. Co, Ni, and Cr are among the most harmful heavy metals present in liquid effluents. Co^{2+} is found in the wastewater of nuclear power plants and many other industries such as mining, metallurgical, electroplating, paints, pigments, and electro-engineering.^{1,2} Co^{2+} ions present in industrial wastewaters can produce various undesirable effects on human beings, such as nausea, vomiting, asthma, damage to heart up to heart failure, damage to thyroid and liver. Ni^{2+} can be found mainly in wastewaters from electroplating, electronics, and metal cleaning industries. Human contact with Ni^{2+} can cause severe damage to lungs and kidneys, gastrointestinal illnesses, pulmonary fibrosis, renal edema, and skin dermatitis.³ Cr^{3+} ions have been commonly found in effluents from industries such as mining, leather tanning, chrome plating, and textiles.⁴ Cr^{3+} is essential to animals and plants and plays an

important role in sugar and fat metabolism, although in excess it can cause allergic skin reactions and cancer.⁵

Various technologies have been applied to remove Co^{2+} , Ni^{2+} , and Cr^{3+} ions from waste streams, such as: chemical precipitation, chemical oxidation/reduction, and electrochemical treatment. However, all of the above methods have disadvantages, which make them less technically appealing in wastewater treatment.⁶ Adsorption is one of the most effective methods for the removal of these heavy metal ions from wastewater streams. Although activated carbons have long been recognized as effective commercial adsorbents for treating industrial wastewaters containing heavy metal ions, their low efficiency have limited their commercial use in actual industrial scenarios.⁷ To reduce the operational costs, the search for a cheap and widely available adsorbent has motivated researchers to focus on naturally available adsorbents.⁸⁻¹⁰ The presence of hydroxyl, acetamido and amino functional groups in chitosan (CS) generates hydrophilicity and excellent chelating properties for heavy metal ions. Furthermore, the reactivity of amine groups

allows the enhancement of its adsorption properties by various chemical reactions.¹¹⁻¹³

In our recent studies, the synthesis of some novel composites obtained by ionic (ionotropic gelation)/covalent cross-linking (with epichlorohydrin, ECH) of a CS/poly(vinyl amine) (PVAm) blend has been reported.^{14,15} The CS/PVAm composites as beads presented a high sorption capacity for Cu²⁺ ions, and a high level of reusability (up to seven consecutive sorption/desorption cycles). This prompted us to extend the investigations on the sorption capacity of these composites against other heavy metal ions such as: Co²⁺, Ni²⁺ and Cr³⁺. Therefore, the factors influencing the adsorption capacity of the CS/PVAm composite beads, such as pH value of the initial metal ions solutions, and the initial concentration of the metal ions in aqueous solutions, were investigated in this work. To the best of our knowledge, this is the first study of sorption of these heavy metal ions on such composite sorbents.

EXPERIMENTAL

Materials

Low molar mass CS was purchased from Sigma-Aldrich and used as received. The average molar mass, determined by viscometry as previously shown,¹⁶ was 467 kDa. The degree of acetylation (DA) of CS was evaluated by infrared spectroscopy using a Vertex 70 Bruker FTIR spectrometer.¹⁷ An average value of DA = 15%, resulted from three measurements, was taken into account. PVAm as aqueous solution with a concentration of 18 wt%, a molar mass of 340 kDa, and a degree of hydrolysis of 95 wt%, was received from BASF (Ludwigshafen, Germany). NiSO₄•6H₂O, CoSO₄•7H₂O and KCr(SO₄)₂•12H₂O used as metal ion sources for the sorption experiments were purchased from Sigma Aldrich. Sodium tripolyphosphate (TPP) (85%) was purchased from Sigma-Aldrich and used as received. ECH purchased from Sigma-Aldrich was distilled twice on KOH. All the other reagents (NaOH, methanol) were of analytical grade, and used without further purification.

Methods

Synthesis of CS/PVAm composite beads

Ionic composite based on CS and PVAm were prepared as microspheres by a "tandem" ionic/covalent cross-linking, according to the method previously presented.^{14,15} The mass ratio between CS and PVAm, selected for this investigation, was 60 wt% of CS and 40 wt% of PVAm, because from previous equilibrium sorption experiments of Cu²⁺ on the composite sorbents different by the ratio between CS and PVAm it was found that the sorption capacity of this composite was higher than that of the composite

consisting of 90 wt% of CS and 10 wt% of PVAm.¹⁴ Therefore, for the investigation of the sorption capacity of Co²⁺, Ni²⁺ and Cr³⁺ ions, only this composite was selected. The synthesis of the composite as beads consisted in the following steps: (1) preparation of the mixture between CS solution with ECH and PVAm solution with ECH, the added ECH being calculated for a molar ratio ECH:NH₂ of 2:1, and stirring until the mixture was completely homogenized; (2) formation of beads occurred by dropping the previously prepared mixture into an aqueous solution of 0.05 M TPP, at room temperature, keeping the beads in TPP for 3 h; (3) the beads were separated from TPP and transferred into a mixture containing ethanol and an aqueous solution of pH 11 with a weight ratio of 50:50, the final solution pH being 9. The composite beads were kept in this solution for 24 h. After that, the microspheres were intensively washed with distilled water in order to remove the excess of small ions and then dried at room temperature for ~24 h, and under vacuum at 40 °C, for 48 h. In order to remove all TPP ions the composites were treated with 0.1 M HCl for 1 h, rinsed with distilled water and treated with 0.1 M NaOH for 1 h. The process was repeated once again and after that the composite beads were washed to neutral pH.

Characterization of CS/PVAm

The structure of the CS/PVAm composite beads, before and after the sorption of all metal ions, was investigated by FTIR spectroscopy. The dried samples were first frozen in liquid nitrogen, and then broken in a mortar to get the samples as powder. FTIR spectra were recorded with a Bruker Vertex FTIR spectrometer, resolution 2 cm⁻¹, in the range of 4000-400 cm⁻¹ by the KBr pellet technique, the amount of the sample being about 5-8 mg in each pellet.

An optical microscope was used to investigate the shape of the CS/PVAm in swollen state, before and after the sorption of Co²⁺, Ni²⁺, and Cr³⁺.

Batch sorption experiments

Batch adsorption studies were used to determine the effect of pH and initial concentration of metal ions (Co²⁺, Ni²⁺, and Cr³⁺) on the sorption capacity of the composite beads. The adsorption capacity of the sorbent, mg/g, was calculated with Equation 1:

$$q = \frac{(C_i - C_e) \times V}{m} \quad (1)$$

where: C_i and C_e are the concentrations of the metal ions in aqueous solution (mg/L) before and after the interaction with the chelating sorbent, respectively, V is the volume of metal ions aqueous solution (L), and m is the amount of the dry composite beads (g). The sorbent dose was around 0.1 g/10 mL aqueous solution of all metal ions, at 25 °C. The sorbent was filtered off, and the residual concentration of the metal cation in the filtrate was measured by UV-Vis spectroscopy at 721 nm (the maximum absorption wavelengths of

$\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$), and 513 nm (the maximum absorption wavelengths of $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$) using a UV-Vis SPECORD200 Carl Zeiss Jena, Germany. The concentration of Cr^{3+} ions was measured by photocolometry using Complexone III.

In the case of the ions investigated in this work, the behavior during the desorption step depended on the nature of the ion. Thus, the desorption of Ni^{2+} was completed with 0.1 M HCl, in two steps each of one hour, and the sorbent could be reused after regeneration with 0.1 M NaOH. On the other hand, various desorption agents have been tested for desorption of Co^{2+} , such as: aqueous solution of 0.2 M EDTA, aqueous solution of 10% NH_3 , aqueous solution of 2 M HCl, but no agent led to satisfactory desorption efficiency. Therefore, the composite sorbents could be reused in successive sorption/desorption cycles only when Ni^{2+} was the ion of interest.

RESULTS AND DISCUSSION

Sorbent characterization

The optical microscopy image in Figure 1A shows the uniform size of the CS/PVAm composite beads, which retain their spherical shape after loading with metal ions. The CS/PVAm composite beads loaded with metal ions were colored in dark plum for Co^{2+} (Figure

1B), light green for Ni^{2+} (Figure 1C), and dark green for Cr^{3+} (Figure 1D). In all three cases, the color is uniformly distributed on the composite surface.

Information about the functional groups of the composite beads, before and after loading with metal ions (Co^{2+} , Ni^{2+} , and Cr^{3+}), was provided by the FTIR spectra (Figure 2). The main peaks visible in the FTIR spectrum of the CS/PVAm composite are located at: 3441 cm^{-1} , assigned to the $-\text{OH}$ and $-\text{NH}$ stretching vibrations as well as to hydrogen bonds, 2924 cm^{-1} and 2855 cm^{-1} , assigned to the CH , and CH_2 stretching vibrations, 1645 cm^{-1} assigned to the stretching vibration of $\text{C}=\text{O}$ in the secondary amide bond of the acetamido groups in CS; 1447 cm^{-1} assigned to $-\text{CH}_2$ groups in PVAm, 1377 cm^{-1} assigned to the secondary $-\text{OH}$ in the anhydroglucose unit (AGU), while the peaks located at 1319 cm^{-1} and 1159 cm^{-1} were assigned to the $\text{C}-\text{N}$ stretching vibration, and to the antisymmetric stretching of the $\text{C}-\text{O}-\text{C}$ bridge, respectively. The peaks located at 1069 cm^{-1} and 1032 cm^{-1} were assigned to the skeletal vibration involving the stretching of $\text{C}-\text{O}$ bonds in AGU.

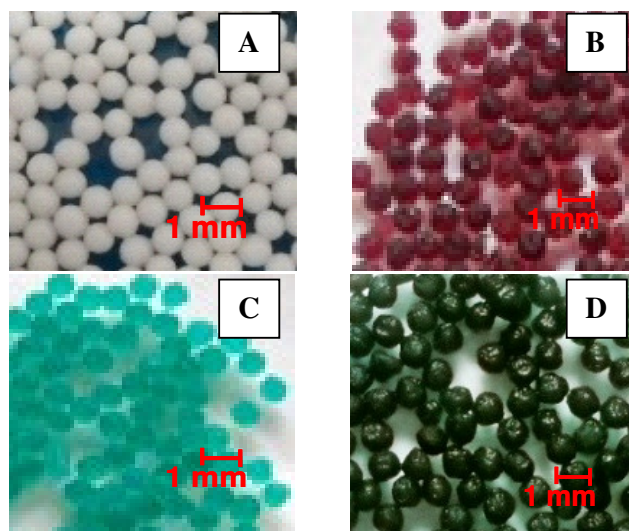


Figure 1: Optical images of CS/PVAm composite beads before (A) and after sorption of: Co^{2+} (B), Ni^{2+} (C), and Cr^{3+} (D)

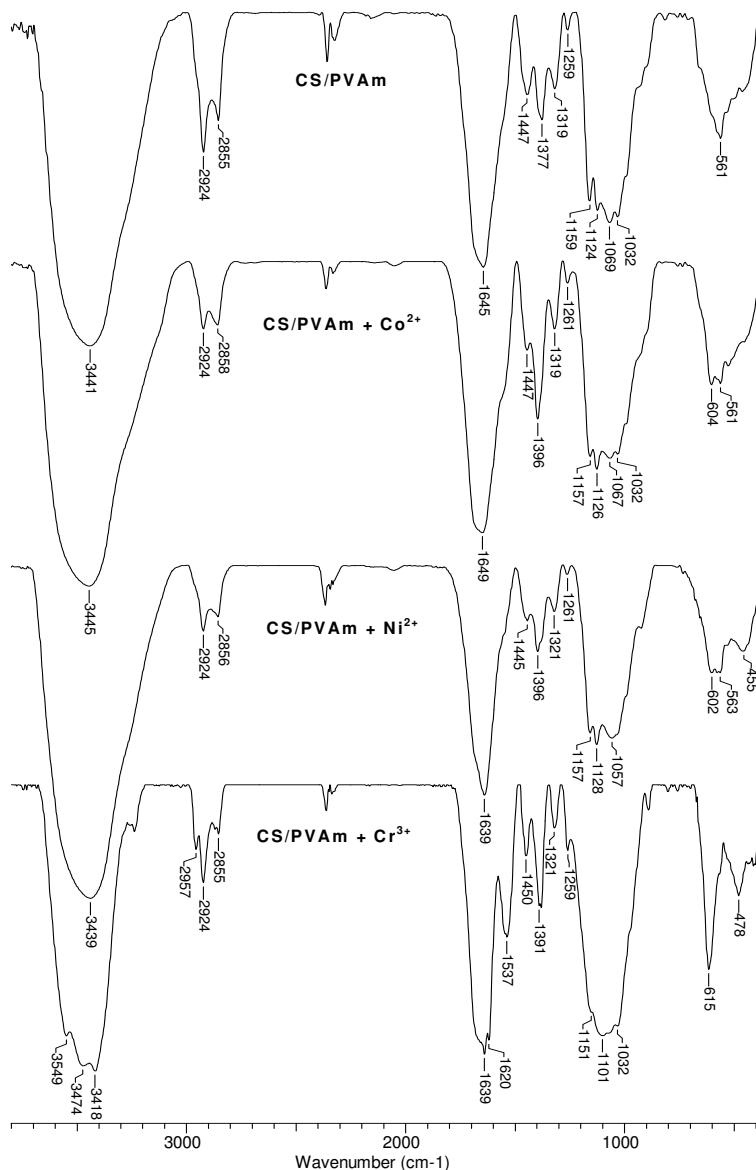


Figure 2: FTIR spectra of CS/PVAm composite beads before and after metal ions sorption

In the spectrum of the CS/PVAm composite loaded with Co^{2+} ions the following changes were observed: the peak located at 1645 cm^{-1} was shifted to 1649 cm^{-1} , the peak at 1377 cm^{-1} increased in intensity and was shifted to 1396 cm^{-1} , the peaks located at 1159 cm^{-1} and 1069 cm^{-1} diminished in intensity and were shifted to 1157 cm^{-1} and 1067 cm^{-1} . Also, the additional peak located at 604 cm^{-1} supports the binding of Co^{2+} ions on the composite beads. The main changes after the adsorption of Ni^{2+} could be seen in the range 1700 cm^{-1} - 500 cm^{-1} . Thus, the peak located at 1645 cm^{-1} was shifted to 1639 cm^{-1} , the peak

from 1377 cm^{-1} was shifted to 1396 cm^{-1} , the peaks located at 1159 cm^{-1} and 1069 cm^{-1} diminished and were shifted to 1157 cm^{-1} and 1057 cm^{-1} , and the peak from 1032 cm^{-1} disappeared. All these changes and the presence of two additional absorption peaks located at 602 cm^{-1} and 455 cm^{-1} support the participation of N and O atoms as the main binding sites in the chelation of Ni^{2+} ions. The structural changes, after the adsorption of Cr^{3+} , are supported by the FTIR spectrum. Thus, the large band at around 3441 cm^{-1} , present in the spectrum of the CS/PVAm composite before the sorption of metal

ion, displays three distinct peaks located at 3549 cm^{-1} , 3474 cm^{-1} , and 3418 cm^{-1} , after the sorption of Cr^{3+} . The main changes can be seen in the range 1700 cm^{-1} - 500 cm^{-1} . Thus, the peak located at 1645 cm^{-1} was shifted to 1639 cm^{-1} , a new peak located at 1537 cm^{-1} appeared and was attributed to the $-\text{NH}$ bending vibration of $-\text{NH}_2$ groups, the peak from 1377 cm^{-1} increased in intensity and was shifted to 1391 cm^{-1} , the peaks from 1159 cm^{-1} and 1069 cm^{-1} were shifted to 1151 cm^{-1} and 1101 cm^{-1} after the sorption of Cr^{3+} . Furthermore, two new peaks located at 615 cm^{-1} and 478 cm^{-1} appeared. These new peaks support the chelation of metal ions and are mainly assigned to the stretching vibrations of M-N and M-O bonds.

Based on the information obtained from the FTIR spectra, a possible mechanism of chelation of metal ions (Co^{2+} , Ni^{2+} , and Cr^{3+}) is presented in Figure 3.

Sorption of Co^{2+} , Ni^{2+} , and Cr^{3+} ions

Effect of initial pH

One of the most critical parameters in the adsorption process of metal ions from aqueous solutions is the medium pH.^{18,19} Different metal ions may have different optimum pH, possibly due to the different solution chemistry of the species.

Figure 4 shows the effect of the initial solution pH on the equilibrium uptake of Co^{2+} and Ni^{2+} ions between pH 2.68 and 7.63, at 298 K, at fixed initial concentrations of metal ions of 7 mmol/L. As can be seen in Figure 4, the amount of Co^{2+} and Ni^{2+} ions sorbed at equilibrium on CS/PVAm composite beads monotonously increased with the increase of pH value from 2.68 to up 7.63. It is well known that the metal ions sorption starts at pH 2-3 and increases with the increase in pH up to the appearance of the precipitate in the system. In the very low acidic region (pH 2), there is a competition between H^+ and metal ions (Co^{2+} , Ni^{2+}) for the same active sites (amine groups in CS and PVAm), the protonation of the amine groups onto the CS/PVAm composite surface decreasing the amount of metal ions sorbed onto the beads at this pH.

The lower adsorption values could be also attributed to the electrostatic repulsion between the positive charges of CS and PVAm, on the one side, and the positively charged metal ions, on the other side. Increasing the pH from 2.68 up to 7.63 led to an enhancement of the sorption capacity because the protonation degree of amine groups decreased, and the surface was getting less positive. The interactions like ion-exchange and chelation between metal ions and the sorbent surface were thus strengthened.

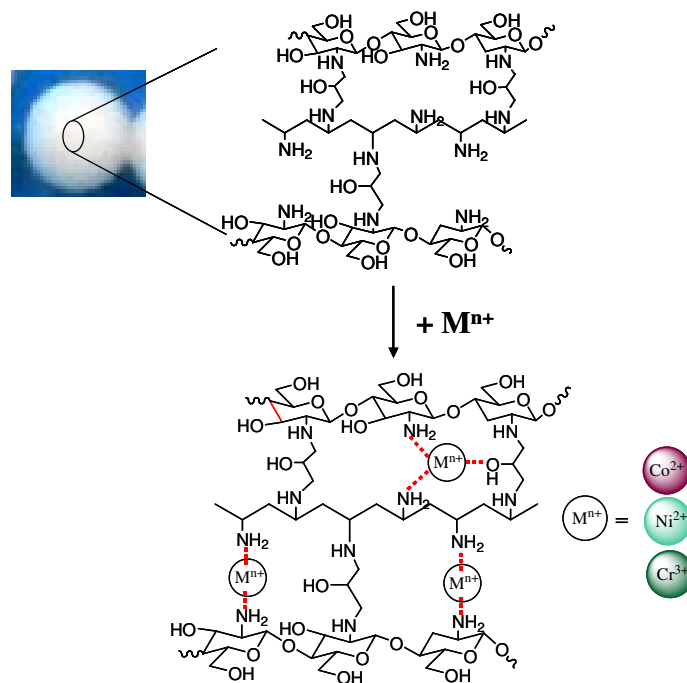


Figure 3: Possible binding mechanism of metal ions onto the CS/PVAm composite beads (Co^{2+} , Ni^{2+} , and Cr^{3+})

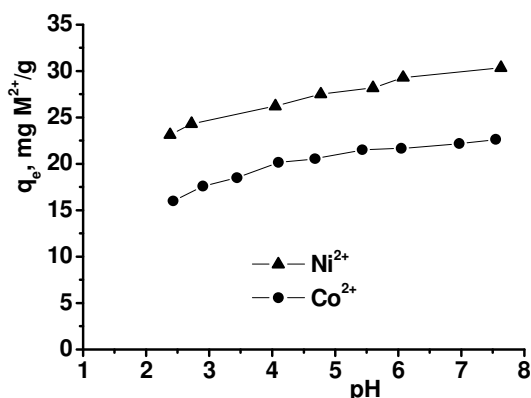


Figure 4: Effect of pH on the equilibrium sorption capacity of Co²⁺ and Ni²⁺ on CS/PVAm composite beads

The pH corresponding to the deposition of Co(OH)₂ and Ni(OH)₂, calculated taking into account the solubility product of Co(OH)₂ (1.1 x 10⁻¹⁵), and of Ni(OH)₂ (5.5 x 10⁻¹⁶) at the initial concentration of metal ions of 7 mmol/L, was 7.68 and 7.72 for Co²⁺ and Ni²⁺, respectively.

Therefore, working at pH values higher than 7.68 and 7.72, when the precipitation of Co(OH)₂ and Ni(OH)₂ is starting, could lead to inaccurate interpretation of the results. In the case of Cr³⁺ sorption, the equilibrium sorption pH was 4 ± 0.1, and it was adjusted periodically from the beginning of the sorption process.

Sorption isotherms

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 the 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.²⁰ Figure 5 shows that the retention capacity of CS/PVAm composites for Co²⁺, Ni²⁺, and Cr³⁺ ions increased with the increase of the equilibrium metal concentration.

Two isotherm models were used to describe the experimental isotherms. The Langmuir isotherm, applicable to homogeneous adsorption, is based on the following assumptions: (1) all the adsorption sites are assumed to be identical; (2) each site retains one molecule of the given compound; (3) all sites are energetically and

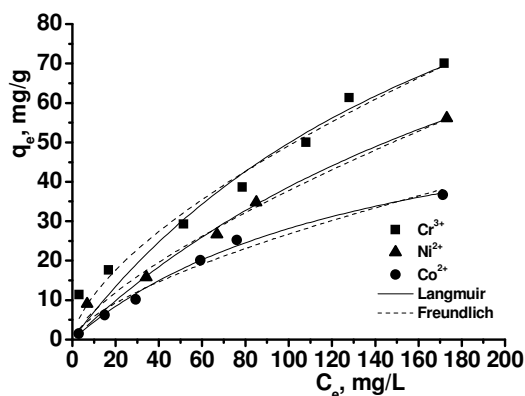


Figure 5: Equilibrium adsorption of Co²⁺, Ni²⁺, and Cr³⁺ ions onto CS/PVAm composite beads at 298 K, and non-linear fitting of two isotherm models (Langmuir and Freundlich) to the experimental data

sterically independent of the adsorbed quantity, the non-linear form of the isotherm being described by Equation 2:²⁰

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (2)$$

where: q_e is the amount of metal ions sorbed per gram of sorbent, at equilibrium (mg/g), C_e denotes the equilibrium concentration of the metal ions in the filtrate (mg/L), q_m is the theoretical limit of adsorption when the monolayer surface is fully covered with metal ions (mg/g), K_L represents the Langmuir constant (L/mg) related to the energy of adsorption, which reflects the affinity between the sorbent and sorbate.

The feasibility of adsorption in a certain concentration range can be expressed in terms of a dimensionless constant R_L (Equation 3), called constant separation factor or equilibrium parameter:²¹

$$R_L = \frac{1}{1 + K_L C_i} \quad (3)$$

where: K_L is the Langmuir adsorption constant (L/mg), and C_i is the initial concentration of metal ions (mg/L).

According to the values of R_L , the adsorption is: unfavorable when $R_L > 1$; linear when $R_L = 1$; favorable when $0 < R_L < 1$; irreversible when $R_L = 0$.

The Freundlich isotherm assumes heterogeneous surface with a non-uniform distribution of heat of adsorption, and is expressed by Equation 4:²²

$$q_e = K_F C_e^{1/n} \quad (4)$$

where: K_F , the Freundlich constant, which predicts the quantity of metal ions per gram of composite at the equilibrium concentration (mg/g); $1/n$, a measure of the nature and strength of the adsorption process and of the distribution of active sites. If $1/n < 1$, bond energies increase

with the surface density; if $1/n > 1$, bond energies decrease with the surface density, and when $1/n = 1$, all surface sites are equivalent.

The isotherm parameters resulted by the non-linear fitting of the Langmuir and Freundlich isotherms are presented in Table 1.

Table 1
Isotherm parameters for the sorption of Co^{2+} , Ni^{2+} , and Cr^{3+} ions at 298 K onto CS/PVAm composite beads

Langmuir isotherm model					
Metal ion	q_m , mg/g	K_L , L/mg	R_L	R^2	χ^2
Co^{2+}	67.89	0.0078	0.877-0.192	0.9932	1.18
Ni^{2+}	143.73	0.0037	0.734-0.304	0.966	11.41
Cr^{3+}	153.35	0.0048	0.985-0.542	0.938	30.01
Freundlich isotherm model					
Metal ion	K_F , mg/g	$1/n$	R^2	χ^2	
Co^{2+}	1.29	0.658	0.974	4.53	
Ni^{2+}	1.41	0.714	0.98	6.55	
Cr^{3+}	2.61	0.638	0.968	15.61	

Table 2
Comparison of maximum equilibrium sorption capacity of Co^{2+} , Ni^{2+} , and Cr^{3+} on different sorbents

Sorbent	Initial pH	q_m , mg/g			Ref.
		Co^{2+}	Ni^{2+}	Cr^{3+}	
Ethylenediaminetetraacetic acid (EDTA) modified chitosan	2.1	65.46	77.07	-	1
Diethylenetriaminepentaacetic acid (DTPA) modified chitosan	2.1	52.86	64.13	-	1
Carbonized coir pith	5	-	62.5	-	3
Aerobic granules	5	-	-	64.1	4
SBA-15 functionalized with 3-aminopropyltrimethoxy-silane	6	0.429	0.720	0.334	23
Coir pith	5	12.82	15.95	11.56	26
Chitosan cross-linked with glutaraldehyde	5-6	99	137.33	-	27
Chitosan/attapulgitite composites (CTS/ATP)	5	-	-	27.03	28
Epichlorohydrin cross-linked Chitosan-clay composite beads	6	-	32.36	-	29
Cross-linked magnetic chitosan-isatin Schiff's base resin	5	53.51	40.15	-	30
Thiourea-modified magnetic chitosan microspheres	5	-	15.3	-	31
C64:2i	4.5	67.89	143.73	153.35	This study

As can be observed in Table 1, the theoretical q_m values estimated by the Langmuir isotherm model show that the CS/PVAm composite beads have a higher sorption capacity for Cr^{3+} ions (153.35 mg/g) compared to the sorption capacity for the Ni^{2+} ions (143.73 mg/g), and Co^{2+} ions (67.89 mg/g). The primary amino groups from the

CS/PVAm structure have a higher affinity for the trivalent Cr^{3+} ions compared to the divalent ions of Ni^{2+} and Co^{2+} .

In the case of the two divalent metal ions, there is a direct relationship between the charge to radius ratio (Z/r) and adsorption capacity.²³ Thus, according to the Z/r ratio of the cations Ni^{2+}

(2.90) and Co^{2+} (2.70),²⁴ the selectivity sequence is expected to be $\text{Ni}^{2+} > \text{Co}^{2+}$, which would be in good agreement with the Irving-Williams series order of metal complex stability.²⁵ The R_L values, calculated for the entire range of initial concentrations of metal ions, show that the sorption process is favourable.

The maximum adsorption capacity, q_m , evaluated by the Langmuir model for the sorption of Ni^{2+} , Co^{2+} , and Cr^{3+} on the CS/PVAm composite sorbents synthesized in this work is compared with the values obtained for other sorbents in Table 2.

As Table 2 shows, the maximum sorption capacity of Ni^{2+} and Co^{2+} onto the CS/ PVAm composite beads is comparable with that reported in literature for other sorbents, and much higher for Cr^{3+} . Therefore, these novel composites could be recommended as an efficient alternative for the sorption of these heavy metal ions.

CONCLUSION

A composite based on CS and PVAm was used for the removal of Co^{2+} , Ni^{2+} and Cr^{3+} , as a function of different parameters, such as pH and metal ion concentration. The optimum adsorption pH of Co^{2+} and Ni^{2+} ions was located at 4.9 for Co^{2+} and 5.6 for Ni^{2+} . The equilibrium data obtained for the adsorption of all metal ions onto the CS/PVAm composite beads fitted well the Langmuir model with a maximum theoretical adsorption capacity of 153.35 mg Cr^{3+} /g composite, 143.73 mg Ni^{2+} /g composite, and 67.89 mg Co^{2+} /g composite, respectively. The R_L values, calculated for the entire range of initial concentrations of metal ions, show that the sorption process was favourable for all metal ions.

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