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Use of Biopolymers for the Removal of Metal Ion Contaminants from Water

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Summary: Naturally abundant biosorbants such as chitin and chitosan are recognized as excellent metal ligands, forming stable complexes with many metal ions, and serving as effective protein coagulating agents. Chitosan is a heteropolymer made of D-glucosamine and a small fraction of N-acetyl-D-glucosamine residues. Therefore, the adsorption ability of chitosan is found to be much higher than that of chitin, which has relatively fewer amino groups. Zeolites are crystalline microporous aluminosilicates with ion exchange properties suitable for a wide range of applications in catalysis and separation of liquid and gaseous mixtures. Incorporation in chitosan membranes is an effective method to control the diffusion outside the zeolite crystals and appropriately designed composite systems can find numerous opportunities for applications in wastewater treatment. In this paper we present the synthesis of zeolite-chitosan and zeolite-ethyl cellulose composites by encapsulation of clinoptilolite using a gelling solution of chitosan or an ethyl cellulose solution in ethyl acetate. The adsorption process of Cu^{2+} and Cd^{2+} on some adsorbents was investigated: clinoptillolite tuff (0.05 mm), chitosan flakes, ethyl cellulose, zeolite-chitosan and zeolite- ethyl cellulose composites. Zeolite-chitosan composites have been prepared by encapsulation of zeolites by a gelling solution of chitosan. Micrometric crystals of clinoptillolite were dispersed in a 3% chitosan solution in 1% aqueous acetic acid. The chitosan gel was formed and the zeolite crystals were encapsulated during the gelling process. The same procedure was used to obtain zeolite – ethyl cellulose composites. Study of the metal ion retention properties of different adsorbent materials was carried out using a steady state regime. The concentration of heavy metal ions in supernatant was determined by the atomic absorption spectrophotometric method. Adsorption isotherms of metal ions on adsorbents were determined and correlated with common isotherm equations such as Langmuir and Freundlich models.

Keywords: adsorption; chitosan; encapsulation; heavy metal; zeolites

Introduction

The presence of heavy metal ions in wastewaters generates problems for the environment and living organisms because of their non-biodegradability and high toxicity. Heavy metals released by a number of industrial processes are major pollutants in marine, ground, industrial and even treated wastewaters.[1–3]

Naturally abundant biosorbants such as chitin and chitosan are recognized as excellent metal ligands, forming stable complexes with many metal ions, and serving as effective protein coagulating agents.[1,2]

Chitosan is a heteropolymer made of D-glucosamine and a small fraction of N-acetyl-D-glucosamine residues (Figure 1).[1–3] Chitosan is found naturally in fungi and arthropods in which it is the

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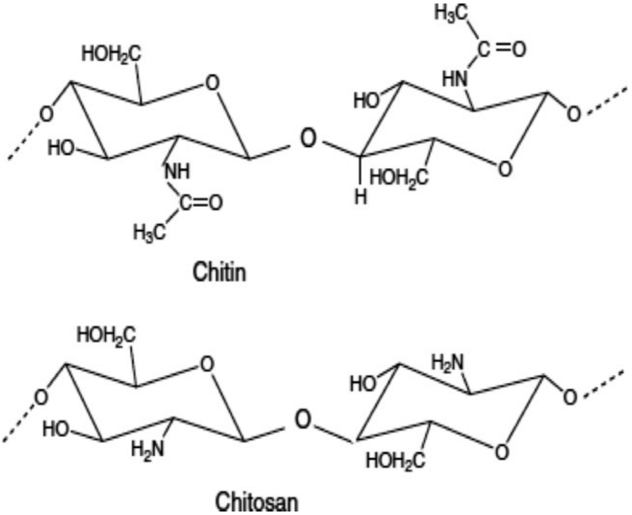

Figure 1.
Structure of chitin and chitosan[1].

main component of the exoskeleton. It can be prepared from fishery wastes and is obtained from shrimp, lobster, or crab shell and from cuttlebone. Previous studies have demonstrated the ability of chitosan to act as an adsorbent of metal ions in aqueous solutions with evidence that sorption occurs through the amine functional groups.[3] Ethyl cellulose is a derivative of cellulose in which some of the hydroxyl groups on the repeating glucose units are converted into ethyl ether groups. (Figure 2) The number of ethyl groups can vary depending on the manufacture. It is mainly used as a thin-film coating material or as a food additive emulsifier.

It is widely known that chitosan can build complexes with certain metal ions. Amino sites are the main reactive groups for metals ions, although hydroxyl groups (especially in the C3 position) may contribute to sorption. Most studies of the chelation mechanism have been focused on the adsorption of copper. Rhazi *et al.* (2002) proposed two types of complex for Cu(II)-chitosan which depend on the pH of the solution. At pH between 5.3–5.8, the complex ($[Cu(-NH_2)]^{2+}$, $2OH^-$, H_2O) is suggested; whereas at $pH > 5.8$, the complex ($[Cu(-NH_2)_2]^{2+}$, $2OH^-$) is considered (Figure 3).[4]

Zeolites are crystalline microporous aluminosilicates with ion exchange properties suitable for a wide range of applications in catalysis and separation of liquid and gaseous mixtures.[5,6]

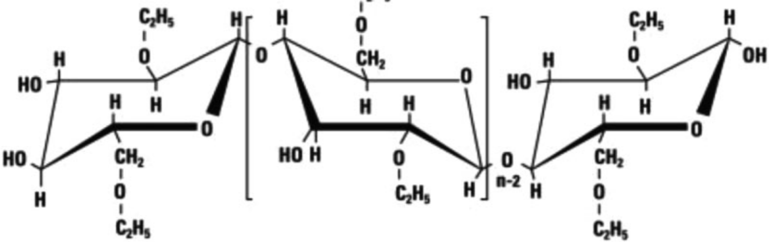

Figure 2.
Ethyl cellulose (EC) structure[3].

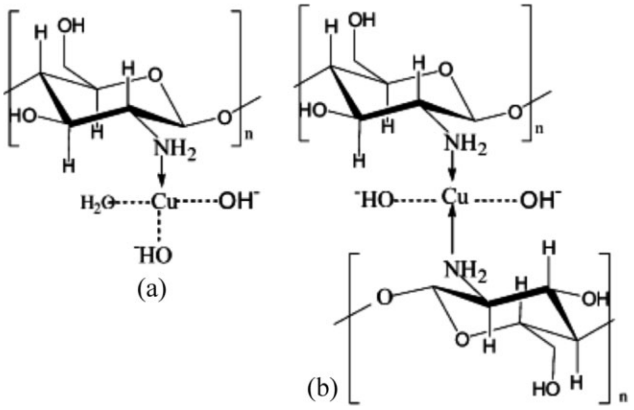

Figure 3.
Proposed structures of Cu-Chitosan complex (a) at pH between 5.3 - 5.8 and (b) at pH > 5.8.[4]

Clinoptilolite (CPL), one of the 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. Incorporation in different biopolymers membranes is an effective method to control the diffusion outside the zeolite crystals and designed composite systems can find many opportunities for applications in wastewater treatment.[7–11]

Considering these aspects, our study presents the synthesis of *zeolite-chitosan and zeolite-ethyl cellulose composites* by encapsulation of clinoptillolite using a gelling solution of chitosan or an ethyl cellulose solution in ethyl acetate.

The adsorption process of Cu^{2+} and Cd^{2+} on some adsorbents was investigated: clinoptillolite tuff (0.05 mm), chitosan flakes, ethyl cellulose, *chitosan-clinoptilolite and ethyl cellulose-clinoptilolite composites.*

Experimental Part

Materials and Methods

The natural clinoptilolite (CPL) sample used in this study comes from volcanic tuffs cropping out in Marsid area, Romania. The natural CPL sample used in this study comes from volcanic tuffs containing 71–73% CPL and has the following ideal composition: $[Ca_{1.24},Na_{1.84},K_{1.76}Mg_{0.2}Al_{16}Si_{30}O_{72}\text{-}(H_2O)_{21.32}]$. The clinoptilolite sample was ground and sieved through a range of sieves, and only the particles that passed through a 0.05 mm sieve were used for this study. The selected fraction was washed three times with distilled water, to remove any soluble salts and dried at 40 °C in the oven, for 24 h.

Chitosan (CS) of low molecular weight and ethyl cellulose (EC) were purchased from Fluka and they were used without further purification.

Preparation of Biopolymers Composites

The chitosan solutions were obtained by dissolving the chitosan powder in 1 vol. % acetic acid solution and intensive stirring for at least 4 h.

Chitosan-clinoptilolite (CS-CPL) composites have been prepared by encapsulation of zeolites by a gelling solution of chitosan. Two volumes of chitosan solution were mixed with one volume of water containing the dispersed clinoptilolite and kept under vigorous magnetic stirring for 6 h. The chitosan gel was formed and the zeolite crystals were encapsulated during the gelling process.

Micrometric crystals of clinoptillolite were also dispersed in an ethyl cellulose solution 1% in ethyl acetate and then it was followed the same procedure presented for chitosan.

The mixture thus prepared was also added by a syringe into an aqueous solution of a surfactant - linear alkyl benzenesulphonate (LAS), with a concentrantion of 0.1 M, under mild stirring. The hybrid microspheres were kept under stirring 5 h at room temperature 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 hybrid microspheres were filtered off, dried at room temperature for 24 h and in the oven at 105 °C, for 12 h.

Study of the metal ion retention properties of the adsorbent materials was carried out using a steady state regime. Thus, 0.25 g of dried microspheres CS/CPL and EC/CPL or 0.1 g of CS, EC and CPL were placed in a flask and contacted with an aqueous solution of Cu^{+2} or Cd^{+2}, having a concentration between 30-100 mg/l, for 72 h. These mixtures were filtered and washed with distilled water. The concentration of heavy metal ions in supernatant was determined by the atomic absorption spectrophotometric method, using a Varian 240F spectrophotometer.

FT-IR spectra were recorded in the domain 4000-400 cm^{-1}, by using a Varian Resolutions Pro 3100 spectrophotometer.

Results and Discussion

Adsorption isotherms of metal ions on adsorbents were determined and correlated with common isotherm equations such as Langmuir and Freundlich models.

Langmuir Model

Original form: $$q = \frac{q_m \cdot K_L \cdot c}{1 + K_L \cdot c} \quad (1)$$

Linearized form :

$$\frac{c}{q} = \frac{1}{K_L \cdot q_m} + \frac{c}{q_m} \quad (2)$$

Freundlich Model

Original form : $$q = K_F \cdot c^{1/n} \quad (3)$$

Linearized form :

$$\log q = \log K_F + \frac{1}{n}\log c \quad (4)$$

where:

q_m: amount of metal ions required to form a monolayer (mg/g)
q: the adsorption capacity (mmol/g)
c: the equilibrium solution concentration of the adsorbed species (mg/l)
K_L: Langmuir equilibrium constant related to the energy of adsorption
n: Freundlich equilibrium constant indicative of bond energies between metal ion and adsorbent

The Langmuir model assumes the following characteristics:[4]

- The energy is the same all over the surface.
- Adsorbed molecules do not interact.
- Molecules adsorb at fixed sites and do not migrate over the surface.
- At the point of maximum adsorption, only a monolayer is formed. The molecules of adsorbate are deposited only on the free surface of the adsorbent.

Linearized forms of Langmuir and Freundlich, models for adsorption of Cu^{2+} and Cd^{2+} are presented in Figure 4–9.

The most precise match was acquired with the Langmuir model. The correlation coefficients (R^2) of Langmuir model for the adsorption of the $Cu^{2+}$and Cd^{2+} were higher than R^2 values of Freundlich models and reveal the good applicability of the Langmuir model to these adsorptions.

This result confirmed that the adsorption of Cu^{2+} and Cd^{2+} on tested adsorbents is monolayer.

The adsorption capacity (q) values increased with increase in initial ion concentration (C_0). This increase is probably

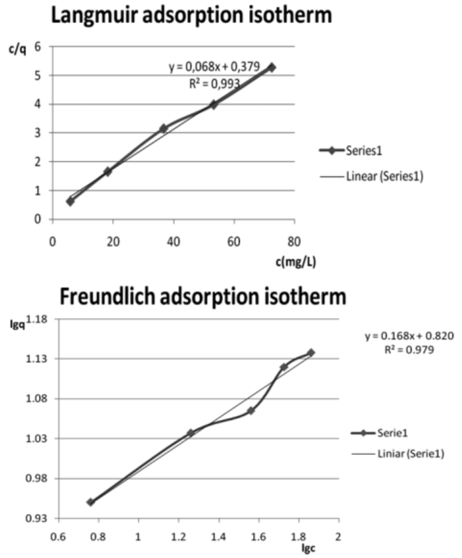

Figure 4.
Adsorption isotherms of Cu^{2+} on clinoptilolite.

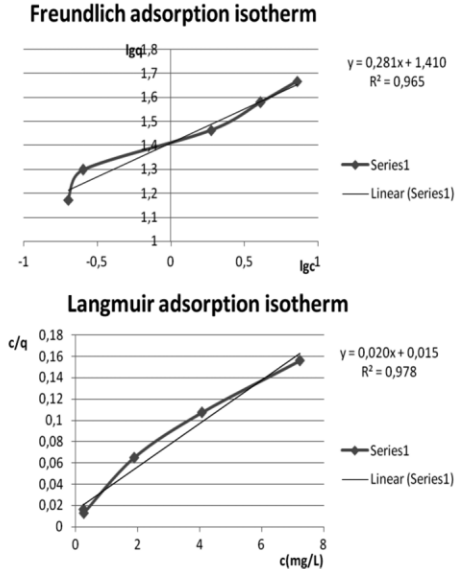

Figure 5.
Adsorption isotherms of Cu^{2+} on chitosan –clinoptilolite composites.

due to a high driving force for mass transfer. When the concentration of metal ions in solution was higher, the adsorption capacity increased.

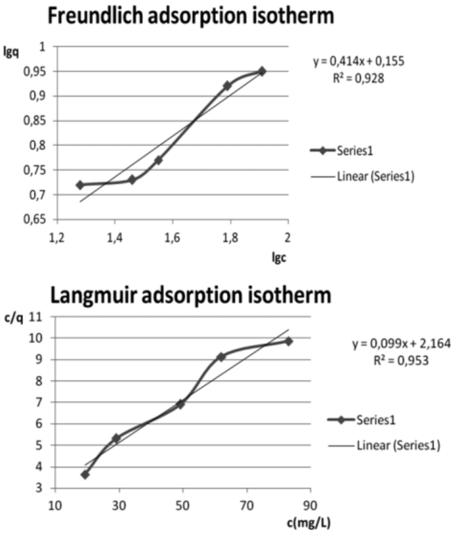

Figure 6.
Adsorption isotherms of Cu^{2+} on ethyl cellulose – clinoptilolite composites.

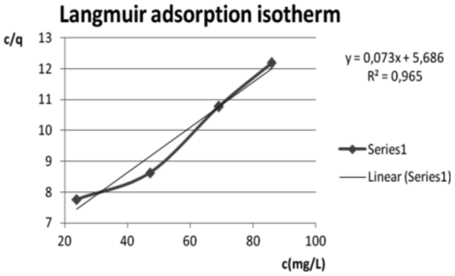

Figure 7.
Langmuir adsorption isotherm of Cd^{2+} on ethyl cellulose –clinoptilolite composites.

The correlation coefficients and other parameters of the two models are presented in Table 1.

Generally, the values of q for adsorption of Cu^{2+} were higher than for adsorption of Cd^{2+}, as well as K_L, which related to the energy of adsorption in Langmuir model. The n and K_F values of Freundlich model were also higher in the case of Cu^{2+} adsorption. These results indicate that adsorption of Cu^{2+} is superior to the adsorption of Cd^{2+} and the affinity of CS-CPL composites for adsorption of Cu^{2+} and

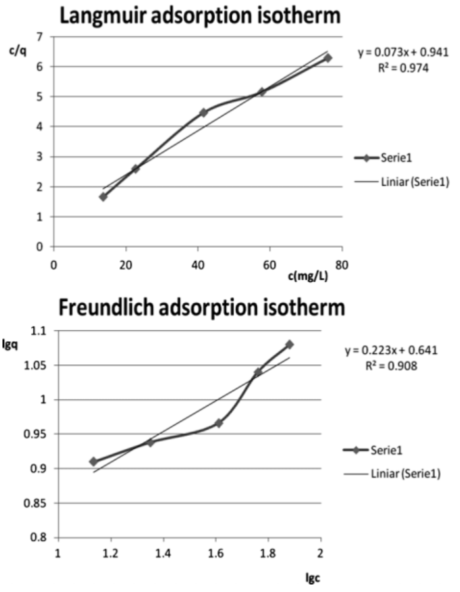

Figure 8.
Adsorption isotherms of Cd^{2+} on chitosan.

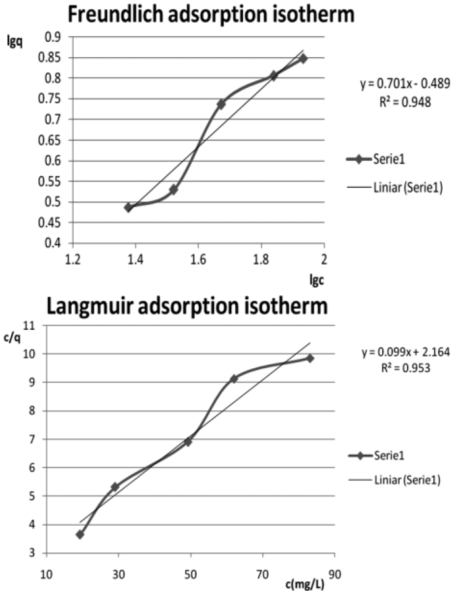

Figure 9.
Adsorption isotherms of Cd^{2+} on chitosan-clinoptilolite composites (CS-CPL).

Cd^{2+} is stronger than the other adsorbents affinity.

The value of ΔG for adsorption of Cu^{2+} on CS-CPL composites was -3.292 kJ/mol. The negative value for Gibbs free energy shows that the adsorption process of Cu^{2+} on this adsorbent is spontaneous in nature. Considering the values $\Delta G < +10$ kJ/mol (Table 1), the adsorption process of Cu^{2+} and Cd^{2+} on the other adsorbents is also spontaneous.

FTIR spectroscopy was performed to identify any changes in the structure of biopolymer-CPL composites compared with chitosan and ethyl cellulose.

The main characteristic bands of CS-CPL composites were found at 487 cm^{-1}, 799 cm^{-1}, 1030 cm^{-1} and 1645 cm^{-1} (Table 2). The band at 487 cm^{-1} resulted from the stretching vibrations of Al–O bonds and the bands at 799 cm^{-1} and 1073 cm^{-1} were assigned to the vibrations of Si–O–Si bonds. These bands were observed in IR spectrum of EC-CPL composites, too.

The characteristic bands of CS were located at 1659 cm^{-1}, assigned to the stretching vibrations of the C=O bond in acetamide groups (amide I band), at 1542 cm^{-1} the vibration of N–H bond

Table 1.
Specific parameters of tested adsorbents.

Adsorbent-heavy metal ion	ΔG (kJ/mol)	Langmuir			Freundlich		
		K_L	q (mg/g)	R^2	K_F	n	R^2
CS-CPL composites, Cu^{+2}	-3.292	1.32	49.01	0.9783	25.73	3.55	0.9651
CS, Cu^{+2}	4.786	0.012	129.87	0.9482	2.01	1.195	0.9971
CPL, Cu^{+2}	1.852	0.180	14.577	0.993	6.608	1.21	0.9798
EC-CPL composites, Cu^{+2}	7.694	0.04573	10.10	0.9534	1.43	2.41	0.9286
CS, Cd^{+2}	6.372	0.0777	13.66	0.979	4.38	4.48	0.9082
EC, Cd^{+2}	2.227	0.1279	12.376	0.9794	5.7279	6.25	0.9603
EC-CPL composites, Cd^{+2}	10.8	0.01229	13.62	0.9653	-	1.42	0.9481

Table 2.
IR main characteristic bands of some adsorbents.

Compound	Assignements, ν_{max} (cm^{-1})				
	ν (C=O)	δ (N–H)	ν (C–O)	ν (Al–O)	ν (Si–O–Si)
CS-CPL composites	1645 ("amide band I")	-	-	487	799 1073
CS	1659, ("amide band I")	1542 ("amide band II")	-	-	-
EC-CPL composites	-	-	1095	467	789 1087

(amide II band) and at 1322 cm^{-1} the characteristic band for the N-acetylglucosamine.

The characteristic band of EC, at 1095-1100 cm^{-1} which is assigned to the stretching vibration of C–O bond, was also found in IR spectrum of EC-CPL composites.

Conclusion

Novel composites with enhanced adsorption capacity for Cu^{2+} and Cd $^{+2}$ were prepared by loading clinoptilolite microparticles in a matrix of chitosan or ethyl cellulose.

The presence of clinoptilolite in the polymer matrix strongly affects the adsorption capacity of composites, at pH 5.

Considering the values $\Delta G < +10$ kJ/mol (Table 1), the adsorption process of Cu^{2+} and Cd^{2+} on the tested adsorbents is spontaneous.

On comparing the efficiency of the assayed absorbers it must be taken into consideration the organic nature of chitosan and its easy availability from fisher factories as a residue, which provides an added value of this adsorbent as a recycled product.

In short, the use of biopolymers and their composites as absorbers for heavy metal removal from aqueous contaminated wastes are an environmentally friendly, highly efficient alternative.

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