Adsorption of Zn(II) by Crosslinked Acrylic Copolymers with Amine Functional Groups

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ABSTRACT: Adsorption of Zn(II) ions from diluted aqueous solutions by the acrylic copolymer based on ethylacrylate : acrylonitrile : divinylbenzene matrix with different crosslinking degrees and ethylenediamine and triethylenetetramine functional groups was investigated. Adsorption experiments were carried out by batch method. The effects of the pH, initial concentration of zinc, time of contact, and the crosslinking degree of the copolymers were studied. On the basis of Langmuir and Freundlich isotherms, the parameters that characterize the adsorption were determined. The maximum Zn(II) retention capacity value (500 mg g^{-1}) was obtained for the acrylic copolymer with 2% crosslinking degree and ethylenediamine, as functional groups. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 93: 803–808, 2004

Key words: ion exchanger; functionalization of polymers; thermodynamics

INTRODUCTION

One of the more important problems of the environment is related to the removal of wastewater polluted by heavy metal ions. At least 20 metals are known to be toxic and fully one-half of these, including zinc, are released into the environment in quantities that pose a risk to human health. Zn(II) ions are frequently encountered in industrial wastewater (e.g., from mining, metal cleaning, plating electroplating).[1]

Metal ions can be removed by adsorption on solid carriers. There are nonspecific adsorbents, such as activated carbon, metal oxides, silica, and ion-exchange resins,[2–4] and specific ones that are considered among the most promising techniques.[5–9] These specific sorbents consist of a ligand that can specifically interact with the metal ion and the carrier, which may be an inorganic material or polymer microbead. The latter carrier is easily produced in a wide range of compositions and can be modified by polymer analogous reactions to introduce a new ligand. The development of metal chelating polymers continues to be a subject of paramount importance. Several criteria must have these types of the compounds for a substantial stability for the selective removal of heavy metal ions: the specific and fast complexation of metal cations and the reusability of them.[10–11] A large number of chelating polymers incorporating amine groups were prepared and their analytical properties were investigated.[12–15]

In our previous studies, the crosslinked acrylic compounds based on ethylacrylate : acrylonitrile : divinylbenzene copolymer, functionalized with different polyalkylenepolyamines, were synthesized and characterized.[16–19] Zn(II) sorption experiments were carried out on the acrylic copolymers with two crosslinking degrees (2 and 8%) having *N*,*N*-dimethylaminopropylamine groups. The results showed that the matrix with low crosslinking degree exhibits high affinity for Zn(II) at pH = 6.[20]

The aim of this article was the adsorption study of the Zn(II) ions by the acrylic copolymers with different crosslinking degrees and functionalized with ethylenediamine and triethylenetetramine under various experimental conditions. The effect of the pH, time of contact, initial concentration of zinc, and temperature were investigated. Also, Langmuir and Freundlich isotherms were used to characterize the interaction of Zn(II) with the functionalized copolymers.

EXPERIMENTAL

Reagents

The ethylacrylate : acrylonitrile : divinybenzene (EA : AN : DVB) copolymers functionalized with ethylenediamine (EDA) and triethylenetetramine (TETA) were synthesized according to refs. [17–19]. Zn(II) stock solution of 1000 μg mL^{-1} as nitrate salt was prepared from metallic zinc (99.99% purity). Amounts of 1*N* HCl and NaOH aqueous solutions (Fluka, Buchs, Switzerland) were used.

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TABLE I
Characteristics of the Studied Functionalized Acrylic Copolymers

Code sample	Crosslinking degree (%)	Functional groups	Weak base exchange capacity	
			mequiv/g	mequiv/mL
S1	2		7.26	0.53
S2	8		3.00	0.97
S3	2		14.66	0.91
S4	8		6.90	1.62

Zn(II) adsorption

Adsorption experiments were carried out by batch method. Sorbent (0.10 g) was stirred with 25 mL solution at previously established zinc concentration and pH value. The pH was adjusted by the addition of the diluted solutions of HCl or NaOH. A pH-meter OP-211/2 Radelkis was used.

The samples of liquid phase were taken at the established times and the Zn(II) remaining in the solution was determined by flame atomic absorption spectrometry with a Perkin–Elmer 3300 spectrophotometer. Reproducibility was verified by duplication.

RESULTS AND DISCUSSION

Table I shows the characteristics of the studied functionalized acrylic copolymers in the retention of Zn(II) ions.

Effect of pH

The pH effect was performed in the pH range of 2–7 at Zn(II) initial concentration of 14 μg L^{-1} and the experiments led to the conclusion that Zn(II) cations were retained from weak acidic solution and the amount of the retained cation increased with increasing pH value up to the maximum retention for pH = 6 (Fig. 1). The retention capacity is different for the studied ion exchangers and depends on the crosslinking degree and the amine functional groups of the resins. It is known that the coordination capacity of the amine groups is maximum at pH = 2–7, when there are unprotonated free base.[10]

Effect of the time of contact

The effect of the contact time on zinc ion retention for S1, S2, S3, and S4 samples is illustrated in Figure 2.

The adsorption capacities of the chelating polymers for the metal ion are given as a function of the initial concentration of the ions within the aqueous phase. It

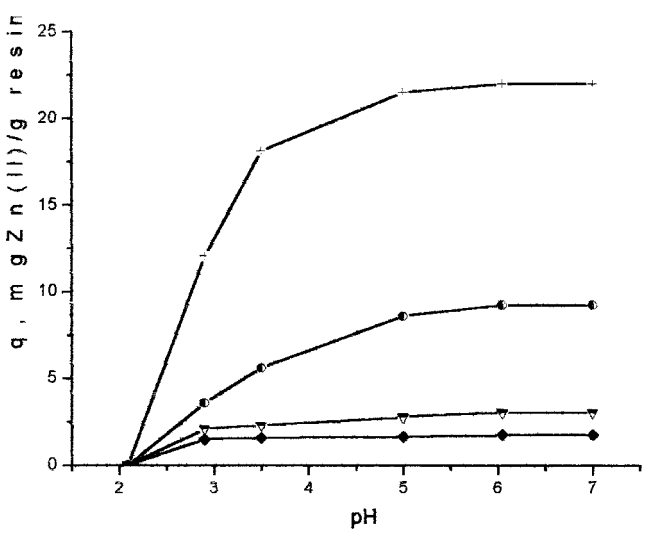


Figure 1 Effect of pH on Zn(II) adsorption of S1 (×), S2 (◐), S3 (▽), S4 (♦) samples at the initial concentration of 14 μg mL^{-1}.

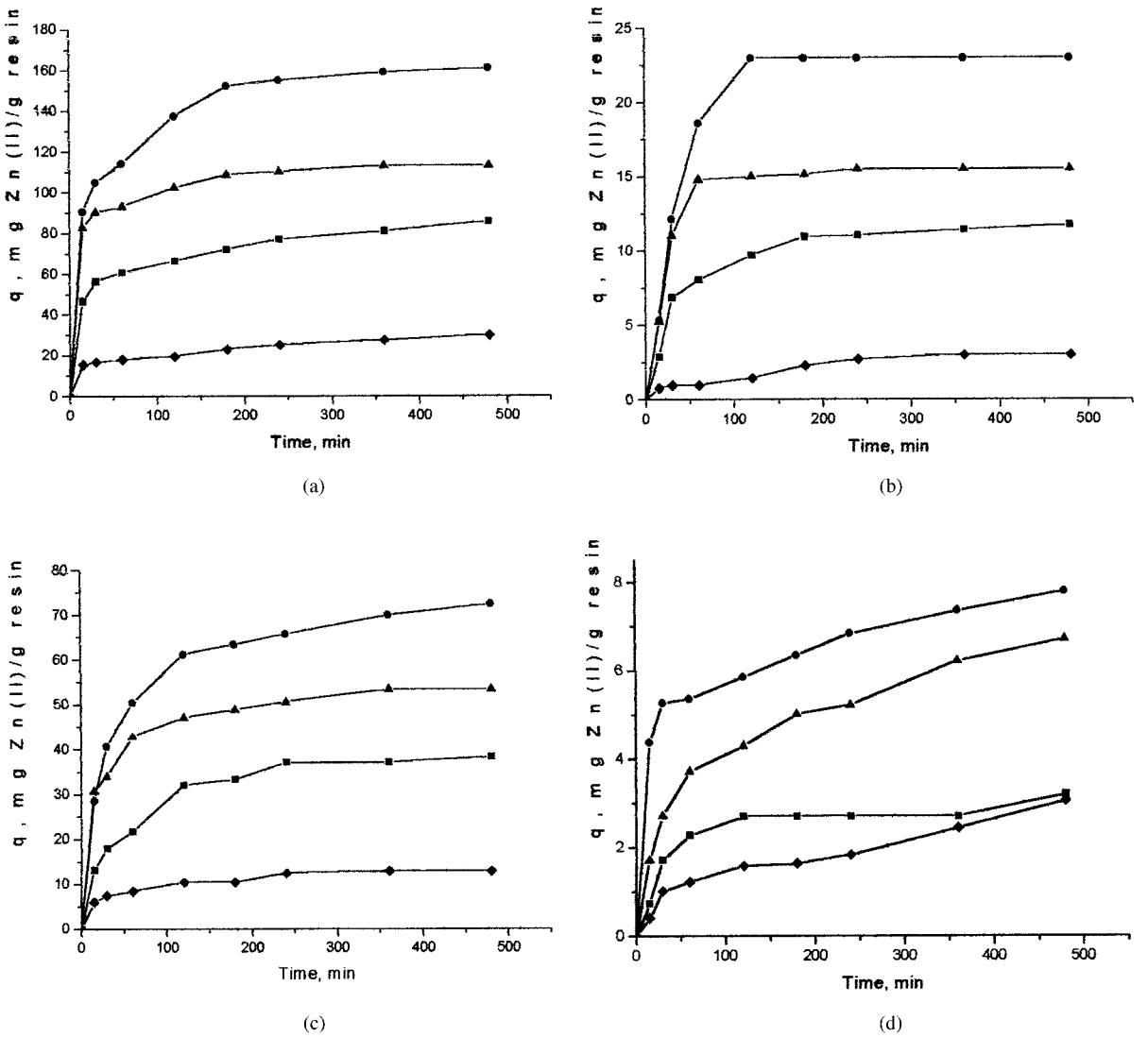


Figure 2 Effect of contact time on Zn(II) retention of S1 (a), S2 (b), S3 (c), S4 (d) samples at different initial concentrations (◆, 19 μg mL^{-1}; ■, 54 μg mL^{-1}; ▲, 67 μg mL^{-1}; ●, 96 μg mL^{-1}).

was found that the amount of Zn(II) adsorbed was significantly increased with an increase of the initial concentration of heavy metal ion and then it reached a equilibrium level. When the initial concentration of Zn(II) ions is lower than 54 μg mL^{-1}, the necessary time for the equilibrium is between 2 and 4 h.

From Figure 2, it can seen that the high Zn(II) retention capacity values were performed on the functionalized copolymers with low crosslinking degree (2% DVB). A network with 2% DVB is a flexible one and it has a high swelling capacity in a suitable medium.

The highest Zn(II) retention capacity was obtained for the acrylic copolymer functionalized with ethylenediamine and 2% DVB (S1 sample). The attached ethylenediamine functional groups to the acrylic copolymer led to a more hydrophilic structure that allows very good interaction with metal cation from the liquid phase.

Adsorption dynamics

The adsorption dynamics for S1 and S3 samples can be appreciated by determining the adsorption rate constant by using the Lagergreen eq. (21)

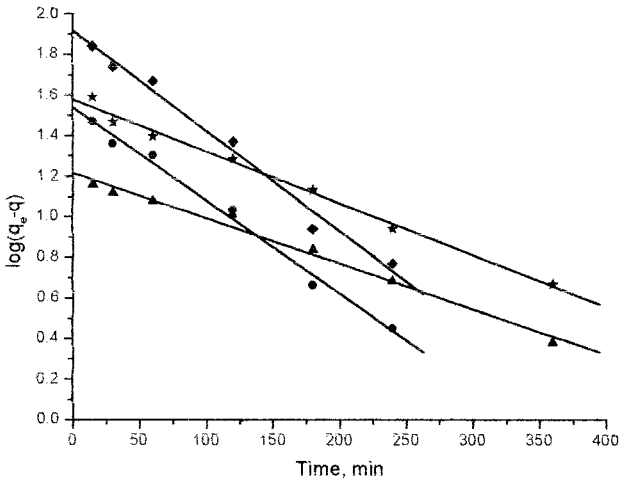
$$\log(q_e - q) = \log q_e - \frac{K'}{2.303} \times t \qquad (1)$$

where q_e and q are the amounts of Zn(II) ions adsorbed (mg g^{-1}) at equilibrium at time t, respectively; and K' is the rate constant.

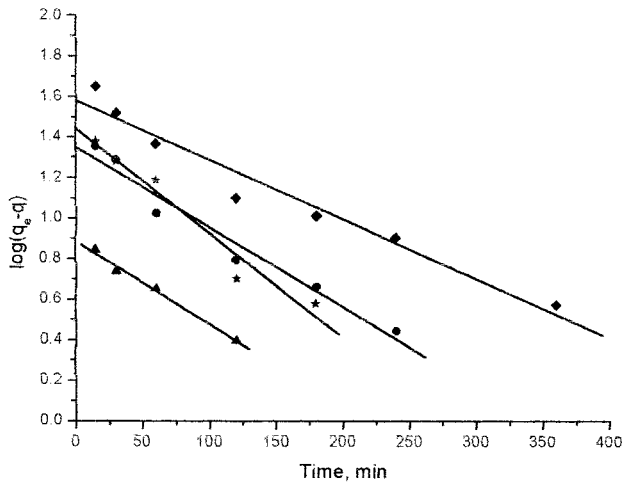
The K' values were calculated from the slope of the linear plot of $\log(q_e - q)$ versus t for the S1 and S3 samples (Fig. 3).

The K' values are presented in Table II.

For the S1 sample, the rate constants increased with the increase of the initial concentration of Zn(II) ions, whereas for the S3 one, the K' values

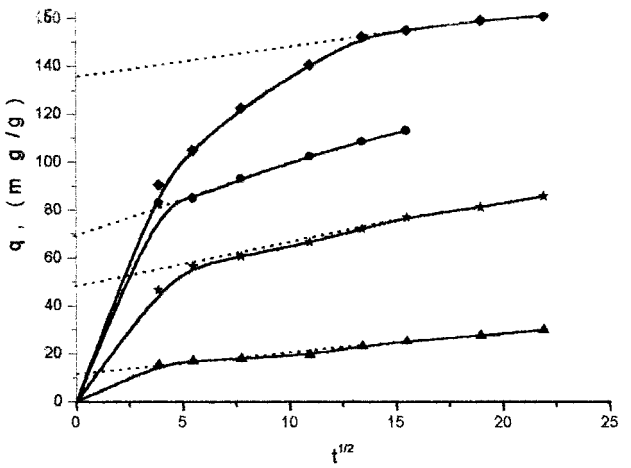


(a)

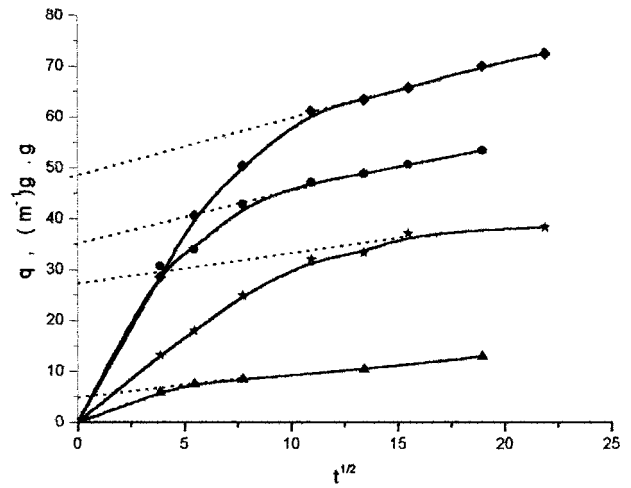


(b)

Figure 3 Lagergreen plot for the adsorption of Zn(II) ions on the S1 (a) and S3 (b) samples (▲, 19 μg mL^{-1}; ⋆, 54 μg mL^{-1}; ●, 67 μg mL^{-1}; ♦, 96 μg mL^{-1}).



(a)



(b)

Figure 4 Amount of Zn(II) ions versus $t^{1/2}$ retained on the S1 (a) and S3 (b) samples (▲, 19 μg mL^{-1}; ⋆, 54 μg mL^{-1}; ●, 67 μg mL^{-1}; ♦, 96 μg mL^{-1}).

did not depend on the amount of the Zn(II) ions in the liquid phase for the studied concentration range.

Intraparticle diffusion

The rate constants of intraparticle diffusion (K_p) were calculated in regard to ref. [21] from the slopes of the last linear domain of the plots q versus $t^{1/2}$ for the S1 and S3 samples (Fig. 4).

TABLE II
Rate Constants for the Zn(II) Adsorption on S1 and S3 Samples

Initial concentration of Zn(II) (μg mL^{-1})	K' (min^{-1})	
	S1	S3
19	0.005066	0.009442
54	0.005987	0.011975
67	0.01059	0.009212
96	0.01151	0.009369

The experimental data led to the finding that curves of their linear domain did not pass through the origin. This meant that the intraparticle diffusion was not the only rate-controlling step. From this figure, it can seen that the adsorption of Zn(II) ions at the surface of beads is very fast; it takes place in a few minutes. Zn(II) ion retention on the ion exchangers is a complex process; in the first stage, it takes place as a physical adsorption, and then the ions diffuse inside of the beads and coordinate with the amine groups of the functionalized acrylic copolymers.

The rate constant values of intraparticle diffusion (K_p) for both S1 and S3 samples increased with the increase of the initial concentrations (19 μg mL^{-1}; 96 μg mL^{-1}) (Table III).

TABLE III
Rate Constants for the Intraparticle Diffusion

Initial concentration of Zn(II) (μg mL^{-1})	K_p (mg g^{-1} min$^{1/2}$)	
	S1	S3
19	0.817	0.434
54	1.811	0.581
67	2.523	0.793
96	2.750	0.996

Langmuir isotherm

Langmuir isotherm constants were determined from the linearized form of the Langmuir equation

$$\frac{C_e}{q_e} = \frac{1}{Q^0 b} + \frac{C_e}{Q^0} \tag{2}$$

where C_e is the equilibrium concentration of Zn(II) ions in the solution (mg L^{-1}), and Q^0 and b are constants indicative of maximum adsorption capacity and the measure of adsorption energy, respectively.

The values of Q^0 and b (Table IV) were calculated from the slope and intercept of a linear plots of C_e/q_e versus C_e for the S1 and S3 samples (Fig. 5).

Experimental data fitted the linearized equation reasonably well for two resins testifying to a monolayer sorption process. The Langmuir constant was calculated with these values on the basis of the relation:

$$K_L = Q^0 b \tag{3}$$

The essential characteristics of Langmuir isotherm can be expressed by a dimensionless constant called equilibrium parameter, R_L, that is defined by

$$R_L = \frac{1}{1 + bC_o} \tag{4}$$

The R_L value between 0 and 1 (Table V) indicates favorable adsorption for Zn(II) on both resins.

From Table IV, it can seen that in the retention of Zn(II) ions the S1 sample is more efficient than S3 sample (Q^0 = 500 mg g^{-1}). Based on our previous study,[20] when the acrylic copolymer functionalized with dimethylaminopropylamine (S) had a maximum adsorption capacity, Q^0 = 100 mg g^{-1}, the following order of the acrylic copolymers selectivity for Zn(II) ions is S1 > S3 > S.

TABLE IV
Langmuir Isotherm Constants

Code sample	Q^0 (mg g^{-1})	B (L mg^{-1})	K_L[a] (L g^{-1})
S1	500.00	0.0441	22.05
S3	169.50	0.1085	8.39

[a] Langmuir constants were calculated with the following equation: $K_L = Q^0$b.

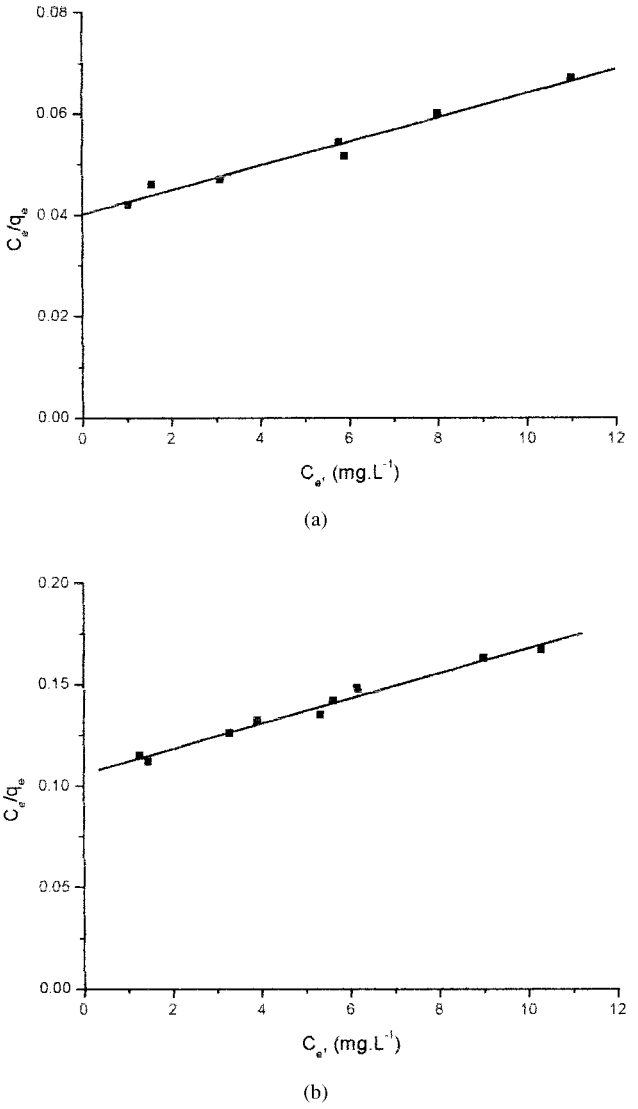


Figure 5 Langmuir isotherms of Zn(II) ions by the S1 (a) and S3 (b) samples.

Freundlich isotherm

Freundlich isotherm was obtained by using

$$\log \frac{x}{m} = \log K_F + \frac{1}{n} \log C_e \tag{5}$$

TABLE V
R_L Values for S1 and S3 Samples

Initial concentration of Zn(II) (μg mL^{-1})	R_L	
	S1	S3
19	0.544	0.326
54	0.295	0.145
67	0.252	0.120
96	0.191	0.087

where x is the amount of Zn(II) adsorbed (mg g^{-1}); m is the quantity of the resin used (g L^{-1}); C_e is the equilibrium concentration of Zn(II) in the solution (mg L^{-1}); K_F and n are constants regarding the adsorption capacity and intensity of adsorption, respectively. K_F and n constants were calculated from the intercept and slope of the linear plots $\log(x/m)$ versus $\log C_e$ for S1 and S3 samples (Fig. 6).

Table VI shows the Freundlich constants of the Zn(II) ions retention by the acrylic copolymers functionalized with ethylenediamine and triethylenetetramine. Values of $1 < n < 10$ show a preference of the studied adsorbents for Zn(II) ions.

Effect of temperature

The effect of temperature on the retention of Zn(II) ions was studied at four values of temperature: 8, 22, 35, and 45°C at the initial concentration of Zn(II) of 19 to 96 μg mL^{-1}. In our studies, no difference was observed between the retention capacity values of Zn(II) at studied temperatures.

It was reported that in the case of the initial concentration higher than 0.6 mmol L^{-1} of Cu(II), Mn(II), Co(II), and Ni(II), the retention capacity is stronger at 20°C than at 40°C for aminoalkyl cellulose. This behavior is attributed to a high stability of the complexes at low temperature.[22]

CONCLUSION

The adsorption of Zn(II) ions on the acrylic copolymers depends on the crosslinking degree of the copolymer and the amine functional groups attached to the matrix. The most efficient acrylic copolymer was that with 2% DVB and ethylenediamine groups (S1) when the maximum retention capacity value for the Zn(II) ions is 500 mg g^{-1}. This functional group led to a more hydrophilic structure that allowed a very good interaction with Zn(II) ions from the liquid phase.

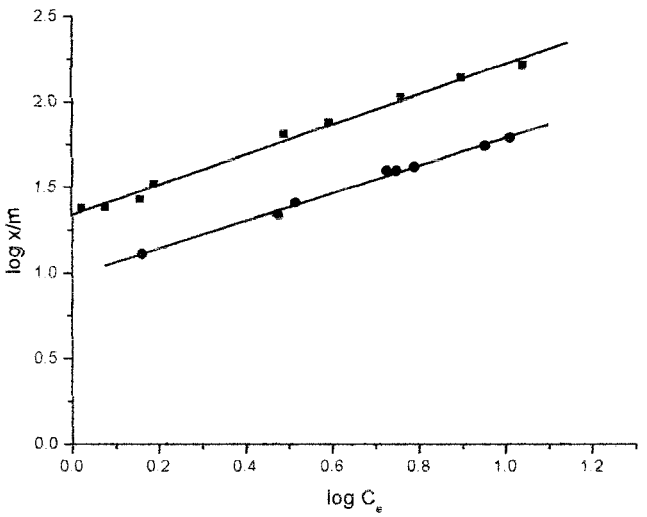


Figure 6 Freundlich isotherms of Zn(II) by the S1 (a) and S3 (b) samples.

TABLE VI
Freundlich Constants for Zn(II) Ions Retention

Code sample	K_F	n
S1	22	1.134
S3	9	1.148

Based on our previous experimental data, the following order of the affinity of the amines for Zn(II) ions has been established: ethylenediamine > triethylenetetramine > dimethylaminopropylamine. Zn(II) ion retention on the ion exchangers is a complex process; in the first stage, a physical adsorption takes place. Then, the ions diffuse inside of the beads and coordinate with the amine groups of the functionalized acrylic copolymers.

The optimal adsorption of Zn(II) ions took place in the weak acidic medium by the complexation process, that is, a preponderant one, with the amine groups attached to the acrylic copolymers.

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