

Kinetic and Thermodynamic Studies Regarding Cu(II) Ions Removal from Aqueous Solution by Poly(Styrene-Divinylbenzene)-Supported Aminophosphonic Acids

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In industrial processes, e. g., the leather industry, mineral extraction and electroplating, there is a considerable emission of residual water contaminated with heavy metals such as cadmium, lead, copper, nickel, zinc, and chromium. The use of chelating polymers for the preconcentration and separation of heavy metals is reasonably well understood and progress today is mainly in improving the specificity of the resin and the techniques of application. In this paper the aminophosphonic resins were used in the removal of Cu(II) ions from aqueous solutions. The kinetic models applied to the experimental data showed that the adsorption of Cu(II) ions onto studied materials is described by the pseudo-second-order kinetic model. Temperature dependence of sorption reveals the increase in sorption performance of the sorbent with temperature increasing. The equilibrium adsorption data were described by the Langmuir model.

Keywords: aminophosphonic acid, copper, removal, isotherm, kinetic

Metals ions are often present in wastewaters from industries such as mining, metallurgy, and surface finishing at a concentration from a few to several hundred milligrams per liter. Elimination of heavy metals from industrial wastewaters is one of the compulsory conditions for their discharge into sewage systems or bodies of waters [1-3]. Metal recovery from solution is typically achieved by techniques including chemical precipitation, solvent extraction and adsorption. Some of these methods are expensive and have limitations. Currently, the usual treatment technology of metal-bearing wastewater is chemical precipitation; however, this method often creates secondary problems with sludge generation. Solvent extraction and resin ion exchange involve similar chemical principles, each offering advantages and drawbacks [4-6]. As examples of the general advantages, solvent extraction is effective for the recovery of metal ions at high concentration with high selectivity and is suitable for continuous operation, while resin ion exchange is effective for the removal of metal ions at low concentration and simplifies the equipment and operation [7-9]. As examples of the general drawbacks, solvent extraction is associated with the loss of organic compounds (extractant and diluents) into the aqueous phase, while resin ion exchange has a low selectivity for metal ions except in the cases using chelating resins, which show slow complexation with metal ions and are expensive. The development of solvent-impregnated resins as a link between solvent extraction and resin ion exchange has become an important direction in separation science and technology. Solvent-impregnated resins have been shown to be effective sorbents for the removal of metal ions at low concentration [10-13].

The purpose of this study is to explore the ability of removing Cu(II) ions from aqueous solutions by using two

synthesized and two commercial aminophosphonic acid grafted on styrene-divinylbenzene copolymer. In order to determine the adsorption performance of the studied materials the equilibrium, kinetic and thermodynamic studies, were performed.

Materials and methods

The studied adsorbent materials were obtained by chemical method, using the "One-Pot" functionalizing reaction, using two materials (benzaldehyde and propionaldehyde), a synthesized co-polymer (S) and a commercial one (C), using different quantities of divinylbenzene grafted with amino groups (1% and 15%) and two types of acids (phosphorous and aminophosphonic acid).

Stock solution of Cu(II) were prepared using Merck Standard Solutions of Cu(NO₃)₂, in HNO₃ 0.5 mol/L.

All other chemicals used for experiments were of analytical reagent grade, and were used without further purification. Distilled water was used in all experiments.

The pH of the solutions was measured with a digital pH meter CRISON Multimeter MM41, using a glass electrode calibrated with buffer solutions.

Cu(II) ions concentrations were determined using a Varian SpectrAA 280 Fast Sequential Atomic Absorption Spectrometer with an air-acetylene flame at wavelengths $\lambda = 324.8$ nm.

For batch experiments a mechanical shaker bath MTA Kutesz, Hungary was used.

In order to establish the adsorption performance of the studied materials, in the process of Cu(II) ions removal from water, kinetic, thermodynamic and equilibrium studies were performed.

The adsorption performance is expressed as the adsorption capacity q_1 (mg/g) of the adsorbent, corresponding to the amount of Cu(II) ions sorbed per g

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adsorbent at a known time, t , and is calculated using the following equation [14-20]:

$$q_t = (C_o - C_t) \frac{v}{m} \quad (1)$$

where:

C_o - initial concentration of Cu(II) ions in solution, mg/L;
 C_t - concentration of Cu(II) ions in solution after a time t (min), mg/L;

v - volume of the solution, L;

m - mass of the adsorbent employed, g.

Kinetic adsorption experiments were carried out with a view to find out the equilibrium time of adsorption and the mechanism of adsorption. Kinetics of adsorption describing the solute uptake rate, which in turn governs the residence time of adsorption reaction, is one of the important characteristics defining the efficiency of adsorption.

In this study, Lagergren-first-order equation and pseudo-second-order equation were used to test the experimental data.

The pseudo-first-order kinetic model can be used to determine the rate constant for the adsorption process and the integrated form is expressed by the following equation [18, 19, 21-23]:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (2)$$

where:

q_t and q_e represent the amounts of the Cu(II) adsorbed on the adsorbent at time t and at equilibrium time, respectively, mg/g;

k_1 - the specific adsorption rate constant, min^{-1} .

The linear form of the pseudo-second-order rate expression of Ho and McKay, based on the solid phase sorption, is given by [18, 19, 21, 24]:

$$\frac{t}{q_t} = \frac{1}{h} + \frac{t}{q_e} \quad (3)$$

where:

$h = k_2 \cdot q_e^2$;

k_2 - the pseudo-second-order constant, $\text{min}^{-1}(\text{mg/g})^{-1}$.

Other terms have their usual meanings.

The study of the temperature effect on Cu(II) removal by studied materials enabled us to determine the thermodynamic parameters (ΔG° , ΔH° and ΔS°) by using the following equation:

$$\ln K_d = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (4)$$

where:

R is the ideal gas constant; T is the temperature, K;

K_d is the distribution coefficient (amount of removed Cu(II) per gram of material divided by its concentration in the liquid phase).

The changes in free energy (ΔG°) have been calculated using the Gibbs-Helmholtz relation as:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (5)$$

where:

the symbols have their usual meanings.

Langmuir and Freundlich isotherm studies were conducted in order to investigate the maximum adsorption capacity of the studied materials towards Cu(II) ions.

The linear form of the Freundlich isotherm equation can be written as:

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (6)$$

and of the Langmuir isotherm as the following equation:

$$\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{C_e}{q_m}, \quad (7)$$

where:

q_e is the amount of Cu(II) ions per gram of sorbent, mg/g;

C_e is the residual concentration of Cu(II) ions in the solution at equilibrium, mg/L;

K_L and $1/n$ are characteristic constants that can be related to the relative adsorption capacity of the adsorbent and the intensity of adsorption, respectively;

q_m is a measure of monolayer adsorption capacity [mg/g] and K_L is a constant related to the free energy of adsorption [14, 16, 18, 19, 21, 24, 26-30].

Results and discussions

The characteristics of aminophosphonic acid groups grafted on polymeric support by polymer-analogous reactions are given in table 1.

Influence of contact time and kinetic studies

The effect of contact time on Cu(II) ions adsorption on the studied materials is presented in figures 1. It should be

Code	Phosphorus content (% w)	Amino residual concentration (mmoles amino group/g of copolymer)	Ligand concentration (mmoles aminophosphonic acid /g of copolymer)	Yield of modification (%)
1S	4.60	0.07	1.39	95.23
3S	3.80	0.47	1.17	71.43
1C	2.03	0.88	0.66	42.73
2C	1.80	0.98	0.55	35.91

Table 1
 CHARACTERISTICS OF THE STYRENE-DIVINYLBENZENE COPOLYMER FUNCTIONALIZED WITH AMINOPHOSPHONIC ACID GROUPS

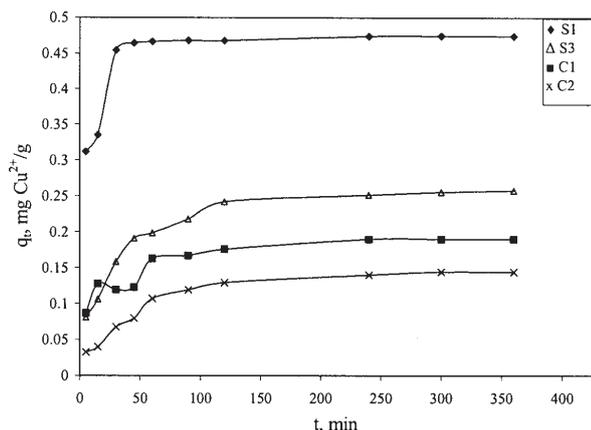


Fig. 1. Effect of contact time on the adsorption capacity in the case of Cu(II) ions adsorption process $C_o = 10$ mg/L, $T = 25 \pm 1^\circ\text{C}$

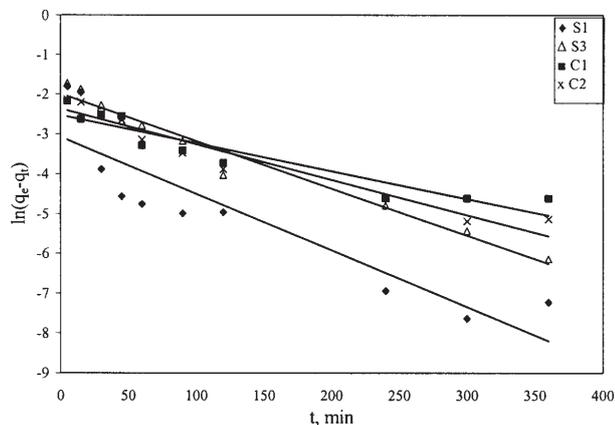


Fig. 2. Pseudo-first-order kinetic plot for Cu(II) ions adsorption process

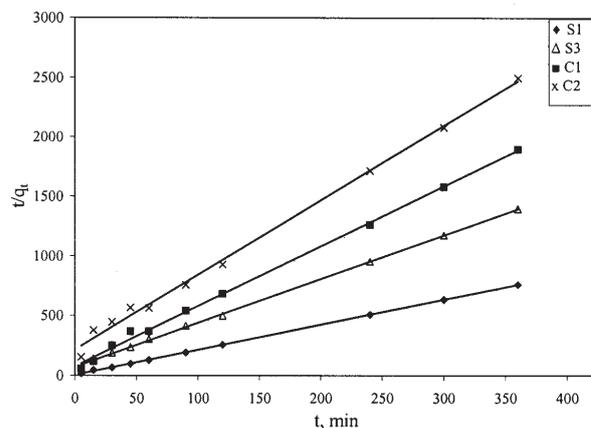


Fig. 3. Pseudo-second-order kinetic plot for Cu(II) ions adsorption process

Table 2
KINETIC PARAMETERS FOR Cu(II) SORPTION ONTO ALL STUDIED MATERIALS

Material	$q_{e, \text{exp}}$, mg/g	Pseudo-first-order model			Pseudo-second-order model		
		$q_{e, \text{calc}}$, mg/g	k_1 , min ⁻¹	R^2	$q_{e, \text{calc}}$, mg/g	k_2 , min ⁻¹ (mg/g) ⁻¹	R^2
S1	0.48	0.046	0.0142	0.8152	0.48	0.783	0.9999
S3	0.20	0.079	0.0070	0.8842	0.20	0.335	0.9977
C1	0.26	0.137	0.0119	0.9695	0.27	0.194	0.9992
C2	0.15	0.093	0.0089	0.9375	0.16	0.182	0.9959

noted that the adsorption capacities of all adsorbents increased as the contact time was increased up to 120 min, but then remained constant as the equilibrium was reached.

Figures 2 display the plot of $\ln(q_e - q_t)$ versus t for Cu(II) adsorption onto all studied materials. The slopes and intercept of the plots are used to estimate the pseudo-first-order rate constant (k_1) and the equilibrium adsorption capacity (q_e), respectively. The pseudo second-order rate constant (k_2) and the equilibrium adsorption capacity (q_e) for all the cases can be estimated from the intercept and slope of t/q_t versus t (fig. 3).

The values of the constants, together with the regression coefficients (R^2) obtained in all cases are summarized in table 2.

Data presented in table 2 show that the correlation coefficients for the pseudo-first-order kinetic model were much lower in all the cases than those obtained for the pseudo-second-order model, where the correlation coefficients are very close to 1. Furthermore, the values of the equilibrium sorption capacities calculated ($q_{e, \text{calc}}$) using the first-order model, are not close to the experimental values ($q_{e, \text{exp}}$). In the case of the pseudo-second-order model the theoretically predicted equilibrium sorption capacities are close to the values experimentally determined, for all studied materials. This shows that the kinetics of Cu(II) removal by adsorption on the studied materials is described by a pseudo-second-order expression. This suggests that the rate-determining step may be chemical adsorption or chemisorptions involving valence forces through sharing or exchange of electrons between adsorbent and adsorbate.

Influence of temperature and thermodynamic studies

The plot of $\ln K_d$ vs. $1/T$ is illustrated in figure 4. The variations for all studied materials are linear, with good correlation coefficients (> 0.98). The thermodynamic parameters calculated from the linear plot and eq. (5) are given in table 3.

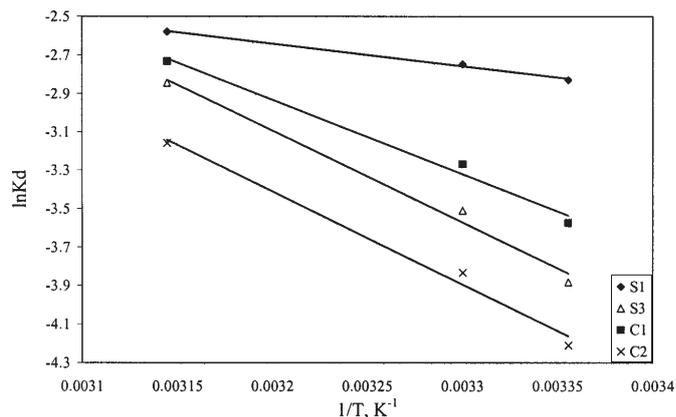


Fig. 4. Effect of temperature on the sorption of Cu(II) onto studied materials $C_0 = 10$ mg/L; $t = 120$ min;

The negative values of ΔG° and positive values of ΔH° indicate that the adsorption of Cu(II) onto the studied materials is a spontaneous and endothermic process. The more negative value of ΔG° implies a higher driving force to the adsorption process. The positive values of ΔS° indicate that the randomness increased at the solid-solution interface during the adsorption of Cu(II) onto the studied materials. The increasing of the adsorption capacities of the studied materials at higher temperatures may be due to the enlargement of pore size and/or activation of the adsorbent surface.

Influence of initial Cu(II) ions concentration and equilibrium studies

Adsorption isotherms are very powerful tools for the analysis of adsorption process. Adsorption isotherms establish the relationship between the equilibrium pressure or concentration and the amount of adsorbed by the unit mass of adsorbent at a constant temperature. The adsorption isotherms of Cu(II) ions are presented in figure 5.

Material	ΔG° , kJ/mol			ΔH° , kJ/mol	ΔS° , kJ/mol·K
	Temperature, K				
	298	303	318		
S1	-16.8	-17.3	-18.6	9.65	0.089
S3	-20.2	-21.2	-24.2	39.7	0.201
C1	-24.4	-25.4	-28.2	32.2	0.190
C2	-23.8	-24.5	-28.1	40.3	0.215

Table 3
THERMODYNAMIC PARAMETERS EVALUATED FOR Cu(II)
SORPTION ONTO STUDIED MATERIALS

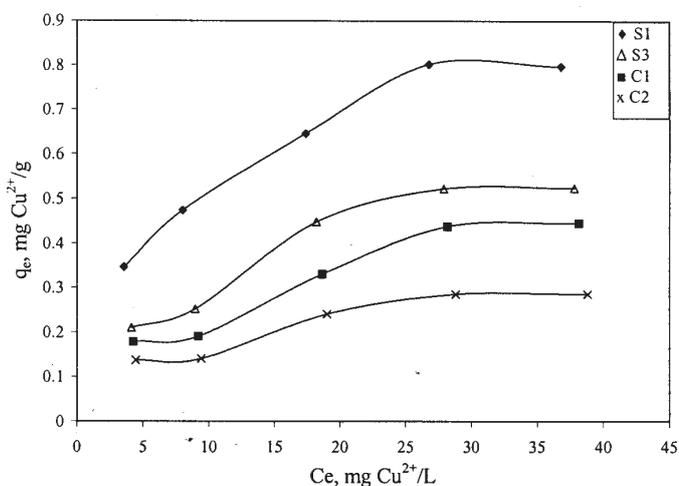


Fig. 5. Adsorption isotherms of Cu(II), $T=25\pm 1^\circ\text{C}$, $C_0 = 5-40 \text{ mg/L}$
 $t=240 \text{ min}$

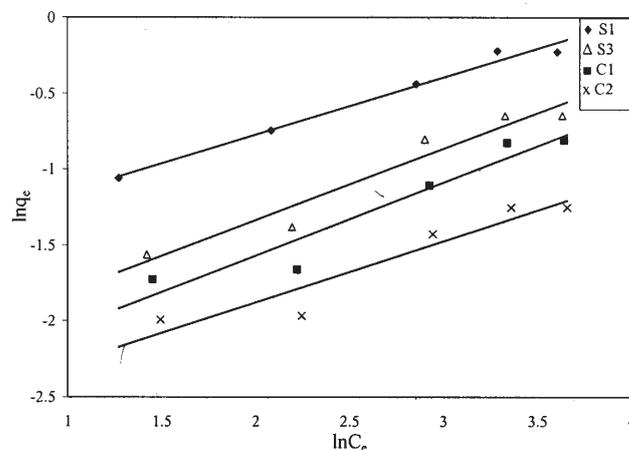


Fig. 6. Freundlich plot for Cu(II) adsorption onto studied materials

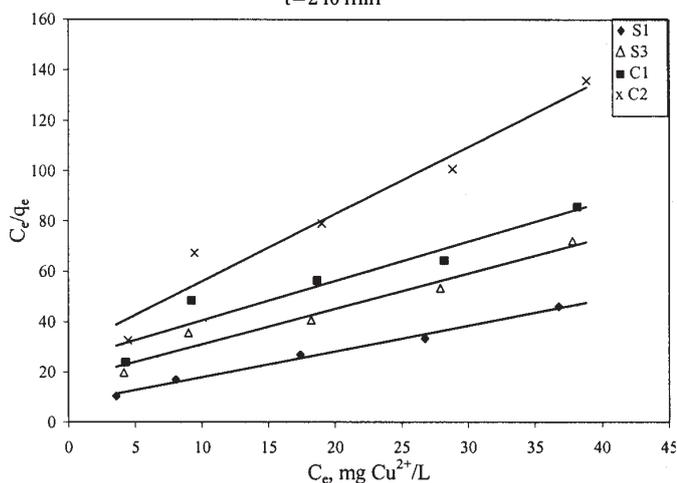


Fig. 7. Langmuir plot for Cu(II) adsorption
onto studied materials

Table 4
PARAMETERS OF FREUNDLICH AND LANGMUIR ISOTHERMS FOR Cu(II) IONS ADSORPTION
ON THE STUDIED MATERIALS

Material	$q_{m, \text{exp}}$, mg/g	Freundlich isotherm			Langmuir isotherm		
		K_F , mg/g	$1/n$	R^2	K_L , L/mg	$q_{m, \text{calc}}$, mg/g	R^2
S1	0.8	0.216	0.3795	0.9842	0.134	0.97	0.9901
S3	0.45	0.079	0.4802	0.9212	0.689	0.64	0.9163
C1	0.52	0.103	0.4691	0.9436	0.084	0.71	0.9602
C2	0.29	0.068	0.4039	0.8997	0.092	0.37	0.9530

The adsorption capacities increased with increasing equilibrium concentration of Cu(II) ions for all the studied materials. Then, they approached a constant value at higher equilibrium concentrations.

The constants K_F and $1/n$ of the Freundlich model, respectively, are obtained from the intercept and the slope of the linear plot of $\ln q_e$ versus $\ln C_e$ (fig. 6). From the intercept and slope of the C_e/q_e versus C_e (fig. 7) can be obtained the K_L and the maximum adsorption capacity of the studied materials for Cu(II) adsorption. The Langmuir and Freundlich constants evaluated from the plots and their correlation coefficients for all the cases are presented in table 4.

The constant K_F can be defined as an adsorption coefficient which represents the quantity of adsorbed metal ions for a unit equilibrium concentration. The slope $1/n$ is a measure of the adsorption intensity or surface heterogeneity. For $1/n = 1$, the partition between the two phases is independent on the concentration. The situation $1/n < 1$ is the most common and correspond to a normal L-type Langmuir isotherm, while $1/n > 1$ is indicative of a cooperative adsorption which involves strong interactions between the molecules of adsorbate. The correlation coefficients are very low suggesting a restriction on the use of Freundlich isotherm.

Correlations coefficients of the Langmuir plot are closer to 1 in all the cases. The essential feature of the Langmuir equation can be expressed in terms of a dimensionless separation factor, R_L defined as [14, 21, 30]:

$$R_L = \frac{1}{1 + K_L \cdot C_0} \quad (8)$$

The value of R_L indicates the shape of the isotherm: unfavourable, $R_L > 1$; linear, $R_L = 1$; favourable, $0 < R_L < 1$; and irreversible, $R_L = 0$. R_L values were found to be between 0 and 1 for all the concentration of Cu(II) ions showing that the adsorption is favourable for all the studied materials. The R_L value decreased with the increase of the initial Cu(II) ions concentration. This indicates that the adsorption is more favourable for the higher initial Cu(II) ions concentrations than for the lower ones. One may also notice that the maximum adsorption capacities of the studied materials calculated from the Langmuir plot ($q_{m, calc}$) are close to the experimental values ($q_{m, exp}$). It is clear that the Langmuir isotherm model provides an excellent fit of the equilibrium adsorption data in all the cases.

It can be concluded that the synthetic materials develop a maximum adsorption capacity closer (or even higher) to that achieved by the commercial materials.

Conclusions

The present investigation shows that the studied materials are effective adsorbents for Cu(II) ions removal. By applying the kinetic models to the experimental data it was found that the adsorption of Cu(II) ions onto studied materials is described by the pseudo-second-order kinetic model. Temperature dependence of sorption reveals the increase in sorption performance of the sorbent with temperature. The values of Gibbs free energy (ΔG°) show the spontaneous nature of Cu(II) sorption and the positive values of the standard enthalpy (ΔH°) show the endothermic nature of Cu(II) sorption on the studied materials. Positive entropy (ΔS°) suggests the affinity of the studied materials for the Cu(II) ions in solution. The equilibrium sorption data were modeled using Freundlich and Langmuir isotherms. For all the studied systems, Langmuir isotherm model provided an excellent fit of the equilibrium adsorption data.

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