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Sorption Isotherms of Heavy Metal Ions onto Semi-Interpenetrating Polymer Network Cryogels Based on Polyacrylamide and Anionically Modified Potato Starch

Diana Felicia Apopei,[†] Maria Valentina Dinu,[†] Andrzej W. Trochimczuk,[‡] and Ecaterina Stela Dragan*,[†]

[†]Department of Functional Polymers, "Petru Poni" Institute of Macromolecular Chemistry, Aleea Grigore Ghica Voda 41A, 700487 Iasi, Romania

[‡]Faculty of Chemistry, Wroclaw University of Technology, Wyspianskiego 27, 50-370 Wroclaw, Poland

ABSTRACT: Semi-interpenetrating polymer network (semi-IPN) cryogels based on polyacrylamide (PAAm) and anionically modified potato starch (PA) were synthesized and tested as sorbents for heavy metal ions like: Cu^{2+}, Cd^{2+}, Ni^{2+}, and Zn^{2+} from aqueous solutions by batch-mode under noncompetitive conditions. Experimental data obtained from batch equilibrium tests have been analyzed using four models: Langmuir, Freundlich, Temkin, and Sips isotherms. The equilibrium data obtained for the sorption of heavy metal ions onto the semi-IPN cryogels were well fitted in the Sips nonlinear regression model with a maximum theoretical sorption capacity of 40.72 mg Cu^{2+}/g composite, 19.27 mg Cd^{2+}/g composite, 9.31 mg Ni^{2+}/g composite, and 7.48 mg Zn^{2+}/g composite.

1. INTRODUCTION

It is known that the presence of heavy metal ions in the wastewaters generates tremendous problems for the living organisms and the environment due to their high toxicity and nonbiodegradability, and therefore, their removal is a stringent requirement. Among the conventional techniques commonly used in the removal of heavy metals from wastewaters like chemical oxidation, biological treatment, and coagulation, the chemical or physical adsorption is perhaps the most widely utilized. It is preferred when either the enrichment of trace metal amounts or a high selectivity for a certain metal ion is required.[1−6] Biosorbents derived mainly from polysaccharides attracted a strong interest in the past decade as a more cost-effective alternative to the existing adsorbents like activated carbon and synthetic ion exchangers, furthermore being biodegradable and nontoxic in nature.[7−16] Among the environmentally friendly sorbents, hydrogels occupy a special place. Hydrogels are usually described as hydrophilic polymers, which swell in water without dissolving, their integrity being stabilized by physical or chemical linkages. The ability of a hydrogel to adsorb ionic species is depending on some of its intrinsic characteristics like: hydrophilic/hydrophobic balance, presence of ionic/ionizable groups, swelling degree, and chemical and mechanical stability. It has been reported that many types of sorbent-based hydrogels are effective in removing heavy metal ions from aqueous effluents.[17−21] As reported in literature, the combination of natural and synthetic polymers in the preparation of multicomponent hydrogels as semi- or interpenetrating polymer networks (IPN) can enhance their properties or even induce novel characteristics for the composite gel.[22−24]

Considerable interest has lately been focused on the macroporous cryogels, characterized by a faster response rate to the small changes of the external stimuli than the conventional hydrogels. By cryogelation, the cross-linking polymerization reactions are conducted below the freezing point of the reaction solutions; when most of the solvent (water) forms crystals, the bound water and the soluble substances (monomers, initiator, polymers) are concentrated in a nonfrozen liquid microphase, where the gel is formed. Cryogels, by their interconnected pore structure, allow the unhindered diffusion of solutes or even colloidal particles.[25−27] Ionic multicomponent cryogels, having enhanced mechanical and chemical resistance, have been tested as novel sorbents in the separation processes of small ionic species.[28−30]

Among the numerous polysaccharides, starch is one of the most promising as raw material for novel sorbents because it is abundant, renewable, biodegradable, biocompatible, and furthermore has a high reactivity in chemical modifications.[12,23,31−34] In a previous study, we have reported the synthesis of some novel semi-interpenetrating polymer network (semi-IPN) composite hydrogels based on polyacrylamide (PAAm) as a matrix and either native potato starch (PS) or the hydrolyzed PS-g-poly(acrylonitrile) (PS-g-PAN) copolymer as entrapped polymer using N,N′-methylenebisacrylamide (BAAm) as cross-linker, ammonium persulfate as radical initiator, and N,N,N′,N′-tetramethylethylenediamine (TEMED) as accelerator of free-radical polymerization.[35] The aim of the present work was the evaluation of the sorption capacities of the semi-IPN cryogels based on PAAm and hydrolyzed PS-g-PAN copolymer (PA), synthesized under the freezing point of the reaction solution (−18 °C), for Cu^{2+}, Cd^{2+}, Ni^{2+}, and Zn^{2+} ions. The modeling of the equilibrium data by applying different isotherm models has been performed.

2. MATERIALS AND METHODS

2.1. Materials. PS from Fluka, moisture content <10%, was used as received. Acrylonitrile (AN) was distilled at about 77 °C and kept at low temperature. $Ce(SO_4)_2$, H_2SO_4, NaOH, methanol p.a., acrylamide (AAm) (Fluka), BAAm (Sigma), ammonium persulfate (APS, Sigma-Aldrich), and TEMED (Sigma-Aldrich) were used as received. The heavy metal salts used were $Cu(CH_3COO)_2\cdot H_2O$, $Cd(CH_3COO)_2\cdot 2H_2O$, $Ni(CH_3COO)_2\cdot 4H_2O$, and $Zn(CH_3COO)_2\cdot 2H_2O$ (all purchased from Aldrich).

2.2. Preparation of PA from PS-*g*-PAN. For the preparation of PS-*g*-PAN copolymer, the redox initiation by Ce^{4+} ions has been adopted because it was demonstrated that the redox-initiated process of graft copolymerization onto the polysaccharide backbone generates free radicals on the polysaccharide backbone itself, a little space remaining for the homopolymerization if the monomer and initiator concentrations are lower than the critical concentrations, 2.0 and 0.1 M, respectively.[36] In our experiments, the concentrations of monomer and Ce^{4+} have been kept lower than the critical concentrations. The details concerning the synthesis of PS-*g*-PAN with $Ce(SO_4)_2$ with a concentration of 0.02 M in 0.4 M H_2SO_4 have been previously presented.[35] Polyanion PA has been obtained by the alkaline hydrolysis of PS-*g*-PAN copolymer, the details concerning the preparation and characterization methods being given elsewhere.[35]

2.3. Preparation and Characterization of Semi-IPN Cryogels. Semi-IPN cryogels based on PAAm and PA were prepared by free-radical cross-linking copolymerization in aqueous medium at −18 °C, as rods and disks. The cross-linker ratio X, defined as the mole ratio of the cross-linker BAAm to the monomer AAm, has been 1:60. The redox initiator system used consisted of APS and TEMED. Stock solutions of APS and TEMED were prepared by dissolving 0.2 g of APS and 0.625 mL of TEMED each in 25 mL of double distilled water. PA as aqueous solution with a concentration of 1 wt % has been prepared by stirring at room temperature, one day before using. The synthesis procedure used in the preparation of semi-IPN composite cryogels is briefly presented below. Typically, 0.4825 g of AAm, 7 mL of PA aqueous solution with concentration of 1 wt %, i.e., 0.07 g of PA, 1 mL of aqueous solution of BAAm (0.436 g in 25 mL of double distilled water), and 1 mL of TEMED stock solutions were first mixed in a 10 mL graduated flask. The solution was cooled at 0 °C in an ice−water bath and purged with nitrogen gas for 20 min; then, 1 mL of APS stock aqueous solution was added, and the whole mixture was further stirred for about 20 s. Thus, the initial concentration of monomers, which represents the total mass of AAm and BAAm in 100 mL of the reaction mixture, was about 5 wt % (Table 1), and the initial concentration of PA in the total mass of the reaction solution was 12.28 wt %,

Table 1. Sample Code and Feed Composition of Semi-IPN Composite Cryogels

sample of CG	BAAm:AAm molar ratio	C_o, wt %	initial content of PA, wt %
CG.R[a]	1:60	5	12.28
CG.D[b]	1:60	5	12.28
CG.Dh[c]	1:60	5	12.28

[a]Cryogel as rod. [b]Cryogel as disk. [c]Cryogel as disk after the treatment with NaOH 0.1 M, 1 h.

calculated taking into account the initial mass of AAm, BAAm, and PA. Portions of this solution, each 1 mL, were transferred into syringes of 5 mm in diameter, in order to prepare gels in the shape of rods, or were transferred to Petri dishes, with diameters of 55 mm, in order to obtain gels in the shape of disks, and after that immersed in a thermostatted bath at −18 °C, and the polymerization was conducted for one day. After polymerization, the gels as rods were cut into pieces of about 10 mm in length. All gels were immersed in large volumes of Milli pore water to wash out any soluble polymers, unreacted monomers, and the initiator, changing the washing water each 4 h. Thereafter, the swollen gel samples were frozen in liquid nitrogen and freeze-dried in a Martin Christ, ALPHA 1-2LD device, 24 h, at −57 °C and 0.045 mbar. In this way, the porosity of the gels in the dried state has been preserved.

2.4. Sorption Experiments. Batch-mode sorption studies were performed from 1 mmol/L solutions of an appropriate metal ion at 20 ± 1 °C, separately for each ion. The pH of aqueous solution was adjusted to 4.7 using an acetate buffer solution, because the pK_a of weak polyacids is around this value. To obtain information about the sorption capacity of semi-IPN cryogels, prepared as monoliths and disks, for the metal ions, 20 mL of the ion solution with a concentration of 1 mmol/L was shaken with 0.01 g of dried cryogel for 24 h. After that time, the cryogel was filtered off and the concentration of metal ion was determined by atomic absorption spectroscopy (AAS) on a Perkin−Elmer AAnalyst 100 with wavelengths set at 324.8 nm for Cu^{2+}, 228.8 nm for Cd^{2+}, 232 nm for Ni^{2+}, and 213.9 nm for Zn^{2+}. The amount of metal ion bound on semi-IPN cryogels was calculated with eq 1:

$$\text{Sorption capacity} = \frac{(C_0 - C)V}{W}, \quad \text{mg/g} \tag{1}$$

where C_0 and C are the concentrations of the metal ion in aqueous solution (mg/L) before and after the interaction with dried cryogel, respectively, V is the volume of the aqueous phase (L), and W is the amount of the dried cryogel (g).

For the determination of sorption isotherms, the metal ion concentration was fixed at 1 mmol/L and the amount of dried cryogel was varied in the range of 0.005−0.040 g, at pH = 4.7 and temperature of 20 ± 1 °C, for 24 h, as previously shown.[5,37] After that time, the cryogel was filtered off and the concentration of metal ion was determined by AAS. Sorption isotherms are useful to relate interaction features among adsorbents (in this case, cryogels) and adsorbates (in this case, metals). There are many isotherms that describe single-component sorption.[38] However, the ones most often employed in the assessment of the sorption of cationic species in anionic sorbents are the Langmuir, Freundlich, Temkin, and Sips isotherms.

Langmuir isotherm is a well-known isotherm model being frequently used to quantify the performance of different sorbents.[14−17,38,39] The Langmuir equation is applicable to homogeneous adsorption based on the following assumptions: (i) all the adsorption sites are assumed to be identical; (ii) each site retains one molecule of the given compound; (iii) all sites are energetically and sterically independent of the adsorbed quantity.[40] The nonlinear and linear forms of the Langmuir isotherm are described by eqs 2 and 3, respectively:

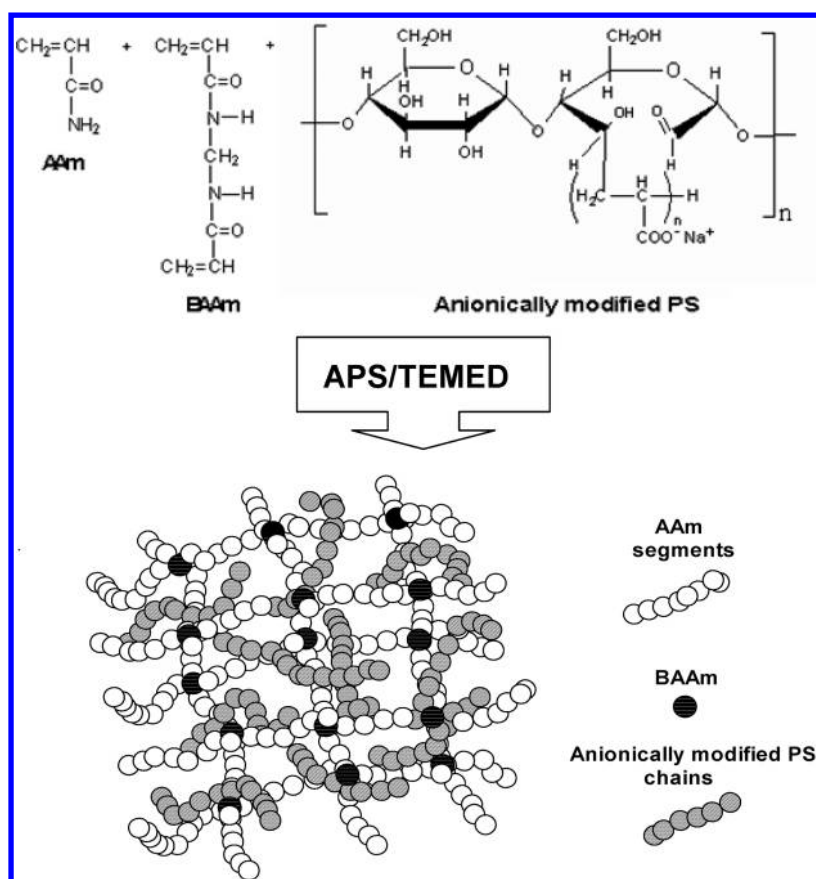$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \tag{2}$$

Figure 1. Schematic representation of the formation of semi-IPN composite cryogels based on PAAm and anionically modified PS.

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{K_L q_m C_e} \tag{3}$$

where q_m is the saturated monolayer sorption capacity (mg/g) and K_L is the Langmuir constant (L/mg) related to the energy of adsorption, which reflects the affinity between the sorbent and sorbate.

Freundlich isotherm assumes heterogeneous surface with a nonuniform distribution of heat of adsorption and is expressed by the following equations:[41]

$$q_e = K_F C_e^N \tag{4}$$

or

$$\log q_e = \log K_F + N \log C_e \tag{5}$$

where K_F is Freundlich constant, which predicts the quantity of metal ion per gram of composite at the equilibrium concentration (mg/g) and N is 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 density, and when $N = 1$, all surface sites are equivalent.

Temkin isotherm is the early model describing the adsorption of hydrogen onto platinum electrodes within the acidic solutions.[42] The assumptions made on the Temkin adsorption model are that: (a) the heat of adsorption of all the molecules in the layer would decrease linearly with coverage due to the adsorbent−adsorbate interactions and (b) adsorption is characterized by a uniform distribution of binding energies.[38]

The Temkin isotherm has commonly been applied in the following forms:

$$q_e = \frac{RT}{b_T} \ln a_T C_e \tag{6}$$

or

$$q_e = \frac{RT}{b_T} \ln a_T + \left(\frac{RT}{b_T}\right) \ln C_e \tag{7}$$

where b_T is the Temkin constant related to the heat of sorption (kJ/mol) and a_T is the equilibrium binding constant corresponding to the maximum binding energy (L/mg).

Sips isotherm is a combination of the Langmuir and Freundlich isotherm type models and is expected to much better describe the adsorption on heterogeneous surfaces. At low sorbate concentrations, it reduces to a Freundlich isotherm, while at high sorbate concentrations, it predicts a monolayer adsorption capacity characteristic of the Langmuir isotherm.[38] The nonlinear and linear forms of the Sips isotherm are described by the following equations:

$$q_e = \frac{q_m a_S C_e^N}{1 + a_S C_e^N} \tag{8}$$

$$N \ln(C_e) = -\ln\left(\frac{q_m}{q_e}\right) + \ln a_s \tag{9}$$

where q_m is monolayer adsorption capacity (mg/g) and a_S is Sips constant related to energy of adsorption.

2.5. Desorption Experiments. Desorption is a very important process; both the regeneration of the sorbent and the recovery of metal ions are strongly required in the sorption experiments. Desorption studies were carried out in a batch system using the metal ions-loaded cryogel immediately after the sorption experiment. HCl (0.1 M) has been used as desorption agent, desorption time being 20 min in all experiments. The concentration of metal ions after desorption has been determined by AAS, as previously shown in Section 2.4. The percentage of metal ion desorbed from semi-IPN cryogels was calculated with eq 10:

$$\text{Metal ion desorbed } (\%) = \frac{M_{\text{des}}^{2+}}{M_{\text{ads}}^{2+}} \times 100 \qquad (10)$$

where M_{ads}^{2+} is the amount of metal ion adsorbed onto cryogel (mg/g) and M_{des}^{2+} is the amount of metal ion desorbed (mg/g).

3. RESULTS AND DISCUSSION

Semi-IPN cryogels composed of PAAm and PA with a cross-linking degree of 1:60 were synthesized at −18 °C and tested, for the first time, as sorbents for Cu^{2+}, Cd^{2+}, Ni^{2+}, and Zn^{2+} ions from aqueous solutions by batch-mode under noncompetitive conditions. During polymerization, the first step was a reaction between APS and TEMED, in which the TEMED catalyzes the decomposition of the persulfate ions to give sulfate and hydroxyl free radicals, which initiate the polymerization of AAm.[23,27,35] In the presence of a cross-linking agent, i.e., BAAm, cross-linking reaction occurred, and finally, a three-dimensional network of PAAm was obtained. The anionically modified PS chains (PA) interdiffuse and get physically entangled within the PAAm 3D network, as can be seen in Figure 1.

The code and some characteristics of the semi-IPN PAAm/PA cryogels have been summarized in Table 1. The code of the gels means: CG, cryogel; R, rod; D, disk; Dh, disk after the treatment with NaOH 0.1 M, 1 h.

By conducting the cross-linking polymerization reactions at −18 °C, semi-IPN PAAm/PA cryogels with macroporous structure were generated, as shown on the SEM images of CG.R presented in Figure 2. As Figure 2 shows, CG.R cryogel exhibits a heterogeneous morphology consisting of polyhedral pores with average sizes of 60 μm. The interconnected character of the pores is also evident.

During the cryogelation, most of the water forms ice crystals, whereas bound water and soluble substances accumulate in a nonfrozen liquid microphase, where the gel is formed.[25] The ice

crystals act as porogen during gelation, leading to a porous structure by thawing at the end of the gel preparation.

3.1. Sorption Studies under Noncompetitive Conditions. Sorption Isotherms. In order to evaluate the sorption capacity of semi-IPN PAAm/PA cryogels, as rods and disks, the sorption of Cu^{2+} ions has been first investigated. Figure 3 presents the amount of Cu^{2+} ions adsorbed at equilibrium onto semi-IPN PAAm/PA cryogels as a function of the equilibrium metal concentration in solution.
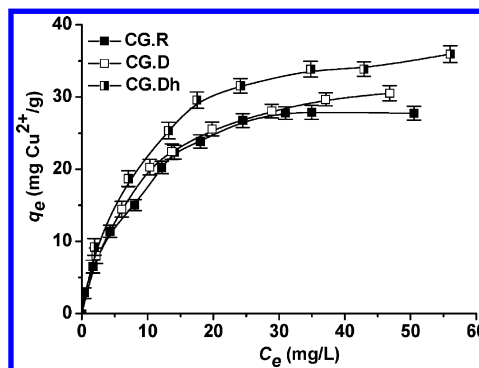

Figure 3. Cu^{2+} retention, q_e as a function of the equilibrium metal concentration, C_e for the semi-IPN PAAm/PA cryogels at pH 4.7, temperature of 22 °C, and contact duration of 24 h.

As can be observed in Figure 3, the semi-IPN PAAm/PA cryogels were able to retain Cu^{2+}, irrespective of the shape of gels (samples CG.R and CG.D). Figure 3 also displayed the results obtained for the sorption of Cu^{2+} ions onto semi-IPN PAAm/PA cryogel prepared as disk but after the treatment with NaOH 0.1 M (CG.Dh). The increase of the sorption capacity of the CG.Dh cryogel (35.93 mg Cu^{2+}/g) compared with the original gel (CG.D having a sorption capacity of 30.51 mg Cu^{2+}/g) could be attributed to the increase of the number of carboxylic groups available for the binding of metal ions.[35] Therefore, the sample CG.Dh has been chosen to carry out the next sorption experiments in all of the investigations.

The sorption isotherm is an invaluable curve describing the phenomenon governing the retention or mobility of a substance from the aqueous media to a solid phase at a constant temperature and pH.[38] A plot of the amount 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 a sorption isotherm. Figure 4A shows that the retention capacity of CG.Dh for Cd^{2+}, Ni^{2+}, and Zn^{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.[43] The experimental values of the maximum sorption capacity ($q_{e,\exp}$) obtained for CG.Dh cryogel were as follows: 35.93 mg Cu^{2+}/g (Figure 3), 14.75 mg Cd^{2+}/g, 8.86 mg Ni^{2+}/g, and 6.57 mg Zn^{2+}/g (Figure 4A).

In the metal removal by hydrogels, it should be considered that the sorption of the metal ions depends on both the amount of available water and the nature of groups attached to the polymer matrix, which in fact allow the interaction with metal ions.[18] In our case, after the hydration of the semi-IPN cryogels, a concentration gradient of metal ions is formed at gel−water interface, and the diffusion of metal ions into cryogel was started.
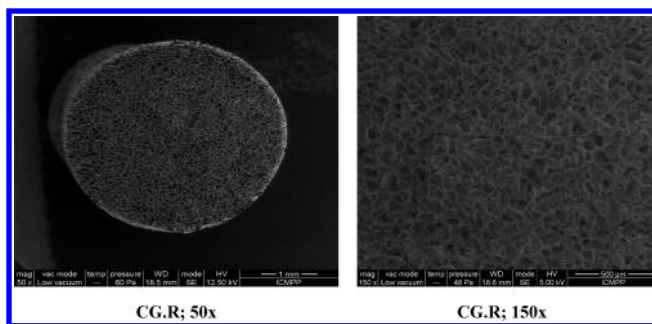

Figure 2. SEM image of CG.R with the scaling bar of 1 mm (left) and 500 μm (right).
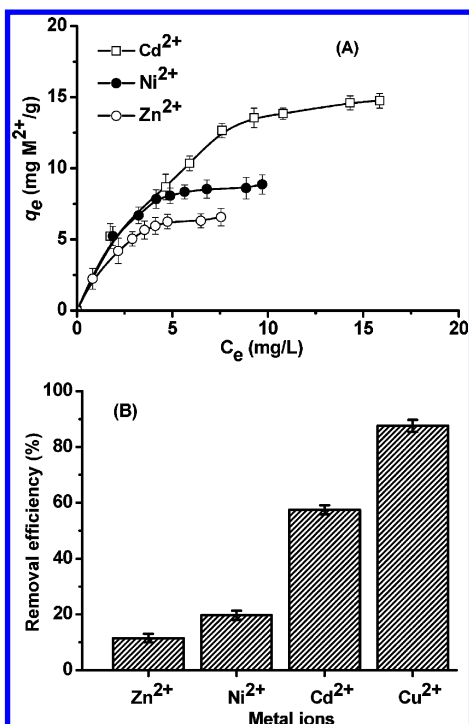
Figure 4. Retention of Cd^{2+}, Ni^{2+}, and Zn^{2+} ions as a function of the equilibrium metal concentration (A) and removal efficiency of Cu^{2+}, Cd^{2+}, Ni^{2+}, and Zn^{2+} ions by CG.Dh (B) at pH 4.7, temperature of 22 °C, contact duration of 24 h; volume of test solution was 20 mL, and the amount of sorbent was 0.04 g.

The removal efficiency of Cu^{2+}, Cd^{2+}, Ni^{2+}, and Zn^{2+} ions from aqueous solution with an initial concentration of 1 mmol/L has been evaluated with eq 11, and the results obtained are presented in Figure 4B.

$$\text{Removal efficiency (\%)} = \frac{C_0 - C}{C_0} \times 100 \qquad (11)$$

where C_0 and C are the concentrations of the metal ion in aqueous solution (mg/L) before and after the interaction with dried cryogel, respectively.

As Figure 4B shows, Cu^{2+}, Cd^{2+}, Ni^{2+}, and Zn^{2+} ions were removed by the semi-IPN cryogels as a function of their chemical nature and ionic size. The removal efficiency of Cu^{2+}, Cd^{2+}, Ni^{2+}, and Zn^{2+} ions by CG.Dh in noncompetitive conditions was $Cu^{2+} > Cd^{2+} > Ni^{2+} > Zn^{2+}$. This result is similar to that reported by Zhao and Mitomo in their study on the sorption of Cu^{2+}, Cd^{2+}, and Zn^{2+} from aqueous solutions using chitosan entrapped CM-cellulose hydrogels.[19]

The mathematical correlation is usually depicted by graphically expressing the amount of metal ions adsorbed on the solid surface (mg/g) as a function of the solute concentration in the solution at equilibrium (mg/L), at constant temperature.[43] In this study, the relationship between the metal ions sorbed onto PAAm/PA cryogels and the aqueous concentrations at equilibrium has been described by Langmuir, Freundlich, Temkin, and Sips sorption isotherm models. A comparison of the nonlinear and linear regression methods of these four widely used isotherms has been performed, because sometimes linearization of a model function has a negative effect on the ability of the model to predict experimental data.[17,37,43-45] Also, several investigations have identified problems in the
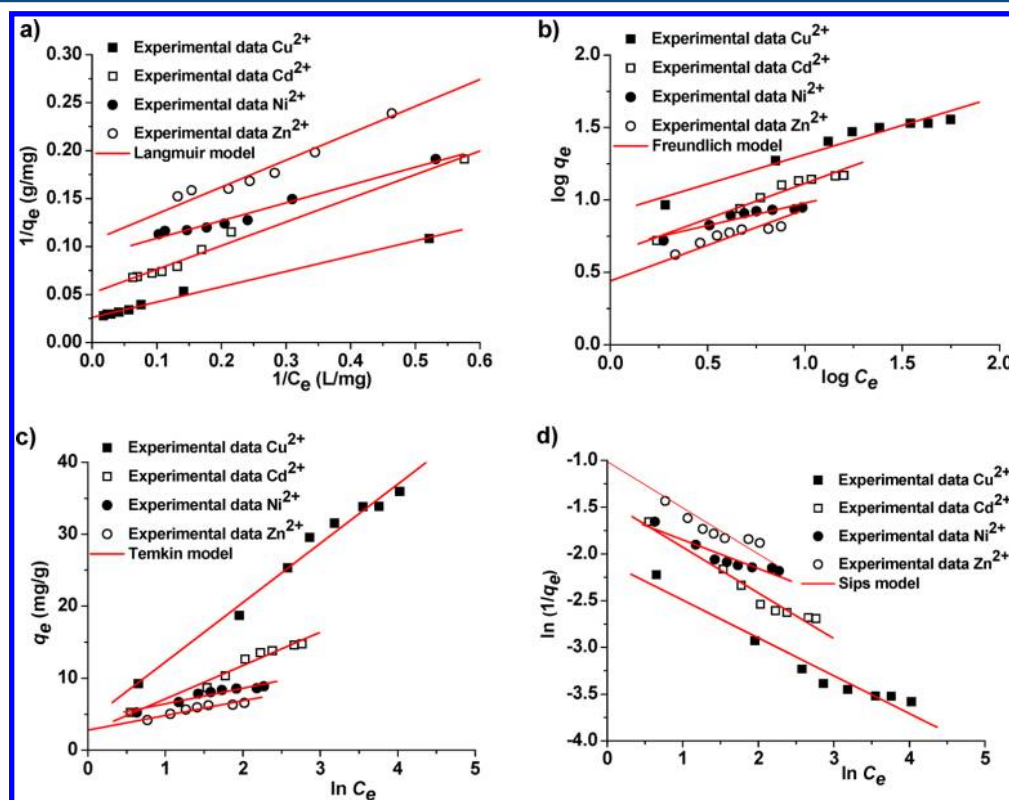

Figure 5. Linear isotherm models of Langmuir (a), Freundlich (b), Temkin (c), and Sips (d) fitted for the sorption of Cu^{2+}, Cd^{2+}, Ni^{2+}, and Zn^{2+} ions onto CG.Dh cryogel; parameters: contact time of 24 h; metal solution pH of 4.7; temperature of 22 °C.

linearization which may lead to violation of the theories behind the isotherm.[17,37,43−46] The equation parameters of these models together with the underlying thermodynamic assumptions provide an insight into the sorption mechanism and the surface properties as well as the affinity degree of sorbents against heavy metals.

3.1.1. Linear Isotherms of Langmuir, Freundlich, Temkin, and Sips. Figure 5a−d illustrates the linear isotherm models for Langmuir (a), Freundlich (b), Temkin (c), and Sips (d) regarding the sorption of Cu^{2+}, Cd^{2+}, Ni^{2+}, and Zn^{2+} ions onto CG.Dh cryogel. The parameters evaluated using eqs 3, 5, 7, and 9 were q_m, K_L, K_F, N, b_T, a_T, a_S, and R^2, their values being displayed in Table 2.

Table 2. Isotherm Parameters of Langmuir, Freundlich, Temkin, and Sips Models Obtained Using Linear Regression Method for the Sorption of Cu^{2+}, Cd^{2+}, Ni^{2+}, and Zn^{2+} Ions onto CG.Dh Cryogel

Langmuir isotherm parameters			
metal ion	q_m, mg/g	K_L, L/mg	R_L	R^2
Cu^{2+}	36.37	0.163	0.859	0.990
Cd^{2+}	18.47	0.209	0.827	0.989
Ni^{2+}	9.87	0.481	0.675	0.986
Zn^{2+}	8.28	0.678	0.596	0.991

Freundlich isotherm parameters		
metal ion	K_F, mg/g	N	R^2
Cu^{2+}	8.07	0.404	0.972
Cd^{2+}	4.67	0.488	0.979
Ni^{2+}	4.22	0.307	0.939
Zn^{2+}	2.75	0.493	0.964

Temkin isotherm parameters		
metal ion	a_T, L/mg	b_T, kJ/mol	R^2
Cu^{2+}	1.63	2.979	0.988
Cd^{2+}	1.71	5.296	0.983
Ni^{2+}	7.29	11.365	0.954
Zn^{2+}	3.94	12.058	0.982

Sips isotherm parameters			
metal ion	q_m, mg/g	a_S	N	R^2
Cu^{2+}	38.46	0.123	0.404	0.972
Cd^{2+}	19.42	0.237	0.489	0.979
Ni^{2+}	11.24	0.214	0.307	0.939
Zn^{2+}	9.44	0.363	0.494	0.964

The plot of $1/q_e$ versus $1/C_e$ (Figure 5a), which corresponds to the linear isotherm model of Langmuir, for the sorption of metal ions onto CG.Dh cryogel provided a line of slope $1/q_m$, which intercepted the y-axis at K_Lq_m. The values of the constant K_L corresponding to the affinity of the metal ions for CG.Dh cryogel and the values of q_m corresponding to the maximum sorption capacity of the cryogel are summarized in Table 2.

As Table 2 shows, the maximum adsorption capacity (q_m) for Cu^{2+}, Cd^{2+}, Ni^{2+}, and Zn^{2+} ions of the CG.Dh cryogel were 36.37 mg/g, 18.47 mg/g, 9.87 mg/g, and 8.28 mg/g, respectively. The theoretical q_m values estimated from the Langmuir model are very close to experimental values, and the correlation coefficients (R^2) were found to be in the range of 0.986−0.991 (Table 2). These results showed that the sorption process of Cu^{2+}, Cd^{2+}, Ni^{2+}, and Zn^{2+} ions onto CG.Dh cryogel could be well described by Langmuir isotherm model.

The essential features of a Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor or equilibrium parameter, R_L (eq 12), which is used to predict if a certain sorption system is "favorable" or "unfavorable":[38,44] unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$), or irreversible ($R_L = 0$).

$$R_L = \frac{1}{1 + K_L C_i} \quad (12)$$

where C_i is the initial metal concentration.

Herein, R_L values obtained for the sorption of Cu^{2+}, Cd^{2+}, Ni^{2+}, and Zn^{2+} ions onto CG.Dh cryogel are listed in Table 2. The fact that all the R_L values for the sorption of metal ions onto cryogel are in the range of 0−1, for 1 mmol/L initial metal ion concentration, confirmed that the cryogels are favorable for sorption of Cu^{2+}, Cd^{2+}, Ni^{2+}, and Zn^{2+} ions under the selected conditions.

The values of Freundlich isotherm constants (K_F and N) determined from the linear plot of log q_e versus log C_e (Figure 5b) are also presented in Table 2. The values of N in the Freundlich model for the sorption of Cu^{2+}, Cd^{2+}, Ni^{2+}, and Zn^{2+} ions onto CG.Dh cryogel were 0.404, 0.488, 0.307, and 0.493, respectively. The values of N in the range of 0−1 indicated favorable sorption of metal ions onto CG.Dh cryogel. The values of correlation coefficients (R^2) are lower than those found for Langmuir model, and this shows that Freundlich model did not fit the experimental data well.

By plotting q_e against ln C_e (Figure 5c), the Temkin constants a_T and b_T were obtained as intercept and slope, their values being given in Table 2. The heat of sorption was found to be in the range of 2.98−12.06 kJ/mol, supporting a mechanism by electrostatic interactions, i.e., the physical sorption. On the basis of R^2 values shown in Table 2, the results indicate that the Temkin model did not fit on experimental data.

The values of Sips isotherm constants (q_m and a_S) determined from the linear plot of ln ($1/q_e$) versus ln C_e (Figure 5d) were collected in Table 2. According to Sips model, the monolayer sorption capacity values, q_m, are close to the experimental sorption capacity values (Table 2 and Figures 3 and 4), while the values of R^2 are lower than those found for the Langmuir model. This result could be attributed to the fact that Sips isotherm is a three parameter isotherm, and therefore, using his linear form for calculation, there were a lot of errors. On the basis of the linear regression models, it could be concluded that the best fitted isotherm on the equilibrium data was the Langmuir model.

3.1.2. Nonlinear Isotherms of Langmuir, Freundlich, Temkin, and Sips. In order to elucidate which isotherm describes our equilibrium data better, the nonlinear forms of Langmuir, Freundlich, Sips, and Temkin isotherms were used. In the case of the nonlinear regression method, an Origin 7.5 program was used to calculate the isotherm parameters by applying eq 2 for Langmuir model, eq 4 for Freundlich model, eq 6 for Temkin model, and eq 8 for Sips model. Figure 6 presents the nonlinear isotherm models of Langmuir, Freundlich, Temkin, and Sips fitted on the equilibrium sorption data of Cu^{2+} (Figure 6a), Cd^{2+} (Figure 6b), Ni^{2+} (Figure 6c), and Zn^{2+} ions (Figure 6d) onto CG.Dh cryogel. The values of the constants corresponding to all isotherms applied are listed in Table 3.

As can be seen in Table 3, the values of the isotherm parameters obtained from nonlinear regression methods were a little different compared to those obtained using the linear regression method. It is because, when the nonlinear regression
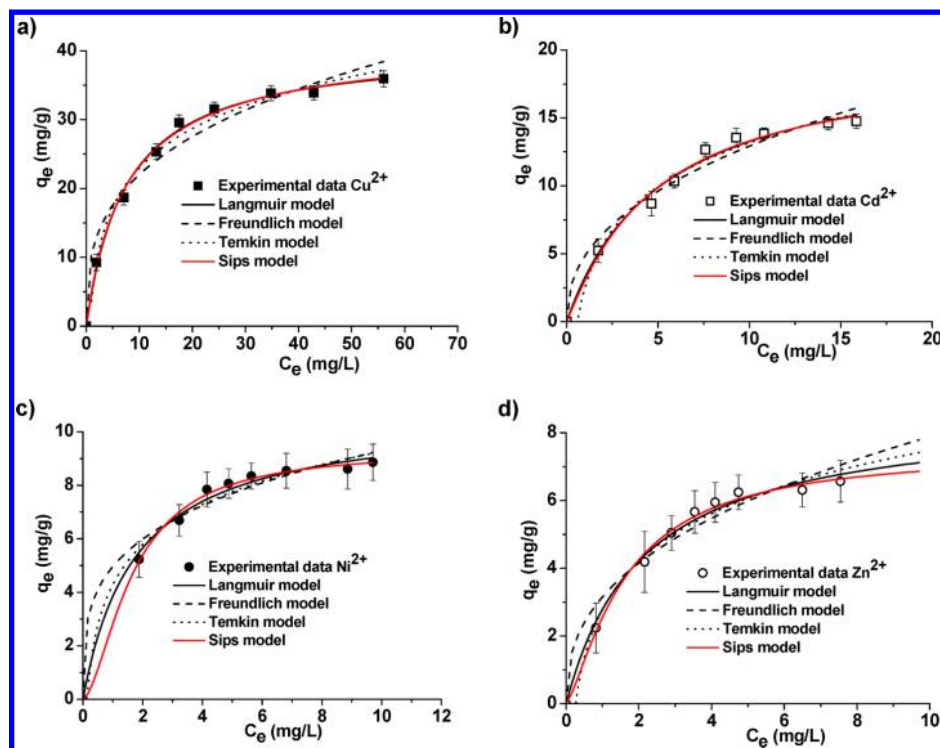
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Figure 6. Nonlinear isotherm models of Langmuir, Freundlich, Temkin, and Sips fitted for the sorption of Cu^{2+} (a), Cd^{2+} (b), Ni^{2+} (c), and Zn^{2+} (d) ions onto CG.Dh cryogel; parameters: contact time of 24 h; metal solution pH of 4.7; temperature of 22 °C.

Table 3. Isotherm Parameters of Langmuir, Freundlich, Temkin, and Sips Models Obtained Using Nonlinear Regression Method for the Sorption of Cu^{2+}, Cd^{2+}, Ni^{2+}, and Zn^{2+} Ions onto CG.Dh Cryogel

Langmuir isotherm parameters					
metal ion	q_m, mg/g	K_L, L/mg	R_L	R^2	χ^2
Cu^{2+}	41.51	0.133	0.882	0.996	0.722
Cd^{2+}	20.22	0.190	0.840	0.990	0.326
Ni^{2+}	10.69	0.562	0.640	0.992	0.065
Zn^{2+}	8.65	0.574	0.635	0.991	0.048

Freundlich isotherm parameters			
metal ion	K_F, mg/g	N	R^2	χ^2
Cu^{2+}	10.45	0.323	0.967	5.760
Cd^{2+}	4.83	0.427	0.975	0.717
Ni^{2+}	4.96	0.273	0.978	0.196
Zn^{2+}	3.15	0.397	0.964	0.198

Temkin isotherm parameters			
metal ion	a_T, L/mg	b_T, kJ/mol	R^2	χ^2
Cu^{2+}	1.63	2.979	0.991	1.538
Cd^{2+}	1.71	5.297	0.987	0.373
Ni^{2+}	2.99	11.371	0.985	0.132
Zn^{2+}	3.94	12.055	0.987	0.073

Sips isotherm parameters				
metal ion	q_m, mg/g	a_S	N	R^2	χ^2
Cu^{2+}	40.72	0.140	0.956	0.996	0.639
Cd^{2+}	19.27	0.186	0.846	0.991	0.286
Ni^{2+}	9.31	0.434	0.602	0.997	0.031
Zn^{2+}	7.48	0.517	0.745	0.995	0.031

fitted isotherm on the equilibrium data was Sips model with a maximum theoretical sorption capacity of 40.72 mg Cu^{2+}/g composite, 19.27 mg Cd^{2+}/g composite, 9.31 mg Ni^{2+}/g composite, and 7.48 mg Zn^{2+}/g composite. Furthermore, the values of exponent N for CG.Dh cryogel, evaluated by Sips model (Table 3), were in the range of 0−1, indicating a favorable sorption of Cu^{2+}, Cd^{2+}, Ni^{2+}, and Zn^{2+} ions onto the composite cryogel under study.

Determining the best-fitting model is a key analysis to mathematically describe the involved sorption system and, therefore, to explore the related theoretical assumptions. Hence, several error calculation functions have been widely used to estimate the error deviations between experimentally and theoretically predicted equilibrium adsorption values, including the average relative error deviation, the Marquardt's percent standard error deviation, the hybrid fractional error function, the nonlinear Chi-square test (χ^2), the correlation coefficient of determination (R^2), Spearman's correlation coefficient, the standard deviation of relative errors, etc.[38] In this study, two statistical functions have been used to investigate their applicability as suitable tools to evaluate isotherm model fitness, namely, the correlation coefficient of determination (R^2) and the nonlinear χ^2 test. The χ^2 test statistic is basically the sum of the squares of the differences between the experimental data and the data obtained by calculating from models, with each squared difference divided by the corresponding data calculated using the models. This can be represented mathematically as:[38]

$$\chi^2 = \sum \frac{(q_{e,exp} - q_{e,cal})^2}{q_{e,cal}} \tag{13}$$

If the data from a model are similar to the experimental data, χ^2 will have a small value, and if they strongly differ, χ^2 will be

method is used, the calculation errors are reduced. By analyzing the values of the isotherm parameters obtained from nonlinear methods displayed in Table 3, it may be affirmed that the best

Table 4. Comparison of Theoretical Sorption Capacities (q_m, mg/g) for Heavy Metal Ions of Different Sorbents

sorbent	sorbent dose, g	pH	q_m, mg/g metal ion Cu^{2+}	Cd^{2+}	Ni^{2+}	Zn^{2+}	ref
starch-graft-acrylic acid	0.5	6			8.85	7.8	12
CM-cellulose/chitosan HG	0.2	4	44.5	27.42		17.67	19
IPNs hydrogels based on poly(polyethylene glycol diacrylate) and poly(methacrylic acid)	0.5	4	47.62	35.2			21
PAAm and 4-vinylpyridine HG	0.1	4	20.13		19.35	11.7	47
adsorption of copper, lead, and nickel using chitosan immobilized on bentonite	0.2	4	23.11		17.51		48
adsorption of Cu(II), Zn(II), and Pb(II) ions on the cross-linked chitosan with epichlorohydrin	0.01	6	35.46			10.21	49
CG.Dh cryogel	0.01	4.7	40.71	19.26	9.31	7.48	this study

bigger. The results of the application of correlation coefficients (R^2) and nonlinear Chi-square test (χ^2) on the experimental data of the equilibrium capacity for all adsorption isotherms are shown in Table 3. The Sips isotherm model appears to be the best fitting model for the sorption of Cu^{2+}, Cd^{2+}, Ni^{2+}, and Zn^{2+} ions onto CG.Dh cryogel, with the highest correlation coefficient (R^2 values were found to be in the range of 0.991−0.997) and the lowest Chi-square values (χ^2 values were found to be in the range of 0.031−0.639). Table 3 also indicates that the Freundlich and Temkin isotherm models have the lowest correlation coefficients and much higher Chi-square (χ^2) values for CG.Dh cryogel used in this study.

A wide variety of sorbents used to remove metal ions from aqueous solutions have been reported in the literature. Table 4 presents a brief list of the published maximum sorption capacity of various sorbents, including also the results obtained in this work.

As Table 4 shows, the sorption capacity of the cryogel CG.Dh for Cu^{2+} ions is comparable with that reported for CM-cellulose/chitosan hydrogels,[19] the cross-linked chitosan,[49] being ca. 50% higher than that reported for hydrogels based on PAAm and 4-vinylpyridine,[47] and chitosan immobilized on bentonite.[48] The sorption capacity of the cryogel CG.Dh for Zn^{2+} ions is comparable with that reported for other sorbents. Comparing the data presented in Table 4, we may conclude that the CG.Dh cryogel is a promising sorbent for the removal of heavy metal ions.

3.2. Desorption Studies. Desorption is a very important process, both the regeneration of the sorbent and the recovery of metal ions being strongly required in the sorption experiments. Desorption studies were carried out in a batch system using the metal ions-loaded cryogel immediately after the sorption experiment. Table 5 presents the data obtained from the desorption experiments.

As can be seen in Table 5, a complete desorption of Cu^{2+}, Cd^{2+}, and Zn^{2+} ions from PAAm/PA cryogels, using 0.1 M HCl, was achieved in 20 min. The desorption level of Ni^{2+} ions from CG.R and CG.D cryogels, using 0.1 M HCl, was around 93% after 20 min; only for CG.Dh cryogel, a complete desorption was achieved after 20 min. Thus, the results of desorption tests show that the sorption process is reversible and also show the possibility of reusing the composite sorbent taking into account the high recovery level of all cations from PAAm/PA cryogels.

4. CONCLUSIONS

The main objective of this work was the investigation of the noncompetitive removal of Cu^{2+}, Cd^{2+}, Ni^{2+}, and Zn^{2+} from

Table 5. Desorption of Cu^{2+}, Cd^{2+}, Ni^{2+}, and Zn^{2+} Ions from PAAm/PA Cryogels Using 0.1 M HCl

cations	sorbent	desorption (%) 5 min	10 min	15 min	20 min
Cu^{2+}	CG.R	56.67	76.86	95.67	100
	CG.D	58.79	80.35	97.75	100
	CG.Dh	60.74	82.34	97.69	100
Cd^{2+}	CG.R	47.68	63.89	92.24	100
	CG.D	50.11	67.45	96.76	100
	CG.Dh	51.23	73.45	97.87	100
Ni^{2+}	CG.R	59.22	66.51	73.98	92.7
	CG.D	71.8	73.16	87.3	93.2
	CG.Dh	58.37	69.54	91.87	100
Zn^{2+}	CG.R	46.87	55.42	97.71	100
	CG.D	48.76	66.05	96.9	100
	CG.Dh	49.54	90.45	100	

aqueous solutions by batch-mode, onto semi-IPN PAAm/PA cryogels. The experimental values of the maximum sorption capacity (q_{exp}) obtained for CG.Dh cryogel were in the order: $Cu^{2+} > Cd^{2+} > Ni^{2+} > Zn^{2+}$. In order to find which isotherm model better describes the equilibrium data, both linear and nonlinear forms of Langmuir, Freundlich, Temkin, and Sips isotherms were used. On the basis of the maximum theoretical sorption capacity, it may be affirmed that the best fitted isotherm on the equilibrium data was Sips model with a maximum theoretical sorption capacity of 40.72 mg Cu^{2+}/g composite, 19.27 mg Cd^{2+}/g composite, 9.31 mg Ni^{2+}/g composite, and 7.48 mg Zn^{2+}/g composite. Additionally, the desorption experiments were performed with 0.1 M HCl. The results of desorption tests showed that the sorption process was reversible and it is possible to reuse the composite sorbent taking into account the high recovery level of all cations from PAAm/PA cryogels.

■ AUTHOR INFORMATION

Corresponding Author
*Tel.: +40.232.219454. Fax: +40.232.211299. E-mail: sdragan@icmpp.ro.

Author Contributions
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