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Co(II) and Ni(II) Removal from Aqueous Solutions by Polymer and Polymer/Silica Adsorbents with Sulfo and Carboxyl groups

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Abstract

Sulfo and carboxyl group-containing polymers and polymer/silica adsorbents poly(acrylonitrile-*co*-2-acrylamido-2-methylpropane-1-sulfonic acid-*co*-acrylic acid-*co-N,N'*-methylene-bis-acrylamide) [poly(AN-*co*-AMPS-*co*-AA-*co*-MBA)] and poly(AN-*co*-AMPS-*co*-AA-*co*-MBA)/SiO_2 were synthesized by a UV-initiated polymerization or simultaneous UV-initiated polymerization and *in situ* sol-gel process and used as adsorbents for removal of Co(II) and Ni(II) ions from aqueous solutions. The adsorption capacity and the effect of the pH in the removal process have been studied. The poly(AN-*co*-AMPS-*co*-AA-*co*-MBA) adsorbent exhibited high efficiency: up to 91.8 % removal of Co(II) and 89.7 % removal of Ni(II). Polymer/silica adsorbents showed higher removal capacity as compared to pure polymer. The adsorption kinetics of Co(II) and Ni(II) ions were found to be satisfactorily described by the pseudo-second-order reaction equation of the Lagergren kinetic model, suggesting the ion-exchange nature of the process.

Keywords: polymer/silica membrane; adsorbent; wastewater treatment; heavy metal ion; kinetic model

1. Introduction

Membrane technologies successfully compete with other methods of wastewater treatment. Contaminants discharged into water without prior treatment can be inorganic and organic substrates, pesticides, radioactive elements, surfactants, detergents and others. Most of the pollutants, especially in hydrometallurgical wastewater, are heavy metal salts.[1] Among the various water treatment techniques, adsorption and ion exchange are of great importance.[2] For the removal of metal ions by these methods, polymer and composite materials are most widely used nowadays.

Numerous ion adsorption and ion exchange polymers have been presented in the scientific literature in recent years.[3-4] The polymers are insoluble and include various functional groups, such as amino, amide, ammonium, carboxyl, *etc*. A large number of research papers are devoted to the development of ion exchange polymers containing sulfo groups. Cavus C. and coauthors[5] studied the removal of heavy metal ions Cu(II), Cd(II) and Pb(II) from aqueous solutions by poly(2-acrylamido-2-methyl-1-propane-sulfonic acid-*co*-itaconic acid). Yiqi Wang and coauthors reported a successful synthesis of a phosphazene-based amine-functionalized porous polymer, which demonstrated an excellent adsorption ability for Hg(II) ions.[6] A significant amount of research in this area was carried out by Rivas B.L. and coauthors. The adsorption of Cu(II), Cd(II), Co(II), Hg(II), Ni(II), Zn(II), Cr(III) and Ag(I) ions by polymers such as poly(2-acrylamido-2-methyl-1-propane-sulfonic acid), poly(methacrylic acid), poly(2-acrylamido-2-methyl-1-propane-sulfonic acid-*co*-methacrylic acid), and cross-linked copolymer poly(4-styrene sodium sulfonate-*co*-acrylic acid) was investigated.[7–8] Recent studies by this research team include the synthesis of cation-exchange resins based on water-soluble copolymers: pol*y(*acrylamide-*co*-styrene sodium sulfonate), poly(2-acrylamido-2-methyl-1-propanesulfonic acid-*co*-acrylic acid), poly(2-acrylamidoglycolic acid-*co*-2-acrylamido-2-methyl-1-propanesulfonic acid).[9–11] The developed ion-exchange copolymers demonstrated the ability to remove Cr(III) ions from aqueous solutions. Synthetic polymer materials for ion exchange adsorbents consisting of 4-styrene sodium sulfonate, methacrylic acid and methyl methacrylate at different ratios were prepared by polymerization in solution.[12] Adsorbents were prepared by cross-linking at heating and esterification reactions. The ion-exchange capacity of the materials was 0.51–0.99 meq/g. The material for the manufacture of the ion-exchange membrane described in[13] is terpolymer of acrylonitrile (AN), styrene sodium sulfonate and *N*-butyl acrylate. The required properties of the material were achieved by selecting the feed composition of monomers: AN : SGS : BA = 75 : 15: 10 wt. %. The process of free radical polymerization took place for 4 h at the temperature of 358 K with 80 % yield. The resulting membrane has an ion exchange capacity of 1.50 meq/g.

It should be noted that polymer adsorbents used for water purification have several limitations, such as the trade-off between water permeability and selectivity for dissolved compounds, low fouling resistance, and others.[14] To improve the performance of the adsorbents, their modification with inorganic fillers are often used. Urbano B. F. and Rivas B. L.[15] investigated the sorption properties of composites based on 2-acrylamido-2-methyl-1-propanesulfonic acid for Pb(II), Cu(II), Cd(II). It was found that the addition of montmorillonite to the polymer increased the mechanical properties of the ion exchange membrane.

A series of new hybrid copolymers was obtained by free radical polymerization and sol-gel process using 3-methacryloxypropyl trimethoxysilane (MAPTMS) and acrylic acid (AA).[16] The obtained copolymers maintain thermal stability up to 693 K. In addition, a more stable molecular structure and desired properties can be obtained by adjusting silica and AA content, respectively. The copolymer showed high adsorption capacity in aqueous solutions containing Cu(II) and Pb(II) ions.

Co(II) and Ni(II) are one of the most common heavy metals in wastewater.[17] Co(II) high concentration in water solution can cause a number of unwanted effects, including low blood pressure, heart failure, thyroid and liver damage in humans. The Contact Dermatitis Society of America named Ni(II) the Allergen of 2008 Year, and its role and impact on breast cancer was also noted.[18] Therefore, the purification of wastewater from Co(II) and Ni(II) salts is extremely necessary. In this study we synthesized new polymer adsorbents based on AN, AA and 2-acrylamido-2-methylpropane-1-sulfonic acid (AMPS) cross-linked with *N,N'*-methylene-bis-acrylamide (MBA) by UV-initiated copolymerization and investigated their adsorption capacity on the removal of heavy metal ions (Co(II) and Ni(II)) from aqueous solutions. In order to improve the efficiency of membrane adsorption, the adsorbents were modified with the precursors tetraethoxysilane (TEOS) and MAPTMS using the sol-gel method.

2. Experiment

2. 1. Materials

The reagents for adsorbent preparation: AN (99%), AMPS (99%), AA (99%), MBA (99%), 2,2-dimethoxy-2-phenylacetophenone (DMPA) (99%), TEOS (99%), MAPTMS (99%), phosphoric acid (PhA) (99%) were purchased from Sigma-Aldrich. Milli-Q® water and ethanol (VWR) were used as solvents. The reagents to study the removal process: nickel (II) nitrate hexahydrate ($Ni(NO_3)_2 \times 6H_2O$) and cobalt (II) nitrate hexahydrate ($Co(NO_3)_2 \times 6H_2O$) were purchased from LLC Sfera Sim.

2. 2. Synthesis of adsorbents

The polymer adsorbents were prepared by UV-initiated polymerization of a mixture of acrylic monomers in the presence of photoinitiator DMPA and cross-linking agent MBA. Water soluble reagents (AA, AMPS) were mixed with the appropriate amount of previously dissolved AN and DMPA and stirred for 35 min (500 rpm) at room temperature to obtain a homogeneous mixture.

The resulting mixture was placed in a handmade glass mold (50 × 20 × 0.15 mm) and covered with thin glass to prevent the inhibitory effect of oxygen. The samples were irradiated with UV light (365 nm, radiation power 15 J/cm^2) using a multi-lamp BIO-LINK® cross-linker (BLX-365, Witec AG, Switzerland) equipped with 5 UV lamps (8 W, output 0.8 W).

In the case of organic/inorganic adsorbent preparation, a sol-gel system (SGS) was prepared according to the appropriate procedure.[19] Sol-gel precursors MAPTMS and

Table 1. Feed composition for adsorbents synthesis.

Sample /Content (mass %)	NSA-613	NSA-613-SGS	NSA-612	NSA-612-SGS
AN	60	60	60	60
AMPS	30	30	25	25
AA	10	10	15	15
MBA*	3	3	3	3
DMPA*	2	2	2	2
SGS*	/	20	/	20

* – from mass of monomers

TEOS are insoluble in water, hence, ethanol-water solvent was used for their dissolution. PhA was used as a sol-gel process catalyst. The components were mixed in a following ratio: MAPTMS : TEOS : C_2H_5OH : H_2O : H_3PO_4 = 0.75 : 0.25 : 4 : 2 : 1.8 (mol) and stirred for 30 min (500 rpm) at 323 K. As a result of hydrolysis of the precursors a silica sol was formed. An appropriate amount of the sol shortly before gelation was added to the monomer mixture under stirring. Further steps of the organic/inorganic adsorbent preparation were the same as for the synthesis of pure polymer adsorbents. The feed compositions for the synthesis of polymer and nanocomposite adsorbents are given in Table 1.

The resulting films were separated from the mold, washed thoroughly to remove the unreacted compounds, and finally dried at 323 K until constant weight.

2. 3. Characterization

IR spectroscopy

The FTIR/ATR spectra were examined in 4000-600 cm^{-1} using FTIR Microscope Hyperion 2000 (Bruker, Germany) equipped with MCT detector and ATR objective connected to spectrometer Vertex 70 (Bruker, Germany). The base lines were corrected and the spectra were normalized with respect to the band of stretching vibration of nitrile group (2243 cm^{-1}).

Morphology

Morphology of polymer and polymer/silica adsorbents were determined by scanning electron microscopy using NEON 40 FIB-SEM (Carl Zeiss Microscopy GmbH, Germany). To visualize the cross section, the samples were fractionated and then immersed in liquid nitrogen. Prior to imaging, all test samples were coated with a layer of carbon ~20 nm thick to avoid accumulation of charge in the electron beam.

Degree of swelling

The degree of swelling of the prepared materials was determined gravimetrically by measuring the difference in dimensions of the samples before and after immersion in Milli-Q® water. Before measurement, the samples were dried at 323 K in a vacuum to obtain a constant mass. The dried and weighed adsorbents were placed and kept in deionized water at different temperatures for 24 h.

Degree of swelling (*DS*) was calculated using the following equation:

$$DS = \frac{d_w - d_d}{d_d} \times 100\%, \quad (1)$$

wher.e d_w and d_d – the dimension (length, width or thickness) of wet and dry samples, respectively.

Adsorption capacity

A batch equilibrium procedure was applied to determine the adsorption capacity of the synthesized materials. Co(II) and Ni(II) solutions were prepared with the initial concentration of 50 mg/L. 150 mg of the synthesized membrane was introduced to 50 mL of metal ion solution. All experiments were performed under ambient conditions without forced stirring. The pH values of the solutions (5, 6) were adjusted with 0.1N NaOH. Metal ions were determined by measuring the optical density of the solution at a wavelength of 516 nm for Co and 395 nm for Ni using a spectrophotometer Spekol 11 (Carl Zeiss Jena, Germany).

The amount of metal ions absorbed by the adsorbent (mol/g) was calculated by the formula:

$$q = \frac{C_0 - C_{eq}}{m} \times V, \quad (2)$$

where C_o is the initial metal ion concentration in mol/L; C_{eq} is the equilibrium metal ion concentration in mol/L; *V* is the volume of the solution in L; *m* is the dry adsorbent mass in g.

The adsorption efficiency, $A_{\text{eff},}$ was calculated as:

$$A_{eff} = \frac{C_0 - C_{eq}}{C_0} \times 100\ \%, \quad (3)$$

3. Results and Discussion

Two series of cross-linked polymer adsorbents were synthesized by photoinitiated radical copolymerization of acrylic monomers – AA, AN, AMPS and *N,N*'-ethylene-bis-acrylamide in the appropriate ratio in the presence of photoinitiator (see Table 1). AMPS and AA include functional sulfo and carboxyl groups which are necessary for metal ion sorption. The AN was chosen to provide mechanical, thermal and film-forming properties. MBA served as a cross-linker providing the cross-linked structure of the material. Fig. 1, 2 illustrate the structure of the synthesized polymer adsorbents.

To compare the adsorption capacity of polymer and polymer/inorganic adsorbents a series of hybrid organic/inorganic adsorbents were synthesized. The preparation of hybrid materials involves two simultaneous processes: radical UV-initiated copolymerization of the monomers and a sol-gel process of silica precursors. We used a mixture of TEOS and MAPTMS as silica precursors. As a result of the sol-gel process silica network is formed in the polymer matrix. The hydrolysis of precursors forms silanol groups, the condensation between silanol groups or between silanol and alkoxy groups creates siloxane bridges (Si-O-Si) that form the entire silica structure (Fig. 3.).[20]

It should be noted that MAPTMS acts as a coupling agent between organic and inorganic phases, hence, the incorporation of the sol-gel precursor into the organic phase leads to the formation of a cross-linked structure.[21–22] As a result, the interpenetrating networks of organic and inorganic phases are covalently linked with each other.

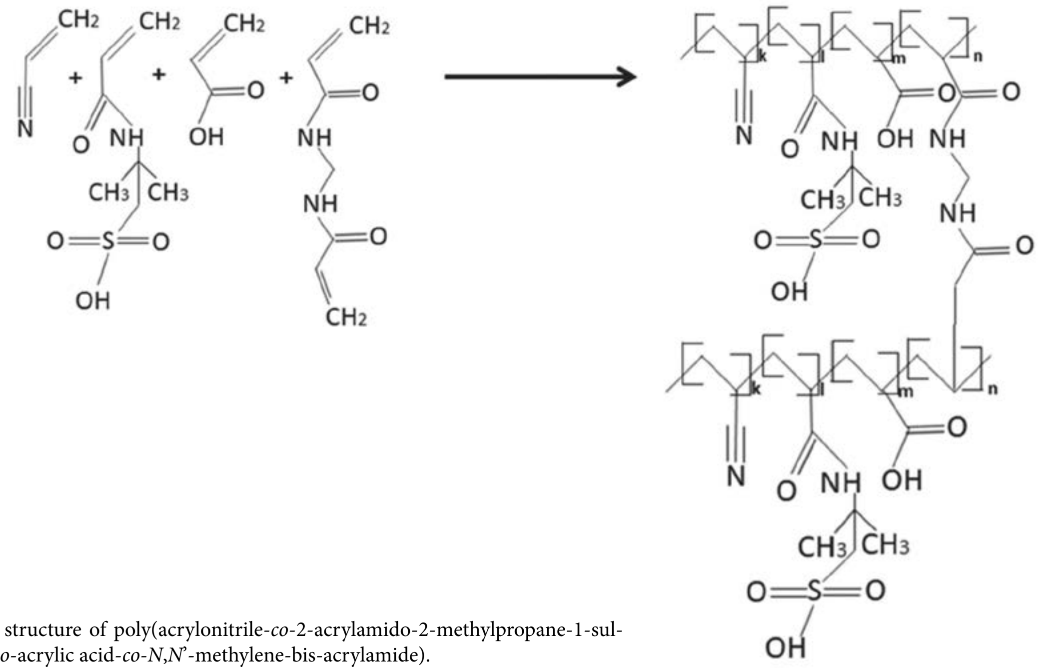


Fig. 1. The structure of poly(acrylonitrile-*co*-2-acrylamido-2-methylpropane-1-sulfonic acid-*co*-acrylic acid-*co*-*N*,*N*'-methylene-bis-acrylamide).

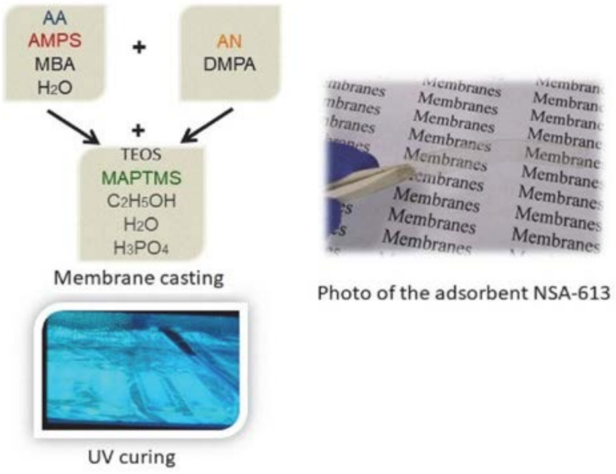


Fig. 2. Scheme of the preparation process polymer/silica materials

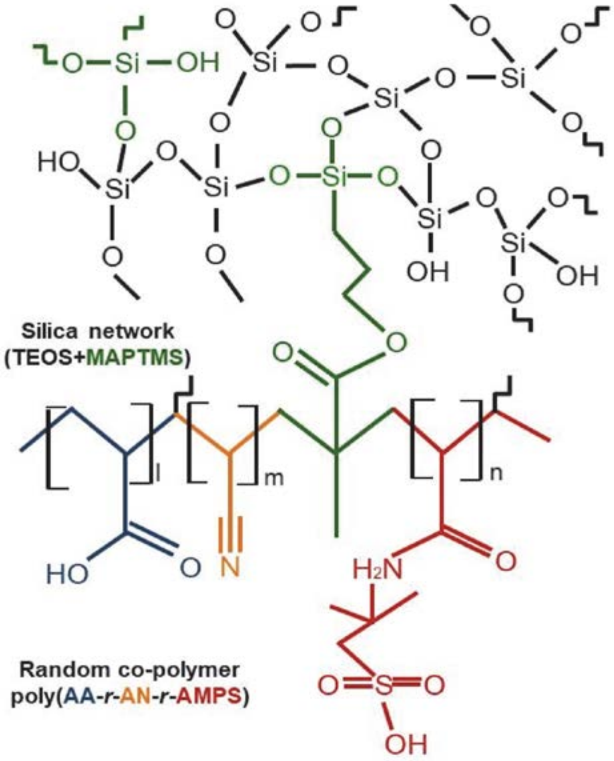


Fig. 3. Chemical structure of polymer/silica adsorbent poly(AN-*co*-AMPS-*co*-AA)

The polymerization yields were estimated by determining the gel fractions of the synthesized materials (Table 2). The gel fractions of the adsorbents were found as the difference in the sample weight before and after keeping them in Soxhlet apparatus for 24 hours. The content of the gel fraction was high in all cases, which indicates the successful completion of the UV polymerization process.

The obtained polymer and organic/inorganic adsorbents were characterized by FTIR spectroscopy to identify the typical absorption signals of the exchange groups. Table 3 summarizes the most important signals in the corresponding spectra of the characteristic functional groups.

The obtained polymer and polymer/silica adsorbents are thin (150–200 μm), transparent, tack-free films evidencing successful synthesis of the materials with homogeneous structure.

Fig. 4 shows SEM photographs of the cross-sectional views of the adsorbents. The adsorbents exhibited a uni-

Table 2. The gel fractions of the adsorbents

Sample	NSA-613	NSA-613-SGS	NSA-612	NSA-612-SGS
GF, mass %	97.1 ± 0.1	96.4 ± 0.1	97.8 ± 0.2	97.5 ± 0.2

Table 3. FTIR absorption signals

Signal, cm^{-1}					
–SO_3H	–OH	C=O	NH–C=O	C≡N	Si–O–Si
1214	3100–3500	1724	1646	2242	1000

form and compact morphology without any visible phase separation and inclusions revealing the structural homogeneity.

Moreover, the degree of swelling (*DS*) is one of the important characteristics for the use of the adsorbents as adsorbents. *DS* value must be sufficient to ensure metal ion diffusion inside the adsorbent, at the same time a significant change in the adsorbent size leads to mechanical fragility.

The synthesized adsorbents contain hydrophilic carboxyl and sulfonic acid groups and therefore they have a high affinity for water. Table 4 presents the results of measured changes in the dimensions of the obtained adsorbents (length (*l*), width (*w*), thickness (*t*)) after swelling in Milli-Q® water for 24 hours at two temperatures.

According to the obtained results, the synthesized polymers and polymer/silica nanocomposites are hydrogel-type materials.[23]

The capacity of the adsorbents depends on pH value of the solutions. With an increase in pH, the protonation of electrically charged functional groups decreases, which leads to the fact that the active centers become increasingly ionized and the competition between hydrogen ions and metal ions decreases, so metal ions are adsorbed to higher values. The highest adsorption capacity of sulfo-containing polyacrylate adsorbents for Cu(II), Ni(II), Co(II), and Zn(II) was observed at pH values of 4-7.[24] Habis Al-Zoubi et al.[18] reported that the ability to remove Ni(II) ions by nanocomposite adsorbents increases with an increase in pH from 3 to 7, low values of Ni(II) adsorption capacity at lower pH values they attributed to the partial protonation of sulfo groups, which prevents the interaction between the adsorbent and metal ions. MAPTMS-based membrane was used as an adsorbent for Ni(II),[25] in the range of pH > 7 a precipitate was observed in the solution. Based on the literature data, the appropriate pH values of the solutions were selected.

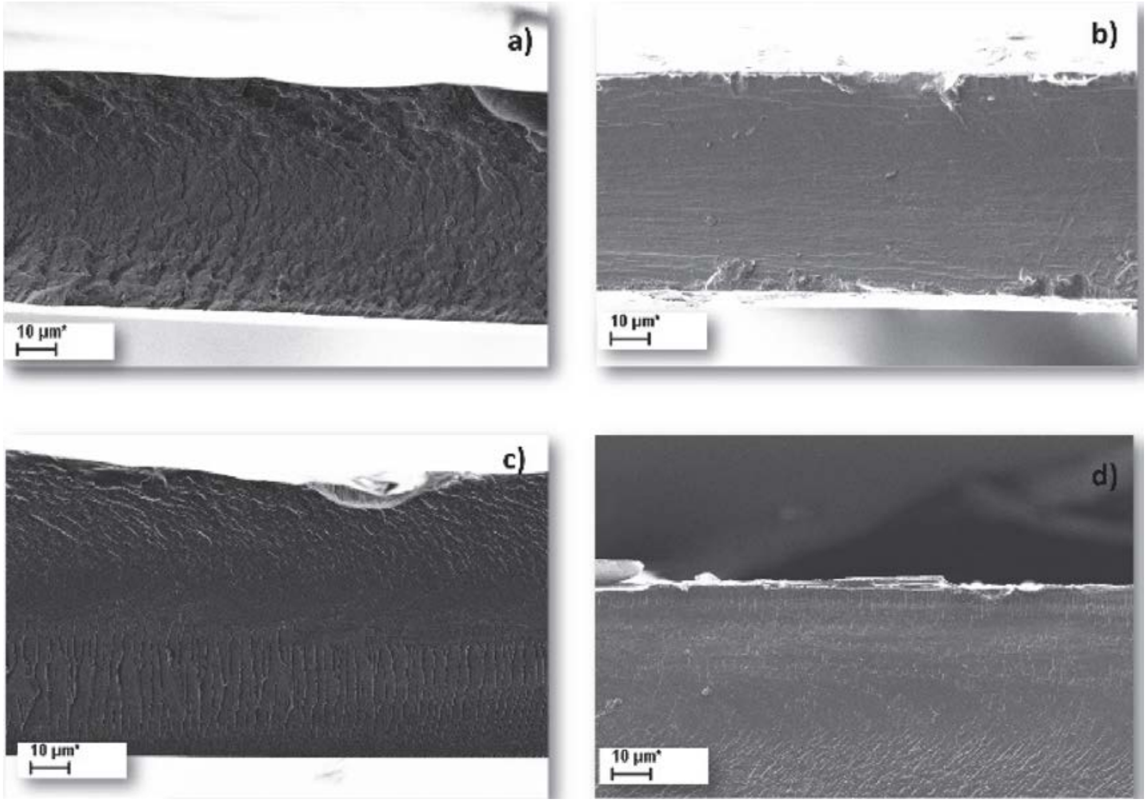
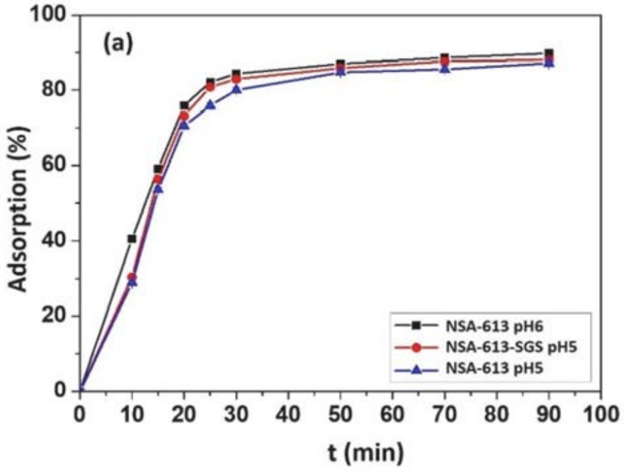


Fig. 4. SEM images of polymer and polymer/silica adsorbents: a) HSA-612; b) HSA-613; c) HSA-612-SGS; d) HSA-613-SGS

Table 4. Adsorbent size changes at swelling

T, °C	*l*, cm	Δl, %	*w*, cm	Δw, %	*t*, µm	Δt, %
			NSA-612			
25	2.8–3.4	21.4 ± 1.9	1.8–2.2	22.4 ± 2.4	130–160	23.0 ± 2.2
50	2.7–3.4	25.7 ± 2.5	1.9–2.4	26.3 ± 2.1	120–150	24.8 ± 3.0
			NSA-612-SGS			
25	2.7–3.3	22.4 ± 2.2	1.6–2.0	25.1 ± 1.8	130–160	25.0 ± 1.6
50	2.6–3.4	26.9 ± 2.0	1.8–2.3	27.7 ± 2.3	150–180	26.7 ± 2.3
			NSA-613			
25	2.7–3.4	25.9 ± 2.0	1.7–2.2	29.4 ± 2.5	130–170	30.7 ± 2.1
50	2.8–3.6	28.6 ± 2.4	1.6–2.1	31.8 ± 2.9	120–160	33.3 ± 2.9
			NSA-613-SGS			
25	2.7–3.4	26.3 ± 2.1	1.7–2.2	30.4 ± 2.3	130–150	31.7 ± 2.3
50	2.7–3.5	29.8 ± 2.1	1.8–2.1	32.7 ± 2.2	150–170	34.3 ± 2.7

The results of the experimental study of the removal capacity of the adsorbents NSA-613, NSA-613-SGS, NSA-612 and NSA-612-SGS for Co(II) and Ni(II) ions are presented in Fig. 5.



As can be seen from the data in Fig. 5, in all cases adsorption proceeds to an equilibrium state. It was found that the studied polymer and polymer/silica adsorbents have a sufficiently high adsorption rate. The maximum values of adsorption are reached during the first 25-30 min contact of the membrane with metal ion solution. The interaction of ion-exchange groups with the metal ion occurs quickly enough, since the degree of swelling of the adsorbents is optimal for the diffusion of the metal ion into the pores of the material and the ion-exchange groups have a high affinity for the metal ions.

The removal of Co(II) and Ni(II) ions increases with increasing pH (6 > 5), as expected. This is due to the fact that the high concentration of H_3O^+ at low pH reduced the number of active ion binding sites, preventing the access of metal ions to the functional groups, and this reduced the adsorption capacity of the synthesized materials.

NSA-613 membrane has a higher adsorption capacity for Co(II) ions as compared to NSA-612 membrane. Obviously, sulfo groups retain Co(II) ion more strongly than carboxyl groups, therefore, a larger number of sulfo

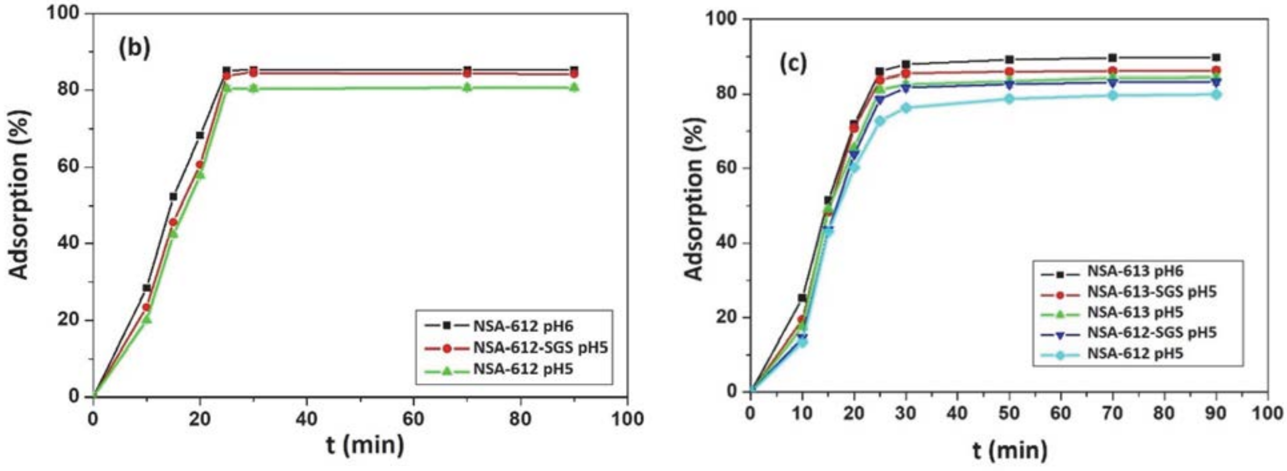


Fig. 5. Co(II) (a, b) and Ni(II) (c) adsorption *vs* time, pH and adsorbent composition

groups in the copolymer leads to an increase in the adsorption value. These results correlated with the data obtained by.[11] The results of the adsorption study are presented in Table 5.

Table 5. Parameters of Co(II) and Ni(II) adsorption

Sample	pH	Co(II) $C_o\times10^{-3}$, g/L	A_{eff}, %	Ni(II) $C_o\times10^{-3}$, g/L	A_{eff}, %
NSA-613	6	2.5	91.80	2.5	89.68
NSA-613-SGS	5	2.5	90.20	2.5	86.18
NSA-613	5	2.5	87.20	2.5	8436
NSA-612	6	2.5	85.40	2.5	83.26
NSA-612-SGS	5	2.5	84.40	2.5	79.87
NSA-612	5	2.5	80.80		

An SEM study of the adsorbents was carried out after their saturation with Co(II) and Ni(II) ions. The results are presented in Fig. 6.

Analysis of the SEM images of the surface and cross-section of the NSA-612 membrane at pH 5 revealed that during the experiment Co(II) ions seeped and "entered" along the entire cross-section of the membrane (a top, middle and bottom) and are available on the surface of the sample. The distribution of the adsorbed elements was also determined (Table 6).

The adsorbed Co(II) and Ni(II) ions are almost uniformly distributed both across the cross-section of the membrane sample and on its surface. It should be noted that according to both to the adsorption isotherms and the results of the SEM analysis, the polymer/silica adsorbents show higher adsorption capacity compared to the polymer ones. For example, the adsorption capacity of the NSA-613 membrane is 85%, while the same characteristic of the NSA-613-SGS adsorbent is 90%. This can be caused by another morphology of the hybrid organic/inorganic adsorbents: they have a branched system of nanopores formed as a result of a sol-gel process of the precursors, which occurs *in situ* in the polymer matrix during UV-initiated polymerization.

Kinetics of the adsorption process

To determine the mechanism of Co(II) and Ni(II) ions adsorption by polymer and polymer/silica adsor-

Table 6. Distribution of adsorbed Co(II) and Ni (II) in the adsorbents

Element, mass. %	Adsorbent	Cross-section part Top	middle	Bottom	Sample surface
Co	NSA-612	1.81 ± 0.12	1.97 ± 0.14	1.99 ± 0.13	1.91 ± 0.12
Ni	NSA-612	2.02 ± 0.17	1.96 ± 0.19	1.94 ± 0.21	2.00 ± 0.24
Ni	NSA-613-SGS	2.30 ± 0.14	2.25 ± 0.19	2.21 ± 0.18	2.14 ± 0.16

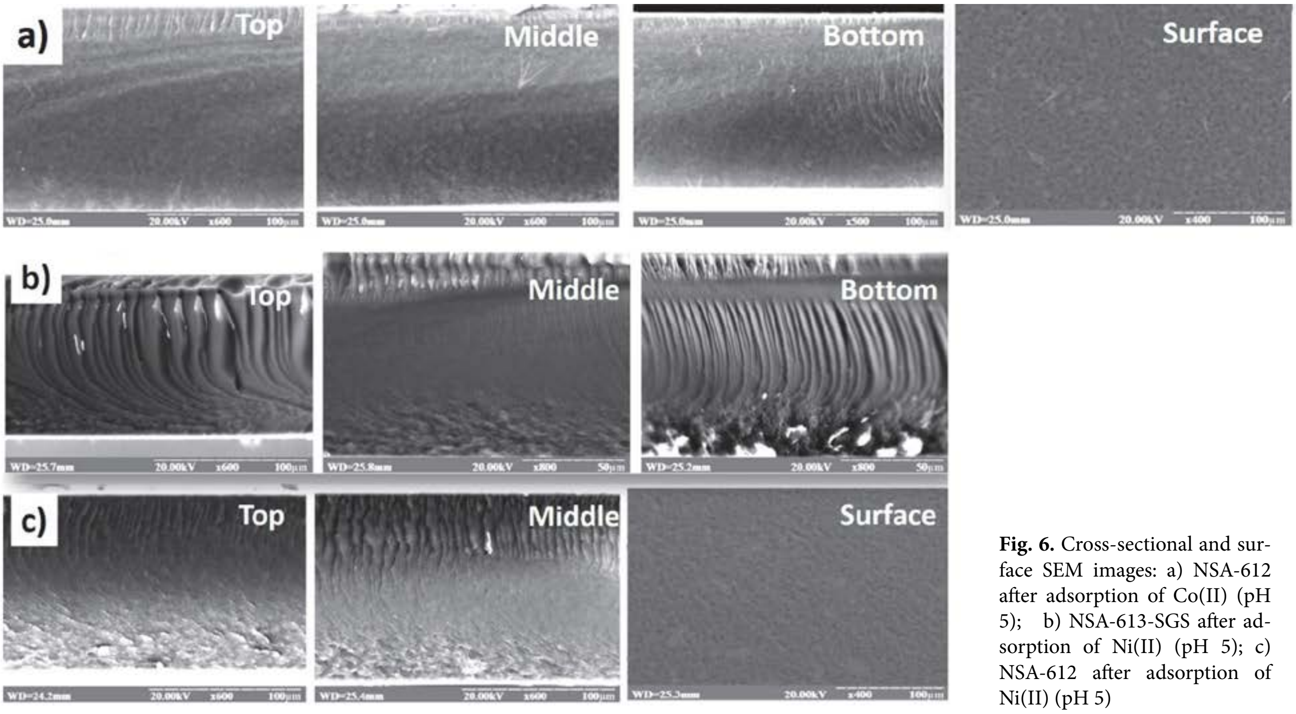


Fig. 6. Cross-sectional and surface SEM images: a) NSA-612 after adsorption of Co(II) (pH 5); b) NSA-613-SGS after adsorption of Ni(II) (pH 5); c) NSA-612 after adsorption of Ni(II) (pH 5)

bents, the kinetics of the process was studied using Lagergren models, similar to the determination of the rate of pseudo-first and pseudo-second order reactions, which are used in modeling sorption processes in the systems solid/liquid.[26]

A pseudo-first-order kinetic model is proposed to describe processes in which the rate of occupation of active centers (binding centers) is proportional to the number of unoccupied sorbent centers, and is represented by the equation:

$$log(qe - qt) = logqe - \frac{k1}{2.303}t \tag{4}$$

where q_t and q_e are the amount of metal ions adsorbed at this moment in time and in a state of equilibrium (mg/g); k_1 is the rate constant of the first-order adsorption process (min^{-1}). It can be determined from the tangent of the slope angle of the direct dependence $log(q_e - q_t) - t$.

The kinetics of the process of adsorption of Co(II) and Ni(II) ions from aqueous solutions with different pH by the investigated adsorbents in the coordinates of the pseudo-first-order equation is shown in Fig. 7. The rate constants of the adsorption process were calculated from the tangent of the angle of the straight lines inclination.

However, the pseudo-first-order equation does not adequately describe the process, as we obtained low determination coefficients ($R^2 \approx 0.9577$). Therefore, the kinetics of adsorption of metal ions was estimated using the pseudo-second-order model, which is described by the equation:

$$\frac{t}{qt} = \frac{1}{k2qe^2} + \left(\frac{1}{qe}\right)t \tag{5}$$

where k_2 is the rate constant of the second-order adsorption process (g/mg min). The initial rate of adsorption h (at $t = 0$) is found from the dependence:

$$h = k_2 \cdot {q_e}^2 \tag{6}$$

Fig. 8 presents the kinetics of the adsorption process of Co(II) and Ni(II) ions in the coordinates of the pseudo-second order equation. The kinetic parameters of the equation were found from the values of the segment cut off on the ordinate axis of the direct dependence $t/q_t - t$.

Table 7 shows the kinetic parameters of the process of metal ion adsorption from aqueous solutions at different pH by the synthesized adsorbents.

Table 7. Kinetic parameters of the adsorption of Co(II) and Ni(II) ions

Parameter		k_1	R^2	k_2	R^2	h	pH
NSA-613	Co(II)	0.0160	0.9715	0.5116	0.9974	5.4525	6
NSA-613-SGS		0.0161	0.9466	0.3236	0.9981	2.5145	5
NSA-613		0.0165	0.9578	0.7617	0.9930	6.9440	5
NSA-612		0.0161	0.9281	0.4422	0.9975	4.3859	6
NSA-612-SGS		0.0161	0.9417	0.6107	0.9964	5.8892	5
NSA-612		0.0162	0.9311	0.8131	0.9969	6.9442	5
NSA-613	Ni(II)	0.0172	0.9577	1.0031	0.9986	10.6750	6
NSA-613-SGS		0.0165	0.8796	0.8272	0.9982	9.6834	5
NSA-613		0.0162	0.9306	0.5706	0.9983	5.4377	5
NSA-612-SGS		0.0161	0.9244	0.8576	0.9982	7.8678	5

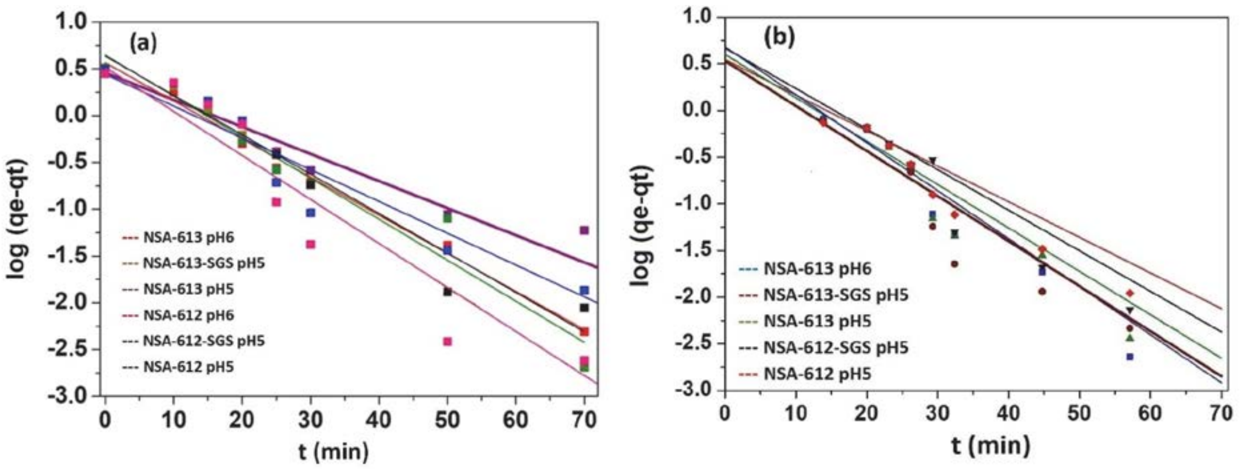


Fig. 7. The adsorption kinetics of a) Co(II) and b) Ni(II) ions in the coordinates of the pseudo-first-order equation

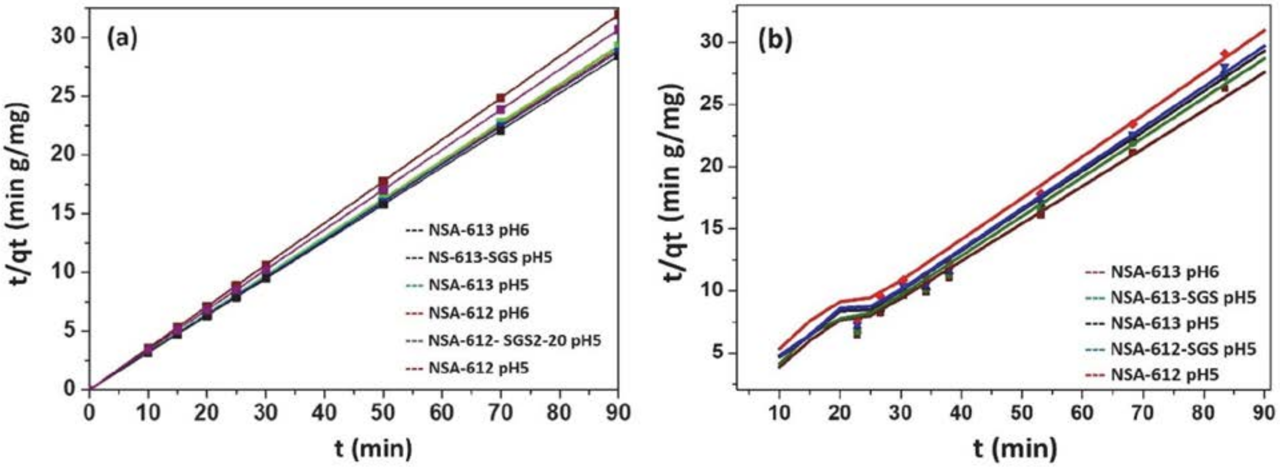


Fig. 8. The adsorption kinetics of a) Co(II) and b) Ni(II) ions in the coordinates of the pseudo-second-order equation

The process of adsorption of metal ions by polymer and polymer/silica adsorbents is better described by the second-order kinetic model, since the values of determination coefficients for the pseudo-second-order model are significantly higher than for the pseudo-first-order model. This can be explained by the fact that the kinetics of metal ion adsorption by adsorbents is influenced not only by the concentration of ions, but also by the concentration of sulfo groups and carboxyl groups in the copolymer. This confirms the mechanism of the electrostatic interaction of metal ions with polymers.

4. Conclusions

The adsorption capacity of the poly(AN-*co*-AMPS-*co*-AA-*co*-MBA) and poly(AN-*co*-AMPS-*co*-AA-*co*-MBA)/SiO_2 adsorbents synthesized in this study for the removal of heavy metal ions from solutions reached 87% for Co(II) ions and 90 % for Ni(II) ions. Due to the formation of a nanoporous structure in the polymer/silica adsorbents, they demonstrate a higher adsorption capacity compared to the polymer adsorbents. A fast rate to the equilibrium state in the adsorption process was revealed for all types of the adsorbents. The effect of pH of metal salt solutions on the adsorption efficiency for Co(II) and Ni(II) ions by the studied adsorbents was found - when pH increases from 5 to 6, the adsorption capacity of the proposed adsorbents increases. The results of the SEM analysis of adsorbents reveal the uniform distribution of Co(II) and Ni(II) on the surface and throughout the adsorbents. The kinetics of adsorption of Co(II) and Ni(II) ions from aqueous solutions by synthesized adsorbents at different the pH was studied. The obtained results were analyzed within the framework of the pseudo-first and pseudo-second order Lagergren kinetic model.

5. References

1. F. Bucatariu, C. Teodosiu, I. Morosanu, D. Fighir, R. Ciobanu, L.-M. Petrila, M. Mihai, *Polymers*, **2021**, *13*, 3963. **DOI:**10.3390/polym13223963.
2. T. A. Saleh, *Environ. Technol. & Innov.,* **2021**, *24*, 101821. **DOI:**10.1016/j.eti.2021.101821
3. Z.-Q. Huang, Z.-Fa Cheng, *J. Appl. Polym. Sci.*, **2019**, *137*, 48579. **DOI:**10.1002/app.48579
4. M. Z. A. Zaimee, M. S. Sarjadi, M. L. Rahman, *Water*, **2021**, *13*, 2659. **DOI:**10.3390/w13192659
5. S. Cavus, G. Gurdag, *Polym. Adv. Technol.*, **2008**, *19*, 1209–1217. **DOI:**10.1002/pat.1113.
6. Y. Wang, N. Yang, M. Soldatov, H. Liu, *React. Funct. Polym.,* **2022,** 173, 105235. **DOI:**10.1016/j.reactfunctpolym.2022.105235
7. B. L. Rivas, C. Muñoz, *J. Appl. Polym. Sci.* **2009**, *114*, 1587–1592. DOI:10.1002/app.30722
8. B. L. Rivas, C. Muñoz, L. Leiton, S. A. Pooley, *J. Appl. Polym. Sci.*, **2011**, *120*, 586–591. **DOI:**10.1002/app.33194
9. B. L. Rivas, I. M. Peric, C. Muñoz, R. Alvear, *Polym. Bull.*, **2012**, *68*, 391–403. **DOI:**10.1007/s00289-011-0551-7
10. B. L. Rivas, C. Muñoz, *J. Appl. Polym. Sci.*, **2007**, *104*, 1769–1774. DOI:10.1002/app.25825
11. B. L. Rivas, D. V. Morales, N. Kabay, M. Bryjak, *J. Chil. Chem. Soc.*, **2018**, *63*, 4012–4018. **DOI:**10.4067/s0717-97072018000204012. **DOI:**10.4067/s0717-97072018000204012
12. N.-S. Kwak, J. S. Koo, T. S. Hwang, E. M. Choi, *Desalination*, **2012**, *285*, 138–146. **DOI:**10.1016/j.desal.2011.09.046
13. V. Bhadja, U. Chatterjee, S. K. Jewrajka, *RSC Adv.*, **2015**, *5*, 40026–40035. **DOI:**10.1039/C5RA07191G
14. J. Yin, B. Deng, *J. Membr. Sci.*, **2015**, *479*, 256–275. **DOI:**10.1016/j.memsci.2014.11.019
15. B. F. Urbano, B. L. Rivas, *Polym. Bull.*, **2013**, *70*, 1143–1162. **DOI:**10.1007/s00289-012-0894-8
16. J. Liu, X. Wang, T. Xu, G. Shao, *Sep. Purif. Technol.,* **2009**, *66*, 135–142. **DOI:**10.1016/j.seppur.2008.11.005

17. J. Kabuba, M. Banza, *Results Eng.*, **2020**, *8*, 100189. **DOI:**10.1016/j.rineng.2020.100189
18. H. Al-Zoubi, K. A. Ibrahim, K. A. Abu-Sbeih, *J. Water Process Eng.*, **2015**, *8*, 19–27. **DOI:**10.1016/j.jwpe.2015.08.002
19. M. M. Zhyhailo, I. Yu. Yevchuk, O. I. Demchyna, V. V. Kochubei, O. I. Makota, *Phys. Chem. Solid St.,* 2021, 22, 775–780. **DOI:**10.15330/pcss.22.4.775-780
20. I. Ab Rahman, V. Padavettan, *J. Nanomater*., **2012**, article ID 132424,. **DOI:**10.1155/2012/132424
21. P. Kapoor, S. T. Mhaske, K. Joshi, *Prog. Org. Coat.*, **2016**, 94, 124–130. **DOI:**10.1016/j.porgcoat.2015.11.021
22. M. Hwang, J. S. Jeong, J. C. Lee, S. Yu, H. S. Jung, B.-S. Cho, K.-Y. Kim, *Korean J. Chem. Eng.*, **2021**, 38, 454–460. **DOI:**10.1007/s11814-020-0695-y
23. D. Morales, B. L. Rivas, *J. Chil. Chem. Soc.*, **2014**, *59*, 2420–2426. **DOI:**10.4067/S0717-97072014000200005
24. B. L. Rivas, E. Pereira, R. Cid, K. E. Geckeler, *J. Appl. Polym. Sci.,* **2005**, *95*, 1091–1099. **DOI:**10.1002/app.21424
25. B. L. Rivas, E. Pereira, A. Maureira, *Polym. Int.*, **2009**, *58*, 1093–1114. **DOI:**10.1002/pi.2632
26. A. Mittal, M. Teotia, R. K. Soni, J. Mittal, *J. Mol. Liq.*, **2016**, *223*, 376–387. **DOI:**10.1016/j.molliq.2016.08.065

Povzetek

Z namenom uporabe kot adsorbenta za odstranjevanje Co(II) in Ni(II) ionov iz vodnih raztopin sta bila sintetizirana dva polimerna adsorbenta s sulfonskimi in karboksilnimi skupinami, poli(akrilonitril-*ko*-2-akrilamido-2-metilpropan-1-sulfonska kislina-*ko*-akrilna kislina-*ko*-*N*,*N*'-metilen-bis-akrilamid) [poli(AN-*ko*-AMPS-*ko*-AA-*ko*-MBA)], pri čemer je drugi adsorbent polimer, kombiniran s silicijevim dioksidom, [poli(AN-*ko*-AMPS-*ko*-AA-*ko*-MBA)]/SiO_2. Sintetizirana sta bila z UV-iniciirano polimerizacijo ali kombinacijo hkratne UV-iniciirane polimerizacije in *in situ* sol-gel postopka. Proučevani sta bili adsorpcijska sposobnost in vpliv pH v procesu odstranjevanja Co(II) in Ni(II) ionov. Poli(AN-*ko*-AMPS-*ko*-AA-*ko*-MBA) adsorbent je pokazal visoko učinkovitost odstranjevanja ionov, do 91,8 % Co(II) in 89,7 % Ni(II) ionov. Poli(AN-*ko*-AMPS-*ko*-AA-*ko*-MBA)/SiO_2 adsorbenti so pokazali večjo učinkovitost odstranjevanja ionov v primerjavi s polimernim adsorbentom. Ugotovljeno je bilo, da je adsorpcijska kinetika ionov Co(II) in Ni(II) zadovoljivo opisana z reakcijsko enačbo psevdodrugega reda Lagergrenovega kinetičnega modela, kar kaže na ionsko-izmenjevalno naravo procesa.