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Novel functional polymers for recovery of silver

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Abstract: In this study, the functional polymers containing heterocyclic ligands were synthesized by microwave modification of a crosslinked poly(vinylbenzyl chloride–divinylbenzene) matrix with 4-tert-butylpyridine, pyrrolidine, and 3-morpholinopropylamine. The sorbents were used to recover Ag(I) from the synthetic and real chloride solutions (4.00 mol/dm^3 of NaCl, 0.100 mol/dm^3 of HCl). The best Ag(I) sorption was achieved from synthetic and real chloride solutions in the case of pyrrolidine resin (16.2 and 16.7 mg/g, respectively). The sorption kinetic data were well fitted to the pseudo-first-order kinetic model. The degree of silver desorption was approximately 90% using a 1.0% potassium cyanide solution in a 0.50% hydrogen peroxide solution. All resins showed good selectivity for Ag(I) compared to Cu(II), Pb(II), Co(II), Ni(II), and Zn(II) in real chloride solution. On the basis of this study, it can be concluded that the obtained sorbents can be used to recover Ag from various sources such as ores, wastewater, and jewelry scraps.

Keywords: synthesis, silver(I), sorption, selectivity, synthetic and real chloride solution

1. Introduction

The intensive development of new technologies is associated with an increased demand for silver, resulting in its greater exploitation and depletion of primary deposits. The high price, small resources, low content in the raw material, significant dispersion, coexistence of other metals, and waste components cause an intensive search for the most effective methods of obtaining silver from poorer deposits or secondary raw materials. These include hydrometallurgical methods. Their effectiveness is determined by the ability to dissolve the recovered metal in the leaching solution, concentrate it, and separate it. The choice of a particular leaching method for silver-bearing raw materials is determined by technical and economic factors, and environmental constraints. Currently, silver hydrometallurgy is dominated by cyanide methods, which account for more than 80% of global production.

Chloride leaching may be an alternative solution. It is characterized by higher leaching, compared to cyanide leaching, process speed, lower price of leaching reagents, and lower toxicity. The advantages of chloride leaching also include high activity in reaction with metals, high redox potential, and ease of regeneration. The use of chloride leaching entails the need to develop selective and efficient methods for the separation of Ag(I) chloride complexes (Puvvada et al., 2000; Liu et al., 2010; Behnajady and Moghaddam, 2011).

Among the methods for obtaining silver from solutions after leaching of low-grade ores or secondary raw materials is sorption on ion-exchange or chelating sorbents currently used as an alternative to solvent extraction methods or the use of liquid membranes and impregnated resins.

Modification of chitosan with 2-mercaptobenzimidazole (2-MBI) and sonication treatment allowed the design of an efficient process for the recovery of Ag from synthetic solution and pregnant leach liquor (PLL) containing Au, Pd, Cu, Al, Fe, Sn, Pb, Ni, and Zn. The strong affinity of silver, which is

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considered soft metal ions, for the S-reactive groups present at the surface of the sorbent (held by 2-MBI) may be explained by the Pearson rules (hard and soft acid base theory). Silver ions have a preference for sulfur compounds (soft base) (Elwakeel et al., 2021).

Functional polymers containing 2-mercapto-1-methylimidazole and guanylthiourea ligands were used for the removal of Ag(I) from synthetic and real chloride solutions. The sorbents were useful for the recovery of Ag(I) from synthetic chloride solution. The highest sorption of Ag(I) was reached in the case of guanylthiourea resin. The 2-mercapto-1-methylimidazole resin was highly selective towards Ag(I) in relation to Pb(II) from real chloride leaching solution. The resins were selective for Ag(I) in real chloride solution and they did not sorb chloride complexes of Co(II), Ni(II), and Zn(II) (Pilśniak-Rabiega and Wolska, 2020).

Corn stalk-based adsorbents, TSC-NH_3-OCS (modified by ammonia–thiosemicarbazide) and OCS-ET-TU (prepared by grafting epithiochlorohydrine and thiourea) were used for recovering Ag(I) from simulate and industrial nickel electrolyte. The TSC-NH_3-OCS adsorbent showed a low affinity for Cu(II)and Ni(II), and had high selectivity to recovery trace amounts of Ag(I) from the mixture solution containing high levels of Cu(II) and Ni(II) (Xiong et al., 2016). The OCS-ET-TU adsorbent had strong adsorption capacity and selectivity to $AgCl_4^{3-}$ in industrial nickel electrolyte. The maximum adsorption capacity of Ag(I) was 3.06 mg/g, but the other competing metal ions (Ni(II), Cu(II)) could not be adsorbed onto the OCS-ET-TU (Li et al., 2018).

Sorbents with imidazole ligands were highly selective for Ag(I) in synthetic chloride solution and did not sorb chloride complexes of Cu(II) (Pilśniak-Rabiega et al., 2019).

Chelating resin containing acyl and thiourea groups showed good selectivity for Ag(I) ions in Ag(I)-Cu(II) binary system in an aqueous solution (Huang et al., 2019).

Thiourea-immobilized polystyrene sorbent (TA-PS) has been reported to exhibit high Ag^+ sorption capacity (190 mg/g) in aqueous phase and high selectivity to alkaline and alkaline earth-metal ions (Yun et al., 2018).

Chemically modified chitosan resin with magnetic properties was tested for the recovery of Au(III) and Ag(I) from their aqueous solutions. Uptake values of 3.6 and 2.1 mmol/g were reported for Au(III) and Ag(I), respectively (Donia et al., 2007).

In this context, the aim of this study was to present the synthesis of novel functional polymers containing heterocyclic groups and their sorptive properties towards Ag(I) from synthetic and real chloride solutions. The effects of hydrochloric acid and sodium chloride concentrations on Ag(I) sorption, sorption isotherms, kinetics, and Ag(I) desorption were also studied.

2. Materials and methods

2.1. Chemical reagents

All chemicals used in this study were purchased from Sigma-Aldrich. The reagents were of analytical grade. Synthetic solution of Ag(I) was prepared by dissolving a known amount of silver nitrate in chloride solution (4.00 mol/dm^3 of NaCl, 0.100 mol/dm^3 of HCl). Concentration of Ag in the synthetic solution was 55.61 mg/dm^3.

Real chloride leach solution was contained 59.38 mg/dm^3 of Ag(I), 453.6 mg/dm^3 of Cu(II), $4.213 \cdot 10^3$ mg/dm^3 of Pb(II), 16.38 mg/dm^3 of Co(II), 5.074 mg/dm^3 of Ni(II), and 20.01 mg/dm^3 of Zn(II). Detailed procedures of chloride leaching solution obtained are presented in (Pilśniak-Rabiega et al., 2019).

2.2. Preparation of VBC/DVB copolymer and polymeric resins

2.2.1. Synthesis of VBC/DVB copolymer

Vinylbenzyl chloride/divinylbenzene copolymer (VBC/DVB) (2.0 wt. % of DVB) with an expanded gel structure was prepared by suspension polymerization. The polymerization was carried out in a thermostatic glass reactor of 1500 cm^3 capacity equipped with a two-blade stirrer with thyristor speed control, a reflux condenser, and a thermometer. 14.0 g of sodium chloride and 0.70 g of poly(vinyl alcohol) (suspension stabilizer) were dissolved in 700 cm^3 of distilled water. Separately, the organic phase consisting of vinylbenzyl chloride (96.3 g), divinylbenzene 80% (2.46 g), benzoyl peroxide (0.99 g) and toluene (43.4 cm^3) was prepared. It was poured into the aqueous phase previously heated to 60°C

while setting the stirrer speed to 180-200 rpm. The reaction was carried out for 10 h, with the reaction at 60°C in the first hour, 70°C in the second hour, 85°C in the third, and fourth hours, and then the temperature was increased to 95°C and left unchanged until the end of the reaction. The mixture was allowed to cool and then the copolymer was separated from the solvent and aqueous phase using a set of sieves. To remove salts and unreacted monomers, the copolymer was washed with hot distilled water followed by cold distilled water and acetone. After drying at room temperature, the polymer was swollen in toluene and extracted with toluene in a Soxhlet apparatus for 8 h to remove the monomers and oligomers present in the obtained material. After the extraction, the copolymer was dried at room temperature and the chlorine content (5.30 mmol/g_{Cl}) was determined.

2.2.2. Synthesis of the studied resins

The functional polymers (I-III) were obtained by modification of VBC/DVB copolymer (2.0 wt. % of DVB) in the reaction of chlorine atom exchange with a selected heterocyclic chemical compound. A microwave modification method was used. The copolymer was placed in a Petri dish and swollen with a heterocyclic compound (98-99%) (5-fold molar excess of the compound relative to the chlorine contained in the copolymer) for 1 h at room temperature. After this time, the reactions were carried out in a microwave reactor for 7-10 min, at 100 W. After completion of the reaction, the product was transferred to a glass funnel with a sintered disc and washed with acetone, acetone/distilled water mixture (1:1), distilled water and then cycled. The cycling process of the material thus obtained was carried out in an ion exchange column by washing the bed with 1 mol/dm^3 of NaOH, distilled water to a column leakage pH of about 7, then with 1 mol/dm^3 of HCl and again with distilled water. This process was repeated three times.

2.3. Methods of analysis

2.3.1. Water regain

Water regain was done by centrifuge method (Jermakowicz-Bartkowiak, 2005). A polymer sample of 1.0 g, swollen in water for 24 h, was placed in a column with a filled Teflon bottom and centrifuged for 5 min (at 2000 rpm) in a laboratory centrifuge to remove water from the grains. After the centrifugation, the sample was transferred to previously weighed weighing vessels and dried at 100°C for 24 h. After this time, the vessels were weighed again. The water regain was determined using Eq. 1:

$$W = \frac{m_w - m_d}{m_d} = \frac{m_w}{m_d} - 1 \ \ [g_{water}/g_{dry\ polymer}] \quad (1)$$

where: W is water regain [$g_{water}/g_{dry\ polymer}$], m_w is wet polymer mass after centrifugation [g], m_d is dry polymer mass [g].

2.3.2. Nitrogen content

Nitrogen content was determined by the Kjeldahl method (Pilśniak-Rabiega and Trochimczuk, 2014). About 0.2 g of dried polymer was placed in a flask, 0.3 - 0.4 g of copper sulfate, about 0.8 - 1.0 g of potassium sulfate, and 20 cm^3 of concentrated sulfuric acid (96-98%) were added. The flask was closed and heated to burn the substance (mineralization). After the cooling, 40 cm^3 of distilled water and 33% NaOH were added to the flask in sufficient quantities to change the color of the solution from blue to brown. The sample thus prepared was subjected to steam distillation for about 5 min (Büchi K-314 distiller). During this time, the ammonia evolved and was absorbed by a 2.0% solution of boric acid (about 60 cm^3) containing a mixture of indicators (bromocresol green and methyl red), placed in a conical flask (receiver). Then, the solution obtained in a conical flask was titrated with 0.1 mol/dm^3 of HCl until the colour changed from green to brown-grey.

2.3.3. Chlorine content

Chlorine content was measured by mineralizing a sample of polymer (Pilśniak-Rabiega and Trochimczuk, 2014). A sample of dried polymer (about 0.03 g) was wrapped in an analytical filter and then attached to a platinum wire. Next, 25.0 cm^3 of 3.0% H_2O_2 solution was introduced into a ground conical flask (500 cm^3). The flask was blown with oxygen and placed in it an on-fire polymer sample.

After complete incineration of the sample, the tightly closed flask was left for about 30 minutes to absorb the vapours. After this time, the walls of the flask were rinsed with distilled water and the chloride ion concentration was determined by Volhard's method.

2.3.4. Infrared spectroscopy analysis

The middle-infrared spectra (4000-400 cm^{-1}) of the resins were collected on a Fourier transform Bruker VERTEX 70V vacuum spectrometer equipped with an air-cooled DTGS detector. The ATR accessory was used for the measurements. The spectral data were recorded at the resolution of 2 cm^{-1} with 64 scans collection.

2.4. Evaluation of the sorption properties

2.4.1. Sorption of metals

The sorption capacity of resins towards Ag(I), Pb(II), Cu(II), Zn(II), Co(II), and Ni(II) from synthetic and real chloride solutions was determined by contacting wet and centrifuged resin samples with 20 cm^3 of metal ion solution. Metal ions solution containing Ag (55.61 or 59.38 mg/dm^3), Cu (453.6 mg/dm^3), Pb ($4.213 \cdot 10^3$ mg/dm^3), Co (16.38 mg/dm^3), Ni (5.074 mg/dm^3), and Zn (20.01 mg/dm^3) was used in the sorption experiments. The ratio of ligands in the resin to Ag in the solution was set to 10:1. The samples were shaken for 24 h at room temperature (23±2 °C) at a shaking rate of 100÷120 cycles/min. After this time, the solution was separated from the polymer grains and the metal concentration was measured using the atomic absorption method on a Varian SpectrAA 20 Plus Atomic Absorption Spectrometer.

The distribution coefficient (K_d) was calculated as the ratio of the amount of metal taken by 1 g of resin and the amount of metal remaining in 1 cm^3 of solution after sorption.

2.4.2. Sorption isotherms

The sorption isotherms were determined by contacting various amounts of wet, centrifuged resin with 10 cm^3 of solution containing 55.61 mg/dm^3 of Ag, 4.00 mol/dm^3 of NaCl, and 0.100 mol/dm^3 of HCl. The ratio of ligands in the resin to Ag in the solution was in the range of 10:1-1:10. The samples were shaken for 24 h at room temperature. After this time, the samples were separated by filtration and the concentration of Ag was determined by AAS.

2.4.3. Sorption kinetics

For the kinetics of sorption, the identical samples of swollen resin were shaken with 10 cm^3 of solution containing 55.61 mg/dm^3 of Ag in chloride solution (4.00 mol/dm^3 of NaCl, 0.100 mol/dm^3 of HCl) at room temperature. The ratio of ligands in the resin to Ag in the solution was set to 10:1. Samples were taken at specific intervals of time from the start of shaking (0.5, 1, 2, 3, 4, 5, 9, 16, 24, 36, 48 h), resin and solution separated, and the concentration of Ag was determined by AAS.

2.4.4. Desorption

Desorption of Ag was determined by contacting an amount of resin, loaded with the known amount of Ag, with 20 cm^3 of an eluent at room temperature (23°C) and at 50°C for 24 h. After that time, the concentration of Ag was determined by AAS and the percentage of Ag eluted was calculated.

3. Results and discussion

3.1. Synthesis and characterization of resins

The functionalized polymers were obtained by immobilization on a carrier, which consists in the covalent bonding of a heterocyclic compound, which is a ligand, to a cross-linked polymer. The immobilization method is a convenient way to obtain polymer resins, as it is easier to covalently bind a specific molecule to an existing polymer, with a fixed structure, mechanical and physicochemical properties, than using a small molecule ligand, catalyst or enzyme to synthesize monomers and subject

them to a difficult polymerization reaction. In addition, it is easy to control the ligand content of the resulting polymer by controlling the reaction time, temperature, or concentration of reactants.

On the basis of the above criteria, it was decided to obtain functionalized polymers to bind covalent 4-tert-butylpyridine, pyrrolidine, and 3-morpholinopropylamine to a solid polymer carrier. To obtain the polymer resin as a carrier, a vinylbenzyl chloride/divinylbenzene copolymer (VBC/DVB) with an expanded gel structure and a content of 2.0% by weight of the networking agent was used. This copolymer is characterized by a low degree of cross-linking, which affects its high swelling (swelling is a function of cross-linking density) and higher segmental mobility. These factors determine the easier accessibility of chloromethyl groups as reactive sites for ligand immobilization. Furthermore, they allow ions to diffuse through the polymer network, e. g: silver(I) during sorption of this metal on resins.

The capacity of incorporation of vinylbenzyl chloride monomers into the polymer network is determined on the basis of the chlorine content of the copolymer. The chlorine content in VBC/DVB copolymer was determined at 5.45 mmol/g by the Volhard's method, which corresponds to 85.0% yield.

The polymer resins (I-III) were prepared by using microwave modification. This method has many advantages regarding the conventional method (Kappe and Stadler, 2005) (modification at the boiling point of the reaction mixture and at room temperature):

- noncontact, rapid and selective heating,
- reduced reaction time and energy input,
- reduced size of laboratory equipment, waste and processing costs,
- no system inertia, e.g., when the source of microwave radiation is switched off, the energy stops being supplied to the system.

Furthermore, internal heating combined with microwave energy can lead to products that cannot be synthesized using conventional methods. There are two mechanisms for the absorption of microwave energy by substances:

- Rotation of dipoles - occurs when polar liquids (water, acids, solvents) are exposed to microwave radiation. In a rapidly changing electric field, molecules change their orientation, trying to arrange themselves in a direction that is consistent with the field lines. In this way, they are put into a rotational and vibratory state. Energy absorption occurs to the greatest extent when the vibrational frequencies of the molecules are close to the field frequency.
- Ionic conductivity - occurs when free ions are present in the field (electrolytes, glassy or ceramic materials).

The efficiency of microwave heating thus depends on the dipole relaxation time, ionic conductivity, and the sample volume. In the case of microwave heating, one should rather talk about the conversion of electromagnetic energy into thermal energy than about heat transfer according to the classical mechanisms of convection, conduction, and radiation. This fundamental difference reduces the process time and saves energy. The advantages of the microwave method motivate the search for new possibilities of using microwave radiation in physical and physicochemical processes and chemical reactions.

The use of the microwave method in chemical preparation requires that the reactants used completely or partially absorb microwave radiation so that the solid or liquid can be heated. A measure of the ability to absorb microwave radiation is the dielectric loss factor tg δ, expressed as the quotient of dielectric loss (ε'') and permittivity (ε') (Kappe and Stadler, 2005) (Eq. 2):

$$\text{tg}\,\delta = \varepsilon'' / \varepsilon' \tag{2}$$

The smaller its value, the lower the ability of the substance to absorb radiation. Some substances, such as water, have a relatively large loss parameter at room temperature, which decreases at higher temperatures.

Synthesized polymer resins were characterised by analytical determinations, i. e., the analysis of Cl and N, water regain, and the results obtained are presented in Table 1.

The best result of chemical modification was obtained for the resin with pyrolidine groups. Elemental analysis gave 4.67 mmol of N/g, which corresponds to 90.0% yield (Table 1). The resins with 3-morpholinopropylamine and 4-tert-butylpyridine ligands displayed a nitrogen content of 6.35 and 2.27 mmol/g, respectively. This corresponds to 85.0% and 56.0% yield of VBC/DVB polymer modification. The absence of chlorine in the resins (I-III) indicated the complete substitution of chlorine

atoms in chloromethyl groups (–CH_2Cl) by the heterocyclic compounds in the copolymer network. The absence of chlorine in Resin I and a lower modification efficiency indicate that there is a cross-linking reaction of chloromethyl groups.

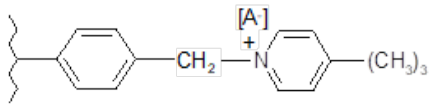
Table 1. Physicochemical properties of the polymeric resins

Resin No.	Water regain [g/g]	Chlorine content [mmol/g]	Nitrogen content [mmol/g]	Yield of modification [%]
I	3.96±0.02	0.00	2.27±0.02	56.0±1.0
II	1.17±0.02	0.00	4.67±0.02	90.0±1.0
III	0.70±0.01	0.00	6.35±0.02	85.0±1.0

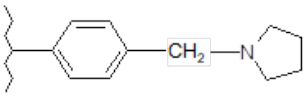
The yield of immobilization of heterocyclic groups on copolymer network (microwave modification), calculated from nitrogen contents was 50–56% (Pilśniak-Rabiega et al., 2019; Pilśniak-Rabiega and Wolska 2020).

The resin with 4-tert-butylpyridine groups was the most hydrophilic, having water regain equal to 3.96 g of water per 1 g of dry polymer. The hydrophilicity of Resin I is due to the large dipole moment value of 4-tert-butylpyridine, which is 2.73 D. For pyrrolidine and 3-morpholinopropylamine, the dipole moment values are 1. 57 and 1.48, respectively. The resin with pyrrolidine ligands (II) shows a higher water regain value than resin 3-morpholinopropylamine groups (III), because it has a free electron pair on nitrogen and is a good proton acceptor in hydrogen bonds formed with water. In the case of Resin III, which is the most hydrophobic, the nitrogen atom is bonded to the aromatic ring, where a hindered free electron pair is observed due to delocalization to the aromatic system. Moreover, the presence of propyl groups increases the hydrophobicity due to the presence of long carbon chains.

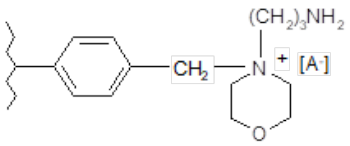
The chemical structures (Fig. 1) of all functionalized polymers were confirmed by FTIR method (Fig. 2).



4-tert-butylpyridine resin (**I**)



pyrrolidine resin (**II**)



3-morpholinopropylamine resin (**III**)

Fig. 1. Structure of the investigated resins

The infrared spectra of polymeric resins are quite complicated due to many overlapping bands. In the FTIR spectrum of the unmodified VBC/DVB copolymer (Fig. 2), a band at a wave number of 1265 cm^{-1}, originating from the C-Cl bonds in the chloromethyl group, is characteristic and was observed by Egawa (Egawa et al., 1990) and Yaacoub (Yaacoub and Le Perchec, 1988). This band, as the modification progresses should disappear, indicating the substitution of chlorine atoms in chloromethyl groups by 4-tert-butylpyridine, pyrrolidine and 3-morpholinopropylamine. The broad band with a wave number of 3427 cm^{-1} comes from the hydroxyl groups that form during the hydrolysis of vinylbenzyl chloride to vinylbenzyl alcohol. The distinct bands with wave numbers 2919 and 2850 cm^{-1}, correspond to the antisymmetric and symmetric valence bands of the methylene groups. The valence vibrations of the bonds between carbon atoms in the ring absorb in the range 1500-1400 cm^{-1}, while the absorption

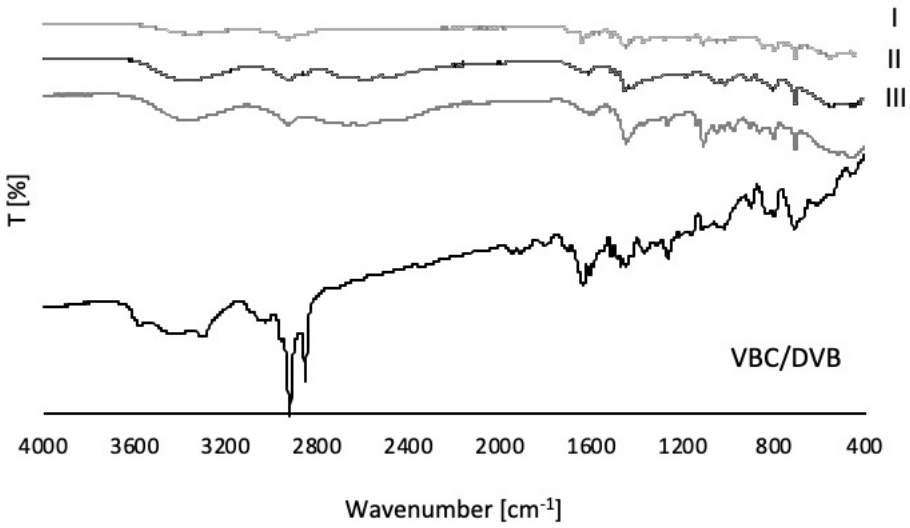


Fig. 2. FTIR spectra of polymeric Resins I-III

bands arising from the non-planar deformation vibrations of the ring occur in the region 900-675 cm^{-1}. As a result of the modifications carried out, the FTIR spectra of the polymeric resins changed most significantly in the wave number range 2684-707 cm^{-1} (Silverstein and Bassler, 1970). Each spectrum shows a valence band of the C-H bond, originating from CH_2 group, falling between 2927 and 2864 cm^{-1}. Strong bands in the range 906-705 cm^{-1} arise from non-flat ring deformational vibrations, while the peaks with maxima at 1513 and 1489 cm^{-1} describe conjugated double bonds in the phenyl ring, and 1450-1445 cm^{-1} deformational shear vibrations of amine-bound CH_2 groups. The absence of absorption at 1265 cm^{-1} in the spectra of functional polymers confirms the substitution of chlorine atoms by amine ligands.

The FTIR spectrum of 4-tert-butylpyridine resin (I) shows a strong stretching valence C-N band at 1275 cm^{-1} characteristic for pyridine ring. The CH_3 asymmetric vibrations of tert-butyl groups are identified at 1468, 1410, and 1367 cm^{-1} (Phan et al., 2020).

The spectrum of pyrrolidine resin (II) shows a valence band of C-H bond at 2683, 2593, 2487 cm^{-1} and an intense C-N band appearing at 3374 cm^{-1}. These bands are characteristic of the pyrrolidone ring (Snavely et al., 1992; Xie et al., 2020).

A band with a maximum at 1589 cm^{-1} appeared in the spectrum of 3-morpholinopropylamine resin (III), which originates from deformational vibrations of the N-H bond. The C-O-C group in the six-member ring absorbs at a vibrational frequency of 1108 cm^{-1}. It is a band of asymmetric valence vibrations (Silverstein and Bassler, 1970).

3.2. Evaluation of the sorption properties

3.2.1. Effect of hydrochloric acid and sodium chloride concentration on the sorption of silver(I)

The acidity of the aqueous solution plays an important role in the chemical sorption of metal ions. To determine the influence of acidity on Ag(I) sorption on polymers (I-III), a series of experiments were performed at 23±2°C using chloride solutions of Ag(I) (55.61 mg of Ag/dm^3) with a fixed sodium chloride concentration of 4.00 mol/dm^3 and varying hydrochloric acid concentrations in the range of 0.0100 - 2.00 mol/dm^3. The results are shown in Fig. 3.

It was observed that that for all resins the Ag(I) sorption decreased with the increasing HCl concentration. The best Ag(I) sorption results can be obtained from the solution containing 0.100 mol/dm^3 of HCl. At relatively low acidity, the functional groups on the adsorbents exist in protonated form and exhibit high electrostatic interaction with the Ag(I) coordination anion according to the hard and soft acid and base (HSAB) theory. At higher concentrations of HCl (0.300-2.00 mol/dm^3) the sorption of Ag(I) decreased because of competition with Cl- ions due to their increased concentration in solution.

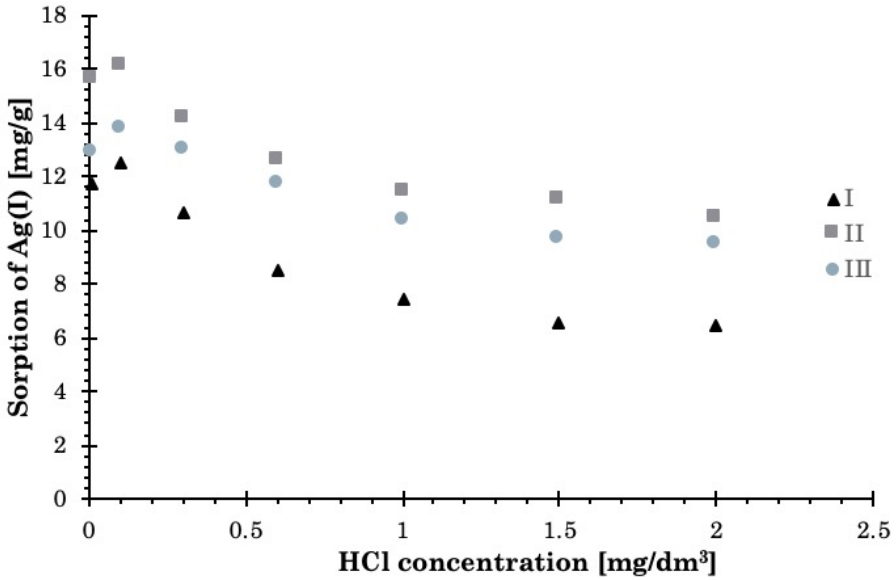


Fig. 3. Ag(I) sorption as a function of HCl concentration

Chloro complexes of Ag(I), $AgCl_4^{3-}$, were successfully adsorbed by natural corn stalk modified by ammonia – thiosemicarbazide (TSC-NH3-OCS) at relatively low acidity (0.1–2.0 mol/dm³). The –C=S group was protonated as $–C=SH^+$ group, which has a high electrostatic interaction with Ag(I) ion based on HSAB theory. At high acidity (2.00-3.00 mol/dm³), the uptake of Ag(I) decreased due to the sorption of NO_3^- ions by the addition of nitric acid (Xiong et al., 2016).

The effect of NaCl concentration on the sorption of Ag(I) at 23±2°C on resins was investigated in the concentration range of 1.0 0- 5.00 mol of NaCl/dm³, 0.100 mol of HCl/dm³, and 55.61 mg of Ag/dm³ (Fig. 4). All resins tested showed the highest affinity for Ag when the concentration of NaCl was 4.00 mol/dm³. The Ag(I) sorption decreased when the NaCl concentration was greater or smaller than 4.00 mol of NaCl/dm³.

The results presented in Fig. 3 and 4 show that the best Ag(I) sorption can be observed from the solution containing 4.00 mol/dm³ of NaCl and 0.100 mol/dm³ of HCl in the chloride solution of silver(I). Therefore, all subsequent experiments, including study of sorption mechanism, sorption isotherms obtaining, and kinetics studies were carried out using this solution.

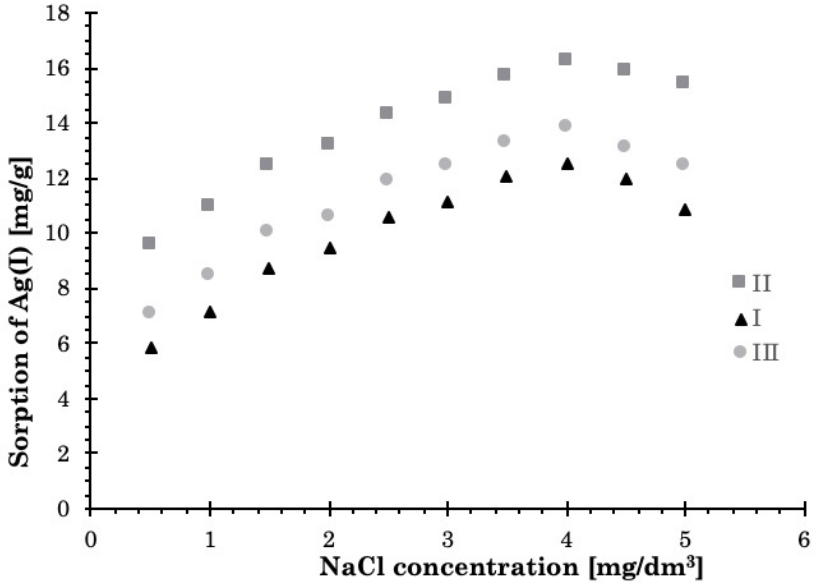


Fig. 4. Ag(I) sorption as a function of NaCl concentration.

3.2.2. Sorption mechanism

The functional polymers with heterocyclic ligands (I-III) were used to recover silver(I) from synthetic chloride solutions. The Ag(I) sorption process was carried out from an aqueous solution containing 55.61 mg of Ag /dm^3, 4.00 mol/dm^3 of NaCl, 0.100 mol/dm^3 of HCl, at room temperature, during 24 hours testing. In this solution, Ag(I) mainly occurs in the form of $AgCl_4^{3-}$ complexes (Liu et al., 2010). Table 2 presents the results of Ag(I) sorption on polymers.

Table 2. Sorption of Ag(I) from synthetic chloride solution

Resin No.	Ligand concentration* [mmol/g]	Sorption of Ag [mg Ag/g resin]	Sorption of Ag [mmol Ag/g resin]	Yield of Ag sorption [%]	K_d
I	2.27±0.02	12.5±1.0	0.116±0.01	46.0±2.0	417
II	4.67±0.02	16.2±1.0	0.150±0.01	28.9±1.0	409
III	3.18±0.02	13.8±1.0	0.128±0.01	36.4±1.0	391

*Calculated from nitrogen content in functional groups

C_{Ag} = 55.61 mg/L (0.5155 mmol/dm^3)

C_{HCl} = 0.100 mol/dm^3, C_{NaCl} = 4.00 mol/dm^3

The best sorption capacity towards Ag(I) is shown by Resin **I** (16.2 mg Ag/g resin) modified with pyrrolidine. The distribution coefficient (K_d) value is 409 (Table 2). According to the theory of hard and soft acids and bases, precious metals (Au, Ag, Pt) are referred to as "soft acids" and tend to form stable complexes with ligands containing "soft" donor atoms ("soft bases"). Nitrogen, which is an intermediate base, also tends to form complexes with precious metals. The pyrrolidine resin (**II**) containing donor nitrogen atoms in functional groups shows affinity to Ag(I) in chloride solution. The silver recovery on this polymer is determined by the presence of a free electron pair on the nitrogen atoms. These atoms can coordinate with silver(I) in chloro complexes, indicating that the coordination of Ag(I) ions is the main sorption mechanism.

The resins with 4-tert-butylpyridine and 3-morpholinopropylamine ligands (Resin I and III, respectively) do not have a free electron pair on the nitrogen atom in the ring, this suggests that Ag(I) coordination is not the mechanism for silver sorption. These resins have a positive charge, so there should be counterions on their surface, e. g.: Cl^-, which are present in the chloride solution of Ag(I). Chloride anions can be exchanged for anionic silver complexes, $AgCl_4^{3-}$.

The sorption of silver chloro complexes, $AgCl_4^{3-}$, on Resin III can also proceed by protonation of the $-NH_2$ amino groups by acid. These groups capture Ag(I) ions due to electrostatic attraction (Eq. 3 and 4).

$$P\text{-}NH_2 + HCl = P\text{-}NH_3^+Cl^- \quad (3)$$

$$P\text{-}(NH_3^+Cl^-)_3 + AgCl_4^{3-} = P\text{-}(NH_3^+)_3AgCl_4^{3-} + 3Cl^- \quad (4)$$

P- polymeric matrix

The high uptake of Ag(I) from aqueous solution by triazole resin and amino/thiol resin is due to the presence of free pair of electrons on nitrogen or sulfur atoms (coordination with Ag(I)) and ion exchange between -SH groups and Ag(I) (Atia et al., 2005).

Melamine-formaldehyde-thiourea (MFT) chelating resin has been used for separation and recovery of silver(I) ions in aqueous solution. Ag(I) ions may interact with functional groups through ionic interaction or with sulphur or nitrogen donor atoms through chelation (Yirikoglu and Gulfen, 2008).

A magnetic chelating resin with amine/thio functionality was found efficient towards the recovery of silver from aqueous solutions. Silver sorption followed two mechanisms, i.e., the coordination mechanism between Ag(I) and nitrogen and sulfur atoms, and cation exchange mechanism (Atia et al., 2014).

3.2.3. Sorption isotherm studies

During evaluating the sorption properties of the synthesized resins also the sorption isotherms at room temperature were determined. The sorption isotherms for all investigated materials are shown in Fig. 5. As can be observed, the capacities of polymers I and III are very similar. The lowest sorption capacity was observed for Resin II during Ag(I) uptake (about 70 mg Ag/g). For resins I and III, sorption capacity towards silver was about 90 mg Ag/g. Additionally, during comparison the concentrations at which the maximum sorption capacities were achieved, it can be seen that for Resin I maximum capacity is reached at lower concentrations than in the case of resins II and III.

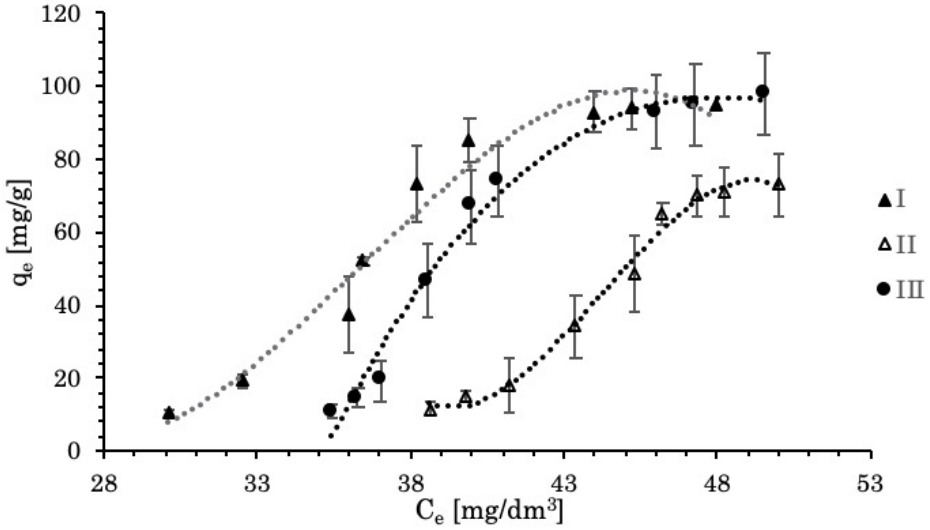


Fig. 5. Ag(I) sorption isotherms for resins I-III. Samples of resin containing 0.1-10x molar excess of ligand were shaken with 10 cm^3 of solution containing 55.61 mg/dm^3 of Ag(I) in chloride solution at 23 ± 2°C

To describe the interaction of Ag(I) with the prepared polymers, three adsorption isotherm models, Langmuir, Freundlich, and Dubinin-Radushkevich were used. The Langmuir isotherm assumes that a monolayer of molecules is formed at surface of adsorbent. The linear form of the Langmuir equation can be given as follows (Eq. 5):

$$\frac{1}{q_e} = \frac{1}{q_m b_L C_e} + \frac{1}{q_m} \tag{5}$$

where q_e (mg/g) is the uptake at equilibrium concentration, q_m (mg/g) is the maximal uptake, C_e (mg/dm^3) is the equilibrium concentration, b_L (dm^3/mg) is the constant related to the binding energy of the sorption system. Parameters q_m and b_L were calculated from the slope and intercept of the linear plot of $1/q_e$ vs. $1/C_e$ (Polowczyk et al., 2016).

Additionally, a separation factor (dimensionless) called the equilibrium or separation parameter (R_L) is determined during the analysis, which allows to determine whether the Langmuir isotherm model is favorable for a given separation process (Eq. 6) (Polowczyk et al., 2016):

$$R_L = \frac{1}{1+b_L C_0} \tag{6}$$

where C_0 is the initial adsorbate concentration [mg/dm^3].

The parameter R_L indicates the efficiency of the adsorption process. The isotherm is (i) unfavourable when $R_L > 1$, (ii) linear when $R_L = 1$, (iii) favourable when $R_L < 1$, and (iv) irreversible when $R_L = 0$ (Polowczyk et al., 2016). Unfortunately, the obtained fitting data did not allow to calculate the characteristic parameters for this isotherm model, which also confirms that this model is not suitable for the analysis of the sorption process of silver(I) on all studied polymers.

Next investigated model was the Freundlich isotherm. This model is assumed as a power function relationship between q_e and C_e and it is easily applicable when the experimental data are plotted in *log* q_e versus *log* C_e format (Eq. 7) (Cela-Pérez et al., 2011). Freundlich isotherm is applicable to adsorption processes that occur on heterogonous surfaces. This isotherm gives an expression which defines the

surface heterogeneity and the exponential distribution of active sites and their energies. The linear form of the Freundlich isotherm is as follows (Polowczyk et al., 2016; Ayawei et al., 2017):

$$\log(q_e) = \frac{1}{n}\log(C_e) + \log(a) \quad (7)$$

In this model, there are two fitting parameters *a* and $1/n$ that both yield a measure of physical binding. The *a* parameter is the constant related to adsorption capacity. The *1/n* parameter is known as the heterogeneity index. For homogeneous materials, *1/n* would be equal to 1, when the adsorption is linear, adsorption sites are homogenous in energy, and no interactions occur between the adsorbed compounds. On the other hand, when values of *1/n* parameter approach to zero increase the heterogeneous character of the polymer. The constant *n* should have a value in the range of 1–10 for the adsorption to be classified as favourable (Cela-Pérez et al., 2011; Wolska and Bryjak, 2014; Polowczyk et al., 2016).

The fitting of experimental data by the Freundlich isotherm allowed to calculate the parameters *a* and *1/n*, which also helped to determine whether the selected model is appropriate. The values of the calculated parameter *a* were $1.3{\cdot}10^{-6}$, $2.0{\cdot}10^{-12}$ and $3.4{\cdot}10^{-9}$ for resins I, II and III, respectively. The values of *n* constant for all of investigated materials were below 1 (0.208, 0.124, and 0.160 for Resin I, II, and III, respectively) therefore it can be assumed that the sorption of Ag(I) onto studied polymers is not favourable. Additionally, comparing the R^2 values for the Langmuir and Freudlich models, it can be seen that the second model is a better fit for silver (I) adsorption onto all resins. All results of Langmiur and Freundlich analysis are given in Table 3.

Table 3. Langmuir and Freundlich fitting parameters for resins I-III

Resin	Langmuir		Freundlich		
No.	R^2	R_L	n	a	R^2
I	0.840	7.94	0.208	$1.3{\cdot}10^{-6}$	0.849
II	0.902	42.3	0.124	$2.0{\cdot}10^{-12}$	0.956
III	0.684	13.5	0.160	$3.4{\cdot}10^{-9}$	0.807

The third investigated sorption model is Dubinin-Radushkevich isotherm model which helps to study interaction between sorbate and sorbent (Cela-Pérez et al., 2011). This approach is used generally to distinguish the kind of sorption: physical or chemical one dominates. The isotherm is expressed by Eq. 8.

$$\ln(q) = \ln(q_m) - K_{DR}\varepsilon^2 \quad (8)$$

where q_m is the maximum adsorption capacity of material [mmol/g], K_{DR} is the Dubinin-Radushkevich constant [kJ^2/mol^2], ε is the Polanyi potential (Eq. 9):

$$\varepsilon = RT\ln\left(1 + \frac{1}{c}\right) \quad (9)$$

K_{DR} is related to the free energy (*E*, [kJ/mol]) of adsorption per molecule of adsorbate when it is transferred to the surface of the solid from infinity (in the solution). The adsorption behavior could predict physical adsorption in the range of 1 – 8 kJ/mol, and chemical adsorption at over 8 kJ/mol. The free energy can be calculated by Eq. 10 (Cela-Pérez et al., 2011).

$$E = (2K_{DR})^{-0.5} \quad (10)$$

During this analysis, the free energy values for all of resins were calculated. For all investigated polymers, the value of E has a value greater than 8 kJ/mol, and they reached the value of 7.76, 12.4, and 10.8 kJ/mol for resins I, II and III respectively. It means that in all cases chemical adsorption dominated. Additionally, as can be seen, the values of calculated parameters were highest for Resin II. It means that the interactions between functional groups of Resin II and sorbate are about 1.6 times and 1.1 higher than Resin I and III forces, respectively. The linear coefficient of determination (^{2}) value closest to 1 was obtained in the case of the Dubinin-Radushkevich isotherm model, and therefore only on the basis of this model the maximum sorption capacities for all investigated resins were calculated. The maximum

sorption capacity of $AgCl_4^{3-}$ for the resins I, II, and III is 120.4, 131.6, and 85.2 mg Ag/g resin, respectively. The parameters of Dubinin-Radushkevich isotherm are given in Table 4.

Table 4. The Dubinin-Radushkevick fitting parameters for all investigated polymers

Resin No.	q_m [mg/g]	q_m [mmol/g]	R^2	E [kJ/mol]
I	120.4±5	1.11±0.05	0.960	7.76 ± 1
II	131.6±7	1.21±0.07	0.975	12.4 ± 1
III	85.2±5	0.787±0.05	0.979	10.8 ± 1

The maximum adsorption capacity of OCS-ET-TU adsorbent (corn stalk-based sulfur-bearing adsorbent) for $AgCl_4^{3-}$ was 107.9 mg/g in single system and 79.94 mg/g in simulate nickel electrolyte system (Li et al., 2018). The best fit was characterized by the Langmuir model for the adsorption of $AgCl_4^{3-}$ on the biomaterial.

The TSC-NH_3-OCS adsorbent based on natural corn stalk modified by ammonia (NH_3)–thiosemicarbazide could selectively adsorb $AgCl_4^{3-}$ from the Ag(I) single and Ag(I)–Cu(II)–Ni(II) simulate nickel electrolyte system (Xiong et al., 2016). The maximum adsorption capacity obtained from Langmuir model in the Ag(I) single and Ag(I)–Cu(II)–Ni(II) ternary system were calculated as 153.54 and 46.69 mg/g, respectively.

3.2.4. Sorption kinetics studies

The relationship between sorption capacity and contact time are displayed in Fig. 6. It was found that sorption capacity increased with prolonging of reaction time. Ag(I) complexes were sorbed faster at the beginning of the process (50% of maximum uptake was reached after 9-16 h). While after 9-16 hours, the sorption curve became gentle and an equilibrium state reached after 48 hours with sorption capacity of 14.56, 19.77, and 19.52 g of Ag/g of resin (for resins **I-III**, respectively).

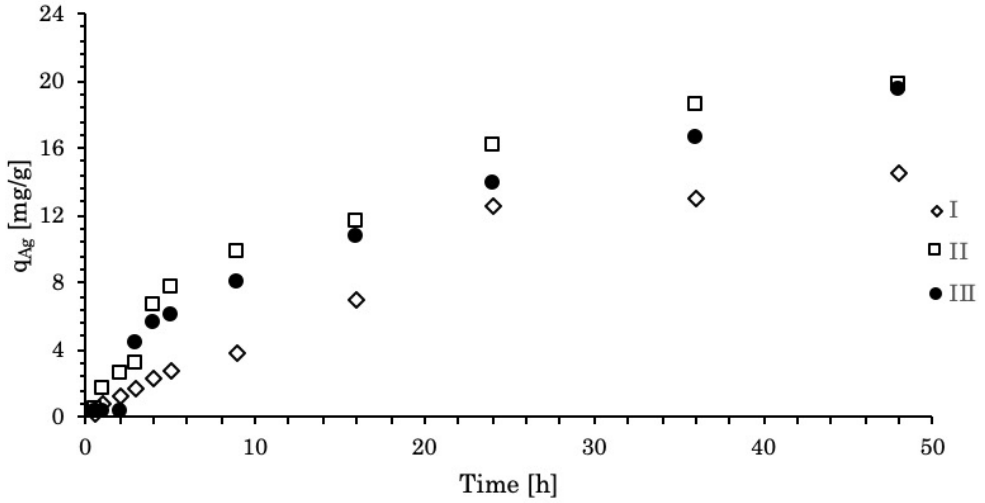


Fig. 6. Kinetics of Ag(I) sorption on polymeric resins. Samples of resin containing 0.01 mmol of ligand were contacted with solutions containing 10x molar excess of an appropriate Ag(I) in chloride solution at 23 ± 2°C and the concentration checked in specified time intervals

Sorption kinetics gives information whether it occurs through diffusion, mass transfer, or chemical reaction. These studies explain the uptake of sorbate by the sorbent, which successively controls the time taken by the sorbate at the interface between the sorbent and bulk solution (Haq et al., 2020). To obtain all such information, the sorption of Ag(I) in the first stage of analysis were fitted to the diffusion

models using the second *Fick's law* (Eq. 11 and 12), to find the rate (film diffusion or particle diffusion) determining steps for the resins (Juang et al., 2002; Kabay et al., 2007; Haq et al., 2020).

$$k_a t = -\ln(1 - \frac{q_t}{q_e}) \tag{11}$$

where q_t and q_e represent the amount of adsorbed species (mg/g) at any time t and at equilibrium time, respectively, and k_a represents the sorption rate constant (1/min). Sorption rate constant k_a (1/min) can be calculated from the plot of $-ln(1 - \frac{q_t}{q_e})$ vs. time.

$$k_b t = -\ln(1 - (\frac{q_t}{q_e})^2) \tag{12}$$

where k_b is the sorption rate constant (min^{-1}), q_e and q_t are the amount of adsorbed species (mg/g) at equilibrium and at time t. Sorption rate constant k_b (1/min) can be calculated from the plot of $-ln(1 - (\frac{q_t}{q_e})^2)$ vs. time.

Table 5 gives the slope values, the linear correlation coefficients, and the calculated values of k_a and k_b. Analyze of k_a and k_b can show for which resins the process of sorption is faster. For resins II and III these parameters are the highest, it means that for this sample the sorption equilibrium was reached in a little shorter time than for Resin I. Analyze of the coefficients of determination can show what kind of diffusion controlled the process mostly. In the case of resins I and III, the film diffusion controls the process mostly, while for Resin II the process of sorption is controlled by the particle diffusion.

Table 5. Analysis of kinetic studies

Resin No	$k_a t = -ln(1 - \frac{q_t}{q_e})$		$k_b t = -ln(1 - (\frac{q_t}{q_e})^2)$	
	k_a	R^2	k_b	R^2
I	$7.0 \cdot 10^{-4}$	0.986	$3.0 \cdot 10^{-4}$	0.920
II	$1.0 \cdot 10^{-3}$	0.905	$5.0 \cdot 10^{-4}$	0.965
III	$1.1 \cdot 10^{-3}$	0.977	$5.0 \cdot 10^{-4}$	0.945

To predict the mechanism involved in the sorption process, several different kinetic models are applied. Among them, the sorption kinetics is usually described by simple kinetic models: by pseudo-first or pseudo-second-order models (Kabay et al., 2007; Santander et al. 2014).

The pseudo-first-order model describes the relationship between the sorption rate and equilibrium time. This model can be described by Eq. 13 (Kabay et al., 2007):

$$\frac{dq}{dt} = k_1(q_e - q_t) \tag{13}$$

where q_t and q_e represent the amount of adsorbed species (mg/g) at any time t and at equilibrium time, respectively, and k_1 represents the sorption rate constant (1/min).

Integrating Eq. 13 with respect to the boundary conditions q=0 at t=0, and q=q_t at t=t, one obtains

$$log(q_e - q_t) = log(q_e) - \frac{k_1 t}{2.303} \tag{14}$$

Sorption rate constant k_1 (1/min) can be calculated from the plot of $log\ (q_e - q_t)$ versus time.

The kinetic data can be analyzed by means of pseudo-second-order kinetics also. According to this model, the sorption behavior is controlled by the chemisorption process occurring either electronic sharing or electronic exchange. This model is represented by Eq. 15 [(Kabay et al., 2007; Haq et al., 2020):

$$\frac{dq}{qt} = k_2(q_e - q_t)^2 \tag{15}$$

where k_2 is the pseudo-second-order rate constant (g/mg min), q_e and q_t are the amount of adsorbed species (mg/g) at equilibrium and at time t. Varying variables in Eq. 15, one gets:

$$\frac{dq}{(q_e - q_t)} = k_2 dt \tag{16}$$

and integrating Eq. 16 for the boundary conditions q=0 at t=0, and q=q_t at t=t, one obtains the final form:

$$\frac{t}{q_e} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \tag{17}$$

A plot t/q versus t gives the value of the constants k_2 (g/mg h). It is also possible to calculate q_e (mg/g).

The experimental data were fitted with Eq. 11 and 16 that served for the calculation of k_1 and k_2 constants and the correlation coefficients (R^2). The results of kinetic analysis are given in Table 6.

Table 6. Kinetic parameters of Ag(I) sorption

Resin No.	Pseudo-first		Pseudo-second	
	k_1	R^2	k_2	R^2
I	$2.0 \cdot 10^{-4}$	0.979	$9.1 \cdot 10^{-2}$	0.551
II	$6.0 \cdot 10^{-4}$	0.983	$3.1 \cdot 10^{-2}$	0.492
III	$4.0 \cdot 10^{-2}$	0.982	$3.6 \cdot 10^{-2}$	0.701

It can be seen that the sorption kinetics for resins fits well to pseudo-first-order mechanism.

Recovery of Ag(I) from aqueous solutions was studied using resin derived from 3-amino-1,2,4-triazole-5-thiol and glutaraldehyde. Kinetic studies indicated that the adsorption reaction follows the pseudo-first-order kinetics (Abd El-Ghaffar et al., 2009).

Modified melamine resin was obtained through treatment with thiourea and tested for selective separation between Cu(II) and Ag(I) from their binary mixtures. Kinetic studies indicated that the adsorption reaction of Ag(I) on sorbent is perfectly fit pseudo-first-order model (Abd El-Ghaffar et al., 2009).

3.2.5. Desorption of Ag(I)

The sorption properties of functional polymers (I-III) presented in the previous sections offer the possibility of removing Ag(I) ions from chloride solutions. In addition to good sorption properties, the sorbent must also have the ability to regenerate. It is very difficult to obtain a sorbent, which at the same time can be easily desorbed, because high sorption capacity means high affinity between metal ions and sorbent, which in turn means difficult desorption. The desorption process depends on several parameters, i. e., static and dynamic conditions of the process, type and amount of eluent, time, temperature, and mixing.

The most commonly used eluents for removing metals from sorbents are mineral acids (HCl, HNO_3, H_2SO_4), hydroxides (NaOH, $NH_3 \cdot H_2O$), and in the case of precious metals also potassium cyanide solutions. The efficiency of acids in metal desorption is due to the fact that H+ ions readily sorb to the electron-donor groups of the sorbent, thus displacing the adsorbed metal ions. However, the desorption efficiency is strongly influenced by the sorption mechanism. Elution with acidic solutions is very effective when sorption occurs by ion exchange. In the case of sorption by chelation, desorption is more difficult, the more stable the complex formed. In such cases, potassium cyanide solutions are used for desorption.

The desorption of Ag(I) from the resins at room and elevated temperatures (23 and 50°C) was investigated. The Ag(I) was desorbed by different eluents: 1.0% potassium cyanide solution, 1.0% potassium cyanide solution in 0.50% hydrogen peroxide solution, 0.50 M sodium hydroxide solution and ammonium buffer (2.86 mol/dm^3 of $NH_3 \cdot H_2O$ and 0.380 mol/dm^3 of $(NH_4)_2SO_4$). Each of the eluents was used for desorption of a similar amount of silver from resin. The results are presented in Table 7.

From the results, it can be concluded that the desorption efficiency of Ag(I) using the selected eluents is higher at elevated temperature than at room temperature. The best eluent for silver sorbed on resins (I-III) with 4-tert-butylpyridine, pyrrolidine, and 3-morpholinopropylamine ligands is 1.0% potassium cyanide solution in 0.50% hydrogen peroxide solution. It can be concluded that during the desorption of Ag(I) from polymers, cyanide anions form $Ag(CN)_4^{3-}$ complexes via a ligand exchange mechanism. The values of logarithm of the stability constant ($\log \beta_4$) of chloride and cyanide silver complexes may suggest that Cl^- ions can be exchanged for CN^- anions in Ag(I) complexes, during the desorption of silver from sorbents. The values of $\log \beta_4$ of $Ag(CN)_4^{3-}$ and $AgCl_4^{3-}$ are 22.3 and 5.30, respectively (Högfeldt, 1982).

Table 7. Elution of silver(I) from resins using different eluents

Eluent	Temp. 23^{0}C			Temp. 50^{0}C		
	%Elution			%Elution		
	I	II	III	I	II	III
1.0 % KCN	44.7±1.0	57.9±1.0	46.5±1.0	62.3±1.0	82.3±1.0	65.6±1.0
1.0% KCN + 0.50% H_2O_2	75.6±1.0	62.0±1.0	77.7±1.0	85.2±1.0	88.7±1.0	92.3±1.0
0.50 mol/dm^3 of NaOH	11.6±1.0	7.64±1.0	2.80±0.5	19.8±1.0	22.5±1.0	6.97±1.0
0.50 mol/dm^3 of $CS(NH_2)_2$ + 0.10 mol/dm^3 of H_2SO_4	7.61±1.0	10.2±1.0	15.8±1.0	18.8±1.0	14.3±1.0	22.7±1.0
Ammonium buffer*	4.85±0.5	8.67±0.5	2.07±0.02	7.23±1.0	15.4±1.0	6.45±1.0

*2.86 mol/dm^3 of $NH_3 \cdot H_2O$ and 0.380 mol/dm^3 of $(NH_4)_2SO_4$

3.2.6. Resin's stability in cycles of sorption/desorption

An important feature of functional polymers is their stability in subsequent processes of sorption and desorption of Ag(I) ions from their surface. It makes it possible to assess the suitability of such materials for cyclic processes, which most often occur in the practical use of sorbents for the recovery of precious metals.

To evaluate the stability of the sorbents (**I-III**) in silver(I) solution and eluent, studies were carried out by cyclic sorption of Ag(I) ions from chloride solution (55.61 mg Ag/dm^3, 4.00 mol/dm^3 of NaCl, 0.100 mol/dm^3 of HCl) and their desorption with a 1.0% solution of KCN in 0. 30% H_2O_2. During the test, the sorbent was treated with a 10-fold relative to the amount of ligand, a molar excess of Ag(I) in solution, then washed with water and desorbed with a 1.0% solution of KCN in 0. 30% H_2O_2. After desorption, the same resin sample was again subjected to Ag(I) sorption. Five cycles of sorption and desorption were performed.

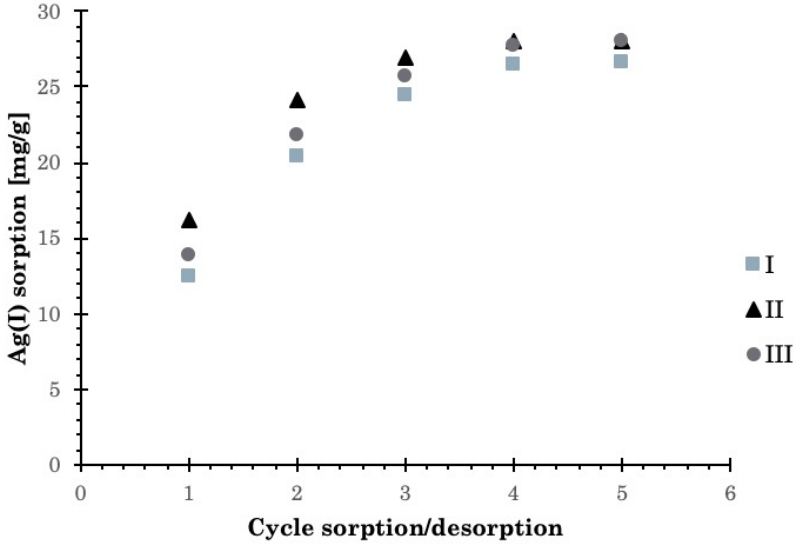


Fig. 7. Sorption properties of resins **I - III** in five cycles of sorption and desorption.

Based on the results presented in Fig. 7, it can be concluded that sorption capacity of Ag(I) increased, sorption capacity was 46.0% (12.5 mg/g), 28.9% (16.2 mg/g), and 36.4% (13.8 mg/g) in the firs cycle, in the case of 2–5 cycles was 75.4-98.0% (20.5-26.7 mg/g), 43.0-50.0% (24.1-28.0 mg/g) and 57.5-76.0% (21.8-28.8 mg/g), for 4-tert-butylpyridine resin (I), pyrrolidine resin (II) and 3-morpholinopropylamine

resin (III), respectively. Desorption efficiency in 1-5 cycles was 75.6-93.0%, 62.0-85.0%, and 77.7-97.2% (for Resin I, II and III, respectively). Elution was carried out at room temperature (23°C).

The more efficient sorption of Ag(I) on resins in cycles 2-5 with respect to cycle 1 can be explained by the presence of cyanide anions derived from potassium cyanide used as eluent. Cyanide ions, CN^-, present on the surface of polymer resins can form $Ag(CN)_4^{3-}$ complexes with Ag(I), which are more stable than $AgCl_4^{3-}$ complexes (Högfeldt, 1982).

Carbonized corn stalk modified by epithiochlorohydrine and thiourea (OCS-ET-TU) has adsorption regeneration ability, which is economic and amicable for the environment. After 6 adsorption-desorption cycles, the adsorption capacity for $[AgCl_4]^{3-}$ anions remained practically unchanged (29-30 mg/g) (Li et al., 2018).

Adsorption capacity of acyl thiourea resin (PTDTR) for Ag(I) ions decreased 2.7% (from 5.57 to 5.42 mmol/g) after five cycles of adsorption-desorption (Huang et al., 2019).

The Ag^+ sorption efficiency of thiourea-immobilized polystyrene (TA-PS) nanoparticles was notessentially decreased after three successive sorption–desorption cycles, (decreased by only ~2%). TA-PS nanoparticles exhibited a high Ag^+ sorption capacity and were very stable under highly acidic conditions (1.0 N HCl) (Yun et al., 2018).

3.2.7. Recovery of Ag(I) from real chloride leach solution

The sorption properties of polymers containing heterocyclic ligands provide the possibility of removing silver from the synthetic chloride solution. Therefore, these materials were used to recover silver from real chloride leaching solution.

Real chloride leach solution was prepared by chloride leaching of a solid residue after atmospheric leaching in sulfuric acid of copper concentrate using Lubin Concentrator (KGHM Polska Miedź S.A.). The concentration of NaCl in the leaching solution was 4.00 mol/dm^3 and 0.100 mol/dm^3 of HCl.

Table 8. Sorption of Ag(I), Cu(II), Pb(II), Co(II), Ni(II) and Zn(II) from real chloride leach solution

Resin No		**I**	**II**	**III**
Sorption [mg metal /g resin]	**Ag**	12.0±0.01	16.7±0.01	14.3±0.01
	Cu	0.401±0.01	0.842±0.01	0.130±0.01
	Pb	5.92±0.01	20.4±0.03	14.9±0.01
	Co	0.270±0.001	0.661±0.001	0.050±0.001
	Ni	0.041±0.001	0.102±0.001	0.051±0.001
	Zn	0.122±0.003	1.26±0.01	0.492±0.005
K_d	**Ag**	389±0.1	431±0.1	416±0.1
	Cu	13.3±0.03	27.9±0.05	4.41±0.01
	Pb	1.41±0.01	4.85±0.01	10.8±0.04
	Co	17.2±0.05	41.9±0.07	2.81±0.01
	Ni	8.24±0.03	21.1±0.05	9.03±0.02
	Zn	6.12±0.01	36.9±0.06	25.2±0.05
$a_{sel.}$	**Ag/Cu**	29.2	15.4	94.3
	Ag/Pb	276	88.7	38.5
	Ag/Co	22.6	10.3	148
	Ag/Ni	47.2	20.4	46.1
	Ag/Zn	63.6	11.7	16.5

C_{Ag} = 59.38 mg/dm^3 (0.5505 mmol/dm^3)

C_{Cu} = 453.6 mg/dm^3 (7.138 mmol/dm^3)

C_{Pb} = 4.213·10^3 mg/dm^3 (20.33 mmol/dm^3)

C_{Co} = 16.38 mg/dm^3 (0.2780 mmol/dm^3)

C_{Ni} = 5.074 mg/dm^3 (0.08645 mmol/dm^3)

C_{Zn} = 20.01 mg/dm^3 (0.3061 mmol/dm^3)

C_{HCl} = 0.100 mol/dm^3, C_{NaCl} = 4.00 mol/dm^3

During the acidic chloride leaching, the solid residue contained silver and lead in the form of insoluble compounds in sulfuric acid, such as Ag_2S and $PbSO_4$.

The selectivity coefficient ($\alpha_{sel.}$) was calculated as the quotient of the distribution coefficients (K_d) calculated for Ag(I) and the specific metal present in the real solution.

Based on the results presented in Table 8, it can be concluded that the polymers are selective towards Ag(I) ions in the presence of Cu(II), Pb(II), Co(II), Ni(II) and Zn(II). This fact could be explained as a result of the presence of ligands with N-donor centers, which had a high affinity for "soft" metals (Au, Ag, Pt), but minor affinity towards other metals referred to as "hard" metals. On the other hand, it could be caused by the fact that resins prefer complexes, which have the highest density of negative charge, what should increase their hydration requirements and facilitate their transport through the VBC/DVB matrices of resins. Chloro complexes of Ag(I), Cu(II), Pb(II), Co(II), Ni(II) and Zn(II) have tetrahedral structure. The complex of $AgCl_4^{3-}$ has a higher density of negative charge (three charges are carried over by five atoms) than $CuCl_4^{2-}$, $PbCl_4^{2-}$, $CoCl_4^{2-}$, $NiCl_4^{2-}$ and $ZnCl_4^{2-}$ complexes.

The best sorption capacity towards Ag(I) from multicomponent solution showed pyrrolidine resin (**II**). The sorption of Ag(I) is 16.7 mg/g. The resin with 4-tert-butylpyridine ligands was selective towards Ag(I) in relation to Pb(II) from real chloride leaching solution. The value of selectivity coefficient, $a_{sel.}$, is 276. This resin showed high selectivity for Ag (I), because $a_{sel.}$ is higher than 100 (Huang et al., 2019).This could be useful in the separation of Ag(I) from the chloride leaching solution containing other metals, especially Pb(II). The concentration of Pb(II) in real chloride solution was 37 times higher than the concentration of Ag(I). The resin with 3-morpholinopropylamine groups was characterized by high selectivity towards Ag(I) in the presence of Co(II) chloro complexes. The value of $a_{sel.}$ is 148.

Based on the literature data (Marhol, 1982), it can be concluded that quantitative separation of the ions is achieved when the corresponding values of the selectivity coefficients comprise 10-30 at least. Thus, polymers with 4-tert-butylpyridine, pyrrolidine and 3-morpholinopropylamine are advanced materials for selective removal of Ag(I) ions from Ag(I)-Cu(II)-Pb(II)-Co(II)-Ni(II)-Zn(II) multicomponent system (Table 8).

The S-bearing corn stalks (OCS-ET-TU) can be used as the adsorbent to selective recover Ag(I) from industrial nickel electrolyte. The maximum adsorption capacity of $AgCl_4^{3-}$ was 3.06 mg/g in the nickel electrolyte, but the other competing metal ions could not be adsorbed onto the OCS-ET-TU (Li et al., 2018).

The 2-MBI (2-mercaptobenzimidazole)-chitosan sorbent has been used to recover precious metals (Ag, Au, Pd) from acid leachate. This material is characterized by its high potential to recover silver even at low metal concentrations from very complex solutions containing a large collection of base metals (Cu, Al, Fe, Sn, Pb, Ni, Zn; at large molar excess, ~67 times) (Elwakeel et al., 2021).

The 2-mercapto-1-methylimidazole resin and guanylthiourea resin were very selective towards Ag(I) in relation to Co(II), Ni(II) and Zn(II) in real solution. The chloride complexes of Co(II), Ni(II), and Zn(II) were not sorbed by these sorbents (Pilśniak-Rabiega and Wolska 2020).

The diethylenetriamine resin and 1,2-dimethylimidazole resin were selective towards Ag(I) in relation to Pb(II), Ni(II), Co(II) and Zn(II) from real chloride leach (Pilśniak-Rabiega et al., 2019).

It could be concluded from these studies that a selective sorption of Ag(I) on functional polymer resins (I-III) from real solutions containing Cu(II), Pb(II), Co(II), Ni(II) and Zn(II), made these materials potentially useful in the recovery of Ag from various sources such as ores, wastewater and jewellery scraps.

4. Conclusions

- Microwave modification of VBC/DVB copolymers with 4-tert-butylpyridine, pyrrolidine, and 3-morpholinopropylamine is an effective method of functional polymers preparation. The best result of the introduction of heterocyclic ligands into the polymer matrix was obtained using pyrrolidine.
- Sorbents are useful for the recovery of Ag(I) from synthetic chloride solutions and show the best sorption properties towards Ag(I) from a solution containing 4.00 mol of NaCl/dm^3 and 0.100 mol of HCl/dm^3.

- The maximum sorption capacity of Ag(I) obtained by that of the Dubinin-Radushkevich isotherm model is 120.4, 131.6, and 85.2 [mg Ag/g resin] for resins I, II and III, respectively.
- The uptake of Ag(I) on sorbents fits well to pseudo-first-order model.
- The loaded resins can be regenerated with 1.0% potassium cyanide solution in 0.50% hydrogen peroxide solution at elevated temperature (50°C).
- All resins retained their capacity towards Ag(I) in five consecutive sorption/desorption cycles.
- Resins are selective towards Ag(I) in relation to Cu(II), Pb(II), Co(II), Ni(II), and Zn(II) in real chloride solution.

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