

## Removal of silver from chloride solutions using new polymer materials

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**Abstract:** This work presents the synthesis of polymer resins with heterocyclic functional groups, that is, N-(3-aminopropyl)-2-pipecoline, N-(3-aminopropyl)-2-pyrrolidinone, and trans-1,4-diaminocyclohexane for the recovery of Ag(I) from chloride solutions. The modification yield was 69.2, 74.6 and 88.3%, respectively. The best Ag(I) sorption was achieved from synthetic and real chloride solutions in the case of trans-1,4-diaminocyclohexane resin (sorption was 26.8 and 21.5 mg/g, respectively). The sorption kinetic data were well fitted to the pseudo-first-order kinetic model. The maximum sorption capacity of Ag(I) is 105.4, 117.8 and 130.7 mg Ag(I)/g for N-(3-aminopropyl)-2-pipecoline resin, N-(3-aminopropyl)-2-pyrrolidinone resin and trans-1,4-diaminocyclohexane resin, respectively. The trans-1,4-diaminocyclohexane modified resin was very selective towards Ag(I) compared to Cu(II), Pb(II), and Zn(II) from the real chloride leaching solution. The N-(3-aminopropyl)-2-pipecoline and N-(3-aminopropyl)-2-pyrrolidinone resins showed high preferences for Ag(I) over Pb(II) in real solution. These results indicated that the polymers can be applied in the recovery of Ag(I).

**Keywords:** synthesis, polymer resins, sorption, desorption, selectivity, chloride solutions

### 1. Introduction

The properties of silver, such as corrosion resistance, thermal and electrical conductance, and antibacterial properties, have attracted the electronics, photography, photonics, industrial catalysis, jewellery, and pharmaceutical industries.

The principal sources of silver are its native state and sulphide and carbonaceous refractory ores. It is commonly found in association with gold, copper, zinc, and lead deposits. Recently, the recovery of secondary silver from waste printed circuit boards (PCBs), solar cell industries, spent catalysts, anode slime, and scraps of plasma TV monitors is being investigated.

Many studies are focused on the development of hydrometallurgical techniques for the recovery of silver from ores, industrial waste, waste electrical and electronic equipment, or jewellery (Mishra et al., 2021; Vlasopoulos et al., 2023). 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. The majority of silver is obtained from ores using alkaline cyanide leaching, but this process is not ideal on account of its toxicity, low leaching rate, and its inefficiency in the treatment of refractory ores. Other leaching processes utilizing thiosulfate, acidified thiourea, hydrochloric acid, and ammonia solutions have also been studied, and some of these processes have found applications in the industry. Chloride leaching has several advantages due to the higher dissolution rate of silver, the low price of leaching reagents, and its non-polluting character (Muscetta et al., 2023). 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).

Different methodologies are proposed for the effective recovery of silver from solutions after leaching of low-grade ores or secondary raw materials, such as cementation, chemical precipitation, membrane processes, solvent extraction, adsorption, and ion exchange.

At present, among the methods for obtaining silver from produced spent solutions 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.

The thiomorpholine modified resin is characterized by a high affinity to Ag(I) from chloride solution (Piłśniak-Rabiega and Wolska, 2022). The maximum sorption capacity of Ag(I) was approximately 1.67 mmol/g. Two magnetic chitosan microparticle (MC) sorbents bearing pyrimidine derivatives (trione or trithione groups for MC-PYO and MC-PYS, respectively) were successfully applied to recover Ag(I) from acidic leachate of photographic waste films (Hamza et al., 2022). Metal removal was enhanced at pH 5.2. MC-PYS was more efficient and selective than MC-PYO at pH 2.2. The sorption capacity of Ag(I) reached 0.82 mmol/g for MC-PYS and 0.70 mmol/g for MC-PYO. The sulfur derivative (trithione-based sorbent) showed a more attractive sorption performance in terms of both sorption capacity and selectivity. The sorbents are very promising for the recovery of silver from complex solutions. The grafting of 2-mercaptobenzimidazole on chitosan microparticles and the sonication treatment allowed the development of highly selective sorbents for the recovery of Ag(I) from synthetic solution and pregnant leach liquor containing Au, Pd, Cu, Al, Fe, Sn, Pb, Ni, and Zn. (Elwakeel et al., 2021). The maximum sorption capacity (up to 3.04 mmol Ag(I)/g) was reached for the non-magnetic sorbent with sonication at the higher frequency. Functional polymers containing heterocyclic ligands, i.e., with 4-tert-butylpyridine, pyrrolidine, and 3-morpholinopropylamine were used for the removal of Ag(I) from synthetic and real chloride solutions (Piłśniak-Rabiega and Wolska, 2021). The best sorption capacity towards Ag(I) from the multicomponent solution showed pyrrolidine resin (sorption was 0.15 mmol/g). The sulfur-containing polymeric sorbents were selective for Ag(I) from chloride solutions (Piłśniak-Rabiega and Wolska, 2020). The resin with guanylthiourea groups (Resin II) showed a greater affinity for Ag(I) relative to the resin modified with 2-mercapto-1-methylimidazole (Resin I). The Ag(I) sorption for Resins I and II was 0.052 and 0.080 mmol/g, respectively. The sorbents were selective for Ag(I) in real chloride solution and did not sorb chloride complexes of Co(II), Ni(II), and Zn(II). Sorbents with imidazole ligands were highly selective for Ag(I) in synthetic chloride solution and did not sorb chloride complexes of Cu(II) (Piłśniak-Rabiega et al., 2019). The highest sorption of Ag(I), 0.18 mg/g, was reached in the case of 1-methylimidazole resin. The corn stalk-based adsorbent (OCS-ET-TU) modified by epithiochlorohydrine and thiourea had a strong adsorption capacity and selectivity to  $\text{AgCl}_4^{3-}$  in industrial nickel electrolyte. The maximum adsorption capacity of Ag(I) was 0.028 mol/g, but the other competing metal ions (Ni(II), Cu(II)) could not be adsorbed onto the OCS-ET-TU (Li et al., 2018). Thiourea-immobilized polystyrene sorbent (TA-PS) has been reported to exhibit high a Ag(I) sorption capacity (1.76 mmol/g) in the aqueous phase and high selectivity to alkaline and alkaline earth metal ions (Yun et al., 2018). The recovery of Ag(I) from aqueous solutions was studied using magnetic resin derived from chemically modified chitosan and chitosan resin modified with ethylenediamine and 3-amino-1,2,4-triazole-5-thiol. The adsorption capacity of Ag(I) was 2.10 and 1.13 mmol/g, respectively (Donia et al., 2007; Elwakeel et al., 2013).

The aim of this work is to present the synthesis of novel polymer resins bearing heterocyclic functional groups. A microwave method for the preparation of a new polymers was presented. The application of the obtained materials for the recovery of Ag(I) from single and multicomponent chloride solutions was also investigated. The polymers studied showed high efficiency and selectivity toward Ag(I) ions. Sorption isotherms, kinetics, and silver desorption have been also studied.

## 2. Materials and methods

### 2.1. Chemical reagents

The chemicals were Sigma-Aldrich and POCH products. A synthetic solution of Ag(I) was prepared by dissolving a known amount of silver nitrate in a chloride solution (4.00 mol/dm<sup>3</sup> of NaCl, 0.100 mol/dm<sup>3</sup> of HCl). The concentration of Ag(I) in the synthetic solution was 58.4 mg/dm<sup>3</sup>.

Real chloride leach solution was contained 61.0 mg/dm<sup>3</sup> of Ag(I), 455.0 mg/dm<sup>3</sup> of Cu(II), 4.30·10<sup>3</sup> mg/dm<sup>3</sup> of Pb(II), 17.0 mg/dm<sup>3</sup> of Co(II), 5.05 mg/dm<sup>3</sup> of Ni(II), and 21.0 mg/dm<sup>3</sup> of Zn(II). Detailed procedures of the chloride leaching solution obtained are presented in (Piłśniak-Rabiega et al., 2019).

## 2.2. Preparation of VBC/DVB copolymer and functional polymers

### 2.2.1. Synthesis of VBC/DVB copolymer

Vinylbenzyl chloride/divinylbenzene copolymer (VBC/DVB) with an expanded gel structure was prepared by suspension polymerization. It contained 2 wt. % of crosslinker. The detailed procedure of synthesis and extraction is presented in (Piłśniak-Rabiega and Wolska, 2021). The VBC/DVB copolymer was dried at room temperature, and the chlorine content was determined.

### 2.2.2. Synthesis of functional polymers

New polymer materials (Resins I-III) were prepared by microwave modification. The VBC/DVB copolymer (2.0 wt. % of DVB) was placed in a Petri dish and swollen with N-(3-aminopropyl)-2-pipecoline, N-(3-aminopropyl)-2-pyrrolidinone or trans-1,4-diaminocyclohexane for 1 h at room temperature. After this time, the reaction mixture was placed in a microwave reactor for 10 min at 100 W. The product was washed with acetone, acetone/distilled water mixture (1:1), distilled water, and then cycled. The beads were placed in the ion exchange column and washed with 1 M HCl, water, 1 M NaOH, and 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. After this time, the polymer was weighted and dried at 100°C for 24 h. After being cooled in a desiccator, the polymer was weighted again. The water regain was determined using Eq. 1:

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

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

### 2.3.2. Nitrogen content

The nitrogen content was determined using the Kjeldahl method after mineralization of the resin sample (about 200 mg) in the concentrated sulfuric acid containing copper sulfate and potassium sulfate (Piłśniak-Rabiega and Wolska, 2021).

### 2.3.3. Chlorine content

The chlorine content is determined by mineralization of the polymer sample and determination of the concentration of chloride ions. The chloride ions concentration was determined by Volhard's method (Piłśniak-Rabiega and Wolska, 2021).

### 2.3.4. Infrared spectroscopy analysis

Middle-infrared spectra (4000-400 cm<sup>-1</sup>) 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<sup>-1</sup> with 64 scans collection.

## 2.4. Evaluation of the sorption properties

### 2.4.1. Sorption of metals

The sorption capacity of the resins towards Ag(I), Cu(II), Pb(II) and Zn(II) from the synthetic and the real chloride solutions was determined by contacting the resin samples with 20 cm<sup>3</sup> of the metal ions

solution. In the sorption experiments a metal ions solution containing Ag(I) (58.4 or 61.0 mg/dm<sup>3</sup>), Cu(II) (455.0 mg/dm<sup>3</sup>), Pb(II) (4.30·10<sup>3</sup> mg/dm<sup>3</sup>) and Zn(II) (21.0 mg/dm<sup>3</sup>) was used. The ratio of ligands in the resin to Ag(I) in the solution was set to 10:1. The samples were shaken for 24 h at room temperature (23±2°C). After this time, the solution was separated from the polymer grains and the metal concentration was measured using the atomic absorption technique (AAS) 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<sup>3</sup> of solution after sorption.

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.

#### 2.4.2. Sorption isotherms

Sorption isotherms were determined by contacting various amounts of resin with 20 cm<sup>3</sup> of solution containing 58.4 mg/dm<sup>3</sup> of Ag(I), 4.00 mol/dm<sup>3</sup> of NaCl and 0.100 mol/dm<sup>3</sup> of HCl. The ratio of ligands in the resin to Ag(I) 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(I) was determined by AAS.

#### 2.4.3. Sorption kinetics

For the kinetics of sorption, the identical samples of resin were shaken with 20 cm<sup>3</sup> of solution containing 58.4 mg/dm<sup>3</sup> of Ag(I) in chloride solution (4.00 mol/dm<sup>3</sup> of NaCl, 0.100 mol/dm<sup>3</sup> of HCl) at room temperature. The ratio of ligands in the resin to Ag(I) 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(I) was determined by AAS.

#### 2.4.4. Desorption

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

### 3. Results and discussion

#### 3.1. Synthesis and characterization of functional polymers

The polymer sorbents were prepared by microwave modification of the VBC/DVB (2 wt.% of DVB) copolymer with N-(3-aminopropyl)-2-pipecoline, N-(3-aminopropyl)-2-pyrrolidinone and trans-1,4-diaminocyclohexane.

The VBC/DVB copolymer with expanded gel structure, containing 2 wt.% of DVB, was obtained in the presence of toluene. The capacity of incorporation of vinylbenzyl chloride monomers into the polymer network is determined on the basis of the chlorine content of the copolymer. Elemental analysis gave 5.30 mmol/g of chlorine, which corresponds to 83% yield of VBC incorporation to the polymer network.

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

Table 1. Physicochemical properties of the polymer resins

Resin No.	Water regain [g/g]	Chlorine content [mmol/g]	Nitrogen content [mmol/g]	Yield of modification* [%]
I	0.41±0.01	0.00	4.22±0.02	69.2±1.0
II	0.98±0.01	0.00	5.19±0.02	74.6±1.0
III	1.43±0.01	0.00	5.75±0.02	88.3±1.0

\* calculated from the nitrogen content

On the basis of nitrogen content (Table 1), the yield of chloromethyl group substitution (yield of modification) in vinylbenzyl chloride/divinylbenzene (VBC/DVB) copolymer was calculated. The chloromethyl groups ( $-\text{CH}_2\text{Cl}$ ) present in its structure served as a reactive place for the immobilization of heterocyclic compounds.

The best result of chemical modification was obtained for the trans-1,4-diaminocyclohexane modified resin. Elemental analysis gave 5.75 mmol of N/g, which corresponds to 88.3% yield (Table 1). The N-(3-aminopropyl)-2-pipecoline, N-(3-aminopropyl)-2-pyrrolidinone resins displayed a nitrogen content of 4.22 and 5.19 mmol/g, respectively. This corresponds to 69.2 and 74.6% yield of VBC/DVB polymer modification. The chlorine analysis results confirmed the complete immobilization of functional groups in the polymer matrix. The absence of chlorine and modification efficiency of 69–88% indicate cross-linked chloromethyl groups. The use of microwave modification to immobilize heterocyclic compounds in the polymer network allowed the introduction of functional groups at the level of 50–90% (Piłśniak-Rabiega and Wolska 2020; Piłśniak-Rabiega and Wolska 2021; Piłśniak-Rabiega and Wolska 2022).

The resin with trans-1,4-diaminocyclohexane groups was the most hydrophilic, having water regain equal to 1.43 g of water per 1 g of dry polymer. The presence of amino groups increases the hydrophilicity of the sorbent due to the possibility of forming hydrogen bonds with water. For sorbents I and II, the water regain value is lower due to the presence of long carbon chains of propyl groups. The N-(3-aminopropyl)-2-pyrrolidinone resin shows a higher water regain value than N-(3-aminopropyl)-2-pipecoline resin, because it has in its chemical structure a carbonyl group ( $\text{C}=\text{O}$ ), which is uncharged but polar (contains partly positive and partly negative charges).

The suggested chemical structures of the prepared polymers shown in Fig. 1 were confirmed by FTIR method (see Fig. 2).

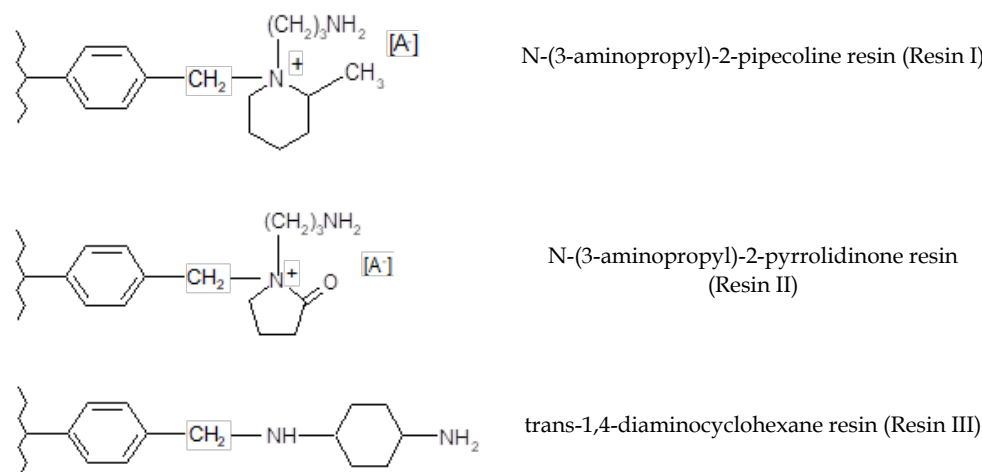


Fig. 1. Proposed structure of the studied polymers

The characteristic peak of the unmodified VBC/DVB copolymer (see Fig. 2) is identified in the spectra, such as the C-Cl bonds in the chloromethyl group at  $1265\text{ cm}^{-1}$  (Yaacoub and Le Perche, 1988; Egawa et al., 1990). This band, should disappear as the modification progresses, indicating the substitution of chlorine atoms in chloromethyl groups by N-(3-aminopropyl)-2-pipecoline, N-(3-aminopropyl)-2-pyrrolidinone and trans-1,4-diaminocyclohexane. The broad band at  $3370\text{ cm}^{-1}$  comes from the hydroxyl groups that form during the hydrolysis of vinylbenzyl chloride to vinylbenzyl alcohol. The distinct bands at  $2924$  and  $2853\text{ cm}^{-1}$  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  $1512\text{--}1422\text{ cm}^{-1}$ , while the absorption bands arising from the non-planar deformation vibrations of the ring occur in the region  $900\text{--}675\text{ cm}^{-1}$ . The appearance of peaks in the range of  $2654\text{--}801\text{ cm}^{-1}$  (Silverstein and Bassler, 1970) confirms the elemental analysis and the successful immobilization of heterocyclic groups on the VBC/DVB copolymer.

Each spectrum shows a valence band of the C-H bond, originating from  $\text{CH}_2$  group, falling between  $2926$  and  $2857\text{ cm}^{-1}$ . Strong bands in the range  $906\text{--}706\text{ cm}^{-1}$  arise from non-flat ring deformational

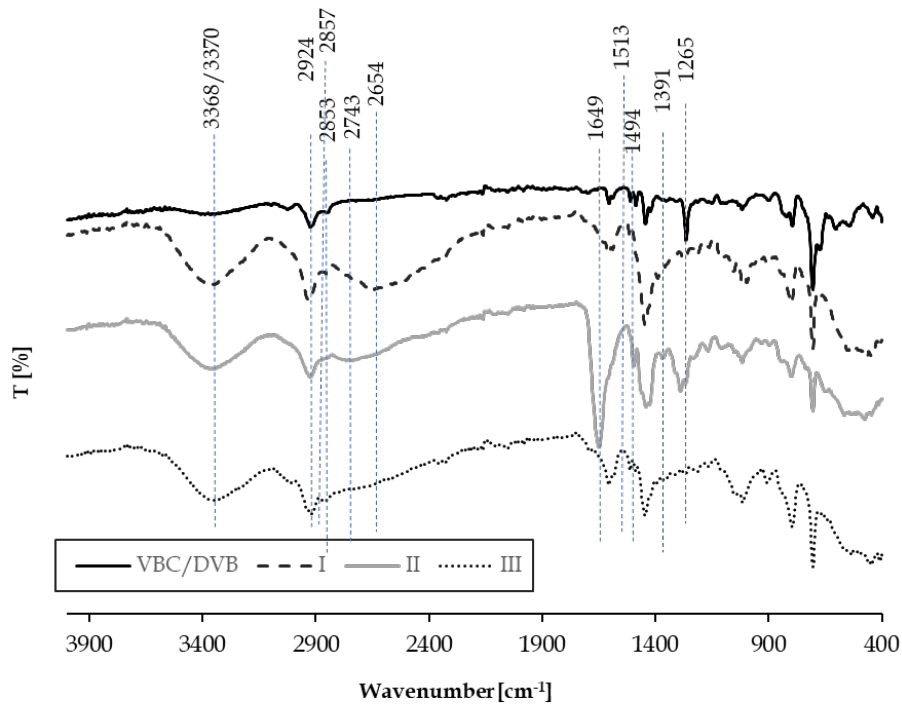


Fig. 2. FTIR spectra of unmodified copolymer VBC/DVB and modified polymers

vibrations, while the peaks with maxima at 1513 and 1494  $\text{cm}^{-1}$  describe conjugated double bonds in the phenyl ring, and 1462–1447  $\text{cm}^{-1}$  deformational shear vibrations of amine-bound  $\text{CH}_2$  groups. Strong and broad bands in the range of 3346–3370  $\text{cm}^{-1}$  are assigned to the presence of the  $\text{NH}_2$  groups in the structure of polymer resins. The absence of absorption at 1265  $\text{cm}^{-1}$  in the spectra of functional polymers confirms the substitution of chlorine atoms by amine ligands.

The FTIR spectrum of N-(3-aminopropyl)-2-pipecoline resin (Resin I) shows a strong stretching valence C-N band at 2654  $\text{cm}^{-1}$  characteristic for piperidine (pipecoline) ring. The deformational symmetric vibration of the  $\text{CH}_3$  group is identified at 1391  $\text{cm}^{-1}$ .

The spectrum of N-(3-aminopropyl)-2-pyrrolidinone resin (Resin II) shows a valence band of C-H bond at 2743  $\text{cm}^{-1}$  and an intense C-N band appearing at 3368  $\text{cm}^{-1}$ . The strong band at 1649  $\text{cm}^{-1}$  is characteristic for valence vibration C=O groups. These bands are characteristic of the pyrrolidinone ring (Silverstein and Bassler, 1970).

A band with a maximum at 1513  $\text{cm}^{-1}$  appeared in the spectrum of trans-1,4-diaminocyclohexane (Resin III), which originates from the deformational vibrations of the NH group. The peak at 1513  $\text{cm}^{-1}$  is attributed to the cyclohexane ring.

### 3.2.2. Sorption mechanism

The polymer sorbents with heterocyclic ligands (Resins I-III) were applied for Ag(I) recovery from synthetic chloride solution (4.0 M NaCl, 0.10 M HCl). The sorption properties were studied under the conditions presented in the Experimental part. The results are shown in Table 2.

Based on the thermodynamics calculation, the silver complex species in the tested solution (4.0 M NaCl, 0.10 M HCl) mainly exist in the form of  $\text{AgCl}_4^{3-}$ , whose proportion is 83%, when  $[\text{Cl}^-]$  is 4.10  $\text{mol}/\text{dm}^3$  (Liu et al., 2010). The proportion of  $\text{AgCl}_2^-$  and  $\text{AgCl}_3^{2-}$  is 3.0% and 14%, respectively.

The best sorption capacity towards Ag(I) is shown by Resin III (26.8 mg Ag(I)/g resin) modified with trans-1,4-diaminocyclohexane. The distribution coefficient ( $K_d$ ) value is 3179 (see Table 2). According to the theory of hard and soft acids and bases, precious metals (Ag, Au, Pt, and Pd) 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 trans-1,4-diaminocyclohexane resin (Resin III) 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 pair of free electrons on the nitrogen atoms. These atoms can coordinate with Ag(I) in chloro complexes. Polymers with N-(3-aminopropyl)-2-pipecoline and N-(3-aminopropyl)-2-pyrrolidinone ligands (Resins I and II, respectively) do not have a free electron pair on the nitrogen atom in the ring, suggesting that Ag(I) coordination is not the mechanism for silver sorption. These materials have a positive charge, so there should be counter ions on their surface, e. g.: Cl<sup>-</sup>, which are present in the chloride solution of Ag(I). Chloride anions can be exchanged for anionic silver complexes, AgCl<sub>4</sub><sup>3-</sup>.

The sorption of AgCl<sub>4</sub><sup>3-</sup> complexes on all functional polymers can also proceed through the mechanism of ion exchange. The -NH<sub>2</sub> amino groups were protonated by hydrochloric acid. These groups capture Ag(I) ions due to electrostatic attraction (Eqs. 2 and 3).

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

Resin No.	Ligand concentration* [mmol/g]	Sorption of Ag(I) [mg Ag(I)/g resin]	Sorption of Ag(I) [mmol Ag(I)/g resin]	Yield of Ag(I) sorption [%]	K <sub>d</sub>
I	2.11±0.01	14.5±1.0	0.134±0.01	63.7±1.0	684
II	2.60±0.01	18.8±1.0	0.174±0.01	67.0±1.0	974
III	2.90±0.01	26.8±1.0	0.248±0.01	85.6±1.0	3179

\* Calculated from nitrogen content in functional groups

C<sub>Ag</sub> = 58.4 mg/ dm<sup>3</sup> (0.5155 mmol/ dm<sup>3</sup>)

C<sub>HCl</sub> = 0.100 mol/ dm<sup>3</sup>, C<sub>NaCl</sub> = 4.00 mol/ dm<sup>3</sup>



P- polymeric matrix.

The concentration of Cl<sup>-</sup> ions in chloride solution was eight thousand times higher than the concentration of Ag(I). The presence of a large excess of chloride anions had a strong influence on the ion exchange and decreased the affinity of the resins towards silver. On the other hand, the small sorption of Ag(I) complexes could be caused by the fact that three ligands participated in the ion exchange of one AgCl<sub>4</sub><sup>3-</sup> complex. This indicates that the coordination of Ag(I) ions is the main sorption mechanism on trans-1,4-diaminocyclohexane modified resin.

Magnetic chitosan microparticles bearing either trione or trithione groups (MC-PYO and MC-PYS, respectively) were tested to recover silver from the complex solution (Hamza et al., 2022). Maximum sorption capacities at pH 6 reach 205 and 248 mg Ag(I)/g for MC-PYO and MC-PYS, respectively. MC-PYO binds silver through binding to N-based carbonyl, hydroxyl, MC-PYS involves sulfur groups in metal binding. The functionalization of chitosan with 2-mercaptobenzimidazole brings to the biopolymer a high affinity for silver (Elwakeel et al., 2021). Sorption capacities are as high as 324 mg Ag(I)/g. The sorption mechanism proceeds mainly through chelation mechanisms following the preference of silver for sulfur groups. However, some complementary binding mechanisms could involve amine groups (by chelation), especially at the highest pH values. Magnetic chelating resin with amine/thio functionality was found efficient towards the recovery of silver from aqueous solutions (Atia et al., 2014). Silver sorption followed two mechanisms, i.e., the coordination mechanism between Ag(I) and nitrogen and sulfur atoms, and the cation exchange mechanism. The maximum uptake capacity showed 669 mg Ag(I)/g.

### 3.2.3. Sorption isotherm studies

During the study of the sorption characteristics of the synthesized resins, the sorption isotherms at room temperature (see Fig. 3) from the Ag(I) solution with a concentration of 58.4 mg/ dm<sup>3</sup> and with a different molar ratio of the ligand to silver ions. From the isotherm curves in Fig. 3, it can be seen that the adsorption capacity for Resin III is the highest, and also the shape of this isotherm is a little different than for the other two materials.

As can be observed, the initial concentration of the ions is an essential driving force to overcome any resistance to mass transfer between the solution and Resins I-III. At a lower concentration of Ag(I), the

solution can interact with the binding sites; therefore, the adsorption capacity increases rapidly with an increase in the initial concentration. At higher concentrations, the adsorption capacity is almost constant as a result of the saturation of the adsorption site. The maximum sorption capacities of Ag(I) for Resins I, II, and III were approximately 100, 120, and 130 mg Ag(I)/g respectively. The adsorption data were described with the Langmuir, Freundlich, and Dubinin-Radushkevich isotherm models. The parameters of the adsorption isotherms along with the coefficient of determination ( $R^2$ ) were calculated and are tabulated in Table 3.

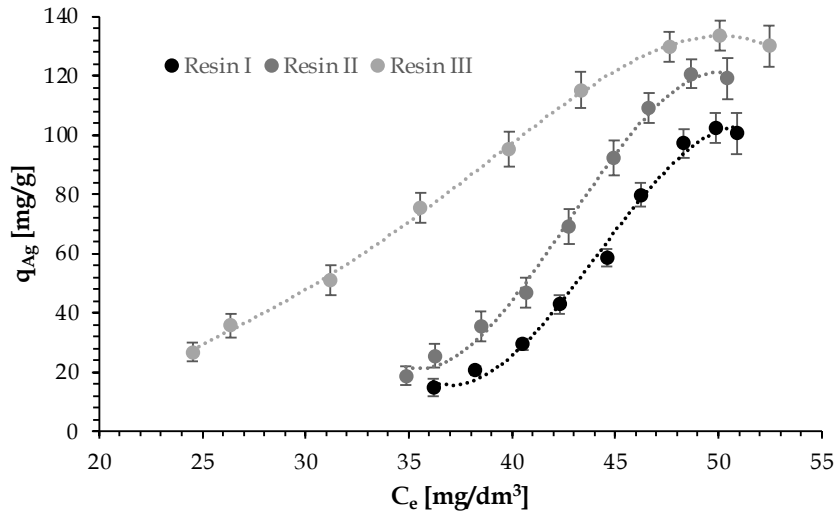


Fig. 3. Sorption isotherms for all resins studied. Samples of resin containing 0.1-10×molar excess of ligand were shaken with 20.0 cm<sup>3</sup> of solution containing 58.4 mg/dm<sup>3</sup> of Ag(I) in chloride solution ( $C_{\text{HCl}} = 0.10 \text{ mol/dm}^3$ ,  $C_{\text{NaCl}} = 4.0 \text{ mol/dm}^3$ ) for 24 h, at  $23 \pm 2^\circ\text{C}$

The Langmuir isotherm is based on the hypothesis that adsorbate molecules form a uniform and finite monolayer on the adsorbent. The non-linear form of this model can be represented according to Eq. (4):

$$q_e = \frac{q_m \cdot b_L \cdot C_e}{1 + b_L \cdot C_e} \quad (4)$$

The linear form of the Langmuir equation can be given as follows (Eq. 5):

$$\frac{1}{q_e} = \frac{1}{q_m b_L C_e} + \frac{1}{q_m} \quad (5)$$

where  $q_e$  (mg/g) is the uptake at equilibrium concentration,  $q_m$  (mg/g) is the maximal uptake,  $C_e$  (mg/dm<sup>3</sup>) is the equilibrium concentration,  $b_L$  (dm<sup>3</sup>/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, Esteves et al. 2022).

Additionally, a separation factor (dimensionless) called the equilibrium or separation parameter ( $R_L$ ) is determined during the analysis, which allows one to determine whether the Langmuir isotherm model is favorable for a given separation process (Eq. 6) (Polowczyk et al., 2016; Esteves et al., 2022):

$$R_L = \frac{1}{1 + b_L C_0} \quad (6)$$

where  $C_0$  is the initial adsorbate concentration [mg/dm<sup>3</sup>].

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 us 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 Ag(I) in the investigated materials. The non-linear regression also confirms that this model is not applicable for all prepared materials (see Fig.4).

The next investigated model was the Freundlich isotherm. This model is commonly adopted to describe non-ideal sorption on highly heterogeneous surfaces that provide adsorption sites of varying



affinities (Esteves et al., 2022). The non-linear form of the model can be represented as described in equation (Eq. 7, Esteves et al., 2022):

$$q_e = aC_e^{1/n} \quad (7)$$

The Freundlich model is assumed as a power function relationship between  $q_e$  and  $C_e$  and is easily applicable when the experimental data are plotted in  $\log q_e$  versus  $\log C_e$  format (Eq. 8) (Cela-Pérez et al., 2011). The Freundlich isotherm is applicable to adsorption processes that occur on heterogenous 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 (Eq. 7) (Polowczyk et al., 2016; Ayawei et al., 2017):

$$\log q_e = \frac{1}{n} \log C_e + \log a \quad (8)$$

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 the 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, the adsorption sites are homogeneous in energy, and no interactions occur between the adsorbed compounds. On the other hand, when the values of the  $1/n$  parameter approach zero, increase the heterogeneous character of the polymer studied. 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 the 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 value of the calculated parameter  $a$  was  $5.9 \times 10^{-9}$ ,  $2.6 \times 10^{-8}$ ,  $2.0 \times 10^{-2}$  for the synthesized Resins I, II and III, respectively. The value of the constant  $n$  for all investigated Resins I, II and III was below 1 and was 0.165, 0.173 and 0.439 respectively, therefore it can be assumed that the sorption of Ag(I) onto all polymers is not favourable. Furthermore, by comparing the  $R^2$  values for the Langmuir and Freundlich models, it can be seen that the second model is a better fit for Ag(I) adsorption onto the synthesized resins. All results of the Langmuir and Freundlich analysis are given in Table 3.

The third investigated sorption model is the Dubinin-Radushkevich isotherm model, which helps to study the interaction between the sorbate and the sorbent (Cela-Pérez et al., 2011). This approach is generally used to distinguish the kind of sorption: the physical or chemical one dominates. The non-linear form of this model can be represented according to Eq. 9 (Ulatowska, 2022):

$$q_e = q_m \exp(-K_{DR} \cdot \varepsilon^2) \quad (9)$$

where  $q_m$  is the maximum adsorption capacity of the material, [mmol/g],  $K_{DR}$  is the Dubinin-Radushkevich constant [ $\text{kJ}^2/\text{mol}^2$ ],  $\varepsilon$  is the Polanyi potential (Eq. 10):

$$\varepsilon = RT \ln\left(1 + \frac{1}{C_e}\right) \quad (10)$$

The linear form of this isotherm can be expressed by Eq. 11:

$$\ln q = \ln q_m - K_{DR} \varepsilon^2 \quad (11)$$

$K_{DR}$  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, where  $E$  is between 8 and 16 kJ/mol, the adsorption process followed by ion-exchange, and for more than 16 kJ/mol it is chemical adsorption. The free energy can be calculated by Eq. 12 (Cela-Pérez et al., 2011; Ulatowska, 2022):

$$E = (2K_{DR})^{-0.5} \quad (12)$$

During this analysis, the free energy values for Resin I were calculated. For the investigated polymer, the value of  $E$  has a value greater than 16 kJ/mol in the case of Resin III and reached the value of 17.6. This means that, in this case, the chemical adsorption is dominated. For Resins I and II, the  $E$  parameter was 10.2 and 9.60 kJ/mol, respectively. This means that in those cases the ion-exchange process is dominated. For Resin III, the value of  $E$  is greater than 16 kJ/mol. The linear coefficient of determination ( $R^2$ ) value closest to 1 ( $> 0.99$ ) was obtained for the Dubinin-Radushkevich isotherm model, and therefore only on the basis of this model the maximum sorption capacity for Resin I was calculated. The maximum sorption capacity of Ag(I) is 105.4, 117.8 and 130.7 mg Ag(I)/g dry resin for Resins I, II and

III, respectively, and these values are close to the experimental capacities obtained during the determination of sorption isotherms. The parameters of the Dubinin-Radushkevich isotherm are given in Table 3.

Table 3. Isotherm constants evaluated for Ag(I) adsorption on Resins I, II, and III (linear analysis)

Resin No.	Langmuir constants			Freundlich constants			Dubinin-Radushkevich constants		
	$R_L$	$q_{max}$ - mg/g(mmol/g)	$R^2$	$a$	$1/n$	$R^2$	E kJ/mol	$q_{max}$ mg/g(mmol/g)	$R^2$
I	na	na	0.921	$5.9 \times 10^{-9}$	6.03	0.983	17.6	105.4 (0.98)	<b>0.991</b>
II	na	na	0.935	$2.6 \times 10^{-8}$	5.75	0.990	10.2	117.8 (1.06)	<b>0.992</b>
III	na	na	0.943	$2.0 \times 10^{-2}$	2.28	0.991	9.60	130.7 (1.21)	<b>0.995</b>

The linear regression method approximates that the scatter of points around the line follows a Gaussian distribution and the standard deviation at every value of  $C_e$ . In reality, this behaviour is impossible with equilibrium isotherm models. The non-linear regression method avoids these types of error, making this technique the most appropriate to estimate the isotherm model parameters. The non-linear regression is a more general method that can be used to estimate models' parameters, and it can be applied even if the isotherm model cannot be linearized. (Nagy et al. 2017). Because of that, the non-linear regression was also performed to find the proper isotherm method. The results of the analysis are given in Fig. 4. During this analysis, the same isotherm models as for linear regression, i.e., Langmuir, Freundlich, and Dubinin-Radushkevich isotherm models were used.

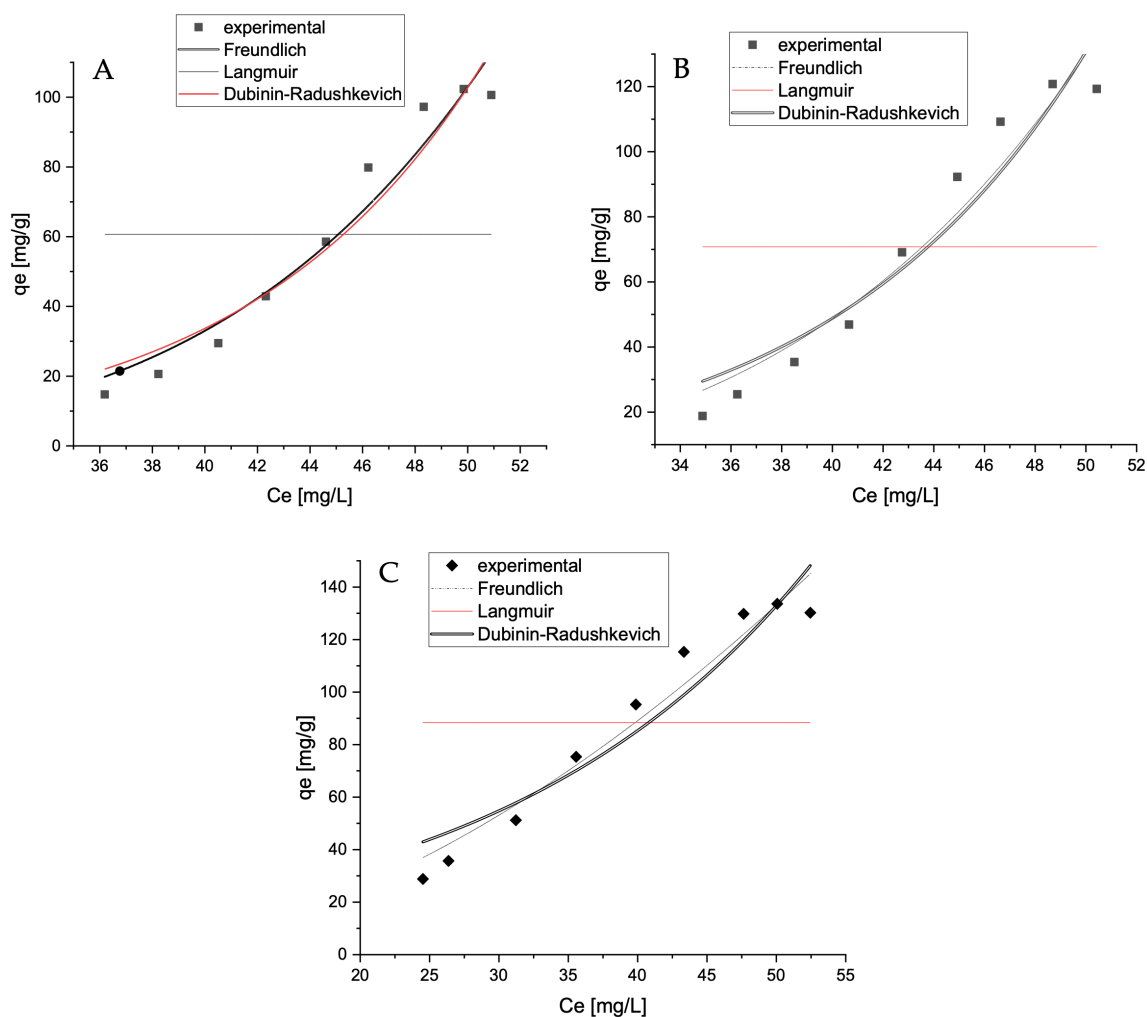


Fig. 4. Non-linear regression analysis by comparison with experimental data for Ag(I) sorption onto synthesized Resin I (A), II (B), and III (C)

This non-linear regression confirmed that the Langmuir isotherm model is also inadequate to describe the sorption process of Ag(I) on all investigated materials. In addition, non-linear regression has shown that the other two models analyzed the sorption of silver quite well. The parameters for the models studied during non-linear regression are given in Table 4. In the case of Langmuir parameters, the results of  $R^2$  and  $R_L$  were unreal because and it was not possible to provide these values, only  $q_{max}$  values are given, but as can be seen the errors are very large. As can be observed, the maximum sorption capacities calculated using the non-linear regression with the Dubinin-Radushkevich model were a little higher for Resins II and III compared to those obtained using the linear analysis. For Resin I, this value was lower than the  $q_{max}$  calculated from the linear regression.

Table 4. Adsorption isotherm models and their coefficients calculated using non-linear regression analysis for Ag(I) onto synthesized Resins I, II, and III

Resin No.	Langmuir constants			Freundlich constants		Dubinin-Radushkevich constants		
	$R_L$	$q_{max}$	$R^2$	$a$	$n$	$R^2$	$q_{max}$	$R^2$
	-	mg/g	-			-	mg/g	-
I	na	60.68±111.88	na	$(2.3±4.9)×10^{-7}$	5.10±0.55	<b>0.953</b>	87.62±10.2	0.939
II	na	70.80±127.74	na	$(4.6±8.6)×10^{-6}$	4.40±0.51	<b>0.943</b>	144.8±15.3	0.924
III	na	na	na	$(1.1±0.8)×10^{-1}$	1.80±0.19	<b>0.956</b>	170.5±14.3	0.927

The maximum sorption capacity of  $AgCl_4^{3-}$  obtained by the Dubinin-Radushkevich isotherm model is 151.3, 120.4, 131.6, and 85.2 [mg Ag(I)/g] for functional polymers containing heterocyclic ligands, i.e., thiomorpholine, 4-tert-butylpyridine, pyrrolidine, and 3-morpholinopropylamine ligands, respectively (Piłśniak-Rabiega and Wolska, 2021; Piłśniak-Rabiega and Wolska, 2022). The OCS-ET-TU adsorbent based on a natural corn stalk modified by grafting epithiochlorohydrine and thiourea could selectively adsorb  $AgCl_4^{3-}$  from the Ag(I) single and Ag(I)-Cu(II)-Ni(II) simulate nickel electrolyte system (Li et al., 2018). The maximum adsorption capacity obtained from the Langmuir model was 107.9 mg/g in the single system and 79.94 mg/g in the ternary system. Xiong (Xiong et al., 2016) investigated the adsorption of  $AgCl_4^{3-}$  from a simulated nickel electrolyte using a corn stalk-based adsorbent modified by ammonia-thiosemicarbazide. The maximum adsorption capacity of the Ag(I) in single and Ag(I)-Cu(II)-Ni(II) ternary systems was obtained and calculated as 153.5 and 46.69 mg/g, respectively. The best fit was characterized by the Langmuir model for the adsorption of  $AgCl_4^{3-}$  on the biomaterial.

It was found that the polymeric materials obtained showed similar sorption capacity with respect to the sorbents presented in the literature (Table 5).

### 3.2.4. Sorption kinetics studies

The effect of contact time on the removal of Ag(I) from the solution with the synthesized resins was studied at room temperature and at an initial concentration of 58.4 mg Ag(I)/dm<sup>3</sup>. The dependence of sorption capacity and contact time is shown in Fig. 5. It can be seen that the removal of Ag(I) from the solution by the investigated polymers increased with the contact time until the equilibrium was attained. The uptake of silver on used adsorbents is the best for Resin III, and the worst for Resin I (see Fig. 5). Moreover, the rate of uptake of Ag(I) is the slowest for Resin I, the 50% adsorption in completed in 9 hours, while for Resins II and III in about 5 hours. Thus, the process for Resin I is about 2 times slower than for the other two materials. The experiments showed that the equilibrium was reached only after about 24 hours for Resin III and after 36 hours for Resins I and II.

The rate-controlling step of the adsorption of Ag(I) ions was determined using five kinetic models. Sorption kinetics gives information on 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 the bulk solution (Haq et al., 2020). To obtain all of this information, the sorption of Ag(I) in the first stage of the analysis was fitted to the diffusion model using the second *Fick's law* (Eq. 13 and 14), 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).

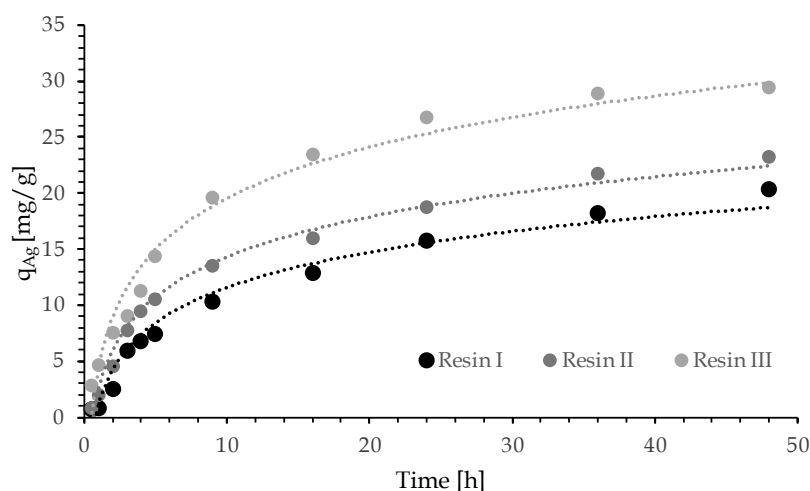


Fig. 5. Kinetics of Ag(I) sorption on polymer resins studied. Samples of resin containing 0.01 mmol of ligand were contacted with 20.0 cm<sup>3</sup> of solution containing 58.4 mg/dm<sup>3</sup> of Ag(I) in chloride solution ( $C_{\text{HCl}} = 0.10$  mol/dm<sup>3</sup>,  $C_{\text{NaCl}} = 4.0$  mol/dm<sup>3</sup>) at 23±2°C and the concentration checked in specified time intervals

Table 5. Adsorption capacity of Ag(I) for different sorbents

Sorbent	Temperature [°C]	pH	$q_m$ [mmol/g]	Ref.
Thiomorpholine resin	23	1.0	1.40	Piłśniak-Rabiega and Wolska, 2022
4-tertbutylpyridine resin			1.11	Piłśniak-Rabiega and Wolska, 2021
Pyrrolidine resin	23	1.0	1.21	
3-morpholinopropylamine resin			0.787	
2-MBI chitosan	25	6.8	1.96	Elwakeel et al., 2021
2-MBI magnetic chitosan			2.02	
2-mercapto-1-methylimidazole resin			0.180	Piłśniak-Rabiega and Wolska, 2020
guanylthiourea resin	23	1.0	1.12	
Thiourea-immobilized polystyrene (TA-PS)	25	6.0	1.76	Yun et al., 2018
OCS-ET-TU adsorbent	30	1.0	1.00	Li et al., 2018
TSC-NH3-OCS adsorbent	30	1.0	1.42	Xiong et al., 2016
thiourea-modified chitosan resin	25	4.0	3.77	Wang et al., 2010
thiourea-formaldehyde chelating resin (TF)	25	3.0-5.0	0.539	Kirci et al., 2009
N-(3-aminopropyl)-2-pipecoline resin			0.980	
N-(3-aminopropyl)-2-pyrrolidinone resin	23	1.0	1.06	This work
trans-1,4-diaminocyclohexane resin			1.21	

$$k_a t = -\ln\left(1 - \frac{q_t}{q_e}\right) \quad (13)$$

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

$$k_b t = -\ln\left(1 - \left(\frac{q_t}{q_e}\right)^2\right) \quad (14)$$

where  $k_b$  is the sorption rate constant (1/min),  $q_e$  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 6 gives the slope values, the linear correlation coefficients and the calculated values of  $k_a$  and  $k_b$ . Analyses of  $k_a$  and  $k_b$  can show which of the processes of sorption is faster for the synthesized polymers. The analysis of the coefficients of determination can show what kind of diffusion mostly controlled the process. In the case of all investigated resins, the film diffusion controls the process mostly, but the differences in the  $R^2$  values are not so significant, because of that it was decided to use a different model that would also allow one to determine which stage of the sorption process is the decisive one.

Table 6. The second Fick's law parameters calculated for the investigated resins

Sample	Film diffusion		Particle diffusion	
	$k_a$ 1/min	$R^2$	$k_b$ 1/min	$R^2$
<b>Resin I</b>	0.0010	<b>0.987</b>	0.0007	0.984
<b>Resin II</b>	0.0012	<b>0.988</b>	0.0007	0.983
<b>Resin III</b>	0.0020	<b>0.995</b>	0.0015	0.986

The limiting step of the Ag(I) adsorption process on synthesized polymeric resin was also determined using the Weber-Morris intraparticle diffusion model (Ulatowska 2022). The equation of this model is described by Eq. 15. The kinetics of intraparticle diffusion is illustrated in Fig. 6 as the relationship of  $q_t=f(t^{0.5})$ .

$$q_t = k_{WM} \cdot t^{0.5} + B \quad (15)$$

where  $k_{WM}$  is the intraparticle diffusion rate constant (mg/g min<sup>0.5</sup>) calculated from the plot  $q_t=f(t^{0.5})$ .

If adsorption occurred solely by intraparticle diffusion, then this relation ( $q_t=f(t^{0.5})$ ) would be rectilinear throughout, and the curve would pass through the origin of the coordinate system. The lack of linearity as in our case (see Fig. 6 and the broken line on the graph) indicates that several processes are involved in the adsorption process and not only intraparticle diffusion. The first section of this curve corresponds to the adsorption on the external surface of the adsorbent grain or the immediate adsorption stage. The second section corresponds to a gentle and gradual adsorption stage, where intraparticle diffusion is the stage that controls the rate of the entire adsorption process (Ulatowska, 2022). As shown in Fig. 6, none of the curves pass through the origin of the coordinate system, suggesting that the intraparticle diffusion is not the only limiting step in the process of silver adsorption from the solution to the synthesized resin. Furthermore, the dependence of  $q_t$  on  $t^{0.5}$  over the whole-time range was not rectilinear, clearly indicating that the adsorption rate depends not only on the intraparticle diffusion. The calculated  $k_{WM}$  values for individual stages are given in Table 7. The analysis of the results obtained suggests that the limiting stage for the Ag(I) adsorption process on all resins studied is the first stage, the  $k_{WM1}$  is the lowest, and indicates that this stage affects the whole process of sorption. This intraparticle diffusion model also confirmed the previous considerations that the adsorption on the external surface of grains is this decisive stage and influences the effectiveness of the sorption process.

Table 7. The Weber-Moris intraparticle diffusion model parameters calculated for the resins studied

Model	Parameter	Unit	Resin I	Resin II	Resin III
Intraparticle diffusion	$k_{WM1}$	mg/g min <sup>0.5</sup>	<b>0.18</b>	<b>0.33</b>	<b>0.33</b>
	$k_{WM2}$	mg/g min <sup>0.5</sup>	1.40	0.94	1.07
	$k_{WM2}$	mg/g min <sup>0.5</sup>	0.36	0.41	0.66

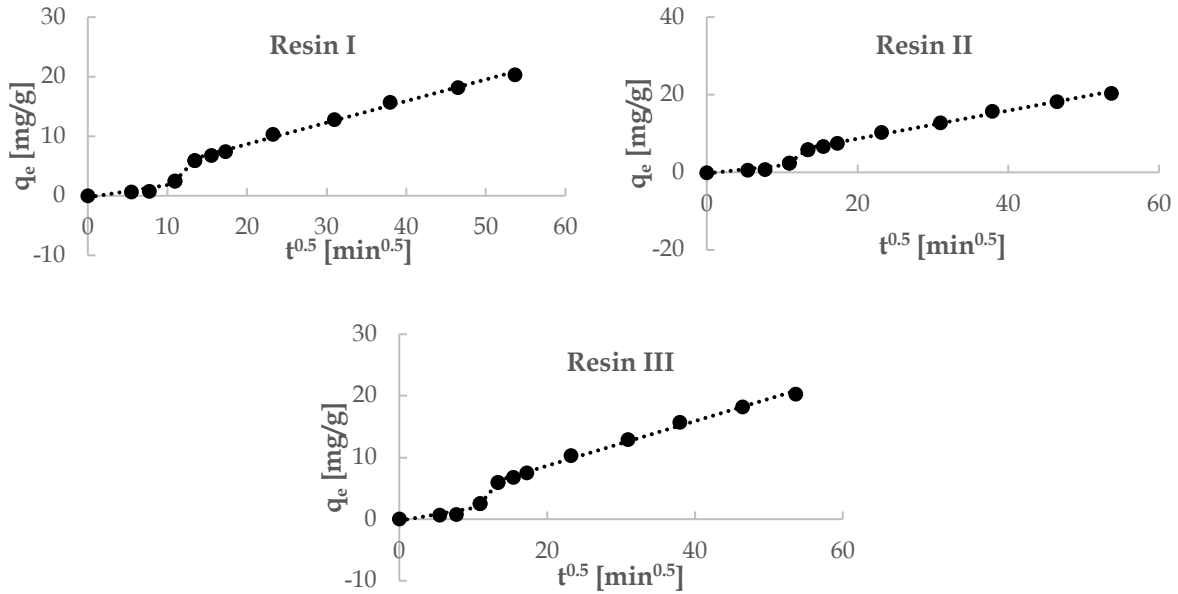


Fig. 6. Intraparticle diffusion model of Ag(I) adsorption on polymer resins

To better understand the adsorption kinetics of Ag(I) and to predict the mechanism involved in the sorption process, several different kinetic models were 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; Lagergren, 1898, Liu et al., 2011, Santander et al., 2014). The models are expressed as follows; the pseudo-first-order model describes the relationship between the sorption rate and the equilibrium time. This model can be described by Eq. 16 (Kabay et al., 2007):

$$\frac{dq}{dt} = k_1(q_e - q_t) \quad (16)$$

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

Integrating Eq. 16 with respect to the boundary conditions  $q=0$  at  $t=0$ , and  $q=q_t$  at  $t=t$ , one obtains Eq. 17:

$$\log(q_e - q_t) = \log(q_e) - \frac{k_1 t}{2.303} \quad (17)$$

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

The kinetic data can also be analyzed by means of pseudo-second-order kinetics. According to this model, the sorption behaviour is controlled by the chemisorption process occurring either electronic sharing or electronic exchange. The non-linear form of this model is represented by Eq. 18 (Kabay et al., 2007; Haq et al., 2020):

$$\frac{dq}{qt} = k_2(q_e - q_t)^2 \quad (18)$$

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  $t$  respectively. Varying variables in Eq. 18, one gets from (Eq. 19):

$$\frac{dq}{(q_e - q_t)} = k_2 dt \quad (19)$$

and integrating Eq. 19 for the boundary conditions  $q=0$  at  $t=0$ , and  $q=q_t$  at  $t=t$ , one obtains the final form (Eq. 20):

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (20)$$

A plot  $t/q$  versus  $t$  gives the value of the constants  $k_2$  (g/mg min). During these analyzes of both models it is also possible to calculate  $q_e$  (mg/g).

The experimental data were fitted with Eq. 17 and 20 that served for the calculation of the characteristic parameters for each model. Linear regression analysis (coefficient of determination ( $R^2$ )) was used to analyse the linear form of the kinetic models. Kinetic constants  $k_1$  and  $k_2$  were determined using the slope and intercept values of the linear plots (see Table 8) which presented pseudo-first-order and pseudo-second-order rate constants, calculated and experimental  $q_e$  values for silver sorption on the synthesized resin. The results of the kinetic analysis are shown in Table 8.

Table 8. Pseudo-first-order and pseudo-second-order rate constants, calculated and experimental  $q_{max}$  values for Ag(I) onto synthesized polymeric resins

Resin No.	$q_{exp}$ mg/g	Pseudo-first			Pseudo-second		
		$k_1$ 1/min	$R^2$	$q_{max1}$ mg/g	$k_2$ g/mg min	$R^2$	$q_{max2}$ mg/g
I	20.33	0.0009	<b>0.989</b>	18.75	0.00059	0.567	41.32
II	23.22	0.0012	<b>0.988</b>	20.58	0.00246	0.924	20.16
III	29.42	<b>0.0019</b>	<b>0.995</b>	27.52	0.00430	0.960	15.24

Based on the high values of the coefficient of determination ( $R^2$ ), it can be concluded that the experimental data obtained during the study of the kinetic of silver adsorption on synthesized resin are better described by the pseudo-first-order model than by the pseudo-second-order model. Additionally, the calculated values of the adsorption capacity from the pseudo-first-order model ( $q_{max1}$ ) are closer to the experimental values ( $q_{exp}$ ) than from the pseudo-second-order model ( $q_{max2}$ ), thus indicating the physical nature of the Ag(I) sorption process in the systems studied rather than the chemical one (see Table 6). Additionally, the value of  $k_1$  parameter is the highest for Resin III and the lowest for Resins I, and this can also confirm a faster Ag(I) sorption process on Resin III than on the other two materials.

The recovery of Ag(I) from chloride solution was studied using sorbents containing heterocyclic functional groups (Piłśniak-Rabiega and Wolska, 2020; Piłśniak-Rabiega and Wolska, 2021; Piłśniak-Rabiega and Wolska, 2022). Kinetic studies indicated that the adsorption reaction follows the pseudo-first-order kinetics. Modified melamine resin was obtained through treatment with thiourea and was tested for selective separation between Cu(II) and Ag(I) from their binary mixtures (Abd El-Ghaffar et al., 2009). Kinetic studies indicated that the adsorption reaction of Ag(I) on the sorbent is perfectly fit pseudo-first-order model. The adsorption of Ag(I) from an aqueous solution on the chelating polymer derived from 3-amino-1,2,4-triazole-5-thiol and glutaraldehyde was also perfectly fit the pseudo-first-order model (Abd El-Ghaffar et al., 2009).

### 3.2.5. Desorption and resin's stability in cycles of sorption/desorption

The Ag(I) elution from the sorbents at room and elevated temperatures (23 and 50°C) was studied. For this purpose, the following eluents were used: 1.0% potassium cyanide solution, 1.0% potassium cyanide solution in 0.50% hydrogen peroxide solution, 0.50% thiourea solution in 0.1 M  $H_2SO_4$  and 0.50 M sodium hydroxide solution. The results are presented in Table 9.

Table 9. Elution of Ag(I) from functional polymers (time: 24 h, T: 23±2 and 50±2 °C)

Eluent	Temp. 23°C			Temp. 50°C		
	%Elution			%Elution		
	I	II	III	I	II	III
1.0 % KCN	25.4±1.0	28.6±1.0	41.2±1.0	41.1±1.0	46.2±1.0	58.3±1.0
1.0% KCN + 0.50% $H_2O_2$	45.4±1.0	50.3±1.0	69.8±1.0	67.6±1.0	69.5±1.0	86.3±1.0
0.50 mol/dm <sup>3</sup> of CS(NH <sub>2</sub> ) <sub>2</sub> + 0.10 mol/dm <sup>3</sup> of $H_2SO_4$	10.6±1.0	15.9±1.0	22.3±1.0	16.4±1.0	19.2±1.0	29.6±1.0
0.50 mol/dm <sup>3</sup> of NaOH	9.76±1.0	10.2±1.0	16.4±1.0	13.3±1.0	14.8±1.0	19.5±1.0

The desorption efficiency of Ag(I) using the selected eluents is higher at elevated temperature than at room temperature. The best eluent for silver adsorbed on polymers (Resins I-III) 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  $\text{Ag}(\text{CN})_4^{3-}$  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  $\text{Ag}(\text{CN})_4^{3-}$  and  $\text{AgCl}_4^{3-}$  are 22.3 and 5.30, respectively (Högfeltdt, 1982). On the other hand, silver can be present on the surface of resins as highly disintegrated metallic silver, which is weakly connected to the polymer and can be better eluted by 1.0% KCN under oxidizing conditions.

To verify the stability of the resins, five cycles of Ag(I) sorption from the chloride solution (58.4 mg Ag(I)/dm<sup>3</sup>, 4.00 mol/dm<sup>3</sup> of NaCl, 0.100 mol/dm<sup>3</sup> of HCl) and desorption with 1.0% KCN in 0.50% H<sub>2</sub>O<sub>2</sub> were performed. Sorption and elution were carried out at room temperature (23°C). 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<sub>2</sub>O<sub>2</sub>. After desorption, the same resin sample was subjected again to Ag(I) sorption. Five cycles of sorption and desorption were performed.

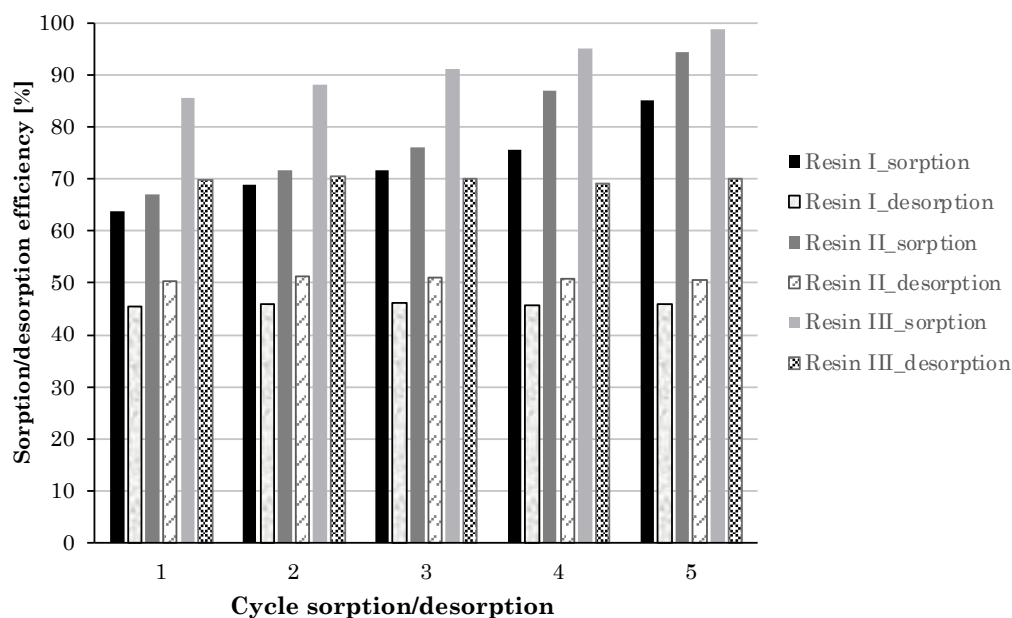


Fig. 7. Resin's stability in cycles of sorption/desorption (time: 24 h, T: 23±2°C)

Based on the results presented in Fig. 7, it can be concluded that the sorption capacity of Ag(I) increased, the sorption capacity was 63.7% (14.5 mg/g), 67.0% (18.8 mg/g), and 85.6% (26.8 mg/g) in the first cycle, in the case of 2–5 cycles was 69.0–85.1% (15.7–19.4 mg/g), 71.6–94.5% (21.1–26.6 mg/g) and 88.2–98.8% (27.6–30.9 mg/g) for Resins I, II and III, respectively. The desorption efficiency values were stable over cycles 1–5 for each sorbent and were 45.4–46.0% (Resin I), 50.3–51.2% (Resin II), and 69.2–70.5% (Resin III). The sorbents were not fully regenerated; nonetheless, sorption of Ag(I) was effective. The better Ag(I) sorption on the synthesized resins in 2–5 cycles than in the first cycle can be explained by the presence of cyanide anions on the polymer surface after the first desorption and the formation of  $\text{Ag}(\text{CN})_4^{3-}$  complexes by ligand exchange mechanism. Cyano complexes of Ag(I) are more stable than chloro complexes of Ag(I) (Högfeltdt, 1982).

The functional polymers with heterocyclic ligands, i.e., thiomorpholine, 4-tertbutylpyridine, pyrrolidine, and 3-morpholino-propylamine, were stable in subsequent sorption and desorption processes of Ag(I) ions from their surface (Piłśniak-Rabiega and Wolska, 2021, Piłśniak-Rabiega and Wolska, 2022). The sorption capacity of functional polymers for Ag(I) ions increased significantly after the first adsorption-desorption cycle (by 49–64% for the second cycle). The desorption efficiency in 1–5 cycles was 62–97%. The functionalized sorbents, MC-PYO and MC-PYS, have a greater stability in



sorption performance at recycling, while using 0.3 M HNO solutions for (total) elution of silver-loaded materials (Hamza et al., 2022). The 2-MBI-chitosan sorbent showed sorption and desorption stability in five consecutive recycling cycles (Elwakeel et al., 2021). Desorption was highly efficient (greater than 98%) and stable along a minimum of five cycles, while sorption slightly decreases with recycling (about 13–16%) at the fifth cycle. The 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<sup>+</sup> sorption efficiency of thiourea-immobilized polystyrene (TA-PS) nanoparticles was not essentially decreased after three successive sorption-desorption cycles (decreased by only ~2%) (Yun et al., 2018). TA-PS nanoparticles exhibited a high Ag<sup>+</sup> sorption capacity and were very stable under highly acidic conditions (1.0 N HCl).

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

The functional polymers modified by N-(3-aminopropyl)-2-pipecoline, N-(3-aminopropyl)-2-pyrrolidinone and trans-1,4-diaminocyclohexane are characterized by a high affinity to Ag(I) from synthetic solutions. Therefore, these materials were used to recover Ag(I) from the real chloride leaching solution. This solution was prepared by chloride leaching of a solid residue after atmospheric leaching in sulfuric acid of copper concentrate (Piłśniak-Rabiega et al., 2019). Table 10 shows the effect of foreign ions on the sorption of Ag(I).

Table 10. Sorption of Ag(I), Cu(II), Pb(II), and Zn(II) from real chloride leach solution ( $C_{Ag} = 61.0 \text{ mg/dm}^3$  (0.565 mmol/dm<sup>3</sup>),  $C_{Cu} = 455 \text{ mg/dm}^3$  (7.16 mmol/dm<sup>3</sup>),  $C_{Pb} = 4.30 \cdot 10^3 \text{ mg/dm}^3$  (20.75 mmol/dm<sup>3</sup>),  $C_{Zn} = 21.0 \text{ mg/dm}^3$  (0.321 mmol/dm<sup>3</sup>),  $C_{HCl} = 0.100 \text{ mol/dm}^3$ ,  $C_{NaCl} = 4.00 \text{ mol/dm}^3$ , time: 24 h, T: 23±2°C)

Resin No.		I	II	III
Sorption [mg metal ion/g resin]	Ag(I)	10.8±0.5	15.2±0.5	21.5±0.5
	Cu(II)	4.68±0.1	3.36±0.1	3.21±0.1
	Pb(II)	9.74±0.1	6.24±0.1	5.89±0.1
	Zn(II)	0.273 ±0.01	0.230±0.01	0.0696±0.001
$K_d$	Ag(I)	325±0.1	516±0.1	1035±0.1
	Cu(II)	10.6±0.1	7.50±0.1	7.15±0.1
	Pb(II)	2.28±0.1	1.46±0.1	1.37±0.1
	Zn(II)	13.4±0.1	11.2±0.1	3.33±0.01
$a_{sel.}$	Ag(I)/Cu(II)	30.7	68.8	144.8
	Ag(I)/Pb(II)	142.5	353.4	755.5
	Ag(I)/Zn(II)	24.3	46.1	310.8

The best sorption capacity towards Ag(I) from the multicomponent solution showed trans-1,4-diaminocyclohexane resin (III). The Ag(I) sorption is 21.5 mg/g. This sorbent showed high selectivity for Ag(I) in the presence of Cu(II), Pb(II) and Zn(II), because the values of selectivity coefficients ( $a_{sel.}$ ) are higher than 100 (Huang et al., 2019).

All sorbents were selective towards Ag(I) in relation to Pb(II) from real chloride leaching solution. The values of  $a_{sel.}$  are 142.5, 353.4 and 755.5 for Resins I-III, respectively. 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 a real chloride solution was 37 times higher than the concentration of Ag(I).

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, sorbents with N-(3-aminopropyl)-2-pipecoline, N-(3-aminopropyl)-2-pyrrolidinone and trans-1,4-diaminocyclohexane ligands are advanced materials for selective removal of Ag(I) ions from real chloride leaching solution.

The selectivity of the polymeric materials to Ag(I) could be explained by the presence of ligands with N-donor centres, which had a high affinity for "soft" Ag(I), but a minor affinity towards Cu(II), Pb(II) and Zn(II) referred to as "hard" metals. On the other hand, this could be caused by the fact that sorbents prefer complexes, that have the highest density of negative charges, which 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), and Zn(II) have tetrahedral structure. The complex of  $\text{AgCl}_4^{3-}$  has a higher density of negative charge (three charges are carried over by five atoms) than  $\text{CuCl}_4^{2-}$ ,  $\text{PbCl}_4^{2-}$  and  $\text{ZnCl}_4^{2-}$  complexes.

The MC-PYO and MC-PYS sorbents are successfully applied to Ag(I) recovery from acidic leachate of waste photographic films (Hamza et al., 2022). MC-PYS is more efficient and selective than MC-PYO at pH 2.2, where the total sorption capacity reaches 88.5 mg Ag(I)/g. The thiomorpholine modified resin is an advanced material for the selective removal of Ag(I) ions from a multicomponent system (Piłśniak-Rabiega and Wolska, 2022). The value of the selectivity coefficient ( $a_{sel.}$ ) for the Ag(I) sorption over Cu(II), Pb(II), Co(II), Ni(II), and Zn(II) is 104, 177, 225, 294, and 213, respectively. The 2-MBI (2-mercaptobenzimidazole)-chitosan sorbent has been used to recover precious metals (Ag, Au, Pd) from acid leachate (Elwakeel et al., 2021). 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 a large molar excess, ~67 times). 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 (Piłśniak-Rabiega and Wolska, 2020). The chloride complexes of Co(II), Ni(II), and Zn(II) were not sorbed by these sorbents. The S-bearing corn stalks (OCS-ET-TU) can be used as the adsorbent to selective recover Ag(I) from industrial nickel electrolyte (Li et al., 2018). The maximum adsorption capacity of  $\text{AgCl}_4^{3-}$  was 3.06 mg/g in the nickel electrolyte, but the other competing metal ions could not be adsorbed onto the OCS-ET-TU.

On the basis of this study, it can be concluded that the obtained sorbents can be used to recover silver from various sources such as ores, industrial waste, and jewelry scraps.

#### 4. Conclusions

- Microwave modification of the vinylbenzyl chloride/divinylbenzene (VBC/DVB) copolymer using heterocyclic compounds such as N-(3-aminopropyl)-2-pipecoline, N-(3-aminopropyl)-2-pyrrolidinone and trans-1,4-diaminocyclohexane is a successful method of polymer resins preparation. The yield of modification was 69.2, 74.6 and 88.3% for Resins I-III, respectively.
- The presented 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 trans-1,4-diaminocyclohexane resin (Resin III) ( $S = 26.8 \text{ mg Ag(I)/g resin}$ ).
- The sorption of Ag(I) by trans-1,4-diaminocyclohexane resin could take place according to the coordination mechanism. The N-(3-aminopropyl)-2-pipecoline and N-(3-aminopropyl)-2-pyrrolidinone resins do not have a free pair of electrons on nitrogen atoms, which suggested that these positively charged sorbents had negatively charged species on their surface, e.g.:  $\text{Cl}^-$  ions present as counter ions. These species could be exchanged for the anionic complexes of silver(I),  $\text{AgCl}_4^{3-}$ . The Ag(I) sorption on all functional polymers can also proceed by the mechanism of ion exchange, due to the presence of amine groups in the functional groups of the polymers.
- The maximum sorption capacity of Ag(I) obtained by the Dubinin-Radushkevich isotherm model is 105.4, 117.8 and 130.7 mg Ag(I)/g dry resin for Resins I-III, respectively.
- The uptake of Ag(I) on sorbents fits well to pseudo-first-order model.
- The loaded sorbents can be regenerated with 1.0% potassium cyanide solution in 0.50% hydrogen peroxide solution at room and elevated temperatures.
- All resins retained their capacity towards Ag(I) in five consecutive sorption/desorption cycles.
- The trans-1,4-diaminocyclohexane modified resin was very selective towards Ag(I) in relation to Cu(II), Pb(II), and Zn(II) from real chloride leaching solution. The values of selectivity coefficients are higher than 100.
- The sorbents with N-(3-aminopropyl)-2-pipecoline, N-(3-aminopropyl)-2-pyrrolidinone ligands showed high preferences for  $\text{AgCl}_4^{3-}$  complexes over  $\text{PbCl}_4^{2-}$  anions from real solution.

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