Silver(I) recovery on thiomorpholine - modified functional polymer

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Abstract: The functional polymer containing heterocyclic ligands was synthesized by microwave modification of a crosslinked poly(vinylbenzyl chloride–divinylbenzene) matrix with thiomorpholine. The modification yield was 89.3%. The sorbent was used to recover Ag(I) from the synthetic and real chloride solutions. The maximum sorption capacity of Ag(I) was approximately 180 mg Ag/g. The sorption kinetic data were well-fitted to the pseudo-first-order kinetic model. The degree of silver desorption was approximately 50.0% using a 1.0% potassium cyanide solution in a 0.50% hydrogen peroxide solution. The resin retained its capacity toward Ag(I) in five consecutive sorption/desorption cycles. The thiomorpholine modified resin was highly selective toward Ag(I) in relation to Cu(II), Pb(II), Co(II), Ni(II), and Zn(II) from the real chloride leaching solution.

Keywords: synthesis, microwave modification, sorption, chloride solutions, selectivity

1. Introduction

Silver is a precious metal found in lead-zinc, copper, tin, nickel, and gold deposits. Most silver comes as a by-product from ores that are mined and processed to make other metals. From a commercial point of view, native silver, which does not contain chemicals or is not associated with other minerals, is also important.

Silver has been known since ancient times. Originally, they were used for jewellery or for the production of everyday objects and for the production of coins. Today, its properties are used in many technical fields, such as electronics, medicine, and photovoltaics. Despite the great demand for this metal, resources are limited. It is estimated that by 2024, the demand for silver will exceed the production of natural raw materials and waste materials (Li and Adachi, 2018). Based on scenarios from the solar industry, the silver shortage will begin in 2030. Therefore, it is necessary to increase the number of potential sources for the recovery of this metal.

In recent years, a great deal of research has been carried out to develop hydrometallurgical methods for recovering silver from industrial waste, waste electrical and electronic equipment, or jewellery. Recycling is also beneficial for environmental reasons.

The most popular hydrometallurgical method of transferring silver into a solution was cyanide leaching, in which up to 90% of silver recovery processes were carried out in this way. This process was not an ideal one on account of its toxicity, low leaching rate, and its inefficiency in treatment refractory ores. Other leaching processes that use thiosulfate, acidified thiourea, hydrochloric acid, and ammonia solution 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, low price of leaching reagents, and non-polluting character (Puvvada et al., 2000; Liu et al., 2010; Behnajady and Moghaddam, 2011).

Different separation processes such as cementation, membrane processes, solvent extraction, or sorption are used to recover metals from solutions after leaching. Different types of sorbents are

currently used for sorption, e. g., activated carbons, zeolites, organically modified porous silica, or polymeric sorbents.

Natural and synthetic polymers, containing selective functional groups, are widely used for the separation of silver ions from various solutions.

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 more attractive sorption performance both in terms of sorption capacity and selectivity. The sorbents are very promising for silver recovery from complex solutions.

The grafting of 2-mercaptobenzimidazole on chitosan microparticles and sonication treatment allowed developing highly selective sorbents for Ag(I) recovery 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/g) was reached for the non-magnetic sorbent with sonication at the higher frequency.

The recovery of Ag(I) from aqueous solutions was studied using chitosan resin modified with ethylenediamine and 3-amino-1,2,4-triazole-5-thiol. The chelating matrix obtained from ethylenediamine showed an uptake capacity of 1.13 mmol/g in 20 min and at 25°C (Elwakeel et al., 2013).

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).

The 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 (Pilśniak-Rabiega and Wolska, 2021). The best sorption capacity toward Ag(I) from the multicomponent solution showed pyrrolidine resin. The sorption of Ag(I) is 0.15 mmol/g. The resin with 4-tert-butylpyridine ligands was selective towards Ag(I) in relation to Pb(II) from the real chloride leaching solution. The value of the selectivity coefficient, $a_{sel.}$, was 276. The resin with 3-morpholinopropylamine groups was characterized by high selectivity toward Ag(I) in the presence of Co(II) chloro complexes. The value of $a_{sel.}$ was 148.

The sulfur-containing polymeric sorbents were selective for Ag(I) from chloride solutions (Pilśniak-Rabiega and Wolska, 2020). Sorbents with 2-mercapto-1-methylimidazole and guanylthiourea groups showed preference for Ag(I) over Cu(II) in a two-component solution. The resin with 2-mercapto-1-methylimidazole ligands was very selective toward Ag(I) in relation to Pb(II) from the real chloride leaching solution. The value of the selectivity coefficient, $a_{sel.}$, was 1583.

The acyl thiourea resin (PTDTR) was used for the removal of Ag(I) from aqueous solution (Huang et al., 2019). The adsorption of PTDTR for Ag(I) reached equilibrium after 12 hours with the adsorption capacity of 5.57 mmol/g at a pH of around 6. The PTDTR resin showed good selectivity for Ag(I) ions in the Ag(I)-Cu(II) binary system.

The 1-methylimidazole resin and the 1,2-dimethylimidazole resin showed preferential sorption of Ag(I) in the presence of Cu(II) from the synthetic chloride solution. The sorbents did not sorb Cu(II) chloro complexes (Pilśniak-Rabiega et al., 2019).

Modified corn stalk adsorbent (OCS-ET-TU) was used for recovering Ag(I) from industrial nickel electrolyte (Li et al., 2018). The maximum adsorption capacity of Ag(I) was 3.06 mg/g, but the other competing metal ions (Ag(I), Ni(II), Cu(II)) could not be adsorbed onto the OCS-ET-TU.

The novel thiourea-immobilized polystyrene nanoparticles (TA-PS) were applied to recover Ag(I) from the $AgNO_3$ solution (Yun et al., 2018). The Ag^+ uptake by TA-PS increased with increasing concentration of Ag(I), and reached a maximum value of 190±5.3 mg/g in an $AgNO_3$ concentration range up to 1000 ppm.

The aim of the work was the synthesis of a functional polymer, containing nitrogen and sulfur atoms, for the recovery of Ag(I) from synthetic single- and two-component chloride solutions as well as a real

chloride leach solution. The effects of hydrochloric acid and sodium chloride concentrations on Ag(I) sorption, sorption isotherms, the effect of contact time, and Ag(I) desorption were also studied.

2.   Materials and methods

2.1.   Chemical reagents

The chemicals were Sigma-Aldrich products. A synthetic solution of Ag(I) was prepared by dissolving a known amount of silver nitrate in a chloride solution (4.0 M NaCl, 0.10 M HCl). The initial concentration of Ag in the synthetic solution was 51.2, 55.6, or 60.0 mg/dm^3.

The solution of Ag(I) and Cu(II) was prepared by dissolving a known amount of copper sulfate and silver nitrate in a chloride solution (4.0 M NaCl, 0.10 M HCl). The concentration of Ag(I) and Cu(II) was 60.0 and 32.1 mg/dm^3, respectively.

The real chloride leach solution was prepared by chloride leaching of a solid residue after atmospheric leaching in sulfuric acid of copper concentrate from Lubin Concentrator (KGHM Polska Miedź S.A.). The concentration of NaCl in the leaching solution was 4.0 mol/dm^3 and 0.10 mol/dm^3 of HCl. During the acidic chloride leaching, the solid residue contained silver and lead in the form of insoluble compounds in sulphuric acid, such as Ag$_2$S and PbSO$_4$. The preparation of Ag(I) and Pb(II) solution could be described using the following reactions:

$$AgS + 2H^+ + 2mCl^- = 2[AgCl_m]^{1-m} + H_2S \quad \text{where m = 1, 2, 3, 4} \tag{1}$$

$$PbSO_4 + nCl^- = [PbCl_n]^{2-n} + SO_4^{2-} \quad \text{where n = 1, 2, 3, 4} \tag{2}$$

The solution after chloride leaching contained 60.0 mg/dm^3 of Ag(I) and 4.20·10^3 mg/dm^3 of Pb(II) as well as 450 mg/dm^3 of Cu(II), 20.0 mg/dm^3 of Zn(II), 16.2 mg/dm^3 of Co(II) and 5.01 mg/dm^3 of Ni(II) (Pilśniak-Rabiega et al., 2019).

The concentration of metal ions in synthetic and real chloride solution was determined using Varian SpectrAA 20 Plus Atomic Absorption Spectrometer.

2.2. Preparation of polymeric resin

The resin presented in this work was prepared from the starting material, the vinylbenzyl chloride/divinylbenzene (VBC/DVB) copolymer. It contained 2.0 wt. % of crosslinker. The polymeric support was obtained by typical suspension polymerization (Trochimczuk, 1998). The prepared resin was characterized by an expanded gel structure.

The polymeric resin was prepared by microwave modification. The VBC/DVB (2.0 wt. % of DVB) copolymer was placed on a Petri dish and swollen with thiomorpholine (five times the molar excess with respect to the chlorine content in the polymer) for 1 h at room temperature. The reaction mixture was then placed in a microwave reactor for 10 min, at 90 W. The resin obtained was washed with acetone, acetone/water (1:1), water. The beads were placed in the column and washed with 1 M HCl, water, 1 M NaOH, and water.

2.3. Methods of analysis

The water regain was measured using a centrifugation method in which about 1 g of polymer swollen in water was placed in a column with filled-glass bottom and centrifuged at 2000 rpm for 5 min., weighted and dried at 100°C for 24 h. After being cooled in a desiccator, the polymer was weighted again. The water regain was calculated as $(m_w - m_d)/m_d$, where m_w is the weight of the swollen polymer after centrifugation, and m_d is the dry weight of the polymer (Jermakowicz-Bartkowiak, 2005).

The nitrogen content was determined using the Kiejdahl method after mineralization of the resin sample (about 200 mg) in the concentrated sulfuric acid containing copper sulfate and potassium sulfate (Pilśniak-Rabiega and Trochimczuk, 2014).

The chlorine content was measured by burning about 20 mg of dry polymer sample in oxygen in a flask containing 25 cm^3 of 3.0% hydrogen peroxide solution. The content of chlorine was determined using the Volhard's method (Pilśniak-Rabiega and Trochimczuk, 2014).

The sulfur content was measured by burning about 20 mg of dry polymer sample in an oxygen-filled flask. The products of burning were adsorbed in 15 cm^3 of 3.0% hydrogen peroxide solution. After 1 h,

the flask was heated in a water bath for 30 min to evaporate carbon dioxide. Then the content of the flask was titrated with 0.01 M NaOH in the presence of bromothymol blue.

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

The sorption capacity of the resin towards Ag(I), Pb(II), Cu(II), Zn(II), Co(II), and Ni(II) was determined from synthetic and real chloride solutions by contacting the resin samples with 20.0 cm^3 of metal ions solution. Metal ions solution containing Ag (51.2, 55.6, or 60.0 mg/dm^3), Cu (450 mg/dm^3), Pb (4.20·10^3 mg/dm^3), Zn (20.0 mg/dm^3), Co (16.2 mg/dm^3) and Ni (5.01 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. After 24 h, the polymer was separated by filtration and the concentration of Ag was measured using the atomic absorption technique (AAS) on a Varian SpectrAA 20 Plus Atomic Absorption Spectrometer.

The sorption isotherm was determined by contacting various amounts of resin (containing 0.1-10×molar excess of the ligand) with 20.0 cm^3 of solution containing 51.2 mg/dm^3 of Ag, 4.0 M of NaCl, 0.10 M of HCl for 24 h, at 23±2°C and plotting the sorption as a function of the equilibrium concentration.

For sorption kinetics, identical resin samples were shaken with 20.0 cm^3 of solution containing 55.6 mg/dm3 Ag in chloride solution (4.0 M NaCl, 0.10 M HCl). The samples were taken at different intervals of time, the resin and solution separated, and the concentration of Ag was determined by AAS.

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. The selectivity coefficient ($a_{sel.}$) was calculated as the quotient of the distribution coefficients for each metal.

Desorption of Ag was determined by contacting an amount of resin, loaded with the known amount of Ag, with 20.0 cm^3 of 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 the resin

The thiomorpholine resin (resin **I**) was prepared by the chemical modification of the VBC/DVB (2 wt.% of DVB) polymer. The VBC/DVB copolymer with expanded gel structure, containing 2 wt.% of DVB was obtained in the presence of toluene. Elemental analysis gave 5.30 mmol/g of chlorine, which corresponds to 83.0% yield of VBC incorporation into the polymeric network. The chloromethyl groups present in the VBC/DVB structure served as a reactive place for the immobilization of thiomorpholine ligands.

The polymeric resin was prepared by microwave modification. Elemental analysis gave 3.95 mmol of N/g, which corresponds to 89.3% yield (see Table 1). The sulfur content in this resin is 3.77 mmol/g. The yield calculated from the sulfur content is 85.0%. The degree of substitution of chlorine in chloromethyl groups by thiomorpholine calculated on the basis of nitrogen and sulfur content was similar. Modification efficiency and chlorine content (0.381 mmol/g) confirmed the effective immobilization of functional groups in the polymer matrix.

The microwave-modified immobilization efficiency of heterocyclic groups in the VBC/DVB copolymer was 50-90% (Pilśniak-Rabiega et al., 2019; Pilśniak-Rabiega and Wolska, 2020; Pilśniak-Rabiega and Wolska, 2021).

Table 1. Physicochemical properties of the polymeric resin

Water regain [g/g]	Chlorine content [mmol/g]	Nitrogen content [mmol/g]	Sulfur content [mmol/g]	Yield of modification* [%]
1.06±0.01	0.381±0.01	3.95±0.01	3.77±0.01	89.3±1.0

*calculated from the nitrogen content

Resin **I** had small values of water regain (1.06 g of water/g of polymer) due to the presence of sulfur atoms, which showed hydrophobic properties.
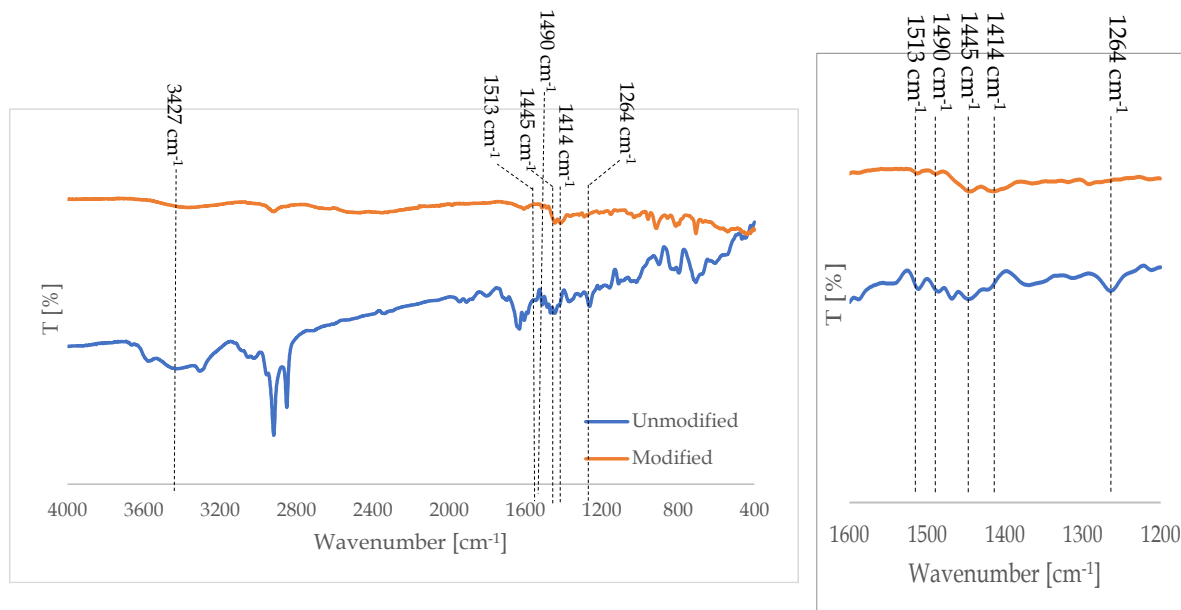

Fig. 1. FTIR spectra of unmodified copolymer VBC/DVB and modified polymer

The FTIR spectrum of the VBC/DVB copolymer (see Fig. 1) shows a characteristic band with a wave number of 1264 cm^{-1} derived from the C-Cl bonds of the chloromethyl group (Yaacoub and Le Perchec, 1988; Egawa et al., 1990). The disappearance of this band indicates the substitution of chloromethyl groups by thiomorpholine ligands. This range is not visible in the spectrum of the thiomorpholine-modified copolymer, suggesting that chlorine atoms in the chloromethyl groups have been substituted by sulfur-containing ligands. The broad band at 3427 cm^{-1} comes from the hydroxyl groups that are formed during the hydrolysis of vinylbenzyl chloride to vinylbenzyl alcohol. In both spectra between 1490 and 1513 cm^{-1}, two skeletal vibration bands emanating from the phenyl rings are visible. In the range from 2850-2920 cm^{-1}, bands are visible that are derived from the tensile vibrations of the aliphatic groups C-H. The FTIR spectrum of a modified polymer (see Fig. 1) shows a strip with a wave number of 1445 cm^{-1} indicating a deformed shear vibration of the N-CH$_2$ bond. At a wave number of 1416 cm^{-1}, a stripe is visible, which may have originated from the -CH$_2$ groups associated with sulfur atoms (Silverstein and Bassler, 1970; Stuart, 2004). Based on the spectrum, the chemical structure of the functional polymer looks as follows (see Fig. 2):
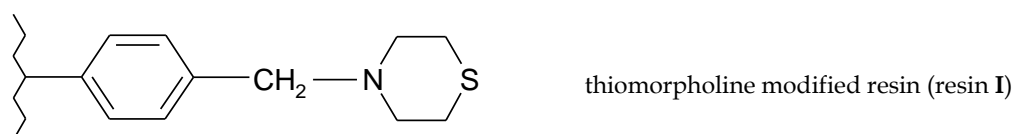

thiomorpholine modified resin (resin **I**)

Fig. 2. Structure of the investigated resin

A similar structure (see Fig. 3) was achieved with the thiomorpholine-functionalized nanoporous mesopore (Ganjali et al., 2010). Construction of a selective sensor, modified with silica-based organic-organic hybrid materials containing thiol groups covalently attached to the solid framework via a propyl chain.

3.2. Evaluation of the sorption properties

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

To determine the influence of acidity on Ag(I) sorption on the functional polymer, a series of experiments were carried out at 23±2ºC using chloride solutions of Ag(I) (60.0 mg of Ag/dm^3) with

a fixed sodium chloride concentration of 4.0 mol/dm³ and varying hydrochloric acid concentrations in the range of 0.010 - 2.0 mol/dm³. The results are shown in Fig. 4.
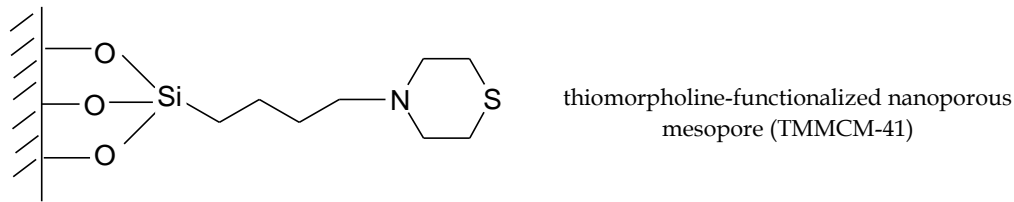

thiomorpholine-functionalized nanoporous mesopore (TMMCM-41)
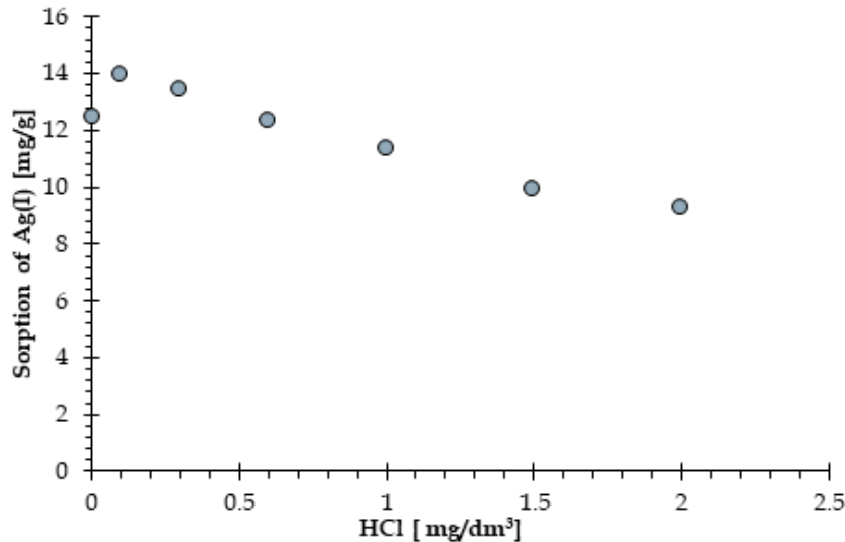
Fig. 3. Structure of the TMMCM-41

Fig. 4. Ag(I) sorption as a function of HCl concentration (C_{Ag} = 60.0 mg/dm³, C_{HCl} = 0.010 – 2.0 mol/dm³, C_{NaCl} = 4.0 mol/dm³, time: 24 h, T: 23±2°C)

It was observed that the Ag(I) sorption decreased with increasing HCl concentration. An exception is the lower sorption capacity at 0.01 mol/dm³ of HCl. This may be caused by the speciation of Ag(I) in chloride solution (Liu et al., 2010). The best Ag(I) sorption results can be obtained from the solution containing 0.10 mol/dm³ of HCl. At relatively low acidity, the functional groups on the adsorbent 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 (Xiong et al., 2016). At higher concentrations of HCl (0.30-2.0 mol/dm³), the sorption of Ag(I) decreased due to competition with Cl⁻ ions due to their increased concentration in solution.

The effect of NaCl concentration on the sorption of Ag(I) at 23±2°C on thiomorpholine - modified functional polymer was investigated in the concentration range of 1.0- 5.0 mol NaCl/dm³, 0.10 mol HCl/dm³, and 60.0 mg Ag/dm³ (see Fig. 5). The resin showed the highest affinity for Ag when the concentration of NaCl was 4.0 mol/dm³. The Ag(I) sorption decreased when NaCl concentration was greater or smaller than 4.0 mol/dm³. The decrease in sorption capacity is due to the speciation of Ag(I) (Liu et al., 2010).

The results presented in Figs. 4 and 5 show that the best Ag(I) sorption can be observed from the solution containing 4.0 mol/dm³ of NaCl and 0.10 mol/dm³ of HCl in the chloride solution of silver(I). Therefore, all subsequent experiments, including the study of sorption mechanism, sorption isotherm obtaining, and kinetic studies, were carried out using this solution.

3.2.2. Sorption mechanism

The thiomorpholine resin was applied for the recovery of Ag(I) from the synthetic chloride solution (4.0 M NaCl, 0.10 M HCl). The sorption properties of resin **I** toward Ag(I) were studied under the conditions presented in the Experimental part. The results are shown in Table 2.
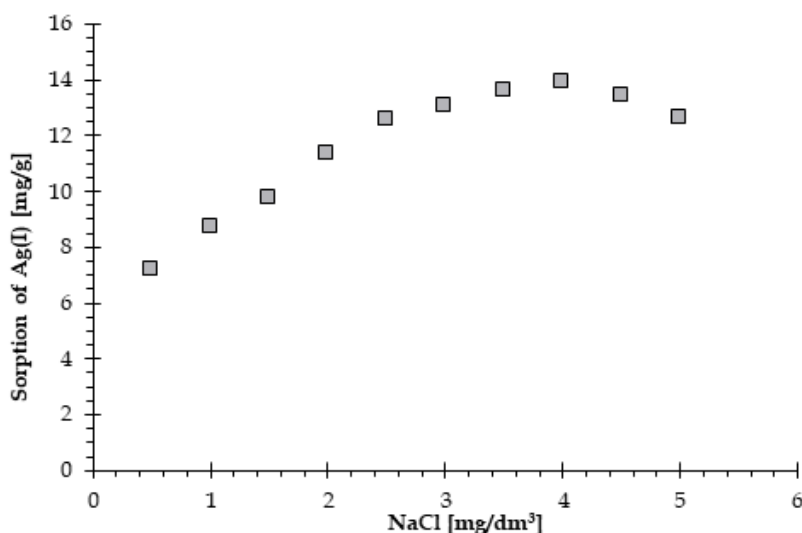
Fig. 5. Ag(I) sorption as a function of NaCl concentration (C_{Ag} = 60.0 mg/dm³, C_{HCl} = 0.10 mol/dm³,
C_{NaCl} = 1.0 - 5.0 mol/dm³, time: 24 h, T: 23±2°C)

Table 2. Sorption of Ag(I) from synthetic chloride solution (C_{Ag} = 60.0 mg/dm³ (0.556 mmol/dm³),
C_{HCl} = 0.10 mol/dm³, C_{NaCl} = 4.0 mol/dm³, time: 24 h, T: 23±2°C)

Ligand concentration*	Ag sorption capacity	Ag sorption capacity	Yield of Ag sorption	K_d
[mmol/g]	[mg Ag/g resin]	[mmol Ag/g ligand]	[%]	
3.95±0.01	13.94±0.2	0.129±0.05	67.3±1.0	389

*calculated from nitrogen content in functional groups

The sorption of silver chloro complexes by resin **I** was 13.94 mg Ag/g resin. These complexes were mainly sorbed in the form of AgCl₄³⁻. The formation of these complexes was suggested by Liu (Liu et al., 2010). According to the thermodynamic calculation, the silver complex species in the tested solution (4.0 M NaCl, 0.10 M HCl) mainly exist in the form of AgCl₄³⁻, whose proportion is 83%, when [Cl⁻] is 4.10 mol/dm³. The proportion of AgCl₂⁻ and AgCl₃²⁻ is 3.0 and 14%, respectively. Therefore, the Ag(I) complexes were mainly sorbed by this resin in the form of AgCl₄³⁻.

Based on the hard and soft acids and bases (HSAB) theory, noble metals are considered "soft acids" and tend to form stable complexes with sorptive materials containing "soft" donor atoms ("soft bases") such as sulfur. Sulfur atoms have an easily polarizable lone pair of electrons and a large atomic/ionic radius. Nitrogen atoms are borderline bases also tend to form complexes with precious metals.

Resin **I** displayed affinity towards Ag(I) due to the presence of donor N- atoms and especially S-atoms in the functional groups. Free pairs of electrons on nitrogen and sulfur atoms should be able to coordinate with Ag(I), which suggested that the main mechanism of metal uptake was the coordination.

It seemed probable that during the sorption of Ag(I) on resin **I**, the thiomorpholine ligands formed specific metal complexes by the ligand exchange mechanism. Ag(I) can be then coordinated to two sulfur donor-ligands and has a linear coordination geometry (see Fig. 6). The formation of these complexes might be the reason of a lower Ag(I) sorption, because two thiomorpholine groups take part in the formation of one complex.
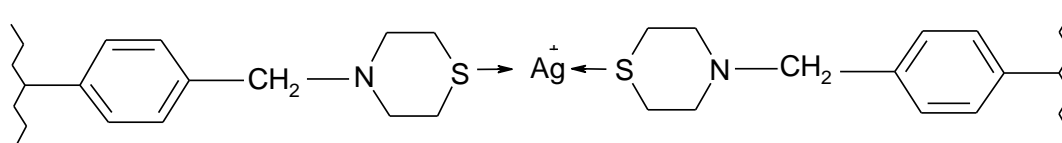

Fig. 6. Suggested mechanism for Ag(I) sorption on thiomorpholine resin

3.2.1. Isotherm of sorption

During the study of the sorption characteristics of the synthesized resin, the sorption isotherm at room temperature was also determined (see Fig. 7) from the silver(I) solution with a concentration of 51.2 mg/dm^3 and with a different molar ratio of the ligand to the silver ions. 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 resin **I**. At a lower concentration of Ag(I), the solution can interact with the binding sites; therefore, the adsorption capacity increases rapidly with increasing initial concentration. At higher concentrations, the adsorption capacity is almost constant as a result of the saturation of the adsorption site. The maximum sorption capacity of Ag(I) for resin **I** was approximately 180 mg Ag/g. The Freundlich, Langmuir, and Dubinin-Radushkevich isotherm models were used to describe the equilibrium data in this study. The adsorption isotherm is given in Fig. 6 and the calculated parameters of the adsorption isotherms along with the coefficient of determination (R^2), are summarized in Table 3.
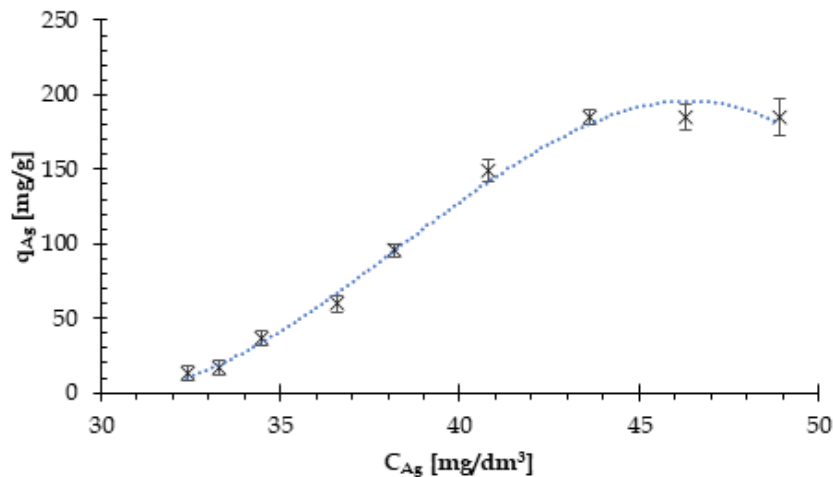

Fig. 7. Sorption isotherm of the studied resin. Samples of resin containing 0.1-10×molar excess of ligand were shaken with 20.0 cm^3 of solution containing 51.2 mg/dm^3 of Ag(I) in chloride solution (C_{HCl} = 0.10 mol/dm^3, C_{NaCl} = 4.0 mol/dm^3) for 24 h, at 23 ± 2°C

To describe the interaction of Ag(I) with the obtained polymer and the equilibrium data in this study, three adsorption isotherm models, Langmuir, Freundlich, and Dubinin-Radushkevich were used. 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. (3):

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

The linear form of the Langmuir equation can be given as follows (Eq. 4):

$$\frac{1}{q_e} = \frac{1}{q_m b_L C_e} + \frac{1}{q_m} \tag{4}$$

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, and 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, 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. 5) (Polowczyk et al., 2016; Esteves et al.,2022):

$$R_L = \frac{1}{1 + b_L C_0} \tag{5}$$

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) favorable 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) on resin **I**.

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. 6)(Esteves et al., 2022):

$$q_e = aC_e^{1/n} \qquad (6)$$

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. 7) (Cela-Pérez et al., 2011). The 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 (Eq. 7) (Polowczyk et al., 2016; Ayawei et al., 2017):

$$logq_e = \frac{1}{n}\, logC_e + loga \qquad (7)$$

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 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, they 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 8.41·10^{-8} for the synthesized resin. The values of n constant for the investigated resin were below 1 and it was 0.176 (therefore it can be assumed that the sorption of Ag(I) onto resin **I** is not favourable. Furthermore, by comparing the R² values for the Langmuir and Freudlich models, it can be seen that the second model is a better fit for Ag(I) adsorption onto the thiomorpholine modified resin. All results of the Langmiur 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. 8 (Ulatowska, 2022):

$$q_e = q_m \exp\left(-K_{DR}\cdot\varepsilon^2\right) \qquad (8)$$

where q_m is the maximum adsorption capacity of the material [mmol/g], K_{DR} is the Dubinin-Radushkevich constant [kJ²/mol²], ε is the Polanyi potential (Eq. 9):

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

The linear form of this isotherm can be expressed by Eq. 10.

$$ln\, q = lnq_m - K_{DR}\varepsilon^2 \qquad (10)$$

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. 11 (Cela-Pérez et al., 2011; Ulatowska, 2022).

$$E = (2K_{DR})^{-0.5} \qquad (11)$$

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, and it reached the value of 17.8 kJ/mol. This means that the chemical adsorption dominated. The linear coefficient of determination (R²) 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 capacity for resin **I** was calculated. The maximum sorption

capacity of Ag(I) is 151.3 mg Ag/g dry resin, and this value is close to the experimental capacity obtained during the determination of the sorption isothrem. The parameters of the Dubinin-Radushkevich isotherm are given in Table 3.

Table 3. Langmuir, Freundlich, and Dubinin-Radushkevich fitting parameters for resin **I**

Model	Parameter	Unit	Value
Experimental	q_{exp}	mg/g	185
		mmol/g	1.72
Langmuir	R_L	-	NA
	R^2	-	0.777
	q_{max}	mg/g	NA
Freundlich	a		$8.41 \cdot 10^{-8}$
	R^2	-	0.883
	n	-	0.176
Dubinin-Radushkevich	E	kJ/mol	17.8
	R^2	-	**0.958**
	q_{max}	mmol/g	151.3
		mg/g	1.40

The maximum sorption capacity of $AgCl_4^{3-}$ obtained by the Dubinin-Radushkevich isotherm model is 120.4, 131.6, and 85.2 [mg Ag/g resin] for resins with 4-tert-butylpyridine, pyrrolidine, and 3-morpholinopropylamine ligands, respectively (Pilśniak-Rabiega and Wolska, 2021).

For functional polymers with 2-mercapto-1-methylimidazole and guanylthiourea ligands, the maximum sorption capacity of $AgCl_4^{3-}$ obtained by those of the Elovich model was 40.7 and 194.2 [mg Ag/g], respectively (Pilśniak-Rabiega and Wolska, 2020).

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. 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 (Li et al., 2018).

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 (Langmuir model) as 153.54 and 46.69 mg/g, respectively.

It could be found that thiomorpholine modified resin exhibited higher sorption capacity than most of the materials presented.

3.2.2. Effect of contact time

The effect of contact time on the removal of Ag(I) from the chloride solution on the thiomorpholine modified resin was studied at an initial concentration of 55.6 mg/dm³ at room temperature. The dependence of sorption capacity and contact time is shown in Fig. 8. It can be seen that the removal of Ag(I) from the solution by the investigated polymer increased with the contact time until the equilibrium was attained. As shown in Fig. 8, the adsorption occurred more rapidly after 2 hours and after 5 hours gradually slowed down as it reached equilibrium. The experiments showed that the equilibrium was reached only after about 36 hours.

The results of the Ag(I) sorption rate on functional polymers presented in the literature are comparable to those obtained on the thiomorpholine-modified resin. The maximum $AgCl_4^{3-}$ adsorption on resins with 2-mercapto-1-methylimidazole and guanylthiourea ligands was reached within 48 hours (Pilśniak-Rabiega and Wolska, 2020). For the 2-mercaptobenzimidazole derivative of chitosan, the maximum Ag(I) adsorption was obtained after 28 hours (Elwakeel et al., 2021). The equilibrium uptake of $AgCl_4^{3-}$ was reached after 48 hours for functional polymers containing 4-tert-butylpyridine, pyrrolidine, and 3-morpholinopropylamine ligands (Pilśniak-Rabiega and Wolska, 2021).
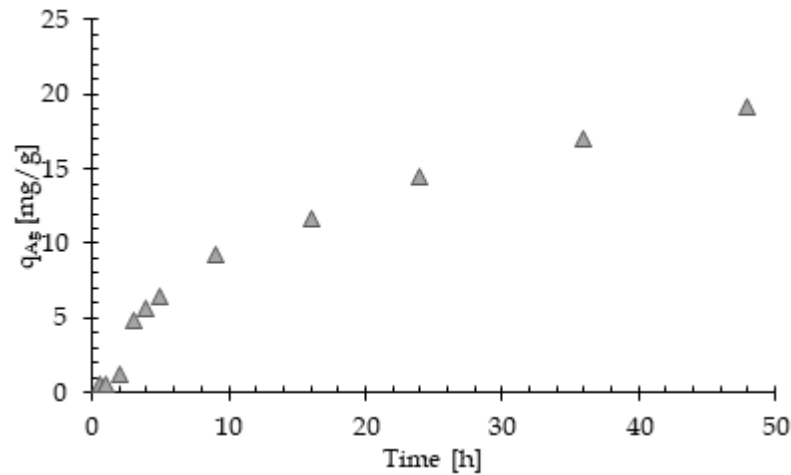
Fig. 8. Kinetics of Ag(I) sorption on resin **I**. Samples of resin containing 0.01 mmol of ligand were contacted with 20.0 cm³ of solution containing 55.6 mg/dm³ of Ag in chloride solution (C_{HCl} = 0.10 mol/dm³, C_{NaCl} = 4.0 mol/dm³) at 23±2°C and the concentration checked in specified time intervals.

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. 12 and 13), to find the rate (film diffusion or particle diffusion) determining steps for resin **I** (Juang et al., 2002; Kabay et al., 2007; Haq et al., 2020):

$$k_a t = -ln\left(1 - \frac{q_t}{q_e}\right) \tag{12}$$

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.

$$k_b t = -ln\left(1 - \left(\frac{q_t}{q_e}\right)^2\right) \tag{13}$$

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 $-ln\left(1 - \left(\frac{q_t}{q_e}\right)^2\right)$ vs. time.

Table 4 gives the slope values, the linear coefficients of determination and the calculated values of k_a and k_b. Analyzes of k_a and k_b can show which of the processes of sorption is faster for the synthetized polymer. The analysis of the coefficients of determination can show what kind of diffusion mostly controlled the process. In the case of the investigated resin, 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. The limiting step of the Ag(I) adsorption process on resin **I** was also determined using the Weber-Morris interparticle diffusion model (Ulatowska, 2022). The equation of this model is described by Eq. 14. The kinetics of intraparticle diffusion is illustrated in Fig. 9 as the relationship of $q_t=f(t^{0.5})$.

$$q_t = k_{WM} \cdot t^{0.5} + B \tag{14}$$

where k_{WM} is the intraparticle diffusion rate constant (mg/g min$^{0.5}$) 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. 9 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. 9, 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 Ag(I) adsorption from the solution to resin **I**. 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 4. The analysis of the results obtained suggests that the limiting stage for the Ag(I) adsorption process on the synthetized resin 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 4. Analysis of kinetic studies

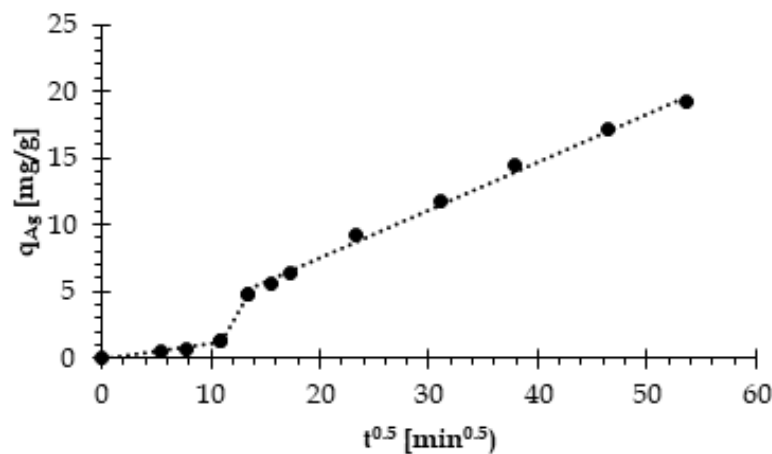| Model	Parameter	Unit	Value
Film diffusion	k_a	1/min	$1.0 \cdot 10^{-2}$
	R²	-	**0.991**
Particle diffusion	k_b	1/min	$4.0 \cdot 10^{-4}$
	R²	-	0.980
Interparticle diffusion	k_{WM1}	mg/g·min$^{0.5}$	**0.11**
	k_{WM2}	mg/g·min$^{0.5}$	1.45
	k_{WM2}	mg/g·min$^{0.5}$	0.36

Fig. 9. Intraparticle diffusion model of Ag(I) adsorption on the polymeric resin

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, Santander et al., 2014). The pseudo-first-order model describes the relationship between the sorption rate and the equilibrium time. This model can be described by Eq. 15 (Kabay et al., 2007):

$$\frac{dq}{dt} = k_1(q_e - q_t) \tag{15}$$

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

$$log(q_e - q_t) = log(q_e) - \frac{k_1 t}{2.303} \tag{16}$$

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. 17 (Kabay et al., 2007; Haq et al., 2020):

$$\frac{dq}{qt} = k_2(q_e - q_t)^2 \tag{17}$$

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. 17, one gets from (Eq. 18):

$$\frac{dq}{(q_e-q_t)} = k_2 dt \tag{18}$$

and integrating Eq. 18 for the boundary conditions $q=0$ at $t=0$, and $q=q_t$ at $t=t$, one obtains the final form (Eq. 19):

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}t \tag{19}$$

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. 16 and 19 that served for the calculation of the characteristic parameters for each model. Linear regression analysis (coefficient of determination (R^2)) was used to analyze the linear form of the kinetic models. The kinetic constants k_1 and k_2 were determined using the slope and intercept values of the linear plots (see Table 5) which presented pseudo-first-order and pseudo-second-order rate constants, calculated and experimental q_e values for Ag(I) sorption on resin **I**. The results of the kinetic analysis are given in Table 5.

Table 5. Pseudo-first-order and pseudo-second-order rate constants, calculated and experimental q_e values for Ag(I) onto synthetized resin I

Model	Parameter	Unit	Value
Experimental	q_{exp}	mg/g	**19.18**
Pseudo-first	k_1	1/min	$9.2 \cdot 10^{-4}$
	R^2	-	**0.991**
	q_1	mg/g	**18.40**
Pseudo-second	k_2	g/mg·min	$2.6 \cdot 10^{-7}$
	R^2	-	0.469
	q_2	mg/g	392

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 Ag(I) adsorption on the thiomorpholine modified 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_1) 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 studied systems rather than the chemical one (see Table 5).

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).

The recovery of Ag(I) from chloride solution was studied using functional polymers containing 2-mercapto-1-methylimidazole and guanylthiourea ligands. Kinetic studies indicated that the adsorption reaction follows the pseudo-first-order kinetics (Pilśniak-Rabiega and Wolska, 2020).

3.2.2. Desorption of Ag(I) from the resin and resin's stability in cycles of sorption/desorption

For the thiomorpholine modified resin, desorption and resin's stability in cycles of sorption/desorption were studied. In this work, the Ag(I) was desorbed by different eluents: 0.50% sodium thiosulphate solution, 0.50% thiourea solution, 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 M

(NH$_4$)$_2$SO$_4$, 0.380 M NH$_3$·H$_2$O). This process was carried out at room temperature (23±2°C) and at elevated temperature (50°C). The results are given in Table 6.

Table 6. Elution of Ag(I) from resin **I** using different eluents (time: 24 h, T: 23±2 and 50±2 °C)

Desorbent	% Desorption	
	Temp. 23°C	Temp. 50°C
0.50% Na$_2$S$_2$O$_3$	6.18±1.0	10.9±1.0
0.50% CS(NH$_2$)$_2$	15.6±1.0	23.2±1.0
1.0% KCN	23.4±1.0	32.5±1.0
1.0%KCN+0.50%H$_2$O$_2$	35.6±1.0	49.8±1.0
0.50 M NaOH	17.2±1.0	20.5±1.0
Ammonium buffer*	12.7±1.0	14.6±1.0

* 2.86 mol/dm³ NH$_3$·H$_2$O and 0.380 mol/dm³ (NH$_4$)$_2$SO$_4$

The eluents more effectively desorbed Ag(I) from resin **I** at elevated temperature, especially 1.0% potassium cyanide solution in 0.50% hydrogen peroxide solution. It seemed probable that during the desorption of Ag(I), cyanide anions formed Ag(CN)$_4$$^{3-}$ complexes by the ligand exchange mechanism. The silver-cyanide complex, Ag(CN)$_4$$^{3-}$, is the most stable complex ion formed by Ag(I), and the logarithm of the stability constant, log β_4, was estimated to be 22.3, for AgCl$_4$$^{3-}$ the value of log β_4 corresponds to 5.30 (Högfeldt, 1982). The values of log β_4 for cyanide and chlorine complexes may suggest that chlorine ligands, Cl$^-$, were substituted for cyanide anions, CN$^-$, in Ag(I) complexes, during Ag(I) desorption from the synthesized resin. On the other hand, Ag can be present on the surface of resin **I** 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 resin, five cycles of Ag(I) sorption of chloride solution (60.0 mg Ag/dm³, 4.0 M NaCl, 0.10 M HCl) and desorption with 1.0% KCN in 0.50% H$_2$O$_2$ were performed on the modified resin thiomorpholine. It could be concluded from these results (see Fig. 10), that the Ag(I) sorption ability increased, the sorption efficiency was 67.3% (13.9 mg/g) in the first cycle, in the case of 2-5 cycles it was 85.2-97.3% (17.6-20.1 mg/g). The desorption efficiency was 35.6-36.2% in 1-5 cycles.

The better Ag(I) sorption on the synthesized resin 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 Ag(CN)$_4$$^{3-}$ complexes by ligand exchange mechanism. Cyano complexes of Ag(I) are more stable than chloro complexes of Ag(I). The thiomorpholine modified resin was not fully regenerated, nonetheless sorption of Ag(I) was effective.
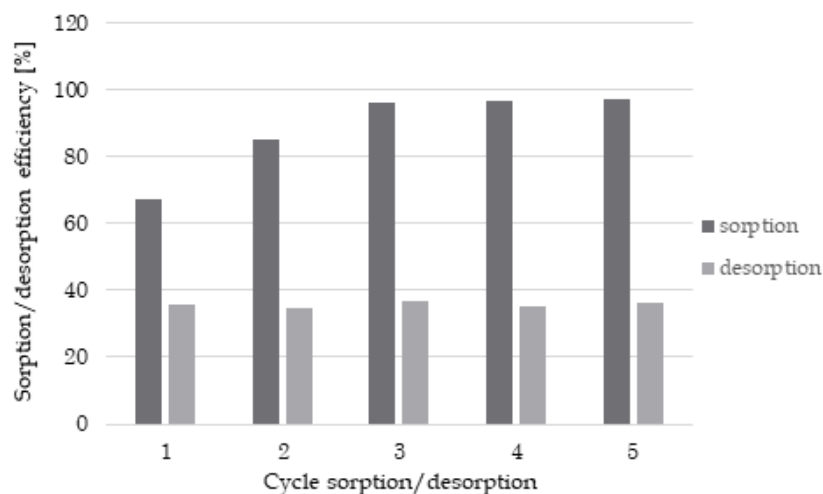

Fig. 10. Sorption properties of resin **I** in five cycles of sorption and desorption (time: 24 h, T: 23±2°C)

The sorbents with heterocyclic ligands, i.e. 4-tertbutylpyridine, pyrrolidine, and 3-morpholino-propylamine, were stable in subsequent sorption and desorption processes of Ag (I) ions from their surface (Pilśniak-Rabiega and Wolska, 2021). Sorption capacity of functional polymers for Ag(I) ions increased significantly after the first adsorption-desorption cycle (by 49-64% for the second cycle). Desorption efficiency in 1-5 cycles was 62-97%. The 2-MBI-chitosan sorbent showed sorption and desorption stability in five consecutive recycling cycles. 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) (Elwakeel et al., 2021).

3.2.3. Selectivity studies

3.2.3.1. Ag(I) sorption from synthetic chloride solution

To determine the selectivity of the thiomorpholine modified resin for Ag(I) and Cu(II), static sorption tests were carried out from a synthetic chloride solution (4.0 M NaCl, 0.10 M HCl) containing Ag(I) and Cu(II) anions. The concentrations of Ag(I) and Cu(II) were 60.0 and 32.1 (0.556, and 0.505 mmol/dm^3), respectively. The selectivity coefficient ($a_{sel.}$) was calculated as the quotient of the distribution coefficients calculated for Ag(I) and Cu(II). The results are presented in Table 9. It could be seen that the featured resin showed preference for $AgCl_4^{3-}$ complexes over $CuCl_4^{2-}$ anions. The value of the selectivity coefficient, $a_{sel.}$, was 194. Quantitative separation of the two ions is achieved, when the corresponding values of the selectivity coefficients comprise 10–30 at least (Marhol, 1982). Thus, the thiomorpholine modified resin is a special material for the selective removal of Ag(I) ions from the Ag(I)-Cu(II) binary system (see Table 7).

The high affinity of the thiomorpholine modified resin to Ag (I) could be explained as a result of the presence of ligands with S- and N-donor centres, which had a high affinity for "soft" Ag, but a minor affinity towards Cu, which is known as a borderline metal and is "harder" than Ag. On the other hand, it could be caused by the fact that resin **I** 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 resin. The Ag(I) and Cu(II) chloro complexes have a tetrahedral structure. The complex of $AgCl_4^{3-}$ has a higher density of negative charge (three charges are carried over by five atoms) than the $CuCl_4^{2-}$ complex.

Table 7. Sorption of Ag(I) and Cu(II) on resin **I** from synthetic chloride solution (C_{Ag} = 60.0 mg/dm^3 (0.556 mmol/dm^3), C_{Cu} = 32.1 mg/dm^3 (0.505 mmol/dm^3), C_{HCl} = 0.10 mol/dm^3, C_{NaCl} = 4.0 mol/dm^3, time: 24 h, T: 23±2°C)

Sorption [mg metal/g resin]		K_d		$a_{sel.}$
Ag	Cu	Ag	Cu	Ag/Cu
12.93±0.01	0.08±0.01	562	2.89	194

The resins with the 2-mercapto-1-methylimidazole and guanylthiourea groups showed good selectivity for Ag(I) ions in the Ag(I)-Cu(II) binary system (Pilśniak-Rabiega et al., 2020). The values of the selectivity coefficient ($a_{sel.}$) were 17.3 and 35.4, respectively.

Functional polymers with imidazole ligands showed preferential sorption of Ag(I) in the presence of Cu(II) from synthetic chloride solution (Pilśniak-Rabiega et al., 2019). The chloro complexes of Cu(II) were not sorbed by these sorbents from a solution containing Ag(I) and Cu(II) anions, each of concentration 0.56 mmol/dm^3.

The melamine resin modified with thiourea (R1) showed high selectivity towards Ag(I) from a binary mixture with Cu(II) (Abd El-Ghaffar et al., 2009). The value of the selectivity coefficient for the adsorption of Ag(I) over Cu(II) is 19.68.

3.2.3.2. Ag(I) sorption from real chloride leach solution

The thiomorpholine modified resin is characterized by a high affinity to Ag(I) from synthetic solutions. Therefore, this functional polymer was used to recover Ag(I) from the real solution.

The sorption ability of resin **I** was investigated in real chloride leaching solution. This solution was prepared by chloride leaching of a solid residue after atmospheric leaching in sulfuric acid of the copper concentrate (Pilśniak-Rabiega et al., 2019). Table 8 shows the effect of foreign ions on the sorption of Ag(I).

Table 8. Sorption of Ag(I), Cu(II), Pb(II), Zn(II), Co(II) and Ni(II) from real chloride leach solution (C_{Ag} = 60.0 mg/dm³ (0.556 mmol/dm³), C_{Pb} = 4.20·10³ mg/dm³ (20.3 mmol/dm³), C_{Cu} = 450 mg/dm³ (7.08 mmol/dm³), C_{Zn} = 20.0 mg/dm³ (0.306 mmol/dm³), C_{Co} = 16.2 mg/dm³ (0.276 mmol/dm³), C_{Ni} = 5.01 mg/dm³ (0.0853 mmol/dm³), C_{HCl} = 0.10 mol/dm³, C_{NaCl} = 4.0 mol/dm³, time: 24 h, T: 23±2°C)

Sorption [mg metal /g resin]	**Ag**	11.28±0.01
	Cu	0.935±0.01
	Pb	0.520±0.01
	Co	0.050±0.01
	Ni	0.030±0.01
	Zn	0.070±0.01
Sorption [mmol metal /g resin]	**Ag**	0.104
	Cu	0.0147
	Pb	2.51·10⁻³
	Co	8.48·10⁻⁴
	Ni	5.11·10⁻⁴
	Zn	1.07·10⁻³
K$_d$	**Ag**	219
	Cu	2.11
	Pb	1.24
	Co	0.973
	Ni	0.744
	Zn	1.03
$a_{sel.}$	**Ag/Cu**	104
	Ag/Pb	177
	Ag/Co	225
	Ag/Ni	294
	Ag/Zn	213

The thiomorpholine modified resin was characterized by high selectivity toward Ag(I) in the presence of chloro complexes of Cu(II), Pb(II), Co(II), Ni(II) and Zn(II), because the values of selectivity coefficient ($a_{sel.}$) were 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) and Cu(II). The concentration of Pb(II) and Cu(II) in the real chloride solution was 37 and 13 times higher than the concentration of Ag(I).

Magnetic chitosan microparticles (MC) containing trione (MC-PYO) or trithione groups (MC-PYS) were applied to Ag(I) recovery from acidic leachate of waste photographic films (Hamza et al., 2022). MC-PYO (hard oxygen-bearing functional groups) was less selective for silver than MC-PYS (soft sulfur-bearing functional groups). Highest selectivity for Ag(I) was reported at pH close to 5.2 with MC-PYS with: Mg(II)>Al(III)>Cu(II)≈Cr(VI)≈Co(II)>Ni(II)>Fe(III).

The 2-mercaptobenzimidazole-chitosan sorbent has been used for the recovery and separation of precious metals (Ag, Au, and Pd) from base metals (iron, copper, aluminum, and tin) in acidic leaching solutions. The results showed the high potential of this material for Ag (and Au, Pd) even at low concentrations of highly complex metal solutions with large base metal collection (in large molars excess, ~67 times) (Elwakeel et al., 2021).

The functional polymers with 4-tert-butylpyridine, pyrrolidine, and 3-morpholinopropylamine ligands are advanced materials for the selective removal of Ag(I) ions from Ag(I)-Cu(II)-Pb(II)-Co(II)-Ni(II)-Zn(II) multicomponent system (Pilśniak-Rabiega and Wolska, 2021).

Sulfur-containing polymeric sorbents were characterized by high selectivity towards Ag(I) in the presence of Co(II), Ni(II), and Zn(II) from a real chloride solution (Pilśniak-Rabiega and Wolska, 2020). These metal complexes were not sorbed by the polymers.

These studies have shown that thiomorpholine modified resin can be used in hydrometallurgical separation processes to recover Ag from different sources such as ore, wastewater, and jewelry scrap.

4. Conclusions

- Microwave modification of the vinylbenzyl chloride/divinylbenzene (VBC/DVB) copolymer with thiomorpholine is an effective method of functional polymer preparation. The yield of modification was 89.3%.
- The sorbent was useful for the recovery of Ag(I) from a synthetic chloride solution (4.0 M NaCl, 0.10 M HCl). The sorption degree of Ag(I) was 67.3%. The value of the distribution coefficient was 389.
- The presence of a large excess of chloride anions in the studied solutions decreased affinity of the resin towards chloro complexes of Ag(I).
- The maximum sorption capacity of Ag(I) obtained by use of the Dubinin-Radushkevich isotherm model was 151.3 mg Ag/g of resin.
- The uptake of Ag(I) on the resin fits well to pseudo-first-order model.
- The loaded resin can be regenerated with a 1.0% potassium cyanide solution in a 0.50% hydrogen peroxide solution at an elevated temperature (50°C).
- The thiomorpholine modified resin retained its capacity towards Ag(I) in five consecutive sorption/desorption cycles.
- The resin showed preferences for Ag(I) over Cu(II) from a two-component Au-Cu solution. The value of selectivity coefficient (Ag/Cu) was 194.
- Thiomorpholine modified resin was very selective towards Ag(I) in relation to Cu(II), Pb(II), Co(II), Ni(II), and Zn(II) from real chloride leaching solution.

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