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Silver(I) recovery on sulfur-containing polymeric sorbents from chloride solutions

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Abstract: This work describes the preparation of functional polymers containing 2-mercapto-1-methylimidazole and guanylthiourea ligands from chemically modified vinylbenzyl chloride/divinylbenzene copolymer (VBC/DVB). The resins were used for the removal of Ag(I) from synthetic and real chloride solutions. The 2-mercapto-1-methylimidazole resin was highly selective towards Ag(I) in relation to Pb(II) from real chloride leaching solution. The resins were selective for Ag(I) from real chloride solution and they did not sorb chloride complexes of Co(II), Ni(II) and Zn(II). The sorption kinetic data were well fitted to the pseudo-first-order kinetic model. The degree of Ag(I) desorption was about 80% using 1% potassium cyanide solution in 0.5% hydrogen peroxide solution. Resins retain their capacity towards Ag(I) in five consecutive sorption/desorption cycles.

Keywords: functional polymers, synthesis, silver(I), sorption, selectivity

1. Introduction

Silver, a precious metal, is extensively applied in different areas: medicine, photography, catalysis, jewelry and electronic industries. Therefore, significant amounts of silver are released in industrial effluents. Silver is also present in its native state and extracted from complex ores such as sulphide and carbonaceous refractory ores. Many studies have been recently focused on the extraction and separation of silver due to both increasing industrial need for this metal and its limited sources. The methods for removal of silver from ores, wastewater and water include zinc cementation, carbon adsorption, solvent extraction and sorption on polymeric resins. The recovery of silver by sorption on polymeric sorbents is a technique of great interest for various applications. This method is the cheapest and effective for the removal of silver. Polymeric materials, ion exchange resins and chelating resins, containing selective functional groups, are widely used for the separation of silver ions from various solutions. According to the theory of hard and soft acids and bases (HSAB) defined by Pearson, silver ions can form a stable ligand structure with sulfur atoms. Chelating resins bearing sulfur in ligands are highly efficient for the selective sorption of silver ions. Therefore, many works were focused on introducing sulfur-containing groups into polymeric matrix. The novel thiourea resin (PTDTR) containing acyl and thiourea groups are used for the removal of Ag(I) from aqueous solution (Huang et al., 2019). The PTDTR resin showed good selectivity for Ag(I) ions in Ag(I)-Cu(II) binary system. The thiourea-grafted mesoporous polystyrene resin showed high selectivity for Ag(I) and can be useful for the selective separation of silver ions from Co(II), Ni(II), Cu(II), Zn(II), Cd(II), Cs(I), Sr(II), Pb(II), La(III) and Pd(II) (Kumar et al., 2013). The resin derived from 3-amino-1,2,4-triazole-5-thiol and glutaraldehyde showed good selective adsorption of Ag(I) from binary mixtures of different metal ions (Cu(II), Pb(II), Cd(II), Zn(II) or Ca(II)) (Abd El-Ghaffar et al., 2009). Thiourea-immobilized polystyrene (TA-PS) nanoparticles were applied to recover of silver(I) from aqueous solution (Yun et al., 2018). The maximum Ag(I) sorption capacity of

TA-PS was estimated to be 190 ± 5 mg/g. Thiourea-formaldehyde (TF) and urea-formaldehyde (UF) chelating resins have been synthesized and they have been used in the adsorptions of Ag(I), Cu(II), and Zn(II) metal ions (Kirci et al., 2009). Ag(I) ions showed higher affinity towards TF resin than UF compared with Cu(II) or Zn(II). Thiourea-modified chitosan resin showed good adsorption capacity and high selectivity for Ag(I) in aqueous solution (Wang et al., 2010). The maximum uptake of Ag(I) exhibited was 3.77 mmol/g, at pH 4.0. Melamine-formaldehyde-thiourea (MFT) chelating resin has been used for separation and recovery of Ag(I) from Cu(II), Zn(II) and Ca(II) metals in aqueous solution (Yirikoglu and Gulfen, 2008). The maximum uptake values of MFT resin were found as 60.05 mg Ag/g resin. The MFT resin showed higher uptake behavior for Ag(I) than other metals due to chelation. The chelating resins containing thiol and amino groups were used for concentrating retrieving of Ag(I) from nitrate solution (Iglesias et al., 2001). Magnetic chelating resin derived from a blend of bithiourea/thiourea/glutaraldehyde had good adsorption properties for recovery of silver and gold from aqueous solutions (Atia et al., 2014). The functional resins containing guanlylthiourea, 2-mercapto-1-methylimidazole ligands were highly selective for the gold(I) and silver(I) from ammonia solution and they did not sorb ammine complexes of copper(II) (Piłśniak-Rabiega and Trochimczuk, 2014). The grafting of 2-mercaptobenzimidazole on chitosan microparticles allowed developing highly selective sorbents for Ag(I) recovery (Elwakeel et al., 2021). Sorption capacities as high as 3 mmol Ag/g could be obtained with contact times as low as 20-30 min. Recovery of Ag(I) from aqueous solutions was studied using magnetic resin derived from chemically modified chitosan. The adsorption capacity of Ag(I) was 2.1 mmol/g (Elwakeel et al., 2007). The corn stalk-based adsorbent (TSC-NH₃-OCS) modified by ammonia-thiosemicarbazide had a good performance for recovery Ag(I) from simulate nickel electrolyte (Xiong et al., 2016). The TSC-NH₃-OCS adsorbent showed a low affinity for Cu(II) and Ni(II), and had high selectivity to recovery trace amounts of Ag(I) from the mixture solution containing high levels of Cu(II) and Ni(II). The maximum adsorption capacities of Ag(I) from Ag(I)-Cu(II)-Ni(II) ternary system was 46.69 mg/g, while it was 153.54 mg/g from the Ag(I) single system. The S-bearing carbonized corn stalk was prepared by grafting epithiochlorohydrine and thiourea onto the corn stalks (OCS-ET-TU) (Li et al., 2018). The OCS-ET-TU adsorbent was used for recovering Ag(I) from industrial nickel electrolyte. The nickel electrolyte contained 24.8 mg/dm³ Ag, 90.0 g/dm³ Ni, 43.0 g/dm³ Cu and 16.6 g/dm³ Fe. The maximum adsorption capacity of Ag(I) was 3.06 mg/g in the nickel electrolyte, but the other competed metal ions could not be adsorbed onto the OCS-ET-TU.

In this work, we focused on the selective uptake of Ag(I) from synthetic and real chloride solutions on resins with 2-mercapto-1-methylimidazole and guanlylthiourea ligands. Sorption isotherms, kinetics and silver desorption have been also studied.

2. Materials and methods

2.1. Chemical reagents

The chemicals were Sigma-Aldrich products. Synthetic solution of Ag(I) was prepared by dissolving a known amount of silver nitrate in chloride solution (4.0 M NaCl, 0.10 M HCl). The initial Ag concentration for synthetic solution was 55.6 mg Ag/dm³.

Solution of silver(I) and copper(II) was prepared by dissolving a known amount of copper sulfate and silver nitrate in chloride solution (4.0 M NaCl, 0.10 M HCl). The concentration of Ag(I) and Cu(II) was 55.6 and 30.8 mg/dm³, respectively.

Real chloride leach solution was contained 60.0 mg/dm³ of Ag(I) and $4.21 \cdot 10^3$ mg/dm³ of Pb(II) as well as 454 mg/dm³ of Cu(II), 20.0 mg/dm³ of Zn(II), 16.3 mg/dm³ of Co(II) and 5.07 mg/dm³ of Ni(II). This solution was prepared by chloride leaching of a solid residue after atmospheric leaching in sulfuric acid of copper concentrate. Detailed procedures of chloride leaching solution obtaining are presented in (Piłśniak-Rabiega et al., 2019).

2.2. Preparation of VBC/DVB copolymer and polymeric resins

2.2.1. Synthesis of VBC/DVB copolymer

VBC/DVB copolymer was prepared from vinylbenzyl chloride (VBC) and divinylbenzene (DVB) using suspension polymerization in the presence of toluene in order to obtain an expanded gel structure. It

contained 0.5 or 2 wt. % of crosslinker. The procedure of synthesis is presented in (Trochimczuk, 1998). The copolymer was washed with hot water, cold water and acetone, dried and extracted with toluene in Soxhlet apparatus for 8 h.

2.2.2. Synthesis of studied resins

The polymeric resin with 2-mercapto-1-methylimidazole groups (**I**) was prepared by microwave modification. The VBC/DVB (2 wt. % of DVB) copolymer was placed on a Petri dish and swollen with 2-mercapto-1-methylimidazole (five times molar excess with respect to the chlorine content in the polymer) for 1 h at room temperature. Then, the reaction mixture was placed in a microwave reactor for 10 min., at 100 W. The reaction temperature in microwave-heated was 120°C. The obtained resin was washed with acetone, acetone/water (1:1) and water. The beads were placed in the column and washed with 1 M HCl, water, 1 M NaOH and water.

The guanylthiourea resin (**II**) was prepared by conventional method. The VBC/DVB (0.5% of DVB), copolymer was modified with ethylenediamine in order to introduce amino groups into its structure. The resin with ethylenediamine ligands was swollen in butanol for 24 h and then was reacted with sodium dicyanamide (four time excess with respect to amino groups) for 20 h, at reflux conditions. After the reaction the polymer was washed with ethanol, ethanol/water, water, acetone and water. The obtained resin with cyanoguanidylethylenediamine groups was reacted with hydrochloric acid solution. After 1 h, sodium thiosulphate solution was added and the reaction mixture was shaken at room temperature for 4 h. Then, 25% of ammonia solution was added. After 2 h the polymer was placed in column and washed with 0.001 M NaOH.

2.3. Methods of analysis

Water regain was measured using centrifugation method in which about 1 g of polymer swollen in water was placed in a column with filled-glass bottom and centrifuged at 3000 rpm for 5 min., weighted and dried at 80°C for 24 h. After cooling 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, m_d is the dry weight of polymer (Jermakowicz-Bartkowiak, 2005).

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

Chlorine content was measured by burning about 20 mg of dry polymer sample in oxygen in a flask containing 25 cm³ of 3% hydrogen peroxide solution. The content of chlorine was determined using Volhard's method (Piłśniak-Rabiega and Trochimczuk, 2014).

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 cm³ of 3% hydrogen peroxide solution. After 1 h the flask was heated in a water bath for 30 min in order 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 to 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 resins towards Ag(I), Pb(II), Cu(II), Zn(II), Co(II) and Ni(II) from synthetic and real chloride solutions was determined by contacting the resin samples with 10 cm³ of metal ions solution. The dry weight of resin samples was 50 mg. Metal ions solution containing Ag (55.6 or 60.0 mg/dm³), Cu (30.8 or 454 mg/dm³), Pb (4.21·10³ mg/dm³), Zn (20.0 mg/dm³), Co (16.3 mg/dm³) and Ni (5.07 mg/dm³) 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 polymers were separated by filtration and the concentration of Ag was measured using atomic absorption technique (AAS) on a Varian SpectrAA 20 Plus Atomic Absorption Spectrometer.

The sorption isotherms were determined by contacting various amount of resins with 10 cm³ of solution containing 55.6 mg/dm³ of Ag, 4.0 M of NaCl, 0.10 M of HCl for 24 h and plotting the sorption as a function of the equilibrium concentration.

For the kinetics of sorption, the identical samples of resin were shaken with 10 cm³ of solution containing 55.6 mg/dm³ of Ag in chloride solution (4.0 M NaCl, 0.10 M HCl). Samples were taken at different intervals of time, 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 cm³ of solution after sorption.

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

Desorption of Ag was determined by contacting an amount of resin, loaded with the known amount of Ag, with 10 cm³ of an eluent at room temperature (23°C) and at 50°C for 24 h. After that time the concentration of Ag was determined by AAS and the percentage of Ag eluted was calculated.

3. Results and discussion

3.1. Synthesis and characterization of the resins

The polymeric resins (I and II) were prepared by the chemical modification of the vinylbenzyl chloride/divinylbenzene copolymers, VBC/DVB, (0.5 or 2 wt.% of DVB). The VBC/DVB copolymers were obtained during suspension polymerization in the presence of toluene giving materials with an expanded gel structure. The efficiency of incorporating vinylbenzyl chloride monomer into the polymer network was determined on the basis of the chlorine content in the copolymer. In the case of VBC/DVB copolymer (2.0 wt.% of DVB), elemental analysis gave 5.30 mmol/g of chlorine, which corresponds to 83% yield. The chlorine content in VBC/DVB polymer (0.5 wt.% of DVB) was determined at 5.15 mmol/g by the Volhard's method, which corresponds to 79% yield. The chloromethyl groups present in VBC/DVB structure served as a reactive place for the immobilization of amine ligands (see Fig. 1).

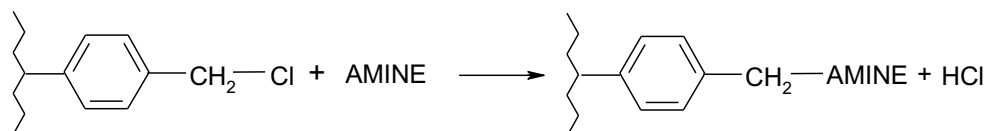


Fig. 1. Introduction of amino groups in the VBC/DVB copolymer

The 2-mercapto-1-methylimidazole resin (I) was prepared by using microwave modification. Elemental analysis gave 4.20 mmol of N/g, which corresponds to 50.0% yield (see Table 1). Sulfur content for this resin is 2.19 mmol/g. The yield calculated from the sulfur content is 51.7%. The substitution degree of chlorine in chloromethyl groups by 2-mercapto-1-methylimidazole calculated on the basis of nitrogen and sulfur content was similar. Modification efficiency and chlorine content (2.05 mmol/g) for resin I confirmed incomplete immobilization of functional groups in the polymer matrix. In relation to sorbent with 2-mercapto-1-methylimidazole ligands (prepared using microwave method) shown in the literature, the yield calculated from the nitrogen content is less and equals 47% (Piłśniak-Rabiega and Trochimczuk, 2007).

Table 1. Physicochemical properties of the polymeric resins

Resin No.	Water regain [g/g]	Chlorine content [mmol/g]	Nitrogen content [mmol/g]	Sulfur content [mmol/g]	Yield of Modification* [%]
I	0.51±0.01	2.05±0.02	4.20±0.02	2.19±0.02	50.0±1.0
II	0.64±0.01	0.00	8.07±0.02	1.73±0.02	41.0±1.0

* calculated from the nitrogen content

The guanylthiourea resin (**II**) was synthesized in a two-step reaction, using conventional method (modification at reflux and room temperature) (see Fig. 2). The resin containing ethylenediamine groups was modified using sodium dicyanamide in butanol (reflux conditions), and then reacted with sodium thiosulfate (modification at room temperature). The yield of the chloromethyl group substitution calculated from the nitrogen and sulfur content was 41.1 and 44.1%, respectively (see Table 1). These values of modification yield were comparable. The modification efficiency of resin **II** with the VBC/DVB (0.5 wt.% of DVB) is lower compared to the efficiency of immobilization of guanylthiourea ligands on a VBC/DVB (2.0 wt.% of DVB), which was 75% (Trochimczuk, 2000). This can be explained by a higher concentration of chlorine (6.25 mmol Cl/g) derived from VBC chloromethyl groups, giving the possibility of introducing more functional groups.

The resin **I** had small values of water regain (0.51 g of water/g of polymer) on account of presence sulfur atoms, which displayed hydrophobic properties.

The resin **II** was more hydrophilic than resin **I**, with water regain equal to 0.64 g of water/g of dry polymer. Amino groups contribute to the hydrophilicity of resins due to possibility of formation of hydrogen bonds with water.

The absence of chlorine in resin **II** and low value of yield reaction suggested that during the modification cross-linking took place (see Fig. 3).

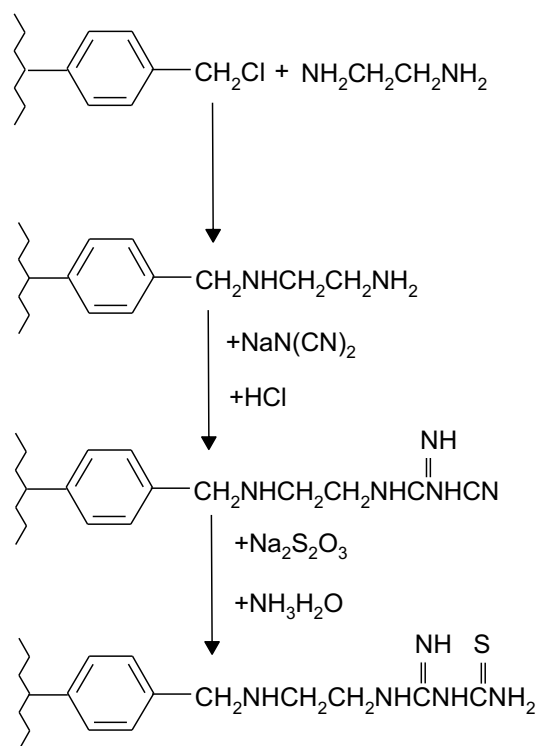


Fig. 2. Synthesis of resin with guanylthiourea ligands

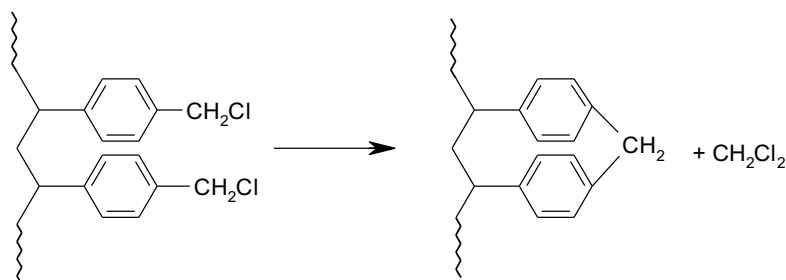


Fig. 3. Cross-linking of chloromethyl groups in VBC/DVB copolymer

The chemical structures (see Fig. 4) of obtained polymeric resins were confirmed by FTIR technique.

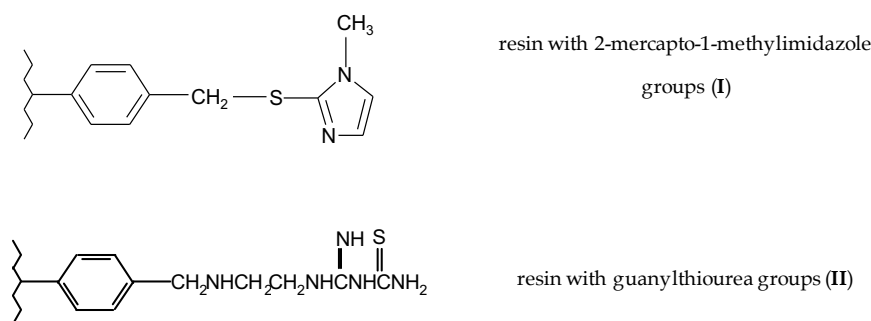


Fig. 4. Structure of investigated resins

In the FTIR (see Fig. 5) spectrum of unmodified VCB/DVB copolymer, the band at the wave number of 1264 cm^{-1} is characteristic, derived from C-Cl bonds in the chloromethyl group, and was observed by Egawa (Egawa et al., 1990) and Yaacouba (Yaacoub and Le Perchec, 1988). The disappearance of this band indicating the substitution of chloromethyl groups by amine ligands. The wide band at 3427 cm^{-1} comes from hydroxyl groups that are formed during the hydrolysis of vinylbenzyl chloride to vinylbenzyl alcohol. The bands at 2920 and 2850 cm^{-1} , correspond to anti-symmetrical and symmetrical valence bands in methylene groups. The valence vibrations of bonds between carbon atoms in the ring absorb in the ranges of $1500\text{--}1400\text{ cm}^{-1}$, while the absorption bands resulting from non-flat deformation vibrations of the ring occur in the area of $900\text{--}675\text{ cm}^{-1}$ (Silverstein and Bassler, 1970). As a result of the modifications carried out in the FTIR spectra of polymer resins, the largest changes occurred in the range of wave numbers $1640\text{--}620\text{ cm}^{-1}$. The strong and wide bands at $3395\text{--}3396\text{ cm}^{-1}$ are assigned to the presence of the -NH groups in the investigated resins. A band with a maximum at 1588 cm^{-1} also appeared in the spectra, which may be due to deformation vibrations of the N-H bond. Strong bands in the range of $899\text{--}704\text{ cm}^{-1}$ arise as a result of non-flat deformation vibrations of the ring, while peaks with a maximum in 1511 and 1488 cm^{-1} describe double bonds coupled in the phenyl ring and 1446 cm^{-1} deformation scissor vibrations of the $-\text{CH}_2$ groups connected with amine.

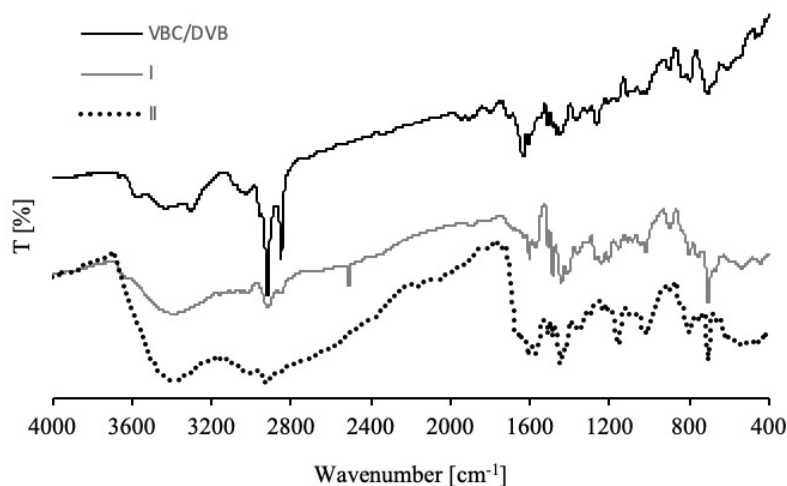


Fig. 5. FTIR spectra of unmodified copolymer VBC/DVB and modified polymers (resin I and II)

The FTIR spectrum of the 2-mercapto-1-methylimidazole resin (I) shows strong valence bands at 1361 cm^{-1} for C-N bonds (see Fig. 5). They appear at higher frequencies than the corresponding bands of aliphatic amines, because the C-N binding force constant is increased by ring resonance. The presence of imidazole rings is confirmed by bands at a maximum of $1509\text{--}1312$, 838 , 758 and 636 cm^{-1} (Silverstein and Bassler, 1970; Stuart, 2004). The strong band at 1411 cm^{-1} suggests the presence of $-\text{CH}_2\text{S}$ groups. The appearance of a broad valence band with a wave number of 2531 cm^{-1} may confirm the presence of

S-H groups. This band is not visible in the spectrum of the resin **I** and suggests attaching 2-mercapto-1-methylimidazole groups via a sulfur atom to the polymer matrix. The strong band at 1411 cm^{-1} comes from $-\text{CH}_2\text{S}$ groups and the invisible broad valence band at 2531 cm^{-1} characteristic for S-H groups, suggests attaching 2-mercapto-1-methylimidazole ligands via a sulfur atom to the polymer matrix.

The spectrum of the resin **II** shows a complex band at 1606 cm^{-1} , which may confirm the presence of a guanylthiourea ligand (see Fig. 5). The peak with a maximum at 1211 cm^{-1} may be from C=S bond vibration, and at 1159 cm^{-1} from C-N bond vibration. The wide band in the area of $615\text{--}405\text{ cm}^{-1}$ can be attributed to the vibrations caused by the interaction between C=S and C-N valence vibrations. The peak at 1558 cm^{-1} is associated with deformation vibrations of NH_2 groups.

3.2. Evaluation of the sorption properties

The polymeric resins with 2-mercapto-1-methylimidazole and guanylthiourea ligands were applied for recovery of Ag(I) from synthetic chloride solution (4.0 M NaCl, 0.10 M HCl). Based on the thermodynamics calculation, the silver complexes species in the tested solution (4.0 M NaCl, 0.10 M HCl) mainly exist in the form of AgCl_4^{3-} , whose proportion is 83%, when $[\text{Cl}^-]$ is 4.10 mol/dm^3 . The proportion for AgCl_2^- and AgCl_3^{2-} is 3.0 and 14%, respectively. The formation of these silver complexes was suggested by Liu (Liu et al., 2010).

The sorption properties of resins towards Ag(I) were studied under the conditions presented in Experimental part. The results are shown in Table 2.

Table 2. Sorption of Ag(I) from synthetic chloride solution ($C_{\text{Ag}} = 55.6\text{ mg/dm}^3$ (0.515 mmol/dm^3), $C_{\text{HCl}} = 0.10\text{ mol/dm}^3$, $C_{\text{NaCl}} = 4.0\text{ mol/dm}^3$)

Resin No.	Ligand concentration * [mmol/g]	Ag sorption capacity [mg Ag/g resin]	Ag sorption capacity [mmol Ag/g ligand]	Yield of Ag sorption [%]	K_d
I	2.10 ± 0.02	5.62 ± 0.5	0.052 ± 0.01	22.3 ± 1.0	130
II	1.61 ± 0.02	8.63 ± 1.0	0.080 ± 0.01	44.5 ± 1.0	280

* calculated from nitrogen content in functional groups

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 large atomic/ionic radius. Nitrogen atoms are borderline bases also tends to form complexes with precious metals.

The resins **I** and **II** displayed affinity towards Ag(I) due to the presence of donor N- and especially S-atoms in functional groups. Free pair of electrons on nitrogen and sulfur atoms should be able to coordinate with the silver in chlorocomplexes, what suggested that the main mechanism of Ag(I) uptake was coordination of metal ions.

It seemed probable that during the sorption of Ag(I) on resins **I**, the imidazole ligands formed specific Ag(I) complexes. Ag(I) can be then coordinated to two nitrogen donor-ligands and has a linear coordination geometry (see Fig. 6).

For silver-imidazole complex, $\text{Ag}(\text{Im})_2^+$, the logarithm of stability constant, $\log \beta_2$, is estimated to be 6.98, for AgCl_4^{3-} the value of $\log \beta_4$ corresponds to 5.30 (Perrin and Sillen, 1979). These values confirm that $\text{Au}(\text{Im})_2^+$ are more stable than AgCl_4^{3-} , what suggest formation of Ag(I) complexes on the resin with imidazole groups. So far, numerous works indicate that imidazole forms with silver some of the most stable complexes of all heterocyclic-N ligands (Bauman and Wang, 1964; Gold and Gregor, 1960; Gold and Gregor, 1960; Barszcz et al. 1985; McCann et al., 2013; Czoik et al., 2008). This is caused by the high acid association constant of imidazole. The formation of $\text{Ag}(\text{Im})_2^+$ complexes might be the reason of a smaller sorption of silver, because two bulky imidazole groups take part in the formation of one $\text{Au}(\text{Im})_2^+$ complex.

The presence of donor nitrogen and sulfur atoms in the functional groups of the resin **I** should also allow the formation of four-membered rings, as shown in Fig. 7. For this resin, the structure was such

that ion-exchange was not possible but sulfur atoms could be involved in the coordination and formation of four-member rings together with the neighbouring nitrogen atoms (see Fig. 7).

In the case of resin with guanyltiourea groups, it was found that sulfur atoms, which are electron donors, could complex Ag(I) and form six-membered rings with neighbouring nitrogen atoms (see Fig. 8).

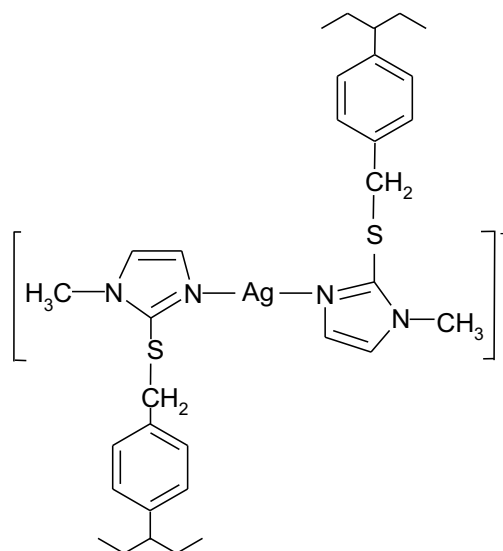


Fig. 6. Suggested mechanism for Ag(I) sorption on 2-mercapto-1-methylimidazole resin

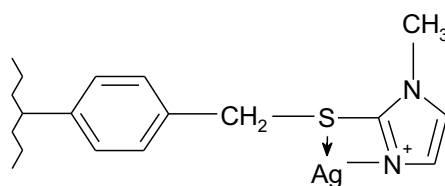


Fig. 7. Proposed structure of resin (I) with sorbed Ag(I)

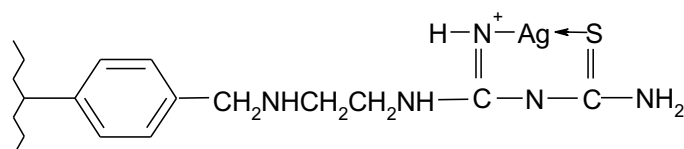
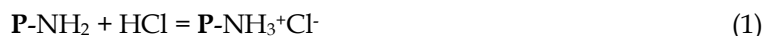


Fig. 8. Suggested mechanism for Ag(I) sorption on guanyltiourea resin

The sorption of silver chlorocomplexes, AgCl_4^{3-} , by resin **II** could also take place according to the mechanism of ion exchange, when nitrogen atoms were protonated (eq. 1 and 2):



where P denotes polymeric matrix.

The complexation abilities of resin **II** were certainly more important and efficient than ion exchange, because the concentration of Cl^- ions in chloride solution was $8.9 \cdot 10^3$ times higher than the concentration of Ag(I). The presence of large excess of chloride anions had strong influence on ion exchange and decreased affinity of the resin towards Ag(I). On the other hand, smaller sorption of Ag(I) complexes could be caused by the fact that three guanyltiourea ligands participated in the ion exchange of one AgCl_4^{3-} complex.

Resin with guanyltiourea groups showed greater affinity for Ag(I) from chloride solution relative to the resin modified with 2-mercapto-1-methylimidazole. Yield of Ag(I) sorption for resin **I** and **II** was

22.3 and 44.5%, respectively (see Table 2). Resin with guanylthiourea ligands was characterized by a structure with a lower degree of crosslinking (0.5 wt.% of DVB) in relation to the resin with 2-mercapto-1-methylimidazole groups, containing 2 wt.% of crosslinking agent. The lower degree of crosslinking had a large influence on polymer swelling and increased segmental mobility. These factors determined the easier access to the ligands and allowed diffusion of Ag(I) in the polymer network during the sorption of this metal on the resin.

3.2.1. Sorption isotherm studies

During the evaluating the sorption properties of prepared sorbents also the sorption isotherms at room temperature were determined (see Fig. 9). As can be observed the capacities of both materials are different. The greatest sorption capacity was observed for resin II during Ag(I) uptake at room temperature (224 mg Ag/g). Resin I has about five times less sorption capacity towards silver(I) than resin II. Additionally, it can be observed also that at lower concentrations, maximum capacity is reached for resin II.

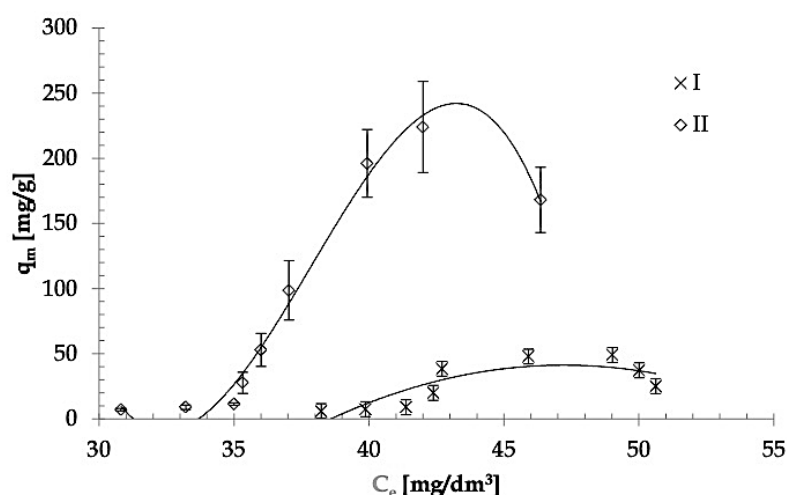


Fig. 9. Ag(I) sorption isotherms for resins. Samples of resin containing 0.1-10 × molar excess of ligand were shaken with 10 cm³ of solution containing 60 mg/dm³ of Ag(I) in chloride solution at 23 ± 2°C

To explore the interaction between the sorbate and sorbent, sorption isotherms are used which provide a relationship between amount of sorbate in liquid phase under equilibrium and sorption capacity at constant temperature. The applicability of the sorption process can be evaluated from the fundamental physicochemical data obtained by applying sorption isotherm models (Haq et al., 2020). In recent times, linear regression analysis has been one of the most applied tools for defining the best fitting adsorption models (Ayawei et al., 2017). In order to examine the model of sorption, the following models were used to evaluate the experimental sorption data obtained.

In the step first the Langmuir isotherm was used. According to this isotherm a monolayer sorption takes place on a homogeneous surface and there is no interaction among the sorbate molecules (Ayawei et al., 2017). The Langmuir equation (eq. 3) served to calculate the maximum uptake q_m of sorbate (Wolska and Bryjak, 2014; Duranglu et al., 2012):

$$q_e = \frac{q_m b_L C_e}{1 + b_L C_e} \quad (3)$$

where q_e is the uptake at equilibrium concentration [mg/g], q_m is the maximal uptake [mg/g], C_e is the equilibrium concentration [mg/dm³], b_L is a constant related to the free energy of adsorption [dm³/mg]. Values of q_m and b_L could be graphically determined from the linear form of Langmuir model (eq. 4):

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

To confirm the favorability of the silver(I) sorption process, a separation factor (dimensionless) called the equilibrium or separation parameter (R_L) can be calculated as (eq. 5) (Polowczyk et al., 2016):

$$R_L = \frac{1}{1+b_L C_0} \quad (5)$$

where C_0 is the initial adsorbate concentration [mg/dm³].

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

We also checked the Freundlich isotherm. This model assumed as a power function relationship between q_e and C_e and it is easily applicable when the experimental data are plotted in $\log q_e$ versus $\log C_e$ format (eq. 6) (Wolska and Bryjak, 2014; Cela-Pérez et al., 2011). Freundlich isotherm is applicable to adsorption processes that occur on heterogeneous 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 (Ayawei et al., 2017):

$$\log q_e = \frac{1}{n} \log C_e + \log a \quad (6)$$

In this model there are two fitting parameters a and $1/n$ that both yield a measure of physical binding. The a parameter is the constant related to adsorption capacity. The $1/n$ parameter is known as the heterogeneity index. For homogeneous materials, $1/n$ would be equal to 1 the adsorption is linear, adsorption sites are homogeneous in energy, and no interactions take place between the adsorbed compounds. On the other hand, when values of $1/n$ parameter approach to zero increase the heterogeneous character of the polymer. The constant n should have a value in the range of 1–10 for the adsorption to be classified as favorable. (Wolska and Bryjak, 2014; Cela-Pérez et al., 2011, Polowczyk et al., 2016). The fitting of experimental data by the Freundlich isotherm allowed to calculate the parameters a and $1/n$ which also helped to determine whether the selected model is appropriate. The values of the calculated parameter a were $1.62 \cdot 10^{-15}$ and $6.67 \cdot 10^{-23}$ for resins **I** and **II**, respectively. The values of n constant for both of investigated materials were below 1 (0.101 and 0.063 for resin **I** and **II** respectively) therefore it can be assumed that the sorption of Ag(I) onto both of resins is not favorable. Compare the R^2 values for the Langmuir and Freundlich models (see Table 3), it can be seen that the second model is a better fit for silver(I) adsorption onto both resins.

The next investigated sorption model is Dubinin-Radushkevich isotherm model which helps to study interaction between adsorbate and sorbent (Cela-Pérez et al., 2011). This approach is used generally to distinguish the kind of sorption: physical or chemical one dominates. The isotherm is expressed by eq. 7:

$$\ln(q) = \ln(q_{max}) - K_{DR} \varepsilon^2 \quad (7)$$

where q_{max} is the maximum adsorption capacity of material [mg/g], K_{DR} is the Dubinin-Radushkevich constant [kJ²/mol²], ε is the Polanyi potential (eq. 8):

$$\varepsilon = RT \ln \left(1 + \frac{1}{c} \right) \quad (8)$$

K_{DR} is related with 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 behaviour could predict physical adsorption in the range of 1 – 8 kJ/mol, and chemical adsorption at over 8 kJ/mol. The free energy can be calculated by eq. 9 (Cela-Pérez et al., 2011).

$$E = (2K_{DR})^{-0.5} \quad (9)$$

During this analysis the free energies values for both of resins were calculated, and they reached the value of 19.22 and 16.11 kJ/mol for resin **I** and **II** respectively. The calculated values of free energy have reached values greater than 8 kJ/mol for both resins, therefore in both cases, as could be expected, the sorption process takes place as a result of chemical interactions between sorbate and the adsorbate. Additionally, as can be seen the values of calculated parameters were higher for resin **II**. It means that the interactions between functional groups of resin **II** and the sorbate are about 1.2 times higher than resin **I** forces.

In the next step we checked the Temkin isotherm. This model takes into account the effects of indirect adsorbate/adsorbate interactions on the adsorption process; it is also assumed that the heat of

adsorption (ΔH_{ads}) of all molecules in the layer decreases linearly as a result of increase surface coverage. The Temkin isotherm is valid only for an intermediate range of ion concentrations. The linear form of Temkin isotherm model is given by the following equation (eq. 10) (Ayawei et al., 2017, Ulatowska et al., 2020):

$$q_e = \frac{RT}{b_T} \ln K_T + \frac{RT}{b_T} \ln C_e \quad (10)$$

where b_T is Temkin constant which is related to the heat of sorption [J/mol] and K_T is Temkin isotherm constant [dm³/g]. During analysis the b_T and K_T parameters for both resins were calculated. Temkin isotherm constant were 2.85 and 1.19 for resin I and II respectively. While the Temkin constants (b_T) have reached values 0.36 for the first of polymer and 1.26 for the second one.

Next investigated model was the Harkin-Jura Isotherm. Harkin-Jura isotherm model assumes the possibility of multilayer adsorption on the surface of adsorbents having heterogeneous pore distribution (Ayawei et al., 2017). This model is expressed as follows (eq. 11):

$$\frac{1}{q_e^2} = \frac{B}{A} - \left(\frac{1}{A}\right) \log C_e \quad (11)$$

where B and A are Harkin-Jura constants that can be obtained from plotting $1/q_e^2$ versus $\log C_e$. Both of constants were calculated. B constant has reached values 1.66 and 1.58 for resin I and II respectively. While the calculated A constant were 3.86 for polymer with with 2-mercapto-1-methylimidazole groups and 5.92 for the second type of material. However, the R^2 coefficient of the trend line is below 0.8, therefore this model does not fully describe the Ag(I) sorption process on synthesized resins.

The Jovanovic model is the next investigated model. The model of an adsorption surface considered by Jovanovic is predicated on the assumptions contained in the Langmuir model, but in addition the possibility of some mechanical contacts between the adsorbate and adsorbent. The linear form of the Jovanovic isotherm can be shown using the following relationship (eq. 12) (Aljaberi et al., 2020, Ayawei et al., 2017, Bharathi et al. 2017):

$$\ln q_e = \ln q_{max} - K_J C_e \quad (12)$$

where q_e is amount of adsorbate in the adsorbent at equilibrium [mg/g], q_{max} is maximum uptake of adsorbate obtained from the plot of $\ln q_e$ versus C_e , and K_J is Jovanovic constant. For this model the calculated parameters were not adequate with the experimental data, therefore this model was also not used to describe the process of silver(I) sorption onto resins.

The last used model is Elovich isotherm. The equation that defines this model is based on a kinetic principle which assumes that adsorption sites increase exponentially with adsorption; this implies a multilayer adsorption. The equation was first developed to describe the kinetics of chemisorption of gas onto solids. The linear form of the Elovich model is expressed as follows (Ayawei et al., 2017, Riyanto et al. 2019) (eq. 13):

$$\ln \left(\frac{q_e}{C_e}\right) = \ln(K_e q_m) - \frac{q_e}{q_m} \quad (13)$$

Elovich maximum adsorption capacity (q_m) and Elovich constant (K_e) can be calculated from the slope and intercept of the plot of $\ln(q_e/C_e)$ versus q_e .

In the next step of analysis, on the basis of determination coefficients (R^2) values, determined from the linear forms of the used sorption models, an attempt was made to determine which model best describes this sorption process (see Table 3). The best determination of adsorption modeling is done by linear regression analysis, because this analysis quantifies the adsorbate distribution, analyses the adsorption system, and verifies the assumption of the consistency of the adsorption isotherm model (Riyanto et al. 2019).

The R^2 value closest to 1 was obtained in the case of the Elovich model, therefore only on the basis of this model the maximum sorption capacities for both of resins were calculated (see Table 4). The maximum sorption capacity of AgCl_4^{3-} for the resins **I** and **II** is 40.7 and 194.2 mg Ag/g resin, respectively.

Recently, many different sorbents have been used for recovery of Ag(I) from aqueous solution. Therefore, we compared some sorbents with resins with 2-mercapto-1-methylimidazole and guanythiourea ligands and their sorption performance are presented in Table 5. Xiong et al. (2016) investigated adsorption of AgCl_4^{3-} from simulate nickel electrolyte using corn stalk based adsorbent

Table 3. Results of isotherm analysis

Model of isotherm	Resin I	Resin II
	R ²	R ²
Langmuir	0.789	0.856
Freudlich	0.866	0.872
Dubinin-Radushkevich	0.850	0.846
Temkin	0.806	0.794
Harkin-Jura	0.709	0.762
Jovanovic	0.835	0.864
Elovich	0.927	0.934

Table 4. Maximum sorption capacities calculated from Elovich model of isotherm

Resin No.	q_m [mg Ag/g resin]	q_m [mmol Ag/mmol ligand]	C_e [mg/dm ³]
I	40.7±1.0	0.180±0.01	42.2±0.2
II	194.2±1.0	1.12±0.10	39.6±0.2

q_m - maximal uptake of silver, calculated from Elovich isotherm,

C_e - equilibrium concentration

Table 5. Ag(I) sorption performance of various sorbents

Sorbent	Temperature [°C]	pH	q_m [mmol/g]	Ref.
PTDTR resin	30	6.0	6.08	Huang et al., 2019
Thiourea-grafted polymeric resin	27-30	1.0-1.5	1.25	Kumar et al., 2013
Chelating resin (P1)	25	6.7	1.73	Abd El-Ghaffar et al., 2009
Thiourea-immobilized polystyrene (TA-PS)	25	6.0	1.76	Yun et al., 2018
thiourea-formaldehyde chelating resin (TF)	25	3.0-5.0	0.539	Kirci et al., 2009
thiourea-modified chitosan resin	25	4.0	3.77	Wang et al., 2010
2-MBI chitosan	25	6.8	1.96	Elwakeel et al., 2021
2-MBI magnetic chitosan	25	6.8	2.02	
TSC-NH ₃ -OCS adsorbent	30	1.0	1.42	Xiong et al., 2016
OCS-ET-TU adsorbent	30	1.0	1.00	Li et al., 2018
2-mercapto-1-methylimidazole resin	25	1.0	0.180	
guanylthiourea resin	25	1.0	1.12	This work

modified by ammonia-thiosemicarbazide. The maximum adsorption capacity in the Ag(I) single and Ag(I)-Cu(II)-Ni(II) ternary system were obtained and calculated as 153.54 and 46.69 mg/g, respectively. The adsorption capacity of corn stalk-based sulfur-bearing adsorbent (OCS-ET-TU) for AgCl₄³⁻ reached to 79.94 mg/g (Li et al., 2018). Thiourea-formaldehyde (TF) and urea formaldehyde (UF) chelating resins have been synthesized and they have been used in the adsorptions of Ag(I) (Kirci and Guelfen, 2009). The adsorption capacities of TF and UF resins were found as 58.14 and 47.39 mg Ag(I)/g by batch method and 30.7 and 4.66 mg Ag(I)/g by the column method. The chelating resin (PTDTR) containing

acyl and thiourea groups exhibited a high adsorption capacity (q_m) (Huang et al., 2019). The maximum q_m of Ag(I) obtained from Langmuir model was 655.8 mg/g at 30°C. It could be found that guanlythiourea resin exhibited higher sorption capacities than most of the presented materials.

3.2.2. Sorption kinetics studies

Fig. 10 shows the sorption of Ag(I) as a function of time. The maximum uptake of Ag(I) was reached within 48 hours. Chlorocomplexes of Ag(I) were sorbed slower at the beginning of the process, but later the rate of uptake increased (77% of maximum uptake was reached after 24 h), and 99.9% of uptake was reached within 48 hours. In relation to resins shown in the literature, the kinetics of Ag(I) sorption on prepared resins is slower.

Atia et al. (2014) described magnetic chelating resin with amine/thio functionalities for silver recovery from aqueous solution. The maximum silver adsorption in the form of Ag(I) (668.8 mg Ag/g of resin) was obtained after 4 hours.

Yirikoglu and Gulfen (2008) separated and recovered Ag(I) using melamine-formaldehyde-thiourea resin (MFT) from Cu(II), Zn(II) and Ca(II) in aqueous solution. Stock solution for Ag(I), Cu(II), Zn(II), and Ca(II) were prepared from AgNO_3 , $\text{Cu}(\text{CH}_3\text{COOH})_2$, $\text{Zn}(\text{NO}_3)_2$ and $\text{Ca}(\text{NO}_3)_2$, respectively. The equilibrium uptake was reached within 40 min. At plateau, the uptake capacity was found to be 60.05 mg Ag/g resin.

Iglesias et al. (2001) investigated sorption capacity towards Ag(I) of three different resins bearing a thiol chelating group, Duolite GT-73, Purolite Thiomethyl and Spheron Thiol, as well as Chelamine. Chelating polymers showed slow kinetics due to coordinating reactions between the chelating group and the silver ions in solution.

For 2-mercaptobenzimidazole derivative of chitosan sorption kinetics was relatively slow (Elwakeel et al., 2021). Under selected experimental conditions 24-28 h were necessary for reaching equilibrium. This was probably due to low specific surface area.

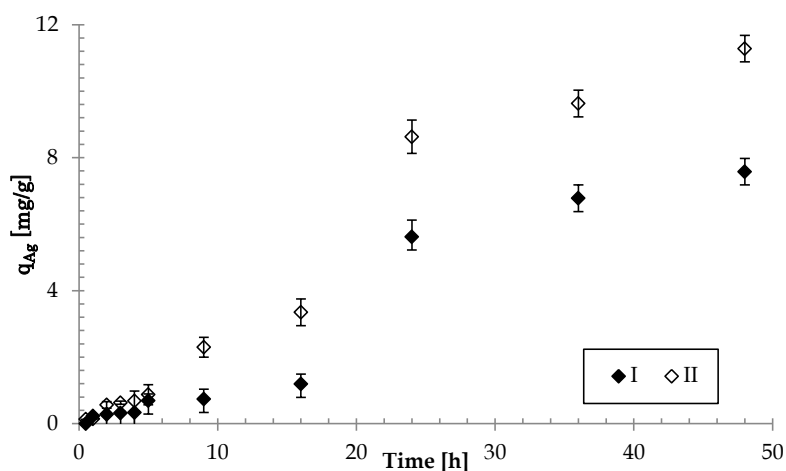


Fig. 10. Kinetics of Ag(I) sorption on polymeric resins. Samples of resin containing 0.01 mmol of ligand were contacted with solutions containing 10×molar excess of an appropriate Ag(I) in chloride solution at $23 \pm 2^\circ\text{C}$ and the concentration checked in specified time intervals

The kinetic data were fitted to diffusion models from the second Fick's law (eq. 14 and 15), to find the rate (film diffusion or particle diffusion) determining steps for resins (Kabay et al., 2007; Juang et al., 2002).

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

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 [min^{-1}]. Sorption rate constant k_a [min^{-1}] can be calculated from the plot of $-\ln\left(1 - \left(\frac{q_t}{q_e}\right)^2\right)$ vs. time.

$$k_b t = -\ln \left(1 - \left(\frac{q_t}{q_e} \right)^2 \right) \quad (15)$$

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

Table 6 gives the slope values, the linear determination coefficients, and the calculated values of k_a and k_b . Analyze of k_a and k_b can show for which resins the process of sorption is faster. For resin **II** these parameters are the highest, it means that for this sample the sorption equilibrium was reached at the little shorter time the for other resins. Analyze of the determination coefficients can show what kind of diffusion controlled the process mostly. In the case of resin **I** it is difficult to say which kind of diffusion controlled the Ag(I) sorption while in the case of resin **II** the film diffusion controlled the process mostly.

Table 6. Analysis of kinetic studies

Resin No.	$k_a t = -\ln \left(1 - \frac{q_t}{q_e} \right)$		$k_b t = -\ln \left(1 - \left(\frac{q_t}{q_e} \right)^2 \right)$	
	k_a [min^{-1}]	R^2	k_b [min^{-1}]	R^2
I	$2.0 \cdot 10^{-3}$	0.937	$3.0 \cdot 10^{-5}$	0.946
II	$5.0 \cdot 10^{-3}$	0.977	$1.0 \cdot 10^{-4}$	0.945

In order to predict the mechanism involved in the sorption process, several different kinetic models are applied. They are as follows: Lagergren pseudo-first and pseudo-second-order, Elovich equation, and parabolic diffusion model. 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 sorption kinetics following the pseudo-first order model is given by eq. 16 (Kabay et al., 2007):

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

where q_t and q_e represent the amount of adsorbed species [mmol/g] at any time t and at equilibrium time, respectively, and k_1 represents the sorption rate constant [min^{-1}].

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

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

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

The kinetic data can be analyzed by means of pseudo-second-order kinetics also (Kabay et al., 2007):

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

where k_2 is the pseudo-second-order rate constant [$\text{g}/\text{mmol} \cdot \text{min}$], q_e and q_t are the amount of adsorbed species [mmol/g] at equilibrium and at time t . Varying the variables in eq. 18 one gets:

$$\frac{dq}{(q_e - q_t)^2} = k_2 dt \quad (19)$$

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):

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

A plot t/q versus t gives the value of the constants k_2 [$\text{g}/\text{mmol} \cdot \text{h}$]. It is also possible to calculate q_e [mmol/g].

The experimental data were fitted with eq. 16 and 18 that served for calculation of k_1 and k_2 constants the determination coefficients (R^2). The results of kinetic analysis are given in Table 7. It can be seen that sorption kinetics for both materials fits well to pseudo-first-order mechanism. The adsorption of Ag(I) from aqueous solution on the chelating polymer derived from 3-amino-1,2,4-triazole-5-thiol and glutaraldehyde was perfectly fit pseudo-first-order model (Abd El-Ghaffar et al., 2009). Abd El-Ghaffar et al. described modified melamine resins (with thiourea or tetraoxaly ethylenediamine) for the

selective separation of Ag(I) from aqueous solution (Abd El-Ghaffar et al., 2009). The sorption kinetic data were well fitted to the pseudo-first-order kinetic model.

Table 7. Kinetic parameters of Ag(I) sorption

Resin No.	Pseudo-first		Pseudo-second	
	k_1 [g/mmol·h]	R^2	k_2 [g/mmol·h]	R^2
I	$7.0 \cdot 10^{-5}$	0.938	$5.9 \cdot 10^{-1}$	0.599
II	$2.0 \cdot 10^{-4}$	0.977	$1.5 \cdot 10^{-1}$	0.231

3.2.2. Desorption of Ag(I) from the resins

Regeneration ability is an important indicator for a sorbent. Based on the mass balance of the Ag(I) sorbed on the polymer bed and then desorbed the elution process was investigated. In this work, the Ag(I) was desorbed by different eluents: 0.5% sodium thiosulphate solution, 0.5% thiourea solution, 1% potassium cyanide solution, 1% potassium cyanide solution in 0.5% hydrogen peroxide solution, 0.5 M sodium hydroxide solution and ammonium buffer (2.86 M $(\text{NH}_4)_2\text{SO}_4$, 0.380 M $\text{NH}_3 \cdot \text{H}_2\text{O}$). The each of eluents was used for desorption of similar amount of silver on resin. This process was carried out at room temperature (23°C) and at elevated temperature (50°C). The results are exhibited in Table 8.

The eluents more effectively desorbed silver from resins at elevated temperature. It was observed that 1% potassium cyanide solution in 0.5% hydrogen peroxide solution at 50°C effectively eluate Ag(I) from resins. It seemed probable that during the desorption of Ag(I) from resins, cyanide anions formed $\text{Ag}(\text{CN})_4^{3-}$ complexes by ligand exchange mechanism. The silver-cyanide complex, $\text{Ag}(\text{CN})_4^{3-}$, is the most stable complex ion formed by Ag(I), and the logarithm of stability constant, $\log \beta_4$, was estimated to be 22.3, for AgCl_4^{3-} the value of $\log \beta_4$ corresponds to 5.30 (Högfeldt, 1982). The values of the $\log \beta_4$ 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 polymeric resins. On the other hand, Ag can be present on the surface of the resin as highly-disintegrated metallic silver, which is weakly connected to the resin and can be better eluted by 1% KCN under oxidizing conditions.

The yields of the silver elution were higher for 2-mercapto-1-methylimidazole resin (I) than for guanlythiourea resin (II). It can be explained that silver bonded to resin I was bonded to less basic ligands (an imidazole ring is not attached to the polymer backbone directly through the nitrogen atom but indirectly through the sulfur).

Table 8. Elution of silver(I) from resins using different eluents

Desorbent	Temp. 23°C		Temp. 50°C	
	% Desorption		% Desorption	
	I	II	I	II
0.5% $\text{Na}_2\text{S}_2\text{O}_3$	7.68±0.5	3.86±0.5	17.9±1.0	6.26±0.5
0.5% $\text{CS}(\text{NH}_2)_2$	12.3±1.0	4.22±0.5	18.9±1.0	5.49±0.5
1% KCN	21.4±1.0	12.5±1.0	65.4±2.0	18.5±1.0
1%KCN+0.5% H_2O_2	45.6±1.0	29.8±1.0	81.0±2.0	59.6±1.0
0.5 M NaOH	11.6±1.0	9.71±1.0	46.5±1.0	16.7±1.0
Ammonium buffer*	14.8±1.0	5.56±0.5	26.8±1.0	6.77±0.5

* 2.86 mol/dm³ $\text{NH}_3 \cdot \text{H}_2\text{O}$ and 0.380 mol/dm³ $(\text{NH}_4)_2\text{SO}_4$

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

In addition to sorption and desorption properties, an important feature of the sorbent is its stability in subsequent sorption processes and desorption of compounds or ions from the surface. It allows to assess

the suitability of such a material for cyclical processes that most often take place in the practical use of sorbent to recover specific compounds or ions.

In order to check the resin's stability, five cycles of Ag(I) sorption from chloride solution (60 mg Ag/dm³, 4.0 M NaCl, 0.10 M HCl) and desorption with 1% KCN in 0.5% H₂O₂ were performed on resins I and II. It could be concluded from these results (see Fig. 11), that the Ag(I) sorption ability increased, sorption efficiency was 22.3 (5.62 mg/g) and 44.5% (8.63 mg/g) in the first cycle, in the case of 2-5 cycles was 54.0-78.6 (13.6-19.8 mg/g) and 86.4-99.6% (16.5-20.5 mg/g), for 2-mercapto-1-methylimidazole (I) and guanylthiourea resin (II) respectively. Desorption efficiency in 1-5 cycles was 21.4-63.0 and 29.8-85.2% (for resin I and resin II, respectively). Elution was carried out at room temperature (23°C).

The better Ag(I) sorption on resins in the 2-5 cycles than in the first cycle, can be explained that during the second sorption of AgCl₄³⁻ on resins, cyanide anions from desorption were present on the polymeric surface, formed Ag(CN)₄³⁻ complexes by ligand exchange mechanism. Ag(I) cyanocomplexes are more stable than chlorocomplexes of Ag(I). Resins I and II were not fully regenerated, nonetheless sorption of Ag(I) was effective.

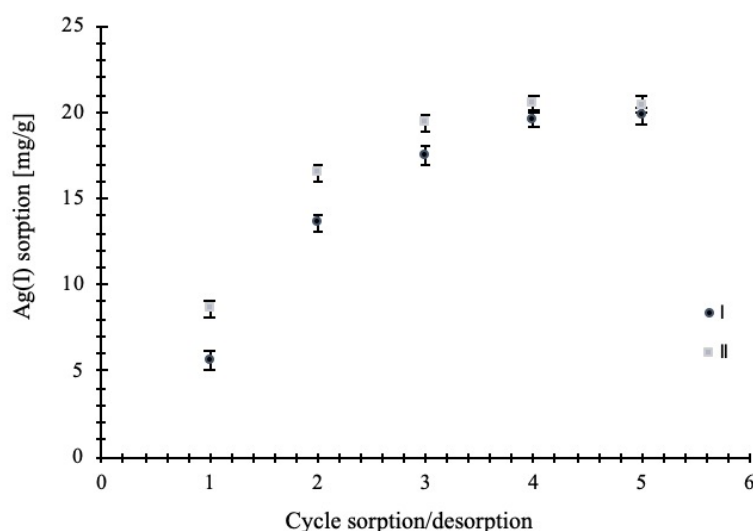


Fig. 11. Sorption properties of resins I and II in five cycles of sorption and desorption

3.2.3. Ag/Cu selectivity studies

The selectivity of functional polymers is a measure of their usefulness in sorption processes, based on the preferential sorption of a given metal, e.g. silver, from multi-component solutions containing other metals and ions. The selectivity of polymeric supports depends among others on: charge of sorbed ion, its polarization and shape, affinity of ligands for sorbed ions, structure of polymeric resin.

In order to determine the selectivity of obtained resins for silver(I) and copper(II), static sorption tests were carried out from 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 0.515, and 0.485 mmol/dm³, respectively. The selectivity coefficient ($\alpha_{sel.}$) was calculated as the quotient of distribution coefficients calculated for Ag(I) and Cu(II). The results are presented in Table 9. It could be seen that featured resins showed preferences for AgCl₄³⁻ complexes over CuCl₄²⁻ anions. This fact 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 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 resins prefer complexes, which have the highest density of the negative charge, what should increase their hydration requirements and facilitate their transport through the VBC/DVB matrices of resins. Ag(I) and Cu(II) chlorocomplexes have tetrahedral structure. The complex of AgCl₄³⁻ has higher density of negative charge (three charges is carried over by five atoms) than CuCl₄²⁻ complex.

Novel resin (PTDTR) with acyl and thiourea groups showed good selectivity for Ag(I) ions in Ag(I)-Cu(II) binary system (Huang et al., 2019). The values of separation factor (K) were higher than 100. The

adsorption capacities of PTDTR for Ag(I) had a bit decrease as the increasing the concentration of Cu(II) ions, suggesting the presence of Cu(II) ions in solution had little effect on Ag(I) adsorption. The 1-methyl imidazole resin and 1,2-dimethylimidazole resin showed preferential sorption of Ag(I) in the presence of Cu(II) from synthetic chloride solution (Piłśniak-Rabiega et al., 2019). The chlorocomplexes of Cu(II)

Table 9. Sorption of Ag(I) and Cu(II) on the resins from synthetic chloride solution ($C_{Ag} = 55.6 \text{ mg/dm}^3$ (0.515 mmol/dm^3), $C_{Cu} = 30.8 \text{ mg/dm}^3$ (0.485 mmol/dm^3), $C_{HCl} = 0.10 \text{ mol/dm}^3$, $C_{NaCl} = 4.0 \text{ mol/dm}^3$)

Resin No.	Sorption [mg metal/g resin]		K_d		$a_{sel.}$
	Ag	Cu	Ag	Cu	Ag/Cu
I	5.55±0.02	0.17±0.01	129	7.45	17.3
II	8.77±0.02	0.25±0.01	291	8.22	35.4

were not sorbed by these resins from solution containing Ag(I) and Cu(II) anions, each of concentration 0.56 mmol/dm^3 . The N-(2-sulfoethyl) chitosan-based sorbent is an advanced material for selective removal of Ag(I) from solutions of complex composition, including separation of silver(I) ions from copper(II) ions (Petrova et al., 2015). It was shown that the basicity of amino groups of the investigated substances decreased with an increase in the degree of sulfoethylation of a sorbent, and that influenced selectivity properties of the sorbent significantly. Particularly an increase in degree of sulfoethylation of chitosan resulted in an increase in selectivity of sorption of silver(I) ions over copper(II) ions, as confirmed by the values of selectivity coefficients. Melamine resin modified with thiourea (R1) showed high selectivity towards Ag(I) from binary mixture with Cu(II) (Abd El-Ghaffar et al., 2009). The value of the separation factor for the adsorption of Ag(I) over Cu(II) is 19.68.

It is interesting to notice, that according to the literature data (Marhol, 1982), quantitative separation of the two ions is achieved, when the corresponding values of the selectivity coefficients comprise 10–30 at least. Thus sorbents with 2-mercapto-1-methylimidazole and guanylthiourea are advanced materials for selective removal of Ag(I) ions from Ag(I)-Cu(II) binary system (see Table 9).

3.2.4. Sorption of Ag(I) from real chloride leach solution

Sorption studies with mixtures of metals (Ag, Cu, Pb, Zn, Co and Ni) were selected with regard to potential applications of resins in hydrometallurgical separation procedures. The sorption ability of resins I and II 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 copper concentrate (Piłśniak-Rabiega et al., 2019). Table 10 shows the effect of foreign ions on sorption of Ag(I).

The best sorption capacity towards Ag(I) from multicomponent solution showed guanylthiourea resin (II). The sorption degree of Ag(I) was 50.0% (10.3 mg/g). The resin with 2-mercapto-1-methylimidazole ligands was selective towards Ag(I) in relation to Pb(II) from real chloride leaching solution. The yield of Ag(I) and Pb(II) sorption was 29.6% and 0.05%, respectively. The value of selectivity coefficient, $a_{sel.}$, was 1583. This resin showed high selectivity for Ag (I), because $a_{sel.}$ was higher than 100 (Huang et al., 2019). This could be useful in the separation of Ag(I) from the chloride leaching solution containing other metals, especially Pb(II). The concentration of Pb(II) in real chloride solution was 37 times higher than the concentration of Ag(I).

The results showed that the resins were selective in respect of Ag(I) in the presence of chloride complexes of Cu(II). The concentration of Cu(II) in chloride solution was 13 times higher than the concentration of Ag(I). For resins I and II, the value of $a_{sel.}$ was 3.87 and 7.80, respectively.

The resins I and II were characterized by high selectivity towards Ag(I) in the presence of chloride complexes of Co(II), Ni(II) and Zn(II). These metal complexes were not sorbed by the obtained sorbents. Virolainen et al. applied several different adsorbents and ion exchangers for recovering Ag in the presence of a large excess of base-metals in concentrated chloride solutions (Virolainen et al., 2015). The recovery yield of Ag(I) was approximately 40% or higher with five materials, including two weak anion exchangers (WP-1, Purolite A830), one chelating resin (Dowex M4195) and both activated carbons (Norit pk 1-3, Univar). Purolite A830 resin had low Ag/Pb and Ag/Zn selectivities, while Dowex M4195 had

low Ag/Zn and especially Ag/Fe selectivity. The highest value of Ag/Cu separation factor ($a_{sel.} = 3.4$) was obtained for polyamine functional resin (WP-1), which also had very high selectivities for Ag over the other impurities except Pb. Affinity order of the metals to the resin was Pb>Ag>Zn>Cu>Fe>Ni>Mg, which can be explained by the tendencies of the metals to form anionic chloride complexes, and by the

Table 10. Sorption of Ag(I), Cu(II), Pb(II), Zn(II), Co(II) and Ni(II) from real chloride leach solution ($C_{Ag} = 60.0 \text{ mg/dm}^3$ (0.556 mmol/dm³), $C_{Cu} = 454 \text{ mg/dm}^3$ (7.14 mmol/dm³), $C_{Pb} = 4.21 \cdot 10^3 \text{ mg/dm}^3$ (20.3 mmol/dm³), $C_{Zn} = 20.0 \text{ mg/dm}^3$ (0.306 mmol/dm³), $C_{Co} = 16.3 \text{ mg/dm}^3$ (0.277 mmol/dm³), $C_{Ni} = 5.07 \text{ mg/dm}^3$ (0.0864 mmol/dm³) $C_{HCl} = 0.10 \text{ mol/dm}^3$, $C_{NaCl} = 4.0 \text{ mol/dm}^3$)

Resin No.		I	II
Sorption [mg metal/g resin]	Ag	7.96±0.01	10.3±0.01
	Cu	20.1±0.01	17.9±0.01
	Pb	0.52±0.01	101.9±0.01
	Co	0.00	0.00
	Ni	0.00	0.00
	Zn	0.00	0.00
	K_d	Ag	190
Cu		49.1	44.6
Pb		0.12	25.9
Co		-	-
Ni		-	-
Zn		-	-
$a_{sel.}$	Ag/Cu	3.87	7.80
	Ag/Pb	1583	13.4
	Ag/Co	-	-
	Ag/Ni	-	-
	Ag/Zn	-	-

affinity of the resin towards the less hydrated Pb and Ag. Polymeric resins with diethylenetriamine and tetraethylenepentamine groups have been used for the separation of Ag(I) from real chloride solution containing Cu(II), Pb(II), Co(II), Ni(II) and Zn(II) (Piłśniak-Rabiega et al., 2019). It was found that chlorocomplexes of Pb(II), Ni(II) and Zn(II) were not sorbed by the diethylenetriamine resin from chloride solution. Tetraethylenepentamine resin was selective towards chloride complexes of Ag(I) in relation to Co(II) and Ni(II).

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

4. Conclusions

- Modification of VBC/DVB copolymers with 2-mercapto-1-methylimidazole and ethylenediamine, is an effective method of polymeric resins preparation.
- Both methods of modification, that is conventional heating in amine solution as well as microwave heating are applicable. The best results of the introduction of functional groups into the polymer matrix were obtained using 2-mercapto-1-methylimidazole (microwave modification).
- The presented sorbents were useful for recovery of Ag(I) from synthetic chloride solution (4.0 M NaCl, 0.10 M HCl). The highest sorption of Ag(I) was reached in the case of guanlylthiourea resin (II).
- The presence of large excess of chloride anions in the studied solutions decreased affinity of the resins towards chlorocomplexes of Ag(I).

- The maximum sorption capacity of Ag(I) obtained from of the Elovich model was 40.7 and 194.2 [mg Ag/g resin] for the resins I and II, respectively.
- The uptake of Ag(I) on resins fits well to pseudo-first-order model.
- The loaded resins can be regenerated with 1% potassium cyanide solution in 0.5% hydrogen peroxide solution at elevated temperature (50°C).
- Resins with 2-mercapto-1-methylimidazole and guanylthiourea ligands retained their capacity towards Ag(I) in five consecutive sorption/desorption cycles.
- The resins showed preferences for AgCl_4^{3-} complexes over CuCl_4^{2-} anions from a two-component Au-Cu solution.
- For resin with 2-mercapto-1-methylimidazole ligands, selective in relation to Ag(I) uptake over Pb(II) was extremely high, from real chloride leaching solution.
- The resins were very selective towards Ag(I) in relation to Co(II), Ni(II) and Zn(II) from real solution. The chloride complexes of Co(II), Ni(II) and Zn(II) were not sorbed by the obtained sorbents.

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