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Modified chitosan as a potential bioresin for Ag(I) recovery

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Abstract: The present study focuses on the preparation of chitosan and chitosan-derived resin and their application in the removal of Ag(I) from aqueous systems. Chitosan was modified with epichlorohydrin, followed by 1-methylimidazole through microwave-assisted modification. The modified chitosan was capable of adsorbing as much as 77 mg of Ag(I) per gram. The sorption kinetics were best described by the pseudo-first-order model. Additionally, the bioresin maintained its Ag(I) sorption capacity after five repeated sorption and desorption cycles.

Keywords: synthesis, microwave modification, epichlorohydrin, 1-methylimidazole, sorption

1. Introduction

One of the greatest challenges the world is currently dealing with is environmental pollution. It can be caused by toxic metals released from various industries, such as the chemical and metallurgical sectors.

Silver, as a precious metal is extensively utilized in various industries because of its outstanding qualities, such as superior thermal and electrical conductivity and corrosion resistance. However, silver-containing waste often ends up in wastewater, which can negatively affect both human health and the environment. Silver compounds can cause various diseases, including a condition known as argyria.

Since silver is both valuable and toxic, increasing efforts are being made to develop methods to recover it from aqueous solutions, including wastewater. Chemists are actively looking for materials that can remove toxic metal contaminants from water. Ideally, these materials should be non-toxic and biodegradable, so they do not become another source of environmental pollution.

Such materials include chitosan, a derivative of the naturally occurring polysaccharide chitin.

Chitin and chitosan are among the most important natural biopolymers, with a wide range of applications. Chitin is a structural polysaccharide occurring in insect and crustacean exoskeletons, built from N-acetyl-D-glucosamine units joined by β-1,4-glycosidic linkages (Kafedjiiski et al., 2021; Shastri, 2017).

The main way to obtain chitosan is by chitin deacetylation. This is an alkaline hydrolysis reaction of the amide groups in the chitin chain. It refers to the elimination of acetyl groups (CH_3-CO-) and the replacement of methylamide groups (CH_3-CO-NH-) with amine groups (-NH_2) (Young et al., 2013; Nabel et al., 2020), which gives chitosan additional biological and chemical properties, such as greater reactivity and chelating abilities, making it extremely useful in various fields (Xiaohong et al., 2001).

The versatility of chitosan, due to its properties and modifiability, makes it a biopolymer with great potential to promote sustainability and environmental protection. Its diverse applications, both in advanced technologies and in everyday products, point to its increasing importance in modern environmental and medical solutions.

One of the most important aspects of the use of chitosan is its modifiability, as it allows its physicochemical, mechanical, and biological properties to be adapted to a wide range of needs in different scientific and industrial fields.

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Chitosan, like many other polysaccharides, can undergo both physical and chemical modifications, with chemical modification being the most commonly used. Modifications are applied to chitosan to change various physicochemical properties, including enhancing its solubility in water, reducing its ability to dissolve in acidic environments, increasing its ability to bind substances, or improving its chemical resistance and mechanical strength. The ability of chitosan to be chemically modified is made possible primarily by the presence of two types of reactive functional groups in its structure: an amine group and two hydroxyl groups (Ostrowska-Czubenko et al, 2016).

Chemical modifications of chitosan, such as cross-linking with, for example, glutaraldehyde, genipin, citric acid, or epichlorohydrin, allow the formation of permanent bonds between polymer chains, leading to a three-dimensional structure with exceptional mechanical, thermal, and chemical properties (Kou et al., 2021).

The process of crosslinking biopolymers allows their properties to be tailored to specific needs. The variety of crosslinking methods allows the structure and properties of materials to be controlled, making cross-linked polymers a key role in modern industry, from automotive to advanced engineering. Their versatility and durability make them essential materials in many fields.

Due to its properties, chitosan has been the subject of numerous scientific studies on its ability to adsorb silver and other metals from aqueous solutions.

The use of epichlorohydrin and 1-methylimidazole as chitosan modifiers results from their complementary chemical properties, which enable the biopolymer to acquire new and advantageous sorption characteristics toward silver ions. Epichlorohydrin is a widely applied crosslinking agent for polysaccharides due to the high reactivity of its epoxy groups, which readily form stable bonds with the –OH and $–NH_2$ groups present in chitosan. The crosslinking process enhances the chemical and mechanical stability of the material, reduces its solubility in aqueous media, and allows controlled structural stiffening. At the same time, epichlorohydrin introduces reactive moieties into the polymer matrix that can serve as anchoring sites for further functional ligands. 1-methylimidazole was selected as the second modifier because of the presence of a heteroaromatic imidazole ring, which is known for its high sorption affinity toward metals, including Ag(I).

Thermosensitive chitosan hydrogels containing β-glycerophosphate (β-GP) were utilized to adsorb Ag(I) from aqueous mediums, achieving a maximum removal efficiency of 34% at the highest initial silver concentration of 10 g/dm^3, with maximum adsorption capacity of q_e=31.52 mmol/g (Skwarczynska-Wojsa and Modrzejewska, 2024).

Magnetic chitosan microparticle sorbents functionalized with pyrimidine derivatives were effectively used for Ag(I) adsorption, achieving maximum sorption capacities of 2.3 mmol/g at pH 6 (Hamza et al., 2022).

Grafting 2-mercaptobenzimidazole onto chitosan microparticles enabled the creation of highly selective sorbents for Ag(I) recovery, achieving sorption capacities up to 3.04 mmol Ag/g (Elwakeel et al., 2021).

The removal of Ag(I) ions from aqueous solutions was studied using chitosan-based resins functionalized with ethylenediamine and 3-amino-1,2,4-triazole-5-thiol. The ethylenediamine-modified chelating resin exhibited an adsorption capacity of 1.13 mmol/g (Elwakeel et al., 2013).

Ag(I) ions were extracted from aqueous solutions using chitosan resin modified with thiourea, reaching a maximum adsorption capacity of 3.77 mmol/g at pH 4.0 (Wang et al., 2010).

A chemically modified chitosan resin exhibiting magnetic properties was evaluated for its ability to recover Au(III) and Ag(I) ions from aqueous solutions, showing uptake capacities of 3.6 mmol/g for Au(III) and 2.1 mmol/g for Ag(I) (Donia et al., 2007).

This paper presents the synthesis of chitosan and chitosan-based resin functionalized with 1-methylimidazolium groups, as well as their sorption properties toward Ag(I) from aqueous solutions. Additionally, sorption isotherms, kinetics, and silver desorption were analyzed.

2. Experimental

2.1. Chemical reagents

Low molecular weight chitosan (20 kDa, degree of deacetylation 75–85%), glutaraldehyde (50% aqueous solution), Span 80, Span 20, and 1-methylimidazole were purchased from Sigma-Aldrich. The solutions of NaCl, $AgNO_3$, glacial acetic acid, ethanol, methanol, and isooctane were obtained from Avantor Performance Materials Poland S.A. Epichlorohydrin was supplied from Acros Organics. Silver standard solution was purchased from Merck. All experiments were conducted using double-distilled water.

Standard Ag(I) solution was obtained by dissolving a weighed amount of silver nitrate in double-distilled water, yielding a concentration of 12.91 mg/dm^3.

Aqueous Ag(I) solutions of 12.91, 24.50, 39.30, 52.03, 65.60, and 78.02 mg Ag/dm^3 were used to determine the sorption isotherms.

2.2. Preparation of the chitosan solution

Chitosan was dissolved in a 5 wt.% aqueous solution of glacial acetic acid containing 0.4 wt.% NaCl. The resulting solution was further filtered to eliminate impurities. This prepared mixture, with a chitosan concentration of 1.5 wt.%, was then used in the membrane emulsification process (Wolska, 2006).

2.3. Preparation of chitosan microspheres

The membrane emulsification (ME) process was performed using a commercial unit supplied by Micropore Ltd, as detailed by Kosvintsev (Kosvintsev et al., 2005).

The system utilized a metallic membrane featuring uniformly distributed pores with a diameter of 20 µm. A volume of 50 cm^3 of the chitosan phase was introduced through the membrane into a tubular reactor equipped with a mechanical stirrer. The reactor contained 90 cm^3 of isooctane, supplemented with 2.5 wt.% Span 20 and 2.5 wt.% Span 80 as surfactants. The chitosan phase was delivered at a flow rate of approximately 1 cm^3/min, while the stirrer operated at a rotational speed of 600 rpm (Wolska, 2017).

Following emulsification, the resulting emulsion was transferred into a round-bottomed flask fitted with a mechanical mixer, and the crosslinking process was conducted at ambient temperature for 24 hours. Glutaraldehyde was added in an amount equal to half the chitosan content present in the emulsion. Upon completion of the crosslinking process, the dispersion was filtered, and the obtained microspheres were washed twice with isooctane and subsequently twice with ethanol via centrifugation. The microspheres were then subjected to drying and further purified using Soxhlet extraction with ethanol for 24 hours to eliminate residual solvents, unreacted glutaraldehyde, and other impurities. Finally, the microspheres were dried at 60°C. Following this step, their physicochemical properties were evaluated, and subsequent surface modification of the chitosan microspheres was carried out.

2.4. Modification of chitosan microspheres

The modification of chitosan microspheres (biopolymer I) was carried out through a two-step procedure.

In the first stage, epichlorohydrin molecules were attached to the free primary amino groups present in chitosan (see Fig. 1). Then the process of attachment of the 1-methylimidazole molecules (see Fig. 2) was performed by substituting the chlorine atoms present in epichlorohydrin.

During the first stage, the swelling time and the microwave modification time were changed to find the appropriate conditions for modification. The weight ratio between the chitosan microspheres and epichlorohydrin in both cases was 1:4.

2.4.1. The first trial

The centrifuged biopolymer was weighed in a beaker on analytical balance, the appropriate amount of epichlorohydrin was added and the mixture was left covered for 1 hour under standard laboratory conditions. Following this period, the mixture was subjected to microwave irradiation at 90 W for 30 seconds, after which it was allowed to cool to ambient temperature. In total, the sample was heated for 20 minutes. After modification, the microspheres were washed 4 times with methanol, then with a 1:1 volumetric mixture of double-distilled water and methanol, and finally 8 times with double distilled water. The washed polymer (biopolymer II) was left in double distilled water for the next stage of modification and for physicochemical analysis.

2.4.2. The second trial

The centrifuged biopolymer was weighed in a beaker on analytical balance, stoichiometrically appropriate quantity of epichlorohydrin was introduced, and the reaction mixture was maintained under covered conditions at ambient temperature for a duration of 24 hours. After this period, the mixture was subjected to microwave irradiation at 90 W for 30 seconds, followed by cooling to ambient temperature. This procedure was repeated until the cumulative irradiation time reached 20 minutes.

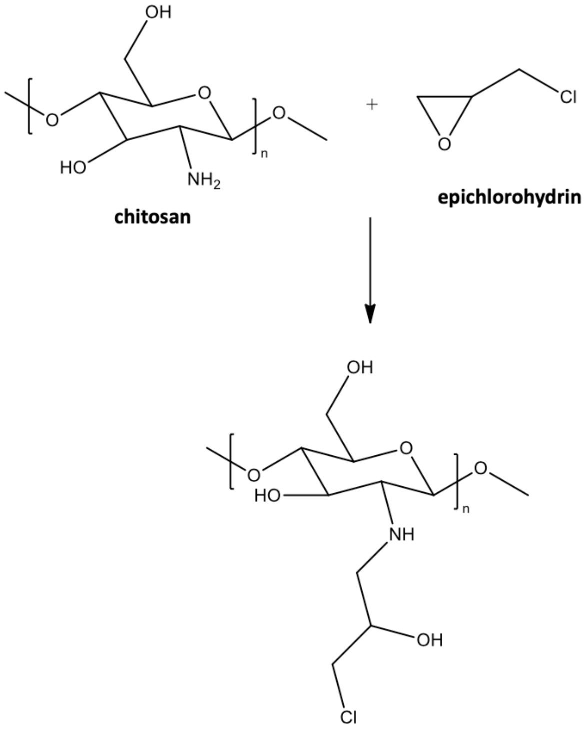

Fig. 1. Scheme of chitosan modification with epichlorohydrin

During the second stage of modification, the certificated biopolymer (biopolymer III) obtained during the second trial was weighted in a beaker and the proper amount of 1-methylimidazole was added (a tenfold molar excess relative to the chlorine content in the chitosan). The prepared mixture was left covered for 1 hour at room temperature. After this time, the swollen microspheres in 1-methylimidazole were modified for 30 seconds in a microwave reactor (90 W) and then cooled to room temperature. This process was repeated until the total modification time was 20 minutes. The polymer was then washed 4 times with methanol, once using a 1:1 volumetric mixture of double-distilled water and methanol, and finally 6 times with double distilled water. The synthesized biopolymer microspheres (biopolymer IV) were left in double distilled water.

2.5. Characterization of biopolymers

2.5.1. Water regain

The water content (W_{H2O}) of the swollen biopolymer sample was determined using a centrifugation technique. Approximately 1 g of swollen polymer spheres was centrifuged at 3000 rpm for 5 minutes, after which the sample was weighed (m_w). The material was then dried at 90°C for 24 hours and weighed again to obtain the dry mass (m_d). The water content was calculated according to Eq. 1:

$$W_{H2O} = (m_w - m_d)/m_d\,, \tag{1}$$

where m_w (g) represents the mass of the swollen biopolymer following centrifugation and m_d (g) denotes the mass of the biopolymer after drying (Wolska, 2016).

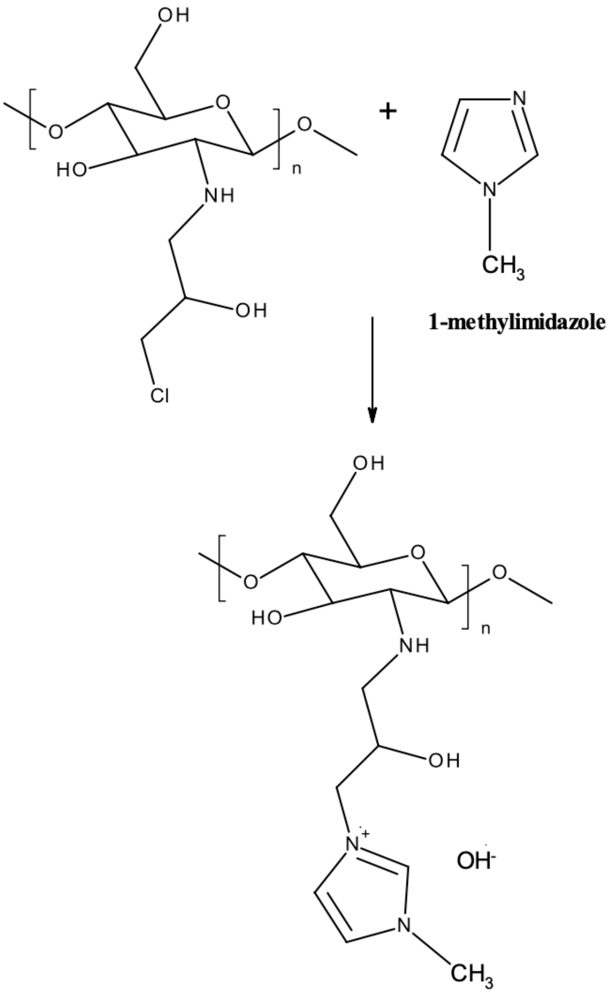

Fig. 2. Scheme of the second stage of modification of chitosan microspheres with 1-methylimidazole

2.5.2. Chloride content

Approximately 20 mg of the dried biopolymer sample was subjected to combustion in an oxygen atmosphere in a conical flask containing 25 cm^3 of a 3% H_2O_2 solution. Chlorine content was determined by applying the Volhard titration method, following the procedure reported by Pilśniak-Rabiega and Trochimczuk (Pilśniak-Rabiega and Trochimczuk, 2014).

2.5.3. Nitrogen content

Nitrogen determination was carried out using the Kjeldahl method, in which approximately 20 mg of the bioresin sample was digested in concentrated H_2SO_4 with $CuSO_4$ and K_2SO_4 serving as catalytic agents (Pilśniak-Rabiega and Wolska, 2021).

2.5.4. Ion-exchanged capacity

The ion exchange capacity (IEC) of the chitosan microspheres was determined by immersing a known mass of the centrifuged, protonated sample in 50 cm^3 of 0.1 M NaOH solution for 24 hours, followed by titration of the resulting solution with 0.1 M HCl, in accordance with the methodology described by Trochimczuk and Czerwińska, and Hajdok (Trochimczuk and Czerwińska, 2005; Hajdok, 2015).

2.5.5. FTIR spectra

Mid-infrared (MIR) spectra were acquired using a vacuum spectrometer equipped with an air-cooled deuterated triglycine sulfate detector (DTGS). The spectral data were collected in the 4000–400 cm^{-1} range with a resolution of 2 cm^{-1}, averaging 64 scans. (Pilśniak-Rabiega and Wolska, 2022).

2.6. Evaluation of the sorptive properties of biopolymers

Batch sorption experiments were conducted using a standard silver solution with an initial Ag(I) concentration of 12.91 mg/dm^3 (0.1197 mmol/dm^3) at an initial pH of 6.70. The process was performed for two different types of samples:

- unmodified chitosan microspheres crosslinked only with glutaral aldehyde (biopolymer I),
- chitosan microspheres after modification with epichlorohydrine and with 1-methylimidazole (biopolymer IV).

The adsorption of Ag(I) ions was examined under batch conditions at room temperature (23 ± 2 °C). A pre-swollen sorbent sample (~0.20 g) was agitated with 20 cm^3 of the model solution for 24 h. Subsequently, the solid material was separated from the liquid phase, and the residual silver concentration in solution was quantified by atomic absorption spectroscopy (AAS) using a Varian SpectrAA 20 Plus instrument.

The distribution coefficient (*Kd*) was defined as the ratio between the amount of Ag(I) adsorbed per unit mass of bioresin and the equilibrium concentration of Ag(I) in 1 cm^3 of solution.

The sorption isotherm was determined by contacting bioresin samples of identical mass (0.20 g - weight of the swollen polymer) with 20.0 cm^3 of Ag(I) solution of different concentrations (concentration range 12.91-78.02 mg Ag/dm^3). The sorption process was carried out over a 24-hour period at a controlled temperature of 23±2 °C, and the results were presented relative to the equilibrium concentration.

To investigate sorption kinetics, resin samples (~0.20 g) were contacted with 20.0 cm^3 of an aqueous solution containing 12.91 mg/dm^3 of Ag. At predetermined time intervals, the resin was separated from the solution, and the silver concentration was measured using analytical technique AAS.

The desorption of silver was evaluated by treating a known quantity of silver-loaded resin with 20.0 cm^3 of eluent at ambient temperature (23 ± 2 °C) for a duration of 24 hours. Following this period, the silver concentration in the solution was quantified using analytical technique AAS (Pilśniak-Rabiega and Wolska, 2023).

3. Results and discussion

3.1. Preparation and physicochemical characterization of biopolymeric materials

Biopolymer sorbents were synthesized through microwave-assisted modification of chitosan using epichlorohydrin and 1-methylimidazole.

The materials were subjected to analytical characterization, including the determination of chlorine content, nitrogen content, ion-exchange capacity, and water uptake. The corresponding results are summarized in Table 1.

Table 1. Physicochemical characteristics of biopolymers

Biopolymer No.	Water regain [g/g]	Chlorine content [mmol/g]	Nitrogen content [mmol/g]	Ion exchange capacity (IEC) [mmol/g]
I	38.4±0.5	---	8.92±0.2	9.16±0.2
II	---	2.01±0.1	8.92±0.2	---
III	---	4.26±0.1	8.92±0.2	---
IV	25.2±0.5	0.725±0.01	13.56±0.2	---

I unmodified chitosan

II epichlorohydrin-modified chitosan (first trial)

III epichlorohydrin-modified chitosan (second trial)

IV chitosan modified with epichlorohydrin (second trial) and 1-methylimidazole

From the water regain values obtained for chitosan before and after modification (see Table 1), it can be concluded that the unmodified biopolymer has free, uncrosslinked primary amino groups, which are hydrophilic groups. This value was decreased after modification with epichlorohydrin and

1-methylimidazole. This may mean that the hydrophilicity of the material has decreased and the attachment of epichlorohydrin to the free -NH_2 groups and subsequent modification with 1-methylimidazole has been successful.

The resulting IEC of 9.16 mmol/g (see Table 1) indicates the ion exchange capacity of the test chitosan and the presence of primary amino groups, –NH_2. The IEC as well as the water regain parameters from which it was concluded that modification of the analysed material by the addition of another compound to the free amine group will be possible.

Moreover, this result allowed us to conclude that chitosan could be further modified by adding other compounds to the amino group -NH_2.

Extending the modification time of chitosan at room temperature from 1 to 24 h and the microwave modification time from 20 to 30 minutes resulted in a more than twofold increase in the chlorine content of the test material. This means that as the modification conditions changed, more epichlorohydrin molecules could be substituted.

More epichlorohydrin was added during the second modification of chitosan (4.26 mmol/g). Accordingly, this material was further modified (1-methylimidazole modification).

The chlorine content of chitosan after modification with 1-methylimidazole decreased more than fourfold. It follows that this reaction was successful and succeeded in replacing the chlorine atoms present in epichlorohydrin with a heterocyclic compound.

The success of the microwave modification of the immobilization of the heterocyclic compound on the chitosan material is also evidenced by the nitrogen content, which increased one and a half times.

The proposed chemical structures of the synthesized biopolymers presented in Fig. 3 were verified using Fourier-transform infrared (FTIR) spectroscopy (see Fig. 4).

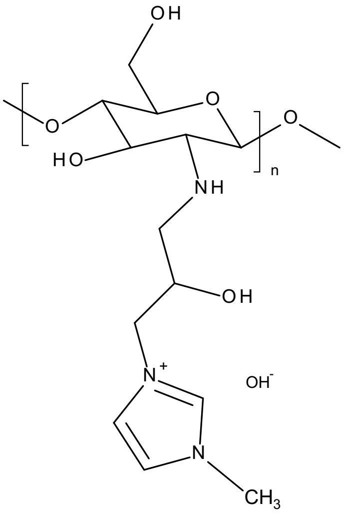

Fig. 3. Proposed structure of chitosan modified with epichlorohydrin and 1-methylimidazole

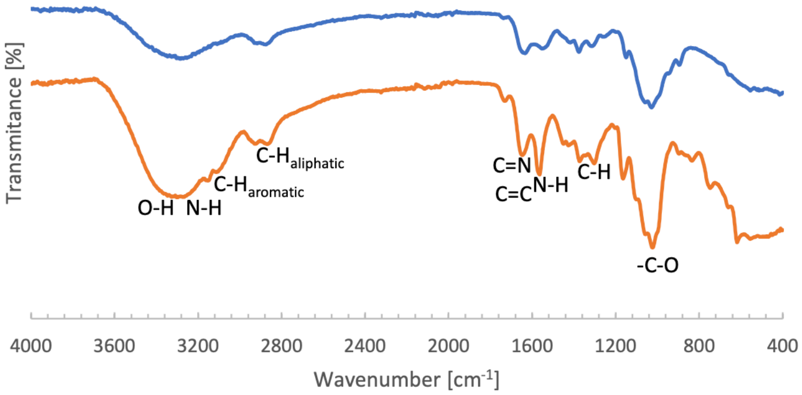

Fig. 4. FTIR spectra of unmodified (blue line) and modified (orange line) chitosan

By analyzing the obtained spectra, it was possible to match individual bands to the functional groups in the materials studied. In Fig. 4, for both samples, a strong band with a wave number of approximately 3285-3346 cm^{-1} and 3285-3346 cm^{-1} can be seen. These bands correspond to the overlapping bands that originate from the vibrations of N-H and O-H bonds. The bands with wave numbers 3112 and 3152 cm^{-1} (orange line) can be attributed to the aromatic C-H bond. It is not as visible in the spectra of unmodified chitosan (blue line). The subsequent absorption bands observed at 2877 cm^{-1} (blue line), as well as at 2869 cm^{-1} and 2925 cm^{-1}, can be assigned to the vibrations of aliphatic C-H bonds. The band in this area is characteristic of other polysaccharides (Wolkers et al., 2004; Melo-Silveira et al., 2012). The bands at wavenumber 1633 cm^{-1} (blue line) and 1647 cm^{-1} (orange line) come from the vibrations of the C=O bond. This means that N-acetyl groups are present in the structure of the tested chitosan. The next band at 1553 cm^{-1} (blue line) and 1565 cm^{-1} (orange line) corresponds to vibrations originating from the N-H bond in the primary amino group. Additionally, in the modified chitosan spectra (orange line), the bands at wave numbers 1565 cm^{-1} and 1647 cm^{-1} are more intense than the bands 1553 cm^{-1} and 1633 cm^{-1} in the spectra of the unmodified sample (blue line). This will be related to the increase in the electron density on the carbon atoms of the heterocyclic ring of attached 1-methylimidazole (Bouchet and Siebert, 1999). Therefore, in the modified chitosan spectra, the band at 1565 cm^{-1} will be superimposed by the vibrational band associated with the C=C bond, while the band at 1647 cm^{-1} will be superimposed by the vibrational contribution of the C=N bond. These bonds are located in the aromatic ring of 1-methylimidazole.

3.2.2. Sorption mechanism

Biopolymer sorbents I and IV were applied for the removal of Ag(I) ions from a model solution. Their sorption performance was evaluated under the experimental conditions described in the Experimental section, with the corresponding results summarized in Table 2.

Table 2. Sorption of Ag(I) from a model aqueous solution

Biopolymer No.	**Ligand* Concentration [mmol/g]**	**Sorption of Ag(I) [mg Ag/g resin]**	**Sorption of Ag(I) [mmol Ag/g resin]**	**Yield of Ag(I) sorption [%]**	**K_d**
I	8.92	11.4±1.0	0.105±0.01	63.4±1.0	2705
IV	4.17	30.9±1.0	0.286±0.01	91.6±1.0	28585

*calculated from nitrogen content in functional groups

I unmodified chitosan

IV chitosan modified with epichlorohydrin (second trial) and 1-methylimidazole

In the tested solution, silver(I) ions predominantly exist as Ag^+. Within the pH range of 2 to 7, free Ag^+ ions constitute over 99% of the total silver species present (Elwakeel et al., 2021).

The highest sorption capacity for Ag(I) was observed in biopolymer IV, which was functionalized with epichlorohydrin and 1-methylimidazole, achieving a value of 30.9 mg Ag(I) per gram of resin. Correspondingly, the distribution coefficient (K_d) reached 28585, as reported in Table 2. This sorbent functions as a medium-strength anion exchanger, characterized by a positively charged polymeric matrix that is associated with hydroxide ions present in the tested Ag(I) solution.

Surface-bound hydroxide ions on the biopolymer sorbent can interact with Ag(I), resulting in the formation of neutral complexes, for example $Ag(OH)(H_2O)_n$ (n=2-6). The Ag^+ ions are hydrated in water solution. The mean coordination number of hydrated Ag^+ ions is reported to be 5.5 (Prasetyo, 2022). The lack of available lone pair electrons on the nitrogen atoms within the imidazole rings indicates that coordination with Ag(I) ions is unlikely to be the primary mechanism responsible for silver sorption.

Both unmodified and chemically modified chitosan sorbents have amine groups (–NH_2, –NHR or –NR_2) and hydroxyl groups (–OH) that can participate in coordination and form complexes with silver ions. These complexes may also result from the cleavage of (1→4)β-glycosidic linkages, accompanied by the surface oxidation of silver on the chitosan molecule (Skwarczynska-Wojsa and Modrzejewska, 2024).

Magnetic chitosan sorbents functionalized with pyrimidine derivatives (MC-PYO and MC-PYS) were evaluated for their efficiency in recovering silver(I) ions from complex aqueous solutions (Hamza et al., 2022). The silver binding mechanism for MC-PYO primarily involves interactions with nitrogen-containing carbonyl and hydroxyl groups, whereas MC-PYS facilitates silver coordination predominantly through sulphur donor atoms.

The modification of chitosan with 2-mercaptobenzimidazole significantly enhances its affinity toward silver ions (Elwakeel et al., 2021). The predominant sorption mechanism involves chelation, primarily driven by the strong affinity of silver for sulfur-containing functional groups. Nonetheless, additional interactions, particularly at elevated pH levels, may involve the participation of amine groups through secondary chelation processes.

The resins functionalized with 1-methylimidazole and 1,2-dimethylimidazole were effective for the recovery of Ag(I) from the synthetic chloride solution (Pilśniak-Rabiega et al., 2019). The absence of lone electron pairs on the nitrogen atoms in the resins indicates that coordination with Ag(I) is unlikely to be the primary mechanism of metal uptake. Instead, the positively charged resins contained counterions, such as Cl^-, which could be exchanged with anionic silver(I) complexes, such as $[AgCl_4]^{3-}$.

Biopolymer IV, i.e. chitosan modified with epichlorohydrin (second trial) and 1-methylimidazole due to its best sorption properties towards Ag(I), was subjected to detailed testing.

3.2.3. Sorption isotherm studies

In the investigation of the sorption behavior of the bioresin IV, the adsorption isotherm at ambient temperature was also established (see Fig. 5) using aqueous silver(I) solutions with initial concentrations ranging from 13 to 78 mg/dm^3. As evident from the results, the initial ion concentration plays a critical role in driving the mass transfer process between the aqueous phase and the bioresin. At lower Ag(I) concentrations, the silver(I) ions readily interact with available active sites on the bioresin, leading to a steep increase in adsorption capacity with rising concentration. However, at higher concentrations, the adsorption capacity approaches a plateau, indicating saturation of the active sites. The maximum adsorption capacity observed for Ag(I) on the bioresin was approximately 80 mg Ag/g. Various adsorption isotherm models exist to describe different adsorption mechanisms; in this study, the experimental data were evaluated using the Langmuir, Freundlich, and Dubinin–Radushkevich isotherm models. The isotherm parameters and coefficients of determination (R^2) are presented in Table 3.

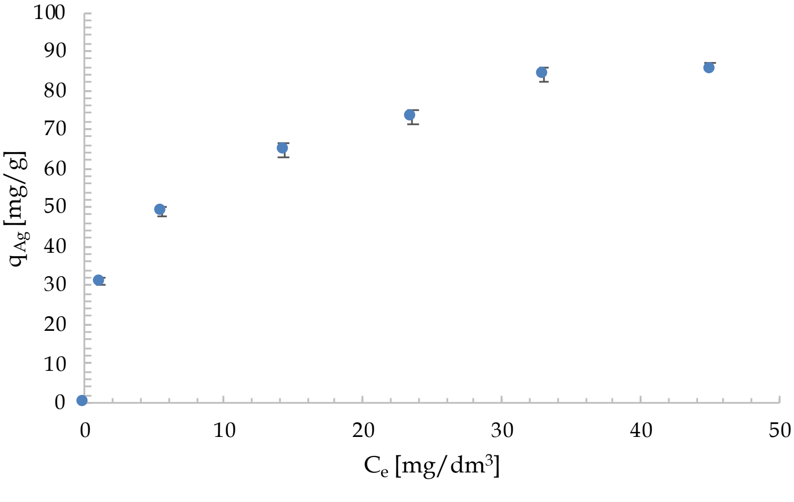

Fig. 5. Sorption isotherm for biosorbent IV. Resin samples (0.20 g - weight of swollen biopolymer) were agitated with 20.0 cm^3 of Ag(I) solutions (12.91-78.02 mg/dm^3); 24 h; 23±2°C

The Langmuir isotherm model assumes that adsorption occurs through the formation of a single molecular layer on the adsorbent surface. It further presumes that the surface contains a finite number of adsorption sites, which are uniform in nature and possess equal affinity for the adsorbate. The linearized expression of the Langmuir equation is presented as Eq. 2:

$$\frac{1}{q_e} = \frac{1}{q_m b_L C_e} + \frac{1}{q_m} \tag{2}$$

The parameter q_e (mg/g) represents the amount of adsorbate taken up at equilibrium, while q_m (mg/g) denotes the maximum adsorption capacity. C_e (mg/dm^3) is the equilibrium concentration of the adsorbate in solution, and b_L (dm^3/mg) is a Langmuir constant associated with the affinity of the binding sites. The parameters q_m and b_L were derived from the slope and intercept of the linearized Langmuir isotherm, obtained by plotting $1/q_e$ against $1/C_e$ (Polowczyk et al., 2016; Esteves et al., 2022).

Furthermore, the equilibrium parameter (R_L), also known as the separation factor (dimensionless), is calculated as part of the analysis to assess the suitability of the Langmuir isotherm model for a particular separation process (Eq. 3) (Polowczyk et al., 2016; Esteves et al., 2022).

$$\mathrm{R_L} = \frac{1}{1+\mathrm{b_L C_0}} \tag{3}$$

where C_0 (mg/dm^3) is the initial adsorbate concentration.

The separation factor R_L serves as an indicator of the favorability of the adsorption process. According to (Polowczyk et al., 2016), the isotherm behavior can be classified as follows: (i) unfavorable when $R_L > 1$, (*ii*) linear when $R_L = 1$, (*iii*) favourable when $R_L < 1$, and (*iv*) irreversible when $R_L = 0$. Based on the obtained fitting results, the characteristic parameters of the isotherm model were determined. Notably, the calculated maximum adsorption capacity q_m closely matched the experimentally observed value, which was approximately 77 mg/g.

The values R_L parameter for each of silver solutions were lower than 1, indicating that the applied model is appropriate for describing the sorption behavior of Ag(I) onto the investigated biopolymer, even the R^2 value very close to 1, which may indicate that this model describes the sorption process on the tested biopolymer material well. Moreover, the shape of the obtained sorption isotherm is also typical for this sorption model, which may also indicate that the Langmuir model, is the right model.

The Freundlich isotherm model describes the heterogeneous adsorption of adsorbate molecules onto a monolayer surface of the adsorbent, assuming the absence of interactions among the adsorbed species (Esteves et al., 2022). The linearized form of the model is expressed by the following equation (Eq. 4):

$$\log q_e = \frac{1}{n} \log C_e + \log a \tag{4}$$

The parameter q_e (mg/g) denotes the adsorption capacity at equilibrium. The constant a (mg/g) refers to the Freundlich adsorption constant, which characterizes the capacity of the adsorbent. The term $1/n$ is a dimensionless empirical constant that indicates the intensity or favorability of the adsorption process. C_e (mg/dm^3) represents the equilibrium concentration of the adsorbate in the solution.

The Freundlich isotherm describes a power-law relationship between q_e and C_e and can be conveniently applied by representing the experimental data in a log–log plot of q_e versus C_e (Eq. 4) (Cela-Pérez et al., 2011). This isotherm characterizes the heterogeneity of the adsorbent surface and reflects an exponential distribution of active sites and their associated energy levels (Polowczyk et al., 2016; Ayawei et al., 2017). The parameters, a and $1/n$, are used to characterize the adsorption behavior, both serving as indicators of the strength of physical binding. The parameter a represents a constant associated with the adsorption capacity of the material. The $1/n$ value, referred to as the heterogeneity index, reflects the energy distribution of adsorption sites. A value of $1/n = 1$ indicates a homogeneous adsorption surface, where the adsorption process is linear, the binding sites possess uniform energy, and no intermolecular interactions among adsorbates are present. Conversely, as $1/n$ approaches zero, the system exhibits an increasingly heterogeneous nature. For adsorption to be considered favorable, the value of n should typically fall within the range of 1 to 10 (Cela-Pérez et al., 2011; Wolska and Bryjak, 2014; Polowczyk et al., 2016).

The application of the Freundlich isotherm to the experimental data enabled the determination of the parameters a and $1/n$, providing insight into the suitability of the model for describing the adsorption process. The calculated value of parameter a was 30.3 for the synthesized bioresin. As can be seen, this value does not closely match the experimental data. The constant values of *n* for the biopolymer ranged from 1 to 10, with a value of 3.55. Therefore, the sorption of Ag(I) onto the studied polymer can be considered favorable. Comparison of the determination coefficients (R^2) for the Langmuir and Freundlich isotherm models could indicate that the Freundlich model provides a superior fit for the adsorption of Ag(I) onto the investigated bioresin. However, even though R^2 for the model is closer to 1, the result of the estimated sorption capacity, as mentioned, is much lower than the values obtained experimentally, which disqualifies this model, therefore, it is not suitable to describe the process of Ag (I) sorption on the synthesized bioresin. A comprehensive summary of the Langmuir and Freundlich model parameters is presented in Table 3.

The Dubinin–Radushkevich (D–R) isotherm model is commonly employed to investigate the nature of interactions between the sorbate and the sorbent (Cela-Pérez et al., 2011). This model is particularly useful for distinguishing whether the sorption process is predominantly physical or chemical. The linearized form of the D–R isotherm can be expressed as shown in Eq. 5 (Ulatowska, 2022):

$$\ln q = \ln q_m - K_{DR}\varepsilon^2 \tag{5}$$

where q_m (mmol/g) represents the maximum adsorption capacity of the adsorbent, while K_{DR} (kJ²/mol²) denotes the Dubinin-Radushkevich constant. The parameter ε corresponds to the Polanyi potential, as defined in Eq. 6:

$$\varepsilon = RT\ln(1 + \frac{1}{c}) \tag{6}$$

The distribution K_{DR} is is associated with the free energy of adsorption (E, in kJ/mol) for a single molecule of adsorbate transitioning from the bulk solution to the surface of the solid adsorbent. The nature of the adsorption process can be inferred based on the magnitude of E. Specifically, values of E in the range of 1–8 kJ/mol indicate physisorption, values between 8–16 kJ/mol suggest adsorption primarily governed by ion-exchange mechanisms, while values exceeding 16 kJ/mol are characteristic of chemisorption. The free energy of adsorption can be calculated using Eq. 7, as described by Cela-Pérez and Ulatowska (Cela-Pérez et al., 2011; Ulatowska, 2022):

$$E = (2K_{DR})^{-0.5} \tag{7}$$

The calculated mean adsorption energy (E) for the biosorbent was 3.55 kJ/mol, indicating a value below the 8 kJ/mol threshold. In this instance, physisorption was the predominant mechanism. The linear coefficient of determination (R^2) value was very close to the value obtained for the Freundlich isotherm model and approached 1. In order to decide which model is better to describe the sorption process, other characteristics of this model were determined. The maximum sorption capacity of Ag(I) was determined to be 55.4 mg Ag/g of dry resin. However, this value deviates notably from the experimentally observed capacity derived from the sorption isotherm study. Consequently, this model does not adequately describe the Ag(I) sorption behavior on the synthesized chitosan resin. In contrast, the Freundlich isotherm provides a more accurate representation of the sorption process.

All results of Langmuir, Freundlich, and Dubinin-Radushkevich analysis are given in Table 3.

Table 3. Adsorption isotherm parameters (Langmuir, Freundlich, and Dubinin–Radushkevich Models) for the investigated chitosan-based resin

Model	Parameter	Unit	Value
Experimental	q_{exp}	mg/g mmol/g	78.0 0.79
Langmuir	**R^2**	-	0.963
	q_m	mg/g mmol/g	**76.9** 0.71
Freundlich	*A*		30.3
	R^2	-	**0.996**
	N	-	3.57
Dubinin-Radushkevich	*E*	kJ/mol	3.55
	R^2	-	0.993
	q_m	mg/g mmol/g	55.4 0.51

The sequence of model suitability based on the coefficient of determination (R^2) follows the order: Freundlich > Dubinin–Radushkevich > Langmuir, indicating that the Freundlich model provides the best fit to the experimental data, while the Langmuir model shows the least agreement. However, as mentioned earlier, not only the R^2 value should be considered when selecting an appropriate model describing the sorption process on a given material. Attention should be paid to the shape of the obtained isotherm and the values of other characteristic parameters for a given model, including the calculated value of the sorption capacity. When comparing the values of maximum sorption capacity determined in individual models, it can be noticed, that the most closely correlate with the experimental sorption values for the Langmuir model, and this model in the case of synthesized bioresin it is most appropriate to describe the process of silver sorption on it.

3.2.4. Sorption kinetics studies

The influence of contact time on the adsorption efficiency of Ag(I) ions by the synthesized chitosan-based resin was evaluated at ambient temperature, using an initial Ag(I) concentration of 12.91 mg/dm^3. As illustrated in Fig. 6, the sorption capacity increased progressively with contact time until equilibrium was achieved. A marked increase in adsorption was observed within the first 5 hours, followed by a gradual deceleration in uptake beyond 10 hours, indicating the approach toward equilibrium. The results demonstrated that adsorption equilibrium was attained after approximately 36 hours.

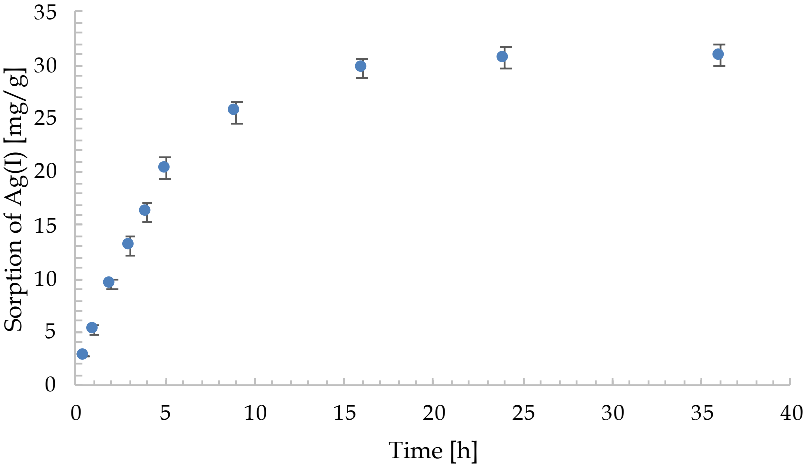

Fig. 6. Sorption kinetics of silver(i) ions on bioresin IV. Resin samples bearing 0.01 mmol of ligand were exposed to 20.0 cm^3 of an aqueous solution with an initial Ag(I) concentration of 12.91 mg/dm^3 at a temperature of 23 ± 2 °C. The silver concentration in the solution was monitored at predetermined time intervals

To investigate the sorption kinetics and gain insight into the underlying adsorption mechanisms, the experimental data illustrated in Fig. 6 were analyzed using five different kinetic models. The corresponding model parameters derived from the fitting process are summarized in Tables 4 and 5. Sorption kinetics offers insight into the underlying mechanism of the process, whether it proceeds via diffusion, mass transfer, or chemical reaction. These studies elucidate the mechanism by which the sorbate is taken up by the biosorbent, ultimately governing the duration required for the sorbate to traverse the interface between the sorbent and the surrounding solution (Haq et al., 2020). In order to determine this, the initial phase of Ag(I) sorption was modeled using a diffusion framework based on Fick's second law (Eqs. 8 and 9), allowing for the identification of the rate-limiting step—either film diffusion or intraparticle diffusion—within the chitosan resin (Juang et al., 2002; Kabay et al., 2007; Haq et al., 2020).

$$k_a t = -\ln\left(1 - \frac{q_t}{q_e}\right) \tag{8}$$

The sorption capacity at a given time q_t and at equilibrium q_e (both expressed in mg/g) describe the amount of adsorbate retained by the adsorbent at time t and and at equilibrium, respectively. The sorption rate constant k_a (1/min) represents the sorption rate constant. Sorption rate constant k_a (1/min) can be determined from the linear plot of $-ln(1-\frac{q_t}{q_e})$ as a function of time.

$$k_b t = -\ln(1-(\frac{q_t}{q_e})^2) \quad (9)$$

The sorption rate constant k_b (1/min) can be determined from the linear plot of $-ln(1-(\frac{q_t}{q_e})^2)$ as a function of time, where q_e and q_t (mg/g) represent the adsorption capacities at equilibrium and at a given time *t*, respectively.

Table 4 presents the slope values, linear correlation coefficients, and the calculated k_a and k_b parameters. The evaluation of k_a and k_b allows for the determination of the faster sorption mechanism for the synthesized biopolymer. Furthermore, the analysis of the coefficients of determination provides insight into the predominant diffusion mechanism governing the process. For the studied chitosan resin, the results indicate that film diffusion is the primary rate-controlling step.

Table 4. Kinetic parameters evaluation

Model	Parameter	Unit	Value
Film diffusion	k_a	1/min	$3.3 \cdot 10^{-3}$
	R^2	-	**0.994**
Particle diffusion	k_b	1/min	$2.3 \cdot 10^{-3}$
	R^2	-	0.975
Interparticle diffusion	k_{WM1}	mg/g $\cdot$min$^{0.5}$	**0.65**
	k_{WM2}	mg/g $\cdot$min$^{0.5}$	1.36
	k_{WM2}	mg/g $\cdot$min$^{0.5}$	0.78

The rate-limiting step of Ag(I) adsorption onto the synthesized polymeric resin was further evaluated using the Weber–Morris intraparticle diffusion model (Ulatowska, 2022), as presented by Eq. 10. This model describes the kinetics of intraparticle diffusion as a function of the square root of time, i.e., $q_t=f(t^{0.5})$.

$$q_t = k_{WM} \cdot t^{0.5} + B \quad (10)$$

The intraparticle diffusion rate constant, denoted as k_{WM} (mg/g min$^{0.5}$) is determined from the linear relationship between q_t and the square root of time $t^{0.5}$.

If adsorption were governed exclusively by intraparticle diffusion, the plot of q_t versus $t^{0.5}$ would exhibit a linear relationship throughout and intersect the origin. The observed deviation from linearity in our results suggests that multiple mechanisms contribute to the adsorption process, indicating that intraparticle diffusion is not the sole rate-controlling step. The initial segment of the curve represents adsorption occurring on the external surface of the adsorbent particles, indicative of the immediate adsorption phase. The subsequent segment reflects a more gradual adsorption phase, during which intraparticle diffusion serves as the rate-limiting step governing the overall adsorption process (Ulatowska, 2022). None of the plotted curves intersect the origin of the coordinate system, indicating that intraparticle diffusion is not the sole rate-controlling mechanism governing the silver(I) adsorption process onto the synthesized bioresin. Moreover, the relationship between q_t and $t^{0.5}$ across the entire time interval was nonlinear, suggesting that the adsorption rate is influenced by factors beyond intraparticle diffusion alone. The calculated k_{WM} values for each stage are presented in Table 4. The analysis of these results indicates that the rate-limiting step in the Ag(I) adsorption process across the examined bioresin is the initial stage, as evidenced by the lowest k_{WM1} value. This suggests that the first stage predominantly governs the overall sorption process, which was also shown in the previous analysis using film or particle diffusion, where diffusion to the grain surface was also the limiting step in the Ag(I) sorption process on the tested bioresin. It can therefore be concluded, on the basis of both analyses, that the adsorption occurring on the external surface of the bioresin particles constitutes the critical step, significantly impacting the efficiency of the sorption process. However, the Weber–Morris intraparticle diffusion model allows us to draw slightly also more deeper conclusions, it can been seen that film diffusion is likely the initial controlling step, while intraparticle diffusion becomes significant in the further part of the sorption process.

To clarify the mechanisms underlying sorption kinetics, the experimental data shown in Fig. 6 were analyzed by fitting them to both pseudo-first-order and pseudo-second-order kinetic models (Kabay et al., 2007; Lagergren, 1898; Liu et al., 2011; Santander et al., 2014).

The pseudo-first-order kinetic model is based on the premise that the sorption rate is directly proportional to the difference between the equilibrium uptake capacity and the amount of sorbate accumulated on the solid phase over time (Rapacz et al., 2025; Revellame et al., 2020). The linearized expression of the pseudo-first-order kinetic model is given by the following equation (Eq. 11). The rate constant k_1 was determined based on the linearization of the plot of $log(q_{eq} - q_t)$ against time, as reported by Rapacz and Revellame (Rapacz et al., 2025; Revellame et al., 2020).

$$\log(q_{eq} - q_t) = \log(q_{eq}) - \frac{k_1 t}{2.303} \tag{11}$$

k_1 (1/min) denotes the sorption rate constant, while q_{eq} and q_t (mg/g) represent the quantities of adsorbate adsorbed at equilibrium and at a given time *t*, respectively.

In the pseudo-second-order kinetic model, the adsorption process is governed primarily by chemisorption at the liquid-solid interface of the adsorbent, enabling accurate prediction of adsorption behavior throughout the entire uptake range The pseudo-second-order model can be expressed in its linearized form using the following equation (Eq. 12). The rate constant k_2 was obtained from the linear regression of the plot of $\frac{t}{q_t}$ against time, as described by Kabay (Kabay et al., 2007).

$$\frac{t}{q_t} = \frac{1}{k_2 q_{eq}^2} + \frac{1}{q_{eq}} t \tag{12}$$

The parameter k_2 (g/(mg×min)) denotes the sorption rate constant, while q_{eq} and q_t (mg/g) refer to the quantities of adsorbate adsorbed at equilibrium and at a given time *t*, respectively.

Linear regression analysis, expressed through the coefficient of determination (R^2), was employed to evaluate the linearized forms of the kinetic models. The rate constants k_1 and k_2 were obtained from the slope and intercept of the corresponding linear plots, as detailed in Table 5. This Table presents the pseudo-first-order and pseudo-second-order kinetic parameters, including both the calculated and experimental equilibrium sorption capacities (q_{exp}) for silver uptake onto the synthesized bioresin.

Table 5. Kinetic parameters and maximum adsorption capacities for Ag uptake onto synthesized chitosan resin based on pseudo-first-order and pseudo-second-order models

Model	Parameter	Unit	Value
Experimental	q_{exp}	mg/g	**30.90**
Pseudo-first	k_1	1/min	$2.0 \cdot 10^{-1}$
	R^2	-	**0.999**
	q_{max1}	mg/g	**31.23**
Pseudo-second	k_2	g/mg·min	$2.0 \cdot 10^{-5}$
	R^2	-	0.976
	q_{max2}	mg/g	50.76

The highest coefficient of determination (R^2) values indicate that the pseudo-first-order kinetic model provides a better fit to the experimental data for silver adsorption onto the synthesized resin compared to the pseudo-second-order model. Furthermore, the adsorption capacities predicted by the pseudo-first-order model (q_{max1}) are in closer agreement with the experimentally determined values (q_{exp}) than those obtained from the pseudo-second-order model (q_{max2}). This suggests that the Ag(I) adsorption process in the studied systems is predominantly governed by physical interactions rather than chemical ones (see Table 5), and the pseudo-first-order kinetic model is the best model that describes the kinetics of sorption of silver (I) ions on the obtained resin.

3.2.5. Elution and sorbent recycling

The desorption process and the stability of the sorbent during repeated sorption/desorption cycles were investigated for chitosan modified with epichlorohydrin and 1-methylimidazole.

Ag(I) was eluted using 20 cm^3 of 0.5 M thiourea solution, acidified with 0.1 M HCl at ambient temperature (23±2°C). The desorption efficiency of Ag(I) achieved under these conditions was 82.3%.

To assess the stability of the bioresin, five consecutive sorption-desorption cycles of Ag(I) were conducted using a model silver solution with a concentration of 12.91 mg Ag/dm^3. Sorption was performed at room temperature (23±2°C) with a tenfold molar excess of Ag(I) relative to the ligand content on the sorbent. Following sorption, the resin was rinsed with water and desorbed using 0.5 M thiourea acidified with 0.1 M HCl. The same resin sample was then reused for subsequent sorption cycles. This procedure was repeated for a total of five cycles to evaluate the bioresin's performance and stability.

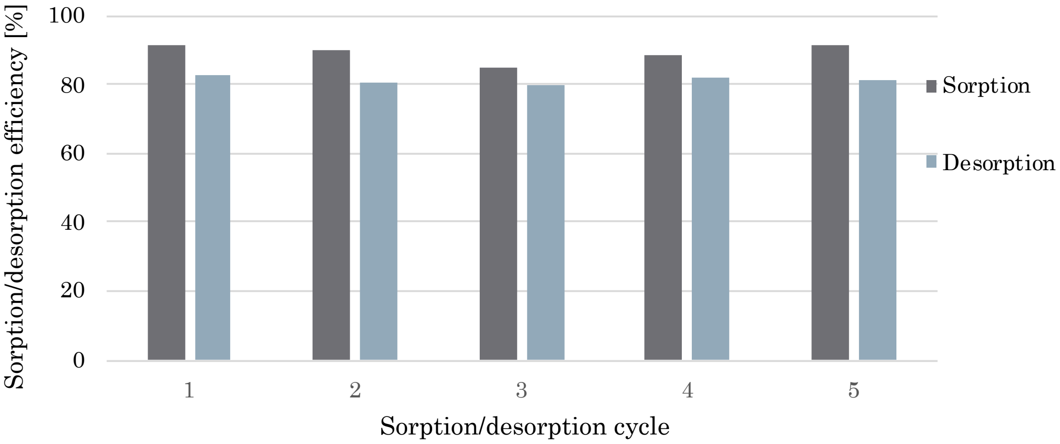

Fig. 7. Stability of bioresin over repeated sorption/desorption cycles

The data illustrated in Fig. 7 indicate that the sorption and desorption efficiencies of biosorbent IV remained consistent across cycles 1 to 5, with values ranging from 85.1% to 91.6% for sorption and 79.8% to 82.3% for desorption.

The functionalized biosorbents MC-PYO and MC-PYS demonstrated enhanced stability in sorption performance during repeated recycling processes, employing 0.3 M HNO_3 solutions for complete elution of silver-laden materials (Hamza et al., 2022). Similarly, the 2-MBI-chitosan sorbent maintained consistent sorption and desorption efficiency over five successive recycling cycles (Elwakeel et al., 2021). Desorption efficiencies exceeded 98% when using acidic thiourea solutions and remained stable for at least five cycles, whereas sorption capacity exhibited a moderate decline of approximately 13–16% by the fifth cycle.

4. Conclusions

- Microwave modification of chitosan with epichlorohydrin and 1-methylimidazole is an effective method for the preparation of functional biopolymers.
- The biosorbent modified with 1-methylimidazole demonstrated effective recovery of Ag(I) from aqueous solutions, achieving a sorption efficiency of 91.6%. The distribution coefficient (K_d) was determined to be 28585.
- The Langmuir isotherm model indicated that the bioresin exhibited a maximum adsorption capacity of 77 mg of Ag(I) per gram.
- The adsorption of Ag(I) onto the bioresin conforms to a pseudo-first-order kinetic model, with the sorption process predominantly governed by film diffusion.

- The loaded bioresin can be regenerated using 0.5 M thiourea solution acidified with 0.1 M HCl, at room temperature (23±2°C).
- The modified chitosan maintained its affinity for Ag(I) across five successive sorption-desorption cycles.

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