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Thiourea Resole Polymers for Recovery of Noble Element

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Abstract

The recovery of noble elements from secondary source, industrial effluent, which are classified as high concentrated noble elements solution are very essential. Liquid-solid extraction systems are an attractive process used for the separation and purification of noble elements. For this purpose, a solid-phase extraction system was investigated for the recovery of noble metals (Au(III), Pd(II), and Rh(III)). Chelating resins were synthesized by a polycondensation reaction between thiourea phenolic monomers and formaldehyde under alkaline conditions. The resulting polymers were characterized and evaluated for their chelating properties with regard to noble metal sorption. Also, the selectivity of sorption of noble elements was studied in the presence of competitive elements that can be present in effluent waste, such as Zn, Cu, Ni, Fe, and Al. Here, we present a promising materials based on formo-phenolic thiourea resins as a potential candidate for high-capacity (> 350 mg/g for Au; > 50 mg/g for Pd; > 30 mg/g for Rh) and high-selectivity solid-liquid sorption of noble elements particularly for Au.

Keywords: Adsorption, chelating resin, thiourea monomers, formo-phenolic resin, noble metals.

1. Introduction

Precious metals (Au, Pd, Pt, Rh, Ru, etc.) are widely used in different sectors (electronics, jewelry, medicine and catalysis) due to their specific physical and chemical properties. Related to their increasing demand and the limitations of the primary nonrenewable sources, the recovery of precious elements from industrial waste has attracted the attention of many researchers from the perspective of both economics and environmental protection (Bigum et al., 2017; Das, 2010; Ding et al., 2019; Tofan & Wenkert, 2022). In addition, the industrial wastewater has been classified as a potential secondary source of noble ions whose concentration is typically much higher than the very low concentration found in the primary source (Hasegawa et al., 2018; Zhang & Xu, 2016).

To recover precious elements from wastewater, industrial techniques including the pyrometallurgical and hydrometallurgical processes have been widely applied (Cyganowski, 2020; Das, 2010). The hydrometallurgical process has been used more frequently for reasons related to its advantages of being relatively inexpensive, requiring low temperature conditions, being efficient, readily available, adaptable, and presenting high metal extraction efficiencies (Ding et al., 2019; Quinet et al., 2005; Tofan & Wenkert, 2022).

Currently, there is a viable interest in the recovery of metals using the standard separation processes, such as precipitation, ion exchange, liquid-liquid extraction, membrane filtration,

and solid-liquid extraction, specifically adsorption (Ding et al., 2019; Ramesh et al., 2008). Adsorption appears to be the most efficient method for recovering precious metals because of its important benefits which include high efficiency, low cost, regeneration of the adsorbent, and no use of organic solvents (Camel, 2003; Ding et al., 2019; Ramesh et al., 2008; Tofan & Wenkert, 2022). Numerous adsorbents with various matrix and functional group compositions have been proposed for the preconcentration of precious metals. Among the wide range, chelating polymers have the highest selectivity (Atia, 2005; Tofan & Wenkert, 2022).

Chelating resins are polymer-based materials with covalent functional groups containing one or more donor atoms that allow them to form complexes with metal ions (Ertan & Gülfen, 2009; Horie et al., 2004; Zuo & Muhammed, 1995). The most commonly used functional groups are those containing N, S, or O donor atoms. According to Pearson rules and hard-soft acid-base theory (HSAB) (Pearson, 1963), sulfur and nitrogen are considered as soft and borderline donating atoms. Therefore, chelating resins containing sulfur and nitrogen ligands in their matrix could be promising adsorbents for the sorption of soft noble elements.

Chelating sorbents based on organic polymers have demonstrated excellent performance for the recovery of precious elements due to their physicochemical stability, regeneration ability, and structural diversity (Tofan & Wenkert, 2022). Different polymers with covalent functional groups have been described in the literature for the selective adsorption of noble elements, such as thiol, thiourea, bithiourea, dithizone, thiosemicarbazide, and other sulfides (Ertan & Gülfen, 2009; Losev et al., 2018).

Chelating resins obtained by polycondensation reactions have received more attention due to the simplicity of the process and their high chemical and physical stabilities (Dzhardimalieva & Uflyand, 2018). Specifically, the formo-phenolic resins, which result from an alkaline polycondensation of aldehydes with a phenolic monomers incorporating chelating groups, have been proposed for the recovery of metal ions of interest (Arrambide et al., 2019; Arrambide Cruz et al., 2018; Bekkar et al., 2023; Mossand et al., 2023).

Meeting these properties, thioureas, sulfur analogues of carbamides, are great chelating candidates for the sorption of precious metals (Ertan & Gülfen, 2009; Zuo & Muhammed, 1995). The covalent introduction of thioureas into the resin matrix is an attractive route for the preparation of high-capacity and selective chelating polymers. Moreover, a variety of formaldehyde thiourea polymerized resins for the recovery of noble metals have been reported in the literature (Atia, 2005; Birinci et al., 2009; Chen et al., 2020; Ertan & Gülfen, 2009; Muslu & Gülfen, 2011).

Due to the selective complexation of noble elements with thiourea, this study aims to explore the possibility of the formation of formo-phenolic resin materials based on phenolic thiourea monomers for the recovery of Au, Pd, and Rh. In fact, among the various materials described in the literature, none of them are based on formo-phenolic resins starting from thiourea phenolic precursors. The advantage of using these resins lies in their properties which include simplicity of processing, robustness and chemical resistance. The adsorption abilities of the different elements were investigated, and kinetic analysis has been carried out. In addition, the selectivity was examined in comparison to the other currently competitive basic ion metals (Fe, Zn, Cu, Al, and Ni).

2. Experimental Section

2.1 Materials and methods

All chemicals and solvent used for the synthesis were analytically pure from Sigma Aldrich, France and used without further purification. The metal solutions were prepared from chlorate salt of Noble elements purchased from Acros (Thermo Fisher Scientific) except for gold which were prepared from the ICP standard (in 1% HCl from ICP Science).

2.2 Characterization

Flash-chromatography runs were performed on silica cartridges using a Reveleris X-2 apparatus.

The ^1H and ^{13}C NMR spectra were carried out in DMSO as a deuterated solvent with a Bruker Advance 400 MHz instrument in order to follow the progress of the reactions. The ^{13}C Solid-state MAS NMR spectra were recorded at rotation speed of 12 KHz (4 mm outer diameter rotors) with a Bruker Advance 400 MHz.

Mechanical grinding of the resins was performed at 50 Hz for 10 min using a Retsch mixer mill MM 200 with a Zr ball.

Thermogravimetric Analysis (TGA) was performed with a Mettler Toledo instrument under air or nitrogen flow with a heating rate of 10 °C/min from 25 to 950 °C. It should be noted that an isothermal treatment of 30 minutes at 100 °C was performed under air to determine the moisture regain by the resins from storage.

Fourier Transform Infrared (FTIR) absorption spectroscopy was carried out on a Perkin Elmer 100 spectrometer between 500 and 4000 cm^{-1} using an ATR crystal with resolution of 4 cm^{-1} .

Elemental analyses were recorded with an Elementar Vario Micro Cube Instrument to determine the composition of the materials.

Scanning Electron Microscopy (SEM) was performed using a Quanta 200 ESEM FEG instrument in order to study and observe the morphology of the resins.

Metal ion concentrations before and after the sorption were determined using Inductively Coupled Plasma/Atomic Emission Spectroscopy (ICP/OES ICAP Pro spectrometer from Thermo Scientific). The wavelengths used for the Au, Pd, and Rh measurements were chosen to avoid spectral interference between the elements.

2.3 Synthesis

2.3.1. General procedure for the synthesis of the ligand

Substituted thioureas were synthesized via a known synthetic route, similar to procedure reported in the literature (Alkherraz et al., 2014).

The isothiocyanate derivatives, (1 eq of benzoyl, benzyl, acetyl or ethyl), commercially available compounds, was added dropwise by a syringe pump to a solution of tyramine (1 eq) in dry toluene preheated at 90 °C for 30 min. The mixture was heated for 12 h and then cooled in an ice bath. The resulting product was precipitated and filtered with cold toluene. Then the pure solid was obtained after washing with ether and pentane. The ^1H and ^{13}C NMR characterizations are reported in the supporting note.

2.3.2 Resins synthesis

The resins were synthesized via alkaline polycondensation of an aldehyde, formaldehyde, with phenolic compounds according to the procedures described in the literature (Arrachart et al., 2015; Arrambide Cruz et al., 2018; Oye Auke et al., 2022).

The phenolic thiourea precursors were dissolved in an alkaline solution using 1.5 eq of sodium hydroxide or 2 eq of 1,8-diazabicyclo(5.4.0)undec-7-ene (DBU) and 80 eq of water. After solubilization of the thiourea ligands by simple stirring at room temperature, formaldehyde was added and the mixture was stirred for 24 h at 60 °C. The reaction progress was monitored periodically by ¹H and ¹³C DEPT 135 NMR measurement. The prepolymers obtained were heated in an oven in air at 130 °C for 72 h. After curing, the polymer was crushed by ball milling and washed with H₂O and 1 mol/L HCl to remove unreacted compounds and the uncrosslinked oligomers. The resin was then dried at 80 °C overnight.

2.4 Desorption

The solution of gold(III) was prepared from a 10 g/L ICP standard (in 1% HCl from ICP Science) after dilution with deionized water. The solutions of palladium (Pd²⁺), rhodium (Rh³⁺), ruthenium (Ru³⁺), and platinum (Pt²⁺) were prepared from their chloride salts. Typical sorption experiments were carried out using 10 mg of resin equilibrated with 10 mL solutions of the metal ions. Batch contacts were generally run for 24 hours to ensure that equilibrium was achieved. After shaking the mixture, it was filtered through a 0.2 μm cellulose filter, and the filtrate was analyzed by ICP OES to determine the residual metal ion concentration.

The sorption efficiency *E* (%) was calculated using Equation 1, where *C_i* is the initial metal ion concentration in aqueous solution (mg/L) and *C_f* is the residual metal ion concentration in aqueous solution after sorption (mg/L).

$$E = \frac{C_i - C_f}{C_i} \times 100 \quad \text{Equation 1}$$

The sorption capacity *Q_e* (mg/g) was estimated from Equation 2, where *V* is the volume of the metal contact solution (mL) and *m* represents the mass of the resin (mg).

$$Q_e = (C_i - C_f) \times \frac{V}{m} \quad \text{Equation 2}$$

The equilibrium of adsorption was described using Langmuir and Freundlich isotherms (Ghosal & Gupta, 2017; Limousin et al., 2007). The two models are defined in Equation 3 and Equation 4, respectively, where *C_e* is the equilibrium metal ion concentration in liquid phase (mg/L), *Q_e* is the equilibrium metal ion concentration in solid phase (mg/g), *Q_{max}* represents the maximum amount of metal ions adsorbed per unit mass of adsorbent (mg/g), and *K* is the Langmuir or Freundlich constant (L/mg).

$$\frac{C_e}{Q_e} = \frac{1}{Q_{max}} \times C_e + \frac{1}{K \times Q_{max}} \quad \text{Equation 3}$$

$$\ln Q_e = \ln K + \frac{1}{n} \ln C_e \quad \text{Equation 4}$$

The selectivity of the resin towards the element *A* in the presence of the element *B* is expressed by the separation factors $S_{A/B}$ obtained according to Equation 5, where K_D is the distribution coefficient (Arrambide Cruz et al., 2018), represented in Equation 6:

$$S_{A/B} = \frac{K_{DA}}{K_{DB}} \quad \text{Equation 5}$$

$$K_D = \left(\frac{C_i - C_f}{C_i} \right) \times \frac{V}{m} \quad \text{Equation 6}$$

Finally, desorption experiments were carried out with a solution of 1 mol/L thiourea. The desorption efficiency DE (%) is represented in Equation 7, where Q_p is the concentration of metal ions adsorbed by the resin and Q_f represents the concentration of residual metal ion content in the resin after desorption.

$$DE = \frac{Q_p - Q_f}{Q_p} \times 100 \quad \text{Equation 7}$$

2.5 Adsorption kinetics

The kinetic experiment was conducted in the same way as the batch contacts, except that the supernatant aliquots were analyzed periodically by ICP-OES. The kinetic data were analyzed using pseudo-first order and pseudo-second order kinetic models (Azizian, 2004; Simonin, 2016; Yuh-Shan, 2004). The two models are defined by the Equation 8 and Equation 9, respectively:

$$\log(Q_e - Q_t) = \log Q_e - \frac{k_1}{2.303} \times t \quad \text{Equation 8}$$

$$\frac{t}{Q_t} = \frac{1}{Q_e} \times t + \frac{1}{k_2 \times Q_e^2} \quad \text{Equation 9}$$

where Q_e is the equilibrium metal ion concentration in solid phase (mg/g), Q_t is the equilibrium metal ion concentration in solid phase at time t (mg/g) and k_1 (min^{-1}) and k_2 ($\text{g mg}^{-1} \text{min}^{-1}$) represent the pseudo-first order and pseudo-second order equilibrium rate constant, respectively.

3. Results and Discussion

3.1 Ligand synthesis and characterizations

The chelating phenolic thiourea monomers were synthesized using tyramine such as amine precursor. The chelating ligand was obtained from nucleophilic addition reaction as shown in Figure 1.

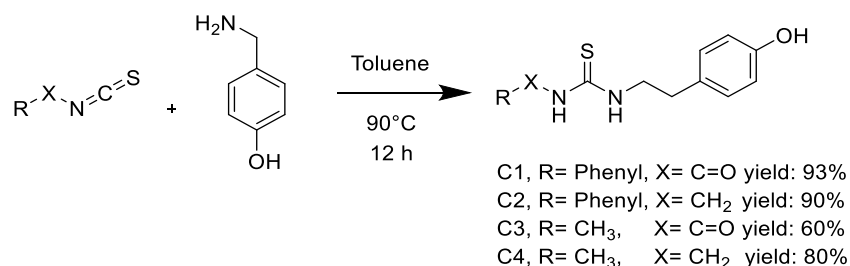


Figure 1: Synthesis of thiourea monomers.

The monomers of the four compounds were synthesized from benzoyl/benzyl, acetyl/ethyl isothiocyanate, and tyramine in dry toluene heated at 90 °C. The monomers were purified after a simple washing in ether and pentane, except for C3 which was purified by chromatography (cyclohexane/ethyl acetate), with yields of 93%, 90%, 60% and 80% as shown in Figure 1. The ¹H and ¹³C NMR, FT-IR spectra were used to confirm the structure of the compounds (see supporting note).

3.2 Resin synthesis and characterizations

Preliminary studies were carried out regarding the synthesis of the prepolymers. Resole resins were prepared using an excess of formaldehyde compared to the monomers in basic medium. As shown in Figure 2, the prepolymers were prepared using 1 equivalent mass (1 eq) of thiourea monomer (C1, C2, C3, or C4) with 2.5 eq of formaldehyde and 1.5 / 2 eq of base in water. Instead of NaOH, DBU (*i.e.*, 1,8-diazabicyclo[5.4.0]undec-7-ene) was used as an alkaline agent for the benzoyl and acetyl derivatives, thus avoiding the hydrolysis of the monomer that occurs in the presence of hydroxide ions.

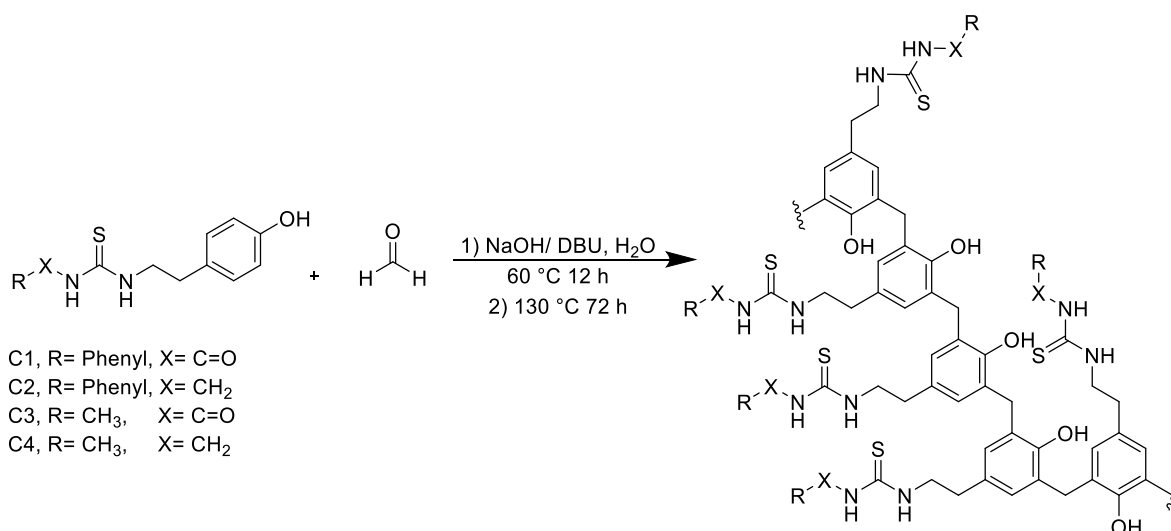


Figure 2: Illustration of the resins synthesis.

The pre-polymerization progress was monitored by using ¹H and ¹³C DEPT-135 NMR spectroscopy by following the consumption of CH aromatics (disappearance of a signal with chemical shift at 115 ppm) of the monomer and the formation of CH₂ methylol (appearance of a signal with chemical shift at around 60 ppm) (Figure S1). After 12 h at 60 °C, no change was noticed related to the consumption of monomer but a problem in the precipitation was appeared related to the beginning of condensation. To prevent this phenomenon, the reaction was stopped after the conversion of 70%–80% of the thiourea monomers. The pre-polymer was then heated in an oven at 130 °C for 72 h. After washing and conditioning of the insoluble resins (H₂O, HCl 1 mol/L, H₂O), a decrease in the mass was detected; this could be attributed to the elimination of excess reagent and the partially soluble oligomeric species.

After curing and washing steps, insoluble, amorphous, infusible polymers (**R1**, **R2**, **R3**, and **R4**) were obtained. In order to obtain a homogeneous particle size and surface contact, each resin was crushed by ball milling. The IR spectra for the four monomers and the resins, highlight the presence of the thiourea precursor in the matrix of the resins R1-R4 (Figure 3). Table 1 shows the characteristic FT-IR spectral data for the phenolic thiourea monomer based on Figure 3, in agreement with the literature (Alkherraz et al., 2014; Binzet et al., 2013; Panicker et al., 2010). The broad peaks at about 3350 cm⁻¹ were attributed to N-H and O-H stretching vibrations, the presence of the thiourea was highlighted by the C=S stretching vibration observed at about 1200 and 800 cm⁻¹, in addition to the absorption band at about 1280 and 1500 cm⁻¹ corresponding to the N-C=S and C-N fragments, respectively. For C1 and C3, the presence of the strong C=O stretching vibration band at about 1670 cm⁻¹ is consistent with their structures.

Elemental analysis of the resins was carried out, giving the elemental composition of the different resins and highlighting the presence of sulfur in the resin (Table S1 see supporting note).

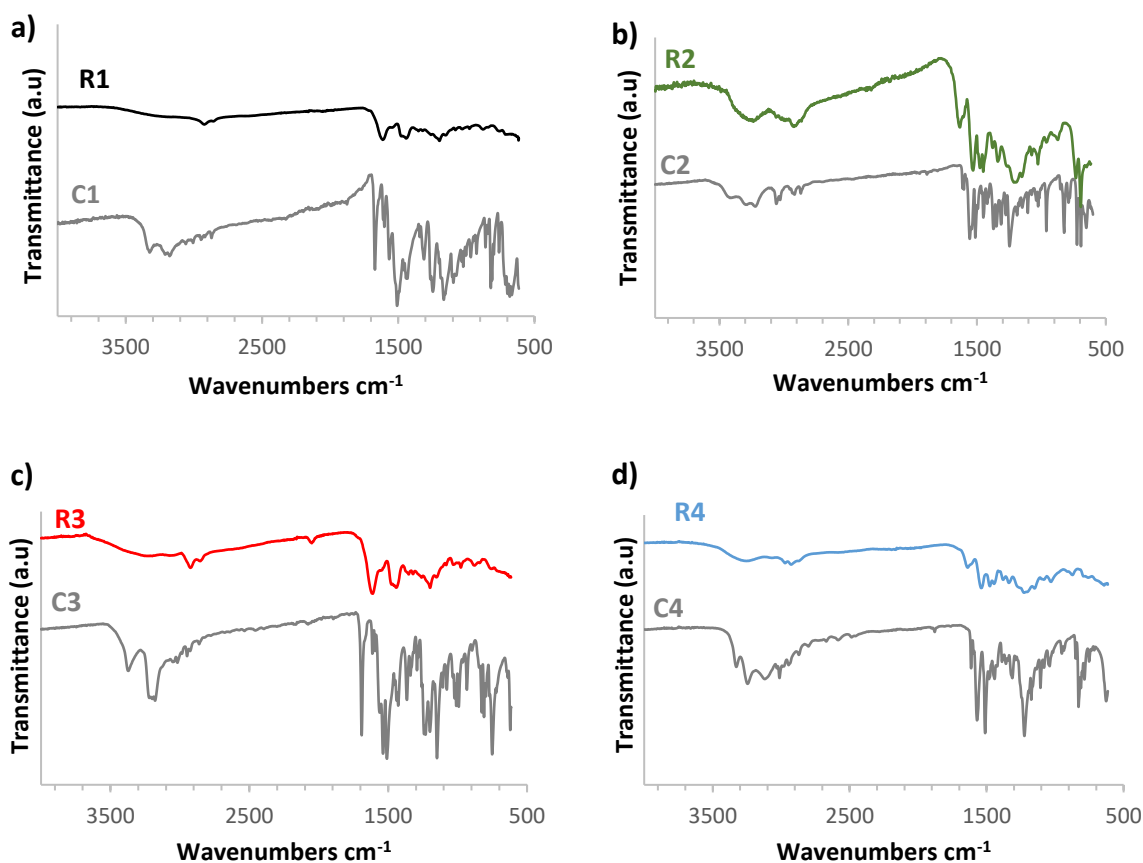


Figure 3: FT-IR spectra for thiourea ligand and their appropriate polymer (resin).

Table 1. Characteristic FT-IR spectral band position for ligand and polymer

Wavenumber (cm ⁻¹)	Band assignment	Reference
3350	N-H ; O-H	Alkherraz et al., 2014 ; Binzet et al., 2013;Panicker et al., 2010
3200	C-H	Alkherraz et al., 2014 ; Binzet et al., 2013;Panicker et al., 2010
1670	C=O	Alkherraz et al., 2014 ; Binzet et al., 2013
1500	C-N; C-C	Alkherraz et al., 2014 ; Binzet et al., 2013;Panicker et al., 2010
1280	N-C=S	Alkherraz et al., 2014 ; Binzet et al., 2013;Panicker et al., 2010
1200	C=S	Alkherraz et al., 2014 ; Binzet et al., 2013;Panicker et al., 2010
800	C=S	Alkherraz et al., 2014; Panicker et al., 2010

This result has been correlated with ¹³C MAS solid state NMR, with the displacement of the aromatic carbon at 125 ppm, the phenolic carbon at 145 ppm, and the methylene bridge carbon at around 30 ppm (Figure 4).

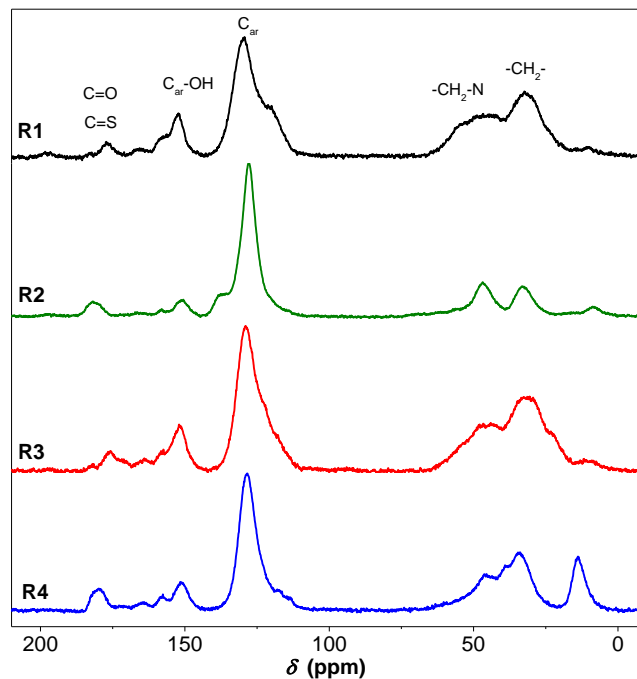


Figure 4: ^{13}C solid state NMR spectra of **R1**, **R2**, **R3** and **R4**.

The thermal properties of the resins, thermal stability, and moisture regain were determined by thermogravimetric analysis (TGA) under air and nitrogen atmospheres (Figure 5). Endothermic peaks in the derivative thermogravimetric curves showed the thermal decomposition of the resins. For all polymers, there are two stages of decomposition. For **R1**, **R3**, and **R4**, the weight loss between 0 and 100 °C was related to the loss of water. Furthermore, from 160 to 250 °C, all the resins showed the beginning of polymer degradation. This degradation could be related to the oxidation of remaining methylols and methylene bridges. The second weight loss from around 500 °C is related to the decomposition of the polymeric matrix, giving CO and CO₂, benzaldehyde, and char (Arrambide et al., 2019; Jackson & Conley, 1964; Jiang et al., 2012).

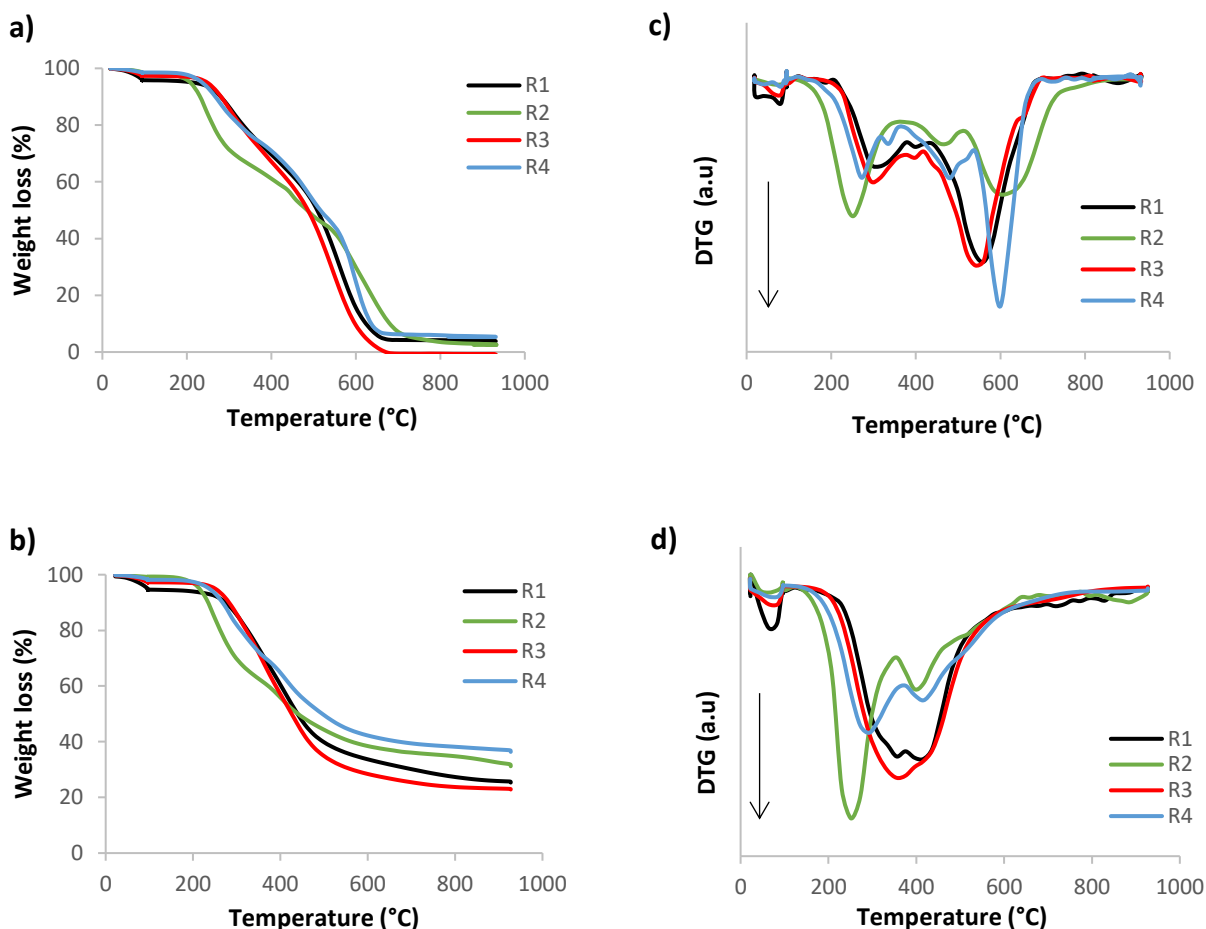


Figure 5: TGA thermogram of resins recorded under air (a) and under nitrogen (b) atmosphere and corresponding derivatives curves under air (c) and nitrogen (d) atmosphere (The arrow indicates the endothermic direction in the derivative thermogravimetric curves).

3.3 Batch contact

First, a study of the influence of pH value on the sorption properties was carried out. During the experiments, special attention was paid to check the precipitation of metals, but nothing was observed at the concentrations used, with batch contact when performed at pH below 7. The adsorption capacities of the different metal ions (Au^{3+} , Pd^{2+} , Rh^{3+}) did not show any significant variation with the change of pH between 0 and 6 (Figure S2 see supporting note). From this point, the strong acid-based desorption theory (Oye Auke et al., 2022) was rejected. For the following studies, a pH=4 was used. Preliminary screening tests were performed to evaluate the affinity of the resins towards the adsorption of noble elements (Au, Pd, Pt, Rh, and Ru). The experiment was carried out by contacting 10 mg of resin with 10 ml of metal ion solution of 20 mg/L concentration of each metal. The results indicate that the **R1** and **R3** resins based on, benzoyl and acetyl thiourea monomers, respectively, present a good affinity for the different noble elements in contrast to **R2** and **R4**, which were based on benzyl and alkyl thiourea monomers, respectively (Figure 6 and Table S2 in the supporting note). This can be explained by the presence of the carbonyl ($\text{C}=\text{O}$), in combination with thiourea, that promotes the sorption of the noble metals considered in this study. Figure S3 (see supporting note) shows the SEM analysis for **R1** and **R3** before and after loading with Au.

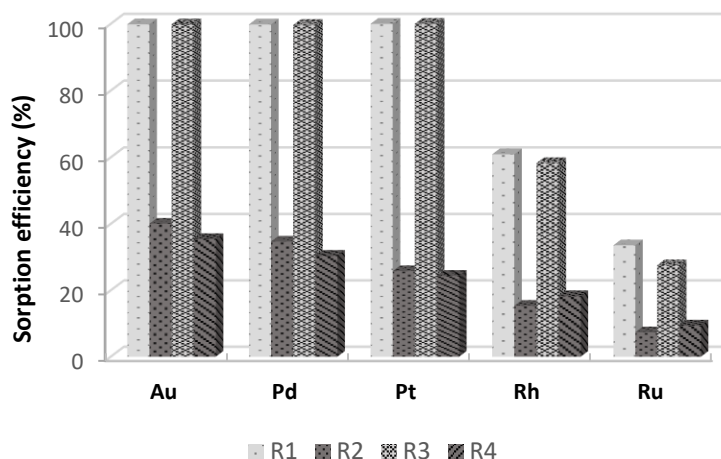


Figure 6: Affinity of the different polymers to noble metals. Sorption experiments: 10 mL of a mixture of Au, Pd, Pt, Rh, and Ru (20 mg/L of each elements at pH=4), contacted with 10 mg of resin **R1**, **R2**, **R3** or **R4** for 24 h at 25°C.

3.4 Adsorption isotherm

Based on the previous results, the sorption capacity and the selectivity of the various noble elements, specifically Au, Pd, and Rh, by **R1** and **R3** were studied.

The adsorption isotherms are based on the relationship between the two parameters: the loading capacity of the resin (Q_e) and the concentration of the metal in the aqueous phase (C_e) measured at equilibrium at constant temperature and pH. The adsorption isotherms of **R1** and **R3** towards Au(III) are shown in Figure 7(a). The initial concentration of metal ions was varied from 10 to 1200 mg/L, while other parameters were kept constant.

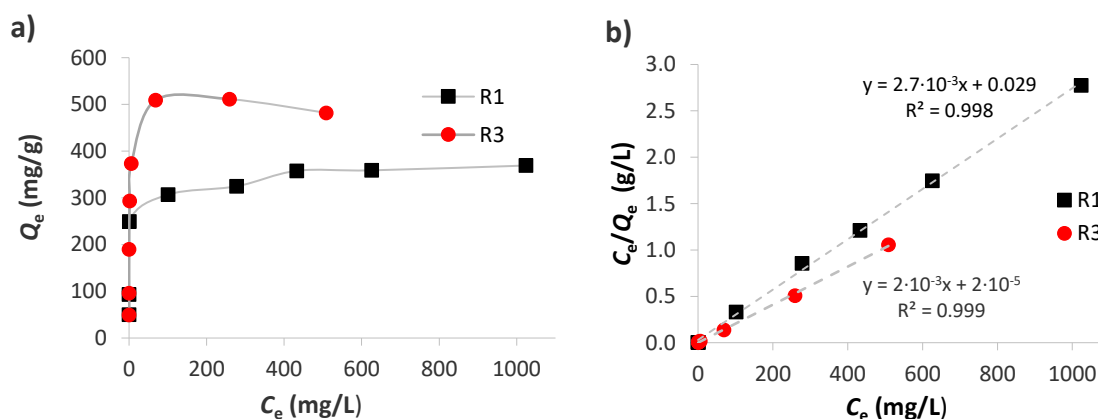


Figure 7: a) Adsorption isotherms yielded for Au(III) on **R1** or on **R3**; b) Plot of Langmuir isotherm equation for Au adsorption by **R1** or by **R3** resins. Sorption experiments: 10 mL of Au (10 to 1200 mg/L of elements at pH=4), contacted with 10 mg of resin **R1** or **R3** for 24 h at 25 °C.

The adsorption data were fitted by Langmuir for Au(III) and Pd(II) and by Langmuir and Freundlich for Rh(III). For Au(III), the models with the best correlation are presented in Figure 7(b). However, the adsorption data for Pd and Rh are represented in Figure S4 (see supporting note). The sorption of Au and Pd for both **R1** and **R3** resins showed a rapid increase at low

concentrations and then a plateau was reached at higher concentrations (Figure 8 and Figure S4 (a)). This was expected to be consistent with the monolayer adsorption phenomenon and was verified according to the Langmuir isotherm, indicating an isothermal chemisorption mechanism. According to the results of the adsorption experiments, it was possible to determine the maximum loading capacity of the resin (Q_{\max}), using the slopes and intercepts of the plots (Figure 8(b) and Figure S4(c)). As a result, the Q_{\max} values of **R1** for Au and Pd were estimated as 350 and 50 mg/g, respectively. Moreover, the results indicated that the Q_{\max} of **R3** for Au and Pd were 500 mg/g and 70 mg/g, respectively.

Compared to some results found in the literature that were obtained with other thiourea resins, **R1** and **R3** showed a higher capacity the recovery of gold (Ertan & Gülfen, 2009; Ronka & Targońska, 2020) and palladium (Birinci et al., 2009; Muslu & Gülfen, 2011). The high capacity achieved by the resins used in this work, compared to the materials described in the literature could be explained by the presence of the carbonyl function, which has made the chelation of noble metals with thiourea more efficient. Indeed, the coordinating properties of the neutral oxygen donor of the amide groups with metal ions are well documented in the literature. This ability to coordinate with metal ions occurs through the carbonyl oxygen of the amide group (Sigel & Martin, 1982).

Due to the rapid increase at low concentration, it was concluded that the resins presented a high affinity towards Au(III) and Pd(II) ions. However, for Rh(III), **R1** presented non-ideal multi-layer adsorption, as it was verified that the adsorption law followed the Freundlich isotherm (Figure S4(b)). According to the experimental data, it was determined that the maximum capacity of **R1** for Rh was found to be 30 mg/g, while the sorption of Rh by **R3** showed a similarity to the sorption of Au and Pd with Q_{\max} equal to 60 mg/g (Oye Auke et al., 2022; Sahoo & Prelot, 2020).

In terms of adsorption energy, considering the interactions of Au and Pd with the **R1** or the **R3** resin, it can be assumed that all adsorption sites are energetically equivalent. For Rh, the adsorption did not occur uniformly at the surface of the **R1** adsorbent, whereas it was found to be homogeneous at the surface of the **R3** material. Moreover, based on the results from this work, it can be established that the different adsorption mechanisms for the three soft noble elements, are influenced by the HSAB rules, the degree of oxidation, and the environment of the binding site. In consequence, both **R1** and **R3** resins have a good affinity for the three noble elements, in a decreasing order from highest to lowest capacity: Au>Pd>Rh.

3.5 Selectivity

Different experiments were carried out to study the selectivity of the resin towards the noble elements compared to the competitive elements (The experimental data are provided in Table S3 in the supporting note).

Figure 8(a, b) shows that the resins have higher selectivity to the noble elements than the other competitive elements, usually found in the industrial waste, such as Fe, Ni, Cu, Al, and Zn. These elements are generally associated with secondary sources (Tofan & Wenkert, 2022). Although, the competitive elements were present in high concentrations (Al: 1620, Fe: 2500, Zn: 970, Ni: 90, and Cu: 150 mg/L) the selectivity of the material was not affected (Figure 8(b)). The S factor of selectivity for the noble elements compared to competitive ones is higher than 500. Regarding the selectivity of noble elements, both resins showed the highest

percentage of sorption for Au (Figure 8(c)). This difference does not seem to be linked to the hardness or softness character, since the three elements are classified as soft acids. The different oxidation state (Au(III), Pd(II) or Rh(III)), as well as the size and hydration of the metal ions could explain the observed differences in terms of sorption efficiency.

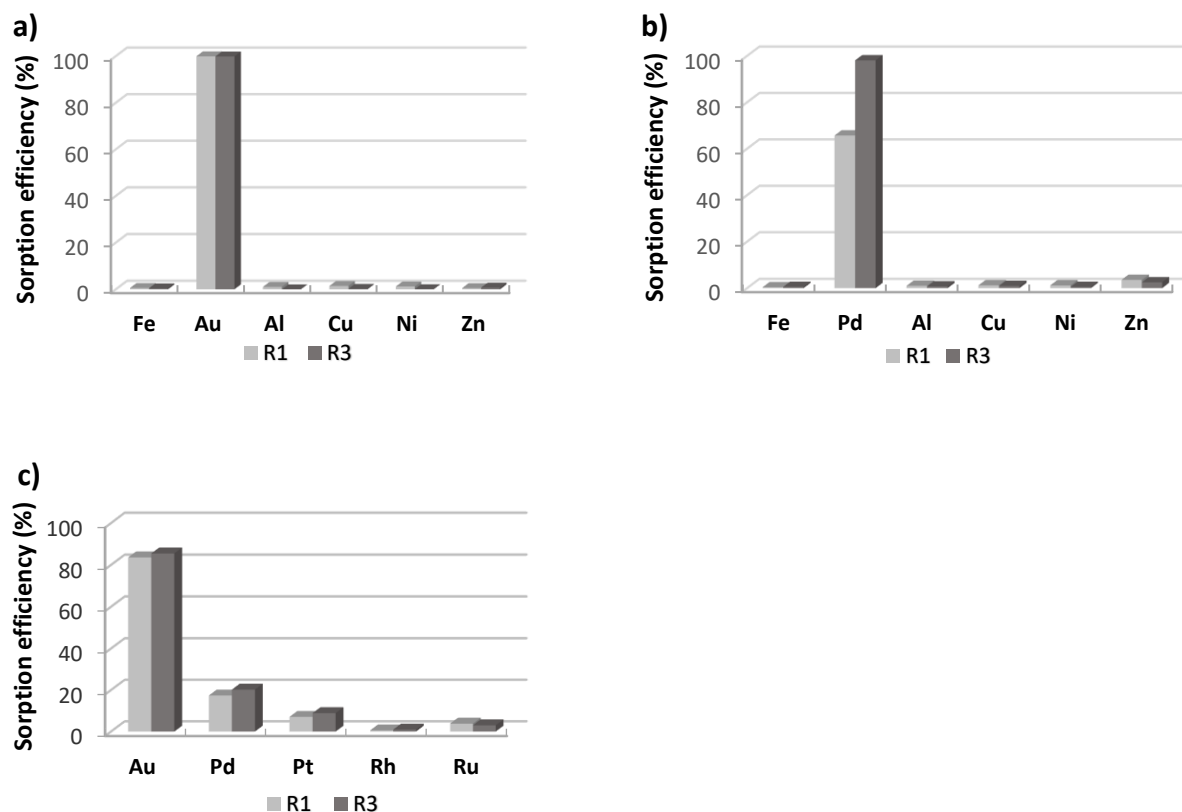


Figure 8: Selective sorption experiments : (a) 10 mL of a mixture of Au, Fe, Al, Zn, Cu and Ni at 20 mg/L of each elements at pH=4 contacted with 10 mg of resin R1 or R3 for 24 h at 25 °C; (b) 10 mL of a mixture of Pd (450 mg/L), Fe (2500 mg/L), Al (1620 mg/L), Zn (970 mg/L), Cu (6 mg/L), Ni (90 mg/L) at pH=1.2 contacted with 60 mg of resin **R1** or **R3** for 24 h at 25°C; (c) 10 mL of a mixture of Au, Pd, Pt, Rh, and Ru at 400 mg/L of each element at pH=3 contacted with 10 mg of resin **R1** or **R3** for 24 h at 25 °C.

3.6 Kinetic studies

Adsorption kinetics provide information about the rate of adsorption and the time required to reach equilibrium. The adsorption kinetics of Au (Figure 9(a)), Pd, and Rh (Figure S5) on the **R1** and **R3** resins have been evaluated at room temperature. The kinetic data were fitted with pseudo-first order and pseudo-second order kinetic models, as discussed in the experimental section, to investigate the mechanism of each adsorption process. For Au, the model with the best correlation is presented in Figure 9(b); for Pd and Rh the kinetic models are presented in the supplementary data (Figure S5).

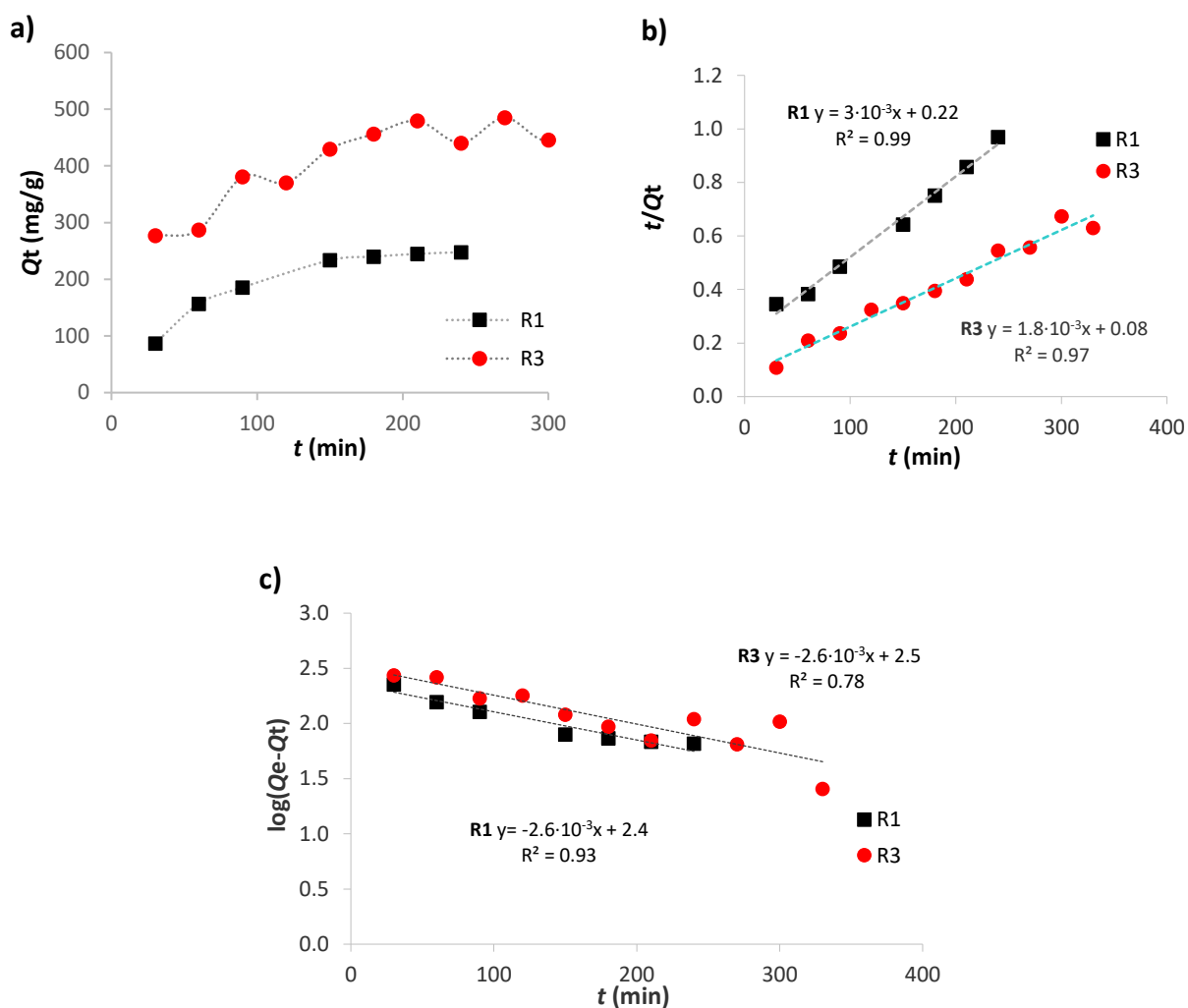


Figure 9: Adsorption Kinetics studies of Au by **R1** and **R3** (a) using pseudo-second order (b) and pseudo-first order (c). Sorption experiments: 10 mL of Au (400 mg/L) at pH=4 contacted with 10 mg of resin **R1** for 0-5 h at 25°C; 10 mL of Au (600 mg/L) at pH=4 contacted with 10 mg of resin **R3** for 0-5 h at 25°C.

For the recovery of Au, it was found that the pseudo-second order model provided a better fit, with a high correlation coefficient of 0.990 (Table 2); the same observations were made for Pd (Table S4) for both resins **R1** and **R3**. However, for Rh adsorption by **R1** (Table S5), the pseudo-first order model was more suitable, consistent with previous studies (Sahoo & Prelot, 2020). The results showed that the recoveries of gold and palladium by both resins were achieved after 5 hours. Furthermore, **R3** showed slow kinetics for rhodium.

In relation to the kinetic adsorption isotherms, the results defined that chemical sorption, or chemisorption, determines the sorption of Au and Pd, where the adsorption rate depends on the adsorption capacity and not on the concentration of adsorbates. However, for Rh adsorption by **R1**, the results suggested a physisorption, where the adsorption rate was related to the difference between the saturation concentration and the amounts that are adsorbed with time (Liu et al., 2019; Vadivelan & Kumar, 2005). The results for Rh by **R3** were similar to the recoveries of Au and Pd, but since the complex formation reaction of Rh(III) complex is extremely slow, this should be taken with caution.

Table 2: Kinetic parameters for Au(III) uptake on **R1** and **R3**.

Kinetic Model	Resins	Q_e (mg g ⁻¹)	k_1 (min ⁻¹)	k_2 (g mg ⁻¹ min ⁻¹)	R ²
Pseudo-First Order	R1	230	6.0x10 ⁻³	-	0.933
	R3	330	6.0x10 ⁻³	-	0.777
Pseudo-Second Order	R1	333	-	4.1x10 ⁻⁵	0.991
	R3	556	-	4x10 ⁻⁵	0.975

3.7 Desorption

The desorption (elution, stripping or back-extraction process), known as adsorbent regeneration, is critical. It allows adsorbents to be reused and regenerated while retaining sorption efficiency, cost reduction and lower environmental impact. Different reagents are used as desorption agents for noble elements. They include acids and chelating complexing agents such as cyanide, thioureas, and thiosulfate (Guo et al., 2022).

The use of acid was eliminated based on the results of the effect of pH on the sorption efficiency. Experiments using thiosulfate and thiourea as desorption agents was carried out for resin **R1** (Table S6). The thiosulfate solution (2 mol/L) offered low desorption. However, the use of thiourea solution at different concentrations and pH values resulted in successful desorption. Three different solutions with 0.5 mol/L and 1 mol/L at pH 4 and pH 2 were examined. The solution prepared from 1 mol/L thiourea at pH 2 produced the best results, with a desorption efficiency of 99%.

The regeneration and reusability of the resin **R1** was investigated for the Au(III) by adsorption-desorption up to five cycles (Table S3 in the supporting note). After adsorption of Au(III) ions, the loaded resin was washed with a 1 M thiourea solution at pH 2. After each adsorption-desorption cycle, the **R1** resin was washed and dried to be reused for other adsorption cycles. After five cycles, the recycled **R1** had almost the same removal affinity as the original **R1** resin (Table 3).

Table 3. Au sorption and desorption efficiencies for **R1**.

	Au sorption (%)	Au recovery (%)
Cycle 1	98.97 ± 0.99	99.47 ± 1.05
Cycle 2	99.89 ± 1.10	98.89 ± 0.97
Cycle 3	98.86 ± 0.96	98.78 ± 0.95
Cycle 4	99.09 ± 0.99	98.50 ± 0.86
Cycle 5	97.97 ± 0.75	98.01 ± 0.81

Sorption experiments: 10 mL of Au solution at 100 mg/L, pH=4, contacted with 10 mg of resin **R1** for 24 h at 25 °C; Desorption experiments: 10 mL of 1 mol/L thiourea solution, pH=2, contacted with 10 mg of resin loaded **R1**-Au for 24 h at 25 °C.

4. Conclusion

Three new chelating sorbents (**R1**, **R2** and **R3**) based on thiourea resole materials were obtained by a polymerization reaction between phenolic thiourea monomers (synthesized from tyramine derivatives) and formaldehyde under basic conditions. The three materials were engaged in sorption experiments with respect to noble elements. The resin **R1** and **R3** based on benzoyl (**C1**) and acetyl (**C3**) thiourea monomers have shown a high affinity for noble metals, with remarkable sorption capacities of 350 – 500 mg/g for Au, 50 – 70 mg/g for Pd, and 30 – 60 mg/g for Rh. This behavior may be related to the combination of carbonyl and thiourea groups in such resins.

In addition, these resins have presented a higher selectivity for noble metals than the competitive metals in industrial effluents, such as Zn, Cu, Ni, Fe, and Al.

The adsorption mechanism towards Au and Pd could be well described by Langmuir monolayer chemical adsorption, while for Rh it was described by Langmuir and Freundlich isotherms. Preliminary studies indicated that noble metals could be stripped from the loaded resins using a 1 mol/L thiourea solution at pH= 2.

As a result, thiourea resole materials are promising candidates for the recovery of noble elements, specifically gold.

Supplementary notes:

Ligand characterizations; Figure S1: ¹³C NMR spectra of prepolymer **R1**; Figure S2: pH sorption experiments; Figure S3: SEM analysis; Figure S4: Adsorption isotherms; Figure S5: Adsorption Kinetics studies; Table S1: Elemental analysis; Table S2 and Table S3: sorption data; Table S4 and Table S5: kinetic parameters. Table S6: Recovery of Au from **R1** loaded resin; Table S7: sorption-desorption data.

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