Syntesis of amine and thiol silica modified: used of removal Ag(I) of aqueous system

Síntesis de sílice mesoporosa amino y tiol modificadas y su aplicación en la remoción de Ag(I) de sistemas acuosos

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Abstract

The recovery of Au from rich cyanidation solutions is usually carried out by adsorption on activated carbon, a process that presents as its main disadvantage the formation of fines in the classifying screens, these fines represent a considerable loss of values in the process, which is why The search for alternatives that allow the recovery of gold and silver from rich cyanidation solutions is of interest to hydrometallurgy. In this sense, magnetic pre-concentration could be an alternative for said process. the present work shows the study of the removal of AgNO3 and [Ag(CN)2]- in synthetic aqueous systems with mesoporous amino and/or thiol silicas modified with magnetite (MS-NH2-Fe3O4 and MS-NH2-SH-Fe3O4) . It is observed that the presence of ligands of a softer nature favors the removal of Ag in Ag-CN systems, showing low removal capacity for amine materials.

Resumen

La recuperación del Au de las soluciones ricas de cianuración se realiza usualmente por adsorción en carbón activado, proceso que presenta como principal desventaja la formación de finos en las cribas clasificadoras, dichos finos representan una considerable pérdida de valores en el proceso, es por ello que la búsqueda de alternativas que permitan la recuperación del oro y la plata de las soluciones ricas de cianuración es de interés para la hidrometalurgia, en este sentido la pre-concentración magnética podría ser una alternativa para dicho proceso; el presente trabajo muestra el estudio de la remoción de $AgNO_3$ y $[Ag(CN)_2]^-$ en sistemas acuosos sintéticos con sílices mesoporosas amino y/o tiol modificadas con magnetita ($MS-NH_2-Fe_3O_4$ y $MS-NH_2-SH-Fe_3O_4$). Se observa que la presencia de ligandos de naturaleza más blanda favorece la remoción de la Ag en los sistemas Ag-CN, mostrando baja capacidad de remoción los materiales aminados.

Mesoporous Silica, Amino and tiol modification, Silver remove

Cinauración, Silice, remoción Ag(I)

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Introduction

In recent years, magnetic hybrid nanomaterials have been studied as adsorbents in the recovery of metal ions, these have been proposed as an alternative in hydrometallurgy for the recovery of precious metals mainly (Pd, Pt, Rh, Ag and Au) and rare earths from e-waste recovery processes [1-10]. These proposals involve the use of a magnetic nanostructured material such as Fe3O4, □-Fe2O3, CoFe2O4, MnFe2O4 among others; these materials are usually coated with a film of a surfactant, polymer or silica as a protective film that favours the modification of the magnet surface with various functional groups that provide selectivity to the metal ion of interest [1]. The principle of these materials is the adsorption of the metal ion with the functionalising group, which can be done by physical adsorption or covalent immobilisation [1-10].

One of the advantages of silica coatings is the ease of anchoring a wide range of functional groups through the condensation of various alkylarylsilanes. [1-10]. Recently, the use of mesoporous silica (MS) type SBA-15, modified with magnetite and chelating groups N, N, O donors for the recovery of Cd(II), Ni(II), Pb(II) and Zn(II) traces in aqueous solutions has been proposed [6-13]. Recently, the use of magnetic composites with metal lattices, polymers and mesoporous silica matrices, activated carbon and other ceramics has been reported for the removal of various contaminants in aqueous media and soil, such as U(VI), Cd, Ni, Pb and various organic contaminants such as oils and dyes [14-19]. The present work shows the study of Ag(I) removal from aqueous systems with mesoporous silica materials modified with magnetic, amino and mercapto groups. Experimental Section.

Synthesis and characterization of the Fe3O4

The synthesis of magnetite was carried out by precipitation techniques according to equation 1, in a $2Fe^{3+}:Fe^{2+}$ ratio [20-22]. In a 250 mL flask, 5.27 g of FeSO4 and 2.7 g of FeCl3 were dissolved in 200 mL of water under constant stirring, then the pH was adjusted to 10-11 with NH4OH and the system was placed at reflux for 24 h. At the end of this time, the magnetite was recovered by filtration and dried at 75°C for 12 h [20-22].

$$2FeCl_3 + FeSO_4 + 8NH_4OH \longrightarrow Fe_3O_4 + (NH_4)_2SO_4 + 6NH_4Cl + 4H_2O$$

Reaction 1

The magnetite was characterized by powder XRD, which was carried out on a RIGAKU ULTIMA IV X-ray diffractometer.

Synthesis and characterization of MS-NH2-Fe3O4 and MS-NH2-SH-Fe3O4

The synthesis of mesoporous silica materials was carried out from sodium silicate using P-123 as molecular sieve according to Salazar et al [23].

The modification with amino and/or thiol groups on the mesoporous silica was carried out by post-synthesis techniques. 0.167 moles of the mesoporous silica was suspended in 100 mL of ethanol and 0.0416 moles of the modifying agent 3-aminopropyltrimethoxysilane and/or 3-mercaptopropyltrimethoxysilane were added, 1 mL of NH4OH was added and the system was left under reflux for 24 h. At the end of this time, the solid was recovered and the system was refluxed. At the end of the time the solid is recovered and washed with 2 portions of 10 mL of ethanol and 10 mL of acetone, to be subsequently dried in the oven for 12 h at 75°C.

The anchoring of the magnetite in the modified silicas was carried out by placing 1 g of the synthesised Fe3O4 under reflux with 10 g of MS-NH2 for 12 h, after which the material was recovered by filtration and dried at 70°C for 12 h.

Adsorption studies of Ag(I) from aqueous systems

The evaluation of the silver adsorption capacity (I) was carried out by determining the adsorption kinetics at 10 min intervals for 1 hour with standard solutions of AgNO3 at different concentrations (100-500 ppm). 0.1 g of the material was placed with 10 mL of a solution at 57, 123, 192, 319 and 694 mgL-1 of Ag and the residual concentration of silver in the solution was determined at the above mentioned times by atomic absorption spectrometry.

The adsorption capacity of silver was determined by equation 1, where qt is the loading at time t, Co and Ct are the initial and at time t silver concentrations in the solution in mgL-1, V is the volume of sample used (L) and m is the mass of material used in g.

$$q_t = \frac{(C_o - C_t)V}{m}$$

(1)

Effect of pH on Adsorption of Ag(I)

The effect of pH on the adsorption capacity of magnetite was evaluated by determining the adsorption capacity of magnetite at pH 3, 4.5, 6 and 10. 0.1 g of the material was placed with 10 mL of Ag(I) solution at the pH under study for 20 minutes and the concentration of residual Ag in the solution was determined.

Results and Discussion

The FTIR characterisation of the silicas modified with the various amino groups, shows the presence of organic matter in the range of 3000-2500 cm-1 and 1600-1200cm-1, in Table 1, summarises the FTIR characterisation of these samples, in all cases a vibrational shift of C-N is observed suggesting NFe interaction in the materials, the assignment of the main vibrations in these materials is summarised in Table 1.

Material	Characterisation (cm^{-1})	
MS-NH$_2$	νC-H	2938-2847
	δC-H	1534
	νN-H, O-H(H$_2$O)	3013-3015
	δN-H, O-H(H$_2$O)	1646
	νSi-O-Si	1065
	δSi-OH	960,793
	δSi-O	464
MS-NH$_2$-Fe$_3$O$_4$	νC-H	2938-2847
	δC-H	1534
	νN-H, O-H(H$_2$O)	3013-3015
	δN-H, O-H(H$_2$O)	1660
	νSi-O-Si	1065
	δSi-OH	793
	δSi-O	464

Table 1 Characterisation by FTIR

Figure 1 shows the diffractogram of the synthesised magnetite, corroborating the obtaining of this phase. The planes are observed at 2 at 30.1, 35.4, 43.1, 54.5, 57.6, 62°, which correspond to magnetite according to Mohammadi et al. [22].
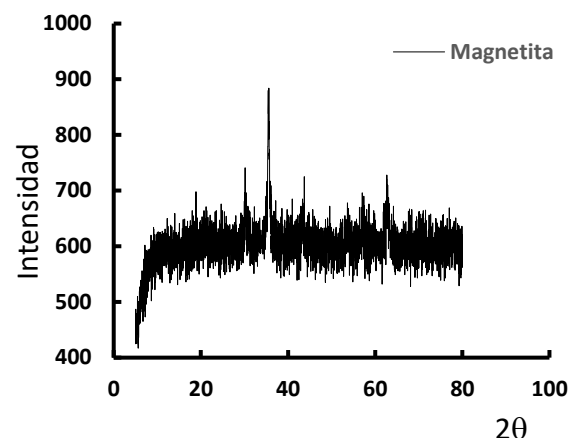

Figure 1 DRX Synthesised Magnetite

Studies on AgNO₃ adsorption from aqueous systems

MS-NH$_2$-Fe$_3$O$_4$, showed a 99% removal at low concentrations of 100 and 200 ppm, decreasing its removal capacity at moderate concentrations of 300 and 500 ppm, removing between 80-75 % of silver only (Figure 2). All the materials showed an adsorption equilibrium after 20 minutes of contact. Table 2 summarises the adsorption parameters observed according to the Langmuir adsorption model, which assumes a monolayer adsorption and no interaction between sorbate-adsorbent and sorbate-sorbate.
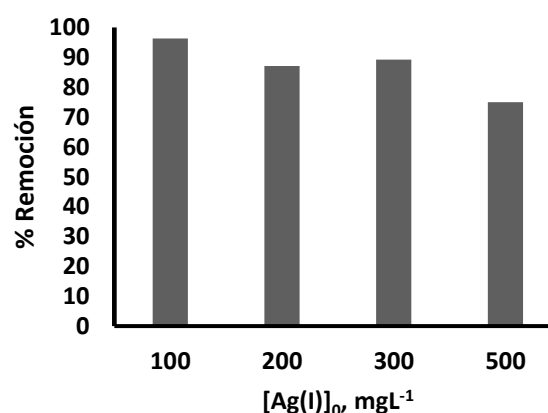

Figure 2 Ag adsorption capacity of the MS-NH$_2$-Fe$_3$O$_4$

$$q_e = \frac{Q_0 K_L C_e}{1 + K_L C_e}$$

(2)

Where:

Q_0 is the charge at equilibrium in mgg-1, K_L the Langmuir constant and C_e the concentration of Ag(I) at equilibrium in mgL $^{-1}$.

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A parameter that allows to identify the type of adsorption in this model is the partition coefficient (RL), which was described by Webber and Chakkravorti in 1974 [24], this parameter is a function of the KL (Langmuir constant) and the initial concentration of the sorbate and is defined by Eq. 2 As already mentioned, the value of RL defines the type of adsorption, so that if RL>1 the adsorption of the system is unfavourable; if RL=1 the adsorption is favourable and linear; values of 0<RL<1 indicate favourable adsorption; while values of RL=0 indicate irreversible adsorption [24, 25].

$$R_L = \frac{1}{1 + K_L C_0} \qquad (3)$$

Where: K_L is the Langmuir constant and C_0 is the initial concentration of sorbate.

Model	Parameters	MS-NH2-Fe3O4
Langmuir	Q_0 [mgg^{-1}]	30.12
	K_L [L mg^{-1}]	0.122
	R^2	0.9242
	$\Delta q(\%)$	6.9
	R_L	0.075-0.14
	ΔG [KJmol^{-1}]	-24.45

Table 2 Experimental parameters of the fit of Ag(I) adsorption data to Langmuir adsorption models
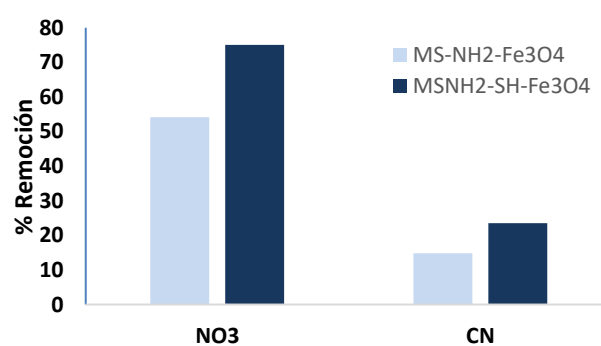
Effect of pH on the Adsorption of Ag(I)

Figure 3, shows the effect of pH on the adsorption of $[Ag(H_2O)_2]+$ with MS-NH2-Fe3O4, it is observed the increase of the adsorption capacity of Ag(I) as the pH of the system increases, it has been reported an isoelectric point close to 9. 0 for polyaminated silicas [23, 25], showing a positive surface charge at acidic pH, which decreases its adsorption capacity due to the repulsive interactions between the positive surface of the material and the $[Ag(H_2O)2]+$, these interactions decrease with increasing pH, favouring the negative charge on the surface at basic pH, which favours the adsorption process.
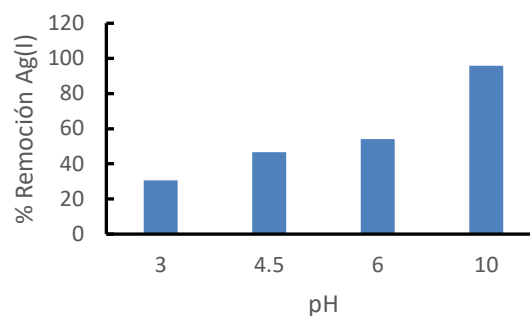
Figure 3 Effect of pH on the adsorption process of Ag (I)

Effect of the counter-anion on Ag adsorption (I)

Figure 4 shows the effect of the counter-anion on the removal of Ag(I), the adsorption of [Ag(H2O)2]NO3 and [Ag(CN)2]-complexes was evaluated. A lower removal capacity of the Ag-CN systems was observed (low removal of 15%) than that observed for silver nitrate, where removal capacities of 80% were observed. The low removal capacity of the Ag-CN system can be attributed to the high affinity of cyanide for silver, being a ligand with a soft nature and high affinity to Ag+. This makes it necessary to use ligands with a higher affinity to this cation, such as mercapto groups, thiophenes, among others. In this sense, the effect of the mercapto group on the removal capacity of Ag in Ag-CN systems was evaluated, observing an improvement in the removal capacity of silver by 25% (Figure 4).

Figure 4 Effect of the counter-anion on the adsorption process of Ag(I)

Conclusions

Polyamino silicas exhibit positive surface charges at acidic pH, which disfavours their ability to remove Ag(I) cation by electrostatic repulsions. The silver nitrate systems show higher removal with the amine silicas compared to the Ag-CN system, this is due to the non-soft nature of the polyamino groups present in the MS.

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The presence of softer ligands favours the removal of Ag by Ag-L interactions, as shown by the presence of mercapto groups in the MS, which favoured the removal of the [Ag(CN)2]- complex.

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