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Cu(I) removal using mesoporous silica (UGM-triamin)

Estudio de la remoción de Cu (I) con materiales mesoporosos de sílice (UGM-triamin)

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Abstract

This paper shows the syntheses and use of hybrid porous silica materials (UGM-triamin) in the adsorption of Cu (I) of the cyanidation effluents of gold and silver. Studies of adsorption of Cu (I) in synthetic solutions of Cu-CN a pH of 11 and at a concentration ratio of 1: 5 Cu: CN, simulating the effluents of cyanide process gold and silver ores, showed maximum adsorption capacity of 7.54 mg of Cu (I) per gram of material and favorable adsorption according to the Langmuir model (R_L of 0.31 to 0.41). The evaluation of the adsorption capacity of the material with real solutions of cyanide, showed 95% removal of copper in the effluent cyanide and 68.5% selectivity for the adsorption of copper. It has been observed free cyanide destruction in the system during adsorption of copper, so that the oxidation of free cyanide may be linked to the mechanism of adsorption of copper.

Cu(I) Adsorption, Cyanidation, UGM-triamin

Resumen

El siguiente trabajo, muestra el uso de materiales porosos de silica poli-amino funcionalizados denominados UGM-triamin, en la adsorción de Cu(I) de efluentes acuosos provenientes de la cianuración de minerales de oro y plata. Los estudios de adsorción de Cu(I) en disoluciones sintéticas de Cu-CN a pH de 11 y bajo una razón de concentración de 1:5 de Cu:CN, simulando los efluentes del proceso de cianuración de minerales de oro y plata, mostraron una capacidad máxima de adsorción de 7.54 mg de Cu(I) por gramo de material y una adsorción favorable de acuerdo con el modelo de Langmuir (R_L de 0.31-0.41). La evaluación de la capacidad de adsorción del material con disoluciones reales de cianuración, mostraron una remoción del 95 % del cobre presente en el efluente de cianuración, así como un 68.5% de selectividad para la adsorción del cobre. Se ha observado la destrucción del cianuro libre en el sistema durante el proceso de adsorción del cobre, por lo que la oxidación del cianuro libre posiblemente se encuentre vinculada con el mecanismo de adsorción del cobre.

Adsorción de Cu(I), Cianuración, UGM-triamin

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Introduction

Nowadays, meso-porous materials based on ordered silica have a growing interest within materials science and technology. Meso-porous materials have high chemical and thermal stability, which allows its use in a wide range of applications that involves biological and chemical processes without meso-porous silica upset these processes. These materials have been used as catalytic supports (Barton T. J. *et al*., 1999; Heikkila I *et al*., 2007), chromatographic supports (Lebeau B. *et al*., 2013), adsorbent materials (Meng M. et al. 2014; Sierra I. *et al*., 2013), drug bio-reservoir and immobilizer of enzymes or proteins (Sierra I. *et al*., 2014; From Muth P. *et al*., 2011), among other applications.

Meso-porous based on ordered silica materials have been widely used as an adsorbent or remover of contaminants, especially for metal ions removal from aqueous effluents. These materials have a high selectivity towards the pollutant to remove, this selectivity is designed from the anchoring of various chelating groups related to the metal ion, in addition to presenting rapid adsorption kinetics and not observing swelling as polymers on contact with water (Jal P. K. *et al*., 2004). thus, there are several industrial processes where the presence of specific metal ions causes low yield or even the economic infeasibility; as an example of this, is the cyanide of minerals process to obtain precious metals, where the presence of Cu into the ore greater than 0.05% makes the cyanide process unfeasible (Dai X. *et al*., 2012).

Therefore, proposals that allow the Cu removal from rich cyanide solutions have special interest on hydrometallurgy. However, a few studies of mesoporous materials for Cu removal are found. In 1990 Talavarides proposed the use of amino polyfunctionalized mesoporous for the removal of copper from Cu:CN systems, however, the removal of the metal ion in these systems is favored at acidic pH and not under the conditions of the cyanidation process (Lee JS *et al*., 1998). Furthermore, our research group recently studied the feasibility of using mesoporous silica for Cu (I) removal from the actual cyanidation effluents, observing that, under the conditions of the process, the removal capacity of the metal ion is feasible in 90%, with moderate load capacities and selectivity (Salazar-Hernández MM *et al*., 2015).

Thus, in this paper is to study more versatile systems that allow greater selectivity for the Cu removal in cyanidation effluents.

Methodology

UGM-triamin: Synthesis and characterization

The synthesis of the mesoporous silica triamin UGM was carried out according to the methodology reported by Rodríguez-Garnica et al. from alkoxysilane derived from diethylene glycol.

UGM-triamin Synthesis

Under nitrogen flow and constant stirring, one mole of the modifying agent (N^1-(3-trimethoxysilylpropyl) diethylenetriamine $(MeO)_3SiCH_2[(CH_2)_2\text{-}NH]_3\text{-}H$, was added to 6 moles of the silica precursor (alkoxide derived from diethyleneglycol) until get a homogeneous solution. 750 ml of reactive grade acetone was added at the mixture in an ultrasound bath with pulses of one minute duration and a frequency of 30 MHz at intervals of one second by an hour. The mixture stands for three days in N_2 atmosphere. The solid obtained was filtered and reflux by 3 day using a solution of ethanol/water (270/30, v / v) and 3mL of HCl. The solid is recovered by filtration and cleaned using ethanol and dried in the vacuum line. Once dry the material, it is washed using 20 ml of an NH_4OH solution for 10 seconds, filtered and dried on a stove at 60 ° C.

UGM-triamin characterization

The UGM-triamin was characterized using infrared spectroscopy with Fourier transform (FTIR), the spectra were acquired under the KBr transmittance methodology, in a Perkin Elmer Spectrum 100 spectrometer, using an average of 32 scans, a resolution of 4 cm^{-1} and a spectral window of 4000 to 400 cm^{-1}.

The NMR CP-MAS ^{29}Si and ^{13}C spectra was obtained in Varian 600 MHz AR-Premium COMPACT with 120 average scans.

The textural characterization of the UGM-triamin was carried out by the adsorption and desorption isotherms of N_2 at 77 K in a Micromeritics ASAP-2010 equipment.

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The samples were degassed prior to analysis at 100 ° C and 8 mmHg. The surface area was determined under the BET model and the analysis of the pore distribution was determined by the BJH model.

Characterization of the ore extracted from "El Porvenir"

The chemical characterization of the mineral (content of Pb, Cu, Zn and Fe), was carried out by atomic absorption, digesting a portion of ore having an average size of 100 microns (5 g) with 10 ml of HNO_3 and 1 ml of $HClO_4$, later, the sample is dried and the cations was dissolved using 20 ml of HCl to determine the content of Pb, Cu, Zn and Fe by atomic absorption. The gold and silver content are determined by gravimetric method.

The mineralogical composition of the ore was determined by scanning electron microscopy (SEM) coupled to an X-ray detector on a PHILLIPS XL30 microscope.

Cyanidation of the ore extracted from el Porvenir, Real de Asientos, Aguascalientes

One kilogram of the dry mineral is grinded for 50 minutes, to reach 60% @ -200 mesh (75 microns). The solid is placed in a reactor with oxygen flow, distilled water is added to reach 42% of solids. 0.5 g of CaO are added to the mixture until a pH of 11 is reached, to add 0.3% NaCN and it is kept under constant stirring at 255 rpm for 72 hours. Finally, the solution is filtered and stored in an amber bottle for later use in adsorption tests.

The chemical composition of the cyanide solution was determined by atomic absorption.

Kinetic Studies of Cu(I) Removal Capacity with UGM-triamin

The evaluation of Cu(I) adsorption isotherms with the UGM-triamin were carried out using synthetic solution and a rich cyanidation solution. 0.5 g of functionalized material were placed in five different test tubes, mixed with 10 ml of Cu (I) stock solution 500, 300, 250, 200, 100 and 50 $mg{\cdot}Cu{\cdot}L^{-1}$) or with the rich cyanidation solution, mounted in a tube rocker model L-TIR200 UNICO working at 24 rpm.

At time study intervals was 3, 6, 9, 14 and 20 minutes, the copper concentration in the solution is determined by atomic absorption.

Results and discussion

UGM-triamin Synthesis and characterization

FTIR study shows that there is organic matter into the silica network within vibrations 2979-2866.9 (υC-H), 1463.3 (δC.H) and the vibrations of υC-N that correspond to primary and secondary amines are 1360.5 y 1395.9 cm^{-1}. RMN spectra in solid state of ^{29}Si y ^{13}C are shown in Figure 1, where the anchoring of organic matter is present in the silica network with the presence of T^3 groups observed by ^{29}Si RMN and the presence of seven aliphatic carbons by RMN 13C, therefore, the functional group is into the silica network.

Adsorption and desorption studies of N_2 using UGM and UGM-triamin have a type IV and V isotherms, respectively, according to the IUPAC classification as shown in Figure 2a. On the other hand, the pore distribution analysis using BJH model, Figure 2b, shows that the UGM have mesopores with an average diameter of 2.6 nm, meanwhile the UGM-triamin shows an average pore diameter of 59 nm and a low presence of mesopores with an average diameter of 3.9 nm. The modified material shows a reduction of the surface area of the material of almost 89.7% (Table 1); this decrease is due to the obstruction of the pores of the material caused by the electrostatic repulsion that the protonated amino groups of the functionalizing group present. For the case of polyamino-functionalized materials. Casasús R. et al. (Casasús R. et al., 2004) reports a basic treatment that allows the deprotonation of the amines suppressing these molecular interactions that the cause of pore obstruction, allowing the unblocking pores. UGM-triamin2 is treated using 1% of NH_4OH. After the treatment, the material shows a 45.9% abatement of the surface area (Table 1), which suggests the unblocking of the pores. Thus, the material UGM-triamin2 shows a type IV isotherm like the unmodified material and a bimodal pore distribution with sizes lying between 2.6 and 3.2 nm (Figure 2).

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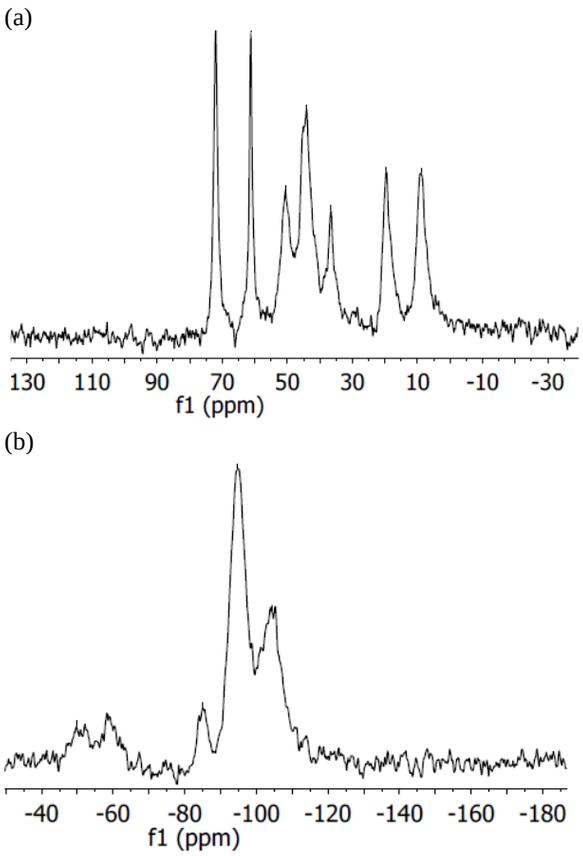

Figure 1 (a) RMN CP-MAS de ^{13}C spectra for UGM-triamin; (b) RMN CP-MAS de ^{29}Si spectra for UGM-triamin

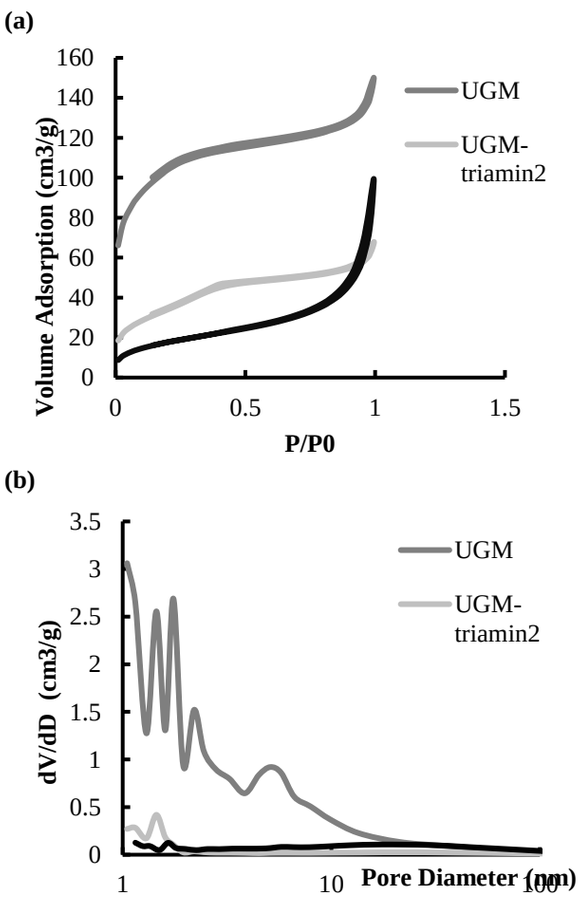

Figure 2 (a) Adsorption-Desorption isotherms of N_2 (b) Pore size distribution using the BJH model

	A_{surf}[m^2g^{-1}]	V_{poro} [cm^3g^{-1}]	D [nm]
UGM	907.53	0.56	2.50
UGM-*triamin*	93.75	0.21	9.06
UGM-*triamin2*	490.40	0.45	3.60

Table 1 UGM and UGM-triamin N_2 Adsorption-Desorption Studies

Cu(I) Adsorption Studies using Synthetic CuCN/KCN Solutions

The adsorption capacity of Cu (I) using UGM-triamin were carried out employing synthetic solutions of Cu / CN at a pH of 11 with a ratio of Cu: CN of 1:3, assuring $[Cu(CN)_3]^{2-}$ as the predominant species in the system, because of this is the one found predominantly in cyanidation effluents with high copper content.

Figure 3 shows the adsorption isotherms of Cu (I) with the UGM-triamin, observing the elimination of more than 90% of the copper in the system with low and moderate concentrations of copper (50–200 ppm).

According to the Langmuir adsorption model, the material has a maximum adsorption capacity of 7.54 mgCu g^{-1} material and an R_L in intervals of 0.31–0.041, which suggests a favorable trend to chemisorption.

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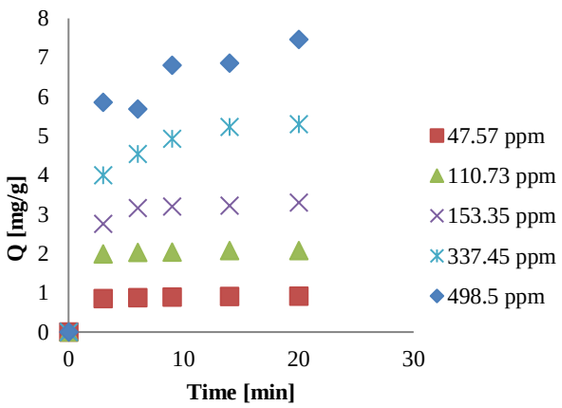
(a)



(b)

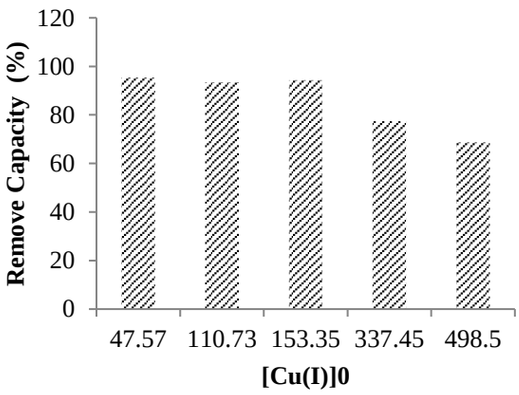


Figure 3 a) UGM-triamin adsorption isotherms for Cu (I) in synthetic Cu-CN solutions; (b) % of removal capacity of Cu (I) in synthetic solutions of Cu-CN using UGM-triamin

Figure 4 shows the UGM-triamine adsorption-desorption capacity for Cu (I) and the recycling cycles of the material, the study shows that with low or moderate concentrations of Cu (I), the material supports up to 3 adsorption-desorption cycles. The UGM-triamin adsorption capacity decreases by 70% in the fourth cycle, while at high concentrations the UGM-triamin allows it to recycle up to 2 adsorption-desorption cycles due by the obstruction of the active sites containing copper not totally desorbed.

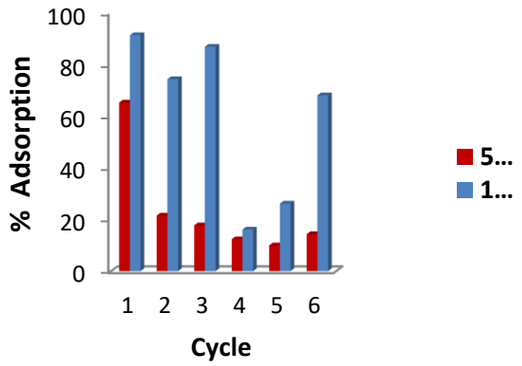


Figure 4 Evaluation of the adsorption-desorption capacity of UGM-triamin

Removal capacity of Cu(I) from cyanide solution

The adsorption capacity of Cu (I) with UGM-triamin, in rich cyanidation solution, was carried out with an ore from "el Porvenir" from the "Real de Asientos" mining district. The mineralogical composition of ore is show in Table 2, where it is shown that copper is present as oxides (malachite), secondary sulfides (covelite and chalcosite) and chalcopyrite. The ore has a composition of 0.126% Cu and an Au and Ag grade of 1.2 and 35.3 g–Ton^{-1} respectively. The cyanidation solution of the ore shows a composition of 137.5 ppm of copper, 1.54 ppm of Au and 9.48 ppm of Ag.

	Mineralogy phase
Gold	Native, free, and finely disseminated.
Silver	Silver sulfides (Ag_2S).
Copper	Oxides (malachite), secondary sulfides (covelite and chalcocite) and chalcopyrite.
Iron	Pyrite.
Another phase	Quartz and a high content of clays.

Table 2 Mineralogical composition of the "El Porvenir" ore from the Real de Asientos Aguascalientes mining district

The UGM-triamin adsorption capacity of Cu (I) in the rich solution of cyanidation of the ore from "El Provenir", shows a 90% removal capacity for copper from the cyanidation solution and a UGM-triamin recycle capacity of two cycles, observing a decrease of 20% in the adsorption capacity for the second cycle, as shown Figure 5 and 6.

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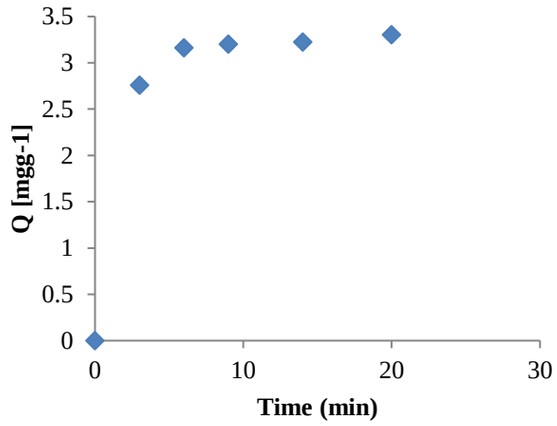

Figure 5 Cu (I) adsorption isotherm from cyanidation of "El Porvenir" ore

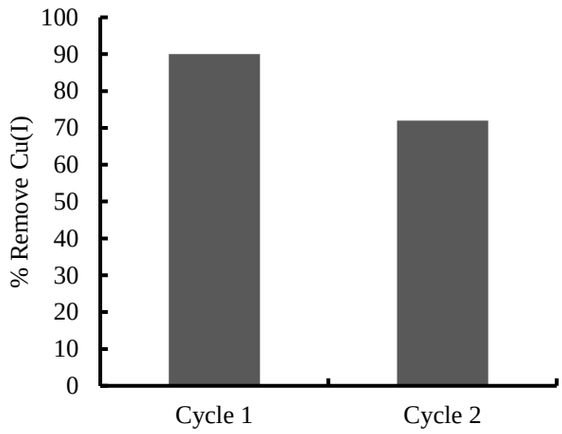

Figure 6 Evaluation of the adsorption-desorption capacity of UGM-triamin for Cu (I) with the rich cyanidation solution from "El Porvenir"

However, the selectivity of the material towards copper was observed in 68.5%. These results suggest the feasibility of copper removal in cyanidation effluents with UGM-triamin.

Conclusions

The results show that UGM-triamine has a maximum Cu (I) adsorption capacity of 7.54 mg–g^{-1}, allowing the Cu (I) removal over 90% in rich cyanidation solutions with high cyanide content. UGM-triamin removes copper from cyanidation solutions with 68% selectivity and a maximum recycling of two adsorption-desorption cycles.

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References

Barton T J, Bull L M, Klemperer W G, Loy D A, McEnaney B, Misono P A, Pez G, Scherer G W, Vartuli J C, Yaghi O M "Tailored Porous Materials" *Chem. Mater*. (1999) 11: 2633-2656.

Casasús R., Marcos M. D., Martínez-Máñez R., Ros-Lis J. V., Soto J., Villaescusa L. A., Amorós P., Beltrán D., Guillem C., Latorre J. "Toward the Development of Ionically Controlled Nanoscopic Molecular Gates" *J. Am. Chem. Soc.* (2004) 126: 8612-8613.

Dai X., Simons A., Breuer P. "A Review of Copper Cyanide Recovery Technologies for the Cyanidation of Copper Containing Gold Ores" *Minerals Engineering* (2012) 25:1-13.

De Muth P, Hurley M, Wu Ch, Galanie S, Zachariah M R, Deshong P, "Mesoscale porous silica as drug delivery vehicles: Synthesis, characterization and pH sensitive relase profiles" *Microporous and Mesoporous Materials* (2011) 141: 128-134

Paulina Rodríguez-Garníca, Ma Mercedes Salazar-Hernández, Jaime Maldonado-Estudillo, Noe Saldaña-Pña, Georgina Sotelo-Rodríguez, Brenda Huichapa-Rocha, Gerardo González-García, Alejandro Alatorre-Ordaz, J. Alfredo Gutiérrez "Nonordered porous silica based pure inorganic and hybrid organic inorganic materials prepared by a nonaqueous, nonthermal sol-gel process" *Materials Chemistry and Physics* (2019) 229: 156-166.

Heikkila T., Salonen J., Tuura J., Hamdy M.S., Mul G., Kumar N., Salmi T., Murzin D.Yu., Laitinen L., Kaukonen A.M., Hirvonen J., Lehto V.P. Int. J. Pharm. (2007) 331: 133–138. c) Zhao D., Nie C., Zhou Y., Xia S., Huang L., Li Q.. "Comparison of disordered mesoporous aluminosilicates with highly ordered Al-MCM-41 on stability, acidity and catalytic activity" *Catal. Today* (2001) 68: 11–20.

Jal P K, Patel S, Mishra B K "Chemical modification of silica surface by immobilization of functional groups for extractive concentration of metals ions" *Talanta* (2004) 62: 1005-1028.

Lebeau Bénedicte, Galarneau Anne, Linden M., "Introduction for 20 years of research on ordered mesoporous materials" *Chem. Soc. Rev.* (2013) 42: 3661-3662.

ISSN: 2410-3934

Lee J. S., Deorkar N. V., Tavlarides L. L. "Adsorpion of Copper Cyanide on Chemically Active Adsorbents" *Ind. Eng. Chem. Res.* (1998) 37: 2812-2820.

Meng M., Meng X., Liu Y., Liu Z., Han J., Wang Y., Luo M., Chen R., Ni L., Yan Y. "An ion-imprinted fuctionalized SBA-15 adsorbent synthesized by surface imprinting technique via reversible addition-fragmentation chain transfer polymerization for selective removal of Ce(III) from aqueous solution" *Journal of Hazardous Materials* (2014) 278: 143-143.

Saldaña Piña N. "Estudio Sobre la Remoción de Cobre de Efluentes Acuosos Provenientes de la Industria Minera Mediante Materiales Mesoporosos Polifuncionalizados" Tesis para la Obtención del Grado de Químico; Universidad de Guanajuto, (2014).

Salazar-Hernández M. M., Salazar-Hernández C., Elorza-Rodríguez E., Juárez-Ríos H. "The Use of Mesoporous Silica in the Removal of Cu(I) from the Cyanidation Process" *J. Mater. Sci.* (2015) 50: 439-446.

Sierra I., Pérez-Quintana D. "Heavy metal complexation on hybrid mesoporous silicas: an approach to analytical applications" *Chem. Soc. Rev.* (2013) 42: 3792-3807.

ISSN: 2410-3934