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FUNCTIONALIZED MESOPOROUS SILICA: AN EFFECTIVE ADSORBENT FOR THE UPTAKE OF GOLD THIOSULFATE

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مادة ماصة فعالة لامتصاص ثيوسلفات الذهب:السيليكا المتوسطة المسامية الوظيفية

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Abstract:
Thiosulfate is recognized as a promising alternative lixiviant to cyanide for the extraction of gold from ore bodies. Gold thiosulfate ($[Au(S_2O_3)_2]^{3-}$), however, is not well-adsorbed by activated charcoal, making industrial scale use of thiosulfate for gold leaching impractical at present. Because of their high specific surface areas (500-1000 m^2g^{-1}) and uniform open-framework nanoporosity (pore channel diameters in the range 3-10 nm), functionalized mesoporous silicas are widely recognized as highly effective materials for the selective, rapid and high capacity uptake of mercury, gold and platinum group ions. In the present work, the efficient and rapid adsorption of gold thiosulfate by thiol-functionalized mesoporous silica (hereafter designated MP-HMS) is demonstrated, whereby the thiol groups in the materials bind with the gold complexes by ligand displacement. The adsorbed gold could be leached out using cyanide, regenerating the adsorbent for further uptake cycles. Functionalized mesoporous silica is thus a promising candidate for the preconcentration of gold from thiosulfate leachate solutions.

الملخص
يتم التعرف على الثيوسلفات على أنها بديل موعود للسيانيد لاستخراج الذهب من الخام. ومع ذلك فإن الثيوسلفات الذهبية (-[Au(S2O3)2]3) لا يتم امتصاصه جيدا بواسطة الفحم المنشط مما يجعل استخدام الثيوسلفات على نطاق صناعي لترشيح الذهب غير عملي في الوقت الحاضر. بسبب ارتفاع مساحاتها السطحية (500-1000 م 2 \جم 1-) والمسامية النانوية ذات الإطار المفتوح الموحد (أقطارمسام القنوات في النطاق من 3 – 10 نانومتر) تم التعرف على المواد الفعالة واسعة النطاق على أنها عالية الانتشارلامتصاص مجموعة الزئبق والذهب والبلاتين بشكل انتقائي وسريع وعالي سعة الايونات. في العمل الحالي الامتصاص الفعال والسريع للثيوسلفات الذهبية بواسطة السيليكا المتوسطة المسامية الوظيفية (المشار إليها فيما بعد MP-HMS) ، حيث مجموعات الثيول ترتبط بمواد مجمعات الذهب عن طريق الإزاحة الترابطية . يمكن ترشيح الذهب الممتص باستخدام السيانيد ، وتجديد المادة الماصة لمزيد من دورات الامتصاص. وبالتالي السيليكا المتوسطة المسامية الوظيفية هي مرشحة واعدة للتركيز المسبق للذهب من محاليل عصارة الثيوسلفات.

INTRODUCTION

Cyanidation has been widely used for the leaching of gold and other metals from ores since the process was patented in 1888 [1]. Technical problems and environmental concerns, however, have prompted the exploration of alternative lixiviants to cyanide for the leaching of gold from ores [2]. One of the most promising lixiviants currently being considered is thiosulfate ($S_2O_3^{2-}$), which forms a stable complex, $[Au(S_2O_3)_2]^{3-}$, with Au(I) ions produced by oxidation of gold ores [3]. Thiosulfate leaching produces similar gold recovery yields as cyanide, while avoiding losses due to peg-robbing and mitigating the health/environmental risks associated with cyanide [3]. One of the main issues preventing the mainstream use of thiosulfate in current gold processing operations is the ineffectiveness of activated carbon to adsorb and separate gold thiosulfate from ore slurries, a phenomenon attributable to the high charge of the complex [3].

The development of high capacity adsorbent materials based on mesostructured silica has undergone significant research during the past 15 years [4]. Using surfactant assembly synthesis techniques, the nanoengineering of high surface area functionalized (500-1000 m^2g^{-1}) silica-based materials with uniform mesoscale pore structures (with typical diameters in the 3-10 nm range) can be achieved [4]. These materials, collectively designated as mesoporous (or mesostructured) silica, have received significant research attention because of their exceptional adsorption properties towards numerous inorganic and organic compounds of environmental and/or industrial interest [4].

One notable example of such an adsorbent with practical application potential is mercaptan- functionalized mesoporous silica, hereafter denoted as MP-HMS [5]. The inclusion of mercaptan (SH) ligands inside the pore channels of mesoporous silica imparts the material with exceptionally high adsorption affinity towards toxic soft metal ions such as Hg^{2+} [4,6,7], as well as towards those of valuable metals including Ag, Au, Pt, Pd and Rh [8-10]. Typically, Hg(II) and Au(III) ion adsorption capacities in the 1-2 mmol/g range are reported for MP-HMS and similar mercaptan-functionalized mesoporous silicas, which corresponds to a maximum loading of 50-100% of the adsorbents' weight in these metals. Thus far, however, all investigation pertaining to gold adsorption with these materials have been performed using Au(III) halide complexes ($[AuX_4]^-$, where X=Cl or Br) [4,10]. In the present study, the adsorption properties of gold-thiosulfate complex ($[Au(S_2O_3)_2]^{3-}$) with MP-HMS are investigated. Based on these findings, the plausibility of using such a material for the capture and concentration of this complex from leachate solutions is discussed.

EXPERIMENTAL

MP-HMS Synthesis and Characterization

MP-HMS was prepared following previously published surfactant asssembly procedures using tetraethoxysilane (TEOS) and 3-mercaptopropyltrimethoxysilane (MPTMS) as structural precursors in a 19:1 molar ratio [5]. The resulting product was characterized by powder X-ray diffraction, N_2 adsorptometry and elemental analysis to verify its pore size uniformity, measure its surface area and pore diameter, and to quantify its functional (mercaptan) group content.

Gold Thiosulfate Preparation

Gold thiosulfate solutions were prepared following previously published procedures [11]. Thus, a 1000 ppm gold stock solution was prepared by dissolving a 1 g gold bar (99.99% purity) in 100 mL Aqua Regia and diluted to 1 L with deionized water. 5 g of KBr (Sigma Aldrich) were added to stabilize the solution. A thiosulfate stock solution was prepared dissolving 13.7 g potassium thiosulfate ($K_2S_2O_3$, Sigma Aldrich) and 25.2 g sodium sulfite ($NaSO_3$, Sigma Aldrich) in deionized water to a volume of 1 L. Solutions of gold thiosulfate, with concentrations in the range 10-100 ppm, were prepared by adding appropriate volumes of gold stock solutions and diluting them to 50 mL with the thiosulfate stock solution.

Adsorption of Gold Thiosulfate with MP-HMS

In a typical adsorption trial (unless indicated otherwise), 40 mL aliquots of each gold thiosulfate solution were stirred with 10 mg portions of MP-HMS. Samples of the aqueous supernatant were then collected using a syringe equipped with a 5 µm Whatmann filter cap. For each adsorption trial, the amount of gold before and after exposure to the adsorbent was measured using flame atomic adsorption spectrometry (AAS). The amount of gold adsorbed by MP-HMS was determined by subtracting the amount measured in the initial solution from that of the post-treated solution and dividing this value by the mass of adsorbent used in the trial.

The effect of pH on the adsorption of $[Au(S_2O_3)_2]^{3-}$ was measured using 10 ppm gold thiosulfate aliquots and varying their pH by judicious additions of 0.1 M NaOH or 0.1 M HCl solutions. The adsorption isotherm of MP-HMS was determined by exposing gold thiosulfate solutions at pH 7 with increasing concentrations ranging from

10 to 100 ppm. Finally, the adsorption kinetics of gold thiosulfate was assessed by collecting samples at different time intervals during the adsorption process.

Gold Recovery and Regeneration of Adsorbent

Gold recovery from loaded MP-HMS samples were investigated by performing cyanide leaching. Thus, a 100 mg sample of gold-loaded MP HMS was placed in 200mL of a 1.32 g/L KCN solution and stirred for 2 hours. Aliquots of the supernatant solution were collected at 5, 20, 45, 120 and 240 minutes of exposure time and the gold concentration in the leachate measured by AAS.

DISCUSSION

MP-HMS Characterization

The presence of a peak in the low angle region (1.8 degree 2□) of the X-ray diffraction pattern of MP-HMS confirmed the periodic mesoscale ordering expected in a mesostructured silica [5]. An average pore-pore distance of 49 Å was measured using Bragg's Law [5]. The nitrogen adsorption isotherm of the material was indicative of a material possessing uniform pore structure with a diameter of 36 Å [5]. The BET surface area of the material calculated from the isotherm data was 1500 m^2g^{-1}, again indicative of the successful preparation of mesostructured silica [5]. By subtracting the pore-pore distance (49 Å) from the pore diameter (36 Å), an average silica wall thickness of 13 Å can be inferred. According to elemental analysis data, the functional group loading of the adsorbent was measured at 0.75 mmol of mercaptan (SH) per g of material. Figure 1 provides a visual depiction of MP-HMS and its structural and functional features.

Diameter = 36Å

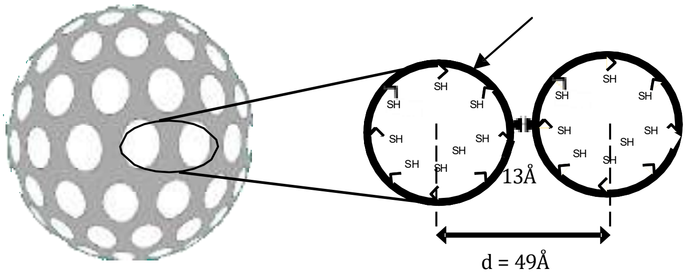

Figure 1 - Depiction of a particle of MP-HMS silica (left) and its pore structure containing mercaptan functional groups lining the pore walls (right)

Adsorption of Gold Thiosulfate by MP-HMS: pH Dependence

Figure 2 shows the effect of pH on the adsorption of $[Au(S_2O_3)_2]^{3-}$ by MP-HMS. The uptake of the complex is found to be negligible in both highly acidic (pH<4) and highly basic (pH>9) media. Optimal adsorption occurs in the pH 5-7 range. One can speculate that, under neutral or slightly acidic environments, the high charge on the complex might become neutralized by the presence sufficient proton concentrations, thereby facilitating its ingress into the pore channels, the environment of which is somewhat hydrophobic because of the presence of the organic mercaptan groups. In highly basic environments, the high negative charge on the complex results in a high degree of hydration, which might preclude its entry into the hydrophobic environment of the pore channels. Likewise, excessive protonation of the complex in highly acidic media might promote a high degree of hydrogen bonding

with water molecules, again curtailing access of the complex to the mercaptan groups in the pore channels. Further investigations, however, are required to elucidate the causes underlying this observation.

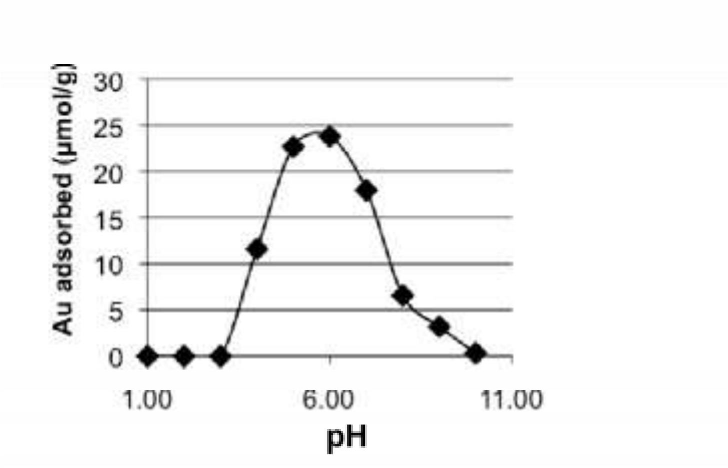

Figure 2 - pH dependence of gold thiosulfate by MP-HMS. For each trial, 25 mg of MP-HMS were stirred with 25 mL of 10 ppm gold thiosulfate for 24 hours

Adsorption of Gold Thiosulfate by MP-HMS: Adsorption Isotherm

Figure 3 shows the adsorption isotherm for $Au(S_2O_3)_2]^{3-}$ under neutral pH conditions. The uptake behaviour shows that the complex is efficiently adsorbed by MP-HMS until saturation is reached at about 0.25 mmol/g. The steep incline of the amount of gold adsorbed at low residual solution concentration indicated strong affinity of the materials towards gold thiosulfate, resulting in the capture of 95% of the gold complex when the initial concentration of gold in the solution was 10 ppm. The adsorption of gold to MP-HMS can be attributed bonding between the mercaptan groups and the gold ions, possibly with the corresponding release of one of the thiosulfate ligands, as depicted in Figure 4.

The relatively low saturation limit (0.25 mmol/g compared with 0.75 mmol/g mercaptan group content in MP-HMS), however, suggests that not every mercaptan binding sites is available for binding with the complex. This might be the result of the high stability of the gold thiosulfate complex (formation constant $K = 5 \times 10^{28}$) [2], which does not easily release its thiosulfate ligands in favour of a Au-S bond with the mercaptan groups of the material. Regardless, the adsorption capacity of MP-HMS is considerably higher that what can be presently achieved using other concentration methods, such as carbon-in-pulp [12].

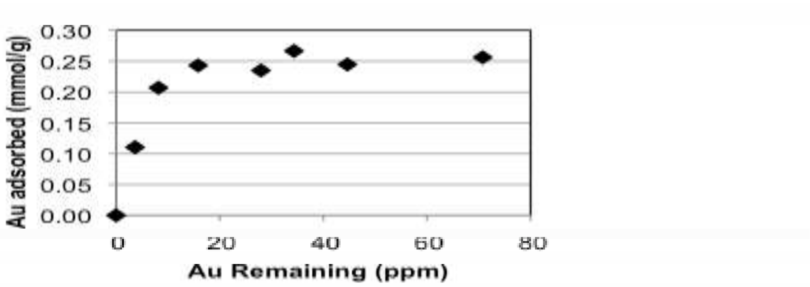

Figure 3 - Adsorption isotherm of gold-thiosulfate by MP-HMS

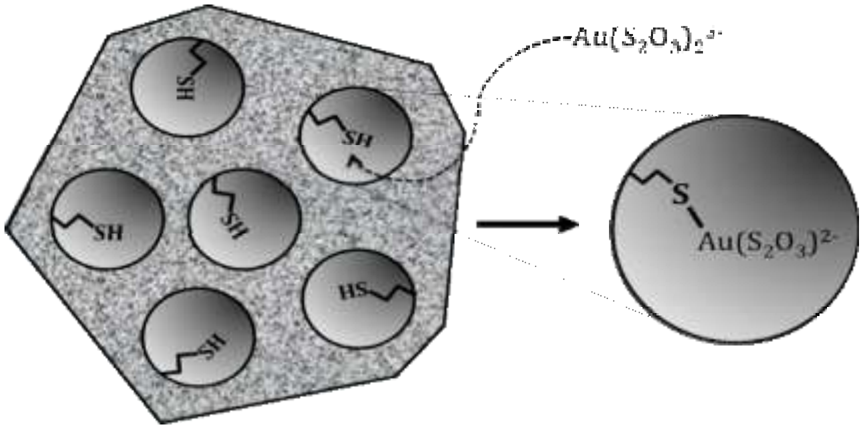

Figure 4 - Depiction of gold thiosulfate binding with the mercaptan functions of MP-HMS

Kinetics of Gold Thiosulfate Adsorption by MP-HMS

Figure 5 shows the kinetic uptake behaviour of MP-HMS towards gold thiosulfate. About 60% of the gold is adsorbed within 5 minutes of exposure to HMS, over 75% after 15 minutes and about 90% after 30 minutes. This very rapid uptake demonstrates the material's potential use in high throughput processing applications.

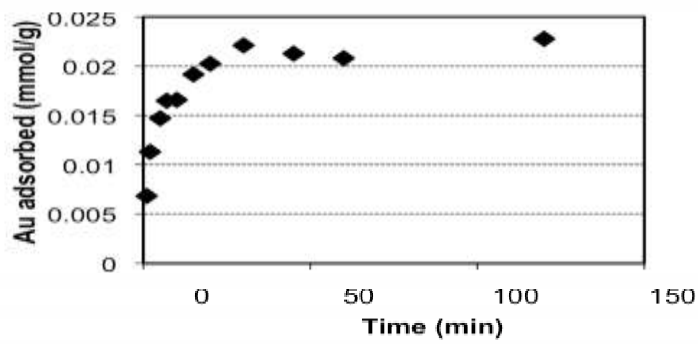

Figure 5 - Kinetic adsorption profile for gold-thiosulfate by MP-HMS (conditions: 20 mL of 9.3 ppm Au stirred with 20 mg MP-HMS at pH 7.02)

Gold Recovery and MP-HMS Regeneration

As shown in Figure 6, gold captured by MP-HMS can be quickly and completely recovered by cyanide leaching (80% recovery after 20 minutes, 100% after 1 hour). In this step, the sequestered gold thiosulfate complex is converted to gold cyanide, $[Au(CN)_2]^-$, thereby regenerating the MP-HMS for further adsorption cycles. Although the aim of this research is to avoid the use of cyanide in gold processing, its application in this step involves much smaller volumes of cyanide eluant compared to what is presently used for leaching gold from activated carbon because of the high gold loading offered by MP- HMS.

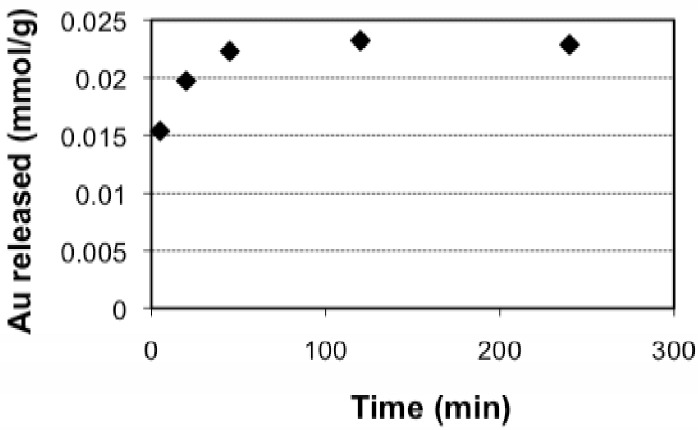

Figure 6 - Desorption Kinetics for 100 mg of gold-loaded MP HMS in 200mL of a 1.3201g/L KCN solution

CONCLUSIONS

Functionalized mesoporous silica are promising materials for environmentally and/or industrially focused applications. In the present work, the ability of one such material, MP-HMS, to effectively and rapidly adsorb gold thiosulfate from low concentration aqueous solutions under near-neutral pH conditions was demonstrated. Cyanide leaching was shown to be a plausible method of recovering adsorbed gold and regenerating the adsorbent for further adsorption cycles.

Given the ineffectiveness of activated carbon to concentrate gold thiosulfate from ore leachate solutions, the effectiveness of MP-HMS towards this end may invigorate new developments in thiosulfate- based gold extraction methods.

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