



# Some insights into the chemistry of gold adsorption by thiol and amine functionalized mesoporous silica in simulated thiosulfate system



Babak Fotoohi\*, Louis Mercier

Centre in Mining Materials Research (CIMMR), Laurentian University, 935 Ramsey Lake Rd., Sudbury, ON P3E 2C6, Canada

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## ABSTRACT

Organic functional groups such as amines and thiols have been widely used to functionalize pore wall surfaces of mesoporous silicas for a variety of applications relying on adsorption of metals. One of the promising applications of such hybrid materials is in hydrometallurgical separation of metals in a leach solution. Toward this aim, mesoporous MSU silica was prepared and functionalized with short-chain thiol and primary amine organic groups. Adsorption of gold from simulated thiosulfate leach solutions was investigated with respect to the adsorption chemistry. Adsorption capacity of thiol-bearing silica was well showing the monolayer behavior approaching an ultimate metal:ligand = 1:1 capacity. Higher capacities were obtained in either alkaline condition (pH ~ 10.5) or at higher oxidation potential ( $E_h \sim 300$  mV) of the solution. Adsorption capacity of amine groups was to some extent proportional to their surface molar concentration, but it was also beyond the monolayer capacity of chemisorption, besides not being explicable by hard-soft acid-base theory. Despite considerable gold recovery by amine functional groups, gold was not detected in XPS analysis unless adsorption was from pure solutions. Partial electrochemical reduction to metallic gold and formation of dispersed tiny nanoparticles during interaction of gold thiosulfate species in solution with amine ligands were proposed.

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## 1. Introduction

Since the advent of thiosulfate leaching of natural gold ores and its introduction as significantly safer and less hazardous alternative to conventional cyanidation extraction, the chemistry of leach solution has been under study from a wide range of aspects. It has long been known that chemistry of gold leaching in thiosulfate system is complicated due to the co-presence of multiple complexing agents and redox couples [1]. Aside from thiosulfate anion as the main leaching agent for gold, other reagents such as ammonium/ammonia and oxidation catalysts (usually copper(II)) are added into the system which impart their specific functions. Inevitable presence of thiosulfate oxidation products (e.g., polythionates or elemental sulfur) are among other complicating factors of the chemistry in such leaching systems.

Despite the reaction complexity, gold thiosulfate leaching has been studied with respect to variety of chemical, electrochemical, thermodynamic and kinetic aspects in the presence of principal as well as contaminant species in solution. Spectrochemical and electrochemical studies on characterization of surface species formed during leaching of metallic gold [2–5] as well as the effect of different sources of reagents and ionic species in solution [6–10] are among the noticeable research published mainly in the past decade.

In a routine hydrometallurgical separation and extraction there comes a stage after leaching wherein the loaded (so-called *pregnant*) solution would be subject to “concentration” process before being fed into the electrochemical metal extraction system. Concentration of gold thiosulfate leach solution has been investigated through applying different methods among which adsorption and ion-exchange are noticeable. Despite relatively extensive study of gold thiosulfate leach concentration by anion-exchange resins and recent success toward commercialization of the process [11], there has been less work on other adsorption methods especially based on chemisorption by ligand-functionalized materials. Significance of directing attention toward such adsorption mechanism arises from the unsuccessful physisorption of gold thiosulfate compound on bare activated carbon surfaces in spite of the latter being the unique adsorbent in commercial gold cyanide hydrometallurgy. Moreover, ion-exchange resin would not be the perfect adsorbent due to inherent drawbacks including non-rigid organic framework, insufficient selectivity and potential for deactivation (poisoning) of the exchange sites by contaminant/competitor species in solution.

On the other hand, organically-functionalized silica gel and relatively novel mesoporous silica with either or both of amine and thiol groups immobilized onto their pore wall surfaces have successfully recovered gold(III) chloride from principally acidic solutions [12–15]. But, it was only recently that hybrid mesoporous silica was found to be efficient in adsorbing gold(I) thiosulfate from copper and ammonia-bearing solutions [16]. In a most recent research by the same authors [17], gold thiosulfate adsorption by both amine and thiol-functionalized

\* Corresponding author at: Department of Chemistry and Biochemistry, Faculty of Science and Engineering, 935 Ramsey Lake Rd., Sudbury, ON P3E 2C6, Canada.  
E-mail address: [babak\\_f8@yahoo.com](mailto:babak_f8@yahoo.com) (B. Fotoohi).

mesoporous silicas was studied in detail with respect to adsorption capacity, kinetics and reagent concentrations for the first time. In that research, several questions regarding the effectiveness of both thiol and amine groups in selective adsorption of gold (complex) were aroused. It has long been known that the bonding mechanism of ionic gold species with sulfur bearing compounds such as thiosulfate [18] is best explained according to the hard–soft acid–base (HSAB) theory [19] in which gold(I) as a soft Lewis acid bonds with sulfur as a soft Lewis base (donor). Same principle is applicable when gold nanoparticles are coated with organic sulfur groups (e.g., thiols, xanthates and disulfides) in the so-called self-assembled monolayers (SAMs) [20,21]. However, with regard to interaction of hard donor atoms (such as  $-\text{NH}_2$  or  $\text{NH}_3$ ) with metal ions of low valency (such as  $\text{Au}^+$ ), chemisorption through (covalent) complexation based on HSAB theory is less predictable and the compounds are regarded as unstable. Most of the published research on adsorption of gold by amine (or polyamine) functional groups have been in the acid environment wherein much of the surface amine groups were expected to become protonated, so that physically (electrostatically) attracting the negatively charged gold compounds such as  $[\text{AuCl}_4]^-$  or even  $[\text{Au}(\text{S}_2\text{O}_3)_2]^{3-}$ .

On the other hand, in a thiosulfate leach solution with a typical higher than neutral pH, such electrostatic interaction could be remote from happening if not completely impossible. Since in the previous research [17] amine functional groups adsorbed high amounts of gold in the simulated leach solutions having a pH  $\sim 7$  or higher (pH  $\sim 10$ ), there was an incentive to find out more details on such adsorption system with respect to both gold speciation and surface functional groups. Therefore in this research, structure and surface chemistry characterizations of the hybrid mesoporous silica exposed to different simulated gold thiosulfate solutions were performed. Behavior of different functional groups on the adsorbent material in different solution chemistries and pH/ $E_h$  conditions was also investigated.

## 2. Materials and Methods

### 2.1. Chemicals

Nonionic surfactants Igepal CO-720 and Pluronic® P123 as structure directing agent, functional organosilanes (3-aminopropyl) triethoxysilane (APTES),  $\geq 98\%$ A and (3-Mercaptopropyl) trimethoxysilane (MPTMS), 95% as well as swelling agent 1,3,5-Trimethylbenzene (TMB) were all provided by Sigma-Aldrich Co., St. Louis, MO, U.S.A. Silica precursor was tetraethyl orthosilicate (TEOS) from Gelest Inc., Morrisville, PA, U.S.A. Sodium fluoride (reagent A.C.S.) was provided by Matheson Coleman & Bell manufacturing chemists, East Rutherford, NJ, U.S.A. In gold adsorption tests, sodium aurothiosulfate(I) purchased from Surepure Chemicals Inc., Florham park, NJ, U.S.A. was used as source of gold(I). Ammonium thiosulfate and Ammonium nitrate, A.C.S. reagent  $\geq 98\%$  were provided by Sigma-Aldrich Co., St. Louis, MO, U.S.A. Cupric carbonate (Baker analyzed reagent) was from J.T. Baker Chemical Co., Phillipsburg, NJ, U.S.A. All other chemicals (acid, base, solvents and hydrogen peroxide) were of reagent grade.

### 2.2. Adsorbent preparation

Mesoporous silica of type MSU-2 and MSU-3 (henceforth in this research, without the “-” in the original nomenclature) was prepared through a two-step sol–gel synthesis by using nonionic poly(ethylene oxide)-based surfactants [22,23]. In a typical synthesis, 0.02 M surfactant solution (15 g/L for MSU3 synthesis) was magnetically stirred in DI water acidified with dilute HCl to pH  $\approx 2$ –2.5 (pH<sub>iep</sub> of  $\text{SiO}_2$ ). In MSU2 preparation swelling agent (TMB) was added in molar TMB/surfactant = 1 for the expansion of pore size. After a homogenous solution was obtained, silica source (TEOS) was added (in MSU2 synthesis: molar TEOS/surfactant = 8, and in MSU3 synthesis: weight TEOS/

surfactant = 2.22). At this step, for thiol functionalization through co-condensation synthesis, mercapto-silane could also be added together with the silica precursor. Upon completion of hydrolysis (in about an hour) at ambient temperatures, sodium fluoride (molar  $\text{NaF}/\text{Si} = 0.04$ ) was introduced to the solution to trigger nucleation. The MSU2 synthesis batch was then transferred to thermostated water bath for condensation at elevated ( $\sim 55$  °C) temperature overnight. The as-obtained (filtered and dried) silica was solvent extracted with hot ethanol in a Soxhlet apparatus (48–72 h) to remove the structure directing agent. In case of amine functionalization, the pristine silica material from the sol–gel synthesis (after solvent extraction) was treated with dry toluene in a boiling reflux system. The reason for using the grafting method for amine functionalization was the acidic medium of the mesoporous silica synthesis in which protonated amines could interfere with the formation of the desired mesoporous framework.

### 2.3. Gold adsorption tests

Adsorption from gold thiosulfate solutions was performed in Erlenmeyer flasks containing 50 mL of test solution and 200 mg/L adsorbent loading. Concentration of the main reagents for a typical simulated thiosulfate leach solution in gold hydrometallurgy was previously determined by the same authors [17]. This included addition of appropriate weights of gold thiosulfate salt to the desired concentration. While ammonium thiosulfate salt was providing 0.1 M thiosulfate concentration, supplementary ammonium/ammonia was added form nitrate salt (or ammonia solution) to make up for a total ammonia concentration of 1.0 M. Copper carbonate hydrate provided 2.5 mM copper(II) in the solution. All reagents were dissolved in DI water. After complete dissolution of all components (usually in a matter of few minutes) a clear colorless solution or a clear blue solution was obtained in neutral pH or alkaline pH systems respectively. In obtaining gold adsorption isotherms for the mesoporous adsorbent, the initial gold concentration in solution was varied within 2–200 mg/L range. After about 24 h orbital shaking (at 150 rpm) of the top-sealed flasks at ambient conditions, samples were taken accurately from the supernatant clear solution given enough sedimentation time in stand-still. The aliquots were then analyzed (after dilution if  $> 50$  mg/L gold was dissolved initially) for the gold remaining in equilibrium solution using a Perkin Elmer AAnalyst 400 atomic absorption spectrometer with a gold lamp (10 mA operating current) and gold chloride standard solutions (1005 mg/L in 5% HCl) for calibration. Adsorption capacities and recoveries were measured using the following formula:

$$\text{Adsorption capacity of the adsorbent } C_a = [(c_i - c_e)(V)]/[196.97(m)]$$

$$\text{Precious metal adsorption or removal recovery } R\% = [(c_i - c_e)/c_i] \times 100$$

wherein “ $C_a$ ” (adsorption capacity) is in [mmol/g], “ $c_i$ ” and “ $c_e$ ” are the initial and remaining gold concentrations respectively in [mg/L],  $V$  is the test volume (0.050 L), “196.97” was considered as gold molar atomic mass in [g/mol] and “ $m$ ” is the adsorbent weight (0.010 g).

### 2.4. Characterizations

Determination of the equilibrium pH and mixed redox potential were conducted at room temperature with a Hanna HI2221 pH/ORP meter. Combination electrodes were used to measure either pH or the electrochemical potential in which Ag/AgCl in 3.5 M KCl was the reference electrolyte. Platinum was the sensing electrode in the ORP measurements. The following relationship was used to report the measured mixed potential in equilibrium solution with respect to the

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