



HIGH-EFFICIENCY NANOPOROUS ADSORBENT IN GOLD EXTRACTION

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ABSTRACT

We report the development of MP-HMS (Mercaptopropyl-Hexagonal Mesoporous Structure), a high-capacity nanoporous adsorbent for gold extraction, designed using nanotechnology. By incorporating thiol groups into the pores of mesoporous silica, MP-HMS can efficiently capture gold ions from ultra-dilute solutions, including mine effluents and leachates from gold mills. Laboratory tests with simulated gold solutions show exceptional adsorption capacities, with up to 370 mg of gold per gram of material ($\approx 37\%$ of its weight) and recovery rates as high as 99.9%. Ongoing studies focus on the interaction of ionic gold complexes with these nanomaterials. Future applications may allow MP-HMS to either supplement or replace conventional CIP/CIL processes, offering a novel approach to gold extraction in pulp (MIP) or leach (MIL) systems.

Key Words: Nanotechnology, gold ion extraction, effluent treatment, ultra-low concentration, high-capacity nanoporous adsorbents.

عملية جديدة عالية الكفاءة لاستخراج الذهب باستخدام تقنية النانو

المخلص

تقدم هذه الدراسة تطوير مواد ماصة عالية السعة ذات مسامية موحدة ، MP-HMS (Mercaptopropyl - هيكل مسامي سداسي) باستخدام التقنية النانوية وقدرتها على استخراج الذهب من المحاليل. تحضير أيونات المعادن الثقيلة عالية الفعالية المتميزات عن طريق دمج شقوق الثيول في قنوات مسام السيليكا المتوسطة المسامية كانت موضوعا للعديد من التحقيقات البحثية في تكنولوجيا النانو. الميزة الفريدة لهذه المتميزات النانوية المسامية هي قدرتها على امتصاص أيونات الذهب من محاليل منخفضة التركيز للغاية مثل النفايات السائلة للمناجم وكذلك من المحاليل المتسربة في مصانع الذهب. تظهر الدراسات الأولية من محاليل الذهب المحاكاة في المختبر أن قدرات الامتزاز من هذه المواد هي أيضا من بين أعلى المواد التي تم الإبلاغ عنها. أظهرت MP-HMS القدرة على امتصاص 370 مجم ذهب لكل جرام واحد من المواد النانوية من محلول رباعي كلورو أورات Tetrachloroaurate (حتى 37% من وزنها). أشارت الدراسات التجريبية إلى أن الحد الأقصى لامتصاص الذهب (معدل استخلاص مرتفع يصل إلى 99.9%). سيتم توسيع نطاق الدراسات الحالية للتحقيق في تفاعل مجمعات الذهب الأيونية بالمواد النانوية. قد يؤدي التطوير المستقبلي لهذا العمل إلى استبدال عمليات CIP / CIL التقليدية أو استخدام المواد النانوية جنباً إلى جنب مع العمليات الأولى ، مما يشير إلى استخدام المواد المسامية في امتصاص الذهب MIP أو في الترشيح ، MIL، كعملية جديدة لاستخراج الذهب.

INTRODUCTION

Gold is typically present in ores at very low concentrations, often below 10 g/t (0.001% by mass), making aqueous chemical (hydrometallurgical) extraction the only economically viable recovery method. Conventional hydrometallurgical processes involve leaching the ore, followed by separation of the gold-bearing solution from residues or adsorption onto activated carbon. Gold is then concentrated through elution, precipitation, or electrodeposition.

Leaching involves dissolving metals into a liquid solvent, with gold requiring both a complexing agent and an oxidant to achieve efficient dissolution. Only a limited number of ligands provide complexes stable enough for practical use (Muir and Aylmore, 2004). Cyanidation, patented by MacArthur and Forrest in 1888, remains the dominant gold leaching method due to its low cost, selectivity for gold and silver, and general safety when properly managed (Hilson and Monhemius, 2005). Oxygen, typically supplied from air, is the most common oxidant. Despite its widespread use, cyanide leaching presents several inherent disadvantages (Marsden and House, 2006):

1. Environmental concerns, and in some cases legal restrictions, make the use of cyanide difficult in some jurisdictions.
2. Cyanide has slower gold leaching kinetics than other reagents.
3. Cyanide can only be applied in alkaline media, whereas acidic media may be more suitable for refractory ore treatment.

Leaching agents other than cyanide have not seen widespread industrial use for gold extraction, pending further technological advances that would justify their adoption (Marsden and House, 2006). Chlorine–chloride leaching was used commercially in the 19th century, but its application declined after the introduction of the cyanide process in 1889 (Tran et al., 1992; Jeffrey et al., 2001; Baghalha, 2007). Other alternative ligands—such as thiosulfate (Zhang and Nicol, 2005; Senanayake, 2006; Feng and Van Deventer, 2007; Xia et al., 2003), thiourea (Zheng et al., 2006), thiocyanate (Wang et al., 2007; Kholmogorov et al., 2002), ammonia, alkaline sulfide, and halides like bromide or iodide (Tran et al., 1991)—have been extensively studied in laboratory settings, and several potential processes have been developed; however, none have yet been applied commercially on a large scale. In gold ore processing, gold ions are first adsorbed from the leach solution onto an extractant, typically activated carbon or a synthetic ion exchange resin. The loaded extractant is then separated from the process stream, and the gold ions are desorbed into a smaller volume of solution for subsequent metal recovery. Activated carbon remains the most widely used extractant, although ion exchange resins have been employed in some applications and continue to be developed (Anthony, 1995; Rajasingam et al., 2006).

Recently, the discovery of a new class of silica–based molecular sieves with ordered pore channels ranging from 1–10 nm, known as MP–HMS (Mercaptopropyl–Hexagonal Mesoporous Structure), has attracted considerable attention for industrial and environmental applications (Beck et al., 1992). Many studies have focused on developing highly effective heavy metal ion adsorbents by incorporating thiol functional groups into the pore channels of these mesoporous molecular sieves (Mercier and Pinnavaia, 1997, 1998). These functionalized adsorbents were shown to exhibit high affinity towards the binding of chalcophilic ions such as Hg(II) and Au(III) (Beck et al., 1992, Mercier and Pinnavaia, 1997, 1998). They have shown unprecedented high loading capacities of Au ions (up to 318 mg/g), exhibit almost exclusive selectivity for adsorption of Au ions from mixed metal ion adsorption studies, and demonstrate very favorable adsorption kinetic (Elhsaeri, Amaratunga and

Mercier 2004). In this work we propose to explore nanomaterials such as MP-HMS to revisit the use of chlorides and other leach ligands to achieve affective gold recovery without the use of cyanide.

EXPERIMENTAL SECTION

Synthesis and Characterization of MP-HMS

Mesostructured HMS silica molecular sieves were synthesized following previously published procedures using a one-step technique (Mercier and Pinnavaia, 1997; 1998). MP-HMS was prepared using neutral amine surfactants as structure-directing agents, with the surfactant subsequently removed via solvent extraction. Specifically, 1.35 g of dodecylamine (DDA) was dissolved in 10 mL of ethanol and 100 mL of water. Tetraethyl orthosilicate (TEOS) and 3-mercaptopropyltrimethoxysilane (MP-TMS) were added to the surfactant solution under vigorous stirring, followed by the addition of 1,3,5-trimethylbenzene (TMB). The reaction mixture was stirred at room temperature for 20 h. The molar ratio of reagents was 1.0 TEOS : 0.05 MP-TMS : 0.23 DDA : 0.23 TMB : 160 H₂O. The resulting precipitate (MP-HMS) was filtered, washed with water, and dried at room temperature for 24 h. Residual surfactant was removed by Soxhlet extraction with ethanol for an additional 24 h.

The adsorbent was structurally characterized using powder X-ray diffraction (XRD), nitrogen adsorption, and transmission electron microscopy (TEM). XRD patterns were recorded on a Rigaku Rotaflex diffractometer using Ni-filtered Cu K α radiation (Ontario Geosciences Laboratory). Nitrogen adsorption isotherms were measured at 77 K using a Micromeritics ASAP 2010 physisorptionmeter. Samples were preheated overnight at 110 °C under 10⁻⁶ Torr. BET surface areas and pore size distributions were calculated using the Horvath-Kawazoe method (Horvath and Kawazoe, 1983). SEM images were obtained using a JEOL JSM-6400 scanning electron microscope (Ontario Geosciences Laboratory).

Simulated Gold Solution

A 100 ppm of gold ions solution was prepared by dissolving 96.6 mg of Ammonium Tetrachloroaurate [(NH₄)AuCl₄.xH₂O] and 3.19 ml of HNO₃ in 500 mL H₂O solution, then diluted with 0.1 M HNO₃ solution to make up standard AuCl₄⁻ solutions with concentrations in the range of 5 to 50 ppm gold.

Adsorption Experiments

Batch adsorption experiments were conducted to assess the effectiveness of MP-HMS for gold removal from low-concentration solutions. In these experiments, 5.05 mg of MP-HMS was suspended in 50 mL of (NH₄)AuCl₄.xH₂O solutions with concentrations ranging from 0 to 50 ppm, and the mixtures were stirred at room temperature for several hours. The suspensions were subsequently filtered, and the gold concentration in the filtrates was determined using Atomic Absorption Spectroscopy (AAS).

RESULTS AND DISCUSSION

Adsorbent Preparation and Characterization

The characterization of the adsorbents conformed to what would be expected for a functional nanoporous adsorbent (Beck et al., 1992), exhibiting ordered framework structure, uniform nanoscale porosity and controlled mercaptan group loading (0.8 mmol/g). Figures 1 and 2 show the XRD patterns and TEM image of HMS functionalized with mercaptopropyltrimethoxysilane. The XRD diffraction pattern of HMS is substantially broad, denoting uniformity in pore channel size although poor long-range order in the material. The broad XRD line, together with electron microscopy images of HMS silica, is consistent with the presence of a material with a wormhole motif pore structure (Figure 2, a and b).

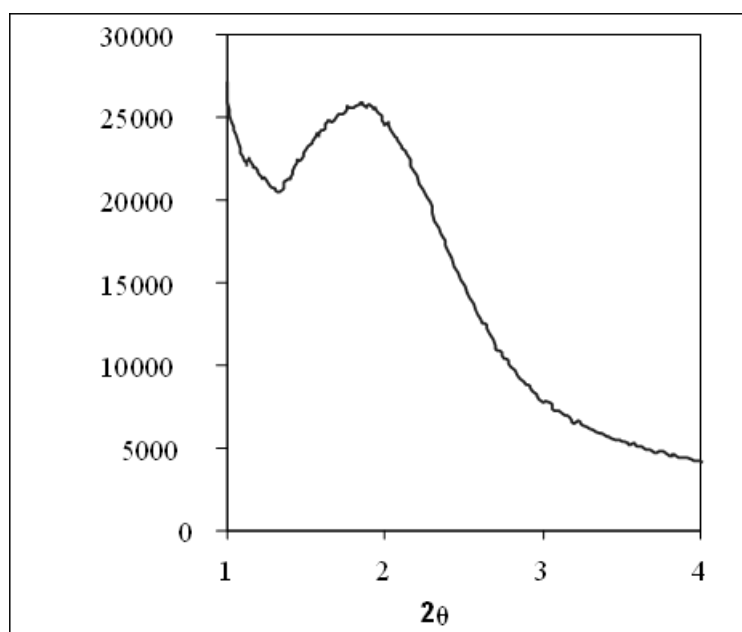


Figure 1: XRD patterns of HMS functionalized with mercaptopropyltrimethoxysilane

The N₂ adsorption isotherms of the functionalized mesostructures are presented in Figure 3. The samples exhibited Type IV isotherms, as expected for mesoporous silica, with inflections observed at relative pressures between 0.2 and 0.5, indicative of nitrogen condensation within the mesopore framework. The materials displayed high BET surface areas—854 m²/g for HMS and 722 m²/g for MP-HMS—typical of mesostructured silica and reflective of their highly open-framework nature. Pore size distributions (Figure 4) confirmed uniform mesoporous channels with an average diameter of 3.6 nm. Incorporation of mercaptopropyl (MP) groups into the framework walls led to a noticeable reduction in surface area, pore volume, and pore diameter, attributable to the thiol moieties lining the pore channels of MP-HMS. Nevertheless, MP-HMS retained substantial surface area and uniform nanoscale porosity despite functionalization. The surface properties of the MP-functionalized adsorbents, along with their parent mesostructures, are summarized in Table 1.

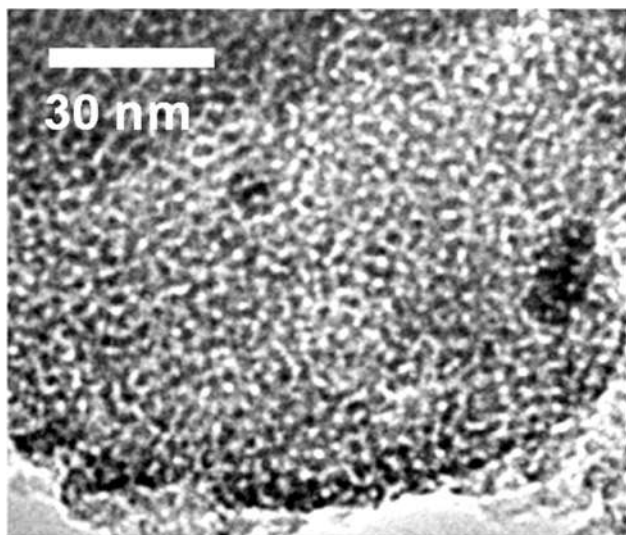
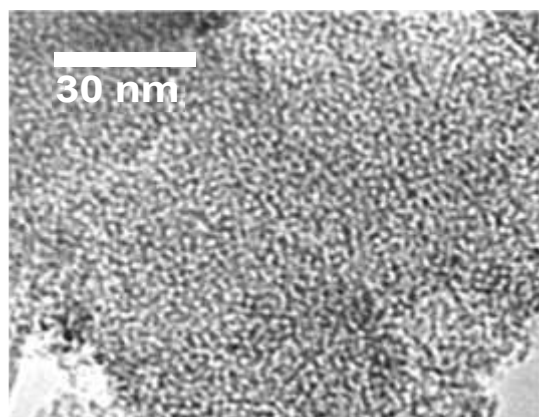


Figure 2: (a) and (b) TEM image of HMS functionalized with mercaptopropyltrimethoxysilane



N₂ Adsorption Isotherm of 5%MP-HMS

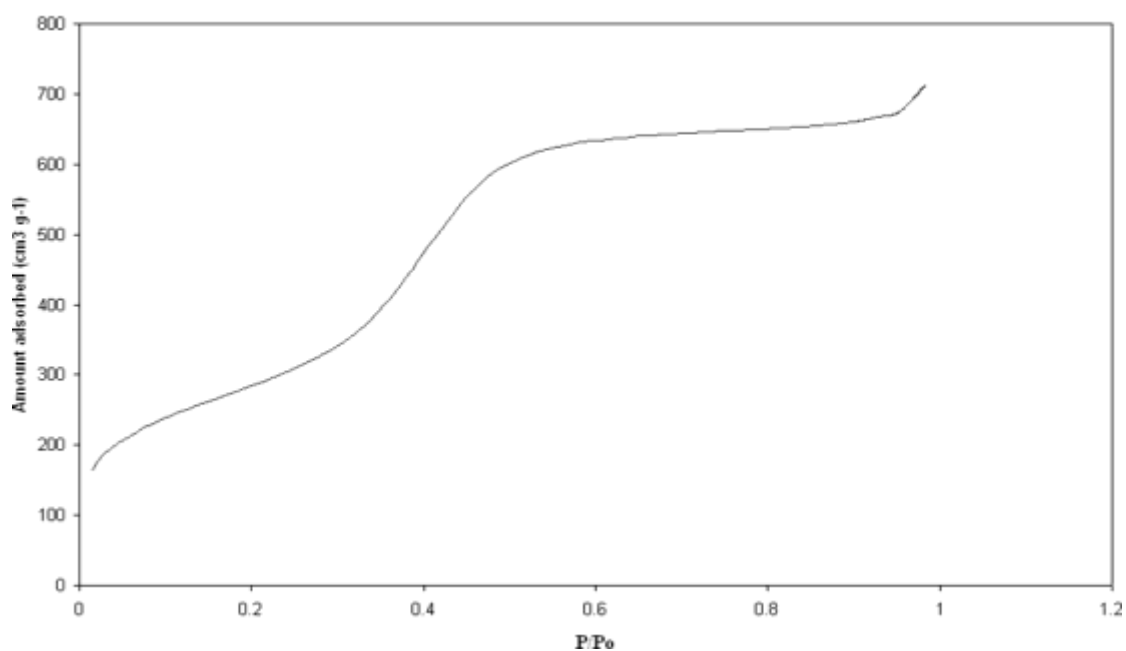


Figure 3: The N₂ (Nitrogen) adsorption isotherms of the functionalized mesostructures

Table 1: Summary of Physical Characteristics for Mesoporous Molecular Sieves and their Mercaptopropyl-Functionalized

| Material | BET surface area (m ² /g) | Pore diameter (nm) | SH content (mmol/g) |
|----------|--------------------------------------|--------------------|---------------------|
| HMS | 854 | 3.6 | 0 |
| MP-HMS | 722 | 2.5 | 0.8 |

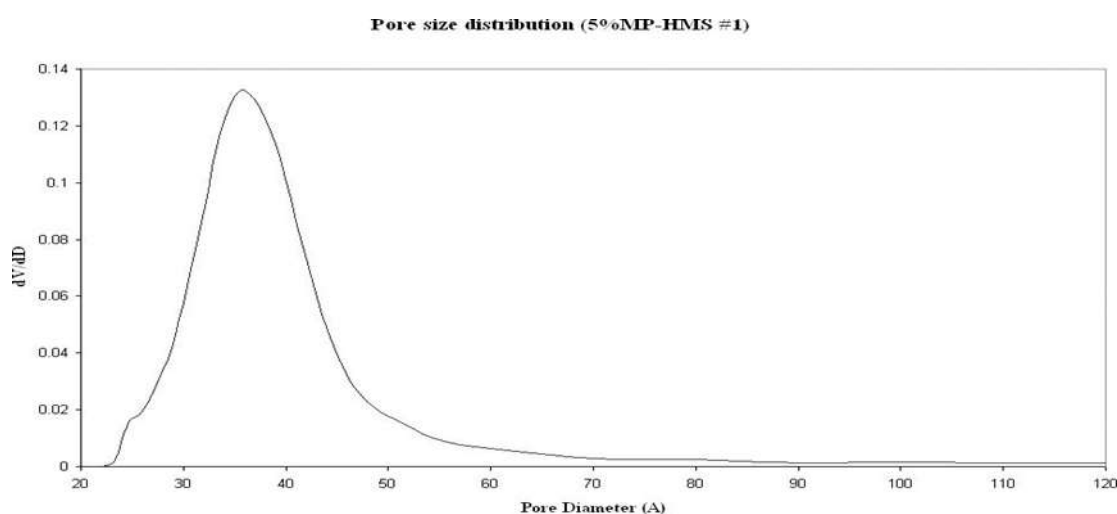
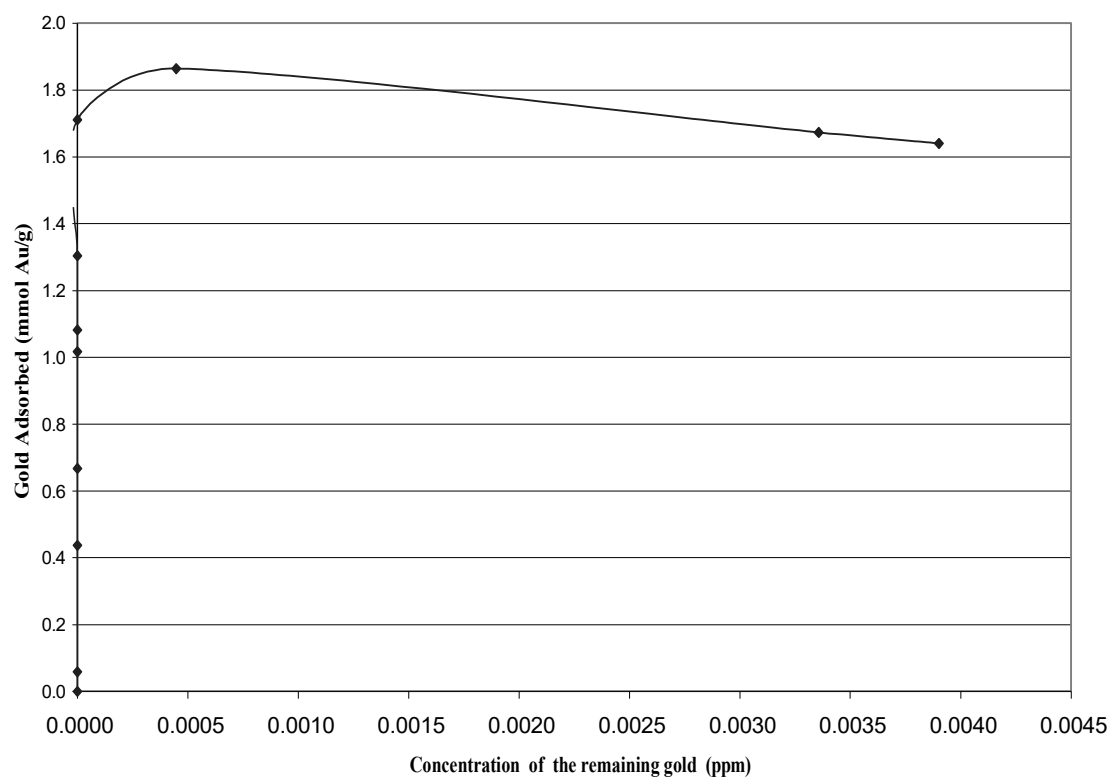


Figure 4: The Horvath–Kawazoe pore size distributions

Gold adsorption

The gold adsorption isotherms of MP-HMS (Figure 5) demonstrate that the material is highly effective at removing gold ions from low-concentration tetrachloroaurate solutions. The isotherms exhibit typical Type I behavior, with the majority of gold ions being adsorbed until the adsorbent reaches saturation. The distribution coefficients of MP-HMS were exceptionally high, ranging from 10^6 to 10^8 across the concentrations studied. Notably, the materials displayed a high adsorption capacity, up to 1.9 mmol/g (equivalent to 37% of the adsorbent's weight), meaning that one gram of MP-HMS can adsorb 0.37 g of gold from solution.

This gold loading corresponds to a relative Au:S molar ratio of 2.37:1, significantly exceeding the expected 1:1 ratio for metal-thiol binding. Such unusually high loading suggests that some of the gold ions may have been spontaneously reduced to metallic gold within the nanoporous structure. This observation is supported by recent literature reporting the formation of metallic gold nanoparticles in similar mesoporous systems (Ghosh et al., 2003; Guari et al., 2001, 2003). Ongoing experiments aim to further investigate and clarify this phenomenon



Concentration of the remaining gold (ppm)

Figure 5: The gold ions isotherms of MP-HMS**CONCLUSION**

The advent of mesoporous silica has enabled the design of materials with open, well-defined pore structures, high surface area, and controlled pore size, making them highly suitable for environmental and industrial applications. MP-HMS, with its outstanding gold adsorption capacity, shows strong potential for recovering and reducing gold from mineral processing streams. This suggests the feasibility of integrating such nanomaterials into conventional gold milling, either as a replacement for activated carbon in CIP/CIL processes or in combination with it, in “mesoporous material in pulp” (MIP) or “mesoporous material in leach” (MIL) approaches. Its unique properties compared to carbon highlight MP-HMS as a promising alternative substrate for gold recovery.

Advantages presented by using nanomaterials such as MP-HMS instead of carbon can be listed as follows:

- Possibility of spontaneous precipitation of metallic gold using MP-HMS.
- The rate and the equilibrium loading of gold to mesoporous adsorbent (370 mg/g or 37% of its weight) is superior to all types of activated carbon.
- Nanotechnology material adsorbents operate efficiently even at ultra-low concentrations (99.9 % Adsorption).
- Operates independent of pH, whereas cyanide operates only at high pH.
- These adsorbents are not likely to be poisoned by organic species such as flotation reagents, machine oils and lubricants (all of which can severely inhibit the loading of gold on activated carbon), because of the stability of the silica framework and the presence of the active binding sites within the framework of the adsorbent particles.
- Selective adsorption of gold in the presence of other metal ions.
- Moreover, the rapid access of the ions to the binding sites, the high loading capacity makes MP-HMS potentially useful under rapid flow conditions used in filtration and fixed/fluidized bed reactors leading to the development of a novel continuous gold extraction process.
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