

Separation of Precious Metals using Selective Mesoporous Adsorbents

Koon Fung Lam, Chi Mei Fong and King Lun Yeung*

Department of Chemical Engineering
Hong Kong University of Science and Technology
Clear Water Bay, Kowloon, Hong Kong,
PR China

* Address all correspondence to King Lun Yeung
Tel: 852-2358-7123; Fax: 852-2358-0054;
E-mail: kekyeung@ust.hk

Abstract

The mesoporous NH₂-MCM-41 adsorbent prepared by grafting aminopropyls on MCM-41 is selective towards gold and palladium adsorptions and can separate these precious metals from complex solutions containing other metal ions such as cobalt, nickel, copper and zinc. Adsorption is rapid and the adsorbent's capacity for gold is better or comparable to most carbonaceous adsorbents including activated carbons. Furthermore, NH₂-MCM-41 can separate palladium from gold solution at pH1.0 with excellent selectivity and capacity. Thus, it is possible to design a two steps separation process for the separation of palladium and then gold from the complex solution. A simple acid wash was sufficient to recover the adsorbed palladium and gold as concentrated, high purity (i.e., > 95%) metal salt solutions and the regenerated adsorbent was reused without lost of performance.

Keywords

MCM-41, gold, palladium, adsorption, separation, mining, recycling

Introduction

The growing industrial demand for precious metals and their increasing scarcity have resulted in their escalating prices [1]. New applications from electronics [2], traditional and fine chemicals as well as environmental catalysis [3-9], medicine and life sciences [10] and hydrogen separation and storage [11-15] are expected to fuel further demand for gold, palladium and platinum in the coming years. There is therefore an urgent need to develop more efficient and environmentally-friendly methods for precious metal extraction and recovery from ores and waste materials (e.g. e-wastes and spent catalysts). Hydrometallurgical processing remains a standard method for metal extraction from ores [16] and is becoming more popular in many metal recycling processes [17] because of its simpler operation and lower cost. The use of new leachants such as chloride and aqua regia also addresses the health, safety and environmental concerns posed by the traditional cyanide process. The dissolved metals could be separated by one of the traditional methods including precipitation, solvent extraction and adsorption. Adsorption has the advantage of easy operation, low energy consumption, simple maintenance and large capacity [18].

Recent years have seen increasing activities in selective adsorption of precious metals from solutions. For instance, Parajuli et al. [19] reported that aminated lignin derivatives are capable of separating gold, palladium and platinum ions from solutions that contain copper, iron, nickel and zinc ions. Doker et al. [20] employed a new hydrogel to separate platinum and palladium from other transition metals. Our recent works [21,22] have shown that the selectivity of mesoporous adsorbents based on MCM-41 could be tailored to selectively remove *only* the precious metals including gold [21] and silver [22] from solutions containing a base metal (e.g., copper and nickel). The gold and silver were recovered as high purity, concentrated metal salt solution by an acid wash and the regenerated adsorbents could be reused without lost of performance. Similar approach was used in the design of other selective mesoporous adsorbents for the separation, removal and recovery of high purity metal salt solution from binary mixtures of Cr₂O₇²⁻ and Cu²⁺ that are found in electroplating waste [23] and of Ni²⁺ and Cd²⁺ from recycling of spent NiCd batteries [24]. In this work, we further demonstrate the feasibility of designing highly selective adsorbents based on mesoporous silica for the selective separation and recovery of high purity gold and palladium from binary and complex mixtures containing these metals. A systematic study was conducted to investigate the effects of solution pH, concentration and composition on the adsorption.

Experimental

The reagents used for the preparation of mesoporous adsorbents include tetraethyl orthosilicate (TEOS, 98%),

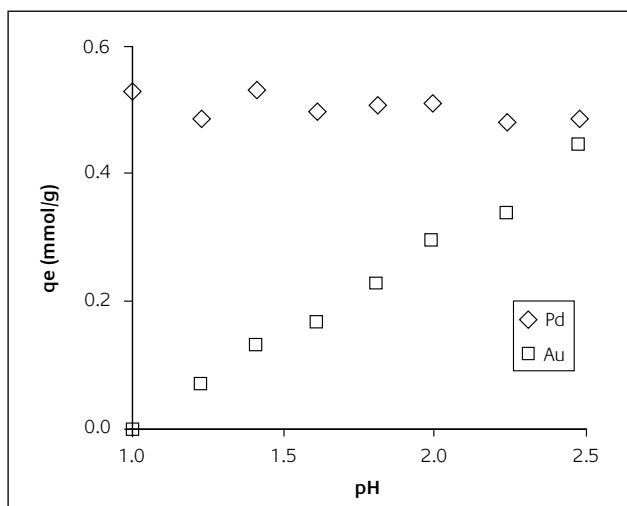


Figure 1
Effects of pH on gold and palladium adsorptions on NH₂-MCM-41 from binary solutions (0.05 g NH₂-MCM-41, 50 ml 2 mM AuCl₃ and 2 mM PdCl₂, 295 ± 2 K, 2h)

cetyltrimethylammonium bromide (CTABr, 99.3%), 3-aminopropyltrimethoxysilane (APTS, 97%) and ammonium hydroxide (NH₄OH, 28-30wt.%) purchased from Aldrich and Fisher Scientific. The dry toluene (> 99.5%) solvent was supplied by Mallinckrodt. Gold (III) chloride (AuCl₃, 99%) from International Lab and palladium (II) chloride (PdCl₂, 99%) from Aldrich were used in the single, binary and multi-components adsorption experiments. The multi-components solutions also contain cobalt (II) nitrate (Co(NO₃)₂, 98%), nickel (II) nitrate (Ni(NO₃)₂, 99%) and copper (II) nitrate (Cu(NO₃)₂, 99%) from Nacalai Tesque Inc. and the zinc (II) nitrate (Zn(NO₃)₂, 99%) bought from Fisher. Dilute hydrochloric acid (HCl, Mallinckrodt) and sodium hydroxide (NaOH, BDH) solutions were added to adjust the pH of the solutions. Standard calibration solutions of 1000 ppm gold and palladium in 2% hydrochloric acid and 1000 ppm cobalt, nickel, copper and zinc in 2% nitric acid were purchased from High-Purity Standards.

The mesoporous MCM-41 silica was prepared at room temperature from an alkaline synthesis solution with mole ratios of 6.6 SiO₂: CTABr: 292 NH₄OH: 2773 H₂O according to the procedure described in the previous work [21]. The amorphous, white precipitates formed early in the synthesis eventually crystallized into MCM-41 powder after two hours of reactions. The MCM-41 was filtered, washed, dried and ground into free flowing powder before calcination in air at

823 K for 24 h to remove the CTA⁺ organic template molecules trapped in the MCM-41 pores. The work by Tikhomirova et al. [25] showed that nitrogen-containing ligands on silica can adsorb group VIII metals including gold, palladium and platinum. The NH₂-MCM-41 adsorbents were prepared by grafting aminopropyls (i.e., C₃H₇NH₂) on the walls of the MCM-41 by refluxing 2.5 g MCM-41 powder in 250 ml dry toluene containing 0.1 mole of APTS for 18 h according to the method described by Ho et al. [26]. The NH₂-MCM-41 powder was filtered, washed with toluene and dried in an oven at 383 K overnight. The dried adsorbent was ground and sieved before use in the adsorption experiments. The prepared MCM-41 and NH₂-MCM-41 were characterized by X-ray diffraction (XRD, Philips 1830), N₂ physisorption (Coulter SA 3100), Fourier transform infrared spectroscopy (FTIR, Perkin-Elmer GX 2000), X-ray photoelectron spectroscopy (XPS, Physical Electronics PHI 5000) and elemental analysis (EA, Elementar Vario EL III) to determine their physical and chemical properties.

Single and binary components gold and palladium adsorptions were measured by adding 0.05 grams of adsorbent powders to 50 ml aqueous metal salt(s) solutions. Small amounts of dilute HCl and NaOH solutions were added to adjust the pH of the metal salt(s) solutions. The batch adsorption was conducted in a shaker bath kept at a constant temperature of 295 ± 2 K. The adsorption rate and equilibrium were determined by taking samples of the adsorption solution at fixed time intervals. The samples were filtered to remove and recover the adsorbent, and the metal concentrations analyzed by inductively coupled plasma, atomic emission spectrometer (ICP-AES, Perkin Elmer Optima 3000XL). Three measurements were made for each sample and the results were averaged. Calibration was made before each set of measurements using ICP standard solutions. The equilibrium adsorption capacity was calculated from equation 1:

$$q_e = \frac{(C_o - C_e) V}{m} \quad (1)$$

where q_e (mmol/g) is the adsorption capacity, C_o (mM) and C_e (mM) are the initial and final metal concentrations, respectively. V (L) is the solution volume and m (g) is the mass of adsorbent used for the adsorption.

The selective adsorptions of gold and palladium

Table 1
Physical, chemical and adsorption properties of MCM-41 and NH₂-MCM-41

	Moiety area	Surface m ² /g	Pore size nm	Specific pore volume cm ³ /g	Loading of functional groups mmol/g	Adsorption capacity mmol/g (mg/g)			
						AuCl ₄ ⁻		PdCl ₄ ²⁻	
						pH1.0	pH2.5	pH1.0	pH2.5
MCM-41	-OH	1140	3.09	0.97	--	0 (0)	0 (0)	0 (0)	0 (0)
NH₂-MCM-41	-RNH ₂	750	2.92	0.56	2.53	0 (0)	1.40 (276.0)	0.55 (58.5)	0.55 (58.5)

were demonstrated using a multi-components solution containing gold, palladium, cobalt, nickel, copper and zinc prepared from metal salts. The complex solution had a composition of 1 mM (197 ppm) AuCl₃, 0.1 mM (10 ppm) PdCl₂, 1 mM (59 ppm) Co(NO₃)₂, 1 mM (59 ppm) Ni(NO₃)₂, 1 mM (64 ppm) Cu(NO₃)₂, and 1 mM (65 ppm) Zn(NO₃)₂. Palladium and gold were adsorbed in two separate steps and high purity palladium chloride and gold chloride solutions were recovered from the spent adsorbents by a simple acid wash with 5 M HCl solution. Acid wash also regenerated the adsorbent for reuse in the subsequent experimental steps. The adsorption, recovery and regeneration were carried out at 295 ± 2 K in a shaker bath. The percent removal and recovery of the precious metals (Eqns. 2 & 3), as well as the adsorption selectivity (Eqn. 4) were determined by ICP-AES analyses:

$$Ads_i = \frac{(C_o - C_e)_i}{C_{o,i}} \times 100 \quad (2)$$

$$RC_i = \frac{(C_{w,i} - V_w)}{(C_o - C_e)_i V} \times 100 \quad (3)$$

$$Sel_i = \text{Log} \frac{(q_e / C_e)_i}{(q_e / C_e)_j} \quad (4)$$

where C_w (mM) and V_w (L) are the concentration of metal cations in the acid wash and the volume of washing solution, respectively. The index *i* pertains to one of the precious metals (i.e., gold or palladium) and index *j* refers to the remaining metals in the solution other than *i*.

Table 2

Gold adsorption on carbonaceous adsorbents

Adsorbent	Max. adsorption capacity mmol/g (mg/g)	Reference
Activated carbon	0.18 (35)	29
Degusorb C25 (granular cocconut-shell carbon)	0.5 (100)	30
Commercial carbon (PICA G210 AS)	0.51 (100)	31
Bagasse	1.16 (229)	31
Rice husk ash	0.11 (22)	32

Results and discussion

Adsorbent characterisation

The detailed description of the mesoporous MCM-41 silica and its derived aminopropylated NH₂-MCM-41 adsorbents was published elsewhere [21]. The calcined MCM-41 powder showed little tendency to agglomerate and had a uniform size and shape. The MCM-41 displayed a flat, disk-like shape with an average diameter of 0.75 ± 0.15 μm and a thickness of 0.10 ± 0.03 μm. The average MCM-41 pore diameter was 3.09 nm calculated according to the method described by Kruk et al. [27] based on the d-spacing measured by XRD and specific pore volume from the N₂ physisorption experiments. The calcined powder had a BET surface area of 1140 m²g⁻¹ and a specific pore volume of 0.97 cm³g⁻¹. XPS detected only silicon and oxygen from the calcined MCM-41 with a trace amount of carbon from adsorbed

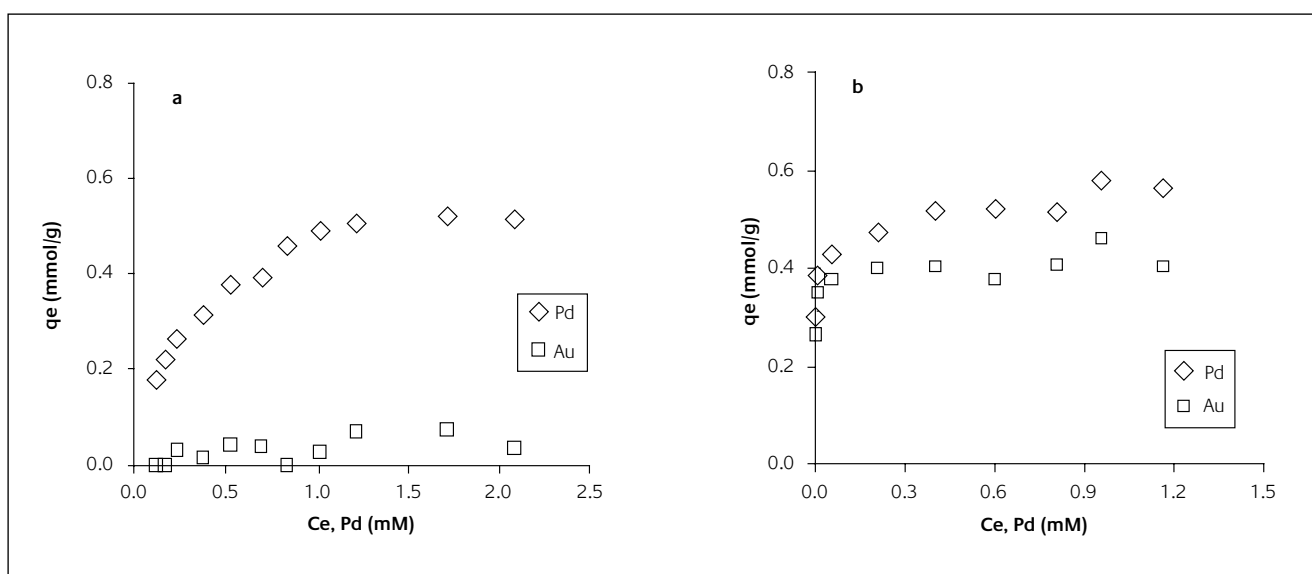


Figure 2

Equilibrium adsorptions of gold and palladium on NH₂-MCM-41 from binary solutions measured at (a) pH1.0 and (b) pH2.5 (0.05 g NH₂-MCM-41, 50 ml [AuCl₃] = [PdCl₂], 295 ± 2 K, 2h)

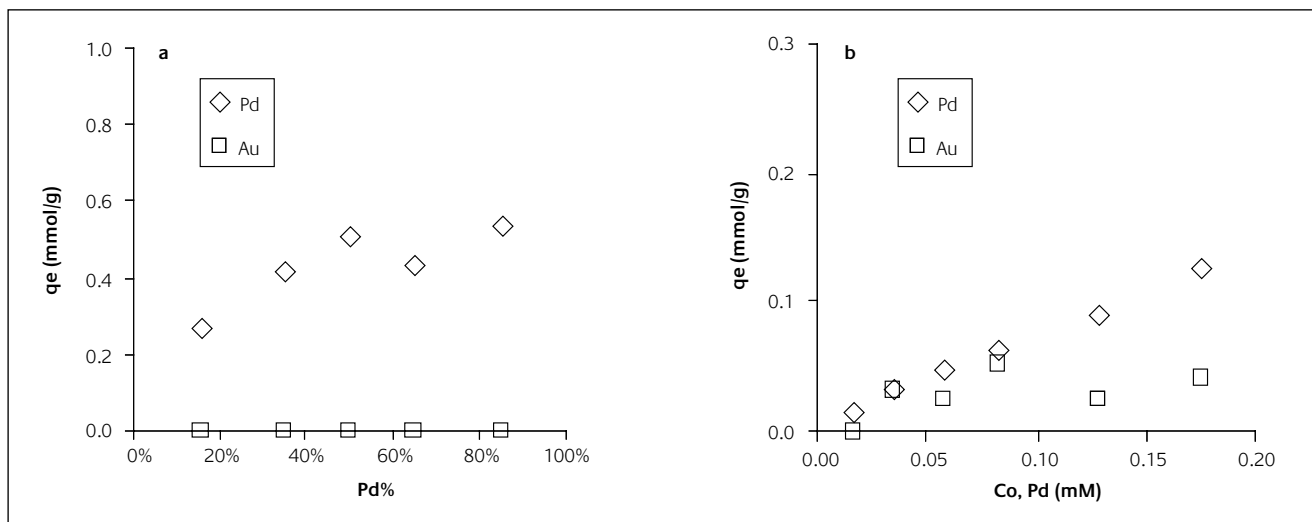


Figure 3

Equilibrium adsorptions of gold and palladium on $\text{NH}_2\text{-MCM-41}$ from binary solutions measured at (a) different solution composition (0.05 g $\text{NH}_2\text{-MCM-41}$, 50 ml $[\text{AuCl}_3] + [\text{PdCl}_2] = 2 \text{ mM}$, $295 \pm 2 \text{ K}$, 2h) and (b) low palladium concentration (0.05 g $\text{NH}_2\text{-MCM-41}$, 50 ml $[\text{AuCl}_3] = 1 \text{ mM}$, $[\text{PdCl}_2] = 0\text{-}0.2 \text{ mM}$, $295 \pm 2 \text{ K}$, 2h)

organic contaminants from the ambient surrounding. The FTIR detected only the surface silanol group and there were no signals from the organic compounds. Table 1 summarizes the BET surface area, the average pore diameter, specific pore volume and the predominant surface chemical moieties found on the MCM-41.

Grafting the aminopropyls on the surface of MCM-41 did not affect the particle size and morphology, but the surface area (i.e., $750 \text{ m}^2\text{g}^{-1}$) and pore size (i.e., 2.92 nm) of the $\text{NH}_2\text{-MCM-41}$ decreased (Table 1). XPS analysis of $\text{NH}_2\text{-MCM-41}$ gave C_{1s} binding energy of 285 eV typical of the carbons in organic alkyl chains and N_{1s} binding energy of 399.5 eV common to many amino compounds [28]. The FTIR spectrum of $\text{NH}_2\text{-MCM-41}$ displays the characteristic signals for the amine (i.e., 3254 cm^{-1} and 3320 cm^{-1}) and alkyl chain (i.e., 2845 cm^{-1} and 2920 cm^{-1}) from the grafted aminopropyls. The infrared signal for surface silanols at 3741 cm^{-1} was absent from the sample. The number of grafted aminopropyls was 2.53 mmolg^{-1} according to elemental analysis.

Single and binary components adsorptions

Gold and palladium were not adsorbed on the mesoporous MCM-41 silica as indicated in Table 1. This suggests that the precious metal ions do not adsorb on the native silanol groups found on the surface of the MCM-41. Gold and palladium adsorbed on $\text{NH}_2\text{-MCM-41}$ through the interactions between the protonated RNH_3^+ surface groups and the AuCl_4^- and PdCl_4^{2-} anions at low pH. The adsorption on the mesoporous adsorbent was rapid and equilibrium was reached in 2 h. This is mainly due to the easy accessibility of the large and straight pore channels of the MCM-41. The pH plays an important role in the adsorption of gold and palladium on $\text{NH}_2\text{-MCM-41}$. Table 1 lists the adsorption capacity of $\text{NH}_2\text{-MCM-41}$ for gold at 0.00 and 1.40 mmolg^{-1} (i.e., 0 and 276 mgg^{-1}) for pH1.0 and pH2.5, respectively. The $\text{NH}_2\text{-MCM-41}$ adsorbed

about 0.55 mmolg^{-1} (i.e., 59 mgg^{-1}) of palladium at pH1.0 and pH2.5. The adsorption capacity of $\text{NH}_2\text{-MCM-41}$ for gold compares favourably to the activated carbons as shown in Table 2. The activated carbons including degusorb and PICA have surface areas in excess of $1000 \text{ m}^2\text{g}^{-1}$ and have particle sizes smaller than the MCM-41 adsorbent reported in this work. The commercial granulated carbons reported by Perry [32] have significantly less capacity for gold adsorption of 19, 24 and 23 Kg/ton (or mg.g^{-1}) for PICA G210 AS, NORIT R03515 and ND CCV/94/295, respectively.

A more detailed study of the effects of pH on the metal adsorption was carried out in binary Au-Pd solutions containing equimolar concentrations of AuCl_3 and PdCl_2 . Dilute HCl solution was added to adjust the solution pH to values between 1.0 and 2.5, below the point of zero charge (i.e., p.z.c = pH3.5) of $\text{NH}_2\text{-MCM-41}$. Figure 1 plots the equilibrium adsorptions of gold and palladium on $\text{NH}_2\text{-MCM-41}$ as a function of solution pH. The data shows that comparable amounts of gold and palladium were adsorbed on $\text{NH}_2\text{-MCM-41}$ from the equimolar solution at pH2.5. The adsorbed gold decreases at lower pH and only trace amount of gold is adsorbed at pH1.0 as shown in the figure. Palladium adsorption was unaffected by pH within the pH range investigated in this study. The low adsorption of gold could be explained by the protonation of AuCl_4^- at pH1.0 to neutral HAuCl_4 that do not adsorb on the RNH_3^+ sites. The speciation PdCl_2 calculated by Visual MINTEQ [34] indicates that the negatively charged PdCl_3^- and PdCl_4^{2-} are predominant species in the solution.

Figure 2 plots the binary adsorption isotherms of gold and palladium at pH1.0 and pH2.5. Less than 0.03 mmolg^{-1} (i.e., 5.9 mgg^{-1}) of gold is adsorbed at pH1 compared to 0.43 mmolg^{-1} (i.e., 84.7 mgg^{-1}) at pH2.5. The amounts of palladium adsorbed at pH1.0 and pH2.5 were comparable and have values of 0.52 and 0.57 mmolg^{-1} , respectively. This

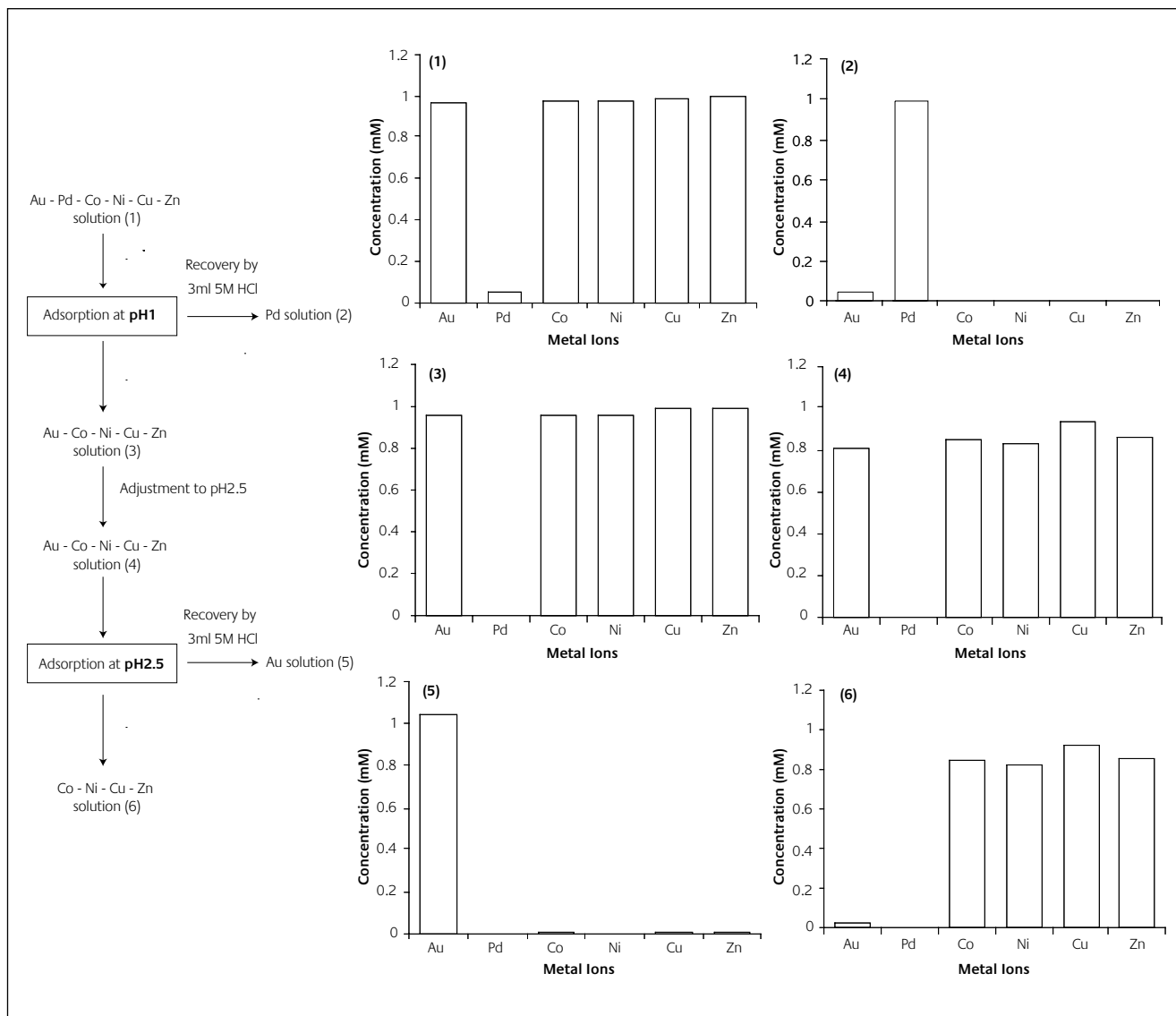


Figure 4

Schematic process diagram of adsorption experiments and the composition of the resulting solutions

is equivalent to about 55 to 60 mg Pd per gram of $\text{NH}_2\text{-MCM-41}$. Figure 3a examines the effects of solution composition on gold and palladium adsorptions at pH1.0. It is clear from the plots that only palladium is adsorbed at this pH and palladium adsorption is insensitive to the solution composition even at low starting PdCl_2 content of 15%. The $\text{NH}_2\text{-MCM-41}$ remained selective to palladium adsorption even in solutions containing trace amount of palladium in large excess of gold as shown in Fig. 3b. The adsorbent removed all the palladium in the solution leaving a palladium-free, high purity gold solution.

Gold and palladium separation and recovery from a complex mixture

The $\text{NH}_2\text{-MCM-41}$ was tested for the separation of precious metals from a six-component metal solution. The separation scheme is illustrated in Fig. 4. The starting solution contained 1mM AuCl_3 , 0.1mM PdCl_2 and 1mM each of $\text{Co}(\text{NO}_3)_2$, $\text{Ni}(\text{NO}_3)_2$, $\text{Cu}(\text{NO}_3)_2$, and $\text{Zn}(\text{NO}_3)_2$ (i.e., solution 1, Fig. 4-(1)) and approximates the pregnant solution from gold refinery

using Miller chlorination process. The concentration was adjusted higher to decrease the uncertainty in the adsorption measurement. In the refining process, it is preferred to immediately remove the palladium from the solution before the electrowinning process. The pH of the solution was first adjusted to pH1.0 and 1 g of $\text{NH}_2\text{-MCM-41}$ was added to each litre of solution. The adsorption was allowed to equilibrate at $295 \pm 2 \text{ K}$ (i.e., room temperature) for 2 h. The spent $\text{NH}_2\text{-MCM-41}$ was filtered and washed with 5 M HCl (i.e., $V_w/V = 33$) to regenerate the adsorbent and recover the palladium as a concentrated PdCl_2 solution of 95% purity (i.e., solution 2, Fig. 4-(2)). However, XPS analysis of the spent adsorbent detected only palladium. This means that the gold was from the liquid solution entrained between the particles as a result of insufficient washing of the filtered adsorbent. The Ads_{Pd} on $\text{NH}_2\text{-MCM-41}$ according to Eqn. 2 approaches 100%, so was the value of Rc_{Pd} calculated from Eqn.3. The selectivity of $\text{NH}_2\text{-MCM-41}$ based on Eqn. 4 was excellent.

The remaining solution was free of palladium (i.e., solution 3, Fig. 4-(3)) and consisted only of gold and the base metals.

The pH of the solution was adjusted to pH2.5 by dilution and addition of NaOH solution. Figure 4-(4) shows the metal concentrations dropped by about 10% after pH adjustment. It is known from previous study [21] that NH₂-MCM-41 selectively adsorbed gold at this pH. The regenerated adsorbent was added to solution 4 and allowed to equilibrate at ambient temperature for 2 h. About 0.80 mmolg⁻¹ or 157 mgg⁻¹ gold was adsorbed less than the single component adsorption capacity of NH₂-MCM-41 for gold at this pH. Solution 5 was obtained after washing the spent adsorbent with 5 M HCl (i.e., V_w/V = 33). Figure 4-(5) shows the solution is mostly AuCl₃ with trace amount of cobalt, copper and zinc. The latter were present probably due to insufficient rinsing of the spent adsorbent after filtration. The calculated values of Ads_{Au} , Rc_{Au} and Se_{Au} are 96, 99 and ∞, respectively. The remaining gold in the solution 6 (Fig. 4-(6)) can be removed and recovered by further adsorption. The experiment showed that selective adsorption is able to recover the precious metals from complex, multi-component metal solution at high purity.

Conclusions

The separation of precious metals from complex mixtures is difficult, but of great economic importance. It is a greater challenge still to separate the individual precious metals from the mixture, so as to recover the metals at sufficiently high purity for immediate reuse. This work has successfully addressed both challenges and demonstrated the use of mesoporous adsorbent to selectively adsorb and separate palladium and gold from a complex, multi-components solution containing other metal ions including cobalt, nickel, copper and zinc. The sequential adsorption at different pHs enabled the separation first of palladium at pH1.0 and then gold at pH2.5 from the solution. The adsorbed metals were recovered by acid wash producing concentrated, high purity metal salt solutions. The regenerated adsorbent was reused without loss of adsorption capacity or selectivity.

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About the authors



Dr. King Lun Yeung is an Associate Professor of Chemical Engineering at the Hong Kong University of Science and Technology. He obtained his Ph.D. in Chemical Engineering at the University of Notre Dame, U.S.A. in the area of surface science and catalysis. His current research focuses on the rational design and molecular-level engineering of functional nanoporous and nanostructured materials with chemical, environmental and bio-related applications.



Dr. Koon Fung LAM is a PhD graduate in Environmental Engineering from Prof. K L Yeung's research group. His research interest is in the design and applications of nanoporous materials for selective adsorption.



Ms. Chi Mei Fong is a Bachelor degree graduate from the Department of Chemical Engineering at HKUST. She is a junior research assistant in Prof. K L Yeung's research group working in selective adsorption of metal ions from industrial wastewater.

References

- 1 C. W. Corti, R. J. Holliday, *Transactions of the Institutions of Mining and Metallurgy*, Section B: *Appl. Earth Sci.*, 2005, **114**, B115
- 2 A. Bischoff, LBMA Precious Metals Conference 2002, San Francisco, 39
- 3 K. L. Yeung, E. E. Wolf, *Catal. Lett.*, 1992, **12**, 213
- 4 K. L. Yeung, E. E. Wolf, *J. Catal.*, 1992, **135**, 13
- 5 M. A. Pena, D. M. Carr, K. L. Yeung, A. Varma, *Chem. Eng. Sci.*, 1998, **53**, 3821
- 6 G. J. Hutchings, *Gold Bulletin*, 1996, **29**, 123
- 7 M. Hurata, *Gold Bulletin*, 2004, **37**, 27
- 8 K. Y. Ho, K. L. Yeung, *J. Catal.*, 2006, **242**, 131
- 9 S.-J. Lee, A. Gavriilidis, Q. A. Pankhurst, A. Kyek, F. E. Wagner, P. C. L. Wong, K. L. Yeung, *J. Catal.*, 2001, **200**, 298
- 10 S.P. Fricker, *Gold Bulletin*, 1996, **29**, 53
- 11 J. W. Phair, S. P. S. Badwal, *Ionics*, 2006, **12**, 103
- 12 Y. H. Ma, I. P. Mardilovich, E. E. Engwall, *Annals. New York Academy of Sciences*, 2003, **984**, 346
- 13 K. L. Yeung, J.M. Sebastian, A. Varma, *Catal. Today*, 1995, **25**, 231
- 14 K. L. Yeung, R. Aravind, J. Szegner, A. Varma, *Stud. In Surf. Sci. Catal.* 1996, **101**, 1349
- 15 Y. S. Cheng, K. L. Yeung, *J. Membr. Sci.*, 2001, **182**, 195.
- 16 W. Petruk, *Applied mineralogy in the mining industry*, New York: Elsevier Science, 2000

- 17 J. Cui, E. Forssberg, *J. Hazardous Mater.*, 2003, **99**, 243
- 18 W. J. Thomas, B. D. Crittenden, *Adsorption Technology and Design*, Oxford: Butterworth-Heinemann, 1988
- 19 D. Parajuli, H. Kawakita, K. Inoue, M. Funaoka, *Ind. Eng. Chem. Res.*, 2006, **45**, 6405
- 20 S. Döker, S. Malci, M. Dogan, B. Salih, *Anal. Chim. Acta* 2005, **553**, 73
- 21 K. F. Lam, K. L. Yeung, G. McKay, *J. Phy. Chem. B*, 2006, **110**, 2187
- 22 K. F. Lam, K. L. Yeung, G. McKay, *Langmuir*, 2006, **22**, 9632
- 23 K. F. Lam, K. L. Yeung, G. McKay, *Microporous Mesoporous Mater.*, 2007, **100**, 191
- 24 K. F. Lam, K. L. Yeung, G. McKay, *Environ. Sci. Technol.*, 2007, **41**, 3329
- 25 T. I. Tikhomirova, V. I. Fadeeva, G. V. Kudryavtsev, P.N. Nesterenko, V. M. Ivanova, A. T. Savitchev, N. S. Smirnova, *Talanta*, 1991, **38**, 267
- 26 K. Y. Ho, G. McKay, K. L. Yeung, *Langmuir*, 2003, **19**, 3019
- 27 M. Kruk, M. Jaroniec, A. Sayari, *Chem. Mater.*, 1999, **11**, 492
- 28 A. E. Hooper, D. Werho, T. Hopson, O. Palmer, *Surf. Interface Anal.*, 2001, **31**, 809
- 29 W. Nakbanpote, P. Thiravetyan, C. Kalambaheti, *Miner. Eng.* 2002, **15**, 549
- 30 K. Kongolo, C. Kinabo, A. Bahr, *Hydrometallurgy* 1997, **44**, 191
- 31 N. Syna, M. Valix. *Miner. Eng.* 2003, **16**, 421
- 32 W. Nakbanpote, P. Thiravetyan, C. Kalambaheti, *Miner. Eng.* 2000, **13**, 391
- 33 G. J. Perry, Activated carbonaceous adsorbents-a production and testing study, LMFS-94-13, 12/31/1994
- 34 Gustafsson, J. P. **2006**. Visual MINTEQ. Version 2.40. KTH, Stockholm, Sweden