Selective mesoporous adsorbents for Ag^+/Cu^{2+} separation

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Three different approaches, including (1) manipulating the site chemistry, (2) controlling the spacing between neighbouring sites and (3) altering the adsorbates by the use of chelates, were successfully used to prepare MCM-41 adsorbents with excellent selectivity for silver adsorption from solutions containing copper.

The rising cost of precious and commodity metals,[1] and the growing awareness of their detrimental impact on health and the environment,[2] has given impetus to the development of effective means for their removal, recovery and reuse from industrial effluent and waste water. The traditional methods of recovering precious metals (*e.g.*, Au and Ag) include chemical precipitation, electrodeposition and adsorption.[3] Adsorption has the advantages of easy operation, low energy consumption, simple maintenance and large capacity.[4] However, common adsorbents, such as activated carbons, are non-selective and adsorb all metal species, making their recovery for reuse a difficult task. An important characteristic of these adsorbents are their heterogeneous surfaces, which host a variety of adsorption sites of differing accessibility. This could explain their poor adsorption selectivity.

Mesoporous MCM-41 is characterized by its straight, cylindrical pore channels and high degree of pore symmetry, giving it an enormous surface area and excellent accessibility. The amorphous SiO_2 pore wall approximates to a Langmuir surface, and can be easily manipulated to create specific adsorption sites for the target chemical species. Fryxell's group are among the pioneers in the design and use of selective mesoporous adsorbents.[5] Hence, various functional groups, including amino, diamino, triamino, ethylenediamine, carboxy and others, were successfully attached to the pore walls of MCM-41, MCM-48 and SBA-15 for the adsorption of groups 6, 10, 11 and 12 metal ions,[6] including the precious metals gold[7] and platinum.[6i] Despite this progress, the design of selective adsorbents remains difficult. This work describes three different approaches for designing selective mesoporous adsorbents, using the separation of Ag^+ and Cu^{2+} as an illustration.

MCM-41 mesoporous silica powder was crystallized from an alkaline synthesis solution with a molar composition of $6.6SiO_2 : CTABr : 292NH_4OH: 2773H_2O$, prepared from tetraethyl orthosilicate (TEOS, 98%, Aldrich), cetyltrimethylammonium bromide (CTABr, 99.3%, Aldrich) and ammonium hydroxide (NH_4OH, 28–30 wt%, Fisher Scientific). White powders were formed within 10 min of adding the silica precursor, but the mixture was allowed to age for 2 h at room temperature (295 ± 2 K) to crystallize the mesopore structures. The powder was filtered, washed and dried before calcining in air at 823 K for 24 h to remove the CTA^+ organic template molecules. The resulting free flowing powder displayed little tendency to agglomerate. Scanning electron microscopy (SEM, JEOL JSM 6300F) and light scattering measurements (Beckman Coulter, Delsa 440SX) indicated that the MCM-41 has a disk-like shape, with an average diameter of 0.80 ± 0.20 μm and a thickness of 0.10 ± 0.03 μm. The MCM-41 displayed an ordered hexagonal pore structure with an average pore diameter of 3.09 nm and a surface area of 1070 $m^2\ g^{-1}$ (Table 1).[8] Despite its enormous surface area, the native surface silanol groups had a poor affinity for Ag^+ and Cu^{2+} adsorption, and did not adsorb these metal cations.

Adsorbents containing amine groups often display an excellent adsorption capacity for metal cations.[9] The NH_2-MCM-41 was prepared by grafting 1.0 mmol g^{-1} of aminopropyl groups onto MCM-41 by reflux with a 3-aminopropyltrimethoxysilane (APTS, 97%, Aldrich) solution in dry toluene (>99.5%, Mallinckrodt) at 383 K for 18 h (Table 1).[10] Pearson's hard–soft, acid–base (HSAB) theory[11] describes the preferential interactions between Lewis acids (*e.g.*, Ag^+ and Cu^{2+}) and Lewis bases (*e.g.*, grafted aminopropyl groups) of similar "hardness". According to the HSAB theory, the grafted aminopropyl groups are borderline hard base and should have a greater affinity for adsorbing Cu^{2+}, a hard acid. Fig. 1a plots the binary adsorption of Ag^+ and Cu^{2+} from the solutions containing equimolar concentration of silver nitrate (99.8%, BDH) and copper nitrate (99%, Nacalai Tesque Inc.) salts. The experiment was carried out at room temperature and pH of 5.0 ± 0.1 under vigorous stirring. The initial and final concentrations of the metals in the solution were analyzed by inductively coupled plasma, atomic emission spectrometer (ICP-AES, Perkin Elmer Optima 3000XL). The adsorption on the submicron-sized, mesoporous adsorbent was rapid and equilibrium was reached within twenty minutes, but the experiments were allowed to last for 8 h. The plots in Fig. 1a show that NH_2-MCM-41 adsorbs *only* Cu^{2+} and displays 100% selectivity for copper over the entire range of concentrations investigated in this work.

By substituting an alkyl group for one of the hydrogens on the NH_2, the hardness of the amino group decreased. RNH-MCM-41 containing 1.0 mmol g^{-1} dipropylamine was prepared by grafting chloropropyltriethoxysilane (95%, Aldrich) onto the MCM-41 by refluxing them in dry toluene, followed by the nucleophilic substitution of propylamine (Table 1). Fig. 1b shows that the substitution of a propyl group

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Table 1 Physical and chemical properties of the mesoporous silica adsorbents

	Surface area/m^2 g^{-1}	Pore size[a]/nm	Moiety	Characteristic FTIR signals/cm^{-1}	Loading of functional groups[b]/mmol g^{-1}	Adsorption capacity[c]/ mmol g^{-1} (mg g^{-1})	
						Ag^+	Cu^{2+}
MCM-41	1070	3.09	–OH	3743 (Si–OH)	—	0	0
NH_2-MCM-41	772	2.82	$-RNH_2$	3288 and 3360 (N–H), 1600 (C–N)	1.01	0.11 (11.8)	0.25 (15.8)
RNH-MCM-41	911	2.83	–RHNR	2973 and 2865 (*n*-propyl), 1500 (CH_2–NH–CH_2)	1.01	0.26 (28.0)	0
R_2N-MCM-41	889	2.79	$-RNR_2$	2973 and 2865 (*n*-propyl), absence of OH and N–H	0.94	0.05	0.05
Spaced-NH_2-MCM-41	670	2.80	$-RNH_2$	3290 and 3359 (N–H), 1643 (C–N)	1.2	1.04 (122.3)	0

[a] Pore size calculated based on XRD (Philips 1830), BET surface area and pore volume (Coulter SA 3100).[8] [b] Amount calculated from elemental analysis (Elementar Vario EL III) and thermogravimetric experiments (Setaram 31/1190). [c] Adsorption capacities of the metals were determined by single component adsorption.

successfully transformed the adsorption selectivity from Cu^{2+} to Ag^+. The RNH-MCM-41 adsorbs *only* Ag^+ and *not* Cu^{2+} from binary metal solutions, and the adsorbent exhibits 100% selectivity for Ag^+ adsorption. Adding another propyl group further decreases the hardness of the grafted amino group, and the R_2N-MCM-41 (Table 1) was expected to be selective for Ag^+ adsorption. Instead, the additional propyl group hindered the adsorption of Ag^+, resulting in poor adsorption, as shown in Fig. 1c. It is clear that both the chemistry and the structure are determining factors in the design of selective adsorbents.

Slow diffusion of the bulky precursor molecules (*e.g.*, APTS) in pore channels often results in an uneven spatial distribution of grafted functional groups in mesoporous materials. Recently, Miyajima and co-workers[12] employed a clever method to quantify pair-spacing between grafted organic moieties, and reported a broader than expected distribution for MCM-41 and SBA-15. The variation in site density affects the distance and interactions between neighboring sites (*e.g.*, hydrogen bonding between the aminopropyl groups, and between an aminopropyl group and a surface silanol), and consequently the sites' energetics and availability for adsorption differed. The adsorption of Cu^{2+} involving two aminopropyl groups resulted in a lower than expected Cu^{2+} adsorption on the NH_2-MCM-41 (Fig. 1a). This also suggests that by properly spacing the aminopropyl groups, it is possible to suppress the adsorption of Cu^{2+} and alter the selectivity of the adsorbent.

Hicks and Jones[13] have reported the use of a new benzyliminosilane to space the aminopropyl groups grafted onto SBA-15. By borrowing the same procedure, benzyliminosilane was prepared by reacting equimolar amounts of APTS and

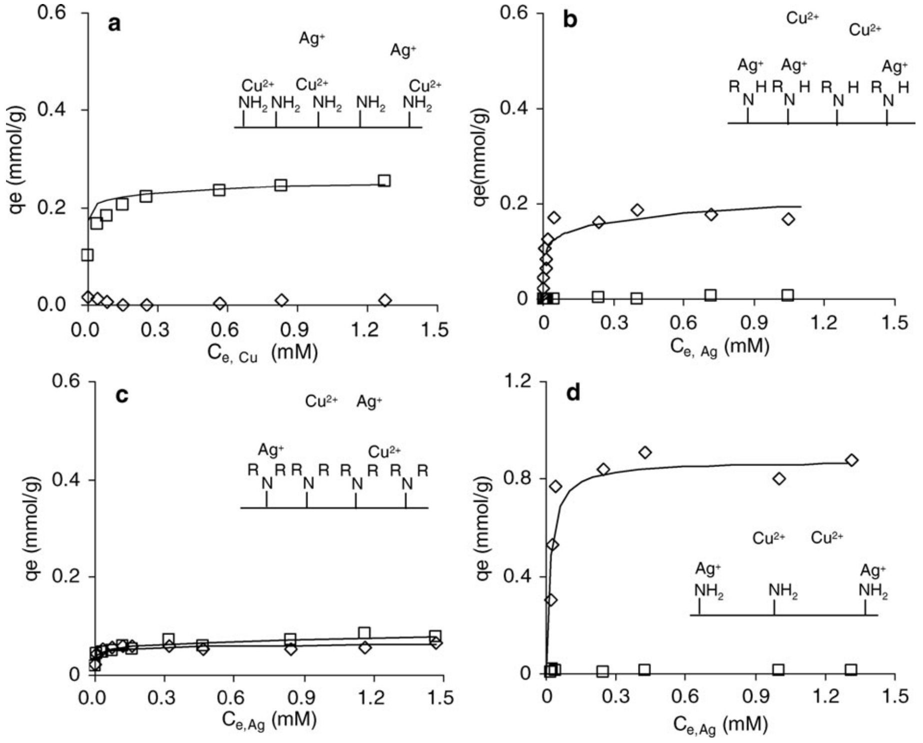

Fig. 1 Plots of binary Ag^+–Cu^{2+} adsorption onto (a) NH_2-MCM-41, (b) RNH-MCM-41, (c) R_2N-MCM-41 and (d) spaced-NH_2-MCM-41. Please note the symbols for copper (□) and silver (◇) adsorption. The lines are drawn for visual guidance.

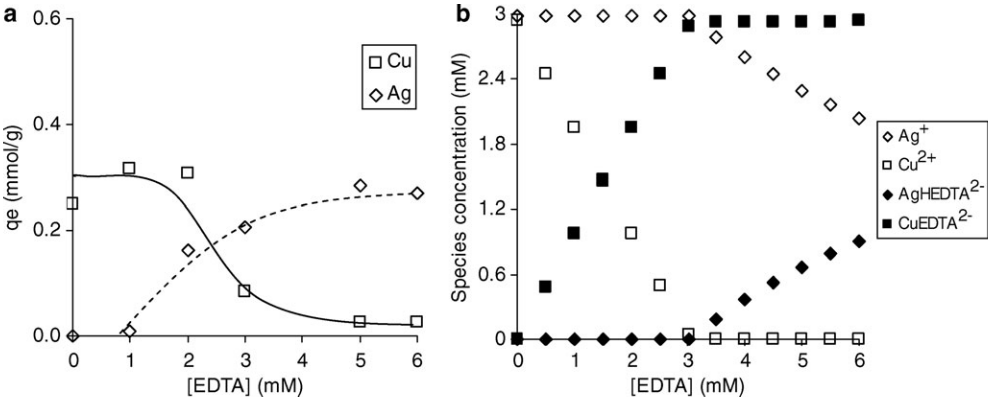

Fig. 2 (a) Binary Ag^+–Cu^{2+} adsorption onto NH_2-MCM-41 at different EDTA concentrations and (b) speciation diagram for Ag^+ (◇), $AgHEDTA^{2-}$ (◆), Cu^{2+}(□) and $CuEDTA^{2-}$ (■). The lines are drawn for visual guidance.

benzaldehyde in toluene at 383 K for 24 h. The MCM-41 was then added to the solution, and the mixture was allowed to reflux for another 18 h under an N_2 atmosphere. The grafted benzyliminosilanes were converted to aminopropyl groups by hydrolysis with a 1 M HCl solution at room temperature for 24 h. The final adsorbent was washed with dilute 0.05 M NH_4OH and distilled water. The unreacted silanols were capped with hexamethyldisilazane (HMDS) in order to suppress undesirable interactions between the grafted aminopropyl groups and the unreacted silanols. Fig. 1d shows that a larger spacing between neighboring aminopropyl groups enabled us to prepare a NH_2-MCM-41 adsorbent that was selective for Ag^+ adsorption. Copper was not adsorbed, and the obtained Ag^+ adsorption capacity of 0.8 mmol g^{-1} was more commensurate with the aminopropyl loading.

Often, the presence of chelates (*e.g.*, EDTA) is considered to be detrimental to adsorption, as it leads to a lower adsorption capacity.[14] However, we found that the judicious use of chelating agents tuned the selectivity of the adsorbent without significantly affecting its adsorption capacity. This is illustrated in Fig. 2 for the separation of Ag^+ and Cu^{2+} on NH_2-MCM-41. The experiments were carried out using equimolar metal solutions of 3 mM $AgNO_3$ and 3 mM $Cu(NO_3)_2$ at pH 5. Fig. 2a shows that it was possible to precisely tune the selectivity of NH_2-MCM-41 from 100% for Cu^{2+} to 100% for Ag^+ by adding measured amounts of EDTA. The effect of EDTA can be seen in the speciation data from Visual MINTEQ,[15] as plotted in Fig. 2b. The EDTA selectively binds to the Cu^{2+} cations, forming a $CuEDTA^{2-}$ complex, and all the Cu^{2+} ions in the solution were bound to EDTA at a [EDTA] above 3 mM. On the other hand, EDTA does not bind as strongly to Ag^+, and the concentration of the $AgHEDTA^{2-}$ complex is only significant above a [EDTA] of 3 mM.

It is clear from the data in Fig. 2 that the aminopropyl groups of NH_2-MCM-41 adsorb metal cations, including Ag^+ and Cu^{2+}, but not the negatively-charged $CuEDTA^{2-}$.

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