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The adsorption of divalent metal cations on mesoporous silicate MCM-41

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ABSTRACT

MCM-41 is a synthetic, mesoporous silicate material, which currently has limited use as an industrial catalyst. This material is considered to have good potential for adsorption/separation applications due to its regular hexagonal structure, uniform pore distribution, large surface area and large pore volume. In order to enhance the adsorption of metal ions on MCM-41, a metal ion chelating agent, acetylacetone is added and the capacity of the adsorbent for three divalent metal cations in aqueous solutions; Cu(II), Ni(II) and Co(II) determined. Adsorption isotherms for these metal ions are presented, along with adsorption selectivity with respect to pH. Metal ion adsorption results are compared with published data for solvent extraction systems utilising pure acetylacetone and acetylacetone in benzene. It was found that the MCM-41/acetylacetone system produced equal or better metals removal in comparison to solvent extraction methods for some of the metal species tested. Further, the pH of maximum adsorption is shifted in the MCM-41 system compared with the solvent extraction case, thus presenting the possibility of processing under different conditions.

1. Introduction

Since the discovery of MCM-41 in 1992, there have been five main areas of interest for research into this material. These include characterization, mechanism of formation, synthesis of other new materials based upon MCM-41, control of morphology and industrial applications [1]. Such applications include its use in adsorption [2], catalysis [3], the immobilization of bio-molecules [4,5] and metal ion extraction [6–8]. Several different analytical techniques have been used to examine the crystal structure, morphology and porosity of mesoporous materials, including X-ray diffraction (XRD), gas adsorption (GA), scanning and transmission electron microscopy (SEM and TEM) and nuclear magnetic resonance (NMR) [3,9].

Possibly the area of greatest interest in mesoporous silicate research to date are the applications of these materials. While there are examples of the use of MCM materials as stated above, these are limited and further work needs to be done to develop the industrial applications of MCM-41. The greatest advantage of mesoporous silicates is their extremely large surface areas and hence their potential for adsorption processes. The study of metal ion adsorption onto MCM-41 could open up new applications for this material in the areas of metals recovery.

The results of studies of the adsorption of various divalent metal ions by MCM-41 have been presented in previous papers [6–8]. These studies reported on the comparative adsorption behaviour of copper, cadmium, zinc and lead as a function of pH, using acetylacetone (Hacac) as a chelating agent. The results showed that the MCM-41/Hacac system has different selectivity for different ions. Further, Hokura et al. [6] investigated the kinetics of copper–acetylacetonate complex adsorption onto MCM-41 and found that equilibrium was reached after 30 min. However, it has been found that the formation of cobalt and nickel–acetylacetonate complexes can be quite slow, of the order of several hours [10]. This investigation builds on the previous studies to look more closely at the adsorption behaviour of MCM-41 for the divalent metal cations, Cu(II), Ni(II) and Co(II) in the presence of Hacac.

2. Experimental

2.1. MCM-41 synthesis and characterisation

The synthesis technique for MCM-41 was performed using a similar technique to that of Edler et al. [9]. Sodium silicate (19.0 g, 27% SiO_2, diluted with 40.6 g MilliQ water) was mixed with a solution of 16.4 g cetyltrimethylammonium bromide (CTAB) in 69.2 g

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of MilliQ water. The sodium silicate/CTAB solution was adjusted to pH 11 by drop-wise addition of 3 mol L^{-1} sulfuric acid. The resulting gel was stirred for 30 min, transferred into a stainless steel jacketed Teflon vessel and heated at 100 °C for 144 h. The resulting silicate solid was then filtered, washed with approximately 2 L of hot water and then dried under vacuum for 48 h.

Four grams of dry mesoporous silicate powder was heated over 8 h to 550 °C in an electric furnace. The silicate was then calcined at 550 °C for 8 h and then allowed to cool slowly for 8 h inside the furnace. Calcination to produce the MCM-41 product was performed immediately before all adsorption experiments. The nitrogen adsorption and desorption isotherms for calcined MCM-41 samples were measured at −196 °C on a Belsorp 18 (BEL Japan Ltd.). Calcined samples were heated at 200 °C for 2 h and degassed overnight. The BET method [11] was used to determine the surface area of each MCM-41 sample from N_2 adsorption data. Pore diameter and pore volume were determined by the Dollimore–Heal method [12], using the N_2 desorption data.

2.2. Adsorption kinetics

Kinetic experiments were performed on the nickel system to determine the optimum reaction time for adsorption experiments. MCM-41 (0.1 g) was contacted with 10 mL of aqueous solution, containing 1×10^{-4} mol L^{-1} of Ni^{2+} ions (made from $Ni(NO_3)_2$) and 1×10^{-2} mol L^{-1} Hacac. The solutions were adjusted to pH 4 using 0.01 mol L^{-1} nitric acid and sodium hydroxide. The kinetics tests were performed at times between 15 min and 30 h. The concentration of metal ion in solution was measured using a VARIAN Vista Pro Inductively Coupled Plasma Adsorption Emission Spectrometer (ICP-AES).

2.3. Metals adsorption with respect to pH

For the metal ion adsorption with respect to pH, 0.1 g of MCM-41 was contacted with 10 mL of aqueous solution, containing 1×10^{-4} mol L^{-1} of M^{2+} ions (made from $M(NO_3)_2$ salts) and 1×10^{-2} mol L^{-1} Hacac. The solutions were adjusted to the desired pH (between 3 and 7) using 0.01 mol L^{-1} nitric acid and sodium hydroxide. The solid and aqueous phases were separated by centrifugation and filtration. The pH of the aqueous phase was determined using a HORIBA F-21 pH meter with a combination glass electrode. The concentrations of metal ions in solution were measured using ICP-AES.

The distribution ratio, K_d, is denoted as:

$$K_d = \frac{[M]_{\text{solid}}}{[M]_{\text{aqueous}}} \qquad (1)$$

where $[M]_{\text{solid}}$ and $[M]_{\text{aqueous}}$ are the metal concentrations in the solid phase (mol g^{-1}) and aqueous phase (mol mL^{-1}). The maximum distribution ratio for each of the metal species tested was calculated from the equilibrium concentrations in the solid and aqueous phase.

2.4. Adsorption isotherms for metal ions

The adsorption isotherms were determined by contacting (for an appropriate time) 0.1 g of calcined MCM-41 with 10 mL of unbuffered aqueous solution, containing between 2.5 mg L^{-1} and 40 mg L^{-1} of M^{2+} ions and 1×10^{-2} mol L^{-1} Hacac. The solid and aqueous phases were separated by centrifugation and filtration. The initial and final solution pH was measured using a HORIBA F-21 pH meter with a combination glass electrode. The concentrations of metal ions in solution were measured using ICP-AES.

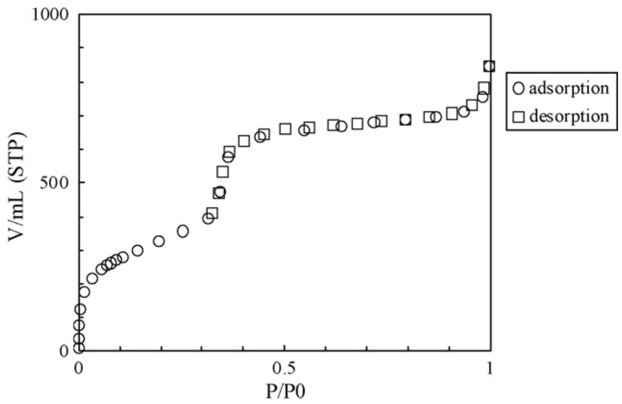

Fig. 1. Nitrogen adsorption and desorption isotherms for synthesised MCM-41 after calcination.

3. Results and discussion

3.1. MCM-41 surface area analysis

In this investigation for each set of metal ion adsorption experiments, a new batch of MCM-41 was synthesised and calcined. The surface area, pore size and pore diameter were measured and used to compare the quality of different samples of MCM-41. Fig. 1 is a typical example of a good quality mesoporous silicate with a distinctive "stepped" gas adsorption isotherm. The sharp step is due to the filling of the mesopores and the sudden increase in adsorbed gas volume indicates a uniform pore size distribution [13]. The surface area, pore diameter and pore volume results for all samples of MCM-41 tested are given in Table 1. Table 1 also gives the measured structural properties of MCM-41 from previous investigations [6,7]. The published results compare well with the results obtained in this study.

3.2. Kinetics of adsorption

A previous study of metal ion adsorption behaviour onto MCM-41 [7] found that the extent of adsorption was almost constant for solid–liquid contact times between 5 min and 24 h. In addition to this, Hokura et al. [6] found that copper ion complexation and adsorption onto MCM-41 reached equilibrium at around 30 min. In this investigation the uptake of Ni(II) onto MCM-41 (Fig. 2) reached a maximum at around 22 h, confirming previous researchers observations that the nickel–acetylacetonate complexation reaction occurs more slowly than for other metals species and is most likely the rate controlling step of uptake onto MCM-41 [6].

3.3. Effect of pH on metals uptake

Plots of adsorption ratio for copper, nickel and cobalt, with respect to pH of the aqueous phase, are shown in Fig. 3. The maximum percentage adsorption for copper was 41% at pH 4.3. Maximum adsorption for nickel was 68% at pH 5.5 and 60% of cobalt was removed from solution at pH 6.4.

Table 1
Structural properties of synthesised MCM-41.

MCM sample	Specific surface area ($m^2\,g^{-1}$)	Pore diameter (nm)	Pore volume ($cm^3\,g^{-1}$)
This study	1090 (±158)	2.87	1.20 (±0.17)
Oshima et al. [7]	1173	3.12	1.45
Hokura et al. [6]	1150	2.52	1.05

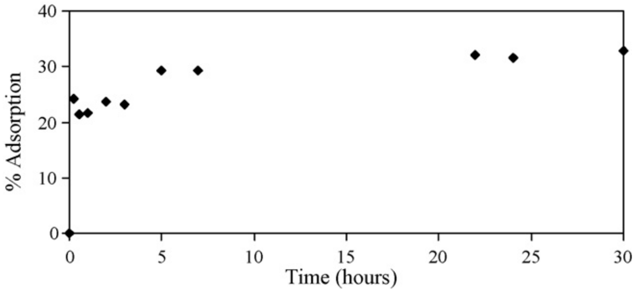

Fig. 2. Kinetics of adsorption of nickel–acetylacetonate complex onto MCM-41 at pH 4. Initial concentration of the metal ion and Hacac was 1×10^{-4} mol L^{-1} and 1×10^{-2} mol L^{-1}, respectively.

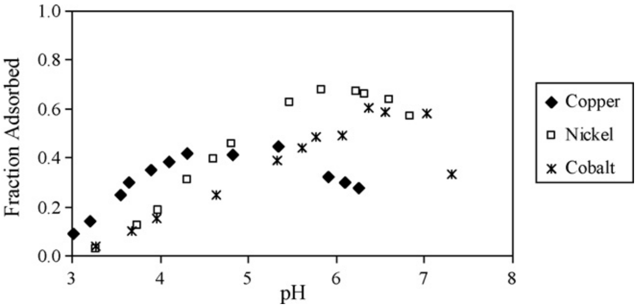

Fig. 3. Adsorption of divalent metal cations by MCM-41/Hacac with respect to pH. Initial concentration of metal ions and Hacac was 1×10^{-4} mol L^{-1} and 1×10^{-2} mol L^{-1}, respectively.

Table 2
Comparison of adsorption properties of the MCM-41/Hacac system with published solvent extraction data.

MCM-41/Hacac	Adsorption (%)	pH	K_d (mL g^{-1})	Loading capacity (mmol g^{-1})
Copper	41	4.3	71	0.0045
Nickel	68	5.5	208	–
Cobalt	60	6.4	152	0.0056

Solvent extraction[a]	Pure Hacac		0.1 M Hacac in benzene[b]	
	Extraction (%)	pH	Extraction (%)	pH
Copper	80	2.0	90	4.0
Nickel	N/A		20	5.0
Cobalt	N/A		30	7.0

[a] Data sourced from Stary [10]. Table 6, pp. 55–60 and references therein; phase ratio 1:1.

[b] 0.1 mol L^{-1} Hacac in benzene; phase ratio 1:1.

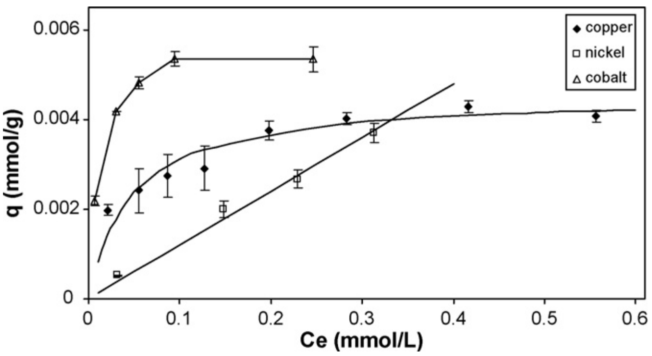

Fig. 4. Adsorption isotherms for copper (pH 3.6 ± 0.4), nickel (pH 4.0 ± 0.2) and cobalt (pH 5.7 ± 0.5). The Cu(II) and Co(II) data were fitted to the Langmuir isotherm (Eq. (2)). The Ni(II) data was fitted ($n = 1$ and $K_f = 0.012$) to the linear isotherm given in Eq. (4). The error bars are the standard deviation for duplicate samples tested.

The maximum distribution ratio for each metal is shown in Table 2. Also included in this table is a comparison of the % removal (adsorption) of each metal investigated in this study with published % extraction data for typical solvent extraction systems [10]. In solvent extraction around 80% of copper can be extracted by pure Hacac at pH 2–5. Hence solvent extraction would be considered more effective than the MCM-41/Hacac system for copper. Only 20% of Ni(II) can be extracted by 0.1 mol L^{-1} Hacac in benzene, compared to 68% for the MCM-41/Hacac system. The results for MCM-41/Hacac adsorption of cobalt show improvement over the Hacac in benzene solvent extraction system, suggesting that the MCM-41/Hacac system is better than solvent extraction for cobalt removal.

There is limited published information regarding the use of MCM-41 for the removal of metals from water. Table 3 gives a comparison of the experimental conditions, % adsorption and distribution ratio for cobalt adsorption for this study and two previous studies [14,15]. In this study, with a solution/adsorbent ratio of 100 and an initial cobalt concentration of 4.3 mg L^{-1}, the maximum adsorption and distribution ratio were 60% and 152 mL g^{-1}, respectively. Sayari et al. [14] investigated a pore expanded MCM-41 containing N,N-dimethylalkylamine inverted cylindrical micelles within the pores of the silicate. They were able to achieve a very high amount of adsorption of cobalt (% adsorption = 99%, K_d = 18600 mL g^{-1}) using a 9.4 mg L^{-1} solution at a solution/adsorbent ratio of 200. However for a test conducted with an initial concentration of cobalt of 1174 mg L^{-1}, the distribution ratio reduced to 90 mL g^{-1}. Hanzel and Rajec [15] studied MCM-41 with imidazol groups bonded to the surface of the silicate. Similar to Sayari et al. [14], Hanzel and Rajec [15] achieved high amounts of adsorption and high K_d at low initial concentrations of cobalt in solution, but K_d decreased with increasing metal concentration.

3.4. *Adsorption isotherms for the metal ions onto MCM-41*

The adsorption isotherms for the three metal ions were investigated. As shown in Fig. 4, the adsorption behaviour of Cu(II) and Co(II) have a distinctive shape which is described well by a Langmuir type isotherm:

$$q = \frac{q_{\max} b C_e}{1 + b C_e} \quad (2)$$

Table 3
Comparison of cobalt adsorption using the MCM-41/Hacac system, with two modified MCM-41 systems.

System	pH	Solution/adsorbent (mL g^{-1})	Co^{2+} initial (mg L^{-1})	Adsorption (%)	K_d (mL g^{-1})
MCM-41/Hacac	6.5	100	4.3	60	152
Pore expanded MCM-41/DMDA[a]	N/A	200	9.4	99	18,600
Pore expanded MCM-41/DMDA[a]	N/A	80	1174	54	90
MCM-41/imidazole[b]	5.6	50	0.35	90	461
MCM-41/imidazole[b]	5.6	50	589	26	17.5

[a] Sayari et al. [14], Pore expanded MCM-41 containing N,N-dimethylalkylamine inverted cylindrical micelles inside pores.

[b] Hanzel and Rajec [15], MCM-41 with immobilized imidazole groups on the surface.

where $q_{\max}$ is the maximum amount of cations adsorbed per gram of MCM-41 ($\mathrm{mmol\,g^{-1}}$), b is a constant which reflects the interaction between the cations in solution and the sorbent surface ($\mathrm{L\,mmol^{-1}}$), q and C_e are the equilibrium concentrations of the metal ion in the solid ($\mathrm{mmol\,g^{-1}}$) and solution ($\mathrm{mmol\,L^{-1}}$), respectively. The Langmuir equation can be re-arranged as follows:

$$\frac{C_e}{q} = \frac{C_e}{q_{\max}} + \frac{1}{q_{\max} b} \qquad (3)$$

This linearised form of the Langmuir equation can be fitted to a plot of C_e/q versus C_e to derive $q_{\max}$ and the constant, b [16]. $q_{\max}$ values of 0.0045 $\mathrm{mmol\,g^{-1}}$ ($b = 22.23$) and 0.0056 $\mathrm{mmol\,g^{-1}}$ ($b = 117.58$) were obtained for the adsorption of Cu(II) and Co(II), respectively. While it would appear that the surface has a preference for Co(II), it must be noted that these isotherms were obtained at different pH.

The nickel data over the concentration range investigated did not exhibit typical Langmuir type behaviour. Linear isotherms are sometimes observed for adsorption at narrow concentration ranges and low concentration levels. This behaviour implies that sorption is not dependent on the initial concentration of metals species in the aqueous solutions. The linear sorption behaviour may be described by the Freundlich equation:

$$q = K_f C_e^n \qquad (4)$$

where K_f and n are empirical constants, q and C_e is as previously defined.

As is shown in Fig. 4, the nickel data is fitted ($n = 1$ and $K_f = 0.012$) more appropriately with a linear isotherm.

4. Conclusions

A novel adsorbent based on synthetic mesoporous silicate with a ligand added specifically to complex divalent transition metal cations, has been characterised in terms of its physical structure and its potential to uptake copper, nickel and cobalt ions over a wide pH range.

Under the experimental conditions described, the adsorption data for Cu(II) and Co(II) obtained from batch studies fitted the Langmuir model while the Ni(II) data was best fitted to a linear isotherm.

The results also show that for the defined pH ranges, the uptake is higher and comparable to the equivalent liquid–liquid extraction system with benzene as the solvent. It is also comparable to other adsorbents reported in the literature. The pH at which the maximum adsorption occurs is shifted in the mesoporous silicate when compared to the benzene system, giving the opportunity to operate a process based on this adsorbent at different process conditions.

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References

[1] U. Ciesla, F. Schuth, Ordered mesoporous materials, Micropor. Mesopor. Mater. 27 (1999) 131–149.

[2] P. Selvam, S.K. Bhatia, C.G. Sonwane, Recent advances in processing and characterization of periodic mesoporous MCM-41 silicate molecular sieves, Ind. Eng. Chem. Res. 40 (2001) 3237–3261.

[3] Q. Wu, Z. Hu, P.L. Yue, Z.S. Zhao, G.Q. Lu, Copper/MCM-41 as catalyst for the wet oxidation of phenol, Appl. Catal. B: Environ. 32 (2001) 151–156.

[4] J.F. Diaz, K.J. Balkus Jr., Enzyme immobilization in MCM-41 molecular sieve, J. Mol. Catal. B 2 (1996) 115–126.

[5] J.M. Kisler, A. Daehler, G.W. Stevens, A.J. O'Connor, Separation of biological molecules using mesoporous molecular sieves, Micropor. Mesopor. Mater. 44–45 (2001) 769–774.

[6] A. Hokura, I. Nakai, H. Yamada, A.J. O'Connor, J.M. Perera, G.W. Stevens, Y. Komatsu, Primary study on capturing behaviour for transition metal ions on mesoporous silicate (MCM-41), J. Ion Exchange 14 (2003) 173–176.

[7] S. Oshima, J.M. Perera, K. Northcott, H. Kokusen, G.W. Stevens, Y. Komatsu, Adsorption behaviour of cadmium(II) and lead (II) on mesoporous silicate MCM-41, Sep. Sci. Technol. 41 (2006) 1635–1643.

[8] K. Northcott, S. Oshima, J. Perera, Y. Komatsu, G. Stevens, Synthesis, characterisation and evaluation of mesoporous silicates for adsorption of metal ions, Adv. Powder Technol. 18 (2007) 751–762.

[9] K.J. Edler, J. Dougherty, R. Durand, L. Iton, G. Kirton, G. Lockhart, Z. Wang, R. Withers, J.W. White, Small angle X-ray scattering from MCM-41 and its synthesis gels: optimization of the synthesis parameters, Colloids Surf. A 102 (1995) 213–230.

[10] J. Stary, The Solvent Extraction of Metal Chelates, Pergamon Press, 1964 (Chapters 2–5).

[11] S. Brunauer, P.H. Emmett, E.J. Teller, Adsorption of gases in multimolecular layers, J. Am. Chem. Soc. 60 (1938) 309–319.

[12] D. Dollimore, G.R. Heal, An improved method for the calculation of pore-size distribution from adsorption data, J. Appl. Chem. 14 (1964) 109–114.

[13] A. Daehler, Development of functional nanoporous silica adsorbents, PhD thesis, University of Melbourne, Australia, 2002.

[14] A. Sayari, S. Hamoudi, Y. Yang, Applications of pore-expanded mesoporous silica. 1. Removal of heavy metal cations and organic pollutants from wastewater, Chem. Mater. 17 (2005) 212–216.

[15] R. Hanzel, P. Rajec, Sorption of cobalt on modified silica gel materials, J. Radioanal. Nucl. Chem. 246 (2000) 607–615.

[16] J.A.A. Sales, A.G.S. Prado, C. Airoldi, Interaction of divalent copper with two diaminealkyl hexagonal mesoporous silicas evaluated by adsorption and thermochemical data, Surf. Sci. 590 (2005) 51–62.