Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Adsorption Behavior of Cadmium(II) and Lead(II) on Mesoporous Silicate MCM-41

Syunichi Oshima[a]; Jilska M. Perera[b]; Kathy A. Northcott[c]; Hisao Kokusen[c]; Geoffrey W. Stevens[b]; Yu Komatsu[c]
[a] Department of Chemistry and Biology Engineering, Fukui National College of Technology, Geshi-cho, Sabae, Fukui, Japan [b] Department of Chemical & Biomolecular Engineering, The University of Melbourne, Victoria, Australia [c] Department of Environmental Chemistry, College of Environmental Engineering and Architecture, Kanazawa Institute of Technology, Nonoichi, Ishikawa, Japan

To cite this Article Oshima, Syunichi , Perera, Jilska M. , Northcott, Kathy A. , Kokusen, Hisao , Stevens, Geoffrey W. and Komatsu, Yu(2006) 'Adsorption Behavior of Cadmium(II) and Lead(II) on Mesoporous Silicate MCM-41', Separation Science and Technology, 41: 8, 1635 — 1643
To link to this Article: DOI: 10.1080/01496390600674786
URL: http://dx.doi.org/10.1080/01496390600674786

Separation Science and Technology, 41: 1635–1643, 2006

ISSN 0149-6395 print/1520-5754 online
DOI: 10.1080/01496390600674786

Adsorption Behavior of Cadmium(II) and Lead(II) on Mesoporous Silicate MCM-41

Syunichi Oshima
Department of Chemistry and Biology Engineering, Fukui National College of Technology, Geshi-cho, Sabae, Fukui, Japan

Jilska M. Perera
Department of Chemical & Biomolecular Engineering, The University of Melbourne, Victoria, Australia

Kathy A. Northcott and Hisao Kokusen
Department of Environmental Chemistry, College of Environmental Engineering and Architecture, Kanazawa Institute of Technology, Nonoichi, Ishikawa, Japan

Geoffrey W. Stevens
Department of Chemical & Biomolecular Engineering, The University of Melbourne, Victoria, Australia

Yu Komatsu
Department of Environmental Chemistry, College of Environmental Engineering and Architecture, Kanazawa Institute of Technology, Nonoichi, Ishikawa, Japan

Abstract: This investigation examines metal ion adsorption on mesoporous silicate, MCM-41, synthesized from sodium silicate solution and cethyltrimethylammonium bromide (CTAB). MCM-41 has potential as an adsorbent material, with a regular hexagonal pore structure, large specific surface area, and large pore volume. The MCM-41 synthesized for this investigation is characterized using powder X-ray

Received 2 June 2005, Accepted 15 February 2006
Address correspondence to Syunichi Oshima, Department of Chemistry and Biology Engineering, Fukui National College of Technology, Geshi-cho, Sabae, Fukui 916-8507, Japan. Fax: (81+) 778-62-3415; E-mail: oshima@fukui-nct.ac.jp

diffraction and nitrogen adsorption and desorption isotherms data. The adsorption behavior for cadmium(II) and lead(II) onto MCM-41 was studied by contacting the mesoporous silicate with an aqueous solution of metal salts and acetylacetone. Both Cd^{2+} and Pb^{2+} were found to quantitatively adsorb onto MCM-41. The results of this study suggest that MCM-41 may have applications in the recovery of toxic metals from waste waters.

Keywords: Adsorption behavior, mesoporous silicate, MCM-41, cadmium, lead

INTRODUCTION

Mesoporous silicates are synthetic, inorganic solids with pores in the 2 to 50 nm size range. The size and arrangement of the pores in these materials are controlled during synthesis by the careful choice of surfactant. MCM-41 is a mesoporous silicate featuring hexagonally packed arrays of one-dimensional, cylindrical pores, with a uniform pore distribution, large specific surface area and large pore volume (1, 2). The characteristics of such mesoporous silicates suggest potential applications in the fields of adsorption, catalysis and nanotechnology due to their large specific surface area and regular porosity (3, 4). As MCM-41 exhibits low hydrothermal stability (4–16), many workers have studied the improvement of stability by modification of the synthesis conditions. Some examples include choice of siliceous source (6), change of pH (7), reaction time (3), temperature (3), and effect of salt addition (8). Previous studies have examined the use of mesoporous silicates for immobilization of globular enzymes (17) and for the adsorption of proteins and vitamins (18). In another investigation, the selective adsorption of mercury was tested using a mesoporous silicate modified with an organic functional group (19). Other studies have examined the inclusion of metals into the structure of MCM-41 for applications in catalysis (20). However, there is little data available regarding the application of MCM-41 for selective adsorption of metal ions in aqueous solution. One previous study examined the adsorption of Cu^{2+} on MCM-41 and established that this material has potential as an adsorbent for metal ions (21). This study focuses on the adsorption behavior of Cd^{2+} and Pb^{2+} to determine the suitability of MCM-41 for the removal of toxic metals from aqueous environments with minimal use of organic reagents.

EXPERIMENTAL

Apparatus

An electric furnace (Vacuum Metallurgical Co., Ltd.) was used for the calcination of the silicate sample. Samples of the silicate product were

characterized by powder X-ray diffraction (XRD; RIGAKU, RINT2100S) using CuKα radiation. The N_2 adsorption and desorption isotherm data for the MCM-41 was determined using a BELSORP 18 apparatus (BEL Japan, Inc.). Prior to nitrogen adsorption, the sample was heated to 200°C and 10^{-1} Pa for 2 hours and degassed overnight. A HORIBA F-21 pH meter with a combination glass electrode was used to determine the pH values. A VARIAN Vista Pro Inductively Coupled Plasma Atomic Emission Spectrometer (ICP-AES) was used for the determination of the concentration of metal ions in aqueous solution.

Reagents

Cethyltrimethylammonium bromide (CTAB) and sodium silicate solution ($\sim$27% SiO_2) were purchased from Sigma-Aldrich and used without the purification. Cadmium nitrate and lead nitrate (Wako Pure Chemical Industries, Ltd.) were used for the adsorption tests. Acetylacetone (Dojindo Laboratories) was used as chelating reagent. All other chemicals were reagent-grade materials and MilliQ water was used throughout.

Synthesis and Characterization of Mesoporous Silicate MCM-41

The synthesis of the mesoporous silicate, MCM-41, was performed using a similar technique to that of Edler et al. (22). A solution of 16.4 g CTAB in 69.2 g of MilliQ water was prepared and heated to 60°C. A sodium silicate solution (19.0 g) was diluted with 40.6 g MilliQ water. The hot CTAB solution was added and the mixture was stirred for 10 minutes. The pH of the mixture was adjusted to 11 by drop-wise addition of 3 mol dm^{-3} sulfuric acid. The resulting gel was stirred for 30 minutes and then transferred into a stainless steel jacketed Teflon vessel. The gel was heated at 100°C for 144 hours and the silicate material produced was then cooled to room temperature. The silicate material was recovered from solution by filtration, washed extensively with hot deionized water, and dried under vacuum.

The silicate product was heated to 550°C in an electric furnace at a rate of 2°C min^{-1} in a nitrogen atmosphere (flow rate of 50 cm^3 min^{-1}). The silicate was then calcined at 550°C in nitrogen for 1 hour, followed by 6 hours in an air atmosphere at 550°C (100 cm^3 min^{-1}). The furnace was then cooled at 0.8°C min^{-1} to 25°C. Calcination was performed immediately before all adsorption experiments.

Adsorption Behavior for Cadmium(II) and Lead(II) onto MCM-41

MCM-41 (0.1 g) was placed in a centrifuge tube and contacted with an aqueous phase (10 cm^3) containing 1×10^{-4} mol dm^{-3} M^{2+} (M = Cd or Pb)

and 1×10^{-2} mol dm^{-3} acetylacetone. The mixture was agitated for 1 hour and then the solid and aqueous phases were separated by filtration. The pH of the aqueous phase and the concentration of metal ions in the aqueous phase were determined. The amount of metal ion adsorbed on the MCM-41 was calculated by subtracting the measured concentration with the initial concentration of metal ion in the aqueous phase.

RESULTS AND DISCUSSION

Characterization of MCM-41

The N_2 adsorption and desorption isotherms obtained for the material synthesized (see Fig. 1) are in good agreement with typical isotherms for mesoporous materials with a regular hexagonal arrangement of cylindrical pores (23). The surface area of the MCM-41 was determined from the linear section of a BET plot. The pore diameter and pore volume were calculated from the N_2 adsorption data, using the Dollimore-Heal (DH) method (24). The surface area and pore size results for MCM-41 are given in Table 1. The surface area and pore volume of the obtained MCM-41 in this work compare well with previous published data (the surface area and pore volume range of 600–1100 m^2 g^{-1} and 0.3–1.2 cm^3 g^{-1}, respectively) (1, 2, 4–8, 10–14, 16, 19, 22, 23, 25–30).

The XRD diffraction pattern for MCM-41, before and after calcination, is shown in Fig. 2 and the hexagonal lattice parameter derived from the XRD analysis is given in Table 1. The four peaks identified at low angles (2–8°, 2θ) are a good indication of the well-ordered hexagonally arranged pore structure typical of MCM-41 (25). The lattice parameter a_0 is a measure of the average distance between two neighboring pore centers in the material structure. The parameter, d_{100}, is the XRD interplanar spacing of the first

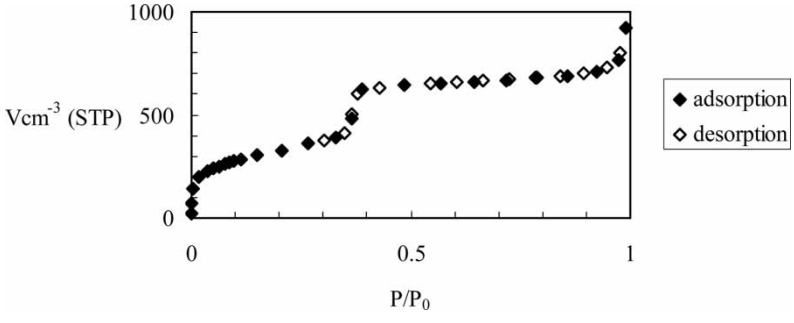

Figure 1. Nitrogen adsorption and desorption isotherms for the synthesized MCM-41 after calcination.

Table 1. Structural properties of synthesized MCM-41

[a]a_0 nm	Specific surface area $m^2 g^{-1}$	Pore diameter nm	Pore volume $cm^3 g^{-1}$
4.7	1173	3.12	1.45

[a]a_0: hexagonal lattice parameter calculated from XRD data using the formula $a_o = 2d_{100}/\sqrt{3}$.

diffraction peak. The wall thickness of MCM-41, which is calculated by subtracting the pore diameter from the lattice parameter, is about 1.6 nm. This result agrees with the reported data (1.3–2.7 nm) (4, 14).

Adsorption Behavior for Cadmium(II) and Lead(II) on MCM-41

Calcined MCM-41 has been found to have a low hydrothermal stability. The structural degradation is caused by hydration of the siloxane structure, that is hydrolysis of Si–O–Si bonds after immersion in aqueous solution (7, 8, 10). Hence, the effect of adsorption time on the % adsorption was examined by changing the contact time of MCM-41 with the aqueous solutions containing Cd^{2+} from 5 minutes to 24 hours. It was found that Cd^{2+} adsorption onto MCM-41 is almost constant for the range of agitation times tested and it was found that MCM-41 could be used as the adsorbent under the these adsorption conditions. It is suggested that the disintegration of the MCM-41 structure by hydrolysis is relatively slow in acidic and neutral aqueous solutions at a room temperature (7, 8). Furthermore, the thicker walls of the synthesized MCM-41, relative to previous investigations, seemed to exhibit

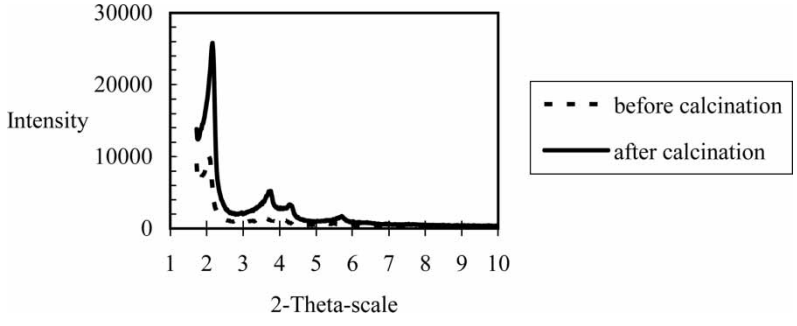

Figure 2. Powder X-ray diffraction pattern of synthesized MCM-41 before and after calcination.

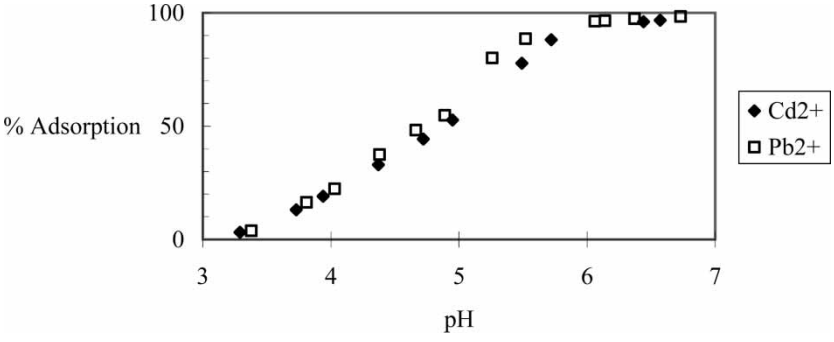

Figure 3. Adsorption behavior for Cd^{2+} and Pb^{2+} on MCM-41. Plots of the % adsorption of the metal ions as a function of the aqueous phase pH after contact with MCM-41. Initial concentration of Cd^{2+} or $Pb^{2+}$and acetylacetone in a solution were 1×10^{-4} mol dm^{-3} and 1×10^{-2} mol dm^{-3}, respectively. MCM-41 was 0.1 g.

a good hydrothermal stability at room temperature (4, 9, 12–14, 16). An agitation time of 1 hour was chosen for subsequent tests.

For adsorption behavior of Cd^{2+} and Pb^{2+} on MCM-41, the adsorption ratios onto MCM-41 were plotted as a function of pH in the aqueous phase (See Fig. 3). As shown in Fig. 3, both Cd^{2+} and Pb^{2+} were quantitatively adsorbed onto MCM-41 at pH = 6.2. A study by Hokura and coworkers (21) found that, for a given pH, metal ion uptake onto MCM-41 increased with an increase in acetylacetone concentration in solution. Hokura and coworkers (21) looked at a case of copper ion extraction and found that the optimum concentration of extractant was 0.001 M. They also found that an excess of acetylacetone impaired metal capture onto MCM-41 by occupation of surface adsorption sites that acetylacetone-metal complexes would otherwise occupy. Other researchers have shown that metal complexes containing nucleophilic ligands such as the acetylacetonate complex, will react with OH groups on oxide surfaces (31). Figure 3 shows adsorption ratios increased as pH value increased, suggesting that Cd^{2+} and Pb^{2+} were adsorbed onto MCM-41 as an acetylacetonate complex by hydrophobic interaction. This is supported by the fact that Cd^{2+} and Pb^{2+} were not adsorbed on MCM-41 without acetylacetone in the aqueous solution (data not shown).

Previous studies of solvent extraction systems, using organic solvents such as benzene and carbon tetrachloride and chelating agents such as acetylacetone, have found that Cd^{2+} is minimally extracted in benzene and carbon tetrachloride with acetylacetone, but up to 80% Pb^{2+} is extracted in benzene from alkaline aqueous solutions (32, 33). The fact that adsorption of metal ions on MCM-41 takes place within a relatively short time is one of the advantages of this method. The results of the adsorption experiments described here have shown that toxic metals such as cadmium and lead can be successfully adsorbed onto MCM-41. Hence the mesoporous silicate, MCM-41, has the

potential to be used in the recovery of toxic metal ions from aqueous systems with minimal use of organic reagents.

ACKNOWLEDGEMENT

We are grateful to Dr. Hirohisa Yamada of the National Institute of Materials Science (NIMS; Tsukuba, Japan), for the XRD measurement of MCM-41.

REFERENCES

1. Kresge, C.T., Leonowicz, M.E., Roth, W.J., Vartuli, J.C., and Beck, J.S. (1992) Ordered mesoporous molecular sieves synthesized by a liquid-crystal template mechanism. *Nature*, 359: 710–712.
2. Beck, J.S., Vartuli, J.C., Roth, W.J., Leonowicz, M.E., et al. (1992) A new family of mesoporous molecular prepared with liquid crystal templates. *J. Am. Chem. Soc.*, 114 (27): 10834–10843.
3. Selvam, P., Bhatia, S.K., and Sonwane, C.G. (2001) Recent advances in processing and characterization of periodic mesoporous MCM-41 silicate molecular seives. *Ind. Eng. Chem. Res.*, 40 (15): 3237–3261.
4. Cheng, C.F., Zhou, W., Park, D.H., Klinowski, J., Hargreaves, M., and Gladdin, L.F. (1997) Controlling the channel diameter of the mesoporous molecular sieve MCM-41. *J. Chem. Soc., Faraday Trans.*, 93 (2): 359–363.
5. Corma, A., Grande, M.S., Gonzalez-Alfaro, V., and Orchilles, A.V. (1996) Cracking activity and hydrothermal stability of MCM-41 and its comparison with amorphous silica-alumina and a USY zeolite. *J. Catal.*, 159 (2): 375–382.
6. Lin, W., Cai, Q., Pang, W., Yue, Y., and Zou, B. (1997) New mineralization agents for the synthsis of MCM-41. *Microporous Mesoporous Mater.*, 33 (1): 187–196.
7. Landau, M.V., Varkey, S.P., Herskowitz, M., Regev, O., Pevzner, S., Sen, T., and Luz, Z. (1999) Wetting stability of Si-MCM-41 mesoporous material in neutral, acidic and basic aqueous solutions. *Microporous Mesoporous Mater.*, 33 (1): 149–163.
8. Ryoo, R. and Jun, S. (1997) Improvement of hydrothermal stability of MCM-41 using salt effects during the crystallization process. *J. Phys. Chem. B*, 101 (3): 317–320.
9. Mokaya, R. (1999) Ultrastable mesoporous aluminosilicates by grafting routes. *Angew. Chem. Int. Ed.*, 38 (19): 2930–2934.
10. Pérez, C.N., Moreno, E., Henriques, C.A., Valange, S., Gabelica, Z., and Monteiro, J.L.F. (2000) On the stability of MCM-41 after ion-exchange and impregnation with cesium species in basic media. *Microporous Mesoporous Mater.*, 41 (1–3): 137–148.
11. Lin, H.P., Shih, P.C., Liu, Y.H., and Mou, C.Y. (2002) Reducing surfactants-silica interactions for high-coverage silane-modification of MCM-41 and MCM-48 silicas. *Chem. Lett.*, 6: 566–567.
12. Kang, K.K. and Rhee, H.K. (2002) Synthesis and characterization of hexagonal mesoporous materials using hydrothermal restructuring method. *Stud. Surf. Sci. Catal.*, 141: 101–108.

13. Pauly, T.R., Petkov, V., Liu, Y., Billinge, S.J.L., and Pinnavaia, T.J.J. (2002) Role of framework sodium versus local framework structure in determining the hydrothermal stability of MCM-41 mesostructures. *J. Am. Chem. Soc.*, 124 (1): 97–103.
14. Chen, H. and Wang, Y. (2002) Preparation of MCM-41 with high thermal stability and complementary textural porosity. *Ceram. Int.*, 28 (5): 541–547.
15. On, D.T. and Kaliaguine, S. (2002) Ultrastable and highly acidic, zeolite-coated mesoporous aluminosilicates. *Angew. Chem. Int. Ed.*, 41 (6): 1036–1040.
16. Lee, H.H., Ahn, J.W., and Kim, H. (2004) Preparation of MCM-41 with high structural stability. *Ceram. Int.*, 30 (6): 817–822.
17. Diaz, J.F. and Balkus, K.J., Jr. (1996) Enzyme immobilization in MCM-41 molecular sieve (MB40). *J. Molecular Catalysis B*, 2 (2–3): 115–126.
18. Kisler, J.M., Dahler, A., Stevens, G.W., and O'Connor, A.J. (2001) Separation of biological molecules using mesoporous molecular sieves. *Microporous Mesoporous Mater.*, 44–45: 769–774.
19. Feng, X., Fryxell, G.E., Wang, L.Q., Kim, A.Y., Liu, J., and Kemner, K.M. (1997) Functionalized monolayers on ordered mesoporous supports. *Science*, 276 (5314): 923–926.
20. Wu, Q., Hu, Z., Yue, P.L., Zhao, Z.S., and Lu, G.Q. (2001) Copper/MCM-41 as catalyst for the wet oxidation of phenol. *Applied Catalysis B*, 32 (3): 151–156.
21. Hokura, A., Nakai, I., Yamada, H., O'Connor, A.J., Perera, J.M., Stevens, G.W., and Komatsu, Y. (2003) Primary study on capturing behavior for transition metal ions on mesoporous silicate (MCM-41). *J. Ion Exch.*, 14: 173–176.
22. Edler, K.J., Dougherty, J., Durand, R., Iton, L., Kirton, G., Lockhart, G., Wang, Z., Withers, R., and White, J.W. (1995) Small angle X-ray scattering from MCM-41 and its synthesis gels: optimisation of the synthesis parameters. *Colloids Surfaces A*, 102: 213–230.
23. Branton, P.J., Hall, P.G., and Sing, K.S.W. (1993) Pysisorption of nitrogen and oxygen by MCM-41, a model mesoporous adsorbent. *J. Chem. Soc. Chem. Commun.*, 16: 1257–1258.
24. Dollimore, D. and Heal, G.R. (1964) An improved method for the calculation of pore size distribution from adsorption data. *J. Appl. Chem.*, 14: 109–114.
25. Broyer, M., Valange, S., Bellat, J.P., Bertrand, O., Weber, G., and Gabelica, Z. (2002) Influence of aging, thermal, hydrothermal, and mechanical treatments on the porosity of MCM-41 mesoporous silica. *Langmuir*, 18 (13): 5083–5091.
26. Urbán, M., Méhn, D., Kónya, Z., and Kiricsi, I. (2002) Production of carbon nanotubes inside the pores of mesoporous silicates. *Chem. Phys. Lett.*, 359 (1, 2): 95–100.
27. Lin, H.P. and Mou, C.Y. (2002) Salt effect in post-synthesis hydrothermal treatment of MCM-41. *Microporous Mesoporous Mater.*, 55 (1): 69–80.
28. Bai, N., Chi, Y., Zou, Y., and Pang, W. (2002) Influence of high pressure on structural property of mesoporous material MCM-41: study of mechanical stability. *Mater. Lett.*, 54 (1): 37–42.
29. Yuan, Z.Y., Zhou, W., Su, B.L., and Peng, L.M. (2002) Mesoporous silicas of hierarchical structure by hydrothermal surfactant-templating under mild alkali conditions. *Stud. Surf. Sci. Catal.*, 141: 133–140.
30. Deere, J., Magner, E., Wall, J.G., and Hodnett, B.K. (2002) Mechanistic and structural features of protein adsorption onto mesoporous silicates. *J. Phys. Chem. B*, 106 (29): 7340–7347.

31. Guzman, J. and Gates, C.B. (2003) Reactions of $Au(CH_3)_2$ (acac) on γ-Al_2O_3: characterization of the surface organic, organometallic, metal oxide, and metallic species. *Langmuir*, 19: 3897–3903.
32. Stary, J. and Hladky, E. (1963) Systematic study of the solvent extraction of metal β-diketonates. *Anal. Chim. Acta*, 28: 227–235.
33. Sekine, T., Iwahori, S., Johnsson, S., and Murai, R. (1977) Formation and extraction equilibria of several cadmium(II) β-diketonates and their triocthylphosphine oxide adducts. *J. Inorg. Nucl. Chem.*, 39 (6): 1092–1094.