Adsorption of heavy metals on amine-functionalized MCM-48

P Taba, P Budi and A Y Puspitasari
Physical Chemistry Laboratory, Universitas Hasanuddin, Jl. Perintis Kemerdekaan
KM. 10, Tamalanrea Indah, Kota Makassar, Sulawesi Selatan 90245, Indonesia

Corresponding author's e-mail: paulinataba@unhas.ac.id

Abstract. The ordered mesoporous silica with cubic structure, MCM-48 was synthesized by post-synthesis under basic media using colloidal silica, cetyltrimethylammonium bromide, and Triton X-100. The modified material, NH$_2$-MCM-48 was prepared using 3-aminopropyl trimethoxysilane (3-APTMS). X-ray diffraction and FT-IR were used to characterize the samples. The modified material was utilized for adsorption of Cu$^{2+}$ and Mn$^{2+}$ from aqueous solution. Parameters used for studying the adsorption process were pH, time of contact, and the initial concentrations of Cu$^{2+}$ and Mn$^{2+}$ ions. Desorption of ions from the adsorbent was also studied using several desorbing agents. The pseudo-second order was found to be the kinetic order for the metals adsorption. The adsorption of Cu$^{2+}$ and Mn$^{2+}$ on NH$_2$-MCM-48 was fixed by the Langmuir model better than the Freundlich model with the capacity of 0.52 and 0.80 mmol g$^{-1}$ for Cu$^{2+}$ and Mn$^{2+}$, respectively. The best desorbing agents for removing the adsorbed Cu$^{2+}$ and Mn$^{2+}$ from the adsorbent were 1 M HNO$_3$ and 1 M HCl, respectively.

1. Introduction
The presence of heavy metals in the water and soil environments is a worldwide concern because the metals are toxic to living organisms, non-degradable, and can accumulate in the food chain. Manganese (Mn) and copper (Cu) are essential metals for human life. However, in high concentration, they can cause health problems. If Cu accumulates inside the body of humans, it will create health problems in some parts, such as brain, skin, pancreas and heart [1, 2], whereas the high levels of Mn exposure can result in a typical Parkinsonism [3]. Therefore, they have to be removed from aqueous solutions the water source. Several ways have been developed to solve the pollution problem caused by metal ions. To name a few are membrane separation [4, 5] bioremediation [6], liquid-liquid and solid phase extractions [7-9], cationic exchange [10, 11], precipitation [12, 13], and adsorption [14-16]. Among them, adsorption is the most popular method in removing heavy metals because it is efficient, simple, and can be applied at low concentration, so it is easy to be conducted [17]. It has been approved that adsorption is effective to reduce the concentration of heavy metal ions from solution as reported by some studies, including the use of zeolite [18-20]. Zeolites were widely used as adsorbents because they have three dimension frameworks with opening pores and high surface area. However, their pores are small (micropores). Therefore, zeolites have limited applications. Many efforts have been performed to find adsorbents with high adsorption capacity. In this case, mesoporous materials, such as mesoporous silica becomes an alternative adsorbent.

Since the recovery of mesoporous silica (M41S family) by Mobile corporation [21], many studies have been conducted using this material as adsorbent because it has pores (higher than zeolites have) that can be adjusted to a wide range sizes using various templates, high surface area, pore volume, thermal stability, and can be made under various pHs, compositions, precursors, temperatures, as well as processing times [22-26]. The materials have been utilized to adsorb organic substances [28-30] and...
heavy metals [28]. One member of the family, MCM-48, has a three-dimensional channels [31]. The material has a greater potency for many applications than other M41S materials (MCM-41 and MCM-50) because it is easier for different host molecules to access the pore [32]. This is due to faster diffusion of adsorbates and resistance of pore blocking [33]. Functionalized MCM-48 has attracted many researchers to use it as adsorbent for heavy metals because the selectivity to remove heavy metals from aqueous solution will be improved as reviewed by Benhamou et al. [34].

The objective of this work is to investigate the capability of functionalized MCM-48 with triaminopropyltrimetoxysilane (3-APTMS) toward adsorption of Cu\textsuperscript{2+} and Mn\textsuperscript{2+} ions.

2. Materials and methods

2.1. Materials
Reagents utilized in this study were produced by Merck or Sigma-Aldrich and used directly without any treatment. Cetyltrimethylammonium bromide (CTAB), Ludox HS-40 (35% b/b SiO\textsubscript{2}, 0.4% b/b Na\textsubscript{2}O, and 60.1% b/b H\textsubscript{2}O), Triton X-100, 3-aminopropyl-trimethoxisilane, 3-APTMS (Sigma-Aldrich), acetic acid, 30%, sodium hydroxide, and hydrochloric acid were used in this research. The solutions of heavy metals (Cu\textsuperscript{2+} and Mn\textsuperscript{2+}) were made in stock solutions up to 1000 ppm of metal from the corresponding nitrate salts (Algara). Solutions of 1 M nitric acid, and 1 M hydrochloric acid were prepared from analytical grade of corresponding materials.

2.2. Synthesis of MCM-48
A hydrothermal method was used to synthesize MCM-48 following the procedure of Ryoo et al. [26] with modification as described elsewhere [35] without addition of sodium chloride as mentioned in the procedure. The removal of surfactant was conducted by washing with a mixture of HCl and ethanol as described in the procedure [35]. However, calcination in a muffle furnace was excluded. After filtering and washing with double distilled water, the remaining water was removed from the product by heating at a temperature of 378 K in an oven. The X-ray powder diffraction (XRD) method was used to characterize MCM-48 before and after the surfactant removal at room temperature with the use of a Panalytical X’Pert Powder diffractometer using a Cu K-alpha as the source of X-ray. The FTIR spectra of the two materials were taken using a Shimadzu: IR Prestige-21 FTIR Spectrometer scanned at wavenumbers ranging from 340-4500 cm\textsuperscript{-1}, a resolution of 4, and the scan number of 300.

2.3. Modification of MCM-48 with 3-APTMS
Modification was conducted following the method of Pirouzmand et al. [36] with some adjustment. In this procedure, 1.3 g of (CH\textsubscript{3}O\textsubscript{3})\textsubscript{3}Si(CH\textsubscript{3})\textsubscript{3}NH\textsubscript{3} was used instead of 1.6 g of (C\textsubscript{2}H\textsubscript{5}O\textsubscript{2})\textsubscript{3}Si(CH\textsubscript{3})\textsubscript{2}NH\textsubscript{2} as mentioned in the method. The functionalized material produced was NH\textsubscript{2}-MCM-48. The FTIR spectrum of the material was taken at the condition mentioned above.

2.4. Adsorption kinetic experiments
To determine the metals removal rate by NH\textsubscript{2}-MCM-48, a kinetic study was separately carried out at series of copper nitrate and manganese nitrate solutions with the same initial concentrations of 50 mg/L (Cu\textsuperscript{2+} and Mn\textsuperscript{2+}). The solutions were stirred in the presence of 100 mg adsorbent at room temperature for various selected times ranging from 100 to 220 min for Cu\textsuperscript{2+} ion and 600 to 1200 min for Mn\textsuperscript{2+} on a magnetic stirrer at the certain stirring rate. The solutions were filtered to remove the solids and analyzed by atomic absorption spectrophotometer (AAS). The amount of ion adsorbed by NH\textsubscript{2}-MCM-48 was calculated by subtracting the initial concentration against the final one at any contact time, \( t \) [37]. The optimum contact times for Cu\textsuperscript{2+} and Mn\textsuperscript{2+} ions were also obtained from these experiments. A blank experiment was conducted without any adsorbent.

The adsorption process was studied using either pseudo-first order or pseudo-second order kinetics. The Lagergren rate equation is generally utilized [38] for pseudo-first order process. The equation is given in equation (1),

\[
\ln (q_e - q_t) = \ln q_e - k_t t
\]
where $q_e$ is the amount of ions adsorbed at equilibrium, $q_t$ is the one adsorbed at time $t$ and $k_1$ is the rate constant of pseudo-first order process. The pseudo-second order process is shown in equation (2)

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$$  \hspace{1cm} (2)

For the equation, $q_e$ is the amount of ions adsorbed at equilibrium, $q_t$ is the one adsorbed at time $t$ and $k_2$ is the rate constant of the pseudo-second order process [38, 39].

2.5. Effect of pH on adsorption of Cu$^{2+}$ and Mn$^{2+}$ ions
The effect of pH on metal adsorption was studied by equilibrating the mixtures at different initial pH values (ranging from 2 to 7) of 50 mg/L of ion solutions before the addition of 100 mg of NH$_2$-MCM-48. The initial pH was adjusted using HCl and NaOH solutions before the addition of the adsorbent. The solution and the adsorbent were stirred at the optimum contact time. Blank experiments were carried out at each pH value without the addition of adsorbent.

2.6. Effect of initial concentration of metal ions on adsorption
The solutions used in these experiments were made by dilution of the stock solution in aquabidest. The experiments were conducted by putting 100 mg of NH$_2$-MCM-48 into beakers containing 50 mL of single metal ion solutions and mixed carefully at the optimum contact time and pH. Concentrations used were in the range of 50-600 mg/L to obtain the data to study the adsorption isotherms.

2.7. Desorption studies
Modified mesoporous silica, NH$_2$-MCM-48, previously in contact with 50 ppm of Cu$^{2+}$ and Mn$^{2+}$ ions, was washed with aquabidest to remove the excess ions from the surface. Furthermore, 0.1 g of adsorbent was inserted into three beaker glasses; each of them contained 50 mL of aquabidest, 1 M HNO$_3$, and 1 M HCl. The mixture was stirred at the optimum time of the ion adsorption. The filtrate was then analyzed to determine the amount of ions removed from the adsorbent. The amount of ions desorbed from the adsorbent was calculated using equation (3).

$$\% \text{ desorption} = \frac{\text{amount of ions desorbed from the desorvent}}{\text{amount of ions desorbed from the adsorbent}} \times 100\%$$  \hspace{1cm} (3)

3. Results and discussion

3.1. Characterization of unmodified and modified MCM-48s
X-Ray diffractograms of unmodified and modified MCM-48s are given in figure 1, which are the characteristic of well-ordered materials as described in previous work [21, 26]. The patterns were indexed in the cubic space group Ia3d. After calcination, the intensities of peaks increased due to the absence of scattering from the surfactant. The peaks also shifted to lower d spacing because of condensation and constriction of the pores.

FTIR spectra of MCM-48 before and after extraction of surfactant are shown in figure 2. Two typical regions for organic molecules (surfactants) are observed in as-synthesized MCM-48. C-H stretching modes consist of CH$_2$ symmetric ($\nu CH_2$ at ca. 2851 cm$^{-1}$), CH$_2$ antisymmetric ($\nu_s CH_2$ at ca. 2920 cm$^{-1}$), and terminal CH$_3$ asymmetric ($\nu_s CH_3$ at ca. 3015 cm$^{-1}$). C-H bending modes are observed at 1512 and 1481 cm$^{-1}$. After the removal of surfactants C-H stretching and bending are almost disappear. The Si-O stretching vibrations of silicate lattice appear with strong bands at 1225 and 1065 cm$^{-1}$ and the weaker ones at 990 and 793 cm$^{-1}$. After the surfactant removal, the peak at 1065 cm$^{-1}$ shifts to a higher wave number by approximately 25 cm$^{-1}$. This indicates that the lattice is contracted during the removal of template as mentioned in the earlier study [27]. The spectra of MCM-48 before and after modification can be seen in figure 2(c). It is clear that after modification of MCM-48 with 3-APTMS, two peaks appear at 4243 and 3368 cm$^{-1}$ indicating the presence of $-\text{NH}_2$ functional group. The stretching
vibrations at 2932 and 2885 cm\(^{-1}\) and bending vibrations at 1643, 1560, and 1491 cm\(^{-1}\) belong to \(-\text{C-H}\) group from 3-APTMS. The shift of peaks at 962 and 800 cm\(^{-1}\) to 793 and 694 cm\(^{-1}\) indicate an interaction between silanol group and 3-AMTMS. The vibration at 1560 cm\(^{-1}\) shows the presence of bending vibration of N-H from the primary amine [40]. The stretching vibration of C-N appears at 1389 cm\(^{-1}\). The peak at the wavenumber of 694 cm\(^{-1}\) belongs to the vibration of Si-CH\(_2\)-R.

3.2. Optimum time of adsorption and kinetic study

Figure 3 shows the amount of ion adsorbed as a function of the contact time and pH. It is obvious that the adsorption of Cu\(^{2+}\) and Mn\(^{2+}\) ions increases with the increase of the adsorption time until the equilibrium is reached. Figure 3a shows that the optimum time to adsorb Cu\(^{2+}\) and Mn\(^{2+}\) ions are 200 and 1200 min, respectively. Therefore, these contact times were used for further experiments.

![Figure 1. XRD patterns of (a) MCM-48 and (b) NH\(_2\)-MCM-48](image)

![Figure 2. FTIR spectra of materials: (a) as-synthesized MCM-48, (b) MCM-48 after removal of template and (c) NH\(_2\)-MCM-48](image)
Using the data of amount adsorbed with contact times, the kinetic study was performed and the kinetic data is given in table 1. All correlation coefficient uses pseudo and second order equations close to 1. However, the amount of ions adsorbed at the equilibrium obtained from the second order equation is closer to the one obtained from experiments. The results indicated that the adsorption of metal ions follow the pseudo-second order with the rate constant ($k_2$) of $3.98 \times 10^{-4}$ and $1.62 \times 10^{-4}$ g mg min$^{-1}$ for Cu$^{2+}$ and Mn$^{2+}$ adsorption, respectively. The rate constant of Cu$^{2+}$ adsorption is higher than that of Mn$^{2+}$ adsorption. The results were in agreement with the results of the optimum contact times where the optimum contact time of Cu$^{2+}$ adsorption is lower than that of Mn$^{2+}$ adsorption.
3.3. The optimum pH of adsorption
The amount of Cu\(^{2+}\) and Mn\(^{2+}\) ions adsorbed on MCM-48-NH\(_2\) with various pH solutions is given in figure 3b. The amount of Cu\(^{2+}\) and Mn\(^{2+}\) ions adsorbed on MCM-48-NH\(_2\) was studied at the pH range of 2-7. It is clear that the amount of ions adsorbed increases sharply from pH of 2 to 3 for both ions. The amount of ions adsorbed increases gradually from pH of 3 to 6 and achieves the optimum at the pH of 6. The amount of ions adsorbed at the pH of 2 is low because the ions compete with the H\(^+\) ion in the solution. In addition, at the lower pH the surface of MCM-48-NH\(_2\) will be protonated to form MCM-48-NH\(_3^+\) that inhibit the ions to be interacted with the adsorbent. At higher pH, the protonated surface is lesser and as a result, the amount of ions adsorbed is higher. At the pH higher than 6, precipitates will be formed so that the amount of ions in the solution will be reduced. From figure 3b, the optimum pH of adsorption for both ions is 6. The pH was used for studying the effect of initial concentrations on the adsorption in order to find the adsorption capacity.

3.4. Adsorption isotherm
The adsorption isotherms of Cu\(^{2+}\) and Mn\(^{2+}\) ions on MCM-48-NH\(_2\) are given in figure 4. The adsorption of ions increases with the increase of initial concentration of ions. Figure 4 shows that the ions adsorption continues to increase at the measured concentration. Therefore, to find the capacity of adsorption, Langmuir and Freundlich isotherms were utilized. In the former isotherm, monolayer adsorption is assumed to be occurred on the adsorbent’s surface with a fixed amount of identical sites \[41-42\]. The isotherm is shown in equation (4) as the form of linear equation:

\[
\frac{C_e}{q_e} = \frac{1}{Q_o b} + \frac{C_e}{Q_o} \tag{4}
\]

where \(C_e\) is the metal ion concentration at equilibrium (mg L\(^{-1}\)), \(q_e\) is the amount of ions adsorbed (mg g\(^{-1}\)), \(Q_o\) is the capacity of adsorption (mg g\(^{-1}\)), and \(b\) is the Langmuir coefficient (L mg\(^{-1}\)). The latter isotherm (empirical equation) assumes that multilayer adsorption occurs on a heterogeneous surface \[41-42\]. The equation can be seen in equation (5):

\[
log q_e = log k + \frac{1}{n} log C_e \tag{5}
\]

where \(q_e\) is the amount of metal ions adsorbed (mg g\(^{-1}\)), \(C_e\) is the concentration of metal ions at equilibrium (mg L\(^{-1}\)), \(k\) is the Freundlich constant associated with the capacity of adsorption (mg g\(^{-1}\)), and \(n\) is the adsorption intensity. Table 2 summarizes the Langmuir and Freundlich constants of the metal ion adsorption on NH\(_2\)-MCM-48.

The adsorption of Cu\(^{2+}\) and Mn\(^{2+}\) ions on MCM-48-NH\(_2\) fits both Langmuir and Freundlich models. Table 2 shows that the adsorption capacity of Mn\(^{2+}\) is higher than that of Cu\(^{2+}\). This is consistent with the Hard Soft Acid Base (HSAB) theory where –NH\(_2\) is a hard base that can well interact with Mn\(^{2+}\) (a hard acid) compared to Cu\(^{2+}\) (a borderline acid).

3.5. Desorption studies
Figure 5 shows the percentage of ions desorbed by several desorbing agent. The amount of both ions desorbed by aquabidest is very small, namely 0.02 and 0.01% for Cu\(^{2+}\) and Mn\(^{2+}\) ions. The amount desorbed by 1 M HNO\(_3\) and 1 M HCl is considerably higher than that by aquabidest. This indicated that the adsorption of ions was mainly occurred by chemical adsorption. The best desorbing agents for Cu\(^{2+}\) and Mn\(^{2+}\) ions were 1 M HCl and 1 M HNO\(_3\), respectively. The desorbing agents that behave as an acid can protonate the surface. As a consequence, the ions will be removed from the surface of the adsorbent.
Figure 4. Adsorption isotherms of Cu$^{2+}$ and Mn$^{2+}$ ions

Table 2. The constants of Langmuir and Freundlich models for the metal ions adsorption on NH$_2$-MCM-48

| Ion    | Langmuir model | Freundlich model |          |          |          |
|--------|----------------|------------------|----------|----------|----------|
|        | $Q_o$ (mg g$^{-1}$) | $b$ (L mg$^{-1}$) | $R^2$    | $k$ (mg g$^{-1}$) | $n$ (g L$^{-1}$) | $R^2$ |
| Cu$^{2+}$ | 33.00          | 0.52             | 0.99     | 13.26    | 0.21     | 6.65    | 0.98 |
| Mn$^{2+}$ | 44.05          | 0.80             | 0.99     | 19.35    | 0.35     | 7.17    | 0.98 |

Figure 5. Percentage of ion desorbed from MCM-48 after the adsorption

4. Conclusions
The study concluded that the amount of Cu$^{2+}$ and Mn$^{2+}$ ions adsorbed on MCM-48-NH$_2$ achieved the optimum at the contact time of 200 and 1200 min, respectively and at the pH of 6 for both ions. Both ion adsorptions fitted the pseudo-second order, in which the rate constant of Cu$^{2+}$ absorption was higher than that of Mn$^{2+}$ adsorption. In addition, both ion adsorptions followed the Langmuir and Freundlich isotherms. The adsorption capacity for Mn$^{2+}$ ion (0.80 mmol g$^{-1}$) was higher than that for Cu$^{2+}$ ion (0.52
mmol g\(^{-1}\)). Furthermore, the best desorbing agent for Cu\(^{2+}\) ion was 1 M HCl solution, whereas for Mn\(^{2+}\) ion was 1 M HNO\(_3\).

Acknowledgements

Professor Russell F. Howe and Bayu Adi Samodro from the University of Aberdeen are greatly acknowledged for their assistance in XRD measurements.

References

[1] Veli S and Alyuz B 2007 J. Hazard. Mater. 149 226-33
[2] Wang N, Han Y, Liu Y, Bai T, Gao H, Zhang P, Wang W and Liu W 2012 J. Hazard. Mater. 213-214 258-64
[3] Guilarte T R and Gonzales K K 2015 Toxicol. Sci. 146 204-12
[4] Fatin-Rouge N, Dupont A, Vidonne A, Dejeu J, Fievet P and Foissy A 2006 Water Res. 40 1303-9
[5] Gao J, Sun S P, Zhu W P and Chung T S 2014 Water Res. 63 252-61
[6] Kang S Y, Lee J U and Kim K W 2007 Biochem. Eng. J. 36 54-8
[7] Mane C P, Mahamuni S V, Kolekar S S, Han S H and Anuse M A 2012 Arabian J. Chem. 9 S1420-7
[8] Su B L, Ma X C, Xu F, Chen L H, Fu Z Y, Moniotte N, Maamar S B, Lamartine R and Vocanson F 2011 J. Colloid Interface Sci. 360 86-92
[9] Al-bishri H M, Abdel-Fattah T M and Mahmoud M E 2012 J. Ind. Eng. Chem. 18 1252-7
[10] Abdel-Aziz M H, Amin N K and El-Ashtoukhy E S Z 2013 Hydrometallurgy 137 126-32
[11] Zewail T M and Youssef N S 2015 Alexandria Eng. J. 54 83-90
[12] Sakai H, Matsuoka S, Zenckeno A A and Murata S 2009 Colloids Surf. A: Physicochem. Eng. Aspects 347 210-4
[13] Fu F, Xie L, Tang B, Wang Q and Jiang S 2012 Chem. Eng. J. 189-190 283-7
[14] Wu S, Li F, Xu R, Wei S and Li G 2010 J. Nanoparticle Res. 12 2111-24
[15] Hu X N, Han Y, Li J Y, Wu J Y, Chen J R and Tang M J 2012 Adv. Mater. Res. 413 148-53
[16] Tresintsi S, Mitrakas M, Simeonidis K and Kostoglou M 2015 J. Colloid Interface Sci. 460 1-7
[17] Cao J, Wu Y, Jin Y, Yihliyan P and Huang W 2014 Taiwan Inst. Chem. Eng. 45 860-8
[18] Oliviera L C A, Petkowicz D I, Smaniotto A and Pergher S B C 2004 Water Res. 38 3699-704
[19] Jamil T S, Ibrahim H S, Abd El-Maksoud I H and El-Wakeel S T 2010 Desalination 258 34-40
[20] Motisi T, Rowson N A and Simmons J M H 2011 Int. J. Miner. Process. 101 42-9
[21] Beck J S et al. 1992 J. Am. Chem. Soc. 114 10834-43
[22] Kresge C T, Leonowicz M E, Roth W J, Vartuli J C and Beck J S 1992 Nature 359 710-2
[23] Vartuli J C, Kresge C T, Leonowicz M E, Chu A S, McCullen S B, Johnson I D and Sheppard E W 1994 Chem. Eng. 360 2070-7
[24] Huo Q, Leon R, Petroff P M and Stucky G D 1995 Science 268 1324-7
[25] Ryoo R, Kim J M, Ko C H and Shin C H 1996 J. Phys. Chem. 100 17718-21
[26] Ryoo R, Joo S H and Kim J M 1999 J. Phys. Chem. B 103 7435-40
[27] Taba P 2001 Mesoporous Solids as Adsorbents PhD Thesis (Sydney: The University of New South Wales, Australia)
[28] Sayar A, Hamoudi S and Yang Y 2005 Chem. Mater. 17 212-6
[29] Taba P, Howe R F and Moran G 2008 Indo. J. Chem. 8 1-5
[30] Taba P 2009 Indo. J. Chem. 9 184-8
[31] Schumacher K, Grün M and Unger K K 1999 Microporous and Mesoporous Materials 27 201-6
[32] Okhovvik O, Antochshuk V and Jaronec M 2004 Colloids Surf. A: Physicochem. Eng. Aspects 236 69-72
[33] Shim W G, Lee J W and Moon H 2006 Microporous and Mesoporous Materials 88 112-25
[34] Benhamou A, Baud M, Derriere Z and Basly J P 2009 J. Hazard. Mater. 171 1001-8
[35] Taba P 2008 Makara Sains 12 120-5
[36] Pirouzmand M, Amini M M and Safari N 2008 J. Colloid Interface Sci. 319 199-205
[37] Deng S and Ting Y P 2005 Environ. Sci. Technol. 39 8490-6
[38] Hossain K Z, Monreal C M and Sayari A 2008 Colloids Surf. B: Biointerfaces 62 42-50
[39] Yurdakoç M, Seki Y, Karahan S and Yurdakoç K 2005 J. Colloid Interface Sci. 286 440-6
[40] Yokoi T, Yoshitake H and Tatsumi T 2004 J. Mater. Chem. 14 951-7
[41] Temoçin Z and Yigitoglu M 2010 Water, Air, and Soil Pollut. 210 463-72
[42] Namasivayam C, Radhika R and Suba S 2001 Waste Manag. 21 381-7