

Amine-functionalized MCM-48 as Adsorbent of Zn²⁺ and Ni²⁺ Ions

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ABSTRACT

A compound, 3-aminopropyltrimethoxy silane, has been used to modify mesoporous silica, MCM-48. The modified silica (NH₂-MCM-48) was utilized to remove Zn²⁺ and Ni²⁺ ions from solutions. The mesoporous material was synthesized in the alkaline solution. Characterization of the unmodified materials was conducted by X-ray diffraction and FT-IR spectroscopy. The ions adsorbed on NH₂-MCM-48 were studied at various pHs, contact times and initial ions concentrations. An Atomic Absorption Spectrophotometer (AAS) measured the ions content in the solution. Pseudo-first-order and pseudo-second-order models performed the kinetic adsorption. The adsorption isotherm was examined by Langmuir and Freundlich isotherms. The result found that optimum contact time for the adsorption of Zn²⁺ ion was lower than that for Ni²⁺ ion. The adsorption followed the pseudo-second-order model with the adsorption rate of 4.56x10⁻² g mg⁻¹ min⁻¹ for Zn²⁺ ion and 7x10⁻⁴ g mg⁻¹ min⁻¹ for Ni²⁺ ion. The optimum pH was 6 and 4 for Zn²⁺ and Ni²⁺ adsorption, respectively. The uptake of both ions from solutions by NH₂-MCM-48 fixed better the Langmuir than the Freundlich model with the adsorption capacity of 0.55 and 0.43 mmol g⁻¹, correspondingly. This research work provides valuable information on the interaction between the ions and the functional group of adsorbent.

Keywords: Adsorption; 3-APTMS; mesoporous silica; heavy metals

1. INTRODUCTION

Heavy metals are well known as one of the toxic compounds to a living organism. Therefore, it is a great concern of many researchers to their presence in the water and soil environments. They are non-degradable and can accumulate in the food chain. Zinc (Zn) and nickel (Ni) are examples of toxic heavy metals especially in high concentration that can cause problems in human's health if they contaminate the water environment. Therefore, their existence in high concentration in the water environment has to be reduced. Several methods, such as sequential removal and separation [1], bioremediation [2], liquid-liquid extraction [3], membrane filtration [4] solid phase

extraction [5], ion exchange [6,7], precipitation [8,9], ultrasonic and mechanical soil washing process [10], adsorption [11-14], biosorption [15-17], electro dialytic treatment [18], ultrafiltration and flocculation [19], phytoremediation [20] have been used to reduce or remove metal ions from aqueous solution. Adsorption was widely applied for removing heavy metals. There were several reasons for the use of the method. It was simple and efficient to be used. In addition, it can be used for removing metal ions with low concentration [21]. Some works have reported the effective use of the method as adsorbent including the utilization of zeolite [22-23]. Although the zeolite materials have some advantages, such as the three dimension of

their frameworks with pores opening and their high surface area, pores over them are small (micropores) that can limit their applications. Therefore, finding other adsorbents having high adsorption capacity have been the interesting matter. Mesoporous materials, such as mesoporous silicas are alternative adsorbents. One kind of mesoporous silicas is the M41S family discovered by Mobile Corporation [24].

M41S materials have higher pores than zeolites have, the pores can be varied using various templates. They have also a high surface area and pore volume. Furthermore, they are thermally stable and can be made under various conditions, such as pH, composition, precursor, temperature, along with time [25-27]. The use of materials as an adsorbent of organic substances [28-30]) and heavy metals [14, 27,31] has been reported. One member of the family is MCM-48 having a three-dimensional channel. The channel makes MCM-48 to have greater potency than other M41S materials (MCM-41 and MCM-50) to be used as adsorbent due to faster diffusion of adsorbates into the pores and resistance of pore blocking [28]. MCM-48 has hydroxyl group that can interact with heavy metal ions. In order to increase the adsorption capacity, modification of the group was widely conducted by functional materials. Benhamou *et al.* [31] reported that the functionalized MCM-48 material has been used by many researchers as an adsorbent for removing heavy metals from aqueous solution due to their improved selectivity after the

modification of the silanol group. One of the functional materials that can be used to modify mesoporous silica is 3-APTMS. The modified silica with the modifying agent has been previously utilized as an adsorbent of Cu^{2+} and Mn^{2+} ions from aqueous solution [14]. Although the material had higher capacity in adsorbing the latter ion (hard acid) than the former one (borderline acid), it had also the potency for the adsorption of the borderline acid. Therefore, it is necessary to study the adsorption of other heavy metal ions on amine-functionalized MCM-48.

In this study, the modified material was used to adsorb other borderline ions, Zn^{2+} and Ni^{2+} , in the aqueous environment. The kinetics and equilibrium adsorption of the ions on $\text{NH}_2\text{-MCM-48}$ were studied. In addition, the effect of pH and concentration on the adsorption was also an important part of the study.

2. METHODOLOGY

A. Materials

Reagents used in this research were Ludox HS-40 (35% b/b SiO_2 , 0.4% b/b Na_2O , and 60.1% b/b H_2O , Du Pont), cetyltrimethylammonium bromide (CTAB, Sigma Aldrich), Triton X-100 (Sigma Aldrich), 3-aminopropyltrimethoxysilane (3-APTMS, Sigma-Aldrich), toluene, chloroform, nitric acid, $\text{Zn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ purchased from Merck. All reagents were used without any treatment.

B. Methods

B.1. Synthesis and Modification of MCM-48

The synthesis of MCM-48 was conducted following the procedure given elsewhere [14]. The X-ray powder diffraction (XRD) was used to prove that the synthesis has been successfully obtained. The XRD patterns were recorded after the removal of surfactant (template) at room temperature by using a diffractometer Shimadzu 6100 using a Cu K-alpha as a source of X-ray at 40 kV dan 30 mA and runned at 2 theta between 1.5-10°, a scan

B.2. Adsorption kinetic experiments

A kinetic adsorption of the Zn²⁺ and Ni²⁺ ions on NH₂-MCM-48 was studied by using zinc nitrate solutions with the Zn²⁺ initial concentrations of 10 mg/L and the Ni²⁺ initial concentration of 20 mg/L. The adsorbent as many as 100 mg was put into 50 mL of the ion solutions and stirred at room temperature for times ranging from 20 to 160 min for Zn²⁺ ion and 30 to 360 min for Ni²⁺ on a magnetic stirrer at the same stirring rate. The solids were removed by filtering and the filtrates were examined by an atomic absorption spectrophotometer. The ion adsorbed by NH₂-MCM-48 was determined by subtracting the initial concentration to the final one at any contact time, t. These experiments can also provide the optimum contact times of Zn²⁺ and Ni²⁺ ions. The blank experiment was also conducted without any adsorbent as the control experiment.

The pseudo-first order or pseudo-second order kinetics was applied to study the adsorption. The Lagergren rate equation is

rate of 5° min⁻¹ using a divergent slit of 1° and a receiving slit of 0.3 mm. The FTIR spectrum before and after the surfactant removal was taken with wavenumbers ranging from 340-4500 cm⁻¹, the resolution and the scan number of 4 and 300, respectively. Modification of MCM-48 was conducted following the method of Pirouzmand, *et al.* [32] with some adjustment as has been described elsewhere [14]. The infrared spectrum of the material was taken in the same condition as that mentioned above.

generally utilized [33] for pseudo-first order process as can be seen in equation (1),

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (1)$$

where q_e and q_t are the amount of ions adsorbed at equilibrium and at time t , respectively and k_1 is the rate constant of the pseudo-first order process.

The pseudo-second order process is shown in equation (2),

$$\frac{t}{q_e} = \frac{1}{k_2 q_e^2} + \frac{t}{C_e} \quad (2)$$

where q_e and q_t are the amount of ions adsorbed at equilibrium and at time t , respectively and k_2 is the rate constant of the pseudo-second order process [34,35].

B.3. Effect of pH on adsorption of Zn²⁺ and Ni²⁺ ions

The influence of pH on the adsorption of Zn²⁺ and Ni²⁺ ions was investigated by carrying out the adsorption experiments at various initial pH (ranging from 3 to 8 for Zn²⁺ ion and 3 to 7 for Ni²⁺ ion). The initial concentration of ions and the amount of adsorbent used in the experiments was the

same as that in the kinetic experiments. Solutions of HCl and NaOH were used to set the initial pH. The pH adjustment was carried out before the addition of the adsorbent. The experiments were performed at the optimum contact time and the blank experiment was also conducted without the addition of adsorbent at each pH value.

B.4. Effect of initial concentration

The effect of the initial concentration of Zn^{2+} and Ni^{2+} solutions on adsorption was studied by putting 100 mg of NH_2 -MCM-48 in beakers containing 50 mL of single metal ion solutions at the optimum contact time and pH. The experiments were performed at the ion concentration range of 20 – 320 mg/L.

3. RESULTS AND DISCUSSION

A. Characterization of MCM Materials

The XRD pattern of unmodified MCM-48 after the removal of the template is given in Fig. 1. The diffraction pattern of MCM-48 shows one peak at 2θ of 2.4° (211). The peak is one of the characteristic peak of MCM-48 as reported previously [14,24,26). Other peaks belong to MCM-48 are not observed in the pattern. This is because of the limitation of the XRD instrument that does not have the facility for low angles.

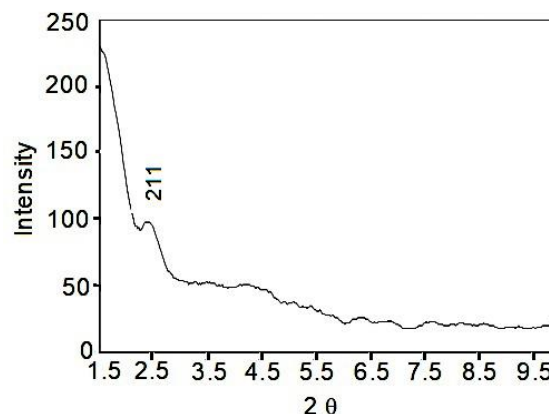


Fig. 1. XRD pattern of MCM-48

FT-IR spectra of MCM-48 before and after extraction of surfactant as well as after modification (NH_2 -MCM-48) can be seen in Fig. 2. It is clear that after the surfactant extraction from MCM-48, almost all surfactants had been removed. After modification, there is an interaction between silanol groups and 3-APTMS shown by the presence of C-H, N-H, C-N and Si- CH_2 -R obtained from 3-APTMS. This is in parallel with the previous study [14].

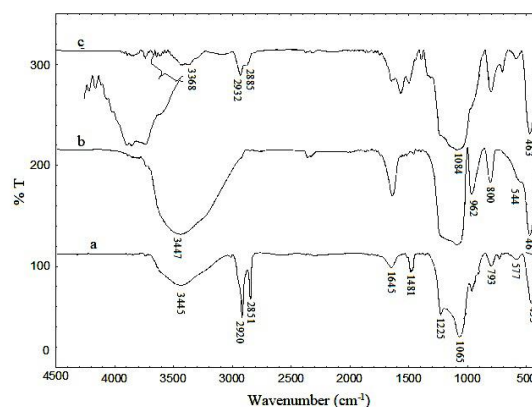


Fig. 2. FTIR spectra of a) MCM-48, b) MCM-48 after removal of the template, and c) NH_2 -MCM-48

B. Optimum time of adsorption and kinetic study

The amount of Zn^{2+} and Ni^{2+} adsorbed by NH_2 -MCM-48 as a function of the contact time is given in Fig. 3. The adsorption of the ion increases with increasing the contact time. The maximum amount adsorbed achieves when the equilibrium reached *i.e.* at the optimum time. The optimum times for the adsorption of Zn^{2+} and Ni^{2+} are 60 and 300 min, respectively. The contact time was applied for experiments at various pHs and concentrations.

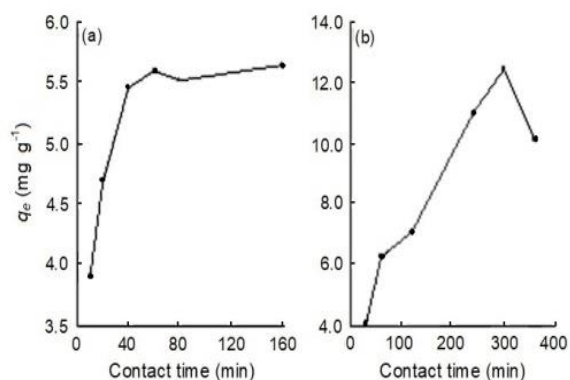


Fig. 3. The influence of contact time on the amount of a) Zn^{2+} and b) Ni^{2+} ions adsorbed on NH_2 -MCM-48- NH_2

Using data of the amount of ions adsorbed at various contact times, the kinetic data can be obtained as given in Table 1. Although the correlation coefficient using the pseudo-first order equation for both ions is close to 1, the amount of ion adsorbed at the equilibrium obtained from the equation for the second order equation is closer to the one obtained from experiments. These indicate that the adsorption of the ions are in parallel with the pseudo- second order equation. The rate

constants (k_2) are 4.56×10^{-2} and $7 \times 10^{-4} \text{ g mg}^{-1} \text{ min}^{-1}$ for Zn^{2+} and Ni^{2+} ions, respectively. The results were in consistent with the optimum contact times mentioned above, the time required to achieve the equilibrium in adsorption of Ni^{2+} ion is higher than that of Zn^{2+} ion.

C. The optimum pH of adsorption

The amount of Zn^{2+} and Ni^{2+} adsorbed on NH_2 -MCM-48 as a function of the pH of solution is clearly illustrated in Fig. 4. The amount of Zn^{2+} ion adsorbed on NH_2 -MCM-48 increases from pH of 3 to 6 for Zn^{2+} ion.

After that, the decrease in the adsorption is observed from pH 6 to 8. The amount of Ni^{2+} ion adsorbed increases from 3 to and the gradual decrease occurs from the pH of 4 to 7. The maximum adsorption of Zn^{2+} ion is at the pH of 6, whereas that of Ni^{2+} ion is at the pH of 4. The low amount of ions adsorbed at the pH of 2 is caused by the competition of the ions to be adsorbed with the H^+ ion found in the solution.

In addition, the surface of NH_2 -MCM-48 will be protonated at the low pH. Therefore, $MCM-48-NH_3^+$ will be formed in the surface and inhibit the ions to interact with the adsorbent. At higher pH, the amount of ions adsorbed is higher because the protonated surface is lower [14] causing the higher negative charge on the surface that can enhance the adsorption. Further increasing of pH (at very high pH), precipitation of metal hydroxide can be formed resulting in the lower concentration of ions detected in solutions. From the results, it is clear that the optimum pH for the adsorption

of Zn^{2+} ion and Ni^{2+} are 6 and 4, respectively. The pH was used for studying the effect of

initial concentrations on the adsorption in order to find the adsorption capacity.

Table 1. Kinetic data of Zn^{2+} and Ni^{2+} ions adsorbed on NH_2 -MCM-48

Data	Zn^{2+}	Ni^{2+}
<i>Pseudo first order</i>		
$k_1(\text{min}^{-1})$	0.02	8.2×10^{-3}
$q_e(\text{mg g}^{-1})$	4.26	11.16
R^2	0.99	0.95
Linear equation	$y = -0.0366x + 0.6294$	$y = -0.0036x + 1.0512$
<i>Pseudo second order</i>		
$k_2(\text{g mg}^{-1} \text{min}^{-1})$	4.56×10^{-2}	7×10^{-4}
$q_e(\text{mg g}^{-1})$	5.80	13.44
R^2	1.00	0.94
Linear equation	$y = 0.1723x + 0.6505$	$y = 0.0693x + 6.1110$
Experimental $q_e(\text{mg g}^{-1})$	5.60	12.46

D. Adsorption Isotherms

The amount of ions adsorbed increases with the increase of the initial concentration of ions. From Fig. 3, it is clear that the amount of ions adsorbed remains increase at the measured concentration. Therefore, Langmuir and Freundlich models were used to determine the adsorption capacity.

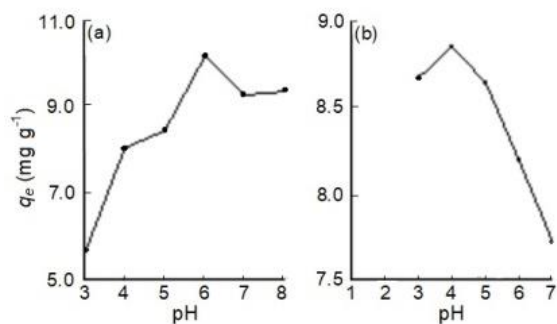


Fig. 4. The effect of pH on the amount of a) Zn^{2+} and b) Ni^{2+} ions adsorbed on NH_2 -MCM-48

The Langmuir isotherm assumes monolayer adsorption on the surface of adsorbent with a finite number of identical sites [33,34]. The linear equation of the model is given in equation (3),

$$\frac{C_e}{q_e} = \frac{1}{Q_0 b} + \frac{C_e}{Q_0} \quad (3)$$

where C_e is the equilibrium concentration of metal ions (mg L^{-1}), q_e is the amount of metal ion adsorbed (mg g^{-1}), Q_0 is the adsorption capacity (mg g^{-1}), and b is the Langmuir coefficient (L mg^{-1}).

The Freundlich isotherm (empirical equation) assumes that the adsorption occurs on a heterogeneous surface through multilayer adsorption [34]. The linear equation can be seen in equation (4),

$$\log q_e = \log k + \frac{1}{n} \log C_e \quad (4)$$

where q_e is the amount of metal ions adsorbed (mg g^{-1}), C_e is the equilibrium concentration of metal ions (mg L^{-1}), k is the Freundlich adsorption constant related to the adsorption capacity of adsorbent (mg g^{-1}), and n is the adsorption intensity.

Table 2 summarized the Langmuir and Freundlich constant of the metal ion adsorption on $\text{NH}_2\text{-MCM-48}$. The adsorption of Zn^{2+} and Ni^{2+} ions on $\text{NH}_2\text{-MCM-48}$ fits better Langmuir equation rather than the Freundlich one indicating that the adsorption is monolayer. It is clear that the adsorption capacity of Zn^{2+} is higher than that of Ni^{2+} . The same trends were reported by other studies [35,36]. By comparing the results with the adsorption of Cu^{2+} ion (Zn^{2+} , Ni^{2+} and Cu^{2+} are borderline acids) on $\text{NH}_2\text{-MCM-48}$ reported previously [14], it was found

that the trend of the adsorption capacity was in the order of $\text{Zn}^{2+} > \text{Cu}^{2+} > \text{Ni}^{2+}$, which coincide reasonably well with the reversed order trend of van der Waals radius as Ni^{2+} (163 pm) $>$ Cu^{2+} (140 pm) $>$ Zn^{2+} (139 pm). This is consistent with the fact that the ion with less-hydrated ionic radius is preferably adsorbed at the surface. All the van der Waals radii were taken from Ref. [35]. Furthermore, the ionic radius of metal ions has been considered to be one factor affecting the adsorption of metal ions. It was reported that the ionic radius affected the amount of metal ions adsorbed in a linear way [37]. The ionic radius of metal ions is in the order of Zn^{2+} (74 pm) $>$ Cu^{2+} (72 pm) $>$ Ni^{2+} (69 pm). Therefore, the results of the adsorption capacity are linear to the ionic radius of metal ions in this study.

Table 2. Langmuir and Freundlich constants for the adsorption of metal ions on $\text{NH}_2\text{-MCM-48}$

Ion	Langmuir model				Freundlich model			
	Q_0 mg g^{-1}	B mmol g^{-1}	B L mg^{-1}	R^2	k mg g^{-1}	n mmol g^{-1}	n g L^{-1}	R^2
Zn^{2+}	35.71	0.56	0.03	0.99	5.68	0.09	3.18	0.98
Ni^{2+}	25.45	0.43	0.07	0.98	11.89	0.2	8.79	0.94
Cu^{2+}	33	0.52	0.05	0.99	13.26	0.21	6.65	0.98 ^a

^a Taken from Ref. [14]

The interaction of Zn^{2+} and Ni^{2+} ions with $\text{NH}_2\text{-MCM-48}$ was studied using FTIR. Functional groups found in $\text{NH}_2\text{-MCM-48}$ before and after are given in Table 3. It is clear that after the adsorption of the metal ions, the absorption bands at 3424 and 3368 cm^{-1} due to -N-H stretching vibrations become one band and shift to 3443 and 3442 cm^{-1} for the adsorption of Zn^{2+} and Ni^{2+} ions, respectively, indicating that both ions interacted with the $-\text{NH}_2$ group of

the adsorbent. The fact was supported by decreasing N-H bending intensity caused by the interaction of ions with $-\text{NH}_2$ groups through electron pair donor from the nitrogen atom in the amino group. In addition, the intensity of absorption band at a wavenumber of 1389 cm^{-1} increases because the interaction of the ions with the $-\text{NH}_2$ groups can cause the increase of the polarity of $\text{NH}_2\text{-MCM-48}$ leading to the increase in the absorption intensity.

Table 3. Vibrations of functional groups in NH₂-MCM-48 before and after adsorption of Zn²⁺ and Ni²⁺ ions

Vibration	Wavenumbers (cm ⁻¹)		
	Before adsorption	After adsorption of Zn ²⁺ ion	After adsorption of Ni ²⁺ ion
-N-H stretching	3424,3368	3443	3442
-N-H bending	1560	1560 (intensity decreased)	1548 (intensity decreased)
-C-N	1389	1383 (Intensity increased)	1383 (Intensity increased)

4. CONCLUSION

The study concluded that the amount of Zn²⁺ and Ni²⁺ ions adsorbed on NH₂-MCM-48 was optimum at a contact time of 60 and 300 min, respectively. The optimum pH of adsorption was 6 for Zn²⁺ ion and 4 for Ni²⁺ ion. The metal ions adsorption fitted the pseudo-second order and the Langmuir isotherm where the adsorption capacity of Zn²⁺ ion was higher than that of Ni²⁺ ion. FTIR data clearly showed that there was an interaction between the ions and the functional group of adsorbent especially with amino groups.

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