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Adsorption of Pb^{2+} on Thiol-functionalized Mesoporous Silica, SH-MCM-48

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Abstract. Modification of mesoporous silica, MCM-48, by using 3-mercaptopropyltrimethoxysilane has been successfully conducted. MCM-48 and SH-MCM-48 were characterized using XRD and FTIR. SH-MCM-48 was used as an adsorbent of Pb^{2+} ions from solution. A number of Pb^{2+} ions adsorbed were studied as the function of time, pH, and concentration. The concentration of the ions after adsorption was determined by an Atomic Absorption Spectrophotometer. The removal of the adsorbed ions from the SH-MCM-48 was also studied using several desorbing agents. The result showed that the optimum time was 20 minutes and optimum pH was 4. The adsorption of Pb(II) ion followed the pseudo-second-order with the rate constant of 0,2632 $g \cdot mg^{-1} \cdot min^{-1}$. Adsorption of Pb(II) ion fitted the Langmuir isotherm with the adsorption capacity of 0,1088 mmol/g. The best desorbing agent to remove the adsorbed ion from SH-MCM-48 was 0.3 M HCl solution with the desorption percentage of 58.6%.

1. Introduction

The fast growth of industry can result in the positive impact into the community. However, it can also create negative impact to the environment due to its waste. One industry that can cause a problem to the water environment is electroplating where its waste contains heavy metals. Heavy metals are toxic and carcinogenic to a human being. Lead is an example of the metals that are *non-biodegradable* in the environment [1]. The metal can cause the toxic effect to people, especially at the concentration is above the threshold value. Therefore, their existence in the waters can be dangerous. Handling of heavy metal waste has been done to overcome pollution and the risk of poisoning for living things [2]. One method that widely used is the adsorption method [3, 4] which is one of the simplest and quite effective processes in removing heavy metals from liquid waste [5, 6, 7].

The adsorption method is generally based on the interaction of metal ions with functional groups present on the surface of the adsorbent through the formation of the complex and usually occurs on the surface of the solid containing the functional groups such as -OH, -NH, -SH and –OOH [8]. Several adsorbents of porous material have been developed to adsorb heavy metals. According to the classification of IUPAC, the porous material is divided into three kinds based on the diameter of the pore, i.e. micropore, material having pore diameter of <2 nm, mesopore with the pore diameter of between 2-50 nm and macropore with the pore diameter of > 50 nm [9]. The development of mesoporous material is now the concern of many researchers, especially since the discovery of M41S family, materials from silicates or aluminosilicates, by researchers from Mobil Corporation United States in 1992. [10]. This mesoporous silica consists of MCM-41 which have hexagonal structures, MCM-48 which has a cubic structure, and MCM-50 with a lamellar (flat) and unstable structure [11, 12]. MCM-48 have been used as an adsorbent for organic compound because MCM-48 has large surface area and regular pores [13]. The material has an advantage compared to MCM-41 and MCM-50. It consists of two mesoporous channel networks that form a three-dimensional channel system that allows the particles to enter easily into the material because the pores are not limited in one direction.

The MCM-48 surface has silanol and siloxane groups that have little role in the metal ion adsorption process so that modification by adding an active functional group will increase its effectiveness and selectivity [14, 15]. Several modifications have been made to increase the adsorption capacity of MCM-48. Wang and Li [16] have modified MCM-48 by adding a thiol group (-SH) on its surface to adsorb Hg^{2+} ions. Modified MCM-48 with thiol (-SH) groups to adsorb Ag^{+} and Cd^{2+} ions [14]. The adsorption capacity for Ag^{+} and Cd^{2+} ions was 2.73 mmol g^{-1} and 0.14 mmol g^{-1}, respectively.

Based on the principle of Hard Soft Acid Base (HSAB), modified MCM-48 with thiol (-SH) groups of the soft base can bind hard acidic of metal ions [17]. But it is possible that the material with the thiol group (-SH) can interact with borderline acidic metal ions such as Pb (II) ions due to other factors, such as surface area large and regular pores that can make it be able to interact with the borderline acid [13].

The adsorption process is usually followed by a desorption process to determine whether adsorbate can be recovered. Desorption can be carried out by contacting the desorbing agent with adsorbents containing the metal ion. The desorbing agent may be acidic, alkaline, or neutral [15].

Based on the above description, the study modified MCM-48 with thiol groups (-SH) of the 3-MPTMS compound. MCM-48-SH is then used to adsorb Pb^{2+} ions. Adsorption of metal ions is strongly influenced by pH, contact time, and solution concentration [14]. Therefore, the effect of these parameters was studied on the adsorption of Pb^{2+} ions to obtain the optimum conditions. To determine the possibility of reuse of the adsorbent, a desorption study of Pb^{2+} ions from MCM-48-SH was also performed.

2. Experimental

2.1. Materials

The materials used in this study were cetyl trimethyl ammonium bromide (CTAB) obtained from Sigma Aldrich, Ludox HS40 consisting of SiO_2 (35% w/w), Na_2O (0.4% w/w) and H_2O (60.1% w/w) obtained from Du Pont, Triton X-100 purchased from Sigma Aldrich, 3-mercaptopropyltrimethoxysilane, 3-MPTMS, (Sigma Aldrich), $Pb(NO_3)_2$, HCl, HNO_3, Na_2-EDTA, NaOH, CH_3COOH, ethanol, toluene (all chemicals were in pro analysis grades), double distilled water, Whatman 42 filter paper, and universal pH papers.

2.2. Equipment

Items of equipment used in this research were oven (SPNI 505FD), Magruch x-stirrer 15 (velp Scientifica), magnetic stirrer (cole-palmer), hotplate stirrer ceramag midi (Ika - Basic 1), NO_2 AP210 analytical balance, vacuum pumps (ABM 4EK F6 3CX-4), pH meters, Atomic Absorption Spectrophotometer (AAS) 205 VGP, Fourier Transform Infra Red (FTIR) (Shimadzu 820 IPC), and X-Ray Diffraction (Paralytical X'-Pert3).

2.3. Procedure

2.3.1. Preparation of Mesoporous Silica (MCM-48). Mesoporous silica, MCM-48, was prepared using previous procedure [11, 18]. The surfactant was removed from the white product using the HCl-ethanol mixture [18] without the addition of sodium chloride and calcination at high temperatures. The washed procedure was repeated two more times and the precipitate was filtered, washed with doubly distilled water and dried at 110 °C. The material was characterized using XRD, and FTIR instruments to ensure that the as-synthesized material has been MCM-48 and the template has been removed, respectively

2.3.2. Modifying MCM-48 with 3-MPTMS. MCM-48 was modified with a thiol group followed the procedures of Wang and Li [16]. The characterization of mesoporous silica materials produced was conducted by XRD and FTIR.

2.3.3. Influence of the contact time on adsorption of Pb^{2+} ion. The modified material, MCM-48-SH, of 0.1 gram was put into an Erlenmeyer containing 50 mL of 10 ppm Pb^{2+} ion solution. The mixture was stirred with a magnetic stirrer for 5 min and then filtered. The filtrate absorbance was measured using AAS. The treatments were repeated with varying stirring times of 10, 20, 40, 60 and 90 minutes respectively. The kinetic of adsorption was studied by a pseudo-first-order equation of Lagergren and a pseudo-order two of Hossain. The equations are given in equations (1) for the former and equation (2) for the later.

$$\log(q_e - q_t) = \log q_e - \left(\frac{k_1}{2{,}303}\right) \tag{1}$$

$$\frac{1}{q_t} = \frac{1}{k_2 q_e^{2}} + \frac{1}{q_e} t \tag{2}$$

where q_e and q_t are the amounts of ion adsorbed at equilibrium and at t, respectively, k_1 is the pseudo-first order rate constant and k_2 is the pseudo-second-order rate constant [19,20].

2.3.4. Influence of pH on adsorption of Pb^{2+} ion. The modified material, MCM-48-SH, of 0.1 g was inserted into an Erlenmeyer glass containing 50 mL of 10 ppm Pb^{2+} ion solution at various pH (2, 3, 4, and 5) the mixture was then stirred during the optimum time. The mixture was filtered and the filtrate absorbance was measured using AAS. Blank experiments (without adsorbent) were also conducted.

2.3.5. Influence of initial concentration of Pb^{2+} on adsorption. The modified material, MCM-48-SH, of 0.1 grams were put into 5 different Erlenmeyer containing 50 mL of Pb^{2+} ion solution with concentrations of 30, 60, 90, 180 and 270 ppm, separately. The solution was then stirred at the optimum pH during the optimum time. The mixture was filtered and the filtrate absorbance was measured using AAS.

2.3.6. Desorption studies. The modified material, MCM-48-SH, that has been in contact with 200 mL of 500 ppm Pb^{2+} ion solution was washed with double distilled water to take out the unbound ions on the surface. After that, 0.1 g of the dried material was put into 4 different Erlenmeyer containing 50 mL of doubly distilled water, 0.3 M HCl, 0.3 M HNO_3, and 0.3 M Na_2-EDTA. The solution was then stirred during the optimum time. The mixture was filtered and the filtrate absorbance was measured using AAS.

3. Results and Discussion

3.1. Characterization of MCM-48 Materials

The X-ray difragtogram of MCM-48 before and after washing as well after modification with 3-MPTMS is given in figure 1. The as-synthesized MCM-48 material has 8 peaks (figure 1a) which are characteristic of well-ordered material known as MCM-48 as has been previously reported [11,21]. After washing with HCl-ethanol, the intensities of the peaks increase because of the removal of surfactant so that there is no scattering. The peaks shift to the lower 2Θ. The same result was reported by the mobile corporation caused by the condensation of silanol groups and constriction of pores [21]. After modification with 3-MPTMS, the diffraction pattern of the modified MCM-48 is similar to that of the unmodified one (figure 1c). This indicates that the structural order of the material remain maintained after the modification.

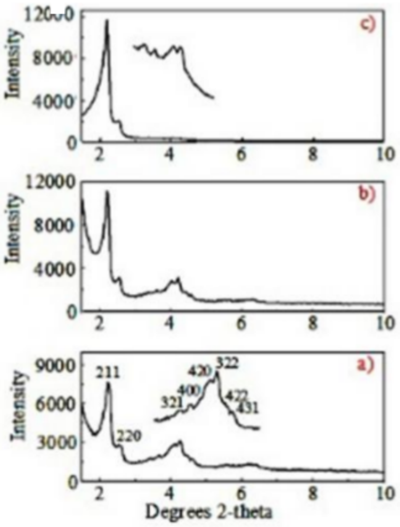

Figure 1. X-ray diffractograms of a) as-synthesized MCM-48, b) washed MCM-48, and c) MCM-48-SH.

FTIR spectra of the used materials are given in figure 2. It is clear that the as-synthesized MCM-48 (figure 1a) contains –OH groups indicated by the presence of a peak at 3442 cm^{-1} for O-H stretching vibration supported by a peak at 1652 cm^{-1} for –O-H bending vibration. Bands at 2852 and 2924 cm^{-1} are associated with C-H stretching vibrations of $–CH_2$ symmetric and $–CH_2$ antisymmetric and the one at 3012 cm^{-1} is for terminal $–CH_3$ asymmetric. The C-H bending vibration is shown at 1481 cm^{-1}. After washing with HCl-ethanol, the peaks of C-H stretching and bending vibrations have nearly been disappeared showing that the surfactants used as the structure-directing agents have almost been removed. The intense peaks at 1226 and 1084 cm^{-1} and the weak bands at 960 and 792 cm^{-1} associated with the vibrations of Si-O stretching in the lattice of silicate. The intense peaks shift to 1228 and 1085 cm^{-1} after washing with HCl-ethanol. This indicates that there is a constriction in the lattice during the removal of surfactants as has been reported before [15, 22, 23].

Figure 2c presents the FTIR spectrum of MCM-48 after modification with 3-MPTMS. It is clear that after modification the FTIR with 3-MPTMS, spectrum changes. Several new peaks appear. Peaks at 2852 and 2931 cm^{-1} are attributed to C-H stretching vibrations from the modifying agent, indicating that 3-MPTMS is grafted on the surface of MCM-48. The presence of methylene groups is supported by small peaks below 1500 cm^{-1}. The S-H vibration is shown at a wavenumber of 2575 cm^{-1}. The peaks at 800 – 900 cm^{-1} are due to the –Si-O (silanol) groups, demonstrating that not all silanol groups of the surface are used during the functionalization of MCM-48. The peak at 690 cm^{-1} associates with the Si-C vibration. After adsorption of Pb^{2+} ion, the band at 2575 cm^{-1} moves to 2563 cm^{-1} with lower intensity. This indicates that there is an interaction between the -SH group with Pb^{2+} ion.

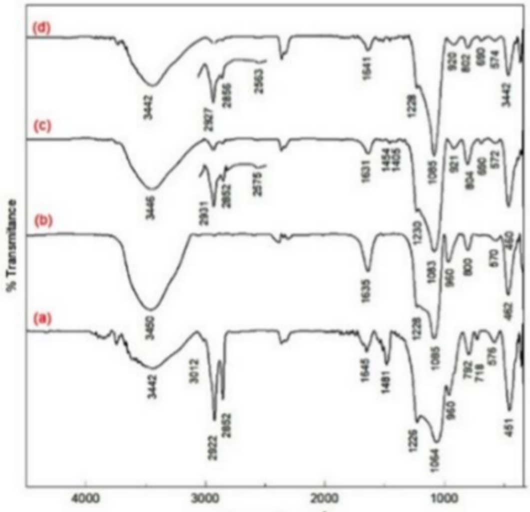

Figure 2. FTIR spectra of a) as-synthesized MCM-48 b) washed MCM-48 c) MCM-48-SH, and d) MCM-48-SH + Pb^{2+} ion.

3.2. *Effect of contact time on adsorption and kinetic study*

The influence of the contact time on the removal of Pb^{2+} by MCM-48-SH is given in figure 3. Adsorption of Pb^{2+} ion on MCM-48-SH enhances with increasing the contact time until achieving the optimum at 20 min. At that time the equilibrium adsorption occurs, the active site of the adsorbent has been saturated to Pb^{2+} ion. The optimum time for the adsorption of the ion was lower than that of Ag^{+} and Cd^{2} using the same modified MCM-48 as has been reported previously [14].

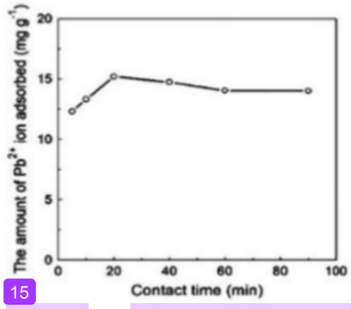

Figure 3. The effect of the contact time on adsorption of Pb^{2+} ion.

Data of the effect of the contact time on the amount of Pb^{2+} adsorbed were used to study the adsorption kinetics that can be seen in figure 4. Both graphs show that the adsorption follows the pseudo-second-order equation because the R^2 value obtained using the pseudo-first-order equation is 0.373, whereas that using the pseudo-second-order equation is 0.999. Calculation from the regression equation resulted in the pseudo-second-rate constant (k_2) of 0.26 g mg^{-1} min^{-1} and the amount of Pb^{2+} adsorbed is 14.06 mg g^{-1} which was closer to the experimental value (15.20 mg g^{-1}).

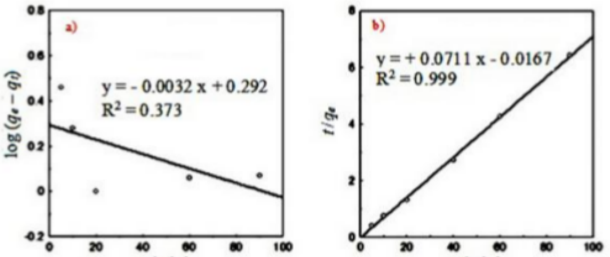

Figure 4. Kinetic study of Pb^{2+} adsorbed using a) pseudo-first-order and b) pseudo-second-order equations.

3.3. Effect of pH on the adsorption

The initial pH of solution affected the amount of ion adsorbed as can be seen in figure 5. The amount of ion adsorbed at a pH of 2 was 4.69 mg g^{-1}. By increasing the solution pH, the amount of ion adsorbed increases until the solution pH of 4 (12.28 mg g^{-1}). The amount of ion adsorbed at a pH of 2 is low because –SH and –OH groups on the surface of adsorbent is protonated at low pH. Therefore, there is competition between H^+ and Pb^{2+} ions leading to the low ability of MCM-48-SH to interact with Pb^{2+} ions. At the pH of 4, the number of H^+ ions to be competitive with Pb^{2+} ions decrease. As a result, the ability of adsorbent to interact with Pb^{2+} ions increases. At higher pH, some of Pb^{2+} ions precipitate causing the concentration of Pb^{2+} ion in the solution decreases. Therefore, the amount of ion adsorbed decreases. Thus, the highest amount adsorbed is at the pH of 4 which is the optimum pH used for determining the adsorption capacity.

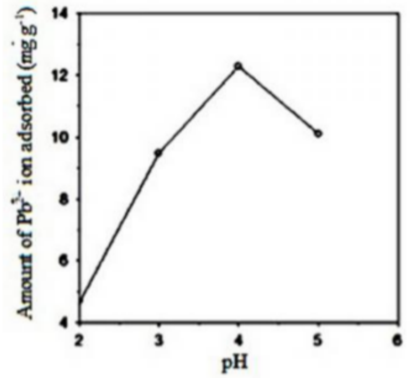

Figure 5. The effect of the initial pH of solution on the adsorption of Pb^{2+} ion.

3.4. Effect of concentration of Pb^{2+} ion

The amount ion of Pb^{2+} adsorbed on MCM-48-SH as a function of the equilibrium concentration of the ion is presented in figure 6.

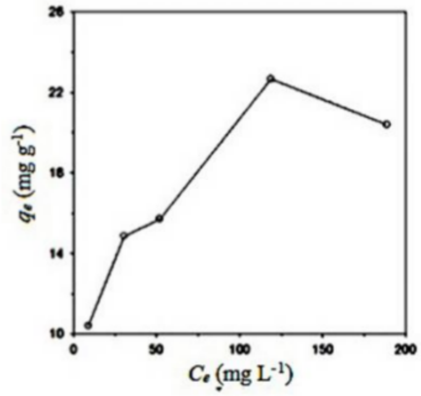

Figure 6. The influence of the equilibrium concentration on the removal of Pb^{2+} ion.

It is obvious that the higher the equilibrium concentration is, the higher the amount of the ion adsorbed is until achieving the maximum at the equilibrium concentration of 118.7 mg L^{-1} and the amount adsorbed of 22.67 mg g^{-1}. To obtain the adsorption capacity, the adsorption isotherms of Langmuir and Freundlich were used. The linear mathematic expression of Langmuir and Freundlich models are given in equations (3) and (4) [24, 25],

$$\frac{C_e}{q_e} = \frac{1}{Q_o b} + \frac{C_e}{Q_o} \tag{3}$$

$$\log q_e = \log k + \frac{1}{n} \log C_e \tag{4}$$

where C_e, q_e, Q_o, b, k, and n are the equilibrium concentration of the ion (mg L^{-1}), the amount of the ion adsorbed (mg g^{-1}), the adsorption capacity of Langmuir (mg g^{-1}), the Langmuir coefficient (L mg^{-1}), the Freundlich adsorption constant related to the adsorption capacity of adsorbent (mg g^{-1}), and the Freundlich adsorption intensity, respectively. The application of data as obtained to both adsorption isotherms can be seen in figure 7.

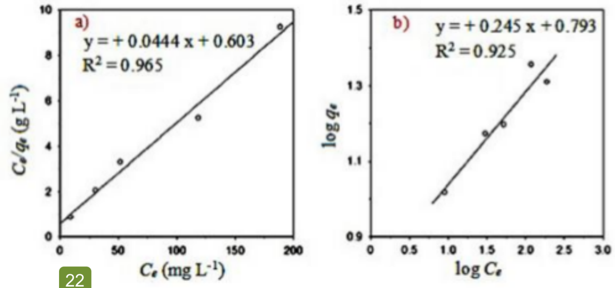

Figure 7. Adsorption isotherms of a) Langmuir and b) Freundlich.

The constants of Langmuir and Freundlich for the adsorption of Pb^{2+} ion on MCM-48-SH are given in table 1. The adsorption of Pb^{2+} ion better fits the model of Langmuir compared to the model of Freundlich shown by the higher of R^2 produced by the former model than that by the later one indicating the occurrence of monolayer adsorption. The same result has been performed when the same functionalized MCM-48 was used to adsorb Ag^+ ion. The adsorption of Pb^{2+} ion is less than that of Ag^+ ion because –SH is known as a soft base that can interact better with Ag^+ (a soft acid) than Pb^{2+} (a borderline one).

Table 1. Langmuir and Freundlich constant for the adsorption of Pb^{2+} ion on MCM-48-SH.

Ion	Langmuir model				Freundlich model			
	Q_o mg g^{-1}	Q_o mmol g^{-1}	b (L mg^{-1})	R^2	k mg g^{-1}	k mmol g^{-1}	n (g L^{-1})	R^2
Pb^{2+}	25.52	0.11	0.06	0.98	6.21	0.03	4.08	0.92
Ag^{+}	294.12	2.73	9.06	1.00	49.91	0.46	2.35	0.93^a

[a] Taken from Ref. [10]

3.5. Desorption of Pb^{2+} ion from MCM-48-SH

The process of desorption was studied by contacting the adsorbent with the desorbing agents used. The amount of Pb^{2+} ion desorbed from the used adsorbent is given in figure 8.

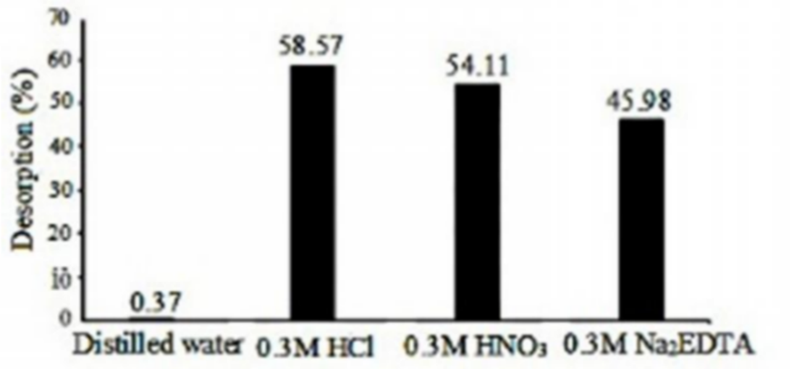

Figure 8. Desorption of Pb^{2+} ion from used MCM-48-SH.

It is clear that the amount of Pb^{2+} ion desorbed from the used MCM-48-SH using distilled water is very small. The amount of ion desorbed decreases using desorbing agents in the order of 0.3 M HCl > 0.3 M HNO_3 > 0.3M Na_2EDTA > distilled water. The fact indicated that the ion strongly interacted with the adsorbent meaning that the adsorption is mainly caused by chemical adsorption. This is supported by FTIR data as given in figure 2d which shows the interaction between the –SH group and the ion. The use of acid in removing the ion from the surface because they can protonate the surface. Therefore, the ion was removed from the surface of the adsorbent. The same trend was reported previously [15] in the removal of Cu^{2+} and Mn^{2+} from used MCM-48-NH_2.

4. Conclusion

Functionalized MCM-48 has been successfully conducted using 3-MPTMS. The material was able to be used as an adsorbent of Pb^{2+} ion with the adsorption capacity of 0.11 mmol g^{-1} at the optimum contact time of 20 min and the optimum pH of 4. The interaction between the adsorbent and the ion occurred between the –SH group of adsorbent and the Pb^{2+} ion.

Acknowledgments

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