https://scilett-fsg.uitm.edu.my/
Vol. 14(1) JANUARY 2020

ISSN: 1675-7785
eISSN: 2682-8626
DOI: 10.1234/jmpc.v14i1.7780

Removal of Lead(II) and Chromium(III) from Aqueous Solution by Using Organic-Functionalized MCM-41

Hamizah Md Rasid*, **Nafisah Aziz, Fazni Susila Abdul Ghani, Noraishah Abdullah**

Faculty of Applied Sciences, Universiti Teknologi MARA, 40450 Shah Alam, Selangor, Malaysia

Corresponding author: hamizah7708@uitm.edu.my

Received: 29 November 2019; Accepted: 2 January 2020; Published: 31 January 2020

ABSTRACT

Ordered mesoporous silica with hexagonal structure, MCM-41 was synthesized under basic media using Ludox as the silica source and cetyltrimethylammonium bromide as the organic surfactant template. Organic-functionalized MPTS-MCM-41 were prepared by grafting method using 3-mercaptopropyltrimethoxysilane. The samples were characterized using FTIR, FESEM and XRD to obtain more detailed structural insights of MCM-41. The synthesized MPTS-MCM-41 were tested for adsorption of Pb(II) and Cr(III) ions in aqueous solution. Adsorption studies were analyzed using atomic absorption spectroscopy (AAS). The effect of adsorbent dose and contact time on the adsorption of Pb(II) and Cr(III) ions from aqueous solution have been investigated. MPTS-MCM-41 was found to be effective adsorbent for metal cation than parent MCM-41 with higher affinity for Pb(II) than Cr(III) from single solution. The highest percentage removal of Pb(II) was achieved at 94.59% using 0.4 g MPTS-MCM-41 at 4 hours contact time whereby the highest percentage removal of Cr(III) ions was achieved at 66.02% using 0.4 g MPTS-MCM-41 at 5 hours contact time.

Keywords: *Modified MCM-41; MPTS; Heavy metals removal*

INTRODUCTION

Nowadays, heavy metals are the major pollutants of both surface and groundwaters. Water pollution by heavy metals is becoming one of the most serious environmental concerns due to the toxicity effects of heavy metal ions, even at low concentrations. With the rapid growth of industries, heavy metals are increasingly discharged into the environment especially in the areas where mining and smelting companies, metal processing plants and paper processing facilities are located [1]. Unlike organic contaminant, heavy metals once introduced into the environment cannot be biodegraded and tend to bioaccumulate in living organisms. Several heavy metals most commonly associated with poisoning of humans are lead, mercury, arsenic, chromium and cadmium. These metals can accumulate throughout the food chain and may affect human beings causing various disease and health disorder such as multiple sclerosis, Parkinson's disease, Alzheimer's disease and cancer [2]. Due to the harmful effects of heavy

ISSN: 1675-7785
eISSN: 2682-8626
DOI: 10.1234/jmpc.v14i1.7780

metals, there are growing public health concerns about removing heavy metal contaminants in wastewater in order to prevent environmental pollution.

Many techniques have been used for heavy metal removal in wastewater such as reverse osmosis, ultrafiltration, nanofiltration and microfiltration but the methods face problems such as high cost, process complexity, membrane fouling and low permeate flux which limited their use in heavy metal removal [3]. Most of the effective and economic method is based on adsorption process due to its high efficiency in removing heavy metal ions at low concentration, the availability of adsorbents which can be regenerated and the simplicity of the process [4]. Different kinds of adsorption materials have been used for the removal of heavy metals such as activated carbon and low-cost adsorbents such as agricultural residues and peat, but these materials have some drawbacks as they have low loading capacities and relatively weak interactions with metallic cations [5]. Polymers, amorphous silica, clays and zeolites have shown several problems like low mechanical stability, high cost and poor removal efficiency. In order to overcome these disadvantages, many investigators developed functionalized adsorbents such as surface modified or functionalized mesoporous materials.

Mesoporous adsorbents are proven to be used as cost-effective adsorbents because they can be economically regenerated and maintaining high adsorption capacities for analyte of interest after multiple uses [6]. Mesoporous silica materials have received considerable attention because of their unique large surface area, well-defined pore size and pore shape [7]. MCM-41 is one of the most popular members in the M41S family and widely used as support material for adsorption because it consists of hexagonal arrays of large and uniform pore size, large surface area, thermal stability and mild acidic property. Solid MCM-41 solid also exhibit high specific surface areas (>1000 m^2g^{-1}) [8].

Mesoporous silica containing functional groups show improved selectivity for the heavy metals in wastewater and natural waters. The key features which determine the improved performance of the functionalized materials are high metal loading capacities due to the ligands and strong binding affinities for the selected metal ions due to the nature of the functional groups [9]. Furthermore, the surface of mesoporous silica without organic functionalized was found to be hydrophilic because of the easy transformation of silanol to hydroxyl group by adsorption of water and causes leaching to occur [10]. MCM-41 has been modified with organic functional group to generate catalysts and adsorbents and to improve its hydrophobicity, hydrothermal and mechanical stabilities. In this research, MCM-41 was functionalized using 3-mercaptopropyltrimethoxysilane (MPTS) to enhance the ability of the material to extract lead and chromium from aqueous solution.

EXPERIMENTAL

The synthesis of MCM-41 was carried out by using Ludox colloidal silica HS-40 (SiO_2, 40 wt.%) with cetyltrimethylammonium bromide (CTABr, ≥98%) as the silica source and precursor agent, respectively. All chemicals including sodium hydroxide (NaOH, ≥98.5%), ammonium hydroxide (NH_4OH, ≥99.9%), 3-mercaptopropyltrimethoxysilane (MPTS, 95%), acetic acid (≥99.8%) and toluene (≥99.5%) were obtained from Sigma-Aldrich (USA) and used without further purification. The synthesis of MCM-41 host matrix was carried out according to the molar composition $6SiO_2$: CTABr: 1.5NaOH: $0.15(NH_4)_2O$: $250H_2O$ as stated by Ng *et al.* [11]. Sodium silicate was prepared by mixing Ludox colloidal silica with NaOH in distilled water in polypropylene bottle. The solution was stirred for 2 hours at 80 °C. In another polypropylene bottle, CTABr was dissolved in distilled water and NH_4OH aqueous solution. The mixture was heated and stirred at 80 °C for 1 hour. Then, sodium silicate solution was added into the polypropylene bottle containing the template solution and was simultaneously stirred vigorously for 15 minutes. The resulting mixture was aged overnight in the oven at 97 °C.

Next, the mixture was cooled to an ambient temperature and the pH of the mix-gel was adjusted to ~10.2 by addition of acetic acid. The product MCM-41 was aged for 24 hours and pH adjustment procedures were repeated two times. The precipitates were filtered, washed with distilled water and dried in the oven at 97 °C. Finally, the product MCM-41 was calcined at 550 °C for 10 hours in order to remove the remaining CTABr surfactant. The organic-functionalized MCM-41 sample was prepared by post-synthesis modification of as-made mesoporous silica. MCM-41 was dispersed in toluene followed by the addition of MPTS (Figure 1). The mixture was then refluxed for 24 hours at 110 °C under nitrogen flow. Finally, the mixture was filtered and the MPTS-MCM-41 solid was washed with toluene and dried at ambient temperature for 24 hours.

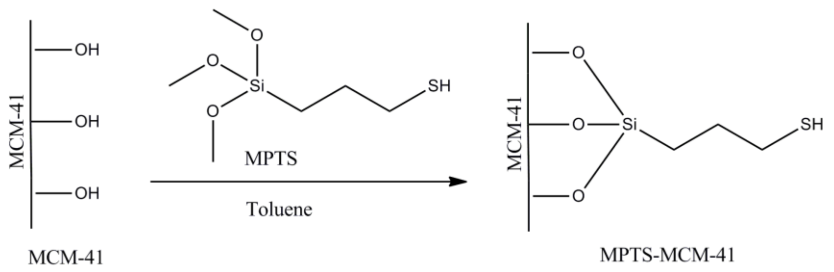

Figure 1: Surface functionalization of MCM-41 using MPTS

To investigate the effect of adsorbent dose, stock solution of lead and chromium was diluted with deionized water to prepare desired concentration of 5 mg/L. Approximately 0.1, 0.2, 0.3 and 0.4 g of MCM-41 and MPTS-MCM-41 was added to the solution containing 5 mg/L Pb(II) and Cr(III), respectively. The adsorption experiments were carried out under stirring at 150 rpm, pH 5 at room temperature for 1 hour contact time. Then, the mixture in the flask was quickly filtered using filter paper to collect and remove the adsorbent solid. To investigate the effect of contact time, 0.4 g adsorbent were added to a solution containing 5 mg/L of Pb(II) and Cr(III). The mixture was stirred at 150 rpm, pH 5 at room temperature for 1, 2, 3 and 4 hours contact time. After that the mixture was quickly filtered over filter paper to collect and remove the adsorbent solid. Finally, the solution was analyzed by using the atomic absorption spectrometer (Thermo Scientific S Series). The percentage removal (%) of Pb(II) and Cr(III) by the adsorbent for both adsorption study was calculated as equation 1 below:

$$\text{Percentage removal (\%)} = \frac{C_o - C_f}{C_o} \times 100\% \qquad (1)$$

where, C_o and C_f are the initial and final concentrations (mg/L) of metal ions present in the adsorption studies, respectively.

ISSN: 1675-7785
eISSN: 2682-8626
DOI: 10.1234/jmpc.v14i1.7780

Several characterization techniques have been utilized in order to elucidate and provide structural information and physicochemical properties of the synthesized materials. X-ray diffraction (XRD) pattern of adsorbents were acquired using Bruker D8 Advance with Cu Kα radiation with $\lambda = 1.5418$ Å at 40 kV and 40 mA. Samples were measured in the range of $2\theta = 1.5\text{-}10°$, with step interval of 0.02° step size and 1 second step time. Fourier transform infrared (FTIR) spectroscopy was used to determine the functional groups present in mesoporous silica prepared. The infrared spectrum of adsorbents was obtained at ambient condition with KBr technique using Perkin-Elmer Spectrum One FTIR spectrometer and measured in the range 4000 to 450 cm^{-1} with 4 cm^{-1} resolutions. The particle size and surface morphology of the adsorbents was observed by using Philips XL40 field emission scanning electron microscopy (FESEM) which performed at voltages of 2 kV.

RESULTS AND DISCUSSION

Calcination of MCM-41 can give better activity in the fields of adsorption because it allows elimination by decomposition of a large part of organic surfactant template from the pores of the as-synthesized MCM-41. In this study, MCM-41 was calcined at temperature of 550 °C because it was suggested that elimination of several species from organic surfactant which bonded to the silica surface occurred at high temperature (450-550 °C). However, at higher temperature (>550 °C), structure breakdown may occur [12]. FTIR spectroscopy was used to confirm whether the organic surfactant template has been removed completely or not.

FTIR spectra of synthesized materials are shown in Figure 2. The FTIR spectrum of the as-synthesized MCM-41 sample (Figure 2a) shows the peak of surfactant around 2921 cm^{-1} and 2851 cm^{-1} corresponding to C-H stretching band of the alkyl group. However, this peak disappeared in calcined MCM-41 sample (Figure 2b) which indicates that the surfactant template was completely removed and decomposed from the pore channels of MCM-41 during calcination process.

In addition, the major peaks of MCM-41 were observed in the FTIR spectrum of calcined MCM-41 consisting asymmetrical Si-O-Si stretching vibration at 1230 cm^{-1} and 1079 cm^{-1}, Si-OH stretching at 963 cm^{-1}, symmetrical Si-O-Si stretching vibration at 802 cm^{-1} and Si-O-Si bending vibrations at 469 cm^{-1} [13]. The existence of characteristics peaks of SiO_2 indicates that the structure of materials is not damaged after calcination at 550 °C [14]. Figure 2c shows the FTIR spectrum of MCM-41 after being modified to MPTS-MCM-41. The spectrum shows the presence of S-H stretching vibration at 2550 cm^{-1} and the asymmetric C-H stretching of the propyl chain from the silylating agent at 2927 cm^{-1} which are absent in MCM-41 sample. The existence of both peaks confirms the successful incorporation of organic functionalized MPTS into MCM-41.

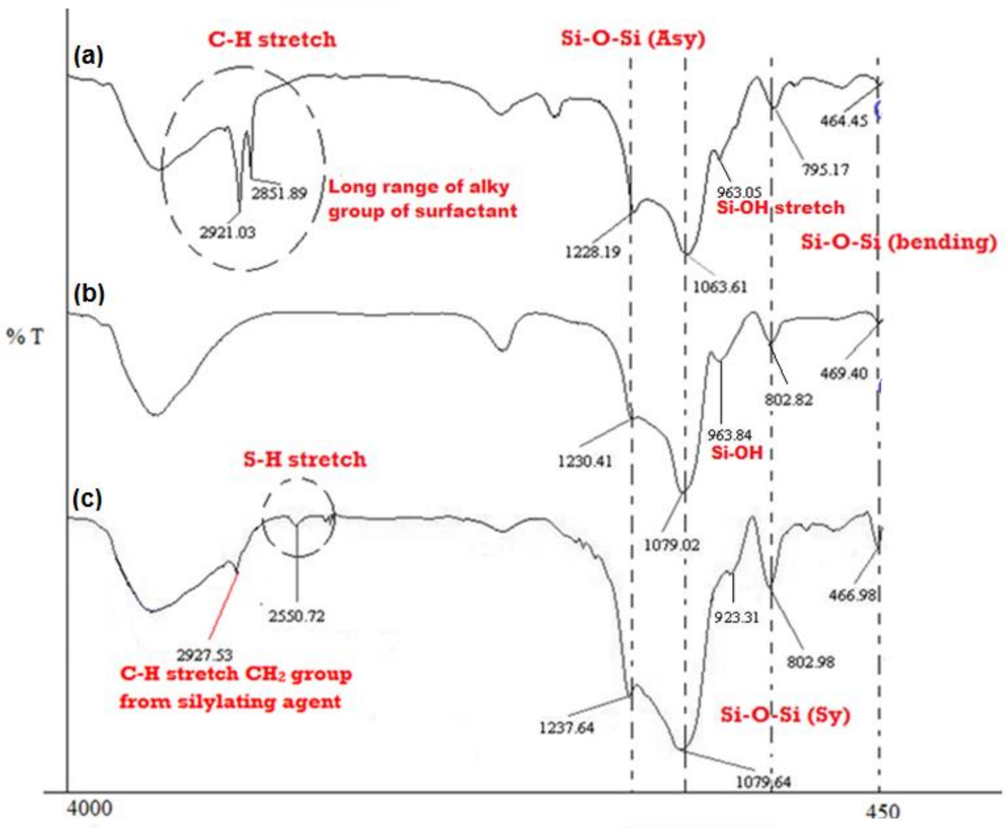

Figure 2: FTIR spectra: (a) as-synthesized MCM-41, (b) calcined MCM-41, (c) MPTS- MCM-41

The morphological differences between calcined MCM-41 and MPTS-MCM-41 were observed by FESEM and presented in Figure 3a and 3b, respectively. The FESEM micrograph reveal the surface texture and porosity of both samples. It was observed that calcined MCM-41 and MPTS-MCM-41 have spherically-shaped particles and are uniform in size. The FESEM micrograph also reveals that the particle morphology of both samples consists of rough surface with many small granular particles of up to 1 - 2 µm in diameter attached on the surface [15].

ISSN: 1675-7785
eISSN: 2682-8626
DOI: 10.1234/jmpc.v14i1.7780

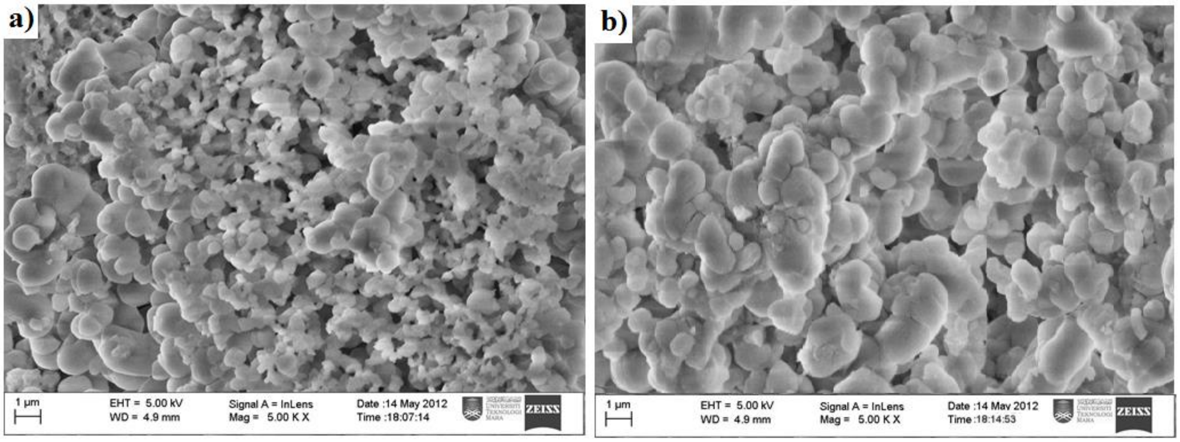

Figure 3: FESEM micrograph: (a) calcined MCM-41, (b) MPTS-MCM-41

Figure 4a and 4b show low angle x-ray diffractogram of as-synthesized MCM-41 and calcined MCM-41, respectively. Both XRD patterns show a typical mesoporous structure with three resolved peaks corresponding to Miller indices (100), (110) and (200). It indicates that the materials possessed a well-ordered hexagonal mesopore system with a clear (100) peak and weaker reflections assignable to (110) and (200) reflections [16].

The position of (100) peak slightly shifts to higher angle after MCM-41 underwent calcination at 550 °C, which may be related to the lattice contraction of MCM-41 during high temperature process [17]. Furthermore, the peak intensity of calcined MCM-41 was higher than the as-synthesized MCM-41, indicating increased in crystallinity of calcined sample due to the successful removal of organic surfactant template [18].

The XRD peak intensity of synthesized materials decreased significantly when the hexagonal pores were filled with organic functionalized MPTS as shown in Figure 4c. This might be due to the reduction of the long order framework in MPTS-MCM-41 whereby the attachment of organic functional group will lead to some structural arrangement in the mesopore channels [19].

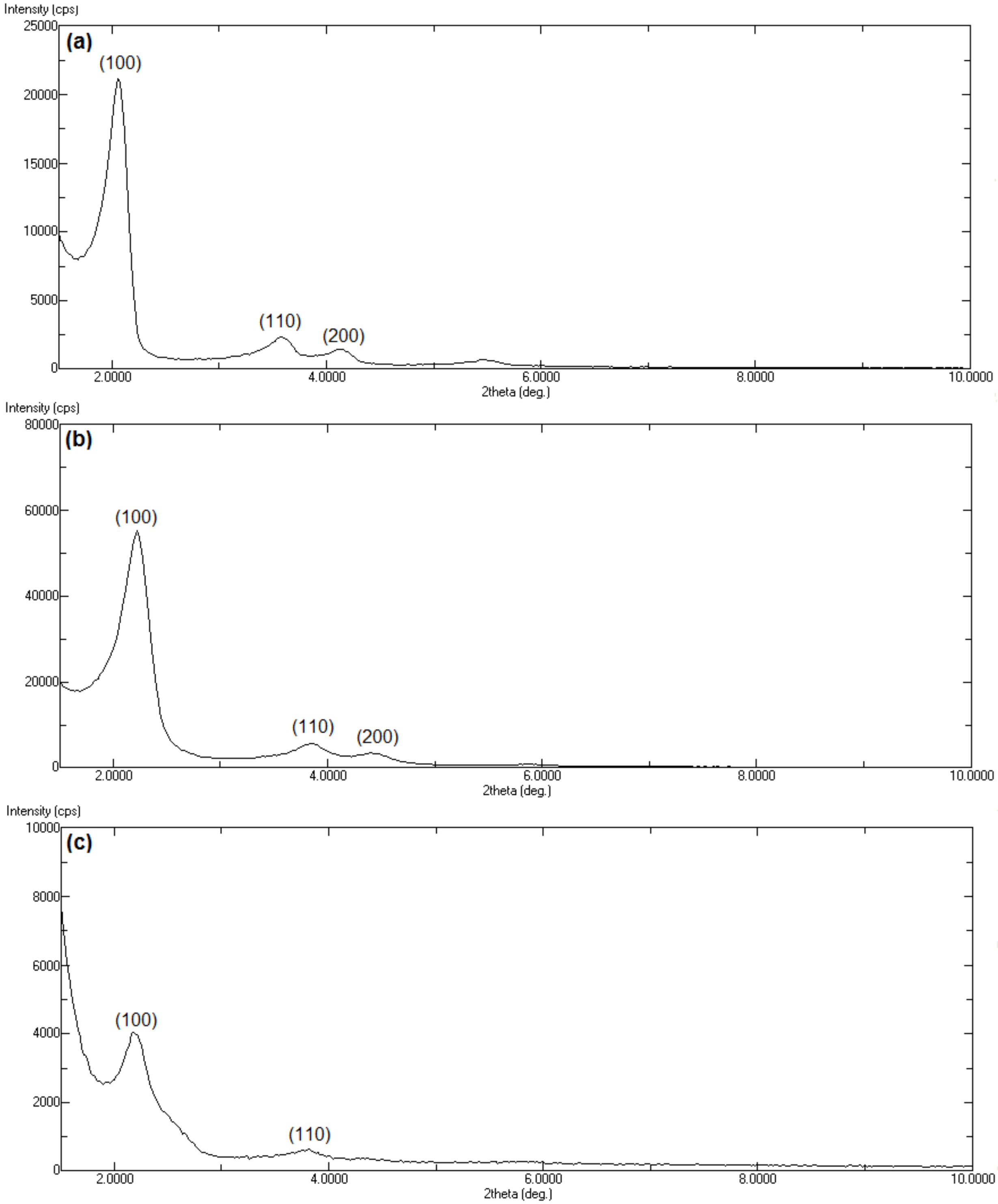

Figure 4: XRD diffractogram: (a) as-synthesized MCM-41, (b) calcined MCM-41, (c) MPTS-MCM-41

ISSN: 1675-7785
eISSN: 2682-8626
DOI: 10.1234/jmpc.v14i1.7780

The percentage removal of Pb(II) and Cr(III) ions on MCM-41 and MPTS-MCM-41 at different adsorbent dose are shown in Figure 5a and 5b, respectively. Both figures show that as the dosage of adsorbent increase, the percentage removal of metal ions in aqueous solution also increases. This might be due to increment of the adsorbent increases the availability of the surface area for the adsorption process, in which more of the heavy metal ions uptake onto the surface of adsorbent could occur [16].

With increase in adsorbent dose, the number of active site unit also increases. At low adsorbent dose, the available sorption sites were quite insufficient compared with the large amount of Pb(II) and Cr(III) ions in solution, resulting in low removal efficiency. In this study, it was found that the highest percentage metal ions removal was achieved when 0.4 g of adsorbent was used.

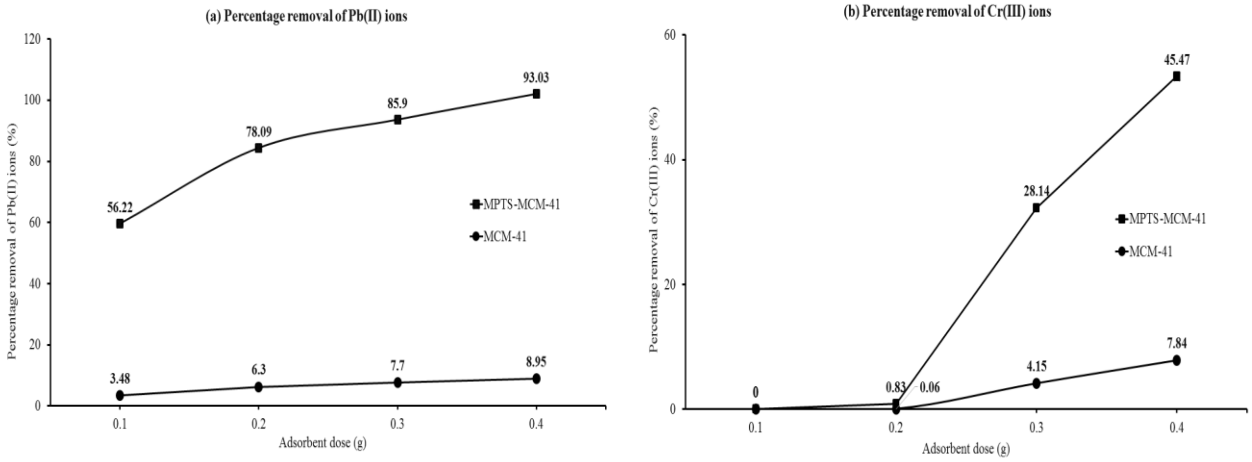

Figure 5: Percentage removal of (a) Pb(II) ions, (b) Cr(III) ions using MCM-41 and MPTS-MCM-41 at 1 hour contact time at different adsorbent dose

MPTS-MCM-41 shows higher metal uptake than parent MCM-41 when the same adsorbent dose was used. MPTS-MCM-41 gives higher percentage removal of Pb(II) ions at 0.4 g adsorbent dose which is 93.03% as compared to MCM-41 which only managed to remove only 8.95% of Pb(II) as shown in Figure 5a. Similarly, MPTS-MCM-41 (0.4 g) shows higher removal of Cr(III) ions which was 45.47% when compared to MCM-41 which only managed to remove only 7.84% of Cr(III) (Figure 5b).

This might be due to organic-functionalization inside the pore channel of MCM-41 which then allowing an easy reaction with metal ions [20]. This performance was attributed to the strong binding affinities of S-H functional group present in the adsorbent with metal cation thus providing effective adsorption sites. The mechanism for the removal of heavy metal ions in an aqueous solution most likely involved either ionic interaction between positively charged metal ions and negatively charged adsorbent surface or by donation of lone-pair electrons of the functional group to metal ions to form coordinate bonds [21].

At pH 5, the surfaces of adsorbent (S-H) became negatively charged which enhanced the adsorption process by electrostatic interaction. Besides, MPTS enhances the hydrothermal stability of MCM-41 materials by raising its hydrophobicity characteristics. Freshly calcined MCM-41 can easily react with water which transform the silanol group to hydroxyl group by adsorption of water and causes leaching to occur. This characteristic is a disadvantage for adsorbent when used in continuous removal process for metal ions in aqueous solution [22]. Hence, functionalization of MCM-41 can help increase the stability and adsorption efficiency of the material [23].

It was also found that removal percentages for Pb(II) (93.03% and 8.95%) were greater than Cr(III) (45.57% and 7.84%) at equilibrium time for both MPTS-MCM-41 and MCM-41 indicating higher affinity of Pb(II) sorption towards the adsorbents than in Cr(III). This is due to the low hydration energy of Pb(II) (1481 kJ mol^{-1}) as compared to Cr(III) (4010 kJ mol^{-1}) which will then separate more easily from the combined H_2O molecules and transforms into bare ions resulting in higher adsorption capacity [24].

Figures 6a and 6b show the percentage removal of Pb(II) and Cr(III) ions on MCM-41 and MPTS-MCM-41 at different contact time. MPTS-MCM-41 gives high percentage of Pb(II) removal (93.03%) at 1-hour contact time but the value slightly decreases to 92.25% when the contact time was increased to 2 hours. When the contact time was increased from 2 to 4 hours, the percentage removal of Pb(II) ions increases until the maximum of Pb(II) percentage removal was achieved at 94.59%. This is because longer contact time provides longer interaction duration between heavy metal ions and adsorbent surfaces [25].

MCM-41 shows similar pattern as MPTS-MCM-41 but the percentage removal is much lower. The highest percentage removal of Pb(II) using MCM-41 was 10.65% which was taken after 4 hours of contact time. On the other hand, the percentage removal of Cr(III) increased as the contact time of the metal ions with sorbent increased until the maximum Cr(III) removal percentages was reached at 5 hours contact time. The highest Cr(III) percentage removal of Cr(III) was 66.02% for MPTS-MCM-41 and 10.48% for MCM-41.

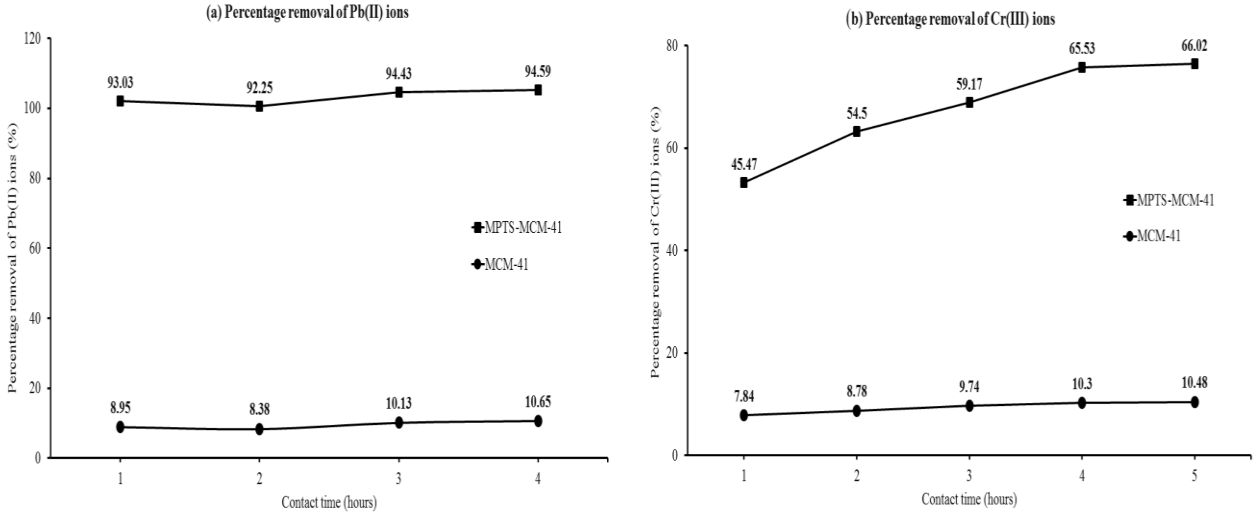

Figure 6: Percentage removal of (a) Pb(II) ions, (b) Cr(III) ions on 0.4 g of MCM-41 and MPTS-MCM-41 at different contact time

ISSN: 1675-7785
eISSN: 2682-8626
DOI: 10.1234/jmpc.v14i1.7780

CONCLUSIONS

The organic functionalized MPTS-MCM-41 was successfully synthesized via post-synthesis method and characterized by using FTIR, FESEM and XRD. The FTIR results displayed the absence of C-H stretching in calcined MCM-41 which suggesting the complete removal of organic surfactant template and the existence of S-H stretching band confirms the incorporation of mercaptan group onto MCM-41 producing MPTS-MCM-41. XRD results indicated that MPTS-MCM-41 has similar XRD pattern as the MCM-41 although the peak intensity decreases. The synthesized MPTS-MCM-41 was tested as adsorbent to remove heavy metal ions in aqueous solution. MPTS-MCM-41 show better efficiency to remove heavy metal ions compared to parent MCM-41 due to the presence of organic-functionalization group. The adsorption study also revealed that MPTS-MCM-41 has better selectivity towards Pb(II) ions than Cr(III). The removal efficiency of MPTS-MCM-41 suggested that the material has the potential to adsorb Pb(II) ions from aqueous solutions in the environmental and industrial cleanup applications to reduce the lead pollution.

ACKNOWLEDGMENTS

The authors would like to acknowledge the Ministry of Higher Education for financing the project under the Fundamental Research Grant Scheme no: 600-RMI/FRGS 5/3(59/2013) and Faculty of Applied Sciences and Faculty of Pharmacy, Universiti Teknologi MARA (UiTM) for their facilities.

REFERENCES

[1] Jawad M.H., Aziz A., Ab Ghani S., Adsorptive Cathodic Stripping Voltammetry of Lead in Water Samples using 2,2'Bipyridine or 1,10-phenanthroline and Nitrite Ions, *Sci. Lett.*, **11**(2):1-10 (2017).

[2] Jaishankar M., Tseten T., Anbalagan N., Mathew B.B., Beeregowda K.N., Toxicity, Mechanism and Health Effects of Some Heavy Metals, *Interdiscip. Toxicol.*, **7**(2):60-72 (2014).

[3] Fu F., Wang Q., Removal of Heavy Metal Ions from Wastewaters: A Review, *J. Environ. Manage.*, **92**:407-418 (2011).

[4] Fiyadh S.S., AlSaadi M.A., Jaafar W.Z., AlOmar M.K., Fayaed S.S., Mohd N.S., Hin L.S., El-Shafie A., Review on Heavy Metal Adsorption Processes by Carbon Nanotubes, *J. Clean. Prod.*, **230**:783-793 (2019).

[5] Rashid R.A, Ishak M.A.M, Mohamed K., Adsorptive Removal of Methylene Blue by Commercial Coconut Shell Activated Carbon, *Sci. Lett.*, **12**(1):77-101 (2018).

[6] Idris S.A., Davidson C.M., McManamon C., Morris M.A., Anderson P., Gibsona L.T., Large Pore Diameter MCM-41 and Its Application for Lead Removal from Aqueous Media, *J. Hazard. Mater.*, **185**:898–904 (2011).

[7] Bois L., Bonhomme' A., Ribes A., Pais B., Raffin G., Tessier F., Functionalized Silica for Heavy Metal Ions Adsorption, *Colloids Surface A.*, **221**:221-230 (2003).

[8] Dimos K., Stathi P., Karakassides M.A., Deligiannakis Y., Synthesis and Characterization of Hybrid MCM-41 Materials for Heavy Metal Adsorption, *Micropor. Mesopor. Mat.*, **126**:65-71 (2009).

[9] Benhamou A., Boudu M., Derriche Z., Basly J.P., Aqueous Heavy Metals Removal on Amine-Functionalized Si-MCM-41 and Si-MCM-48, *J. Hazard. Mater.*, **171**:1001–1008 (2009).

[10] Li X.D., Zhai Q.Z., *Characterization of Methylated Nanoscale MCM-41 Material Research Center for Nanotechnology*, Changchun University of Science and Technology, Changchun 130022, P.R. China. (2011).

[11] Ng E.P., Nur H., Wong K.L., Muhid M.N.M., Hamdan H., Generation of Brönsted Acidity in AlMCM-41 by Sulphation for Enhanced Liquid Phase Tert-butylation of Phenol, *Appl. Catal. A-Gen.*, **323**:58-65 (2007).

[12] Keene M.T.J., Gougeon R.D.M., Denoyel R., Harris R.K., Rouquerol J., Llewellyn, P.L., Calcination of the MCM-41 Mesophase: Mechanism of Surfactant Thermal Degradation and Evolution of the Porosity, *J. Mater. Chem.*, **9**: 2843-2850 (1999).

[13] Abdel Salam M.S., Betiha M.A., Shaban A.A., Elsabagh A.M., Abd El-Aal R.M., El Kady F.Y., Synthesis and Characterization of MCM-41-Supported Nano Zirconia Catalysts, *Egypt. J. Pet.*, **24**(1):49-57 (2015).

[14] Yang G., Deng Y., Ding H., Lin Z., Shao Y., Wang Y., A Facile Approach to Synthesize MCM-41 Mesoporous Materials from Iron Ore Tailing: Influence of the Synthesis Conditions on the Structural Properties, *Appl. Clay Sci.*, **111**:61-66 (2015).

[15] Malek N.N.A., Laiman R., Adsorption of Sulfur Dioxide (SO_2) Gas Using Treated Rice Husk Ash (RHA) Adsorbent, *Sci. Lett.*, **12**(1):63-76 (2018).

[16] Heidaria A., Younesia H., Mehraban Z., Removal of Ni(II), Cd(II), and Pb(II) from a Ternary Aqueous Solution by Amino Functionalized Mesoporous and Nanomesoporous Silica, *Chem. Eng. J.*, **153**:70–79 (2009).

[17] Guo F., Guo S., Wei X., Wang X., Xiang H., Qiu Z., Zhao L., The Effects of MCM-41's Calcination Temperature on the Structure and Hydrodenitrogenation Over NiW Catalysts, *Korean J. Chem. Eng.* **31**(11):1973-1979 (2014).

[18] Singh R.P.P., Hudiara I.S., Rana S.B., Effect of Calcination Temperature on the Structural, Optical and Magnetic Properties of Pure and Fe-doped ZnO Nanoparticles, *Mater. Sci. Poland*, **34**(2):451-459 (2016).

[19] Joseph T., Kumar K.V., Ramaswamya A.V., Halligudi, S.B., Au Pt Nanoparticle in Amine Functionalized MCM-41: Catalytic Evalution in Hydrogenation Reactions, *Catal. Commun.*, **8**:629-634 (2007).

[20] Taib N.Z., Endud S., Katun M.S., Functionalization of Mesoporous Si-MCM-41 by Grafting with Trimethylchlorosilane, *Int. J. Chem.*, **3**(3): 1-10 (2011).

[21] Quintanilla D.P., Hierro I.D., Fajardo M., Sierra I., 2-Mercaptothiazoline Modified Mesoporous Silica for Mercury Removal from Aqueous Media, *J. Hazar. Mater.*, **134**(1-3):245-256 (2006).

[22] Zhao X.S., Lu G.Q., Hu X., Characterization of the Structural and Surface Properties of Chemically Modified MCM-41 Material, *Micropor. Mesopor. Mater.*, **41**:37-47 (2000).

[23] Lee B., Kim Y., Lee Hi, Yi J., Synthesis of Functionalized Porous Silicas via Templating Method as Heavy Metal Ion Adsorbents: The Introduction of Surface Hydrophilicity onto the Surface of Adsorbents, *Micropor. Mesopor. Mater.*, **50**:70-90 (2001).

[24] Liu W., Wang T., Borthwick A.G.L., Wang Y., Yin X., Li X., Ni J., Adsorption of Pb^{2+}, Cd^{2+}, Cu^{2+} and Cr^{3+} onto Titanate Nanotubes: Competition and Effect of Inorganic Ions, *Sci. Total. Environ.*, **456-457**: 171-180 (2013).

[25] Mubarak N.M., Thobashinni M., Abdullah E.C., Sahu J.N., Comparative Kinetic Study of Removal of Pb^{2+} Ions and Cr^{3+} Ions from Waste Water using Carbon Nanotubes Produced using Microwave Heating, *Carbon,* **2**(1):1-16 (2016).