MCM-41 and Functionalized MCM-41 as Adsorbents to Remove Heavy Metals and Hardness from Contaminated Water and Groundwater

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ABSTRACT

Mining operating and abandoned mines often have resulted in waste rock dumps and open pits that contain materials high in heavy metals and toxic elements. These contaminants are known to be present in groundwater, surface water, sediment, soils and plants and can be transported beyond the former mining areas through the surface and ground water system. Exposure to high level of these contaminants can cause adverse effects in humans, wildlife, and other animals. An effective technology to remove these pollutants is needed.

MCM (Mobil Composition of Matter) is a mesoporous material that forms a family of silicate solids (such as MCM 41, MCM 48, etc.) that consist a regular arrangement of cylindrical mesopores that form an one-directional pore system. These mesoporous solids are widely used as absorbents, catalysts, or catalyst supports due to their large surface area to mass ratio. However, MCM materials are not structurally stable and their lattices may collapse with time, which will alter the properties of the materials. Addition of moieties on the surface of the MCM surface structure stabilizes the lattice but also changes the surface properties, thus this technique can serve as a "tuner" for the properties of MCM materials. The properties that are altered are depending on the molecules being attached onto the surface.

This report will focus on MCM-41 and its functionalized product as an adsorbent to remove heavy metals and hardness simultaneously from polluted water and groundwater. In this study, MCM-41 was first synthesized by a hydrothermal method, functionalization was prepared by using $ZnCl_2$ to form $ZnCl_2$-MCM-41 with the use of a microwave procedure. MCM and $ZnCl_2$-MCM-41 surface were characterized by SEM, TEM, AFM, and FTIR. Surrogate heavy metals used in the study were Hg, Pb, and Cr, while Ca was used as a major component of the hardness in water. Systematic experiments were performed to investigate the capabilities of these MCM adsorbents at various concentrations of absorbates and durations at neutral pH. Comparisons of adsorption capabilities with activated carbon were also performed.

It was found that $ZnCl_2$-MCM-41 could adsorbed 3 times as much as its original weight, and the amount of metal absorbed by $ZnCl_2$-MCM-41 increased with molecular weight of the metals. Among other applications, the results of selective sorption phenonium can be useful for some particular water treatment alternatives, such as nuclear engineering industry.

Keywords: MCM, adsorption, heavy metals, functionalized MCM, calcium, removal

1 INTRODUCTION

Heavy metals, such as Pb, Hg, Cr, Mn and Cd found in the liquid effluents from different industrial sources can be harmful for human bodies. These heavy metals are toxic even at low concentrations, and can impact the environment as well as human health in a negative way. For example, lead is a toxic carcinogen, and even at low concentration can lead to bone degradation, liver and lung damage (Ghorbani et al. 2016, Raji 2016) as well as high damage to nervous system, brain, kidney, cardiovascular, and reproductive system [1].

Different industries such as electroplating, leather, textiles, dyes, mining, etc. are often the sources for heavy metals discharged into the surface water and contaminate the environment with toxic metals (Culita et al. 2016); these toxic pollutants must be removed from the wastewaters before they are discharged.

Many techniques such as chemical precipitation, oxidation/reduction, sedimentation, ion exchange, membrane filtration and extraction are used for removal of heavy metals such as mercury, chromium, and lead (Aryan et al. 2016; Xu, & Qian 2015). But many recent developments have provided

evidence that sorption can be a more suitable method for extraction of heavy metals from water.

Ordered mesoporous material MCM-41 displays adsorption features such as well-defined pore-size with uniform shapes of hexagonal arrays. These features help the adsorption process through greater thermal, hydrothermal, and hydrolytic abilities. These mesoporous structures can be further modified to make them more stable and enhance their characteristics be more suitable for adsorption, catalysis, and sensor fabrication.

The objective of this research is to synthesize and study the characteristics of MCM-41, and its modified product with $ZnCl_2$, ($ZnCl_2$-MCM-41), and then apply it for the removal of different heavy metal ions such as Pb(II), Hg (II), Cr (III) through adsorption process as well as other ions in water such as calcium (Ca^{2+}), potassium (K^+) and nitrate (NO^{3-}).

2 MATERIALS AND METHODS

2.1 Materials

Cetrimethylammonium bromide (CTAB), tetraethylorthosilicate (TEOS), tetramethylammonium hydroxide (TMAOH), zinc chloride ($ZnCl_2$), lead nitrate ($Pb(NO_3)_2$), mercuric chloride ($HgCl_2$), chromium chloride hexahydrate ($CrCl_3.6H_2O$), calcium chloride ($CaCl_2$), potassium nitrate (KNO_3^-), hydrochloric acid (HCl), and nitric acid (HNO_3^-) were supplied from Aldrich Sigma. All the other chemicals were of analytical grade, all experiments were carried out at pH 7.0. and all solutions were prepared with double deionized water (DI).

2.2 Synthesis of MCM-41

The synthesis of MCM-41 was done according to the method provided in (Gaydhankar et al. 2007). 2.04 g CTAB was dissolved in 114 mL of distilled water under constant stirring. 16.33 g of aqueous ammonia (TMAOH) solution was added to it, and the solution was stirred in a magnetic stirrer for 10 minutes. 10 g of TEOS was then added drop-wise with continuous stirring, which was continued for 4 hours at room temperature. The molar composition of the product obtained was SiO_2: 0.12CTAB: 2.50NH_4OH: 150H_2O. The product was filtered and washed thoroughly with distilled water, and dried in an oven at a temperature of 373K. Then it was calcined in air in a furnace, with a rate of 1K/min, 2 hours each at temperature 373K, 473K and 623K, and then at 813K for 6 hours to remove the organic shell from the CTAB.

2.3 Synthesis of $ZnCl_2$-MCM-41

$ZnCl_2$-MCM-41 was synthesized using a microwave method, in which 1 .0 g of the calcined MCM-41 was added to a flask containing 50 mL distilled water in an Erlenmeyer flask, and 4 mmol of anhydrous $ZnCl_2$ was added to it and stirred well. This solution was then heated in a microwave at 650W for 15 minutes. DI water was added at intervals to compensate the drying of the solution and keep the volume at 50 mL, and overflow was prevented to avoid spilling and loss of the materials. The solution was filtered using a 0.45 µm filter paper, and washed slightly with distilled water to remove unreacted zinc chloride. The recovered solid was then dried up in an oven at 373K to get the final modified $ZnCl_2$-MCM-41 powder.

2.4. Procedures for Batc Adsorption Studies

Batch adsorption experiments were conducted to explore the adsorption capabilities of MCM-41 and $ZnCl_2$-MCM-41 for heavy metals (Pb^{2+}, Hg^{2+}, and Cr^{3+}) as well as other ions such as nitrates, calcium, and potassium in solution. Experiments of all different ions were conducted in similar procedures: 15 mg of MCM-41 or $ZnCl_2$-MCM-41 sorbent was placed in a vial containing 30 mL of ion solution (e.g., Pb) at initial concentration ranging from 0.001 to 0.1 M. The vial was then shaken continuously for a specific time period, ranging from 10 to 300 minutes and 24 hours, in a shaker at 300 rpm before sampling for measurements.

2.5. Detection of metals and ions

Detection of metals and ions were conducted by using ICP-OES or electrodes. All results were measurements of at least 2 samples with duplicates.

3 RESULTS AND DISCUSSIONS

In this study, Pb, Hg, and Cr presented the surogates of wasted heavy matels in solution, whereas Ca presented hardness in water or groundwater. The following 4 figures show the comparisons of results between MCM-41 and $ZnCl_2$-MCM-41 for Pb, Hg, Cr, and Ca. $ZnCl_2$-MCM-41 consistently out-performed MCM-41 at pH 7 for the 5-hour batch adsorption experiment.

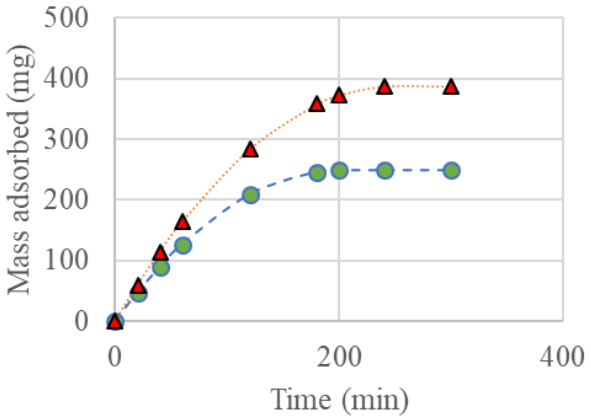

Figure 1: Mass of 0.1M Pb (II) (mg) adsorbed by MCM-41 & $ZnCl_2$-MCM-41. Circle is mass of 0.1 M Pb adsorbed by MCM-41, triangle is mass of 0.1 M Pb adsorbed by $ZnCl_2$-MCM-41.

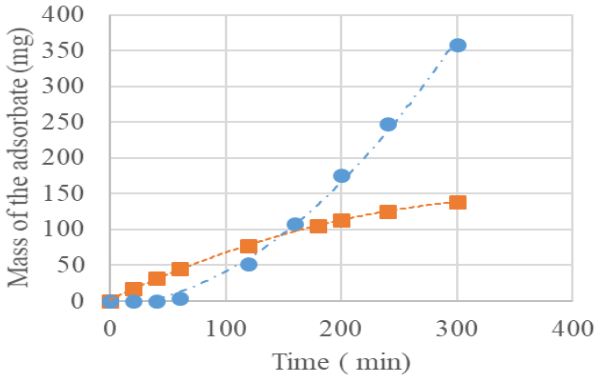

Figure 2: Mass of 0.1M Hg (II) adsorbed by MCM-41 & $ZnCl_2$-MCM-41. Square is mass of 0.1 M Hg adsorbed by MCM-41, circle is mass of 0.1 M Hg adsorbed by $ZnCl_2$-MCM-41.

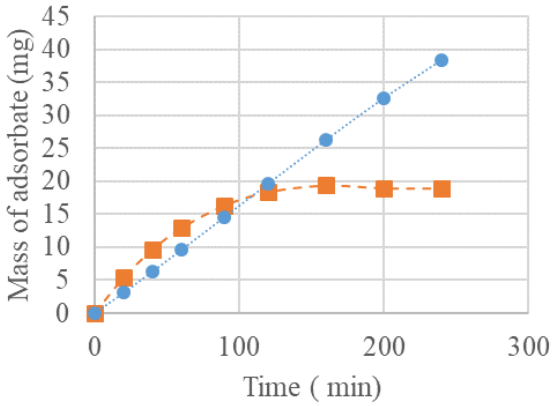

Figure 3: Mass of 0.1M Cr (III) adsorbed by MCM-41 & $ZnCl_2$-MCM-41. Square is mass of 0.1 M Cr adsorbed by MCM-41, circle is mass of 0.1 M Cr adsorbed by $ZnCl_2$-MCM-41.

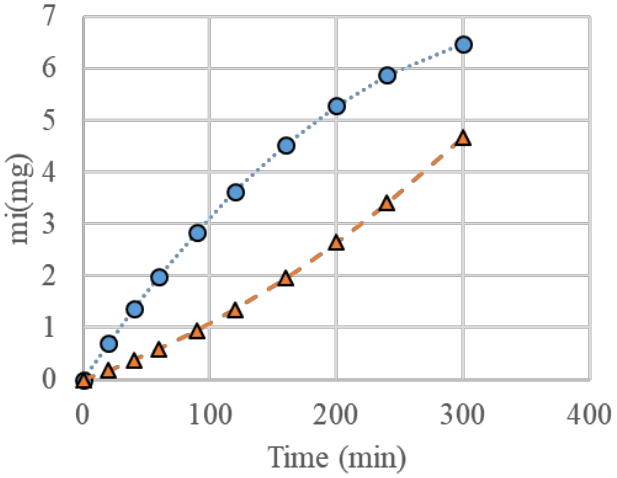

Figure 4: Mass of 0.1M Ca^{2+} ions adsorbed by MCM-41 and $ZnCl_2$-MCM-41, Triangle is mass of 0.1 M Ca^{2+} adsorbed by MCM-41, circle is mass of 0.1 M Ca^{2+} adsorbed by $ZnCl_2$-MCM-41.

In the following, Table 1 summaries the adsorpion capacity of MCM-41 and $ZnCl_2$-MCM-41 at various concentrations of adsorbates, that shows the functionalized MCM-41 consistently outperformed MCM-41. For example, $ZnCl_2$-MCM-41 could nearly adsorbed 3x the mass of Pb, that was substantially more than the capacity of common activated carbon.

Table 1: Summary table of adsorption capacity (mg/g)

Adsorbate	**MCM-41**	**$ZnCl_2$-MCM-41**
0.1M Pb	1657.6	2846.4
0.01M Pb	32.82	14.92
0.001M Pb	12.979	18.648
0.1M Hg	505.55	1302.74
0.01M Hg	160.6	184.75
0.001M Hg	12.91	10.53
0.1M Cr	70.42	139.27
0.01M Cr	27.37	25.44
0.001M Cr	3.501	3.788
0.1M Ca^{2+}	63.95	47.94
0.01M Ca^{2+}	10.56	12.62
0.001M Ca^{2+}	1.116	4.87
0.1M K^+	219.48	279.28
0.01M K^+	50.07	47.1
0.001M K^+	5.283	5.092
0.1M NO_3^-	297.28	219.479
0.01M NO_3^-	50.07	47.1
0.001M NO_3^-	5.283	5.092

4. CONCLUSIONS

As expected, the capacity of the adsorbent increases with the concentration of adsorbate in the testing solutions from 0.001 M to 0.01 M; in adddition, the adsorption capacity increases with contact time. Most importantly, the adsorption capacity of the both adsorbents increases with the moleccular weight of the adsorbates (Pb>Hg>Cr>Ca). This property is important in waste management of cleaning up water and/or wastewater containing mixture of different metals. However, more research is needed to substantiate such claim.

5 ACKNOWLEDGMENT

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REFERENCES

[1] Culita, D. C., Simonescu, C. M., Patescu, R. E., Dragne, M., Stanica, N., & Oprea, O. (2016). o-Vanillin functionalized mesoporous silica - coated magnetite nanoparticles for efficient removal of Pb(II) from water. *Journal of Solid State Chemistry, 238*, 311-320.