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MCM-41 AND $ZnCl_2$-MCM-41 AS ADSORBENTS TO REMOVE HEAVY METALS AND CALCIUM, POTASSIUM, AND NITRATE IN WATER

by

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To the Graduate Faculty:

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ABSTRACT

Mobil Composition of Matter-41 (MCM-41) is a mesoporous molecular sieve formed by silicate and alumosilicate solids, which can be synthesized through different methods. The most common one is a hydrothermal method using cetyltrimethylammonium bromide (CTMABr). With its large surface area, high thermal stability, uniform pore system with adjustable pore sizes, and ultra-high adsorption quality, MCM-41 is used in many environmental, industrial, and biological applications as adsorbent, sensor, and catalyst.

MCM-41 has been used in wastewater dye removal, adsorption of organic and inorganic pollutants, and drug delivery system devices. Examples include removal of organic materials such as nitrobenzene and phenol, and inorganic materials such as lead, copper, cadmium, and radioactive wastes from water. MCM-41 can also be used for sensor application and has many advantages over traditional methods for metals detection.

This systematic study will focus on MCM-41 as an adsorbent to remove heavy metals and hardness simultaneously from water that can be useful for cleanup and water treatment application. In this study, MCM-41 was first synthesized by hydrothermal method, and functionalized with zinc chloride, to form $ZnCl_2$-MCM-41, with the use of microwave method. The final product was characterized by TEM images to demonstrate its mesoporous structure. The adsorption capacities of $ZnCl_2$-MCM-41, achieved from batch studies, were as high as 2846.4 mg/g, 1302.74 mg/g, and 139.27 mg/g for lead (Pb^{2+}), mercury (Hg^{2+}), and chromium (Cr^{3+}) respectively. The capacities for removal of the cations and anions by $ZnCl_2$-MCM-41 were found to be 47.94 mg/g, 279.28 mg/g, and 219.48 mg/g for calcium (Ca^{2+}), potassium (K^{+}), and nitrate (NO_3^{-}), respectively.

CHAPTER 1 - INTRODUCTION

1.1 Background

Heavy metals, like Pb, Hg, Cr, Mn and Cd, found in the liquid effluents from different chemical sources can be harmful for human bodies (Tavakoli et al. 2013, Chen et al. 2014). These heavy metals are toxic even at low concentrations, and can impact the environment as well as human health in a negative way. Lead is a toxic carcinogen, and can even at low concentration can lead to bone degradation, and liver and lung damage (Ghorbani et al. 2016, Raji 2016) as well as high damage to nervous system, brain, kidney, cardiovascular, and reproductive systems (Culita et al. 2016).

Different industries such as electroplating, leather, textiles, dyes, mining, etc. are often the sources for heavy metals in water, and contaminate the wastewater with toxic metals (Culita et al. 2016). These can be removed from the wastewaters before they are discharged back to the environment.

Many techniques like chemical precipitation, oxidation/reduction, sedimentation, ion exchange, membrane filtration and solid phase extraction are used for removal of heavy metals like mercury, chromium, and lead (Aryan et al. 2016; Xu, & Qian 2015). But many recent developments provide proof that sorption can be a 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 (Alothman 2012). And though

activated carbon or alumina are efficient, they are expensive when pure solvents are involved (Algarra 2005).

The synthesis of mesoporous structures has been studieds for a while now, and its applications on adsorption, sensors, as catalysts and separation materials have been researched over the years. Hydrothermal synthesis and liquid templating method have been widely used for the synthesis of MCM-41, which produces uniformly shaped and sized hexagonal channels, with surface area ranging from 700-1500 m^2/g (Mehdinia 2015).

These mesoporous structures can be further modified to make it more stable and enhance its characteristics to make it more suitable for adsorption, catalysis, and as sensors. This report reviews MCM-41 as an adsorbent and reports its functionalization to make it more efficient as an adsorbent towards heavy metals like lead, chromium, and mercury. Similarly, it will also present the adsorption of other ions as potassium, calcium and nitrates that are found in water.

1.2 Objectives

The objective of this research is to synthesize and study the characteristics of MCM-41, and its modified product $ZnCl_2$-MCM-41, and apply these adsorbents for 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-}).

While adsorption of lead by pure MCM-41 has been studied, it needs to be functionalized by other groups to achieve specific characteristics. Grafting of different functional groups on the surface of mesoporous structures makes the adsorption process more effective. Different studies have already been done using a variety of modifications to MCM-41 (Behbahani 2014, Etienne 2002).

For this, another goal of this research is to modify the synthesized MCM-41 with $ZnCl_2$ and apply it for removal of heavy metal ions found in wastewater. Then the results obtained with MCM-41 and $ZnCl_2$-MCM-41are compared with the widely used adsorbent, activated carbon as a sorption standard.

1.3 Thesis Overview

This Thesis report has overall five chapters.

Chapter 1 Introduction: This chapter presents the background and introduction on MCM-41, its structure and synthesis, and the objectives of the thesis research.

Chapter 2 Literature Review: This chapter provides literature review of the research topic, with references and examples of previously done works on similar research of adsorption of heavy metals.

Chapter 3 Methodology: The third chapter is to describe the methodology used in this research, including the synthesis process used, the batch isotherms and their models applied to calculate their adsorption capacities.

Chapter 4 Results and Discussion: Chapter four reports the results of experiments to determine the adsorption capacity of the synthesized material, MCM-41 as well as that of $ZnCl_2$-MCM-41, and their comparisons with that of Activated Carbon (AC).

Chapter 5 Conclusion and Recommendations: The final chapter summarizes the conclusions and recommendations on the use of MCM-41 and $ZnCl_2$-MCM-41 for adsorption of heavy metals and removal of hardness from water.

CHAPTER 2 - LITERATURE REVIEW

2.1 Porous Materials

Zeolites and porous silica are a family of crystalline aluminosilicate and they are used for applications in separation and catalysis, due to their small pore diameters (Prasomsri et al. 2015). Conceptually, molecular sieves are materials that can retain the particles which fit in the channels while letting the larger ones through (Alothman 2012). Thus, they exhibit excellent adsorption properties.

Porous materials are formed in stages by crystallization and consists of interconnected pores. The porous materials are categorized according to its pore size by IUPAC as microporous materials (pore size diameters 2 nm), mesoporous materials (pore size diameters from 2-50 nm), and macroporous materials (pore sizes more than 50 nm) (Alothman 2012).

Porous silica materials have three-dimensional structure with internal pores interconnected through SiO_4 tetrahedra, which can be processed using sol-gel method. These materials possess better physical and chemical properties, and exhibit better ion exchange abilities than amorphous materials (Prasomsri et al. 2015). But these zeolites have diffusion limitations, and zeolites below the size of 100 nm may cause filtration problems due to their colloidal nature (Prasomsri et al. 2015). And while zeolite itself has weak stability and small pore size, mesoporous materials similar to MCM-41 have large pore sizes and are more stable. The preparation of these materials is attained by synthesizing long chains of alkyltrimethylammonium cations into layers of silicate kanemite, and then calcining it to remove any organic species remaining. This produces a mesoporous material, which was later developed by the Mobil Corporation as M41S family of aluminosilicate molecular sieves (Alothman 2012).

2.2 MCM-41

"Mesoporous structure is defined by IUPAC as porous materials with pore sizes between 2.0 to 50.0 nm. Mesoporous material was first introduced in 1992, when Mobil Corporation researchers discovered large uniform pore structures family MCM 41S, which is synthesized with sol-gel and surfactant method (Alothman 2012). The M41S family was developed with a soft-templating method using ammonium surfactant micellar aggregates which work as organic templates (Prasomsri et al. 2015).

MCM-41 is one of the three mesoporous family, lamellar (MCM-50), hexagonal (MCM-41) and cubic (MCM-48) as shown in Figure 1. MCM-41 is one of the widely researched hexagonal mesoporous molecular sieves, due to its large surface area, uniformed-sized pores, controllable pore sizes, thermally more stable, and capabilities as adsorbent, sensors and catalysts (Bao et al. 2004; Dai et al. 2014; Raji et al. 2016). These mesoporous structures possess surface areas of about 1000 m^2/g, and a large pore volume (as large as 1.0 cm^3/g) which can be measured by electron microscopy (TEM) and X-ray powder diffraction (XRD) (Alothman 2012; He et al. 2015). MCM-41 also has high adsorption capacity, and large amount of internal hydroxyl groups (40-6-%), and high surface reactivity (Mehdinia et al. 2015).

Figure 1- Schematic Diagram of MCM-50 (layered), MCM-41 (hexagonal), and MCM-48 (cubic) (Alothman 2012)

Besides all its suitable characteristics as an adsorbent, it also has well defined surface properties, and low toxicity, as well as fine pore dimensions (1.5-20 nm) with stable thermal, hydrothermal, chemical and mechanical properties (Mehdinia et al. 2015). These features provide easily tunable surface to make modification possible with other materials to yield better ionic and binding properties (Dimos et al. 2009, Egodawatte et al. 2015).

But mesoporous silica powders are difficult to separate and recover due to their small sizes (Behbahani et al. 2014). Although their recovery is difficult to attain, silica mesoporous material is a suitable adsorbent (Prelot et al. 2012).

2.3 Synthesis of MCM-41

In the early 1990s, mesoporous material similar to MCM-41 was synthesized from alkyltrimethylammonium cations, into the layered silicate kanemite, then calcined to remove moieties (Alothman 2012). The synthesis by liquid crystal templating is used, in which a liquid crystal forms a mesostructure with formation of continuous centimeter scale morphologies. Templating is a process in which an organic species acts as a central structure, and the other entities form a crystalline network around it. When the organic templates are removed by calcination, the inorganic materials take their geometry, hence forming the new crystalline lattice structure

(Alothman 2012). And different organic groups can be incorporated into the pores when the templates are extracted instead of calcinations (Melde et al. 2008).

MCM-41 were synthesized using pure silica, CTAB and tetramethylammonium hydroxide. It was tested for adsorption of Cd^{2+}, Co^{2+}, Cu^{2+}, and Pb^{2+} in aqueous solution. The aminated materials were found to have fast adsorption capacity for the metallic cations, with Cu^{2+} and Pb^{2+} having the greatest affinity amongst all the metals.

There are many ways to prepare mesoporous structured particles. Sol-gel process is one of the processes, which is the transformation of a sol to a gel. A sol is a colloid of small particles (agglomerate) that are dispersed into a liquid which eventually link together to form a coherent network (gel), and MCM-41 has been prepared using sol-gel method (Heidari et al. 2009). The hexagonal structure is a result of condensation of silicate species adsorbed into external surfaces of randomly ordered rod-like micelles. These pack into ordered species to form a mesoporous material (Alothman 2012). The concentration of the surfactant employed affects the structure of the material and for use of tetraethylorthosilicate as silica source, the surfactant's concentration should be equal or higher than the micelle concentration (Alothman 2012). The room temperature synthesis of Si-MCM-41 with CTMABr and TEOS gives the gel with composition of SiO_2: xCTMABr: yNH_4OH: zH_2O, and according to literature, the optimal composition to produce hexagonal pores in MCM-41 is SiO_2: 0.12CTMABr: $2.5NH_4OH$: $150H_2O$ (Gaydhankar et al. 2007).

Figure 2 shows the synthesis of MCM-41 from silica materials to form the final hexagonal array of MCM-41. The structure is affected by the type of template used or any modification compounds added to it, but the resultant pore structure are regular mesoporous channels (Raji & Pakizeh 2013).

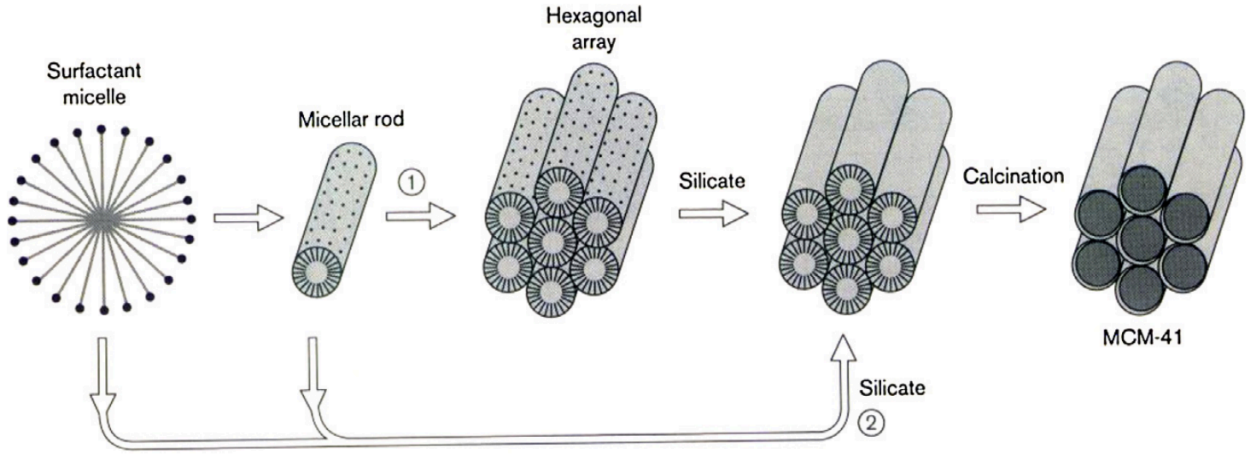

Figure 2-Synthesis scheme for MCM-41 (Raji & Pakizeh 2013)

2.4 MCM-41 Structure

MCM-41 hexagonal structure formation is based on the surfactant concentration as the surfactants exist as monomolecules at low concentrations, and only come together as the concentration increases in order to decrease system entropy. At high concentration, hexagonal arrays are formed, and these combine to form parallel cylinders known as lamellar phase (Alothman 2012).

XRD pattern shows the hexagonal cylindrical channels, which are represented by (100), (110) and (200) reflections (Anbia and Mohammadi 2009, Kuster et al. 2014). The silicon and oxygen bonds (Si-O-Si) are seen from FT-IR spectrum in many experimental results (Anbia and Mohammadi 2009, Chen et al. 2015). Similarly, SEM micrographs of various samples have shown a spherical morphology of MCM-41, with larger particles and less monolithic aggregates (Anbia and Mohammadi 2008). The adsorption-desorption studies done for MCM-41 confirms the mesoporous nature of the MCM-41 (Lu et al. 2016; Raji et al. 2015).

MCM-41 displayed a strong band of 3200-3800/cm (FT-IR) that verifies the Si-OH bonds of silanol groups (Cao et al. 2014; Lu et al. 2016). These features show hydroxyl groups in the

MCM which are the physically adsorbed water molecules (Anbia & Mohammad 2009; Chen et al.2015).

Figures 3 and 4 are images from different experiments that show the hexagonal pattern of the MCM-41 pores. The TEM images show the uniform distribution of hexagonal pores that represent a crystalline structure of MCM-41 and the SEM image shows the cylindrical tube formation.

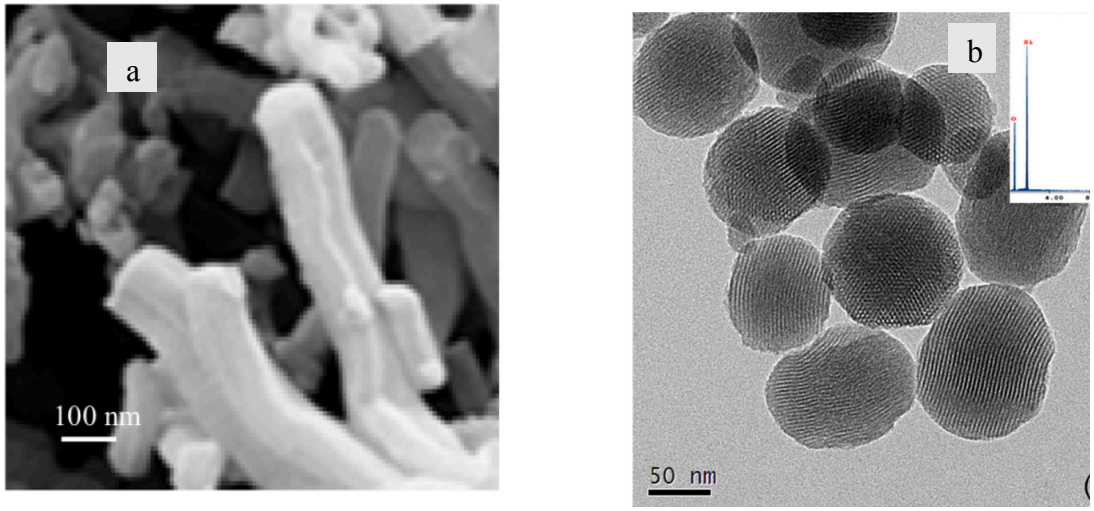

Figure 3 -a) SEM image of MCM-41 (Bao et al. 2015) and b) TEM image of MCM-41 (Dai et al. 2014)

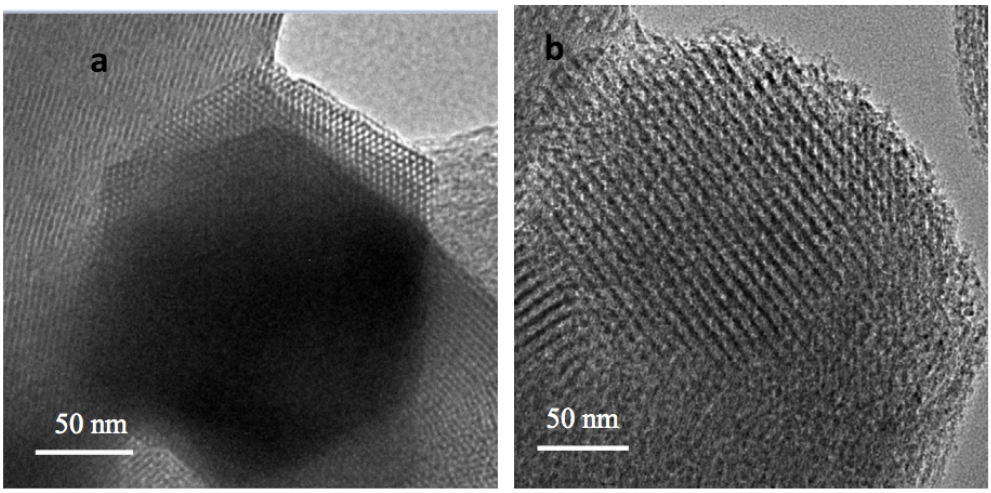

Figure 4 -a) TEM image of MCM-41 b) TEM image NH_2-MCM-41 (Bao et al. 2015)

2.5 Applications

Functionalized MCM-41 exhibits properties that can be used in catalysis, adsorption and other environmental remediation (Alothman 2012; Showkat et al. 2007) as well as in other applications such as biosensors, electrolyte, semiconductors, drug delivery systems, solar cells, gas separation, molecular shuttles, coatings for corrosion protection, etc. (Samiey et al. 2014).

2.6 Adsorption

Although various water and wastewater treatment methods have been researched and developed, ion exchange using zeolites, kaolinite, vermiculite, attapulgite, other artificial mesoporous silica (Bao et al. 2015), and clays or ionic resins are more effective for adsorption of different compounds (Algarra et al. 2005). Similarly, alternatives like reverse osmosis, electrodeposition, cementation, selective liquid-liquid extraction, and Nano-filtration requires higher energy, especially with low metal concentration (Bao et al. 2015; Culita et al. 2016; Raji et al. 2015). Ultrafiltration and microfiltration would not separate heavy metals from water sources

normally due to large pore sizes. And, even though polymer enhanced adsorbent in filtration can be useful, but it requires energy for sludge management (Bao et al. 2015).

Adsorption is more effective method than other methods like precipitation, chemical oxidation-reduction, ion exchange, filtration, membrane separation and photocatalytic reduction, as adsorption is free from chemical sludge and has higher efficiency to remove heavy metals and is low cost as well (Cao et al. 2014; Culita et al. 2016; Ghorbani et al. 2016). It can effective for extraction of heavy metals from water and sludge as it has advantages of easy handling, reduction of the volume of solid wastes, and reversibility of removal process so that the raw materials are retainable (Prelot et al. 2012).

Recent works show that mesoporous materials and magnetic particles can be used to achieve greater adsorption capacity, removal and recovery of the toxic compounds from the aqueous solutions (Anbia & Mohammadi 2009). Ordered mesoporous silica products may attract metal cationic species within the pH range from 3 to 9 as they have point of zero charge between 1.3 and 3.7 (pH) (Prelot et al. 2012).

Adsorption occurs in two steps-transport of the metal ion to the external surface of the adsorbent and pore diffusion of the metal ion into the interior surface of the adsorbent. The first step is a rapid one, while pore diffusion is a slow process (Ghorbani et al. 2016).

2.7 Sensors

Silica materials can be used for their capabilities as a sensor due to their stable nature over a wide range of pH and their applications in fields such as optical sensing, electrochemical sensing, and biosensing. (Melde et al. 2008). Some mesoporous materials have been used in electrochemical sensors due to their special structure, and their good stability to adsorbates, which

can improve detection of trace heavy metals (Dai et al. 2014). Metal ions can be separated with the use of supramolecular recognition and fluorescent chemical sensor principle. The fluorescent sensors can be utilized for a highly selective ion recognition receptor and can be combined with other materials to form a novel material for detection of metal ions (He et al. 2015).

An example of sensing ability of MCM-41 was presented to detect Pb^{2+} and Cd^{2+} in tap water, lake water, and tea samples, and compared with ICP-OES results, which showed the reliability of MCM-41 sensor, along with the recovery rate of heavy metals up to 106.4% for Pb(II) and 102.3% for Cd (II) (Dai et al. 2014). MCM-41 can be a capable material for an electrode if modified properly so that it can detect metal ions even at low concentration.

2.8 Removal of Heavy Metals

Heavy metals such as Pb, Cr, Cu, Zn, Cd, As, Hg, and Mn are present as toxic materials in the environment and some of these are the ones present as the most hazardous metal ions found in liquid effluents from different industries (Cao et al. 2014; Culita et al. 2016). The removal of these heavy metals has been important due to their toxicity. Their removal from the water/wastewater, and thus from environment overall, has been incorporated in environmental legislature in many countries (Culita et al. 2016).

MnO_4^-, if exceeds the concentration of 0.1 mg/L in water bodies, reduces the biological oxygen demand, and can affect the central nervous system (Cao et al. 2014). Gasoline can be a source of air pollution by releasing several heavy metals in the environment through combustion or even while refining, distilling, transporting or storage (Behbahani et al. 2014).

Adsorptive membranes have been used in several studies to gain a better and faster removal efficiency of heavy metals, higher flow rate, lower pressure drop, reusability, and ease to use as well as for being environmentally friendly (Bao et al. 2015).

Various factors play important roles on adsorption of heavy metals from aqueous solutions. With the decrease in solution pH, the sorption can be increased. pH decrease means more H^+ and so more active sites for heavy metals uptake. Similarly, sorbent dosage and contact time also affect the equilibrium capacity (Ghorbani et al. 2016).

a) **Lead**

Among the heavy metals, Pb^{2+} is one of the toxic materials and has been categorized as hazardous by US Environmental Protection Agency (Chen et al. 2015). Lead can cause hypertension, hepatic injury, bone degeneration, and liver and lung damage because of its toxic nature (Ghorbani et al. 2016; Heidari et al. 2009). Lead pollution can arise from industries like alloys, metal plating, mining, ceramics, etc. (Heidari et al. 2009). Due to its toxic nature, lead is the only metal with limitation not only in drinking water but also in allowable concentration (5μg/L) by the National Agency of Petroleum, Natural gas and Biofuels (ANP) (Behbahani et al. 2014).

Different experiments using MCM-41 and its other modified forms have already showed their adsorption capacity for lead. Py-Fe_3O-MCM-41 was synthesized for selective solid phase extraction and to trace lead and copper in fuel products (Behbahani et al. 2014).

Lead removal has been tried in a few experiments with modifications of MCM-41, as shown in Table 1, and the sorption of lead by $ZnCl_2$-MCM-41 has been successful, with adsorption capacity in Langmuir isotherm as high as 479 mg/g of sorbent (Raji et al.2015).

Table 1 Adsorption of Lead ions

Adsorbent used	Details	Capacity	References
Amine-MCM-41 for Cr(VI), As(V), Pb(II), Hg(II) removal	BET: 1045 m^2/g for CTAB, Volume: 248 mm^3/g	-	(Showkat et al., 2007)
MCM-41, NH_2-MCM-41 for Ni(II), Cd(II) and Pb(II) removal	BET: 966 and 1387 m^2/g; size: 4.85 and 4.88 nm for MCM-41 and nano MCM-41 resp.	12.36, 18.25, and 57.74 mg/g for Ni, Cd & Pb resp.	(Heidari et al., 2009)
MCM-41 for removal of Cu (II), Pb (II), Ag (I), Cr (III)	BET: 421.9 m^2/g, volume: 0.556 cm^3/g, pore dia: 5.27 nm	-	(Wu et al.,2010)
MCM-41 for Cd, Co, Pb, Sr removal	-	Pb<Cd<Co<Sr	(Prelot et al., 2012)
ALG-MCM-41 for Pb (II) adsorption	BET: 915 m^2/g for 12.7 m^2/g; volume: 0.67 & 0.02 cc/g, dia: 1.93 & 1.79 for MCM-41 & ALG-MCM-41	140.84 mg/g	(Tavakoli et al., 2013)
MCM-41 for Hg, Cd & Pb removal	3 nm size	81.5%,55.6%,92.5% removal rate for Hg, Cd & Pb resp.	(Zhao et al., 2013)
Py-Fe_3O_4-MCM-41 for Pb (II) & Cu(II) ions removal	-	287 mg/g for Pb and 194 mg/g for Cu	(Behbahani et al., 2014)
NH_2-MCM-41 for removal of lead and cadmium	-	Sensor for Pb and Cd	(Dai et al., 2014)
NH_2/MCM-41/NTAA for removal of Pb^{2+} and MnO_4^-	Pure MCM-41-BET: 916 m^2/g, pore volume: 0.68 cm^3/g, dia: 2.59 nm	147 mg/g for Pb^{2+} and 156 mg/g for MnO_4^-	(Chen et al., 2015)
$ZnCl_2$-MCM-41 for Pb removal	BET: 754 m^2/g; dia: 2.86 nm	479 mg/g	(Raji et al., 2015)
Fe_3O_4@MCM-41-N-oVan for Pb (II) removal	Fe_2O_3@ MCM-41 BET: 555 m^2/g, volume: 0.59 cm^3/g	155.71 mg/g	(Culita et al., 2016)
MCM-41 +/-IIP for removal of Pb	BET: 1073 and 189 m^2/g resp.; 0.93 and 0.17 cm^3/g; dia: 3.46 and 3.65 nm resp.	57.7 and 27 mg/g resp. for ion-imprinted and non-ion imprinted MCM-41.	(Ghoohestani & Faghihian, 2016)
MCM-41/TMSPDETA for Pb (II) and Ni (II) removal	BET: 1063 and 867 for MCM-41 and MCM-41/TMSPDETA resp.; volume: 1.082 and 0.782 cm^3/g, dia: 13.88 and 3.61 nm resp.	77.52 and 58.47 mg/g for Pb (II) and Ni (II) ions	(Ghorbani et al., 2016)
Nanoscale Zero Valent Irons (nZVI) coupled with Rice Husk MCM-41 for Pb (II) removal	-	233 mg/g Pb	(Kaewbuddee et al., 2016)
NZVI MCM-41 for removal of Pb(II)	Specific Surface area: 744.27 & 247.41 m^2/g for MCM-41 and MSNZVI resp.;	416.17 mg Pb/g	(Lu et al., 2016)

b) Mercury

Mercury is one of the most toxic heavy metals due to its high affinity to thiol groups in proteins and enzymes. Accumulation of mercury in the body can lead to systemic poisoning and cause death (Zhai 2016). Mercury (II) can exist in aqueous forms at different pH and in combination with chloride, as $HgCl_2$, $HgCl_3$, $HgCl_4$ (Etienne et al. 2002). Mercury removal using different functionalized mesoporous materials have been studied. MCM-41 was utilized to adsorb mercury with adsorption capacity of 56.48 mg/g (Zhai et al. 2016). In a recent study, MCM-41 functionalized with magnetic di-thiocarbamate groups, which provided a high efficiency of Hg^{2+} removal in environmental samples, with an adsorption capacity of 538.9 mg/g of adsorbent (Mehdinia et al. 2015). Different experiments of its removal have been compared as shown in Table 2.

Table 2 Adsorption of Mercury ions

Adsorbent used	Details	Capacity	References
MCM-41/APTES-10%, and MCM-41/MPTMS-10% for Hg removal	BET: 1040 m2/g for APTES; 1580 for MPTMS; volume: 0.64 cm3/g & 0.78 cm3/g resp.	10-02 mmol/g for APTES, and 0.6 mmol/g for MPTMS	(Etienne et al., 2002)
MCM-41 for removal of Hg (II)	-	0.70 mmol/g	(Puanngam & Unob, 2008)
Mercaptopropyl(MP) or diethylenetriamine (DETA) functionalized MCM-41 for Hg removal	BET: 760.21, 448.83, 237.56 m2/g for MCM-41, MP-MCM-41, DETA-MCM-41 resp., pore size: 6.74, 6.67, 5.48 nm, porevolume:0.9868,0.5924,0.409 cm3/g resp.	1245 µmol/g Hg(II)	(Idris et al., 2011)
Thiol-functionalized magnetic mesoporous microsphere (TMMM)	Surface area: 913.14 m^2/g; pore dia: 2.48 nm	185.19 mg/g for Hg (II) and 114.7 mg/g for Pb (II)	(Tao et al., 2012)
$ZnCl_2$-MCM-41 for Hg removal (Thermodynamic study)	BET: 602.3 m2/g, pore size: 2.37 nm; volume: 0.46 cm3/g	204.1 mg/g	(Raji & Pakizeh, 2013)
Core shelled Fe_3O^4 NPs MCM-41 /rhodamine for removal of Hg (II)	-		(Chen & Mu, 2014)
MCM-TEOS for removal of Hg (II)	-	47.50 mg/g	(Saman, Johari, & Mat, 2014)
Aminopropyl MCM-41SM for Hg removal	BET: 1138 m2/g; pore volume: 0.875 cm3/g; pore size: 1.384 nm	21 mg Hg2+/g Separation Material (SM)	(He et al., 2015)
Di-thio-MCM-41(DT-MCM-41) for Hg removal	BET: 1207 m2/g, & 830 m2/g for magnetic MCM-41, and magnetic DT-MCM-41 resp.	538.9 mg/g	(Mehdinia et al., 2015)
$ZnCl_2$-MCM-41 for Hg removal	-	Recovery of Hg (II) upto 75%	(Raji et al., 2016)
Polyacrylamide (PAAM)-NH_2-MCM-41 for Hg (II) removal	-	177 mg/g	(Saad et al., 2016)
MCM-41 for Hg removal	110 nm average size	56.48 mg Hg/g sorbent	(Zhai et al., 2016)

c) Chromium

Chromium is another industrial heavy metal which is highly toxic and can cause health issues such as bronchitis, liver damage and ulcer formation, and is also highly carcinogenic (Bao et al. 2015). It is released into the environment through industrial wastewater of dyes and pigments, films and photography, metal cleaning, plating, leather and mining (Cao et al. 2014). In general, Cr (VI) is considered the most toxic state of Chromium, but Cr (III) which is a vital trace element for human body, can cause poisoning if it is absorbed in excessive amount. Adsorption of Cr (III) and Cr (VI) has been studied in a few studies lately, and some of them have showed the modification of MCM-41 with iron oxide nanoparticles yielded successful magnetic separation (Egodawatte et al. 2015).

In a study with three amino-functionalized (hexadecylamine, dodecylamine, and dimethyldodecylamine) MCM-41 and MCM-48, adsorption of chromate and arsenate ions increased with its functionalization as the sorption capacity increased with the chain length of functionalized groups (Benhamou et al. 2013). Other studies for adsorption of chromium by use of MCM-41 as well as its functionalized product are shown in Table 3.

Table 3 Adsorption of Chromium ions

Adsorbent used	Details	Capacity	References
Cationic MCM-41 for removal of dichromate ion and furfural/ used a little for MCM structure	-	126.39 mg Cr (VI) /g (2.43 mmol/g) for as-MCM-41; 0.5 mg/g (1.21 mmol/g) for calcined MCM-41	(Anbia & Mohammadi, 2009)
Magnetic MCM-41 for removal of Cr (VI)	550 m^2/g; 10 nm	1.9 mmol/g (100 mg/g)	(Chen, Lam, & Yeung, 2011)
MCM-41 for removal of Cr (VI)	Surface area: 1040 m^2/g; dia: 2.8 nm	904 mg/g	(Tian et al., 2011)
TiO_2-MCM-41 for removal of Cr (VI)	-	91% at 100 mg/L Cr (VI)	(Parida, Mishra, & Dash, 2012)
Terpyridine-functionalized MCM-41 for removal of chromate	-	114 mg/g (0.97 mmol/g)	(Sattari et al., 2013)
NH_2-MCM-41 for removal of Chromium (VI)	Pure MCM- BET: 41: 821 m^2/g, Pore size:3.02 nm & pore volume: 0.94 cm^3/g	38.55 mg/g for Cr (VI), 94.6 mg Cr/g for $Cr_2O_7^{2-}$	(Cao et al., 2014)
Grafted NH_2-MCM-41 for removal of Chromium (VI) & Copper (II)	Pure MCM-41: 1025 m^2/g,2.71 nm; NH_2-MCM-41: 437.2 m_2/g, 2.21 nm	2.8 mg Cr/g & 3.7 mg Cu/g (Adsorption equilibrium=5 min)	(Bao et al., 2015)
Fe_3O_4@MCM-41 for Chromium removal	Pure MCM BET: 1032 (+/- 15) m^2/g, pore volume: 0.61 cm^3/g, dia: 3.2 nm	0.17 mmol Cr/g for pureMCM-41and 0.71 mmol Cr/g for magnetic iron oxide/mesoporous silica	(Egodawatte et al., 2015)
MnO_2/MCM-41 for Cr (VI) and As (III) removal	-	3.872 mg/g for Langmuir	(Wu et al., 2015)
2-ureylenemethyl-pyridine functionalized MCM-41 for Cr(III) removal	BET: 983 m^2/g for MCM-41, pore volume: 0.55 cm^3/g, dia: 29 nm	36% & 64% selectivity in water & seawater resp. with other interfering ions like Zn, Cd, Co & Cu.	(Mathew et al., 2015)
NH_2-MCM-41 for removal of Chromium (III)	BET: 155.1 m_2/g	83.33 mg/g for Cr (III)	(Kaur et l., 2016)
MCM-41 for chromate removal	BET: 718 m^2/g, pore size: 3.6 nm, volume: 0.76 cm^3/g	4.10 mg/g when initial conc. was 50 mg/L	(Wei et al., 2016)

d) Other Metals

Other metals such as nickel, cadmium and copper which are also harmful to the environment as well as human body, can be removed through adsorption. Copper, which is used in industries for electroplating and alloy preparation, can cause skin, brain, pancreas, and heart diseases if accumulated in the human body (Bao et al. 2004). The maximum allowable concentration of copper in fuel is 0.07 mg/kg (Behbahani et al. 2014). Toxic metals in fuel (gasoline) is a major cause of pollution, even in low concentrations. Nickel and cadmium were successfully removed with the use of amine functionalized MCM-41with a capacity of 12.36 mg Ni (II)/ g sorbent and 18.25 mg Cd (II)/g sorbent (Heidari et al. 2009). In other studies, silver and arsenic were adsorbed alongside other metals like copper, lead and chromium (Wu et al. 2010; Wu et al. 2015). Table 4 shows a few research details for removal of other metals.

Table 4 Adsorption of other metals

Adsorbent used	Details	Capacity	References
Aminopropyl-Si MCM-41 for Ni (II) & Cu (II) removal	S_{BET}: Na_{50}, Na_{25}, Na_5 has 869, 881 & 649 m^2/g resp.	128,75 & 54 meq/100 g for Cu; & 36,21 & 34 meq/100 g for Ni	(Algarra et al., 2005)
Cationic MCM-41 for removal of copper –phthalocyanine anion $(Cu(tsPc)^{-4})$	-	300.5 mg/g of $(Cu(tsPc)^{-4})$ for as-MCM-48 & 285.5 mg/g for as-MCM-41	(Anbia & Mohammadi, 2008)
MCM-41 @ NH_4 for removal of heavy metals	BET: 948 m_2/g, Volume: 0.80 cm_3/g		(Dimos et al., 2009)

2.9 Modified MCM-41

Pure MCM-41 has low adsorption of heavy metals as it does not have enough capacity for the adsorption process, which is the reason for many new studies functionalizing different groups into MCM structure to achieve higher adsorption capacity (Ghorbani et al. 2016; Raji & Pakizeh 2013). To increase the adsorption capacity, modifications can be made by organic compounds or

metal salts, and there are several examples of incorporation of different compounds into MCM-41 pores to create a more capable sorbent (Algarra et al. 2005, Dimos et al. 2012, Raji and Pakizeh 2013, Ghorbani et al. 2016).

Other additional techniques have been applied to improve the thermal stability. Grafting of functional groups like amino, diamino, triamino, malonamide, carboxyl, dithioc arbamate, humic acid, and imidazole to the mesoporous silica structure (Cao et al. 2014). Large pore groups are preferred to incorporate these functional groups so that there is no pore blockage and the grafting is uniformly done (Melde et al. 2008).

Functionalization can be done by grafting organic groups on the surface of the silica or by the co-condensation method (Melde et al. 2008). Such examples are illustrated in Figures 5 & 6, which show MCM-41 functionalized with different functional groups for adsorption. Amine functionalized MCM-41 (NH_2-MCM-41) was reported to have high adsorbent capacity towards heavy metals like Ni (II), Cd (II), Pb (II), Cu (II) and As (II) (Bao et al. 2015).

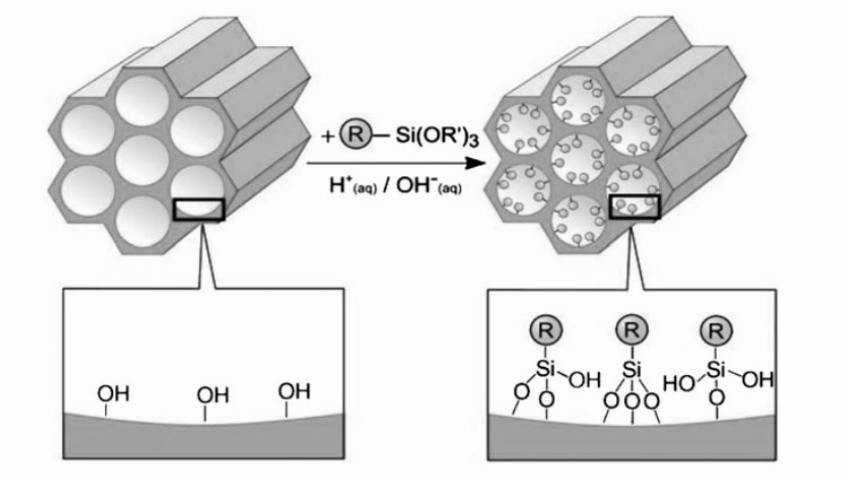

Figure 5 - Polymer Grafting on MCM-41 (Ghoohestani & Faghihian 2016)

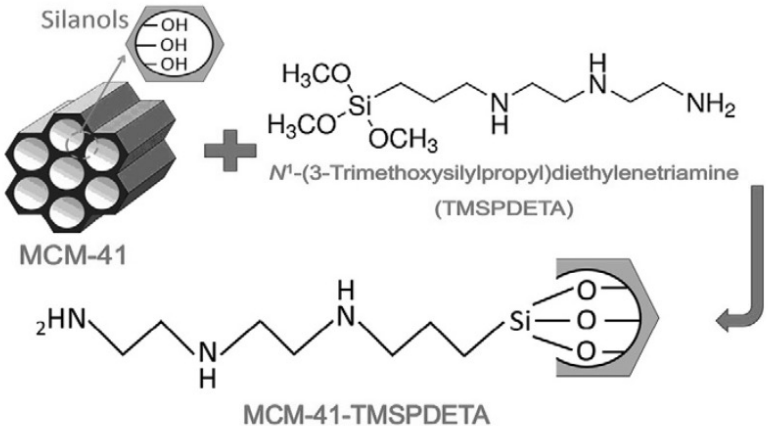

Figure 6 - Structure of MCM-41/TMSPDETA (Ghorbani et al. 2016)

TEM images in several recent studies show the stability of the mesoporous form after it is functionalized (Chen et al. 2015; Ghorbani et al. 2016; Raji & Pakizeh 2013; Zhao et al. 2013). Cations and anions cannot be simultaneously removed in a single reactor, and so even if the toxic metal ions are removed, the anions remain in the solution. For adsorption of both anions and cations, amino functionalized MCM-41 have the capacity to target and remove both cations and anions simultaneously in a solution (Chen et al. 2015).

To achieve easy separation and recovery of mesoporous silica, novel materials can be prepared by introduction of magnetic nanoparticles into the mesoporous structures (Behbahani et al. 2014). These can be useful in the fields of drug delivery for controlled release, bioseparation, biocatalysis and separation. (Behbahani et al. 2014). Magnetic properties of iron oxide have been used to adsorb Cr (VI), Hg, and Cu (II) in some studies, and this is possible due to the effectiveness of iron oxides when coupled with a mesoporous silica particle (Egodawatte et al. 2015).

2.10 $ZnCl_2$-MCM-41

$ZnCl_2$, an inorganic metal salt, can be loaded in the pores of MCM-41 due to the high surface area and easily accessible pores of MCM-41 (Raji & Pakizeh 2013). And while many other organic groups and metal salts have been used to modify MCM-41, $ZnCl_2$-MCM-41 has shown better results in adsorption of lead and mercury. Figure 7 shows the TEM structure of $ZnCl_2$-MCM-41, which shows that even after the addition of $ZnCl_2$, the material still retains its original structure. There are not many studies on modification of MCM-41 with $ZnCl_2$ currently; and thus, research investigates the adsorption capacity affected by addition of $ZnCl_2$ to MCM-41 structure.

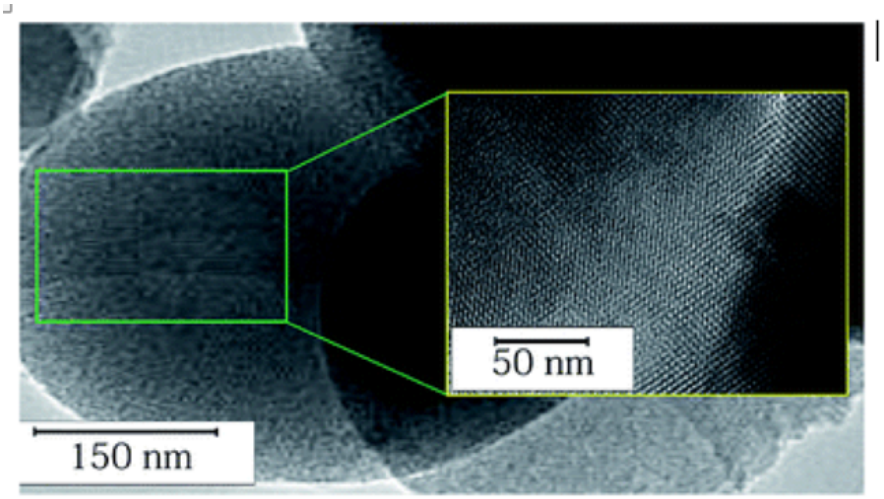

Figure 7 - TEM image of $ZnCl_2$-MCM-41 (Raji et al. 2015)

MCM-41 particles synthesized using hydrothermal method was modified using $ZnCl_2$ for Hg(II) removal from aqueous solution (Raji & Pakizeh 2014; Raji et al. 2016). $ZnCl_2$-MCM-41 has also been used for Pb (II) adsorption and the structure of the modified MCM-41 can be seen in Figure 8. The uptake of mercury ions by $ZnCl_2$-MCM-41 is shown in the Figure 9. N_2

adsorption-desorption isotherm on these studies show that the loading of $ZnCl_2$ particles into MCM-41 surface decreases the surface area, but tfhese pores are still mesoporous (Raji & Pakizeh 2014; Raji et al. 2016).

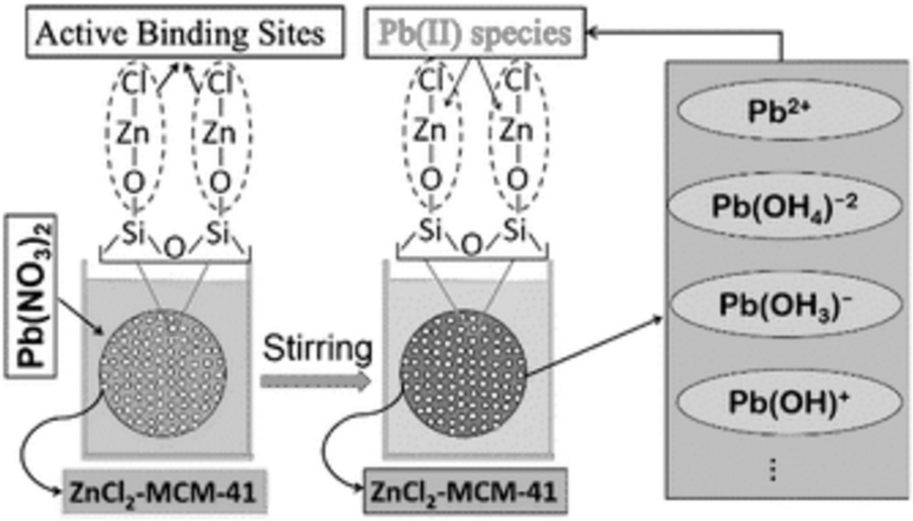

Figure 8 - Adsorption mechanism of Pb (II) species by $ZnCl_2$-MCM-41 (Raji et al. 2015)

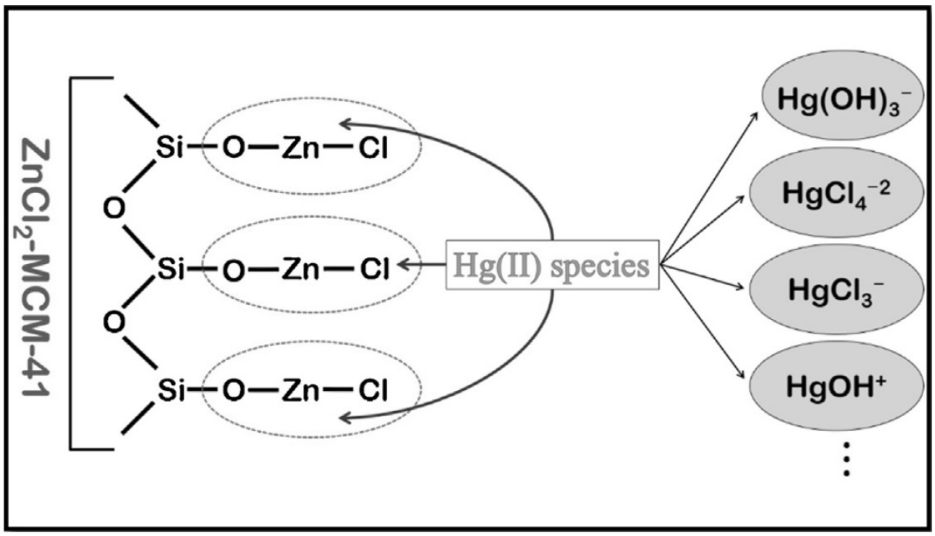

Figure 9 - Adsorption mechanism of Hg (II) species by $ZnCl_2$-MCM-41 (Raji & Pakizeh 2014)

2.11 Effect of various factors

a) Effect of pH

pH is one of the most important factor for obtaining an efficient adsorption capacity and has a considerable effect on the adsorption process as pH causes changes in properties of both adsorbent and adsorbate (Ghorbani et al. 2016).

For magnetic particles like Fe3O4 –MCM-41, adsorption of lead and copper increased from pH 2.0 to 6.0, but decreased slightly from pH 7.0 to 9.0 (Behbahani et al. 2014). This was due to electrostatic repulsion of the protonated active sites on the sorbent with cationic adsorbates lead and copper: thus, as the pH decreases, the removal also decreased.

The removal efficiency of chromium increased with increase of pH from 2.5 to 3.5, and the removal decreased for pH>3.5 (Cao et al. 2014). And the maximum adsorption capacity for Cr (III) was found to be at pH 3 (Kaur et al. 2016). Similarly, the sorption efficiency for metal ions Cd(II), Ni(II), and Pb(II) increased as pH was increased from 1.5 to 5.0 (Heidari et al. 2009). In this case, it was due to increase in the number of binding sites for ion uptake as the protonated size decreases when the acidity decreases.

b) Effect of the adsorbent concentration

Adsorbent dosage is another important factor. As the dose of the adsorbent increases the adsorbent, so is the surface area as there are more available sites for adsorbate (Kaur et al., 2016). Magnetic mesoporous materials have higher surface area to volume ratio, which increases the extraction capacity (Behbahani et al. 2014). Cr (VI) removal increased from 42.7 to 98.6% when the adsorbent dosage was increased from 1.0 to 5.0 g/L (Cao et al. 2014).

On the other hand, when the dosage of the adsorbent was increased, the removal efficiency increased, but the adsorbed amount per unit adsorbent decreased after a certain dosage. This is the result of the lack of saturation of the adsorbent surface with adsorbate after a certain concentration (Lu et al. 2016).

c) Effect of Temperature

Sorption was more for Pb(II) at 20°C than at 30, 40 and 50°C. (29.1, 27.2, 24.1, and 21.2 mg/g respectively). Adsorption of metal ions like Pb (II) and Ni (II) is an exothermic process and the adsorption capacity decreased with temperature (Ghorbani et al. 2016). Also, the sorption amount decreased from 20 to 50°C from 58.08 mg/g to 54.18 mg/g for Pb (II) (Raji et al. 2015). This might be due to the tendency of Pb (II) and Ni (II) species to escape from the sorbent surface as the temperature increases (Ghorbani et al. 2016). But with Cr (VI), its adsorption increased with increasing temperature, which might be due to increase in movement of ions across the boundary and into the adsorbent pores (Cao et al. 2014).

d) Effect of sorption time

Contact time is an important factor for adsorption process to be effective in batch adsorption. The adsorption of Cr (III) increased from 85% to 92% from 30 minutes to 2 hours (Kaur et al. 2016). Another study of Pb adsorption showed the contact time, when increased from 0.5 to 5 hours, also increased the adsorption during the first 4 hours (Lu et al. 2016).

e) Effect of other competitive ions:

The adsorption of various metal ions can be affected by the competitive adsorption of different ions on the binding sites available on the adsorbents, which can create difficulty in precise removal of targeted ions. The adsorption capacities were highest for Hg among Pb, Cd, and Zn in a study

using magnetic NH_2-MCM-41, with Zn having the lowest interference (Mehdinia et al. 2015). Another experiment shows high selectivity of chromate when MCM-41 was used to adsorb metal ions from a solution of Ni^{2+}, Cu^{2+}, Cd^{2+}, and Pb^{2+} and Cr^{3+} (Wei et al. 2016).

2.12 Techniques for sorbent characterization and detection

Techniques such as atomic absorption spectroscopy, atomic fluorescence spectrometry, inductively coupled plasma-mass spectrometry, colorimetry, have been used for detection of heavy metals in solution (Dai et al. 2014). For the characterization of the sorbent before and after the adsorption process, analysis techniques of Fourier Transform Infrared Spectroscopy (FTIR), Transmission Electron Microscopy (TEM), and Scanning Electron Microscope (SEM) are mostly for characterizing the material. And for detection of the metals in solution, ion selective electrode (ISE) for lead and inductively coupled plasma optical emission spectrometry (ICP-OES) for all the other metals can be used.

CHAPTER 3- METHODOLOGY

This chapter includes the methodology for synthesis of MCM-41 and $ZnCl_2$-MCM-41 as well as their application in adsorption studies.

3.1 Chemicals

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 sodium hydroxide (NaOH) were purchased from Aldrich Sigma.

3.2 Synthesis of MCM-41

The synthesis of MCM-41 was carried out according to the procedure of Gaydhankar et al. (2007). 2.04 g of 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 with 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. Figure 10 shows the stepwise procedure for synthesis of MCM-41. Figure 11 shows the solution after being stirred magnetically for 4 hours. The molar composition of the product obtained was SiO_2: 0.12CTAB: 2.50NH_4OH: 150H_2O. The product was filtered, washed thoroughly with distilled water, and dried in an oven at a temperature of 373K. Figure 12 shows the filtration process, and Figure 13 shows the MCM-41 after drying at 373 K. 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. The final product after calcination can be seen in Figure 14.

Figure 10 – Room temperature synthesis of MCM-41

Figure 11 – Synthesis of MCM-41 (Solution with CTAB, TMAOH, and TEOS after stirred together for 4 hours)

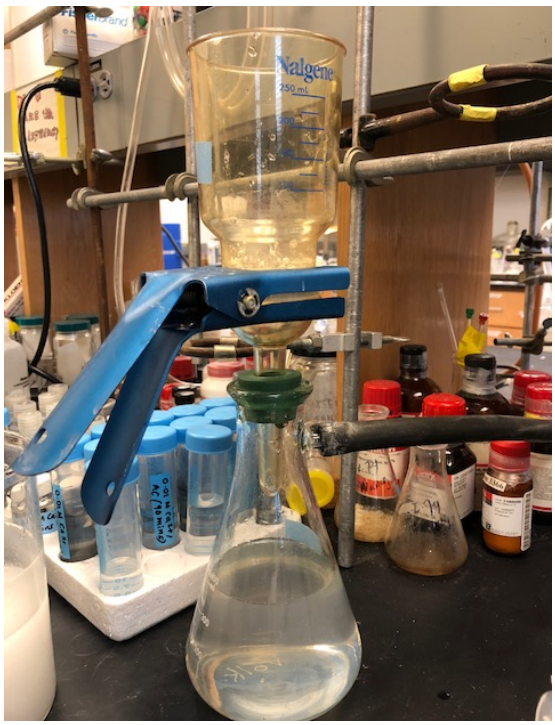

Figure 12 – Filtration Process for separation of MCM-41 from the solution

Figure 13 – Filtered and washed MCM-41 (after 4 hours stirring)

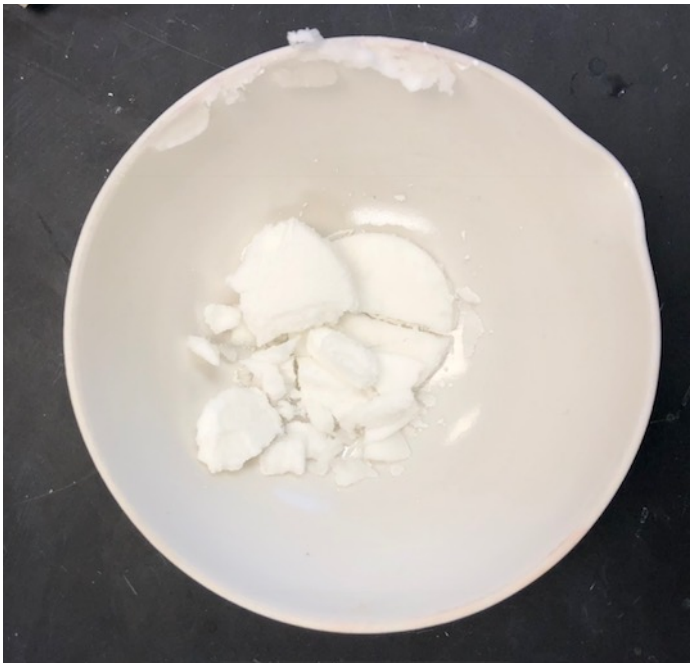

Figure 14 – MCM-41 after completion of calcination at 813K

3.3 Synthesis of $ZnCl_2$-MCM-41

$ZnCl_2$-MCM-41 was synthesized using the 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 for the evaporation of the solution and the volume was kept 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 a little with distilled water to remove unreacted zinc chloride. The recovered solid was then dried up in an oven at 373K to yield the final modified $ZnCl_2$-MCM-41 powder, as shown in Figure 15.

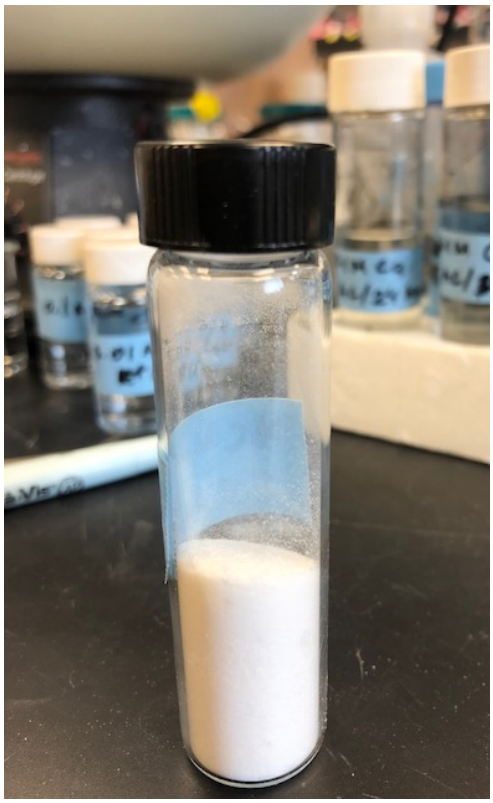

Figure 15 – $ZnCl_2$-MCM-41 after drying in an oven at 373K

3.4 Preparation of lead solutions

A stock solution of 0.1M of Pb (II) was prepared by dissolving 3.312 g of lead nitrate ($Pb(NO_3)_2$ in 100 mL deionized water. This standard solution was used for other concentrations for experiment. Other solutions ranging from concentrations 1 x 10^{-02} M to 1 x 10^{-05} M were prepared using the standard solution. The pH for the solutions were adjusted to a neutral 7 using 0.1M HCl or NaOH.

3.5 Preparation of mercury solutions

A stock solution of 0.1M of Hg (II) was prepared by dissolving 4.073 g of mercuric chloride ($HgCl_2$) in 150 mL deionized water. This standard solution was used to prepare other concentrations for the experiments. Other solutions from concentrations ranging from 1 x 10^{-02} M to 1 x 10^{-04} M were prepared using the standard. The pH for the solutions were adjusted to a neutral 7 using 0.1M HCl or NaOH.

3.6 Preparation of chromium solutions

A stock solution of 0.1M of Cr (III) was prepared by dissolving 6.624 g of chromium chloride hexahydrate ($CrCl_3.6H_2O$) in 150 mL deionized water. This standard solution was used to prepare solutions to be used for experiments ranging from concentrations 1 x 10^{-02} M to 1 x 10^{-04} M. The pH for the solutions were adjusted to a neutral 7 using 0.1M HCl or NaOH.

3.7 Preparation of combined heavy metals solutions

A stock solution of 0.1M combined heavy metal solutions with all 3 metals ($Pb^{2+,}$ Hg^{2+}, and Cr^{3+}) was prepared by dissolving 11.592 g of lead nitrate, 9.503g of mercuric chloride, and 9.323 g of chromium chloride hexahydrate in 350 ml of DI water. This stock solution was used to

prepare other solutions for the experiments, ranging from concentrations 1 x 10^{-01} M to 1 x 10^{-03} M. The pH for the solutions were adjusted to a neutral 7 using 0.1M HCl or NaOH.

3.8 Preparation of calcium solutions

A stock solution of 0.1M Ca^{2+} solution was prepared by dissolving 5.549 g of calcium chloride in 500 ml of DI water. This stock solution was used to prepare other concentrations for the experiment. Series dilution was used to prepare standard solutions from 1 x 10^{-01} M to 1 x 10^{-04} M. The pH for the solutions were adjusted to a neutral 7 using 0.1M HCl or NaOH.

3.9 Preparation of nitrate solutions

A stock solution of 0.1M NO_3^- solution was prepared by dissolving 5.055 g of potassium nitrate in 500 ml of DI water. This stock solution was used to prepare other solutions from 1 x 10^{-01} M to 1 x 10^{-04}. The pH for the solutions were adjusted to a neutral 7 using 0.1M HCl or NaOH.

3.10 Preparation of potassium solutions

A stock solution of 0.1M K^+ solution was prepared by dissolving 5.055 g of potassium nitrate in 500 ml of DI water. This stock solution was used to prepare other solutions from 1 x 10^{-01} M to 1 x 10^{-04} M. The pH for the solutions were adjusted to a neutral 7 using 0.1M HCl or NaOH.

3.11 Procedure for Batch Adsorption Studies

Batch adsorption experiments were conducted in different studies 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 in water like nitrates, calcium and potassium. All the standard solutions were neutralized at pH 7 during preparation.

Batch experiments were conducted for Pb (II) adsorption by placing 15 mg of MCM-41 and $ZnCl_2$-MCM-41 sorbent in a vial containing 30 mL Pb (II) at initial concentration ranging from 0.001 M to 0.1M. These vials were then shaken continuously for specified times, ranging from 10 minutes to 300 minutes, in a shaker at 300 rpm. Readings were taken by a standard ISE electrode at specified time intervals. The final reading of 24 hours was taken for each solution to make sure that the reaction reached equilibrium point.

Batch experiments for Hg (II), Cr (III), and combined heavy metals solution adsorption were carried out by placing 0.275 mg of MCM-41 and $ZnCl_2$-MCM-41 sorbent in a vial containing 60 mL Pb (II) at initial concentration, 0.001,0.01, and 0.1M. These vials were then shaken continuously for specified times in a shaker at 300 rpm. 5 mL of sample was taken out from the vial at each interval, and the concentration in each sample was measured using Varian 715-ES ICP-OES with plasma flow rate of 11L/min, and nebulizer pressure of 300kPa.

Batch experiments were conducted for Ca^{2+}, NO_3^-, and K^+ adsorption by placing 15 mg of MCM-41 and $ZnCl_2$-MCM-41 sorbent in a vial containing 30 mL of the respective ions at initial concentration ranging from 0.001 to 0.1M. These vials were then shaken continuously for specified times in a shaker at 300 rpm. Readings were taken with the standard ISE electrode at specified intervals.

The adsorption per gram can be calculated according to the equation:

$$m_i = \frac{(C_0 - Ce)V}{m}$$

Here, m_i is the equilibrium Pb (II) concentration in mg/g; C_e and C_o are the equilibrium and initial concentrations, respectively; V is the volume of the solution in liters (L); and m is the mass of the sorbent in grams (g).

The removal percentage can be calculated according to the equation:

$$\text{Removal } \% = = \frac{(C_o - Ce)}{Co} * 100\%$$

Table 5 shows the list of all the experiments conducted in the order they were performed.

Table 5 List of all the adsorption experiments conducted

#	Adsorbent and adsorbate used	Mass of adsorbent used & Volume of the solution (mL)
1	0.1M Pb with MCM-41	0.15g in 30 mL
2	0.1M Pb with $ZnCl_2$-MCM-41	0.15g in 30 mL
3	0.01M Pb with MCM-41	0.15g in 30 mL
4	0.01M Pb with $ZnCl_2$-MCM-41	0.15g in 30 mL
5	0.001M Pb with MCM-41	0.15g in 30 mL
6	0.001M Pb with $ZnCl_2$-MCM-41	0.15g in 30 mL
7	0.1M Hg with MCM-41	0.275g in 60 mL
8	0.1M Hg with $ZnCl_2$-MCM-41	0.275g in 60 mL
9	0.01M Hg with MCM-41	0.275g in 60 mL
10	0.01M Hg with $ZnCl_2$-MCM-41	0.275g in 60 mL
11	0.001M Hg with MCM-41	0.275g in 60 mL
12	0.001M Hg with $ZnCl_2$-MCM-41	0.275g in 60 mL
13	0.1M Cr with MCM-41	0.275g in 60 mL
14	0.1M Cr with $ZnCl_2$-MCM-41	0.275g in 60 mL
15	0.01M Cr with MCM-41	0.275g in 60 mL
16	0.001M Cr with MCM-41	0.275g in 60 mL
17	0.001M Cr $ZnCl_2$-MCM-41	0.275g in 60 mL
18	0.1M combined heavy metals (Cr, Hg and Pb) with MCM-41	0.275g in 60 mL
19	0.1M combined heavy metals (Cr, Hg and Pb) with $ZnCl_2$-MCM-41	0.275g in 60 mL
20	0.1M Ca^{2+} with MCM-41	0.15g in 30 mL
21	0.1M Ca^{2+} with $ZnCl_2$-MCM-41	0.15g in 30 mL
22	0.01M Ca^{2+} with MCM-41	0.15g in 30 mL
23	0.01M Ca^{2+} with $ZnCl_2$-MCM-41	0.15g in 30 mL

24	0.001M Ca^{2+} with MCM-41	0.15g in 30 mL
25	0.001M Ca^{2+} with $ZnCl_2$-MCM-41	0.15g in 30 mL
26	0.1M K^+ with MCM-41	0.15g in 30 mL
27	0.1M K^+ with $ZnCl_2$-MCM-41	0.15g in 30 mL
28	0.01M K^+ with MCM-41	0.15g in 30 mL
29	0.01M K^+ with $ZnCl_2$-MCM-41	0.15g in 30 mL
30	0.001M K^+ with MCM-41	0.15g in 30 mL
31	0.001M K^+ with $ZnCl_2$-MCM-41	0.15g in 30 mL
32	0.1M NO_3^- with MCM-41	0.15g in 30 mL
33	0.1M NO_3^- with $ZnCl_2$-MCM-41	0.15g in 30 mL
34	0.01M NO_3^- with MCM-41	0.15g in 30 mL
35	0.01M NO_3^- with $ZnCl_2$-MCM-41	0.15g in 30 mL
36	0.001M NO_3^- with MCM-41	0.15g in 30 mL
37	0.001M NO_3^- with $ZnCl_2$-MCM-41	0.15g in 30 mL
38	0.1M Pb with AC	0.15g in 30 mL
39	0.1M Ca^{2+} with AC	0.15g in 30 mL
40	0.01M Ca^{2+} with AC	0.15g in 30 mL
41	0.001M Ca^{2+} with AC	0.15g in 30 mL
42	0.1M K^+ with AC	0.15g in 30 mL
43	0.01M K^+ with AC	0.15g in 30 mL
44	0.001M K^+ with AC	0.15g in 30 mL
45	0.1M NO_3^- with AC	0.15g in 30 mL
46	0.01M NO_3^- with AC	0.15g in 30 mL
47	0.001M NO_3^- with AC	0.15g in 30 mL

3.12 Characterization of samples

TEM was used to examine the pore structure of MCM-41 and $ZnCl_2$-MCM-41 adsorbents. TEM images were taken using Tecnai G2 F30 STEM-FEG, operated at 300 kV. TEM samples were prepared using the crash and float technique, with Lacey carbon film coated copper grid supporting the powders.

CHAPTER 4- RESULTS AND DISCUSSION

4.1 Adsorbent Characterization

TEM images. The TEM image of MCM-41 are shown in Figures 16, 17, and 18, and TEM images for $ZnCl_2$-MCM-41 are shown in Figures 19, 20, and 21. The images show the porous nature of MCM-41 and $ZnCl_2$-MCM-41. Figure 21 shows the presence of silica and oxygen in the material confirming the silica-based structure of the adsorbent. Figures 23 and 24 show TEM of a $ZnCl_2$-MCM-41 sample after adsorption of lead, and shows the presence of lead on the sample.

$ZnCl_2$-MCM-41 still retains the form of MCM-41, but it shows stronger adsorption qualities. This can be due to the formation of O-Zn-Cl bonds in MCM-41, which increases the adsorption properties of heavy metals into it.

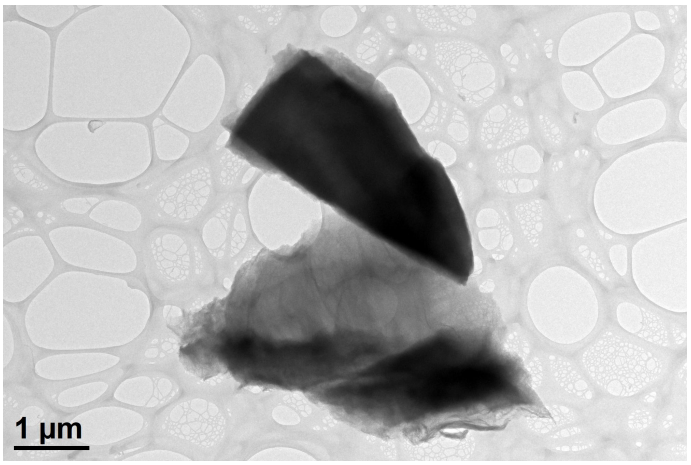

Figure 16 - TEM image of MCM-41 taken at low magnification (the sample overlays with Lacey Carbon film)

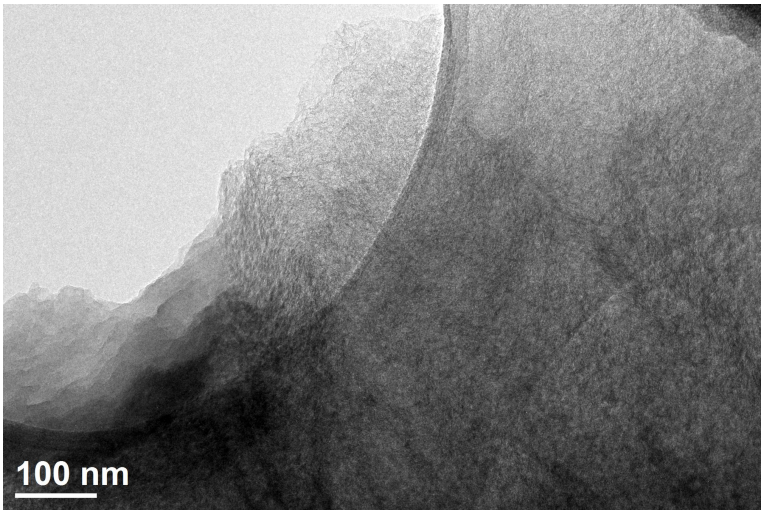

Figure 17 - TEM image of MCM-41 taken at higher magnification (100nm), showing the morphologies in the sample

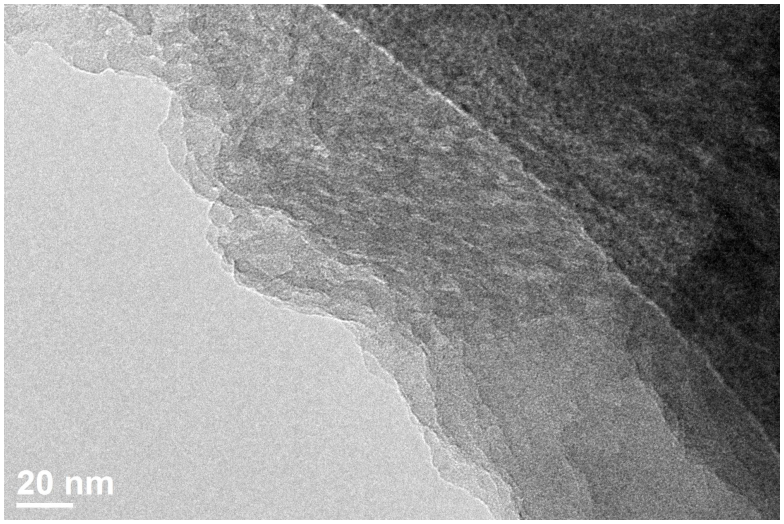

Figure 18 - TEM image of MCM-41 taken at higher magnification (20 nm), showing the morphologies in the sample

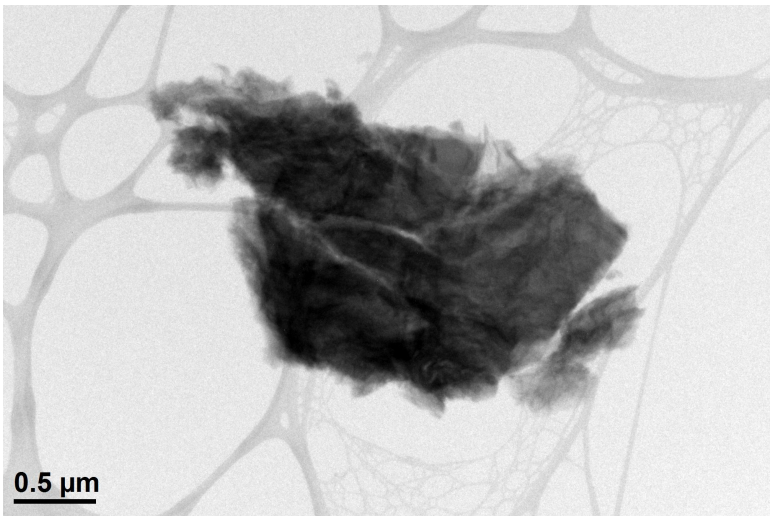

Figure 19 - TEM image of $ZnCl_2$-MCM-41, taken at low magnification (the sample overlays with Lacey Carbon film)

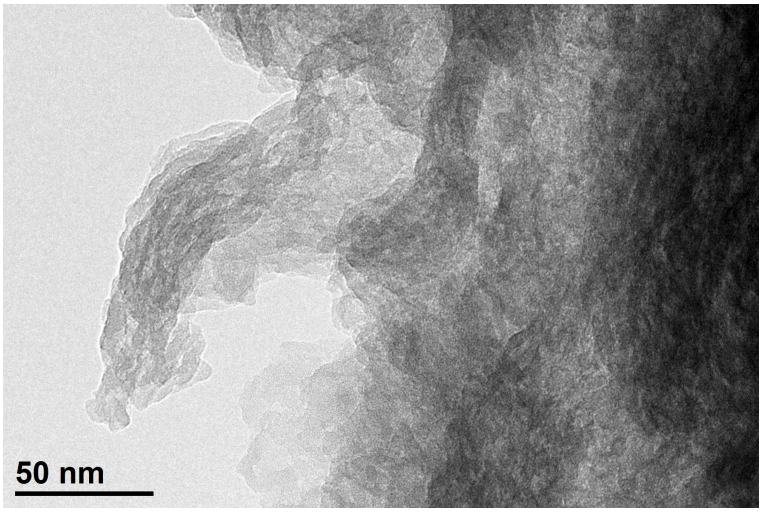

Figure 20 - TEM image of $ZnCl_2$-MCM-41, taken at higher magnification (50nm), showing the morphologies in the sample

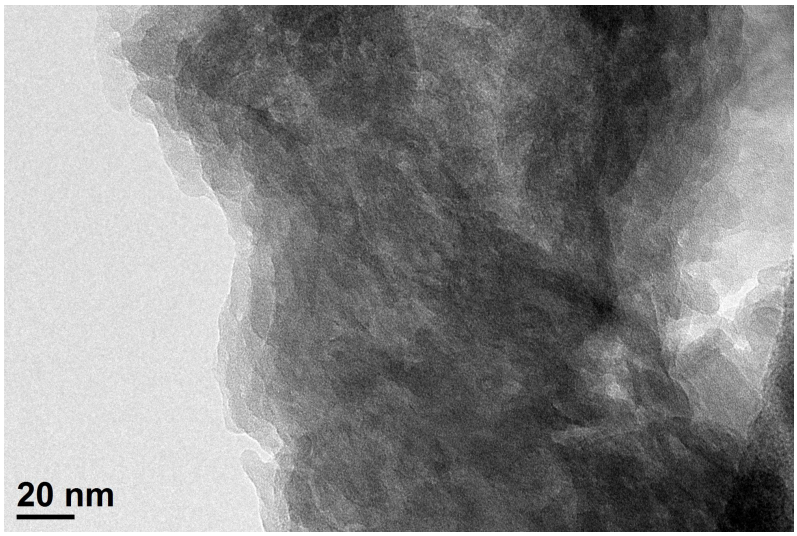

Figure 21 - TEM image of $ZnCl_2$-MCM-41, taken at higher magnification (20nm), showing the morphologies in the sample

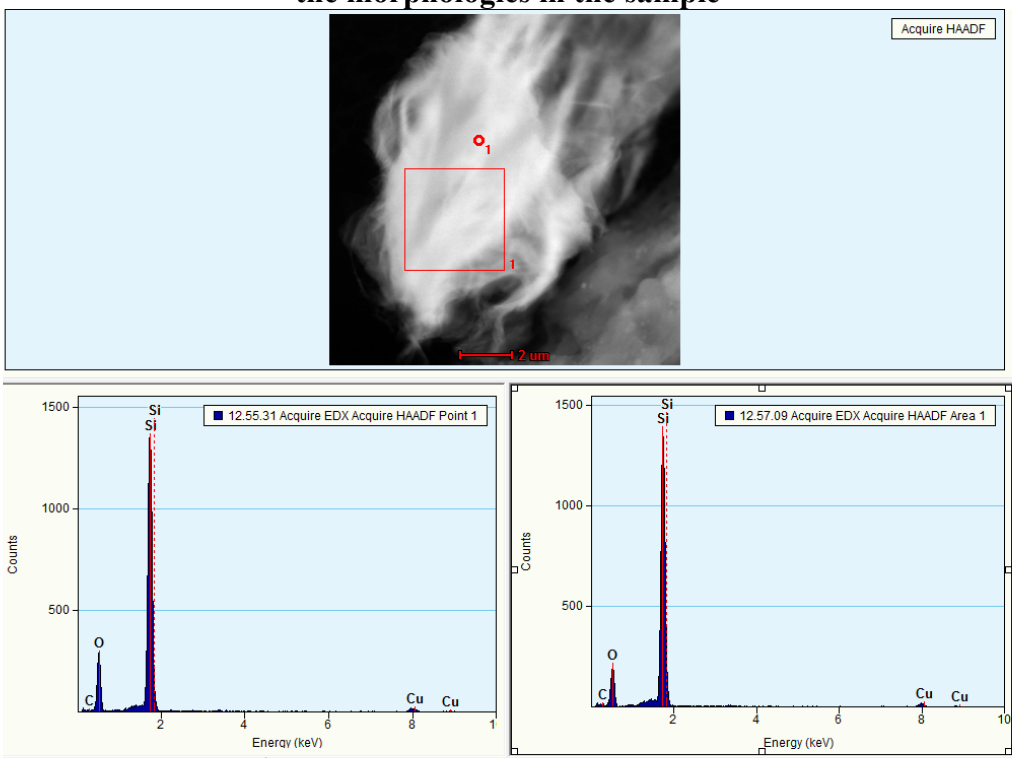

Figure 22 - STEM Z-contrast image of $ZnCl_2$-MCM-41 showing presence of oxygen and silica in the material

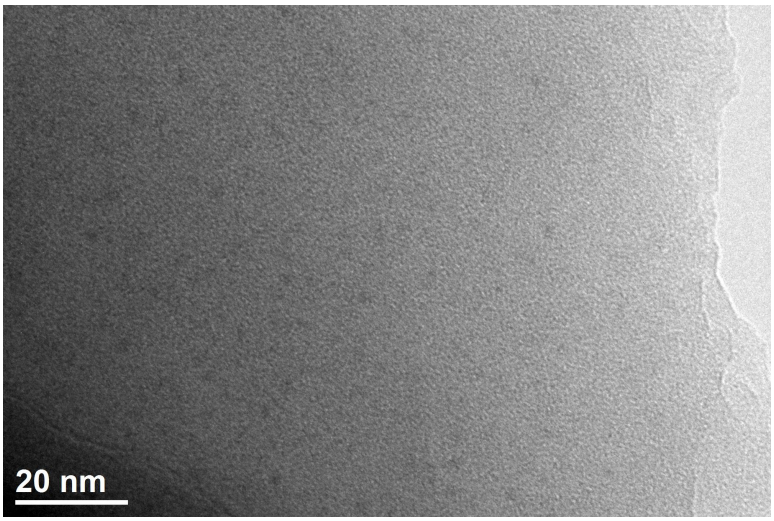

Figure 23 - TEM image of $ZnCl_2$-MCM-41 with the randomly distributed features (approx. 2nm) in darker contrast

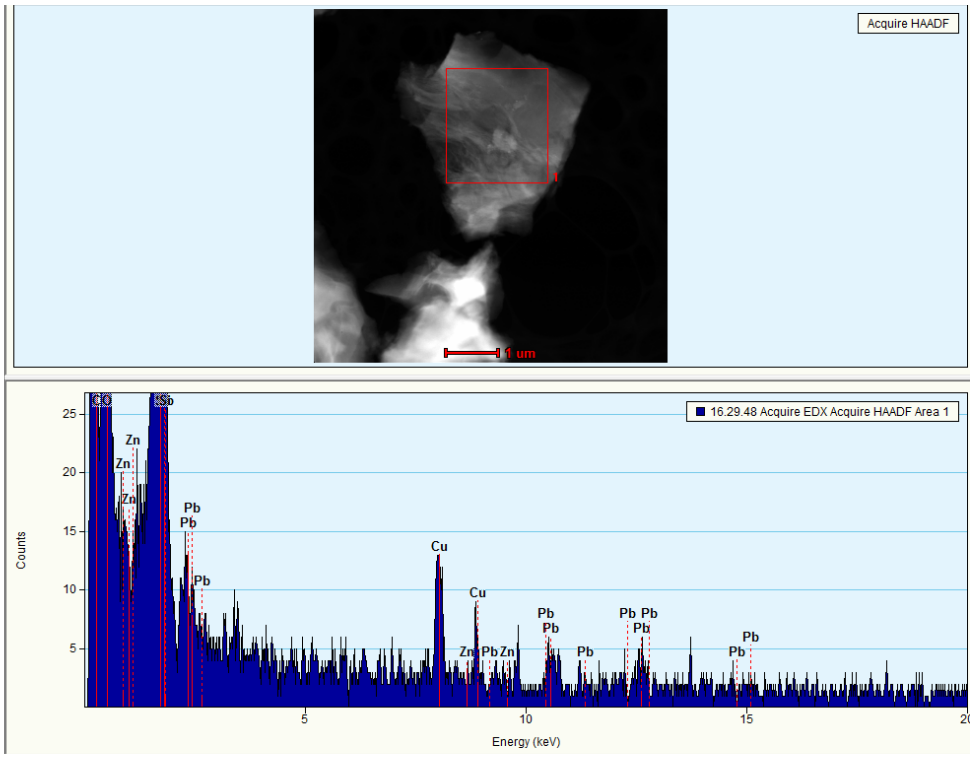

Figure 24 - STEM Z-contrast image of $ZnCl_2$-MCM-41 showing presence of lead

4.2 Structure of MCM-41 and $ZnCl_2$-MCM-41

The structure of MCM-41 can be seen as amorphous silica, as seen in TEM images in results. The structure is amorphously packed hence no crystallinity can be seen at the atomic level.

Figure 25 shows the hexagonal structure of MCM-41, and the major bond of Si-O-Si in MCM-41. Other possible bonds are Si-OH, Si-O-R, and Si- carbon bonds. Figure 26 is a representation of possible bond structure in MCM-41. Figure 27 shows the adsorption and bonding of heavy metals after being adsorbed into the structure.

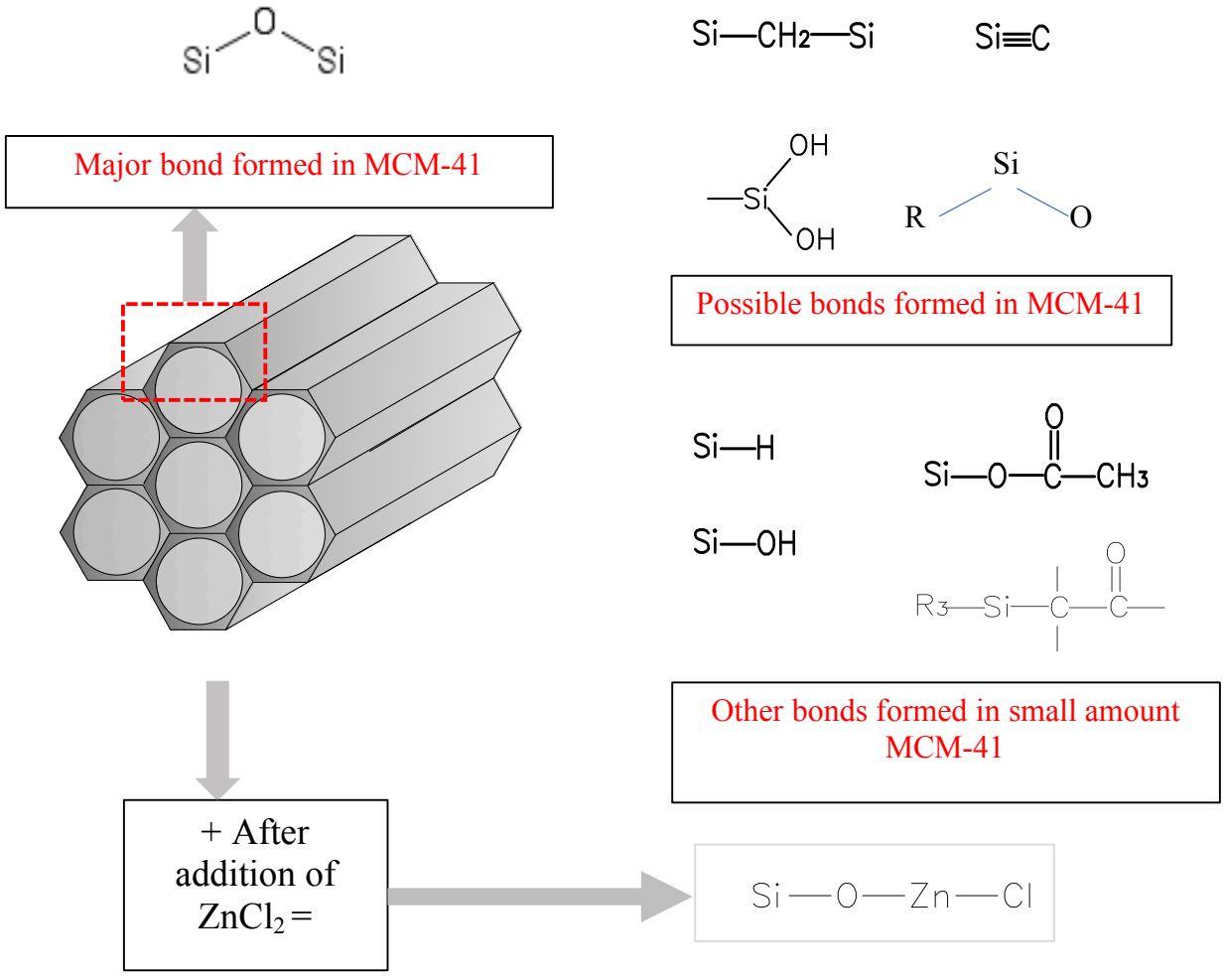

Figure 25 MCM-41 and $ZnCl_2$-MCM-41 structure

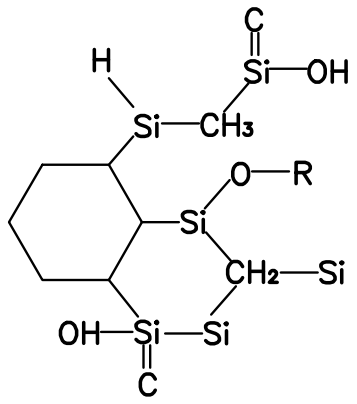

Figure 26 Possible bonds in MCM-41 structure

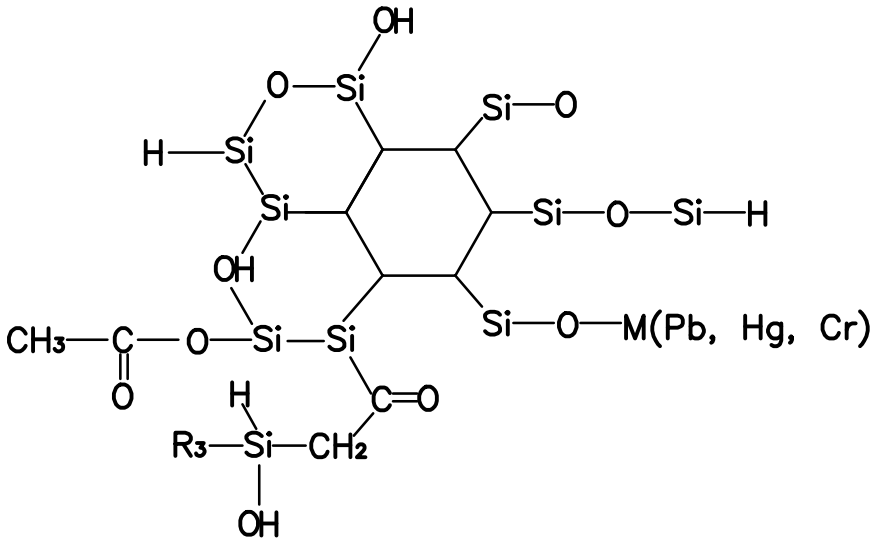

Figure 27 MCM-41 structure after adsorption of heavy metals

MCM-41 is porous materials with hexagonal pores packed in it, with its major composition being silica and oxygen bonds. Other structures are –OH bonds with silanol groups and the adsorbed water molecules. In case of $ZnCl_2$-MCM-41, $ZnCl_2$ binds to MCM-41 structure forming –O-Zn-Cl bonding. Figure 28 represents the bonding of $ZnCl_2$ with MMC-41's silica and oxygen bonds, and the binding of lead ions after adsorption in the silanol.

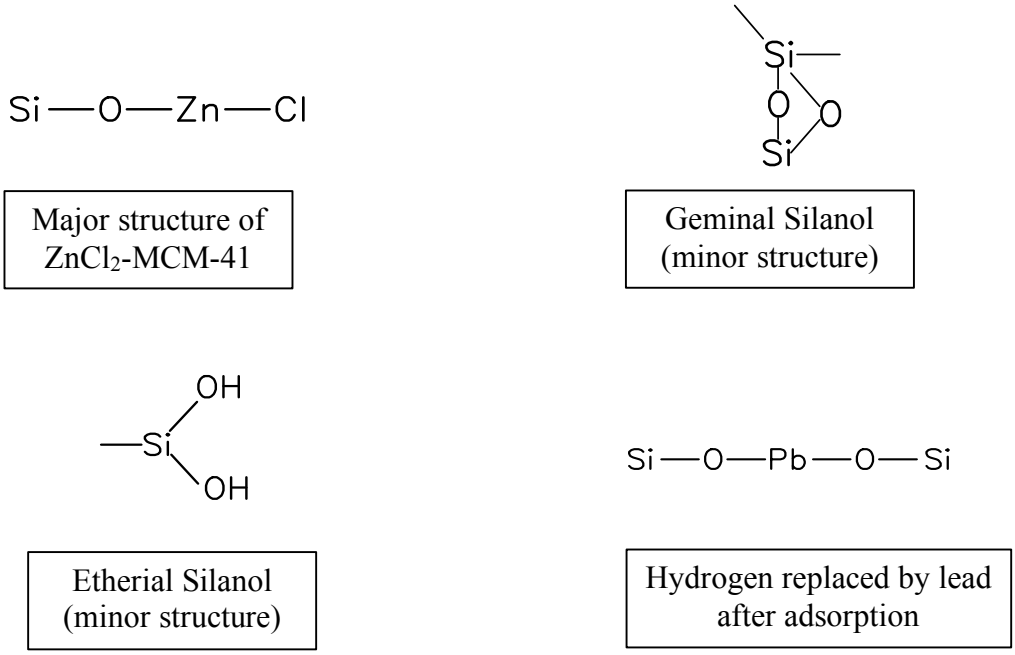

Figure 28 $ZnCl_2$-MCM-41 structure composition before and after adsorption

4.3 Solubility test

The solubility of MCM-41 was tested. 0.50 grams of MCM-41was placed in 100 mL DI water. It was stirred magnetically for 15 minutes. The solution was then filtered and dried up in an oven. The final mass of the dried material was weighed. The final mass was still 0.50 grams, which shows that MCM-41 is not soluble in water.

4.4 Batch Adsorption Studies- Adsorption of heavy metals

The results from the batch adsorption studies for lead, chromium, mercury, and the combination of all three are shown in the Tables 6 to 27. The tables show the calculated values from excel sheet, and the calculation are shown in Appendix.

4.3.1 Adsorption of Pb (II) species

In order to obtain the maximum adsorption capacity of Pb (II) ions by MCM-41 and $ZnCl_2$-MCM-41, lead samples of concentration 0.001M, 0.01M, and 0.1M were tested with MCM-41 and $ZnCl_2$-MCM-41. The adsorbent used was 15 mg in a 30mL solution of the adsorbate concentration. The lead samples were all tested with an ISE lead electrode for up to 24 hours adsorption, and the final solution taken after 5 days was tested with ICP-OES to confirm the results. Table 6 shows the initial calibration of lead electrode. The other calibration data are shown in the Appendix. The results for lead adsorption are shown from Table 6 to Table 12. Figures 29 to 41 are the graphs for concentration versus time and the mass adsorbed by the adsorbents. The results show that as the concentration increases, the amount of lead adsorbed also increases. And as more time increases, the adsorption also increases till it reaches equilibrium point.

A. Calibration Curve for Lead electrode

Table 6 shows the initial calibration curve of lead electrode. The electrode was calibrated after certain intervals (1 hour to 5 hours) to ensure the stability of the electrode. The remaining calibration data are presented in Appendix, with the calculation of concentration from the calibration charts.

Table 6 Initial Calibration curve for Pb^{2+} ions			
Original Conc. (M)	**Log10 (Conc)**	**abs value of Conc**	**mV Reading**
1.00E-02	-2.00	2.00	-207
7.00E-03	-2.15	2.15	-211
5.00E-03	-2.30	2.30	-213
4.00E-03	-2.40	2.40	-215
2.00E-03	-2.70	2.70	-222
1.00E-03	-3.00	3.00	-228
5.00E-04	-3.30	3.30	-237
2.00E-04	-3.70	3.70	-247
1.00E-04	-4.00	4.00	-255
5.00E-05	-4.30	4.30	-264
2.00E-05	-4.70	4.70	-271
1.00E-05	-5.00	5.00	-278

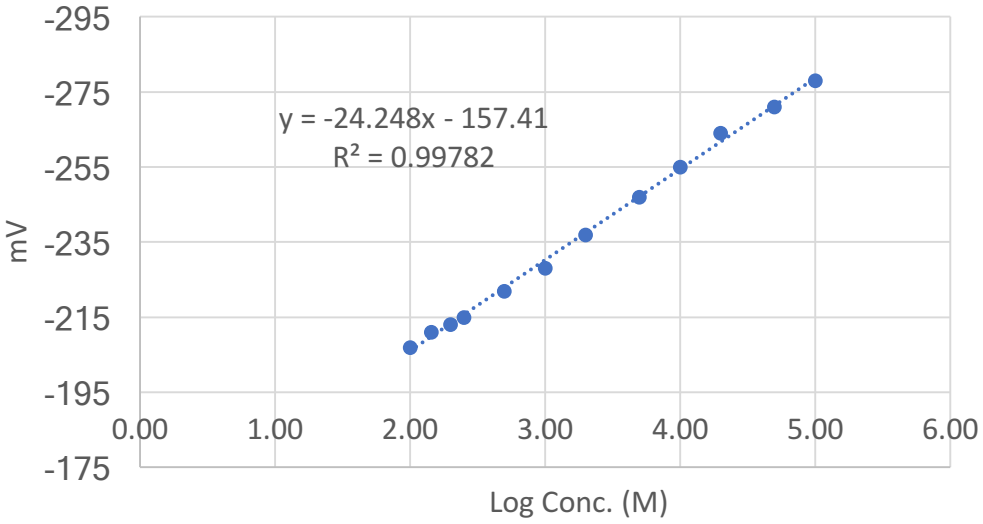

Figure 29 – Initial Calibration Curve for Lead

B. Adsorption of 0.1M Pb (II) ions measured by ISE lead electrode

Tables 7 & 8 show the concentration of 30 mL 0.1M lead solution after addition of 0.15g MCM-41, and $ZnCl_2$-MCM-41 respectively. Figure 30, 31 & 32 show experimental, model, and normalized graphs for concentration versus time respectively. The mass adsorbed by MCM-41 and $ZnCl_2$-MCM-41 is shown in Figure 33. The detailed calculations are shown in Appendix. The graphs show that the concentration decreases with the increase in time. Equilibrium was reached

at 200 minutes. The adsorption capacity for MCM-41 was calculated as 1657.6 mg/g, and 2846.4 mg/g for $ZnCl_2$-MCM-41.

Table 7 Adsorption of 0.1 M Pb (II) by MCM-41					
Time (min)	**Conc (M)**	**Model conc (M)**	**Normalized Conc (M)**	**Mass of the adsorbate (m_i), mg**	**Cumulative mass of adsorbate ($\sum m_i$), (mg)**
0	0.1322	0.1208	0.100	0.00	0.00
20	0.1180	0.1132	0.094	47.242	47.24
40	0.1116	0.1064	0.088	42.269	89.51
60	0.0708	0.1004	0.083	37.296	126.81
120	0.0844	0.0872	0.072	82.051	208.86
180	0.0794	0.0812	0.067	37.296	246.15
200	0.1035	0.0808	0.067	2.486	248.64
240	0.0918	0.0824	0.068	-9.946	248.64
300	0.0815	0.0908	0.075	-52.214	248.64
24 hours	0.0945				**Σm_i= 248.64 mg**
Adsorption= Σm_i/0.15g adsorbent = 1657.6 mg/g					

Table 8 Adsorption of 0.1 M Pb (II) by $ZnCl_2$-MCM-41					
Time (min)	**Conc (M)**	**Model conc (M)**	**Normalized Conc (M)**	**Mass of the adsorbate (m_i), mg**	**Cumulative mass of adsorbate ($\sum m_i$), (mg)**
0	0.1310	0.1267	0.100		
20	0.1310	0.1171	0.092	59.674	59.670
40	0.0943	0.1083	0.085	54.701	114.37
60	0.0943	0.1003	0.079	49.728	164.10
120	0.0834	0.0811	0.064	119.347	283.45
180	0.0800	0.0691	0.055	74.592	358.04
200	0.0842	0.0667	0.053	14.918	372.96
240	0.0941	0.0643	0.051	14.918	387.88
300	0.0863	0.0667	0.053	-14.918	387.88
24 hours	0.0340				**Σm_i=387.88 mg**
Adsorption= Σm_i/0.15g adsorbent= 2846.4 mg/g					

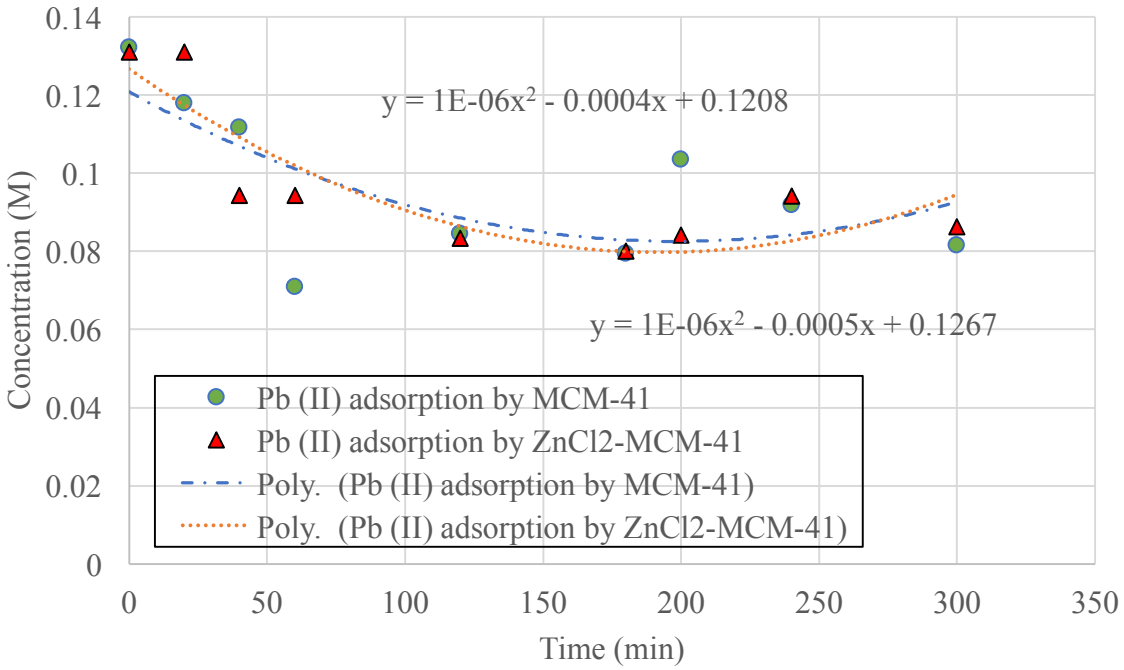

Figure 30 - Experimental: Adsorption of 0.1M Pb (II) by MCM-41 & $ZnCl_2$-MCM-41

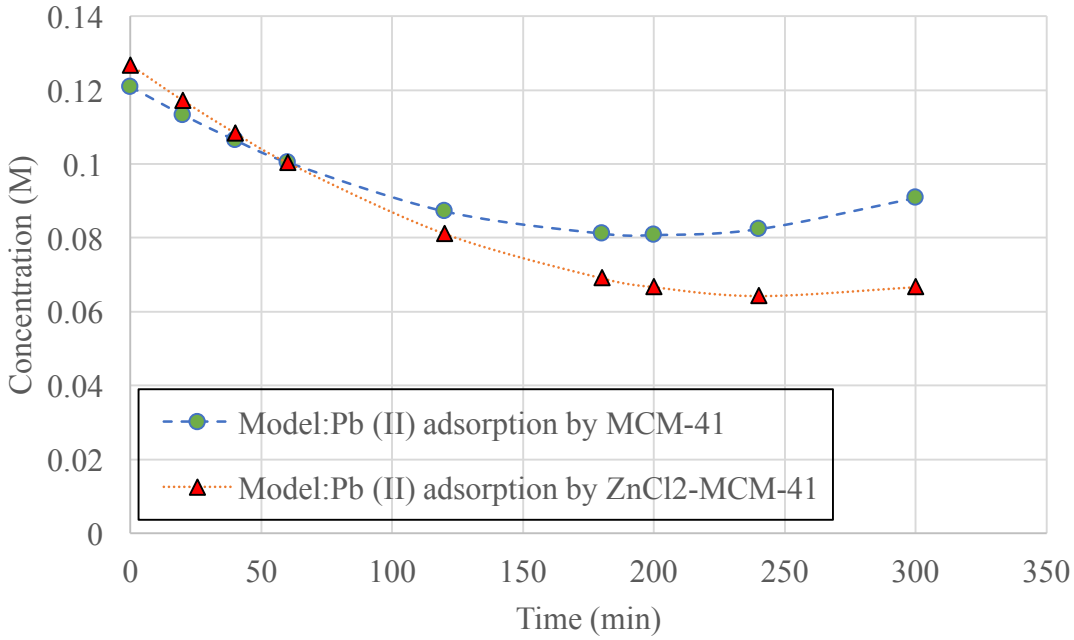

Figure 31 - Model: Adsorption of 0.1M Pb (II) by MCM-41 & $ZnCl_2$-MCM-41

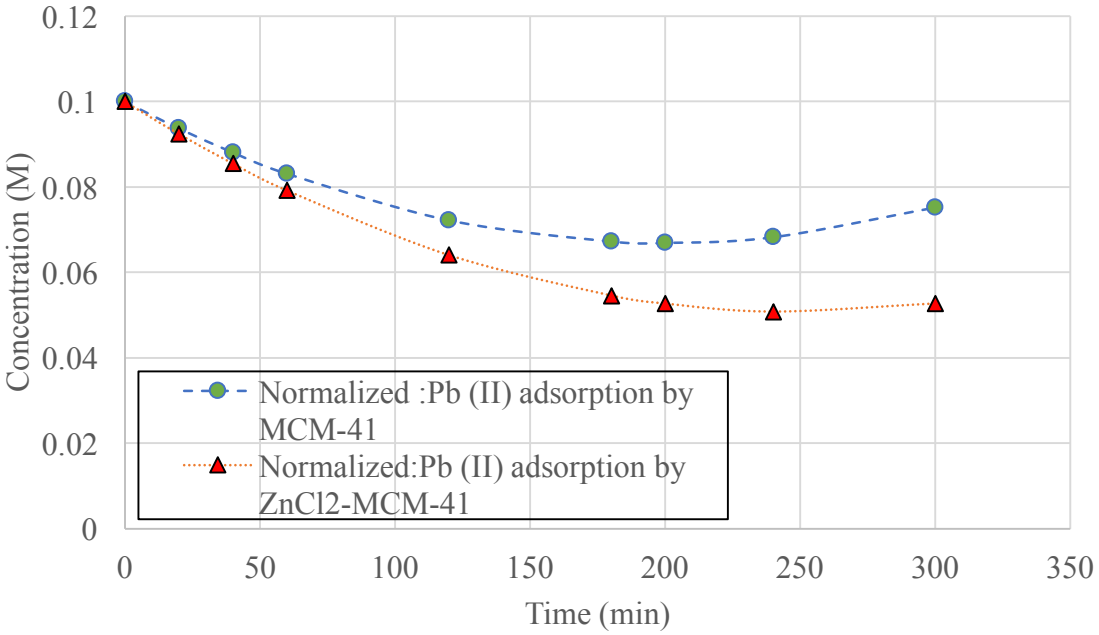

Figure 32 - Normalized: Adsorption of 0.1M Pb (II) by MCM-41 & $ZnCl_2$-MCM-41

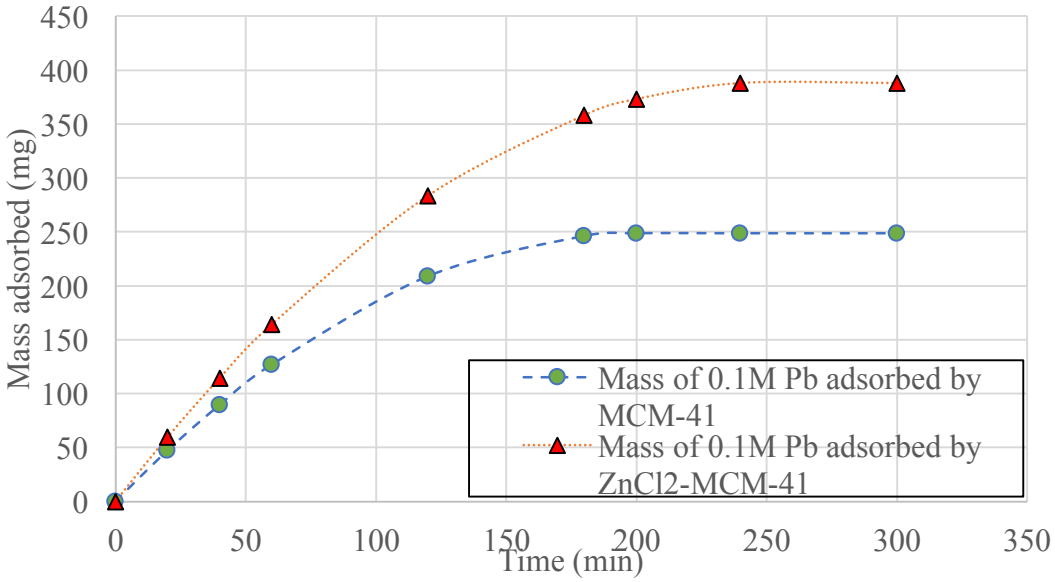

Figure 33 - Model: Mass of 0.1M Pb (II) (mg) adsorbed by MCM-41 & $ZnCl_2$-MCM-41

C. Adsorption of 0.01M Pb (II) ions measured by an ISE electrode

Tables 9 & 10 show the concentrations of 30 mL 0.01M lead solution after addition of 0.15g MCM-41, and ZnCl2-MCM-41 respectively. Figure 34, 35 & 36 show experimental, model, and normalized graphs for concentration versus time respectively. The mass adsorbed by MCM-41 and $ZnCl_2$-MCM-41 is shown in Figure 37. The detailed calculations are shown in Appendix. The adsorption capacity of MCM-41 for 0.01M is calculated to be 32.82 mg/g, and for $ZnCl_2$-MCM-41 is 99.456 mg/g.

Table 9 Adsorption of 0.01 M Pb (II) by MCM-41

Time (min)	**Conc. (M)**	**Model conc. (M)**	**Normalized Conc (M)**	**Mass of the adsorbate (m_i), g**	**Cumulative mass of adsorbate ($\sum m_i$), (mg), (mg)**
0	0.009893	0.00980	0.01000	-	-
10	0.009893	0.00972	0.00992	0.48	0.48
20	0.009432	0.00965	0.00984	0.46	0.94
30	0.009432	0.00958	0.00977	0.44	1.38
40	0.009432	0.00951	0.00971	0.41	1.79
50	0.009432	0.00945	0.00964	0.39	2.18
60	0.009432	0.00939	0.00958	0.36	2.54
90	0.009432	0.00924	0.00943	0.93	3.47
120	0.009013	0.00913	0.00931	0.71	4.18
180	0.008970	0.00901	0.00919	0.75	4.92
300	0.008970	0.00920	0.00939	-1.19	4.92
24 hours	0.008970				**Σm_i=4.92**
Adsorption= Σm_i/0.15g adsorbent=32.82mg/g					

Table 10 Adsorption of 0.01 M Pb (II) by $ZnCl_2$-MCM-41					
Time (min)	**Conc (M)**	**Model conc (M)**	**Normalized Conc (M)**	**Mass of the adsorbate (m_i), g**	**Cumulative mass of adsorbate ($\sum m_i$), (mg)**
0	0.00989	0.00960	0.01000	-	-
10	0.00989	0.00940	0.00980	1.22	1.22
20	0.00855	0.00922	0.00960	1.17	2.39
30	0.00855	0.00904	0.00941	1.12	3.51
40	0.00855	0.00886	0.00923	1.07	4.57
50	0.00855	0.00870	0.00906	1.02	5.59
60	0.00855	0.00854	0.00890	0.97	6.56
90	0.00855	0.00812	0.00846	2.61	9.17
120	0.00738	0.00778	0.00810	2.16	11.34
180	0.00703	0.00730	0.00760	2.98	14.32
300	0.00669	0.00720	0.00750	0.60	14.92
24 hours	0.00669				**Σm_i=14.92**
Adsorption=Σm_i/0.15g adsorbent= 99.456 mg/g					

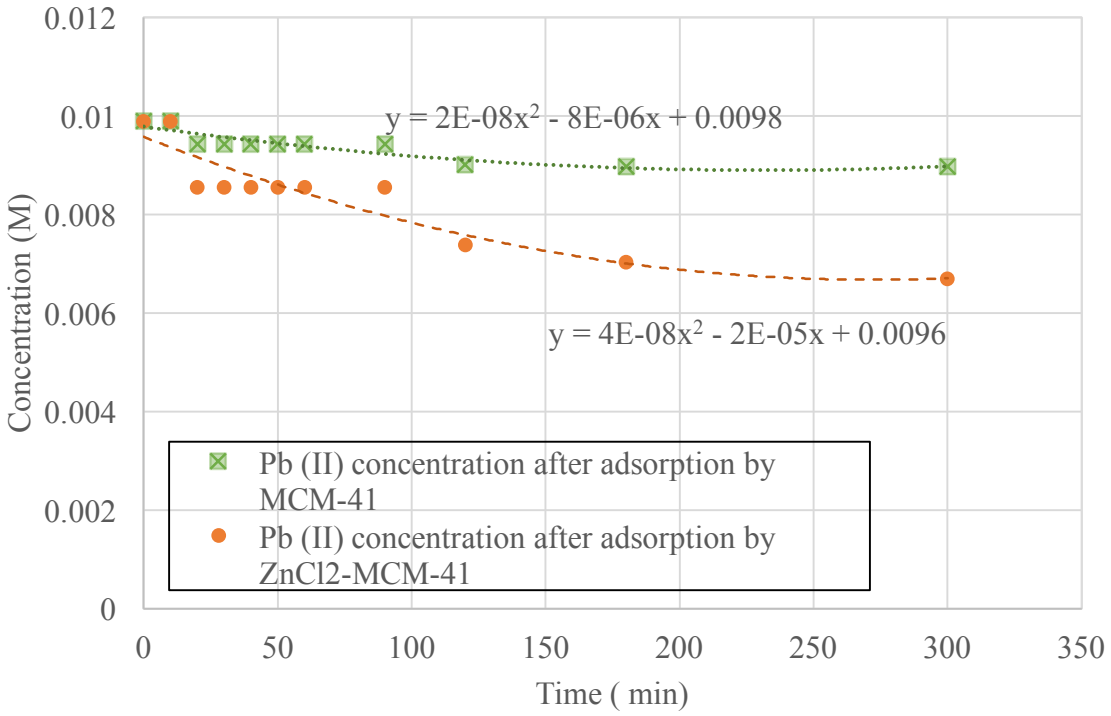

Figure 34 - Experimental: Adsorption of 0.01M Pb (II) by MCM-41 & $ZnCl_2$-MCM-41

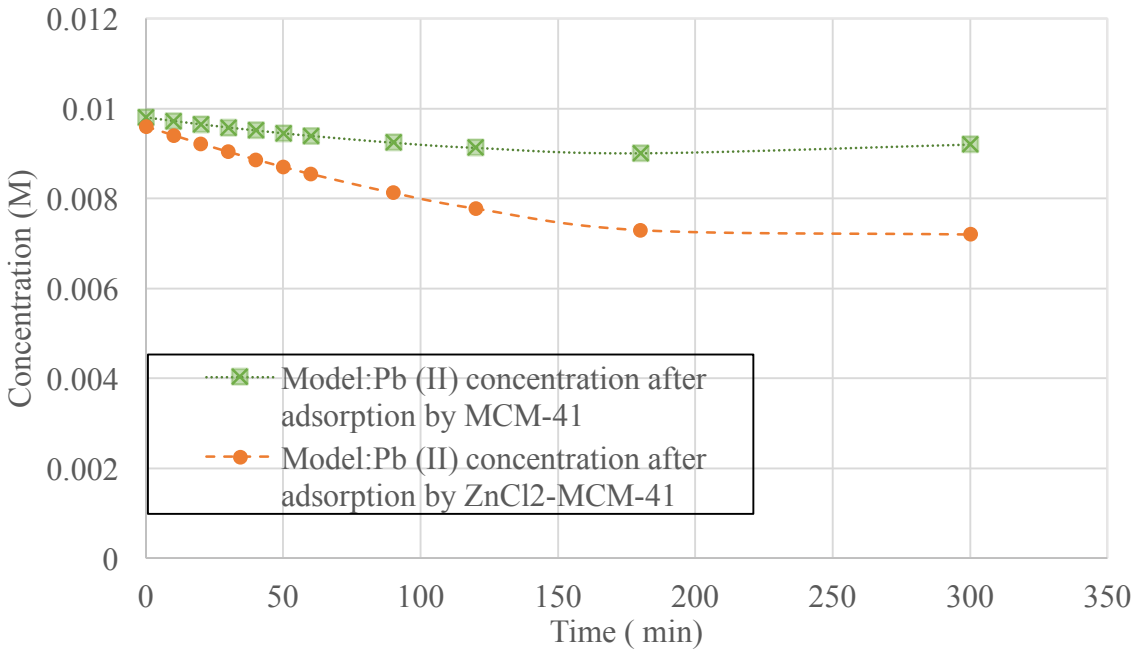

Figure 35 - Model: Adsorption of 0.01M Pb (II) by MCM-41 & $ZnCl_2$-MCM-41

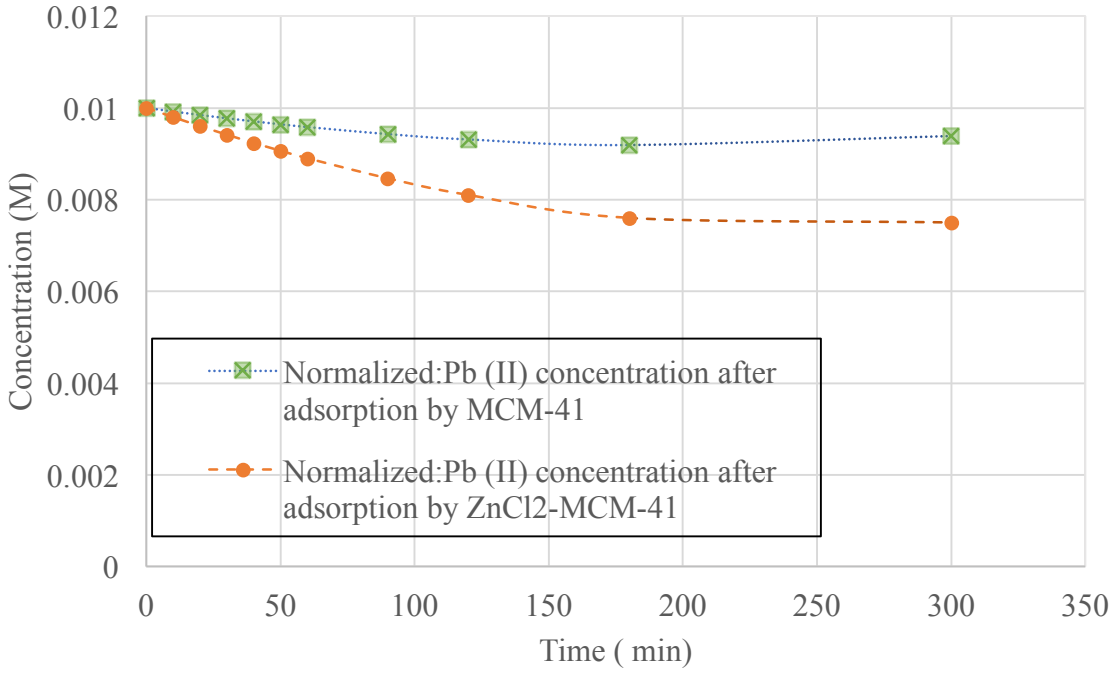

Figure 36 - Normalized: Adsorption of 0.01M Pb (II) by MCM-41 & $ZnCl_2$-MCM-41

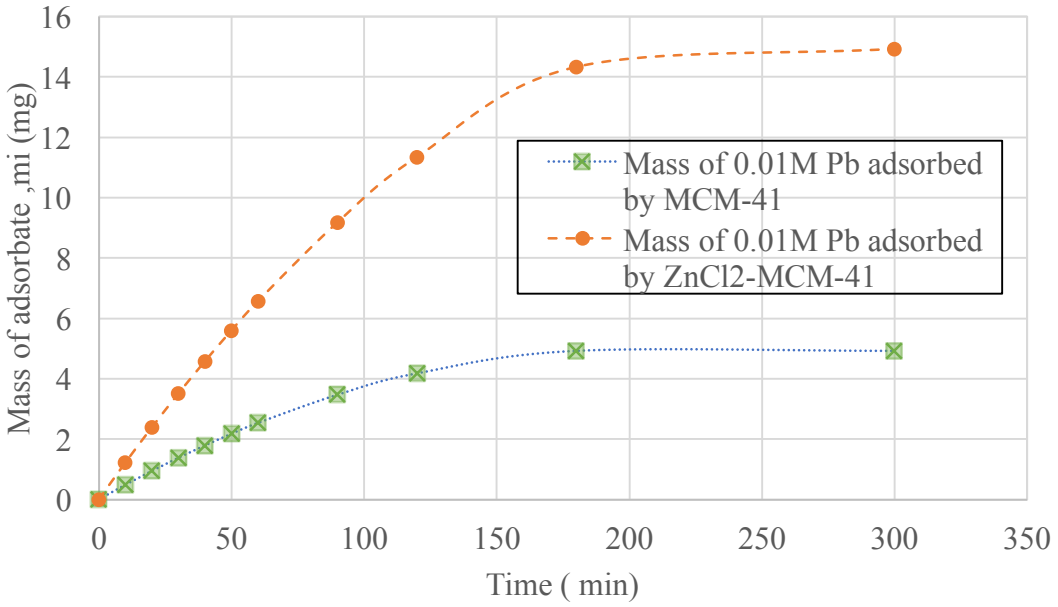

Figure 37 - Model: Mass of 0.01M Pb (II) adsorbed by MCM-41 & $ZnCl_2$-MCM-41

D. Adsorption of 0.001M Pb (II) ions

Tables 11 & 12 show the concentrations of 30 mL 0.001M lead solution after addition of 0.15g MCM-41, and $ZnCl_2$-MCM-41 respectively. Figure 38, 39 & 40 show experimental, model, and normalized graphs for concentration versus time respectively. The mass adsorbed by MCM-41 and $ZnCl_2$-MCM-41 is shown in Figure 41. The detailed calculations are shown in Appendix. The adsorption capacity of MCM-41 for 0.01M is calculated to be 12.979 mg/g, and for $ZnCl_2$-MCM-41 is 18.65 mg/g.

Table 11 Adsorption of 0.001 M Pb (II) by MCM-41					
Time (min)	**Concentration (M)**	**Model concentration (M)**	**Normalized Concentration (M)**	**Mass of the adsorbate (m_i), g**	**Cumulative mass of adsorbate ($\sum m_i$), (mg)**
0	0.001015	0.001000	0.001000	0.182	0.182
10	0.000923	0.000961	0.000967	0.173	0.356
20	0.000923	0.000924	0.000936	0.165	0.520
30	0.000839	0.000889	0.000907	0.156	0.676
40	0.000694	0.000856	0.000879	0.147	0.824
50	0.000763	0.000825	0.000853	0.139	0.962
60	0.000631	0.000796	0.000828	0.649	1.611
120	0.000694	0.000664	0.000712	0.336	1.947
180	0.000763	0.000604	0.000652	-0.269	1.947
300	0.000631	0.000700	0.000700		0.182
24 hrs	0.000574				**Σm_i=1.97 mg**
Adsorption=Σm_i/0.15g adsorbent= 12.979 mg/g					

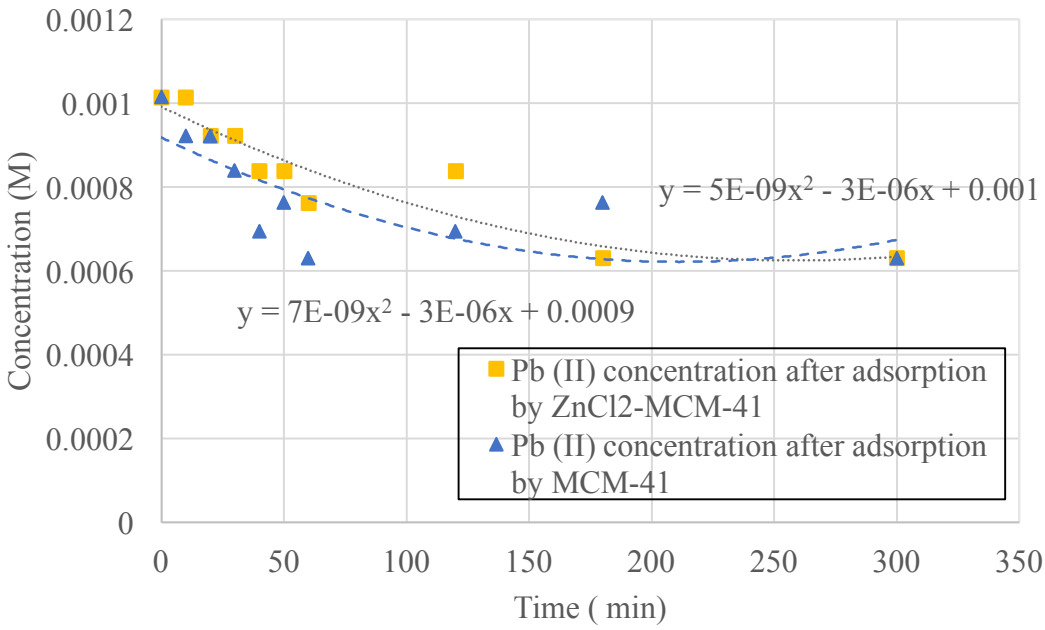

Figure 38 - Model: Mass of 0.001M Pb (II) adsorbed by MCM-41 & $ZnCl_2$-MCM-41

Table 12 Adsorption of 0.001 M Pb (II) by $ZnCl_2$-MCM-41					
Time (min)	**Concentration (M)**	**Model concentration (M)**	**Normalized Concentration (M)**	**Mass of the adsorbate (m_i), g**	**Cumulative mass of adsorbate ($\sum m_i$), (mg)**
0	0.001015	0.001000	0.000		
10	0.001015	0.000971	1.218	0.183	0.183
20	0.000923	0.000942	2.387	0.177	0.361
30	0.000923	0.000915	3.506	0.171	0.531
40	0.000839	0.000890	4.575	0.165	0.696
50	0.000839	0.000865	5.594	0.159	0.855
60	0.000763	0.000842	6.564	0.152	1.007
120	0.000839	0.000726	11.338	0.783	1.790
180	0.000631	0.000654	14.322	0.559	2.350
300	0.000631	0.000640	14.918	0.448	2.797
24 hrs	0.000475				**Σm_i=2.79 mg**
Adsorption=Σm_i/0.15g adsorbent= 18.648 mg/g					

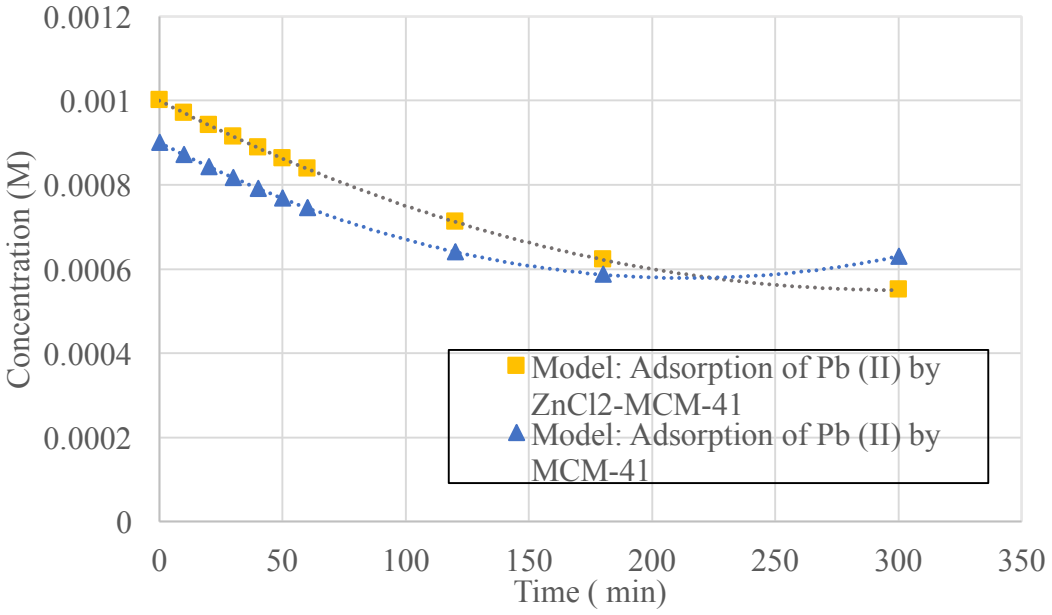

Figure 39 - Model: Mass of 0.001M Pb (II) adsorbed by MCM-41 & $ZnCl_2$-MCM-41

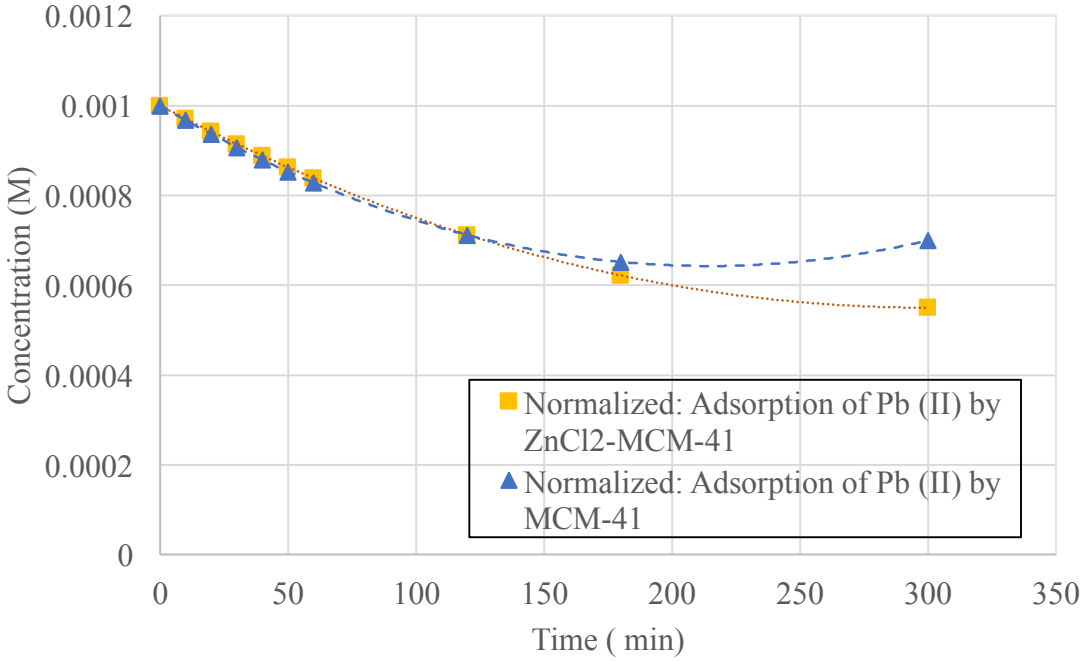

Figure 40 - Normalized: Adsorption of 0.001M Pb (II) by MCM-41 & $ZnCl_2$-MCM-41

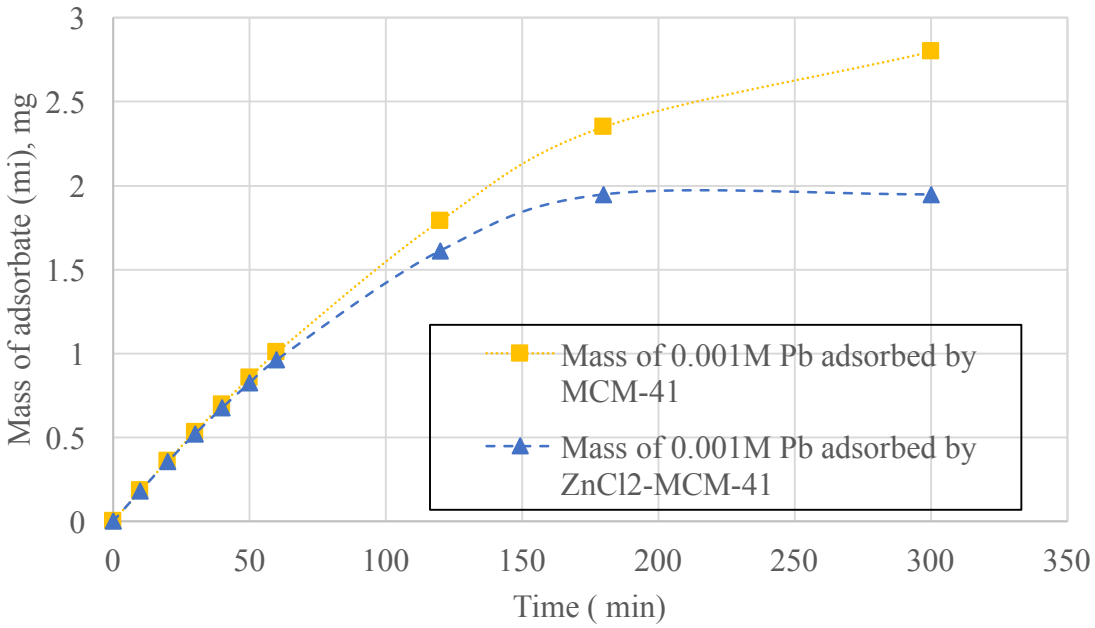

Figure 41 - Model: Mass of 0.001M Pb (II) adsorbed by MCM-41 & $ZnCl_2$-MCM-41

E. Comparison of data taken by electrode, and by ICP for lead

Since the readings for the lead experiments were taken by an ISE electrode for up to 24 hours reading, the results for lead are all based on those readings. But to check the data taken with an electrode, the final solution reading after 5 days adsorption was taken with an ICP-OES for each concentration, for each adsorbent. The Table 13 shows the reading taken by ICP for different samples and different concentration of lead. These values were averaged for each two samples taken for a single concentration using the same adsorbent. The averaged value was compared with the final reading taken with the ICP, as shown in Table 14. The data shows that concentration for 5 days was similar to or less than that taken on 24 hours for most concentrations.

Table 13 ICP measurement for adsorption of 0.1M Pb (II) by MCM-41 & $ZnCl_2$-MCM-41

Samples	Time (min)	Adsorbent	Initial conc.	Pb^{2+} Conc. after adsorption
Sample 1	5 days	MCM-41	0.001	4.75E-04
Sample 2	5 days	$ZnCl_2$-MCM-41	0.001	1.54E-03
Sample 1	5 days	MCM-41	0.001	3.09E-04
Sample 2	5 days	$ZnCl_2$-MCM-41	0.001	3.83E-04
Sample 1	5 days	$ZnCl_2$-MCM-41	0.01	5.17E-03
Sample 2	5 days	MCM-41	0.01	2.47E-03
Sample 1	5 days	MCM-41	0.01	6.84E-03
Sample 2	5 days	$ZnCl_2$-MCM-41	0.01	7.05E-03
Sample 1	5 days	$ZnCl_2$-MCM-41	0.1	1.36E-02
Sample 2	5 days	MCM-41	0.1	9.99E-02
Sample 1	5 days	MCM-41	0.1	1.07E-01
Sample 2	5 days	$ZnCl_2$-MCM-41	0.1	9.72E-02

Table 14 Comparison of ICP measurement & electrode measurement for adsorption of 0.1M Pb (II) by MCM-41 & $ZnCl_2$-MCM-41			
Adsorbent	**Initial Conc. (M)**	**Average of S1 & S2 of Pb^{2+} Conc. (by ICP) (M) (5 days reading)**	**Average of S1 & S2 of Pb^{2+} Conc. (by electrode-24 hours reading) (M)**
MCM-41	0.001	0.000392	0.000574
$ZnCl_2$-MCM-41	0.001	0.000963	0.000475
MCM-41	0.01	0.00465	0.008970
$ZnCl_2$-MCM-41	0.01	0.00611	0.00669
$ZnCl_2$-MCM-41	0.1	0.0554	0.0834
MCM-41	0.1	0.103	0.0945

4.3.2 Adsorption of Hg (II) species

All the measurements here forward for the heavy metals were taken with ICP-OES. The concentration used was again 0.001M, 0.01M, and 0.1M Hg (II). The time interval ranges from 20 minutes to 300 minutes, and lastly a 24 hours reading was taken for each sample. The results for mercury are shown in Table 15 to 20. They show a similar trend, with adsorption increasing as the concentration and time increases until it reaches equilibrium.

A. Adsorption of 0.1M Hg (II) species

Table 15 and 16 shows the data for 0.1M Hg (II), with experimental, model, and normalized concentration at specific time interval. The adsorption capacity of MCM-41 is calculated to be 505.55 mg/g, and for $ZnCl_2$-MCM-41, it is 1302.74 mg/g. The trend for the concentration versus time can be seen in Figures 42 to 44, with concentration decreasing with time. Figure 45 shows the mass of 0.1M Hg adsorbed by the adsorbents, and it increases with time.

Table 15 Adsorption of 0.1 M Hg (II) by MCM- 41

Vol of the solution (L)	Time (min)	Conc (M)	Model conc (M)	Normalized Conc (M)	Mass of the adsorbate (m_i), g	($\sum m_i$), (mg)
0.060	0	0.09475	0.0962	0.100	-	
0.055	20	0.10924	0.0946	0.098	17.61	17.612
0.050	40	0.08788	0.0938	0.098	14.34	31.957
0.045	60	0.08769	0.0930	0.097	12.69	44.651
0.040	120	0.08742	0.0914	0.095	33.02	77.667
0.035	180	0.08726	0.0867	0.090	27.91	105.577
0.030	200	0.08613	0.0821	0.085	7.68	113.258
0.025	240	0.08015	0.0806	0.084	12.20	125.460
0.020	300	0.08015	0.0775	0.081	13.57	139.025
0.015	24 hours	0.07213				**Σm_i=139.823**
Adsorption=**Σm_i/0.275g adsorbent= 505.55 mg/g**						

Table 16 Adsorption of 0.1 M Hg (II) by $ZnCl_2$-MCM-41						
Vol of the solution (L)	**Time (min)**	**Conc (M)**	**Model conc (M)**	**Normalized Conc (M)**	**Mass of the adsorbate (m_i), g**	**($\sum m_i$), (mg)**
0.060	0	0.09635	0.0941	0.100	-13.24	
0.055	20	0.09454	0.0953	0.101	-4.01	-13.24
0.050	40	0.09376	0.0957	0.102	3.61	-17.25
0.045	60	0.09371	0.0953	0.101	48.14	3.61
0.040	120	0.08788	0.0893	0.095	56.17	51.75
0.035	180	0.08583	0.0813	0.086	67.40	107.92
0.030	200	0.08476	0.0701	0.074	72.21	175.32
0.025	240	0.03424	0.0557	0.059	110.73	247.53
0.020	300	0.03359	0.0281	0.030	-13.24	358.25
0.015	24 hours	0.008933				**Σm_i=358.25**
Adsorption=**Σm_i/0.275g adsorbent= 1302.74 mg/g**						

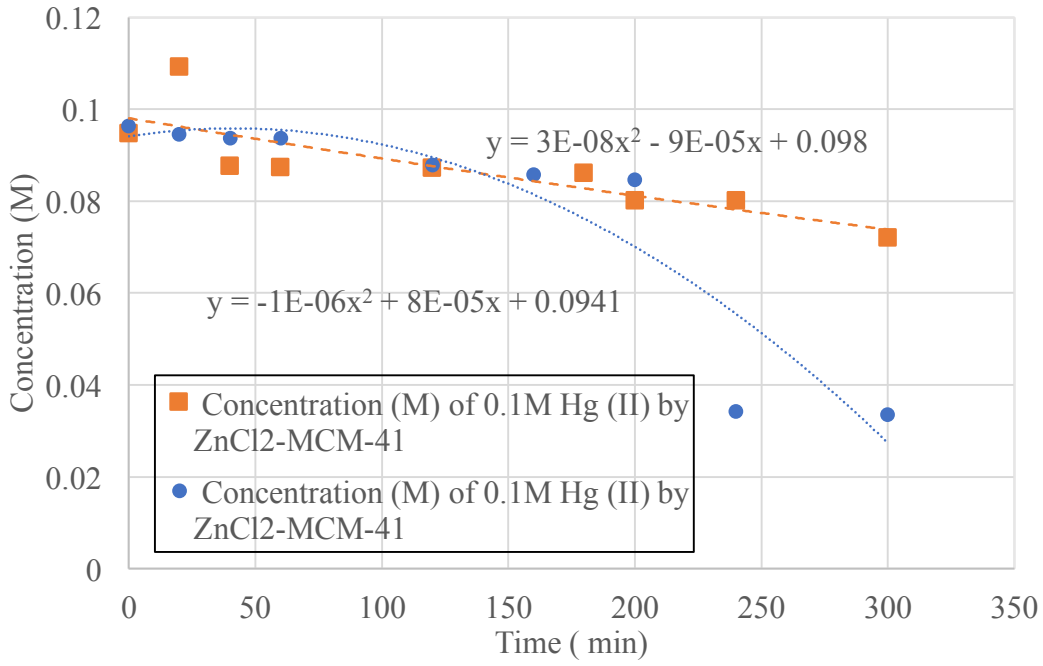

Figure 42 - Experimental: Adsorption of 0.1M Hg (II) by MCM-41 & $ZnCl_2$-MCM-41

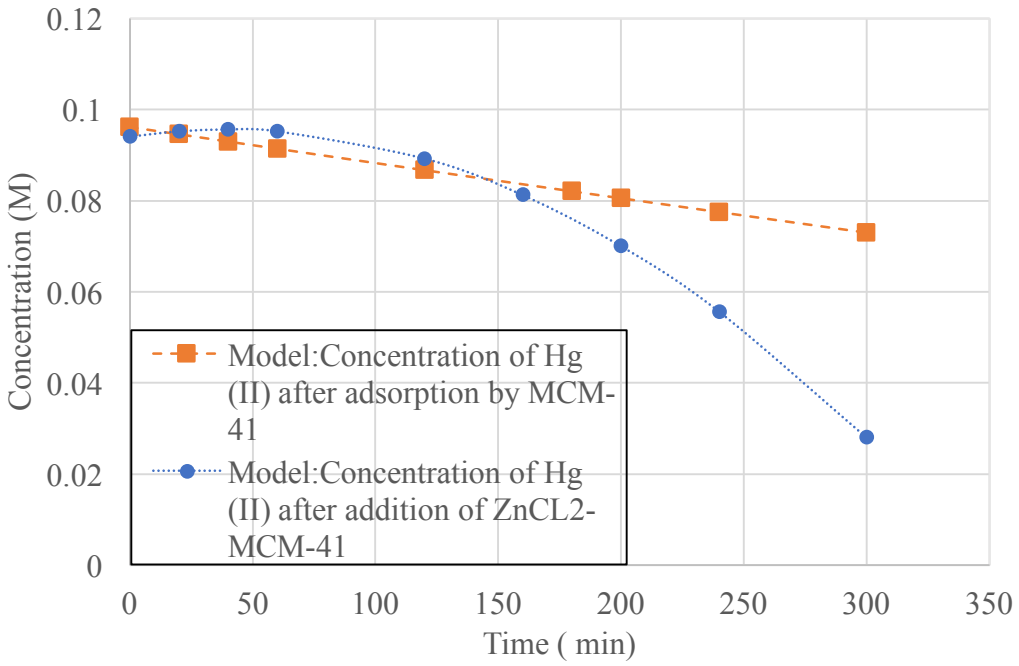

Figure 43 - Model: Adsorption of 0.1M Hg (II) by MCM-41 & $ZnCl_2$-MCM-41

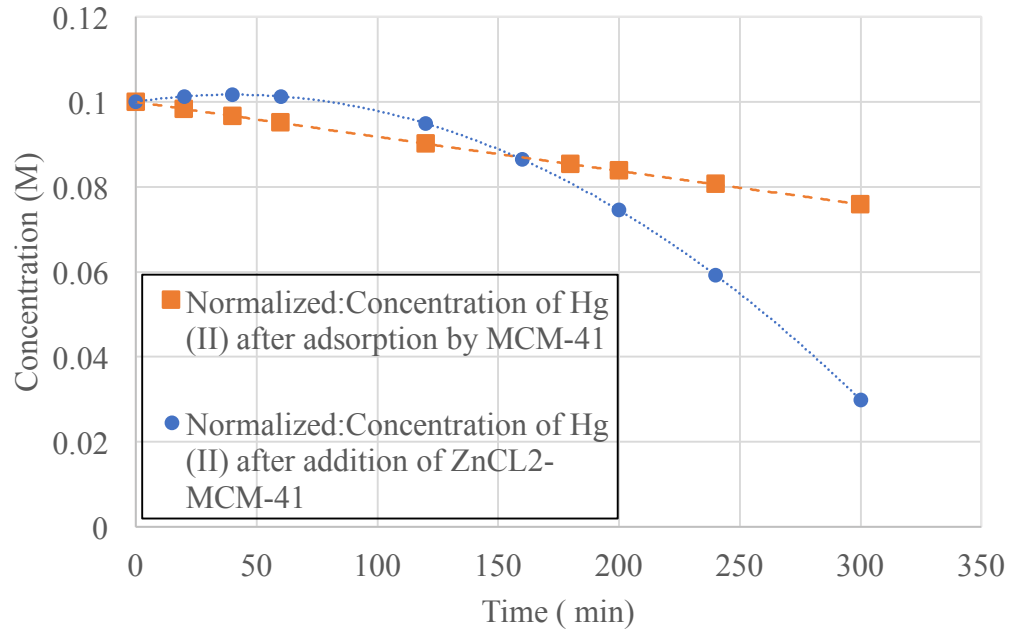

Figure 44 - Normalized: Adsorption of 0.1M Hg (II) by MCM-41 & $ZnCl_2$-MCM-41

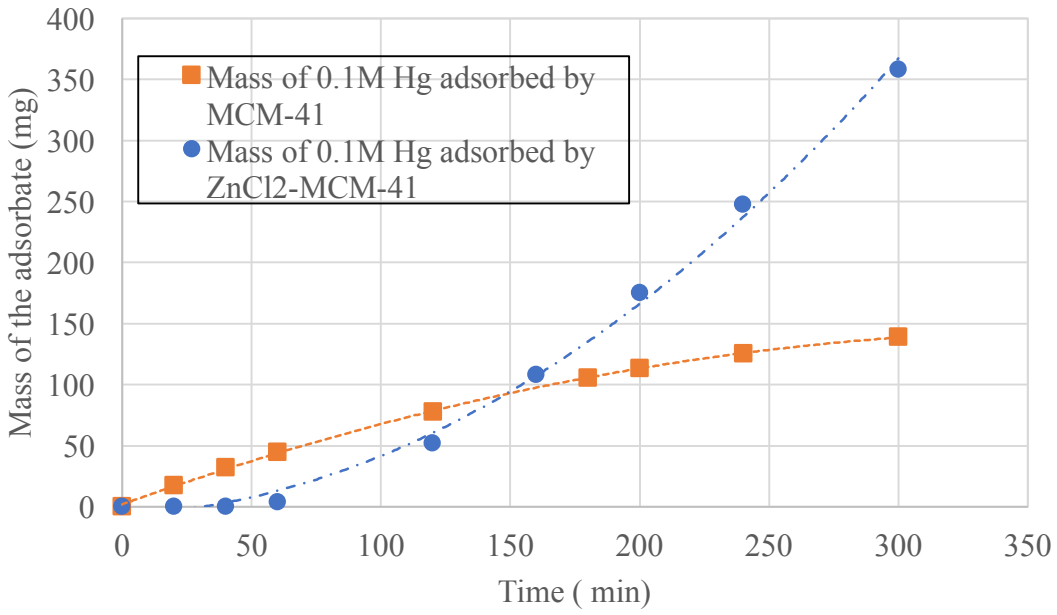

Figure 45 - Model: Mass of 0.1M Hg (II) adsorbed by MCM-41 & $ZnCl_2$-MCM-41

B. Adsorption of 0.01M Hg (II) species

Table 17 and 18 shows the data for 0.01M Hg (II), with experimental, model, and normalized concentration at specific time interval. The adsorption capacity of MCM-41 is calculated to be 160.6 mg/g, and for $ZnCl_2$-MCM-41, it is 180.74 mg/g. The trend for the concentration versus time can be seen in Figures 46 to 48, with concentration decreasing with time. Figure 49 shows the mass of 0.01M Hg adsorbed by the adsorbents, and it increases with time. The adsorption capacities for both adsorbents are not significantly different as in case of 0.1M Hg adsorption. The equilibrium point was at 250 minutes.

Table 17 Adsorption of 0.01 M Hg (II) by MCM- 41						
Vol of the solution (L)	**Time (min)**	**Conc (M)**	**Model conc (M)**	**Normalized Conc (M)**	**Mass of the adsorbate (m_i), g**	**($\sum m_i$), (mg)**
0.060	0	0.01262	0.0120	0.0100		
0.055	20	0.01121	0.0112	0.0094	8.52	8.52
0.050	40	0.01092	0.0105	0.0088	7.18	15.70
0.045	60	0.00920	0.0099	0.0082	5.96	21.66
0.040	90	0.00898	0.0090	0.0075	7.10	28.76
0.035	120	0.00892	0.0082	0.0068	5.33	34.09
0.030	180	0.00851	0.0071	0.0059	6.86	40.95
0.025	200	-	0.0068	0.0057	1.34	42.29
0.020	240	0.00751	0.0064	0.0054	1.48	43.77
0.015	300	0.00733	0.0063	0.0053	0.40	44.16
0.015	24 hours	0.00787				**Σm_i=44.16**
Adsorption=**Σm_i/0.275g adsorbent= 160.6 mg/g**						

Table 18 Adsorption of 0.01 M Hg (II) by $ZnCl_2$-MCM- 41						
Vol of the solution (L)	**Time (min)**	**Conc (M)**	**Model conc (M)**	**Normalized Conc (M)**	**Mass of the adsorbate (m_i), g**	**($\sum m_i$), (mg)**
0.060	0	0.01321	0.01270	0.01000		
0.055	20	0.01317	0.01174	0.00924	10.591	10.59
0.050	40	0.00922	0.01086	0.00855	8.826	19.42
0.045	60	0.00886	0.01006	0.00792	7.221	26.64
0.040	90	0.00850	0.00901	0.00709	8.425	35.06
0.035	120	0.00826	0.00814	0.00641	6.108	41.17
0.030	180	0.00826	0.00694	0.00546	7.221	48.39
0.025	240	0.00809	0.00646	0.00509	2.407	50.80
0.020	300	0.00809	0.00670	0.00528	-0.963	50.80
0.015	24 hours	0.00787				**Σm_i=50.80**
Adsorption=**Σm_i/0.275g adsorbent= 184.75 mg/g**						

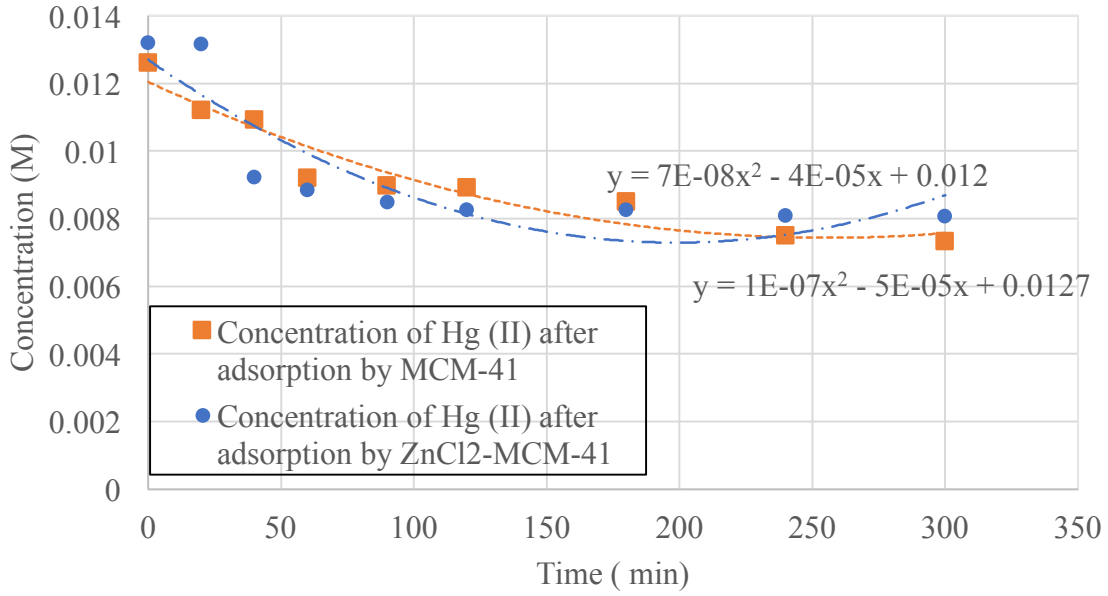

Figure 46 – Experimental: Adsorption of 0.01M Hg (II) by MCM-41 & $ZnCl_2$-MCM-41

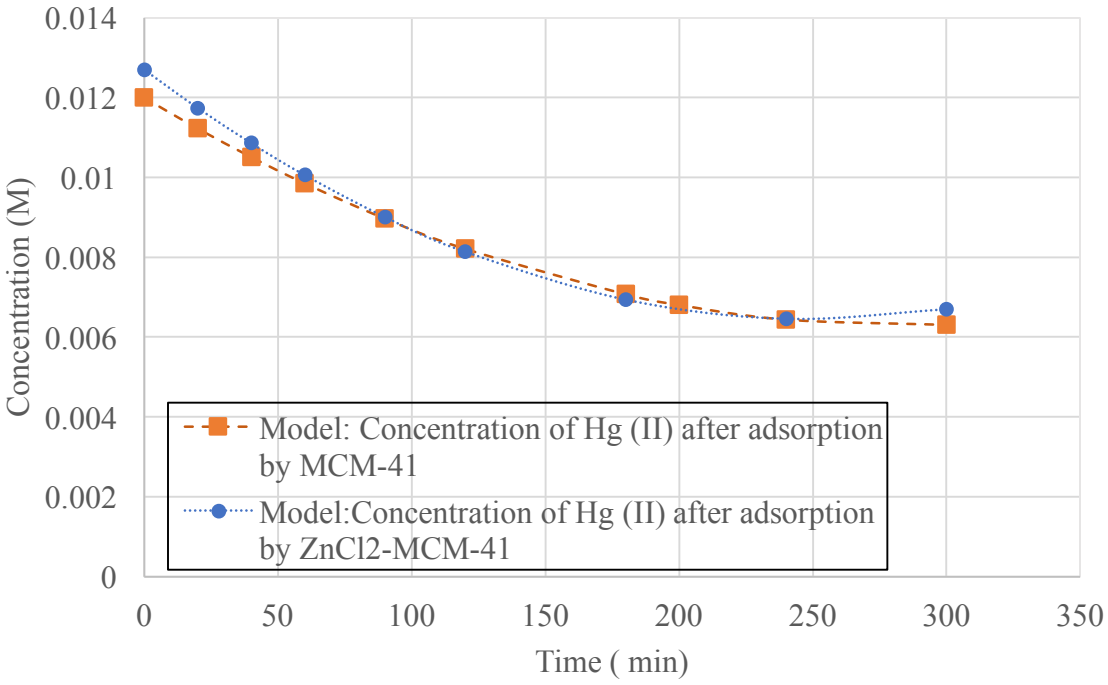

Figure 47 - Model: Adsorption of 0.01M Hg (II) by MCM-41 & $ZnCl_2$-MCM-41

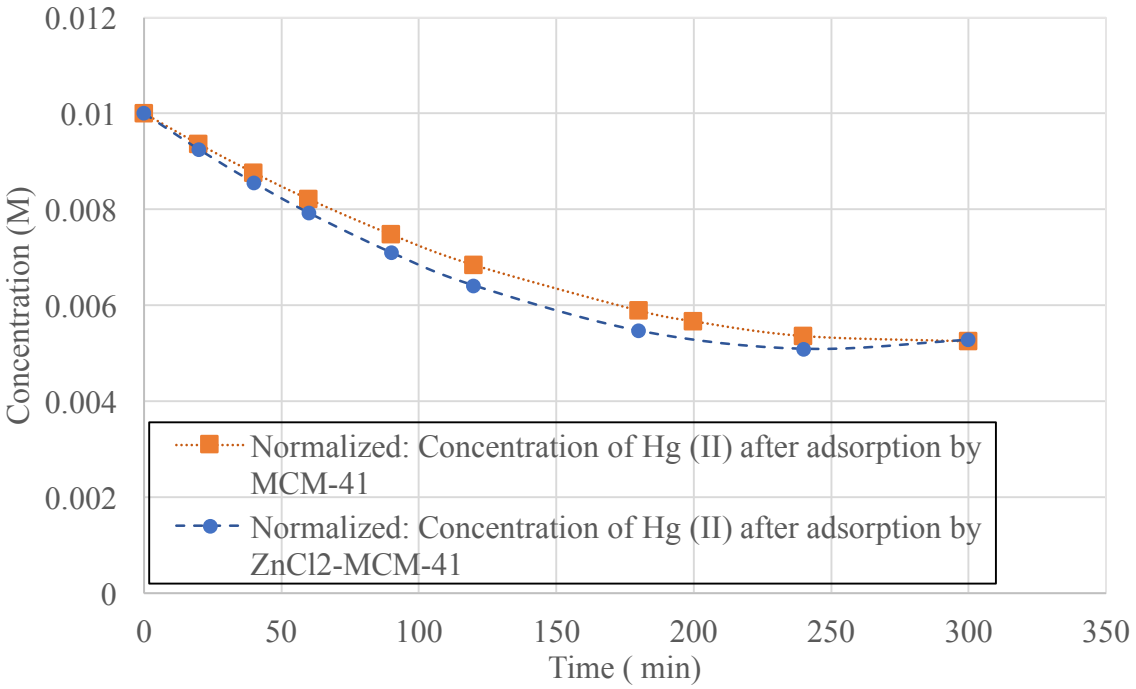

Figure 48 - Normalized: Adsorption of 0.01M Hg (II) by MCM-41 & $ZnCl_2$-MCM-41

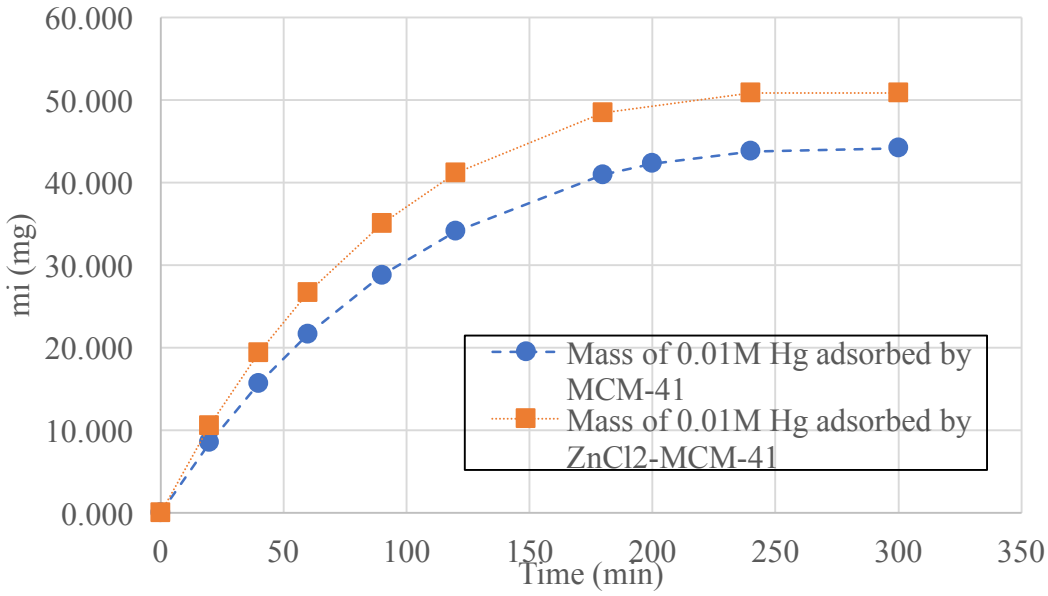

Figure 49 - Model: Mass of 0.01M Hg (II) adsorbed by MCM-41 & $ZnCl_2$-MCM-41

C. Adsorption of 0.001M Hg (II) species

Tables 19 and 20 show the data for 0.001M Hg (II), with experimental, model, and normalized concentration at specific time interval. The adsorption capacity of MCM-41 is calculated to be 12.91 mg/g, and for $ZnCl_2$-MCM-41, it is 10.53 mg/g. The trend for the concentration versus time can be seen in Figures 50 to 52, with concentration decreasing with time. Figure 53 shows the mass of 0.001M Hg adsorbed by the adsorbents, and it increases with time. MCM-41 was found to be performing a little better than $ZnCl_2$-MCM-41, but the adsorption capacities for both adsorbents are similar, with not a significant difference.

Table 19 Adsorption of 0.001 M Hg (II) by MCM- 41

Vol of the solution (L)	Time (min)	Conc (M)	Model conc (M)	Normalized Conc (M)	Mass of the adsorbate (m_i), g	($\sum m_i$), (mg)
0.060	0	0.00141	0.00140	0.00100	-	-
0.055	20	0.00112	0.00136	0.00097	0.441	0.44
0.050	30	0.00112	0.00134	0.00096	0.201	0.64
0.045	40	0.00108	0.00132	0.00094	0.181	0.82
0.040	60	0.00107	0.00128	0.00091	0.321	1.14
0.035	120	0.00097	0.00116	0.00083	0.842	1.99
0.030	160	0.00095	0.00108	0.00077	0.481	2.47
0.025	200	0.00093	0.00100	0.00071	0.401	2.87
0.020	240	0.00086	0.00092	0.00066	0.321	3.19
0.015	300	0.000841	0.00080	0.00057	0.361	3.55
0.015	24 hours	0.00080				**Σm_i=3.55**
Adsorption=**Σm_i/0.275g adsorbent= 12.91 mg/g**						

Table 20 Adsorption of 0.001 M Hg (II) by $ZnCl_2$-MCM- 41						
Vol of the solution (L)	**Time (min)**	**Conc (M)**	**Model conc (M)**	**Normalized Conc (M)**	**Mass of the adsorbate (m_i), g**	**($\sum m_i$), (mg)**
0.060	0	0.001438	0.00130	0.00100	-	-
0.055	20	0.001363	0.00124	0.00096	0.635	0.64
0.050	30	0.001323	0.00122	0.00093	0.271	0.91
0.045	40	0.001214	0.00119	0.00092	0.233	1.14
0.040	60	0.001212	0.00114	0.00088	0.385	1.52
0.035	120	0.001191	0.00103	0.00079	0.809	2.33
0.030	180	0.001117	0.00095	0.00073	0.433	2.77
0.025	200	0.000957	0.00094	0.00072	0.072	2.84
0.020	240	0.000956	0.00093	0.00071	0.058	2.90
0.015	300	0.000901	0.00094	0.00072	-0.043	2.90
0.015	24 hours	0.000836				**Σm_i=2.90**
Adsorption=**Σm_i/0.275g adsorbent= 10.53 mg/g**						

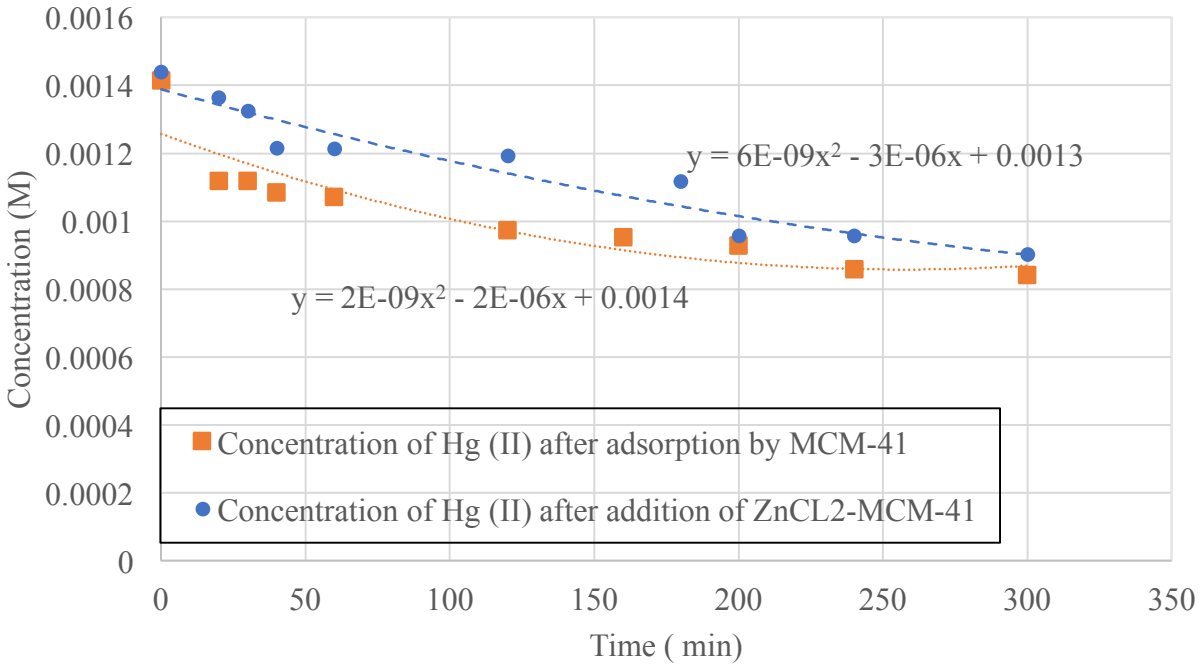

Figure 50 – Experimental: Adsorption of 0.001M Hg (II) by MCM-41 & $ZnCl_2$-MCM-41

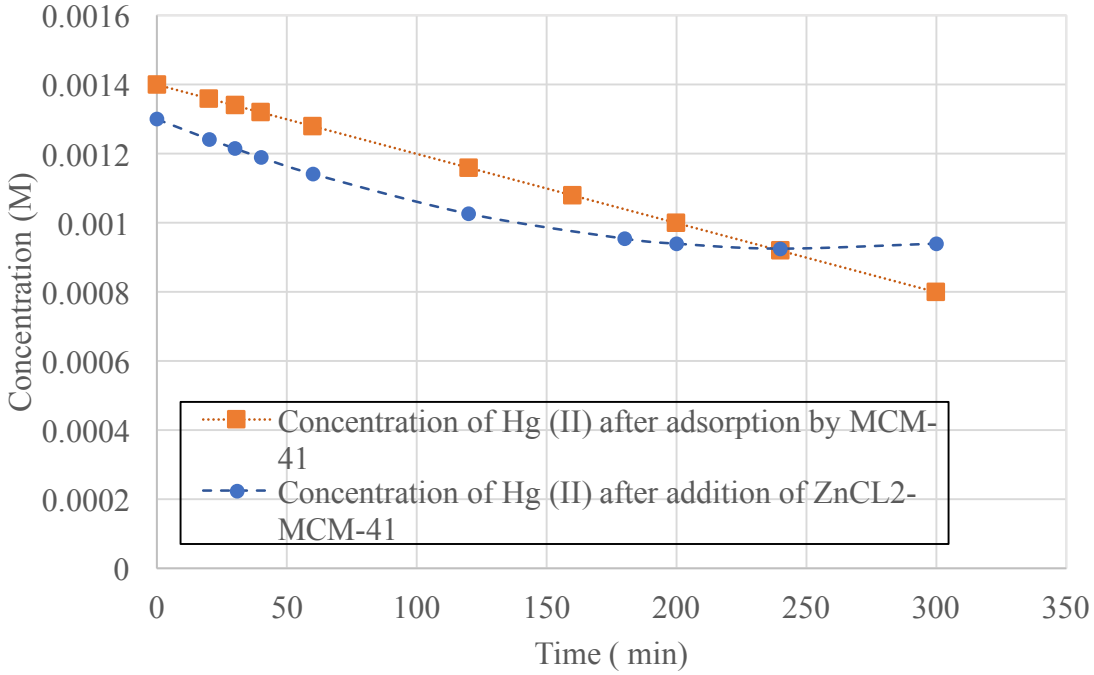

Figure 51 – Model: Adsorption of 0.001M Hg (II) by MCM-41 & $ZnCl_2$-MCM-41

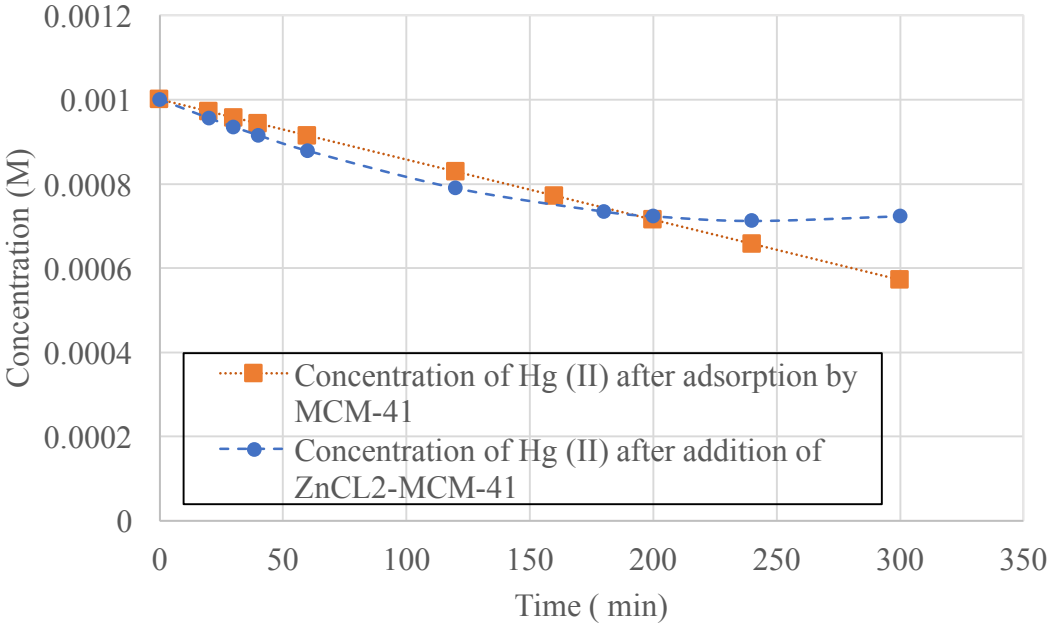

Figure 52 – Normalized: Adsorption of 0.001M Hg (II) by MCM-41 & $ZnCl_2$-MCM-41

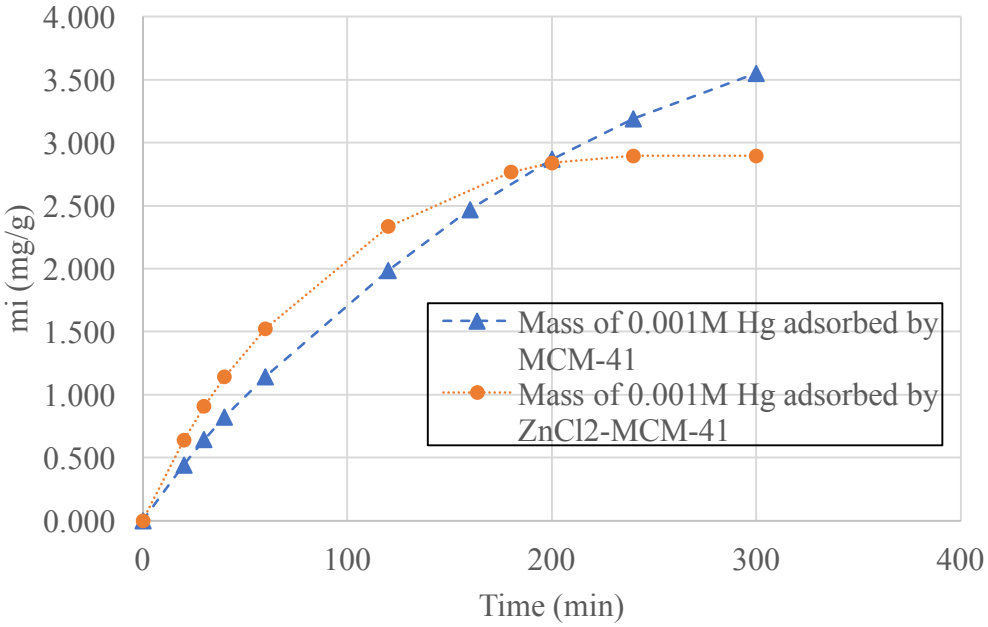

Figure 53 – Model: Mass of 0.001M Hg (II) adsorbed by MCM-41 & $ZnCl_2$-MCM-41

4.3.3 Adsorption of Cr (III) ions

Chromium ions experiments were done in the same method as the mercury. The results for chromium were taken with an ICP-OES instrument. The calibration, and other data are presented in the Appendix section. In case of Chromium 0.001M, only sample 2 was taken into consideration because of high data discrepancy with sample 1. The results are shown in the Tables 21 to 26. The experiments with chromium showed similar results as in mercury, only the adsorption capacity of the adsorbents was less in case of chromium than for mercury.

A. Adsorption of 0.1M Cr (III) ions

Tables 21 and 22 show the data for 0.1M Cr (III), with experimental, model, and normalized concentration at specific time interval. The adsorption capacity of MCM-41 is calculated to be 70.42 mg/g. ZnCl2-MCM-41 performed better than MCM-41, with adsorption capacity of 139.27 mg/g. The trend for the concentration versus time can be seen in Figures 54 to 56, with concentration decreasing with time. Figure 57 shows the mass of 0.1M Cr (III) adsorbed.

Table 21 Adsorption of 0.1 M Cr (III) by MCM-41

Vol of the solution (L)	Time (min)	Conc (M)	Model conc (M)	Normalized Conc (M)	Mass of the adsorbate (m_i), g	($\sum m_i$), (mg)
0.060	0	0.09753	0.0961	0.1000	-	-
0.055	20	0.09440	0.0942	0.0980	5.376	5.376
0.050	40	0.09081	0.0926	0.0963	4.264	9.640
0.045	60	0.08844	0.0912	0.0949	3.276	12.916
0.040	90	0.08822	0.0895	0.0932	3.432	16.348
0.035	120	0.08782	0.0884	0.0920	2.020	18.368
0.030	160	0.08761	0.0878	0.0913	0.998	19.366
0.025	200	0.08586	0.0881	0.0917	-0.416	18.950
0.020	240	0.08553	0.0894	0.0930	-1.331	18.950
0.015	24 hours	0.08245				**Σmi=18.950**
Adsorption=Σm_i/0.275g adsorbent= 70.42 mg/g						

Table 22 Adsorption of 0.1 M Cr (III) by $ZnCl_2$-MCM-41						
Vol of the solution (L)	**Time (min)**	**Conc (M)**	**Model conc (M)**	**Normalized Conc (M)**	**Mass of the adsorbate (m_i), g**	**($\sum m_i$), (mg)**
0.06	0	0.09423	0.0925	0.1000		
0.055	20	0.09058	0.0914	0.0988	3.089	3.089
0.050	40	0.08836	0.0902	0.0975	3.224	6.312
0.045	60	0.08805	0.0888	0.0960	3.276	9.588
0.040	90	0.08743	0.0864	0.0934	4.992	14.580
0.035	120	0.08645	0.0836	0.0904	5.023	19.603
0.030	160	0.07982	0.0794	0.0858	6.614	26.216
0.025	200	0.07500	0.0745	0.0805	6.344	32.560
0.020	240	0.07128	0.0690	0.0746	5.740	38.300
0.015	24 hours	0.05301				**Σmi=38.300**
Adsorption=Σm_i/0.275g adsorbent= 139.27 mg/g						

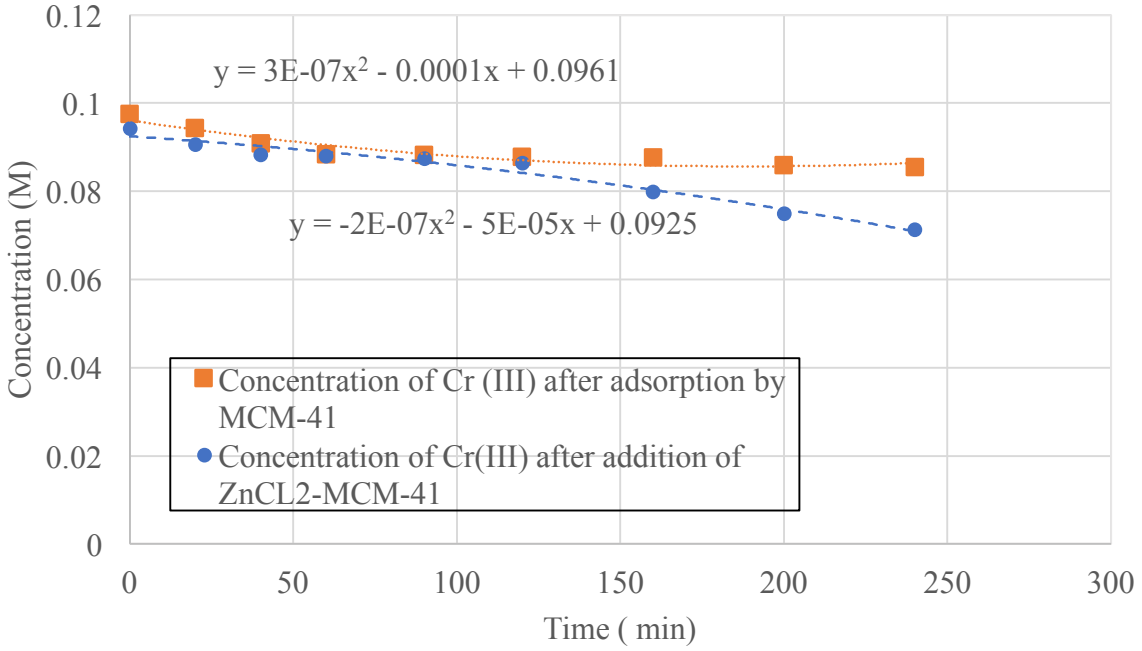

Figure 54 - Experimental: Adsorption of 0.1M Cr (III) by MCM-41 & $ZnCl_2$-MCM-41

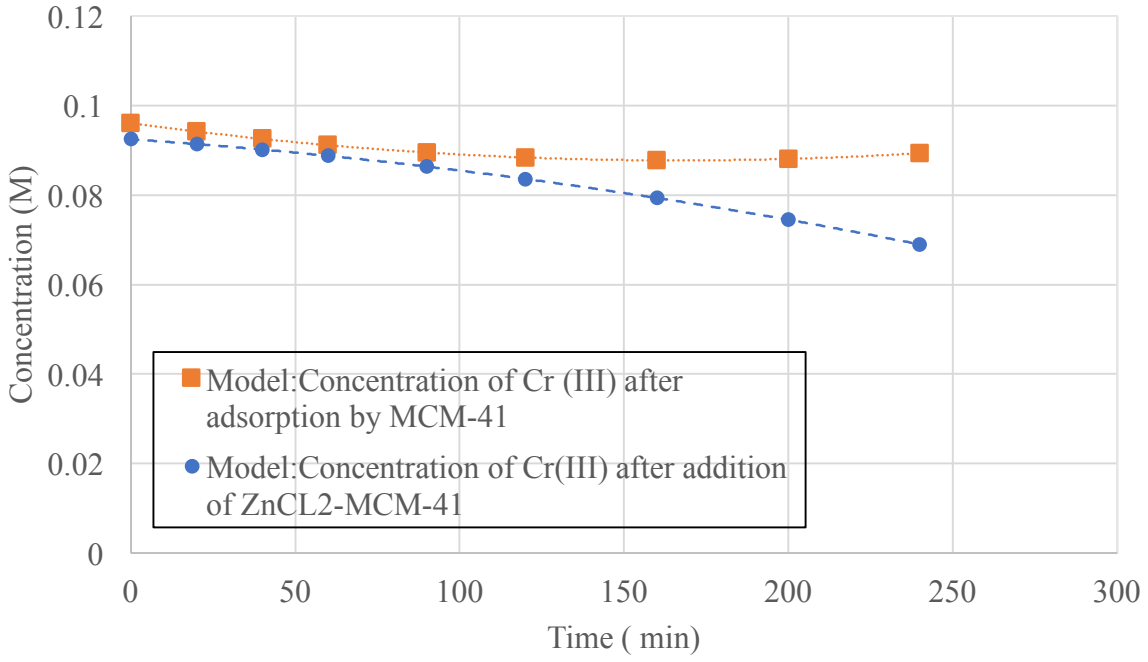

Figure 55 - Model: Adsorption of 0.1M Cr (III) by MCM-41 & $ZnCl_2$-MCM-41

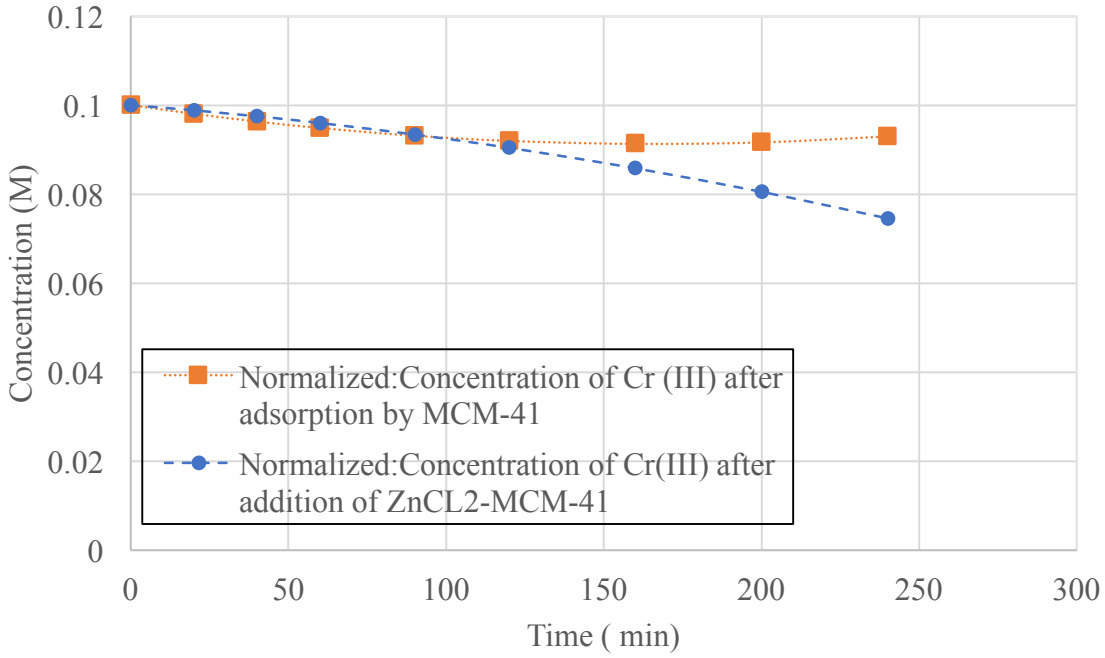

Figure 56 - Normalized: Adsorption of 0.1M Cr (III) by MCM-41 & $ZnCl_2$-MCM-41

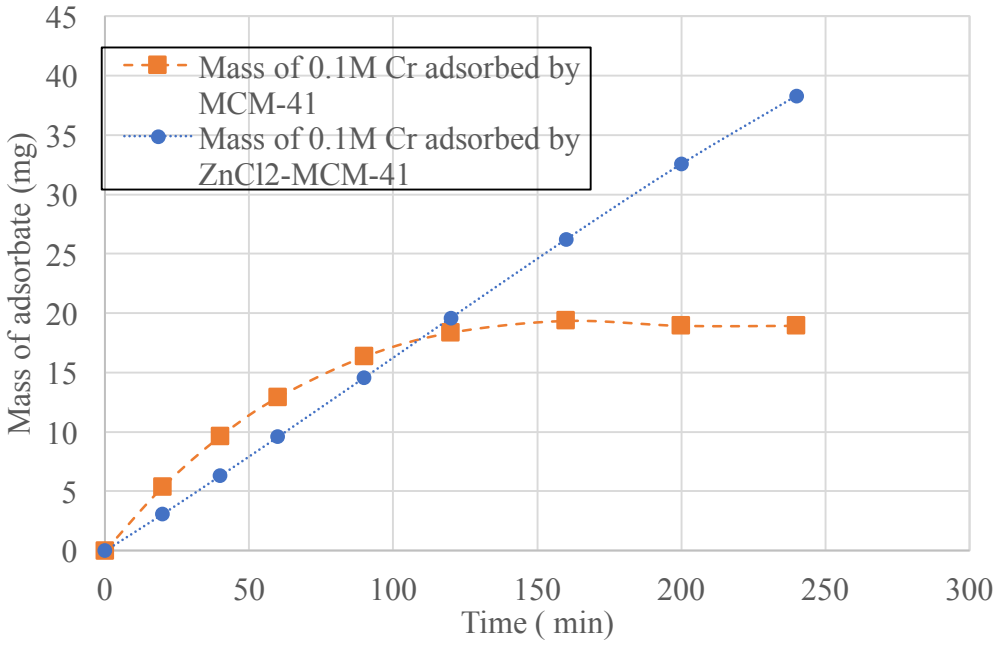

Figure 57 - Model: Mass of 0.1M Cr (III) adsorbed by MCM-41 & $ZnCl_2$-MCM-41

B. Adsorption of 0.01M Cr (III) species

Tables 23 and 24 show the data for 0.01M Cr (III), with experimental, model, and normalized concentration at specific time interval. The adsorption capacity of MCM-41 is calculated to be 27.37 mg/g. $ZnCl_2$-MCM-41 performed better than MCM-41, with adsorption capacity of 25.44 mg/g. The trend for the concentration versus time can be seen in Figures 58 to 60, with concentration decreasing with time. Figure 61 shows the mass of 0.01M Cr (III) adsorbed by the adsorbents, and it increases with time. The adsorption capacity is similar for both adsorbents for 0.01M Cr (III).

Table 23 Adsorption of 0.01 M Cr (III) by MCM-41						
Vol of the solution (L)	**Time (min)**	**Conc (M)**	**Model conc (M)**	**Normalized Conc (M)**	**Mass of the adsorbate (m_i), g**	**($\sum m_i$), (mg)**
0.06	0	0.00938	0.00910	0.0100		
0.055	20	0.00923	0.00852	0.0094	1.647	1.647
0.050	40	0.00771	0.00800	0.0088	1.373	3.020
0.045	60	0.00723	0.00752	0.0083	1.123	4.143
0.040	90	0.00700	0.00689	0.0076	1.310	5.453
0.035	120	0.00692	0.00636	0.0070	0.950	6.403
0.030	180	0.00664	0.00564	0.0062	1.123	7.526
0.025	200	0.00663	0.00550	0.0060	0.187	7.714
0.020	240	0.00653	0.00536	0.0059	0.150	7.863
0.015	300	0.00645	0.00550	0.0060	-0.112	7.863
	24 hours	0.00645				**Σm_i = 7.863**
Adsorption=Σm_i/0.275g adsorbent= 27.37 mg/g						

Table 24 Adsorption of 0.01 M Cr (III) by $ZnCl_2$-MCM-41						
Vol of the solution (L)	**Time (min)**	**Conc (M)**	**Model conc (M)**	**Normalized Conc (M)**	**Mass of the adsorbate (m_i), g**	**($\sum m_i$), (mg)**
0.06	0	0.01000	0.00850	0.0100		
0.055	20	0.00708	0.00793	0.0093	1.636	1.636
0.050	40	0.00679	0.00741	0.0087	1.341	2.977
0.045	60	0.00671	0.00695	0.0082	1.076	4.054
0.040	90	0.00650	0.00637	0.0075	1.217	5.270
0.035	120	0.00650	0.00591	0.0070	0.835	6.106
0.030	180	0.00647	0.00537	0.0063	0.842	6.948
0.025	240	0.00630	0.00533	0.0063	0.047	6.995
0.020	300	0.00628	0.00580	0.0068	-0.487	6.995
0.015	24 hours	0.00609				**Σm_i = 6.99**
Adsorption=Σm_i/0.275g adsorbent= 25.44 mg/g						

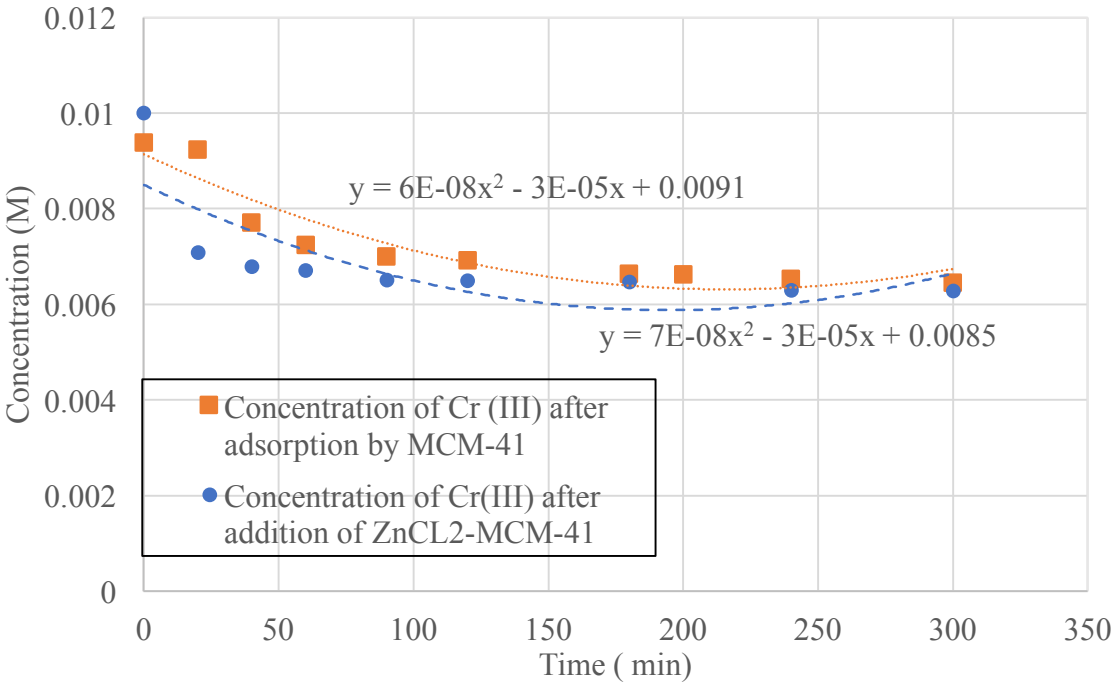

Figure 58 - Experimental: Adsorption of 0.01M Cr (III) by MCM-41 & $ZnCl_2$-MCM-41

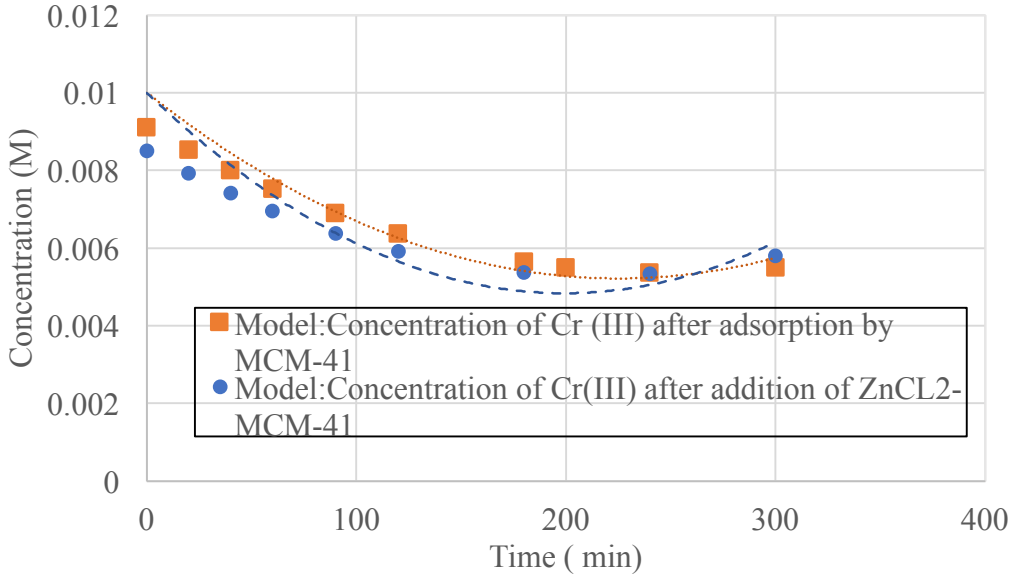

Figure 59 - Model: Adsorption of 0.01M Cr (III) by MCM-41 & $ZnCl_2$-MCM-41

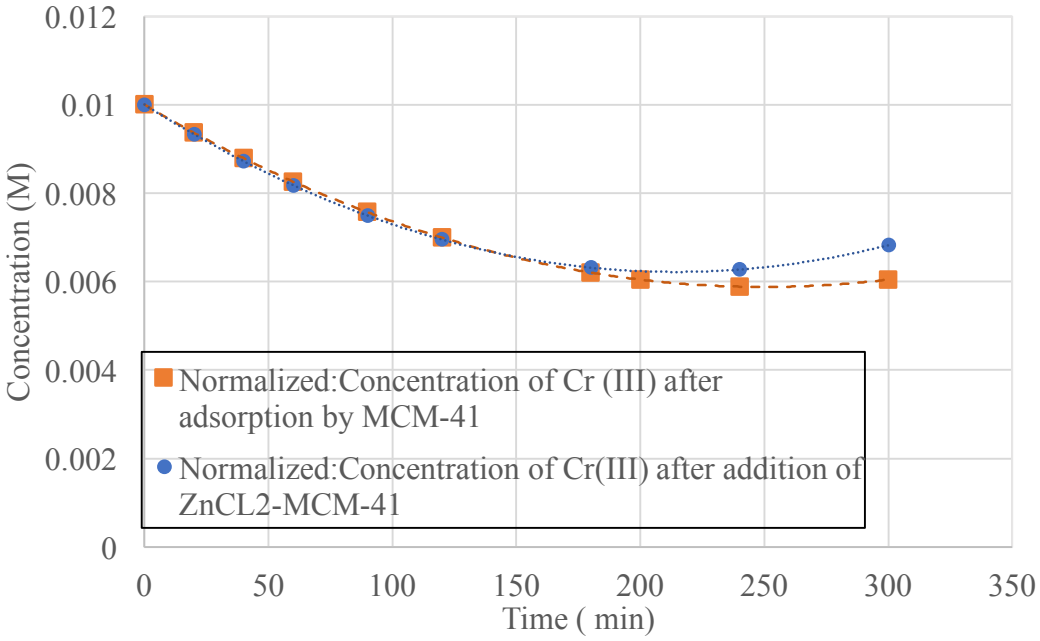

Figure 60 - Normalized: Adsorption of 0.01M Cr (III) by MCM-41 & $ZnCl_2$-MCM-41

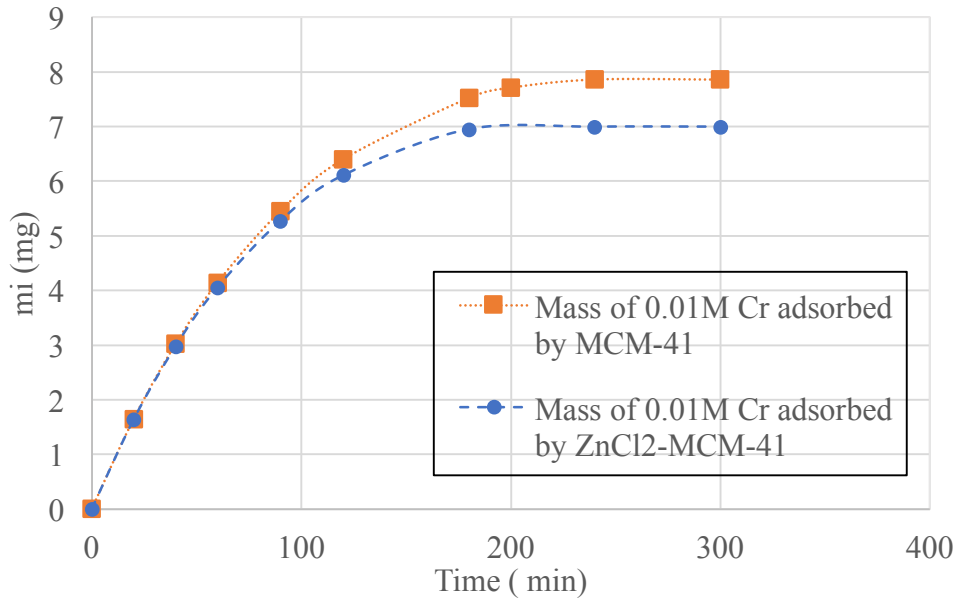

Figure 61 - Model: Mass of 0.01M Cr (III) adsorbed by MCM-41 & $ZnCl_2$-MCM-41

C. Adsorption of 0.001M Cr (III) species

Tables 25 and 26 show the data for 0.001M Cr (III), with experimental, model, and normalized concentration at specific time interval. The adsorption capacity of MCM-41 is calculated to be 3.501 mg/g. $ZnCl_2$-MCM-41 performed similar to MCM-41, with adsorption capacity of 3.788 mg/g. The trend for the concentration versus time can be seen in Figures 62 to 64, with concentration decreasing with time. Figure 65 shows the mass of 0.01M Cr (III) adsorbed by the adsorbents, and it increases with time. The adsorption capacity is similar for both adsorbents for 0.001M Cr (III).

Table 25 Adsorption of 0.001 M Cr (III) by MCM-41

Vol of the solution (L)	Time (min)	Conc (M)	Model conc (M)	Normalized Conc (M)	Mass of the adsorbate (m_i), g	($\sum m_i$), (mg)
0.06	0	0.00100	0.00090	0.00100	-	-
0.055	20	0.00088	0.00082	0.00092	0.218	0.218
0.050	40	0.00071	0.00075	0.00084	0.180	0.398
0.045	60	0.00070	0.00069	0.00077	0.145	0.543
0.040	90	0.00061	0.00061	0.00068	0.165	0.709
0.035	120	-	0.00055	0.00061	0.115	0.824
0.030	180	0.00060	0.00047	0.00052	0.122	0.946
0.025	240	0.00056	0.00046	0.00051	0.017	0.963
0.020	300	0.00054	0.00051	0.00057	-0.054	0.963
0.015	24 hours	0.00050				**Σm_i = 0.963**
Adsorption=Σm_i/0.275g adsorbent= 3.501 mg/g						

Table 26 Adsorption of 0.001 M Cr (III) by $ZnCl_2$-MCM-41						
Vol of the solution (L)	**Time (min)**	**Conc (M)**	**Model conc (M)**	**Normalized Conc (M)**	**Mass of the adsorbate (m_i), g**	**($\sum m_i$), (mg)**
0.06	0	0.00100	0.00090	0.00100		
0.055	20	0.00067	0.00082	0.00091	0.220	0.220
0.050	40	0.00066	0.00075	0.00084	0.183	0.403
0.045	60	0.00063	0.00069	0.00077	0.150	0.552
0.040	90	0.00063	0.00060	0.00067	0.175	0.727
0.035	120	0.00061	0.00054	0.00059	0.127	0.854
0.030	160	0.00049	0.00046	0.00052	0.110	0.964
0.025	200	0.00049	0.00042	0.00047	0.058	1.022
0.020	240	0.00042	0.00040	0.00045	0.020	1.042
0.015	24 hours	0.00040				**Σm_i = 1.042**
Adsorption=Σm_i/0.275g adsorbent= 3.788 mg/g						

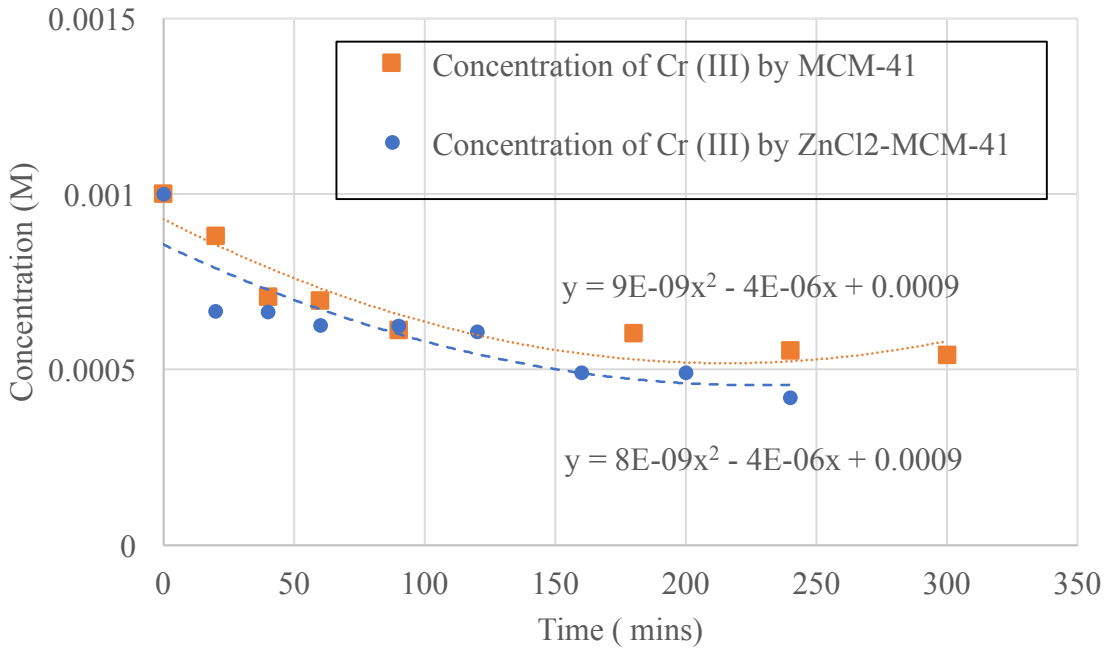

Figure 62 - Experimental: Adsorption of 0.001M Cr (III) by MCM-41 & $ZnCl_2$-MCM-41

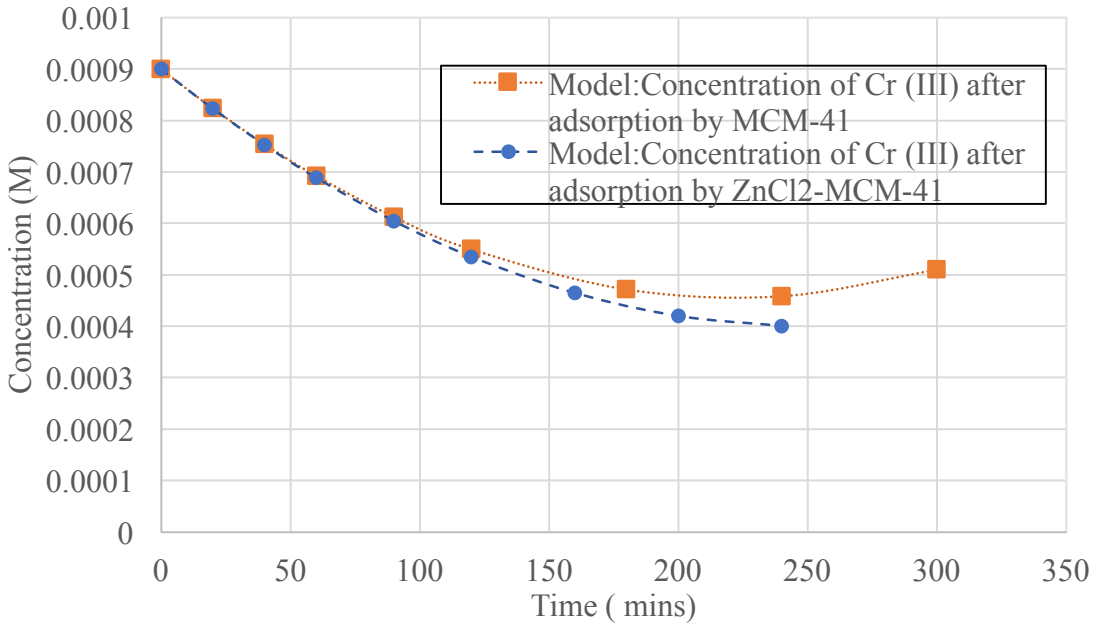

Figure 63 - Model: Adsorption of 0.001M Cr (III) by MCM-41 & $ZnCl_2$-MCM-4

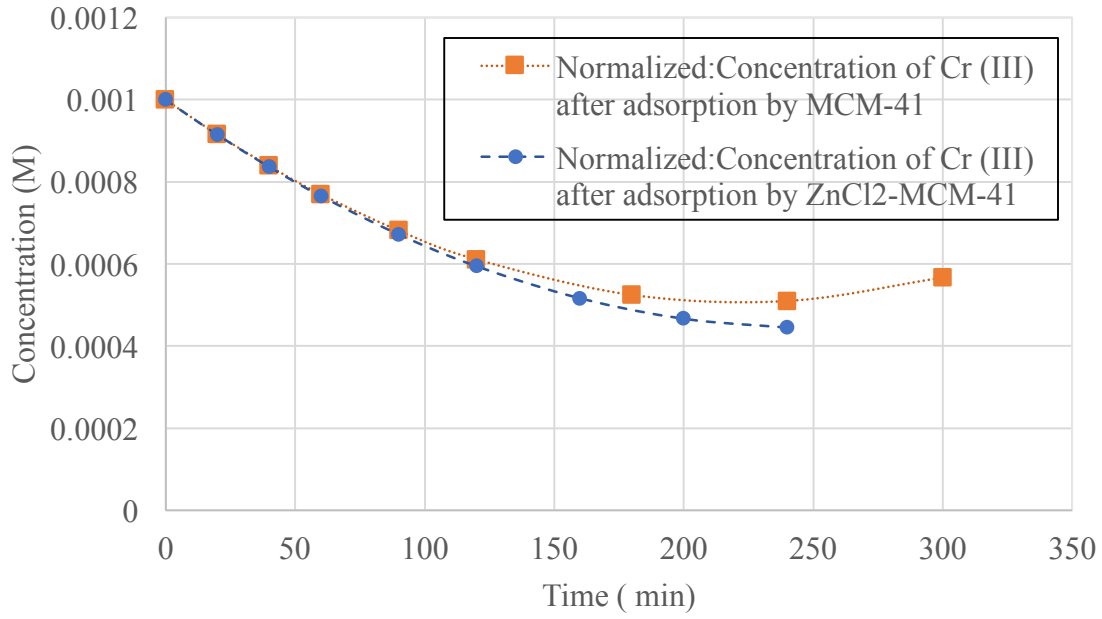

Figure 64 - Normalized: Adsorption of 0.001M Cr (III) by MCM-41 & $ZnCl_2$-MCM-41

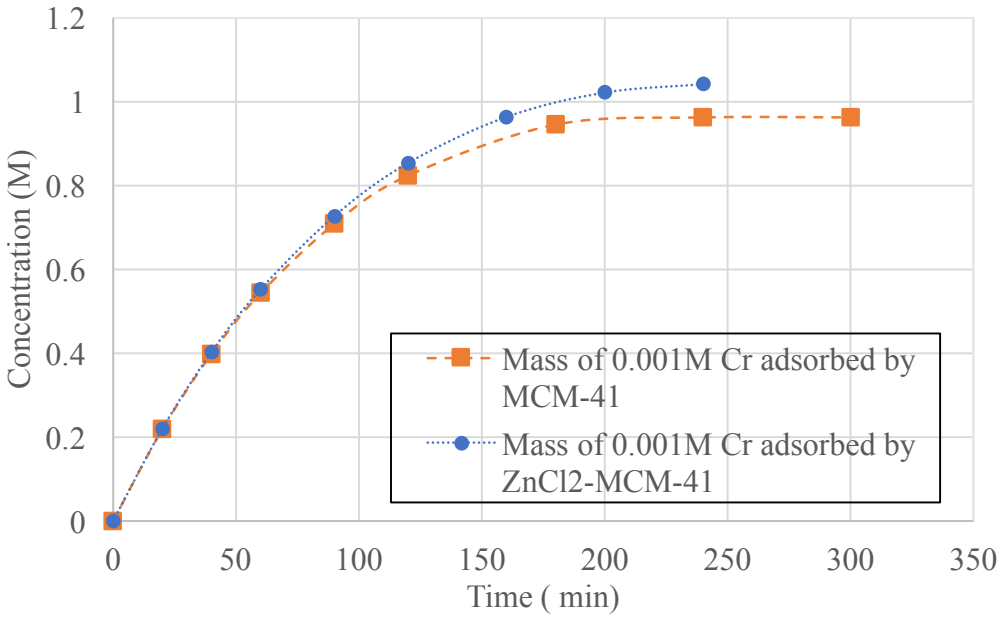

Figure 65 - Model: Mass of 0.001M Cr (III) adsorbed by MCM-41 & $ZnCl_2$-MCM-41

4.3.4 Competition of metal ions in a solution in an adsorption

Three different heavy metal ions, Pb(II), Hg(II), and Cr(III), were used to find out the highest adsorption capacities of MCM-41 and $ZnCl_2$-MCM-41. The results are presented in the tabular format from Table 27 to 32. Figures 66 to 68 show the adsorption of heavy metals in solution by MCM-41. Figures 70 to 72 show the adsorption by $ZnCl_2$-MCM-41. The adsorption capacities of MCM-41and $ZnCl_2$-MCM-41 can be seen in Figures 69 and 73 respectively. The results from the combined heavy metals experiments show that lead is the most adsorbed metal amongst the three metals tested. Mercury is the second most adsorbed, making chromium the least adsorbed one. This shows the adsorption is in order of Pb>Hg>Cr.

Table 27 Adsorption of 0.1M heavy metals by MCM-41 Experimental Results

Samples	Volume of the solution (L)	Time (min)	Cr^{3+} concentration after adsorption	Hg^{2+} concentration after adsorption	Pb^{2+} concentration after adsorption
1	0.060	0	0.106615	0.101741	0.098995
2	0.055	20	0.097653	0.100833	0.075845
3	0.050	40	0.100872	0.100518	0.074143
4	0.045	60	0.097721	0.102426	0.075919
5	0.040	90	0.099060	0.103035	0.076369
6	0.035	120	0.099827	0.102238	0.073371
7	0.030	160	0.097662	0.101715	0.064701
8	0.025	200	0.096930	0.099492	0.065800
9	0.020	240	0.099561	0.102756	0.067352
10	0.015	300	0.074718	0.085541	0.052216
		24 hours	0.065013	0.066112	0.041599

Table 28 Adsorption of 0.1M heavy metals by MCM-41 Model & normalized concentration						
Time (min)	**Cr III - Model conc. (M)**	**Hg II- Model conc. (M)**	**Pb II- Model conc. (M)**	**Cr III- Normalized Conc. (M)**	**Hg II- Normalized Conc. (M)**	**Pb II- Normalized Conc. (M)**
0	0.09970	0.09950	0.0867	0.1000	0.1000	0.1000
20	0.10074	0.10094	0.0848	0.1010	0.1014	0.0978
40	0.10146	0.10206	0.0830	0.1018	0.1026	0.0958
60	0.10186	0.10286	0.0814	0.1022	0.1034	0.0939
90	0.10186	0.10346	0.0793	0.1022	0.1040	0.0915
120	0.10114	0.10334	0.0776	0.1014	0.1039	0.0895
160	0.09906	0.10206	0.0758	0.0994	0.1026	0.0875
200	0.09570	0.09950	0.0747	0.0960	0.1000	0.0862
240	0.09106	0.09566	0.0742	0.0913	0.0961	0.0856
300	0.08170	0.08750	0.0747	0.0819	0.0879	0.0862

Table 29 Adsorption of 0.1M heavy metals by MCM-41 Adsorption capacity (mg/g)						
Time (min)	**Cr III, m_i (mg)**	**Hg II, m_i (mg)**	**Pb II, m_i (mg)**	**Cr III, ($\sum m_i$), (mg)**	**Hg II, ($\sum m_i$), (mg)**	**Pb II, ($\sum m_i$), (mg)**
0						
20	-3.245	-15.887	21.880	0.000	0.000	21.880
40	-2.059	-11.233	18.234	0.000	0.000	40.114
60	-1.040	-7.221	14.918	0.000	0.000	55.032
90	0.000	-4.814	17.405	0.000	0.000	72.437
120	1.497	0.842	12.618	1.497	0.842	85.056
160	3.785	7.703	10.940	5.283	8.545	95.996
200	5.241	12.838	5.802	10.524	21.383	101.797
240	6.032	15.405	1.989	16.556	36.788	103.786
300	9.734	24.552	-1.492	26.289	61.340	103.786
				Σm_i=26.289	**Σm_i**=61.340	**Σm_i**=103.786
			Adsorption=	**95.6 mg/g**	**223.056 mg/g**	**377.405 mg/g**

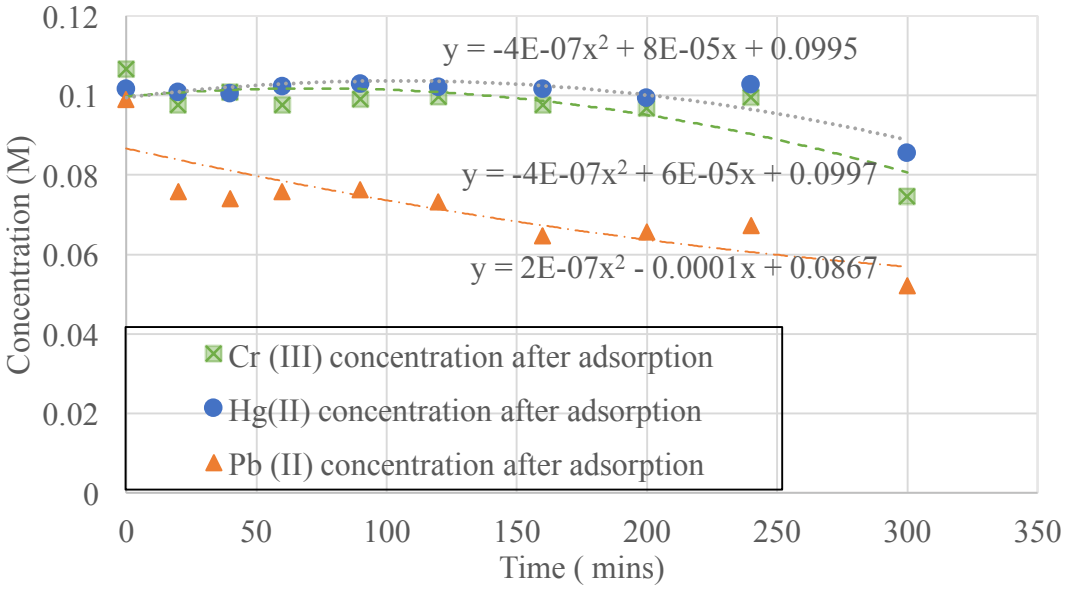

Figure 66 Experimental: Adsorption of 0.1M heavy metals (Cr^{3+}, Hg^{2+}, & Pb^{2+}) by MCM-41

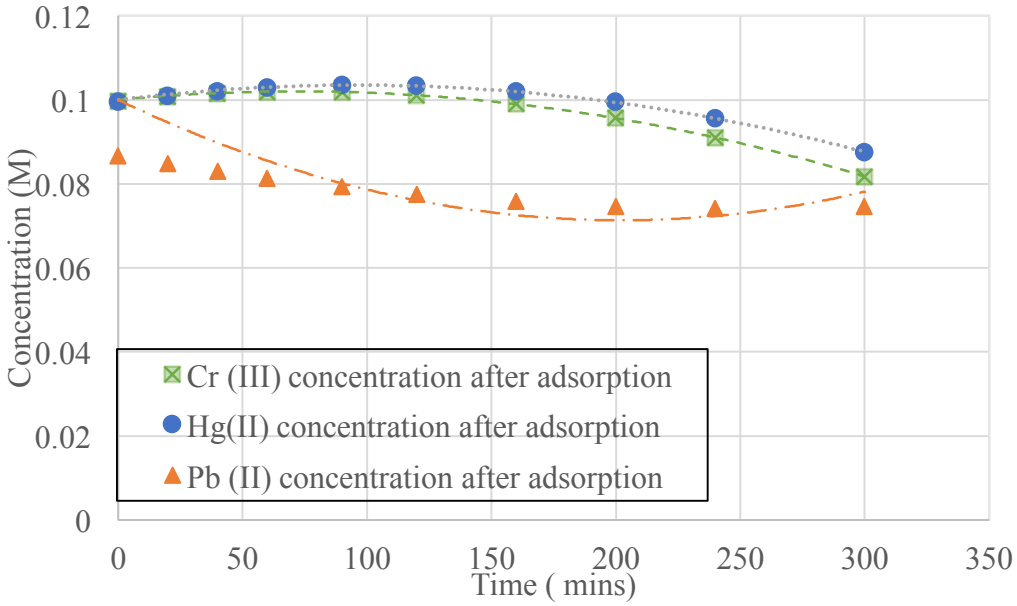

Figure 67 Model: Adsorption of 0.1M heavy metals (Cr^{3+}, Hg^{2+}, & Pb^{2+}) by MCM-41

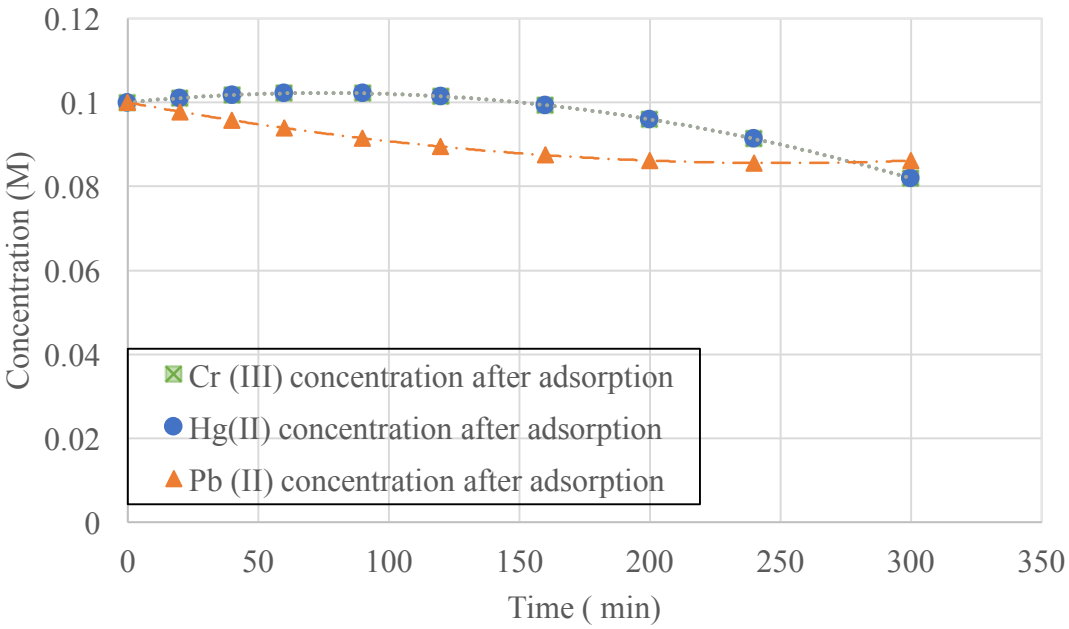

Figure 68 Normalized: Adsorption of 0.1M heavy metals (Cr^{3+}, Hg^{2+}, & Pb^{2+}) by MCM-41

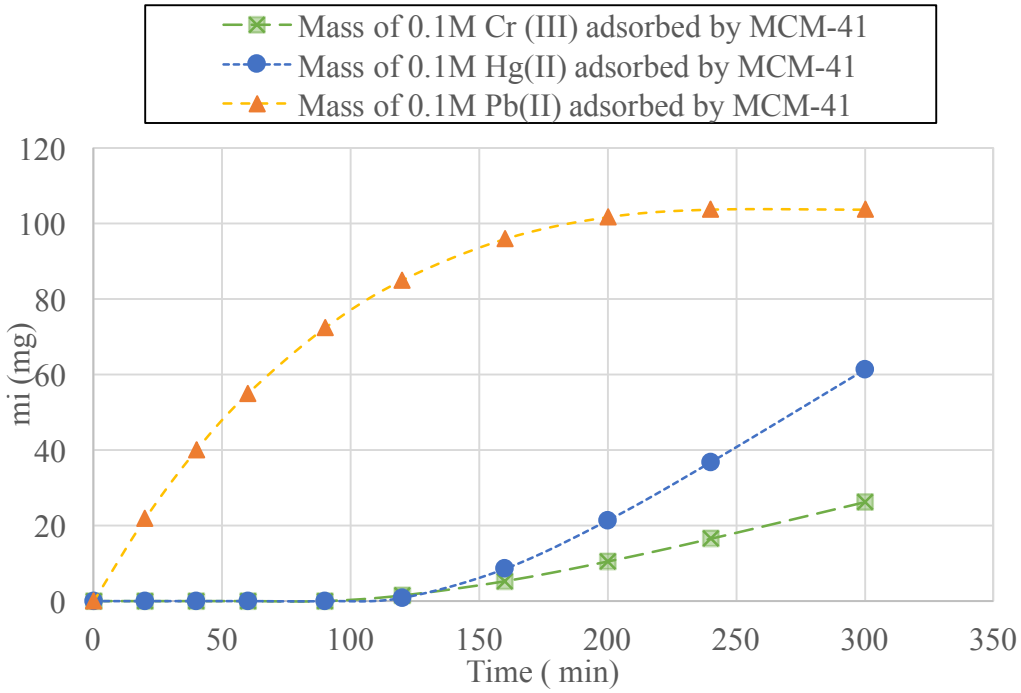

Figure 69 Mass of the adsorbate (mg) 0.1M heavy metals (Cr^{3+}, Hg^{2+}, & Pb^{2+}) adsorbed by MCM-41

Table 30 Adsorption of 0.1M heavy metals by $ZnCl_2$-MCM-41 Experimental Results					
Sample	**Volume of the solution (ml)**	**Time (min)**	**Cr^{3+} concentration after adsorption**	**Hg^{2+} concentration after adsorption**	**Pb^{2+} concentration after adsorption**
1	0.060	0	0.101457	0.102097	0.099248
2	0.055	20	0.097164	0.100150	0.075760
3	0.050	40	0.101922	0.101346	0.076392
4	0.045	60	0.099124	0.101315	0.074908
5	0.040	90	0.103227	0.104429	0.076956
6	0.035	120	0.099087	0.101508	0.072256
7	0.030	160	0.098242	0.101003	0.069053
8	0.025	200	0.099409	0.101725	0.066199
9	0.020	240	0.099798	0.102498	0.066957
10	0.015	300	0.098461	0.100310	0.069006
		24 hours	0.064403	0.06726	0.038747

Table 31 Model: Adsorption of 0.1M heavy metals by $ZnCl_2$-MCM-41 Model & normalized concentrations						
Time (min)	**Cr III - Model conc. (M)**	**Hg II- Model conc. (M)**	**Pb II- Model conc. (M)**	**Cr III- Normalized Conc. (M)**	**Hg II- Normalized Conc. (M)**	**Pb II- Normalized Conc. (M)**
0	0.10030	0.1012	0.089	0.10000	0.10000	0.09966
20	0.10028	0.1014	0.085	0.09998	0.10018	0.09539
40	0.10025	0.1015	0.082	0.09995	0.10032	0.09157
60	0.10020	0.1016	0.079	0.09990	0.10042	0.08820
90	0.10009	0.1017	0.075	0.09979	0.10049	0.08399
120	0.09995	0.1017	0.072	0.09965	0.10047	0.08079
160	0.09971	0.1015	0.070	0.09941	0.10032	0.07809
200	0.09940	0.1012	0.069	0.09910	0.10000	0.07719
240	0.09903	0.1007	0.070	0.09873	0.09953	0.07809
300	0.09835	0.0997	0.074	0.09806	0.09852	0.08281

Table 32 Adsorption of 0.1M heavy metals by $ZnCl_2$-MCM-41 Adsorption capacity (mg/g)						
Time (min)	**Cr III, m_i (mg)**	**Hg II, m_i (mg)**	**Pb II, m_i (mg)**	**Cr III, ($\sum m_i$), (mg)**	**Hg II, ($\sum m_i$), (mg)**	**Pb II, ($\sum m_i$), (mg)**
0						
20	-3.245	-15.887	21.880	0.051	-1.986	43.305
40	-2.059	-11.233	18.234	0.139	-3.390	78.529
60	-1.040	-7.221	14.918	0.256	-4.293	106.501
90	0.000	-4.814	17.405	0.474	-4.894	137.581
120	1.497	0.842	12.618	0.730	0.105	158.249
160	3.785	7.703	10.940	1.109	1.068	173.167
200	5.241	12.838	5.802	1.508	2.673	177.311
240	6.032	15.405	1.989	1.894	4.599	177.311
300	9.734	24.552	-1.492	2.421	7.668	177.311
				Σm_i=2.421	**Σm_i=7.668**	**Σm_i=177.311**
			Adsorption=	**8.804 mg/g**	**27.882 mg/g**	**644.77 mg/g**

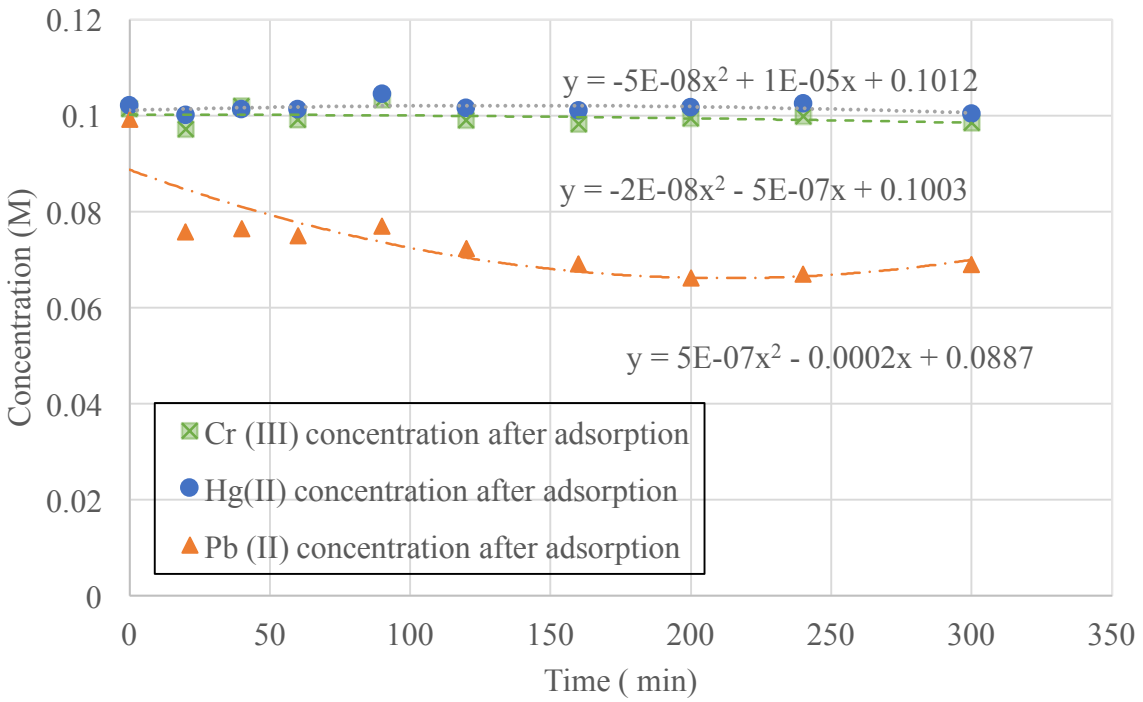

Figure 70 Experimental: Adsorption of 0.1M heavy metals (Cr^{3+}, Hg^{2+}, & Pb^{2+}) by $ZnCl_2$-MCM-41

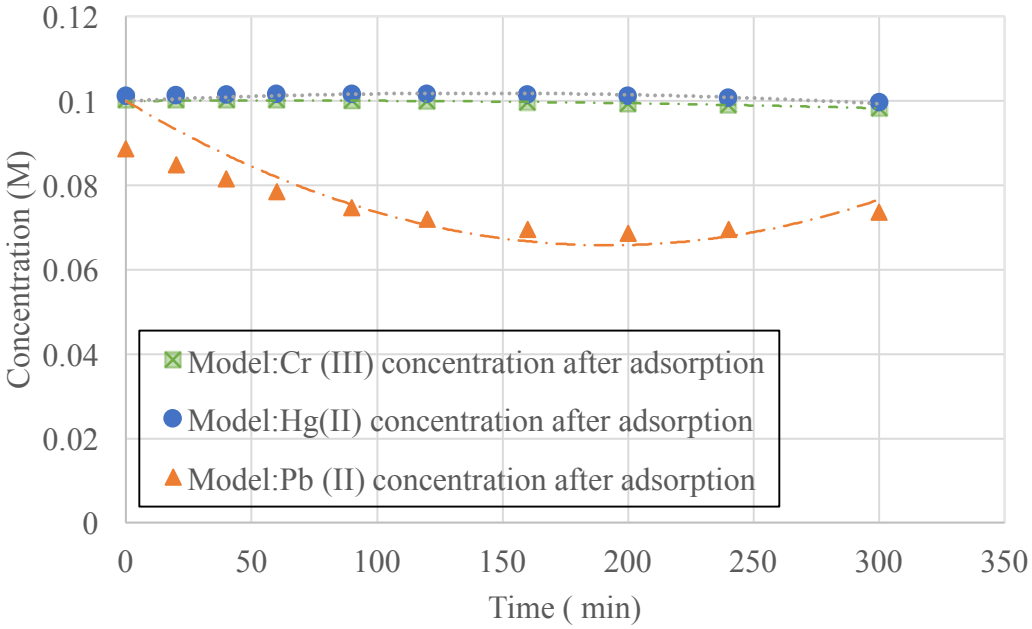

Figure 71 Model: Adsorption of 0.1M heavy metals (Cr^{3+}, Hg^{2+}, & Pb^{2+}) by $ZnCl_2$-MCM-41

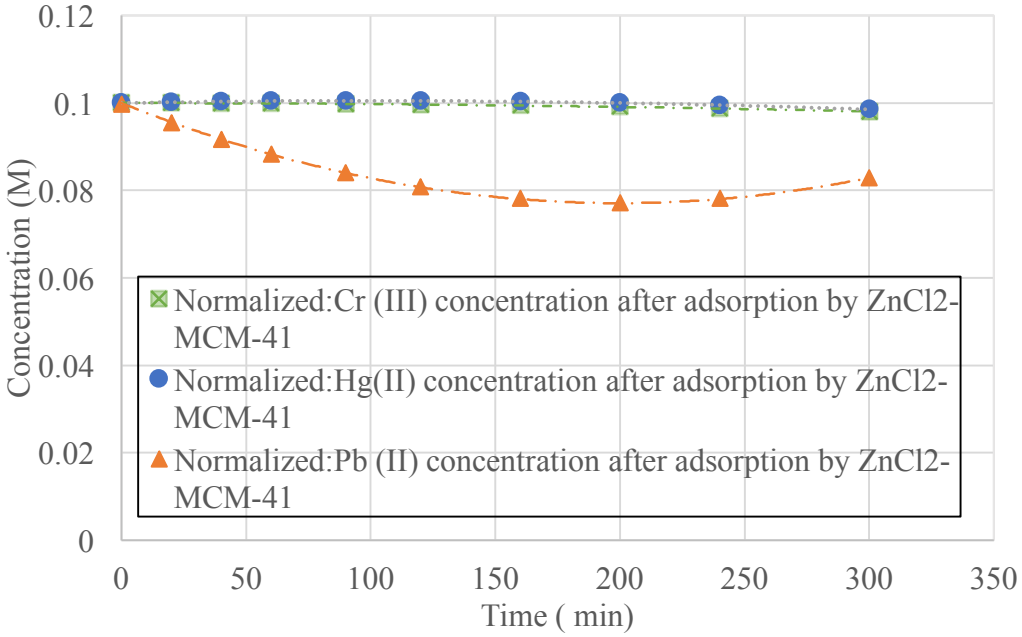

Figure 72 Normalized: Adsorption of 0.1M heavy metals (Cr^{3+}, $Hg^{2+,}$ & $Pb^{2+)}$ by MCM-41

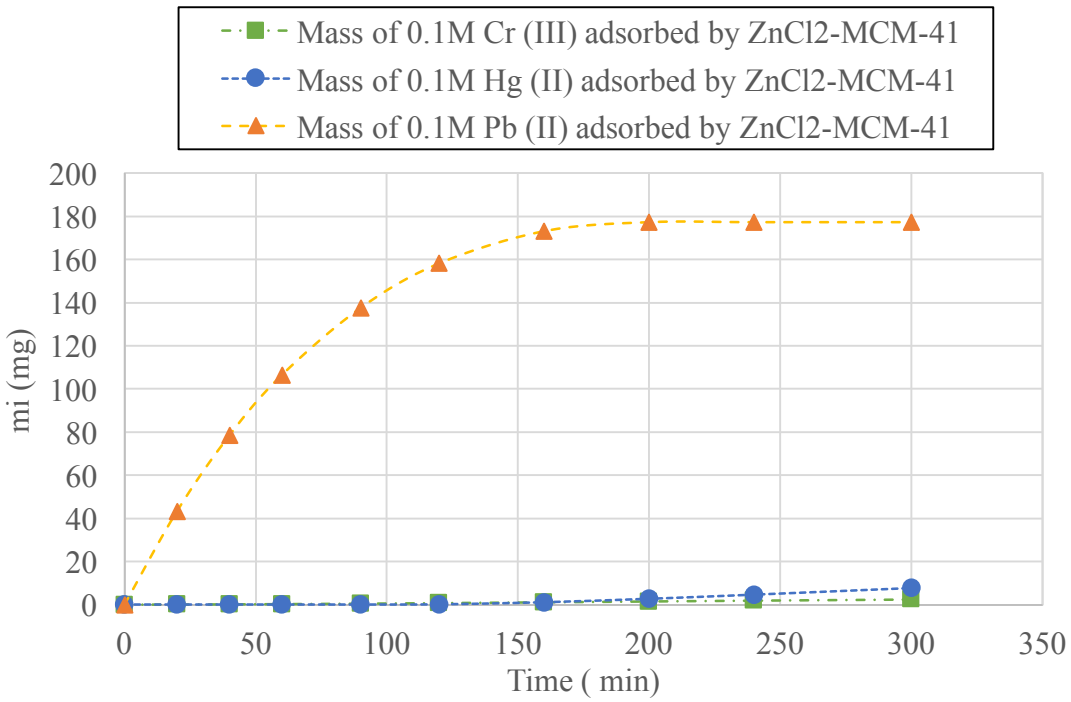

Figure 73 Model: Mass of the adsorbate (mg) 0.1M heavy metals (Cr^{3+}, Hg^{2+}, & Pb^{2+}) adsorbed by $ZnCl_2$-MCM-41

4.5 Batch Adsorption Studies: Adsorption of Ca^{2+}, K^{+}, and NO_3- ions in a solution in an adsorption

All the measurements for the cations calcium and potassium, and anion nitrate were taken with an ISE electrode. The detailed calculations are shown in the Appendix. The concentrations used were 0.1M, 0.01M, and 0.001M.

4.4.1 Adsorption of Ca^{2+} ions in a solution in an adsorption

The adsorption of calcium ions in a solution by MCM-41 and $ZnCl_2$-MCM-41 was tested with electrode similar to the lead ions presented in this research previously. The initial calibration curve is presented in Table 33. The initial calibration curve is shown in Figure 74. The rest of the calculations and calibration data are presented in the Appendix.

A. Initial Calibration Curve for Calcium ions (Ca^{2+})

Table 33 Initial Calibration curve for Ca^{2+} ions

Original Concentration (M)	Log10 (Conc)	abs value of Conc	mV Reading
1.00E-01	-1.00	1.00	71.8
5.00E-02	-1.30	1.30	66
3.00E-02	-1.52	1.52	61.2
1.00E-02	-2.00	2.00	51.6
5.00E-03	-2.30	2.30	43.9
3.00E-03	-2.52	2.52	40.1
1.00E-03	-3.00	3.00	32.8
5.00E-04	-3.30	3.30	25.6
1.00E-04	-4.00	4.00	7.9

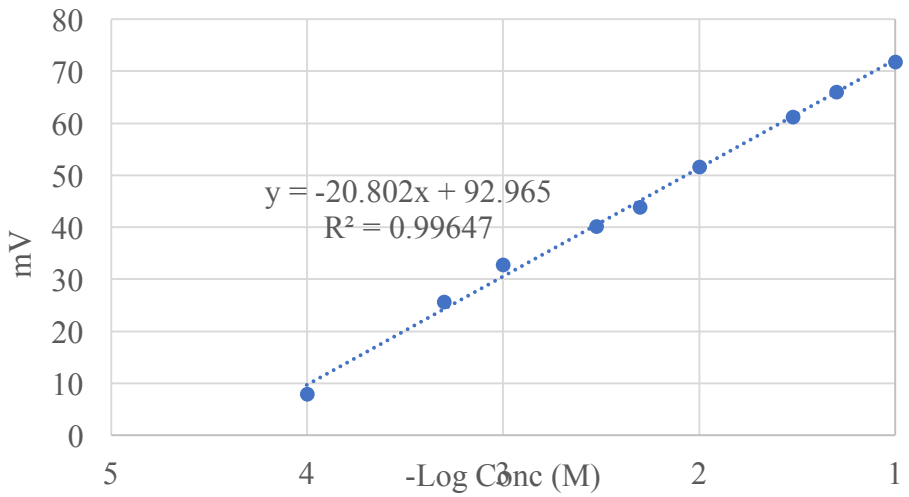

Figure 74 Initial Calibration Curve for Ca^{2+} electrode

A. Adsorption of 0.001M Calcium ions (Ca^{2+}) by MCM-41 and $ZnCl_2$-MCM-41

Table 34 shows the experimental data calculated from the calibration data. Tables 35 and 36 presents the model and normalized concentration after adsorption, and the mass adsorbed by the adsorbents. The adsorption capacities for MCM-41 and $ZnCl_2$-MCM-41 are 4.992 mg/g, and 2.56 mg/g respectively. Figures 75 to 77 show the experimental, model and normalized graphs, and Figure 78 shows the mass adsorbed by the adsorbents.

Table 34 Adsorption of 0.001M Ca^{2+} ions

	MCM-41		$ZnCl_2$-MCM-41	
Time (min)	**0.001M MCM-41**	**Conc. after adsorption by MCM-41 (M)**	**0.001M $ZnCl_2$-MCM-41**	**Conc. after adsorption by $ZnCl_2$MCM-41 (M)**
0	32.6	0.00125	31.9	0.00116
20	32.7	0.00127	27.3	0.00070
40	32.5	0.00124	28.5	0.00080
60	32	0.00117	28	0.00075
90	28.9	0.00083	27.5	0.00071
120	28.9	0.00083	27	0.00067
160	28.6	0.00081	27.1	0.00068
200	28.7	0.00081	26.8	0.00066
240	28.5	0.00080	26.4	0.00063
300	28.6	0.00081	26.2	0.00062

Table 35 Adsorption of 0.001 M Ca^{2+} by MCM-41					
Time (min)	**Conc (M)**	**Model conc (M)**	**Normalized Conc (M)**	**Mass of the adsorbate (m_i), g**	**($\sum m_i$), (mg)**
0	0.00125	0.00130	0.00100		
20	0.00127	0.00120	0.00093	0.11520	0.11520
40	0.00124	0.00112	0.00086	0.10560	0.22080
60	0.00117	0.00104	0.00080	0.09600	0.31680
90	0.00083	0.00093	0.00072	0.12600	0.44280
120	0.00083	0.00084	0.00065	0.10440	0.54720
180	0.00081	0.00076	0.00058	0.10560	0.65280
240	0.00081	0.00070	0.00054	0.06720	0.72000
300	0.00080	0.00068	0.00052	0.02880	0.74880
24 hours	0.00050				**Σm_i = 0.7488**
Adsorption=Σm_i/0.15g adsorbent= 4.992 mg/g					

Table 36 Adsorption of 0.001 M Ca^{2+} by $ZnCl_2$-MCM-41					
Time (min)	**Conc (M)**	**Model conc (M)**	**Normalized Conc (M)**	**Mass of the adsorbate (m_i), g**	**($\sum m_i$), (mg)**
0	0.00116	0.00090	0.00100		
20	0.00070	0.00084	0.00094	0.06864	0.06864
40	0.00080	0.00079	0.00088	0.06192	0.13056
60	0.00075	0.00075	0.00083	0.05520	0.18576
90	0.00071	0.00069	0.00076	0.07020	0.25596
120	0.00067	0.00064	0.00071	0.05508	0.31104
180	0.00068	0.00060	0.00067	0.04992	0.36096
240	0.00066	0.00058	0.00064	0.02304	0.38400
300	0.00063	0.00058	0.00065	-0.00384	0.38400
24 hours	0.00062				**Σm_i = 0.384**
Adsorption=Σm_i/0.15g adsorbent= 2.56 mg/g					

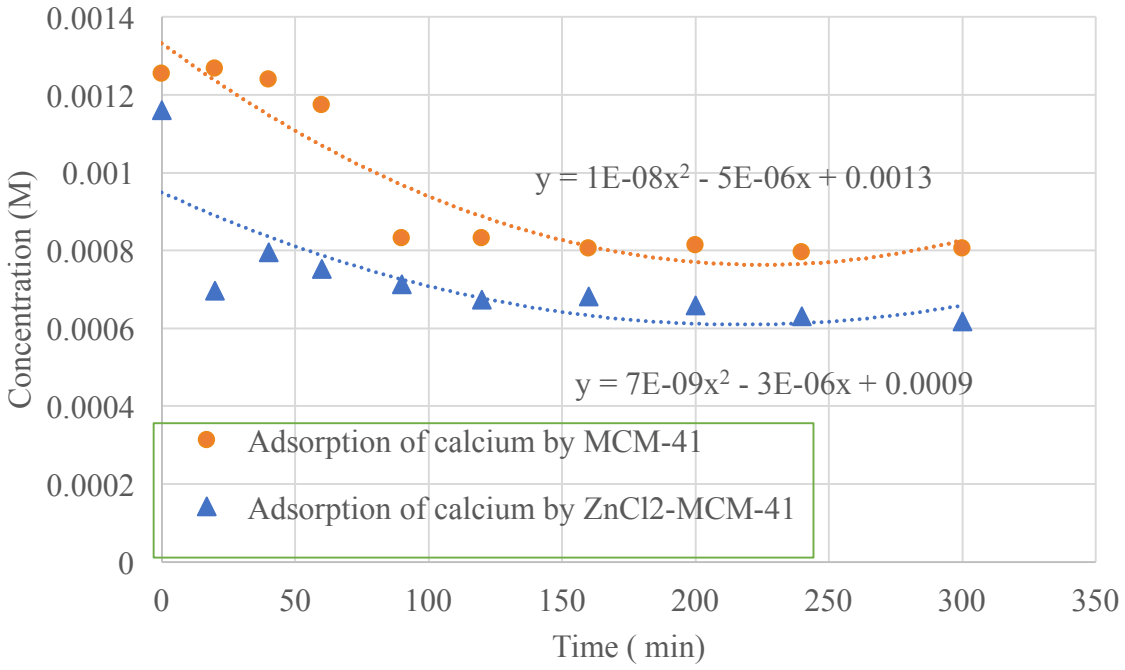

Figure 75 Experimental: Adsorption of 0.001M Ca^{2+} ions by MCM-41 and $ZnCl_2$-MCM-41

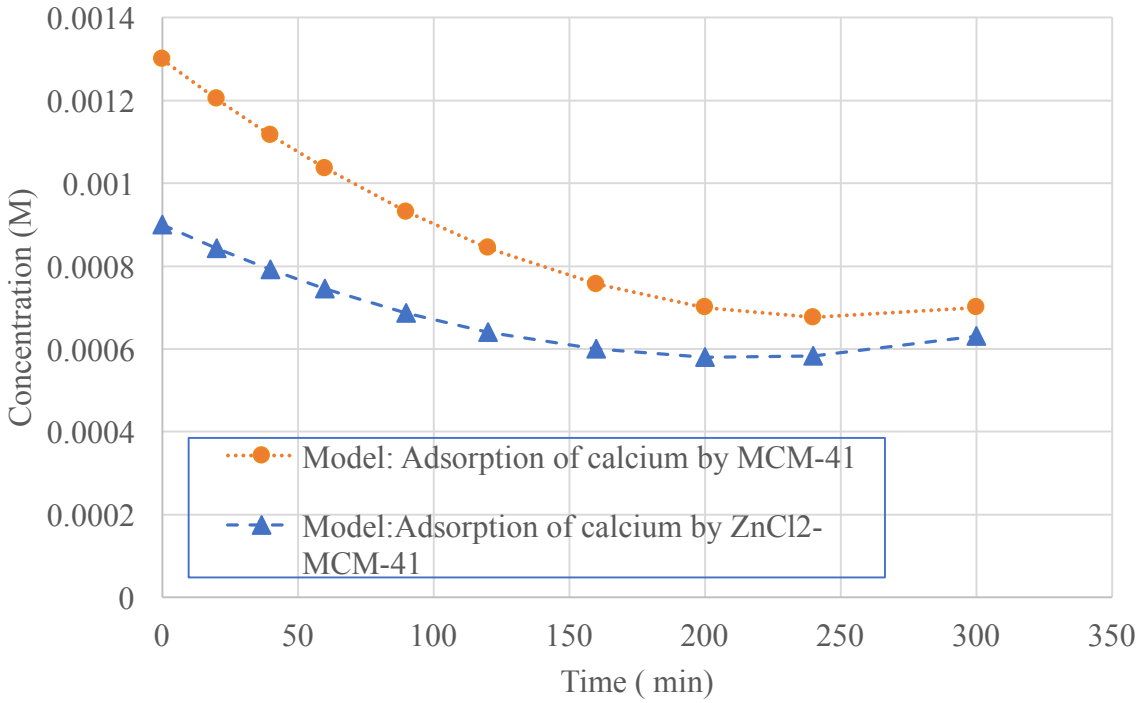

Figure 76 Model: Adsorption of 0.001M Ca^{2+} ions by MCM-41 and $ZnCl_2$-MCM-41

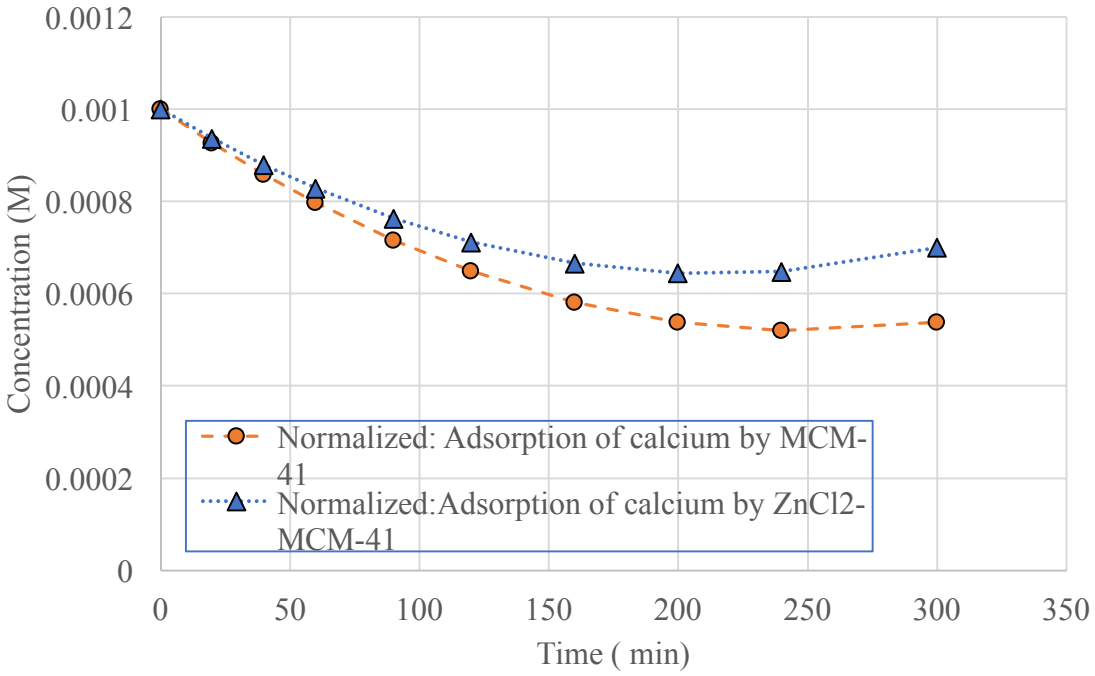

Figure 77 Normalized: Adsorption of 0.001M Ca^{2+} ions by MCM-41 and $ZnCl_2$-MCM-41

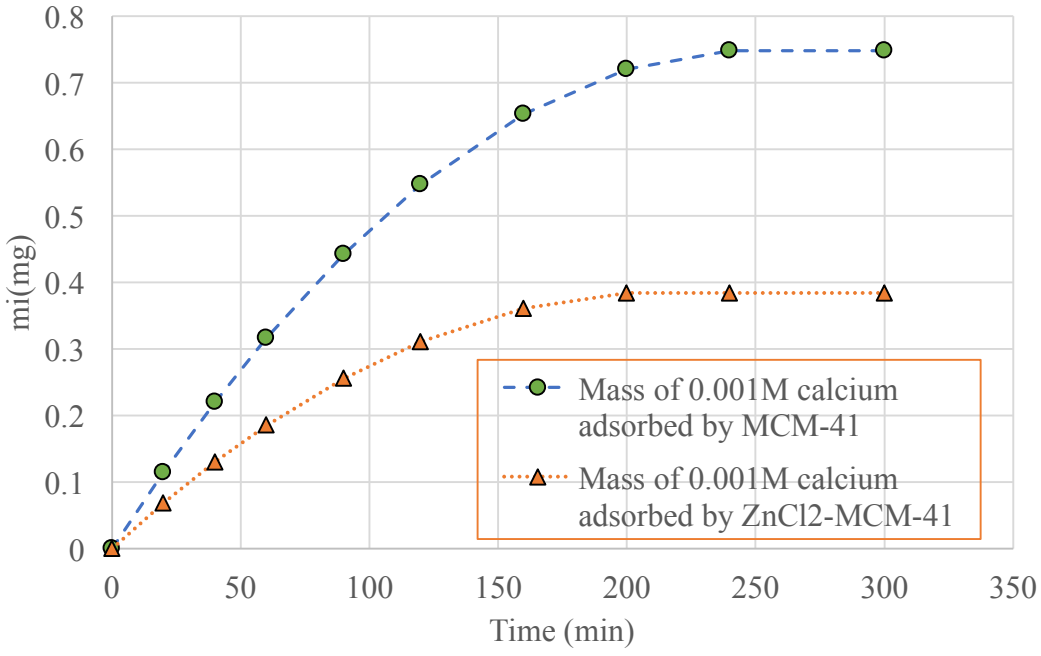

Figure 78 Mass of 0.001 Ca^{2+} ions adsorbed by MCM-41 and $ZnCl_2$-MCM-41

B. Adsorption of 0.01M Calcium ions (Ca^{2+}) by MCM-41 and $ZnCl_2$-MCM-41

Table 37 shows the experimental data calculated from the calibration data. Tables 38 and 39, and Figures 79 to 82 present the model and normalized concentration after adsorption, and the mass adsorbed by the adsorbents. The adsorption capacities for MCM-41 and $ZnCl_2$-MCM-41 are 4.080 mg/g, and 9.600 mg/g respectively.

Table 37 Adsorption of 0.01M Ca^{2+} ions

	MCM-41		$ZnCl_2$-MCM-41	
Time (min)	**0.01M MCM-41 (mV)**	**Conc. after adsorption by MCM-41 (M)**	**0.01M $ZnCl_2$-MCM-41 (mV)**	**Conc. after adsorption by $ZnCl_2$MCM-41 (M)**
0	51.60	0.0103	51.60	0.0103
20	51.60	0.0103	51.60	0.0103
40	51.50	0.0102	51.40	0.0100
60	51.40	0.0100	51.00	0.0096
90	51.50	0.0102	51.00	0.0096
120	51.00	0.0096	50.80	0.0094
160	51.40	0.0100	50.70	0.0093
200	51.60	0.0103	50.70	0.0093
240	51.30	0.0099	50.80	0.0094
300	51.10	0.0097	50.20	0.0088
24 hours	51.2	0.0097	50.10	0.0080

Table 38 Adsorption of 0.01 M Ca^{2+} by MCM-41					
Time (min)	**Conc (M)**	**Model conc (M)**	**Normalized Conc (M)**	**Mass of the adsorbate (m_i), g**	**($\sum m_i$), (mg)**
0	0.0103	0.01020	0.00100		
20	0.0103	0.01016	0.00100	0.04752	0.04752
40	0.0102	0.01012	0.00099	0.04656	0.09408
60	0.0100	0.01008	0.00099	0.04560	0.13968
90	0.0102	0.01003	0.00098	0.06660	0.20628
120	0.0096	0.00997	0.00098	0.06444	0.27072
160	0.0100	0.00991	0.00097	0.08256	0.35328
200	0.0103	0.00984	0.00096	0.07872	0.43200
240	0.0099	0.00978	0.00096	0.07488	0.50688
300	0.00969	0.00095	0.10512	0.61200	0.00969
24 hours	0.00968				**Σm_i = 0.6120**
Adsorption=Σm_i/0.15g adsorbent= 4.080 mg/g					

Table 39 Adsorption of 0.01 M Ca^{2+} by $ZnCl_2$-MCM-41					
Time (min)	**Conc (M)**	**Model conc (M)**	**Normalized Conc (M)**	**Mass of the adsorbate (m_i), g**	**($\sum m_i$), (mg)**
0	0.0103	0.01030	0.01000		
20	0.0103	0.01016	0.00987	0.16320	0.16320
40	0.0100	0.01004	0.00974	0.15360	0.31680
60	0.0096	0.00992	0.00963	0.14400	0.46080
90	0.0096	0.00975	0.00947	0.19800	0.65880
120	0.0094	0.00960	0.00932	0.17640	0.83520
160	0.0093	0.00944	0.00916	0.20160	1.03680
200	0.0093	0.00930	0.00903	0.16320	1.20000
240	0.0094	0.00920	0.00893	0.12480	1.32480
300	0.0088	0.00910	0.00883	0.11520	1.44000
24 hours	0.0087				**Σm_i = 1.440**
Adsorption=Σm_i/0.15g adsorbent= 9.600 mg/g					

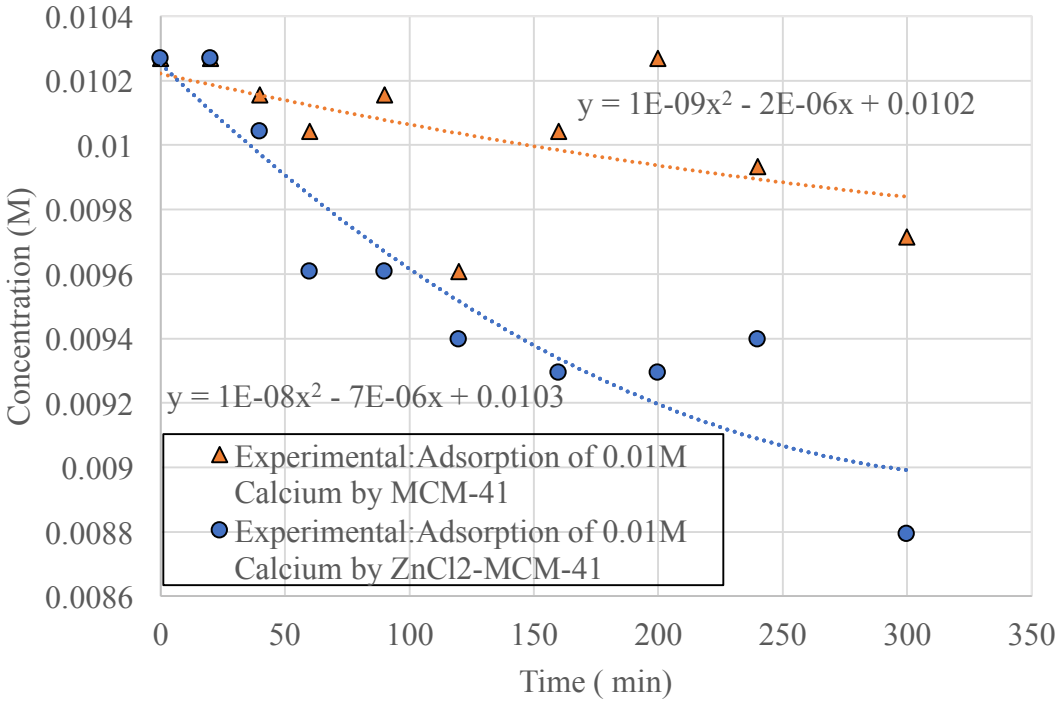

Figure 79 Experimental: Adsorption of 0.01M Ca^{2+} ions by MCM-41 and $ZnCl_2$-MCM-41

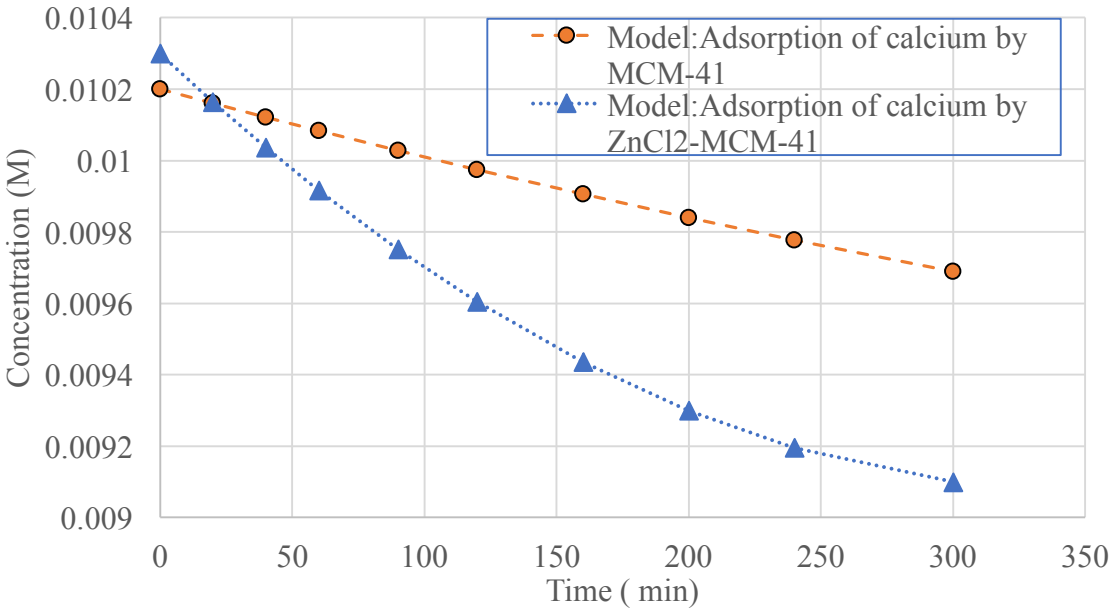

Figure 80 Model: Adsorption of 0.01M Ca^{2+} ions by MCM-41 and $ZnCl_2$-MCM-41

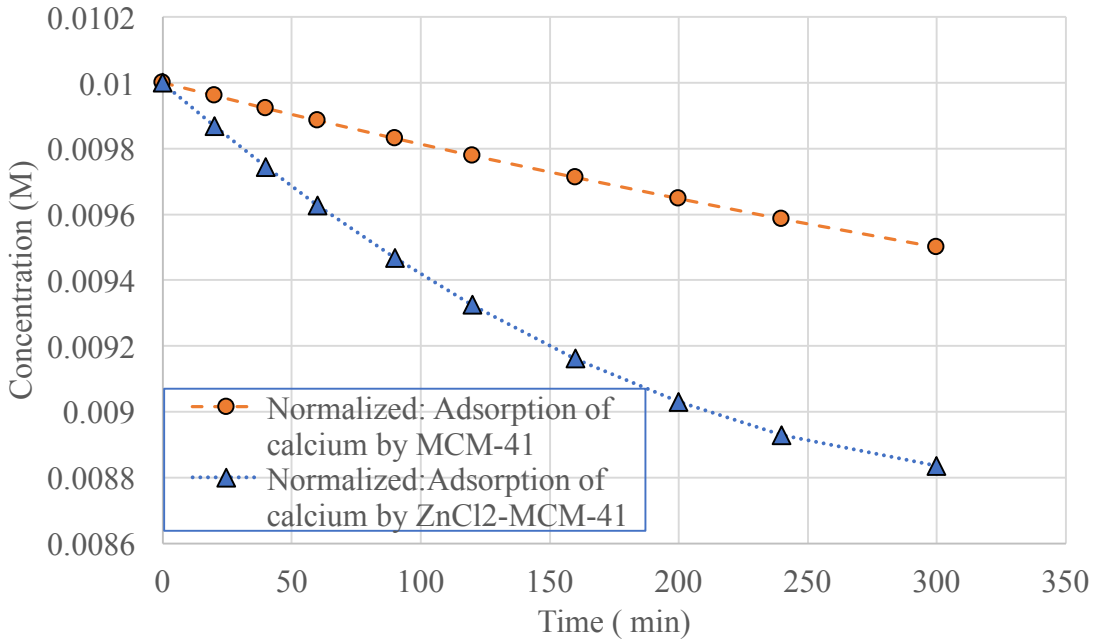

Figure 81 Normalized: Adsorption of 0.01M Ca^{2+} ions by MCM-41 and $ZnCl_2$-MCM-41

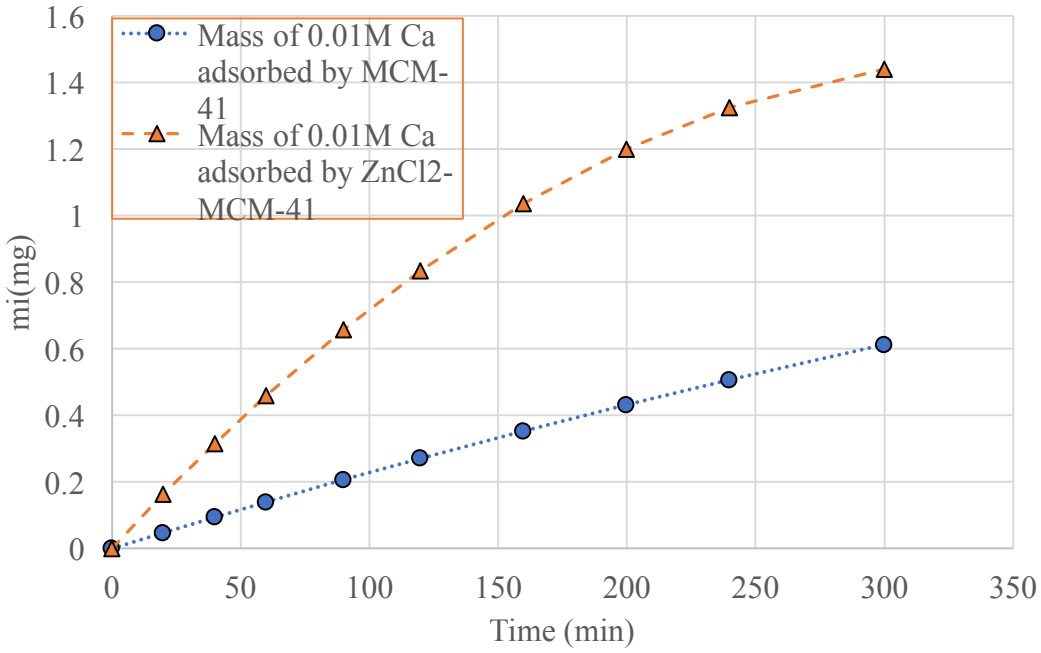

Figure 82 Mass of 0.01 Ca^{2+} ions adsorbed by MCM-41 and $ZnCl_2$-MCM-41

C. Adsorption of 0.1M Calcium ions (Ca^{2+}) by MCM-41 and $ZnCl_2$-MCM-41

Table 40 shows the experimental data calculated from the calibration data. Tables 41 and 42, and Figures 83 to 86 present the model and normalized concentration after adsorption, and the mass adsorbed by the adsorbents. The adsorption capacities for MCM-41 and $ZnCl_2$-MCM-41 are 31.20 mg/g, and 43.20 mg/g respectively. These values are nor significantly different from each other, so both adsorbents seem to be working in similar manner.

Table 40 Adsorption of 0.1M Ca^{2+} ions

	MCM-41		$ZnCl_2$-MCM-41	
Time (min)	**0.01M MCM-41 (mV)**	**Conc. after adsorption by MCM-41 (M)**	**0.01M $ZnCl_2$-MCM-41 (mV)**	**Conc. after adsorption by $ZnCl_2$MCM-41 (M)**
0	71.4	0.092	71.4	0.092
20	71.4	0.092	71.3	0.091
40	71.5	0.093	71.2	0.090
60	71.2	0.090	71.4	0.092
90	71.4	0.092	71.4	0.092
120	71.2	0.090	71.2	0.090
160	71	0.088	71.2	0.090
200	71	0.088	71.1	0.089
240	71.1	0.089	71.1	0.089
300	71	0.088	71	0.088
24 hours	67	0.056	66	0.051

Table 41 Adsorption of 0.1 M Ca^{2+} by MCM-41					
Time (min)	**Conc (M)**	**Model conc (M)**	**Normalized Conc (M)**	**Mass of the adsorbate (m_i), g**	**($\sum m_i$), (mg)**
0	0.092	0.09150	0.10000		
20	0.091	0.09135	0.09984	0.17760	0.17760
40	0.090	0.09119	0.09966	0.19680	0.37440
60	0.092	0.09101	0.09946	0.21600	0.59040
90	0.092	0.09071	0.09913	0.36000	0.95040
120	0.090	0.09037	0.09877	0.40320	1.35360
160	0.090	0.08987	0.09822	0.60480	1.95840
200	0.089	0.08930	0.09760	0.68160	2.64000
240	0.089	0.08867	0.09690	0.75840	3.39840
300	0.088	0.08760	0.09574	1.28160	4.68000
24 hours	0.0510				**Σm_i = 4.680**
Adsorption=Σm_i/0.15g adsorbent= 31.20 mg/g					

Table 42 Adsorption of 0.1 M Ca^{2+} by $ZnCl_2$-MCM-41					
Time (min)	**Conc (M)**	**Model conc (M)**	**Normalized Conc (M)**	**Mass of the adsorbate (m_i), g**	**($\sum m_i$), (mg)**
0	0.092	0.09260	0.10000		
20	0.092	0.09202	0.09937	0.70080	0.70080
40	0.093	0.09146	0.09877	0.66240	1.36320
60	0.090	0.09094	0.09821	0.62400	1.98720
90	0.092	0.09022	0.09743	0.86400	2.85120
120	0.090	0.08958	0.09673	0.77760	3.62880
160	0.088	0.08882	0.09592	0.90240	4.53120
200	0.088	0.08820	0.09525	0.74880	5.28000
240	0.089	0.08770	0.09471	0.59520	5.87520
300	0.088	0.08720	0.09417	0.60480	6.48000
24 hours	0.056				**Σm_i = 6.480**
Adsorption=Σm_i/0.15g adsorbent= 43.20 mg/g					

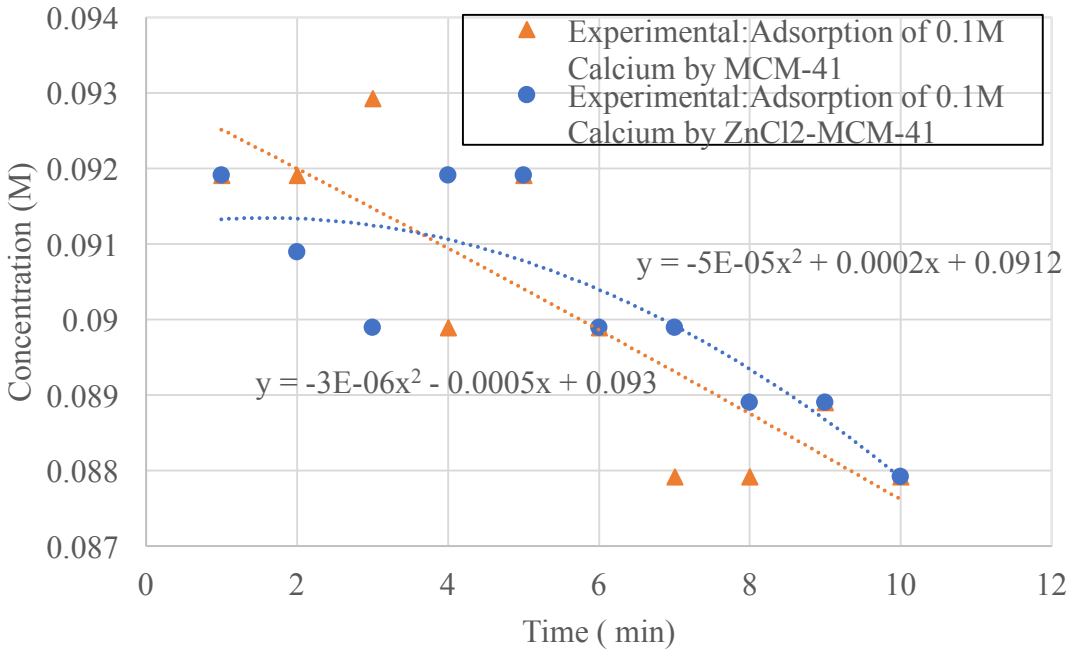

Figure 83 Experimental: Adsorption of 0.1M Ca^{2}+ ions by MCM-41 and $ZnCl_2$-MCM-41

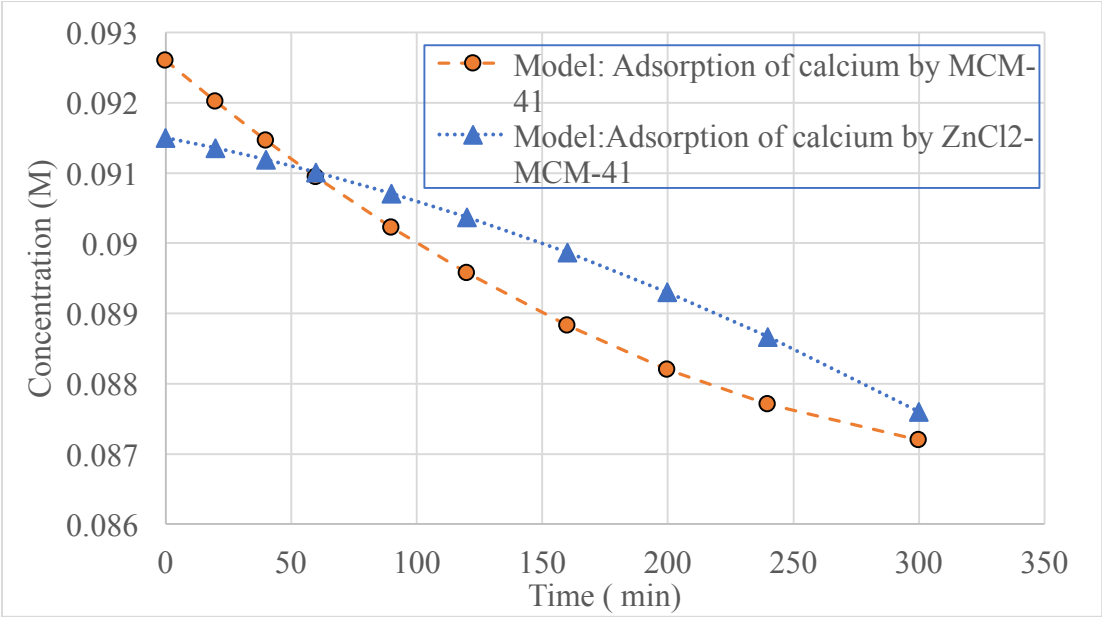

Figure 84 Model: Adsorption of 0.1M Ca^{2}+ ions by MCM-41 and $ZnCl_2$-MCM-41

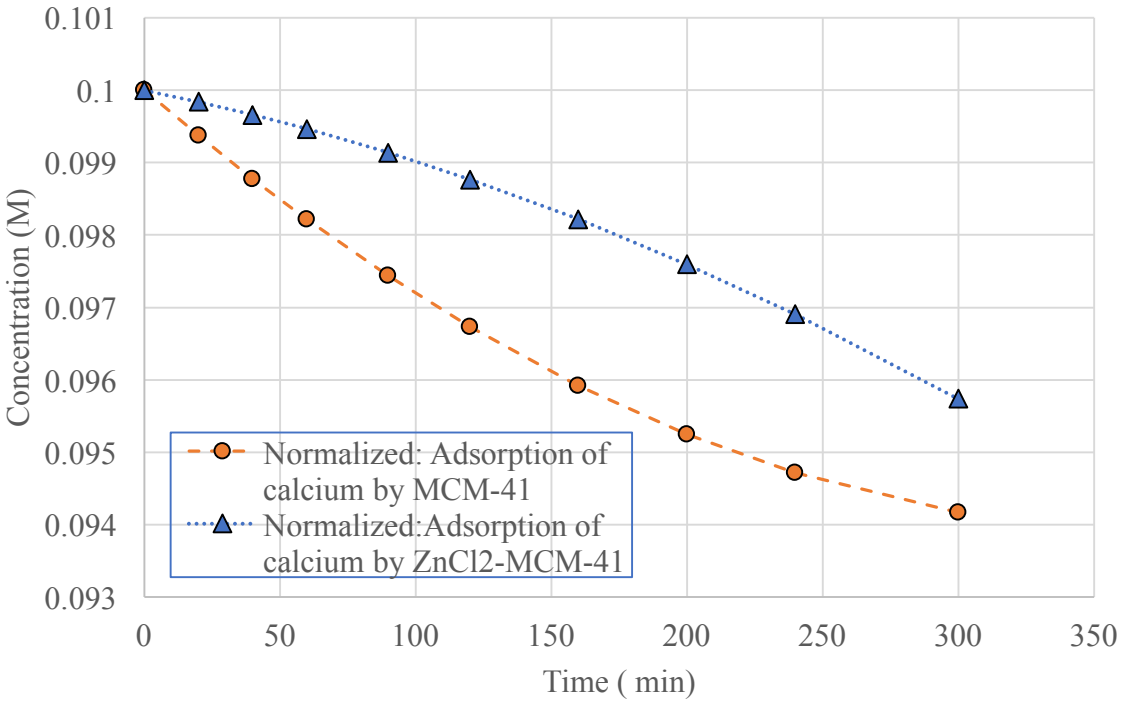

Figure 85 Normalized: Adsorption of 0.1M Ca^{2}+ ions by MCM-41 and $ZnCl_2$-MCM-41

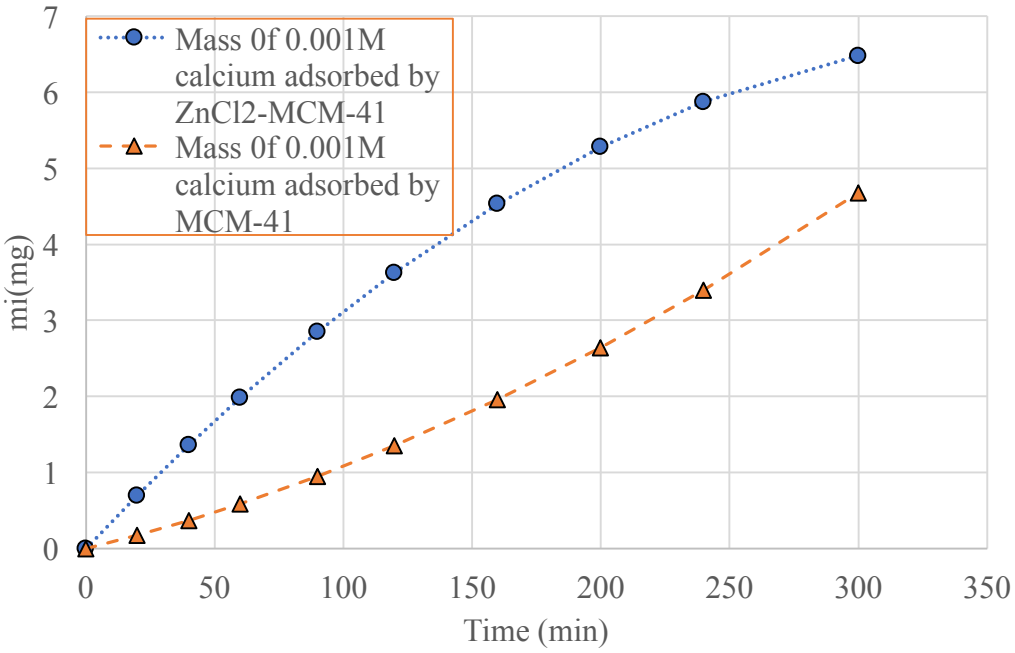

Figure 86 Mass of 0.1M Ca^{2}+ ions adsorbed by MCM-41 and $ZnCl_2$-MCM-41

4.4.2 Adsorption of K^+ ions by MCM-41 and $ZnCl_2$-MCM-41

Potassium ions were tested for adsorption with MCM-41 and $ZnCl_2$-MCM-41. Table 43 is the initial calibration data for the ISE potassium electrode calibration. Other data are presented in the Appendix.

A. Initial Calibration data for potassium electrode

Table 43 shows the initial calibration data, and Figure 87 shows the initial calibration curve. The rest of the data and the calculations are shown in the Appendix.

Table 43 Initial Calibration curve for K^+ ions

Original Conc. (M)	Log10 (Conc)	abs value of Conc	mV Reading
1.00E-01	-1.00	1.00	-38.8
5.00E-02	-1.30	1.30	-55.4
3.00E-02	-1.52	1.52	-69.4
1.00E-02	-2.00	2.00	-102
5.00E-03	-2.30	2.30	-122.7
3.00E-03	-2.52	2.52	-137.8
1.00E-03	-3.00	3.00	-166.1
5.00E-04	-3.30	3.30	-189.5
1.00E-04	-4.00	4.00	-213

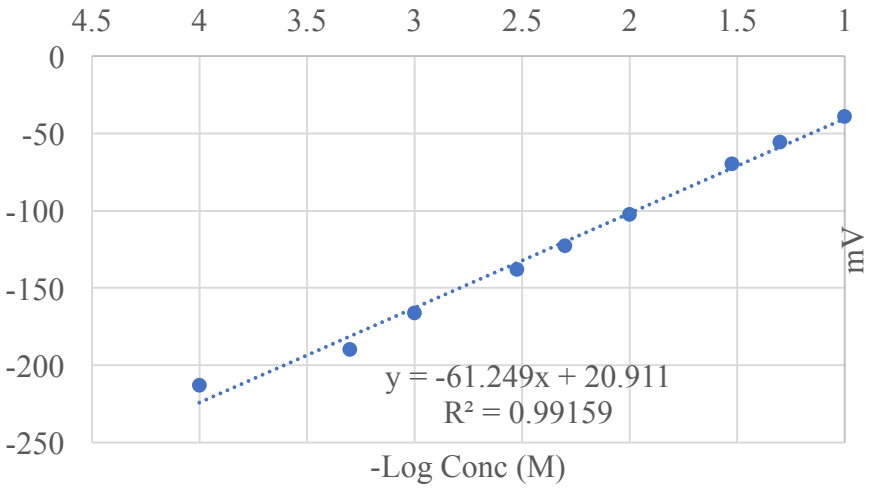

Figure 87 Initial Calibration Curve for K^+ electrode

B. Adsorption of 0.001M K^+ ions by MCM-41 and $ZnCl_2$-MCM-41

Table 44 shows the experimental data for adsorption of potassium ions by MCM-41 and $ZnCl_2$-MCM-41. Tables 45 and 46, ad Figures 88 to 91 show the data for model and normalized concentrations, with the total mass adsorbed by the adsorbents. Both adsorbents seemed to work similar, with not a significant amount of adsorption as compared to the heavy metals. The adsorption capacities for MCM-41 and $ZnCl_2$-MCM-41 are 0.1101 mg/g and 0.2377 mg/g respectively.

Table 44 Adsorption of 0.001M K^+ ions

	MCM-41		$ZnCl_2$-MCM-41	
Time (min)	**0.001M MCM-41 (mV)**	**Conc. after adsorption by MCM-41 (M)**	**0.001M $ZnCl_2$-MCM-41 (mV)**	**Conc. after adsorption by $ZnCl_2$MCM-41 (M)**
0	-168.4	0.00082	-168.3	0.00083
20	-166.3	0.00089	-166.1	0.00090
40	-164.7	0.00095	-165.1	0.00093
60	-165.6	0.00092	-165.4	0.00092
90	-165.2	0.00093	-165.9	0.00091
120	-166.4	0.00084	-166.5	0.00084
160	-166.8	0.00083	-166.5	0.00084
200	-166.6	0.00083	-166.8	0.00083
240	-164.2	0.00091	-167.1	0.00082
300	-164.7	0.00090	-167.5	0.00081
24 hours	-161.1	0.0008	-163.5	0.0007

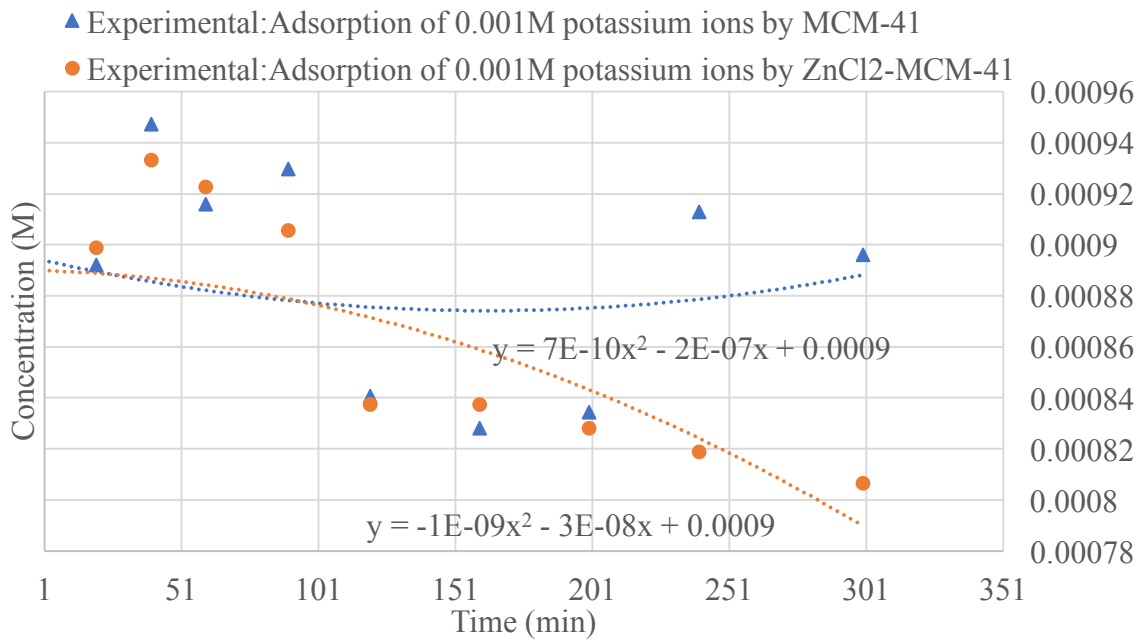

Figure 88 Experimental: Adsorption of 0.001M K^+ ions by MCM-41 and $ZnCl_2$-MCM-41

Table 45 Adsorption of 0.001 M K^+ by MCM-41					
Time (min)	**Conc (M)**	**Model conc (M)**	**Normalized Conc (M)**	**Mass of the adsorbate (m_i), g**	**($\sum m_i$), (mg)**
0	0.00082	0.00090	0.00100		
20	0.00089	0.00090	0.00100	0.004	0.00436
40	0.00095	0.00089	0.00099	0.004	0.00807
60	0.00092	0.00089	0.00099	0.003	0.01112
90	0.00093	0.00089	0.00099	0.003	0.01446
120	0.00084	0.00089	0.00098	0.002	0.01633
160	0.00083	0.00089	0.00098	0.000	0.01652
200	0.00083	0.00089	0.00099	-0.002	0.01652
240	0.00091	0.00089	0.00099	-0.005	0.01652
300	0.00090	0.00090	0.00100	-0.013	0.01652
24 hours	0.00080				**Σm_i = 0.01652**
Adsorption=Σm_i/0.15g adsorbent= 0.1101 mg/g					

Table 46 Adsorption of 0.001 M K^+ by $ZnCl_2$-MCM-41					
Time (min)	**Conc (M)**	**Model conc (M)**	**Normalized Conc (M)**	**Mass of the adsorbate (m_i), g**	**($\sum m_i$), (mg)**
0	0.00083	0.00090	0.00100		
20	0.00090	0.00090	0.00100	0.001	0.00117
40	0.00093	0.00090	0.00100	0.002	0.00328
60	0.00092	0.00089	0.00099	0.003	0.00633
90	0.00091	0.00089	0.00099	0.006	0.01267
120	0.00084	0.00088	0.00098	0.008	0.02111
160	0.00084	0.00087	0.00097	0.015	0.03566
200	0.00083	0.00085	0.00095	0.018	0.03566
240	0.00082	0.00084	0.00093	0.022	0.03566
300	0.00081	0.00080	0.00089	0.040	0.03566
24 hours	0.00070				**Σm_i = 0.03566**
Adsorption=Σm_i/0.15g adsorbent= 0.2377 mg/g					

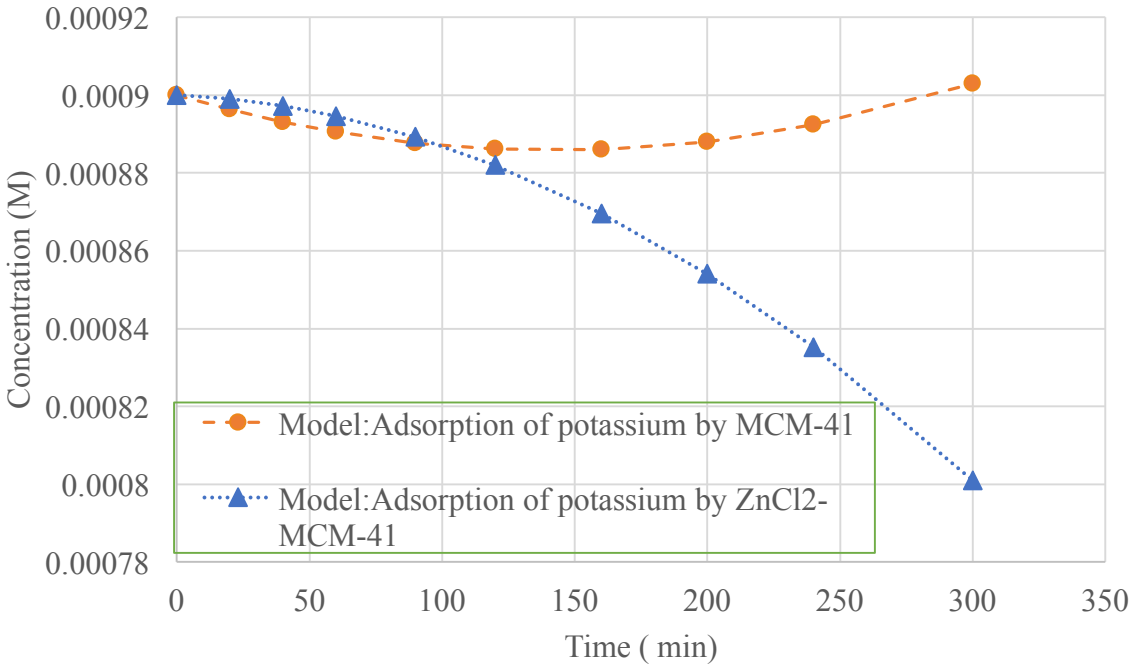

Figure 89 Model: Adsorption of 0.001M K^+ ions by MCM-41 and $ZnCl_2$-MCM-41

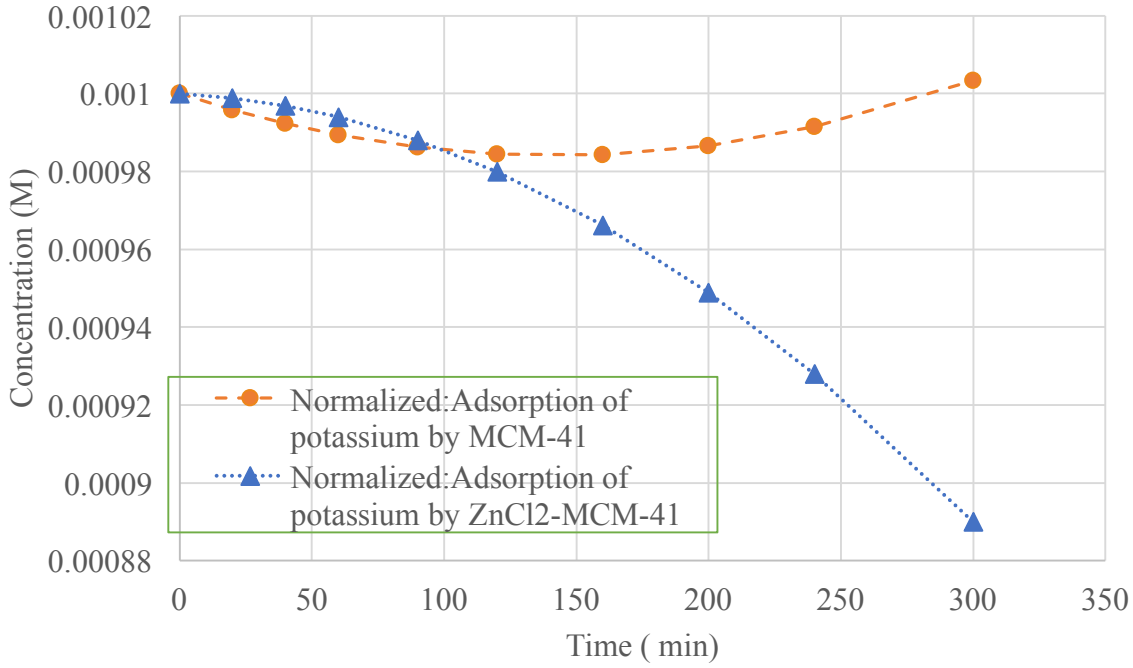

Figure 90 Normalized: Adsorption of 0.001M K^+ ions by MCM-41 and $ZnCl_2$-MCM-41

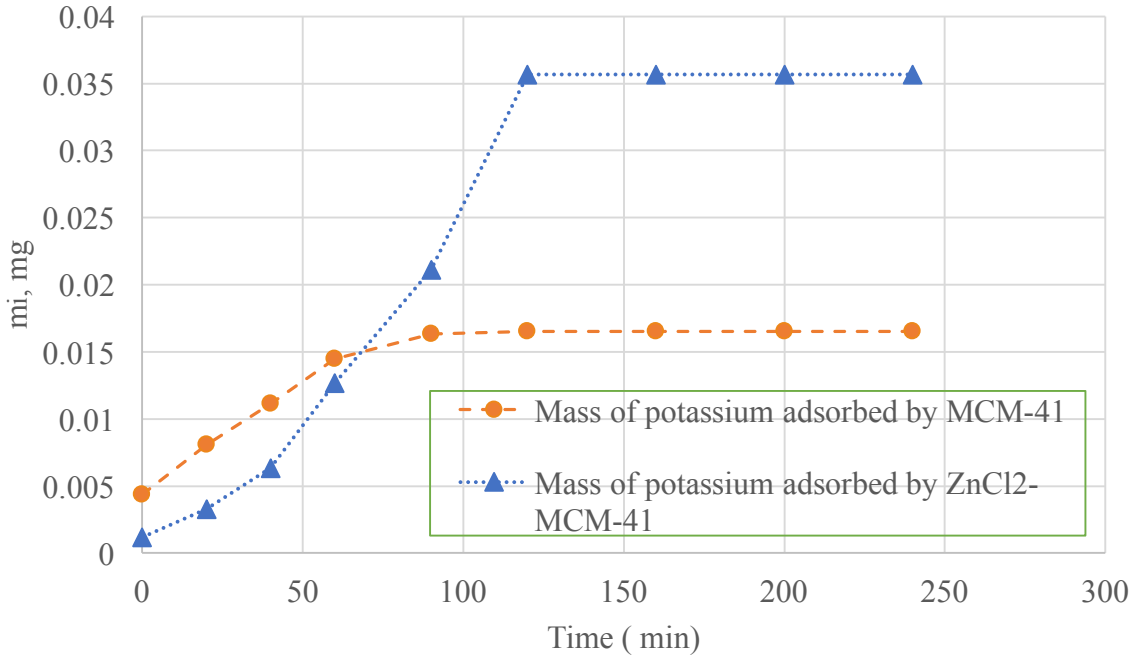

Figure 91 Mass of 0.001 K^+ ions adsorbed by MCM-41 and $ZnCl_2$-MCM-41

C. Adsorption of 0.01M K^+ ions by MCM-41 and $ZnCl_2$-MCM-41

Table 47 shows the experimental data for adsorption of potassium ions by MCM-41 and $ZnCl_2$-MCM-41. Tables 48 and 49, and Figures 92 to 95 show the data for experimental, model and normalized concentrations, with the total mass adsorbed by the adsorbents. Both adsorbents seemed to work similar, with not a significant amount of adsorption as compared to the heavy metals. The adsorption capacities for MCM-41 and $ZnCl_2$-MCM-41 are 0.0375 mg/g and 0.782 mg/g respectively. These values show that there was very low amount of adsorption by both adsorbents. Figures 92 to 95 show there was no reduction in concentration even after 5 hours of time interval.

Table 47 Adsorption of 0.01M K^+ ions

	MCM-41		$ZnCl_2$-MCM-41	
Time (min)	**0.01M MCM-41 (mV)**	**Conc. after adsorption by MCM-41 (M)**	**0.01M $ZnCl_2$-MCM-41 (mV)**	**Conc. after adsorption by $ZnCl_2$MCM-41 (M)**
0	-103.1	0.0095	-103	0.00955
20	-98.3	0.0114	-99.1	0.01106
40	-98.3	0.0114	-98.9	0.01114
60	-98.1	0.0115	-98.6	0.01127
90	-98	0.0115	-98.1	0.01148
120	-99.8	0.0103	-99.7	0.01030
160	-99.2	0.0105	-99.2	0.01049
200	-99.1	0.0105	-98.8	0.01065
240	-98.3	0.0109	-98.1	0.01094
300	-97.5	0.0112	-98	0.01098
24 hours	-95	0.0110	-96.4	0.0104

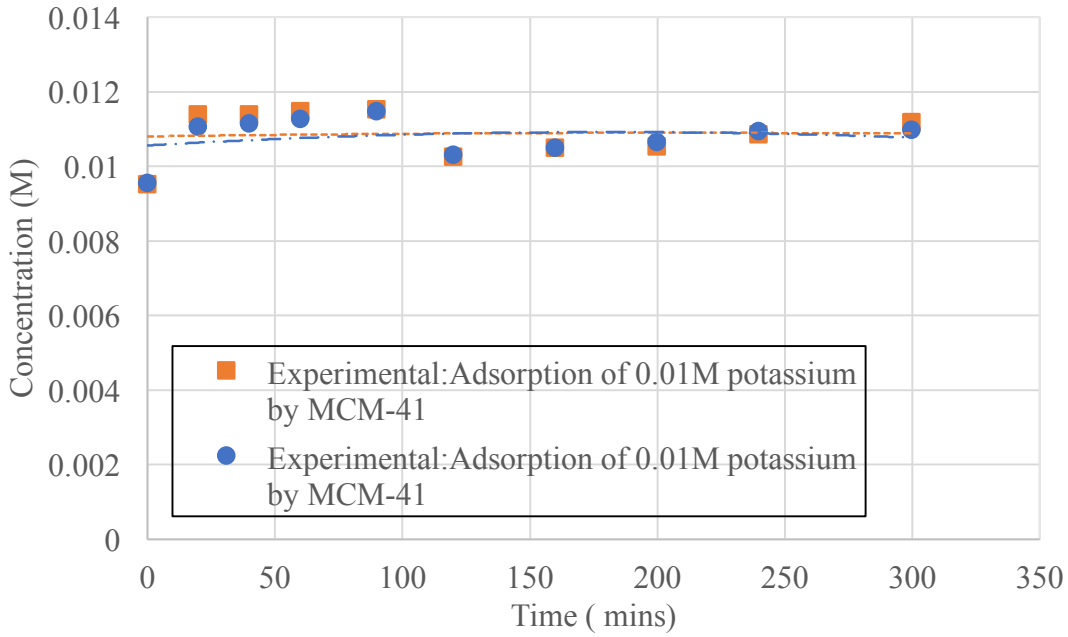

Figure 92 Experimental: Adsorption of 0.01M K^+ ions by MCM-41 and $ZnCl_2$-MCM-41

Table 48 Adsorption of 0.01 M K^+ by MCM-41					
Time (min)	**Conc (M)**	**Model conc (M)**	**Normalized Conc (M)**	**Mass of the adsorbate (m_i), g**	**($\sum m_i$), (mg)**
0	0.0095	0.01080	0.01000		
20	0.0114	0.01082	0.01002	-0.023	0.00000
40	0.0114	0.01084	0.01003	-0.021	0.00000
60	0.0115	0.01085	0.01005	-0.019	0.00000
90	0.0115	0.01087	0.01007	-0.025	0.00000
120	0.0103	0.01089	0.01008	-0.020	0.00000
160	0.0105	0.01091	0.01010	-0.021	0.00000
200	0.0105	0.01092	0.01011	-0.013	0.00000
240	0.0109	0.01092	0.01012	-0.006	0.00000
300	0.0112	0.01092	0.01011	0.006	0.00563
24 hours	0.0110				**Σm_i = 0.00563**
Adsorption=Σm_i/0.15g adsorbent= 0.03753 mg/g					

Table 49 Adsorption of 0.01 M K^+ by $ZnCl_2$-MCM-41					
Time (min)	**Conc (M)**	**Model conc (M)**	**Normalized Conc (M)**	**Mass of the adsorbate (m_i), g**	**($\sum m_i$), (mg)**
0	0.00955	0.01060	0.01000		
20	0.01106	0.01068	0.01007	-0.089	0.00000
40	0.01114	0.01074	0.01014	-0.080	0.00000
60	0.01127	0.01080	0.01019	-0.070	0.00000
90	0.01148	0.01088	0.01026	-0.088	0.00000
120	0.01030	0.01094	0.01032	-0.067	0.00000
160	0.01049	0.01098	0.01036	-0.056	0.00000
200	0.01065	0.01100	0.01038	-0.019	0.00000
240	0.01094	0.01098	0.01036	0.019	0.01877
300	0.01098	0.01090	0.01028	0.099	0.11729
24 hours	0.0104				**Σm_i = 0.1173**
Adsorption=Σm_i/0.15g adsorbent= 0.782 mg/g					

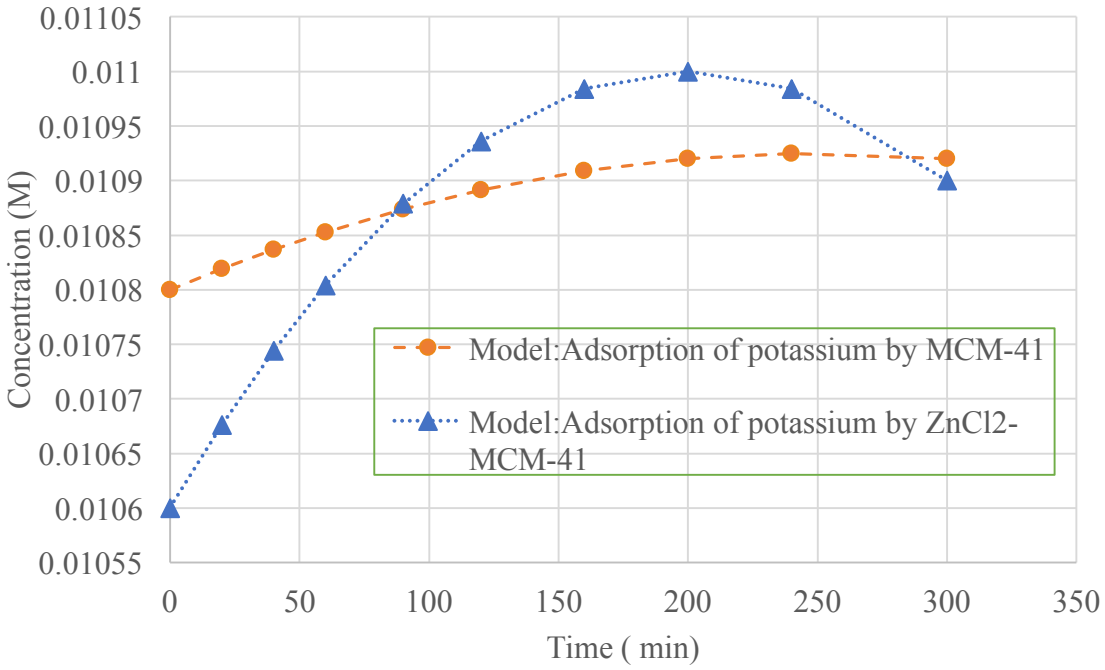

Figure 93 Model: Adsorption of 0.01M K^+ ions by MCM-41 and $ZnCl_2$-MCM-41

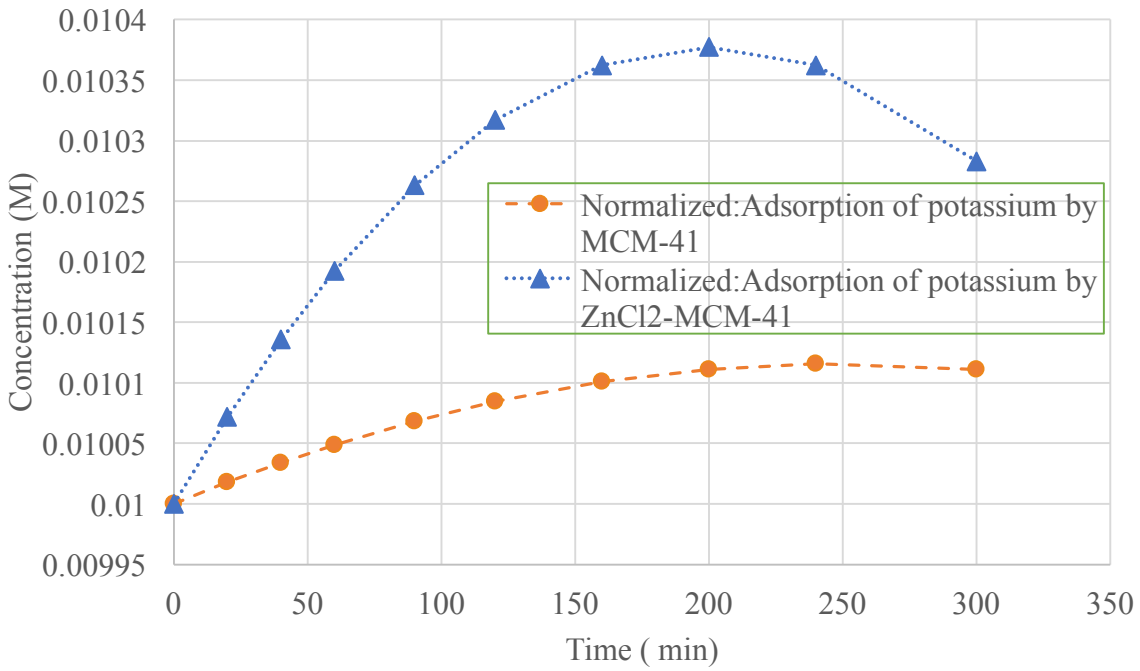

Figure 94 Normalized: Adsorption of 0.01M K^+ ions by MCM-41 and $ZnCl_2$-MCM-41

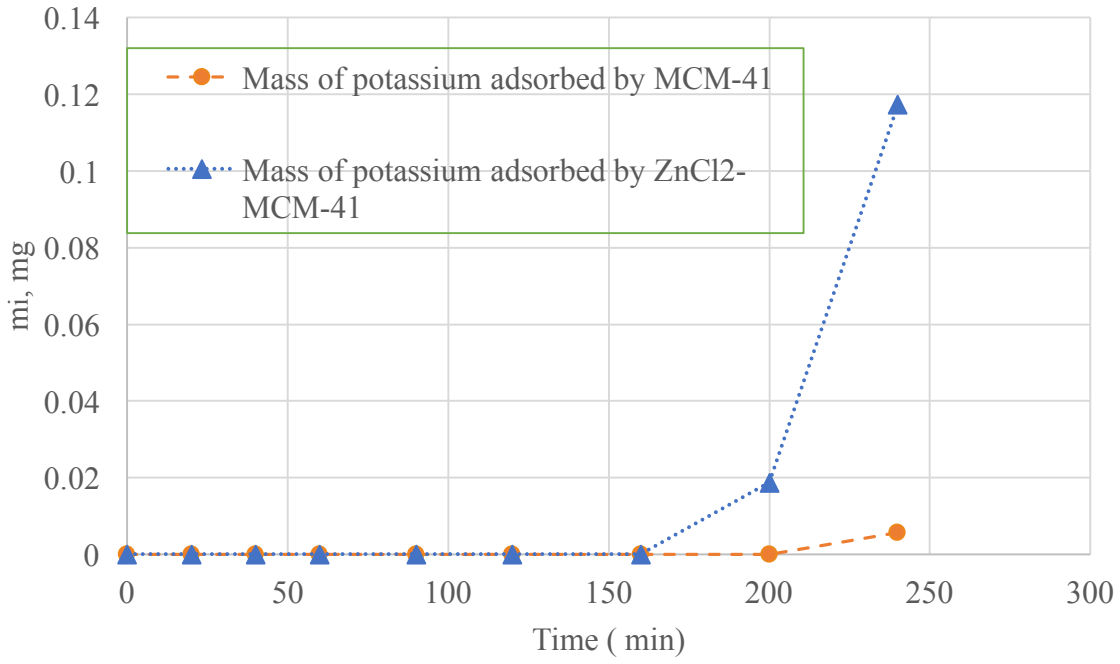

Figure 95 Mass of 0.01 K^+ ions adsorbed by MCM-41 and $ZnCl_2$-MCM-41

D. Adsorption of 0.1M K^+ ions by MCM-41 and $ZnCl_2$-MCM-41

Table 50 shows the experimental data for adsorption of potassium ions by MCM-41 and $ZnCl_2$-MCM-41. Tables 51 and 53, and Figures 96 to 99 show the data for model and normalized concentrations, with the total mass adsorbed by the adsorbents. Both adsorbents seemed to work similar, with not a significant amount of adsorption as compared to the heavy metals. The adsorption capacities for MCM-41 and $ZnCl_2$-MCM-41 are 65.060 mg/g and 62.557 mg/g respectively. These values show that there was very low amount of adsorption by both adsorbents. The adsorption was similar for both adsorbents.

Table 50 Adsorption of 0.1M K^+ ions

	MCM-41		$ZnCl_2$-MCM-41	
Time (min)	**0.1M MCM-41(mV)**	**Conc. after adsorption by MCM-41 (M)**	**0.1M $ZnCl_2$-MCM-41 (mV)**	**Conc. after adsorption by $ZnCl_2$MCM-41 (M)**
0	-38.4	0.107	-38.4	0.107
20	-38.2	0.108	-38.3	0.108
40	-38.3	0.108	-38.2	0.108
60	-38.8	0.106	-38.8	0.106
90	-38.4	0.107	-38.2	0.108
120	-39.8	0.098	-39.5	0.099
160	-39.6	0.098	-39.1	0.100
200	-38.8	0.101	-38.4	0.103
240	-37.5	0.107	-38	0.105
300	-37.3	0.107	-38	0.105
24hours	-36.9	0.1098	-37.4	0.1076

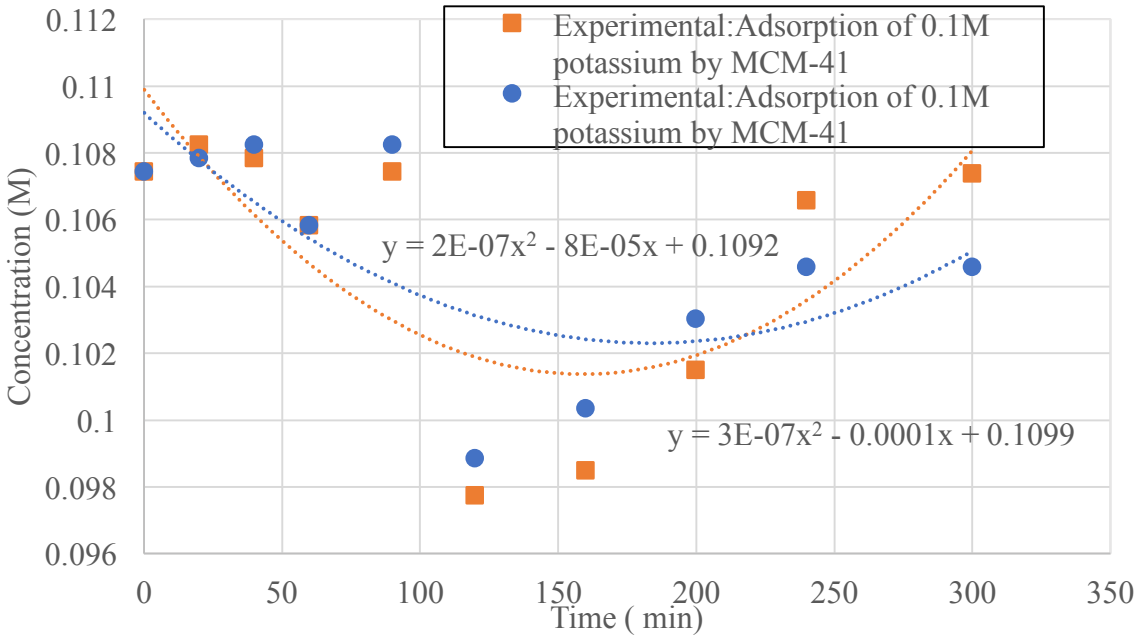

Figure 96 Experimental: Adsorption of 0.1M K^+ ions by MCM-41 and $ZnCl_2$-MCM-41

Table 51 Adsorption of 0.1 M K^+ by MCM-41					
Time (min)	**Conc (M)**	**Model conc (M)**	**Normalized Conc (M)**	**Mass of the adsorbate (m_i), g**	**($\sum m_i$), (mg)**
0	0.107	0.10990	0.10000		
20	0.108	0.10802	0.09829	2.205	2.205
40	0.108	0.10638	0.09680	1.924	4.129
60	0.106	0.10498	0.09552	1.642	5.771
90	0.107	0.10333	0.09402	1.935	7.706
120	0.098	0.10222	0.09301	1.302	9.008
160	0.098	0.10158	0.09243	0.751	9.759
200	0.101	0.10190	0.09272	-0.375	9.759
240	0.107	0.10318	0.09389	-1.501	9.759
300	0.107	0.10690	0.09727	-4.363	9.759
24 hours	0.101				**Σm_i = 9.759**
					Adsorption=Σm_i/0.15g adsorbent= 65.060 mg/g

Table 52 Adsorption of 0.1 M K^+ by $ZnCl_2$-MCM-41					
Time (min)	**Conc (M)**	**Model conc (M)**	**Normalized Conc (M)**	**Mass of the adsorbate (m_i), g**	**($\sum m_i$), (mg)**
0	0.107	0.10920	0.10000		
20	0.108	0.10768	0.09861	1.783	1.783
40	0.108	0.10632	0.09736	1.595	3.378
60	0.106	0.10512	0.09626	1.408	4.786
90	0.108	0.10362	0.09489	1.759	6.545
120	0.099	0.10248	0.09385	1.337	7.882
160	0.100	0.10152	0.09297	1.126	9.008
200	0.103	0.10120	0.09267	0.375	9.384
240	0.105	0.10152	0.09297	-0.375	9.384
300	0.105	0.10320	0.09451	-1.971	9.384
24 hours	0.101				**Σm_i = 9.384**
					Adsorption=Σm_i/0.15g adsorbent= 62.557 mg/g

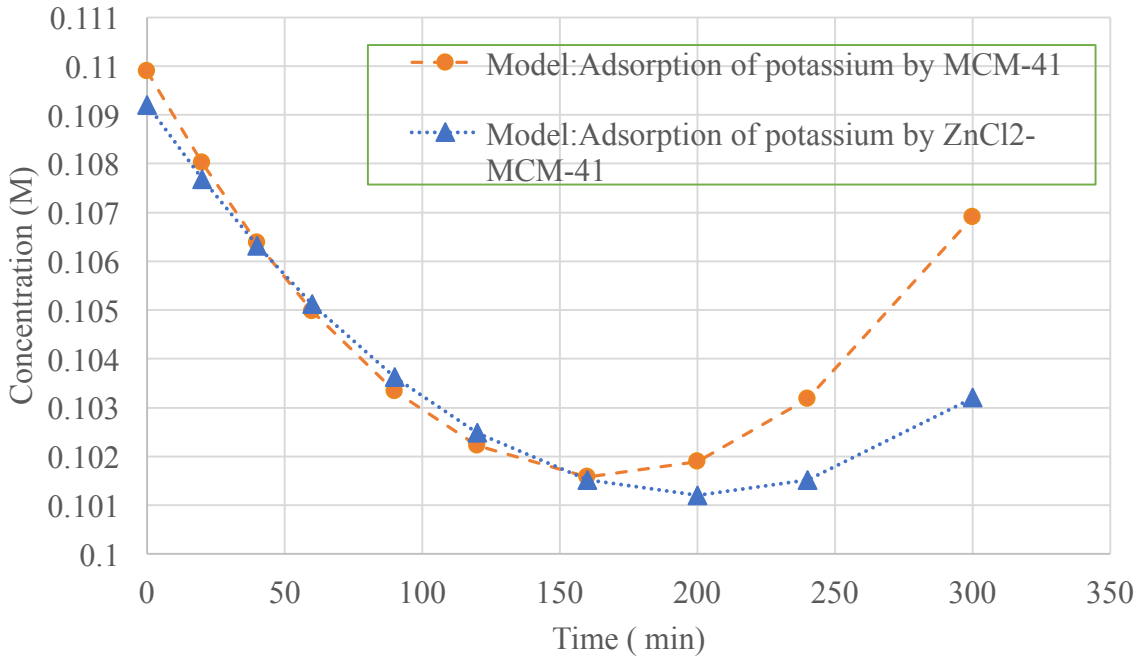

Figure 97 Model: Adsorption of 0.1M K^+ ions by MCM-41 and $ZnCl_2$-MCM-41

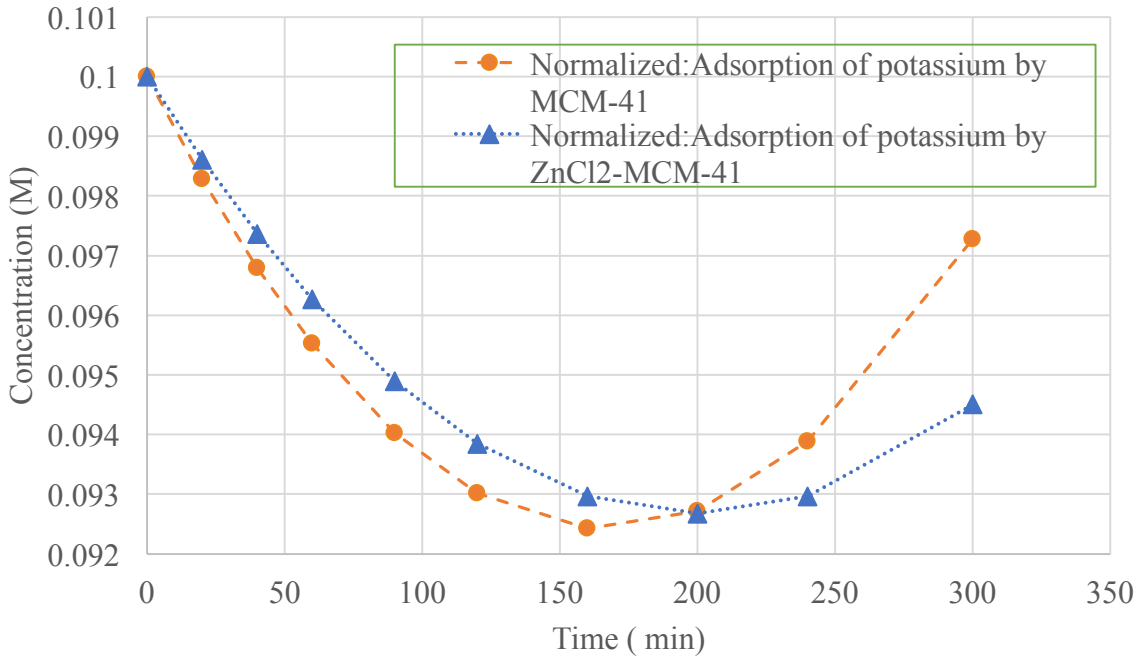

Figure 98 Normalized: Adsorption of 0.1M K^+ ions by MCM-41 and $ZnCl_2$-MCM-41

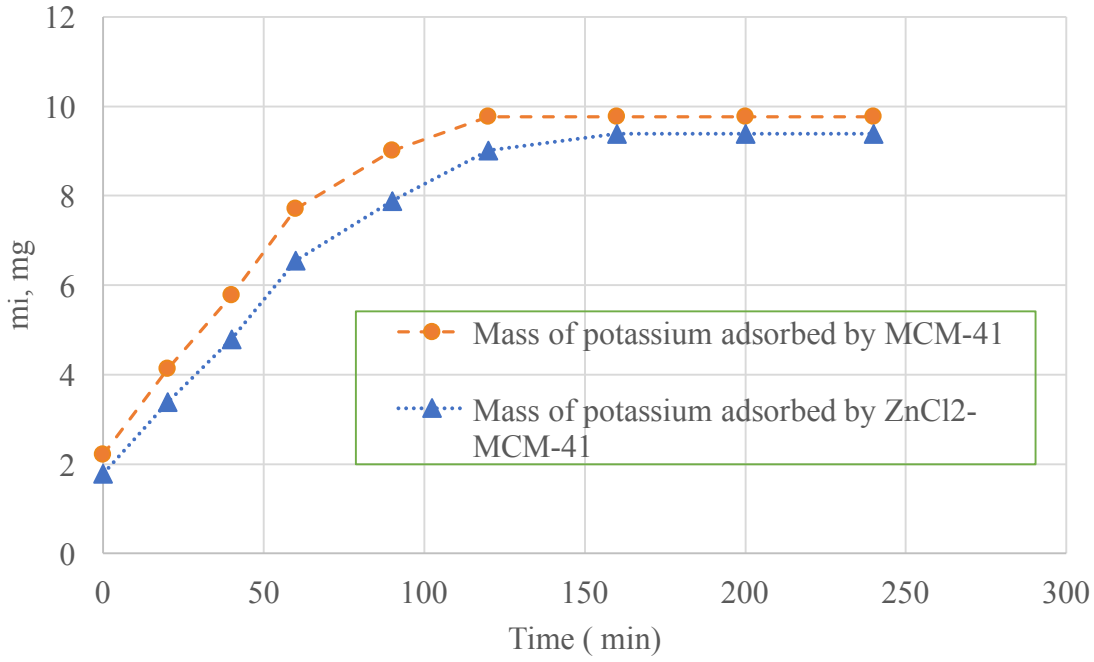

Figure 99 Mass of 0.1 K^+ ions adsorbed by MCM-41 and $ZnCl_2$-MCM-41

4.4.3 Adsorption of Nitrate (NO_3^-) ions by MCM-41 and $ZnCl_2$-MCM-41

Nitrate ions were placed in a 30-mL solution with 0.15g of the adsorbents for each concentration 0.001M, 0.01M, and 0.1M.

A. Calibration of potassium electrode

Table 53 is the calibration data for initial calibration of nitrate electrode. Figure 100 shows the calibration curve data.

Table 53 Initial Calibration curve for NO_3^- ions

Original Conc. (M)	Log10 (Conc)	abs value of Conc	mV Reading
1.00E-01	-1.00	1.00	-104
5.00E-02	-1.30	1.30	-86.4
3.00E-02	-1.52	1.52	-72.9
1.00E-02	-2.00	2.00	-43.0
5.00E-03	-2.30	2.30	-26.2
3.00E-03	-2.52	2.52	-11.6
1.00E-03	-3.00	3.00	11.8
5.00E-04	-3.30	3.30	22.6
1.00E-04	-4.00	4.00	40.7

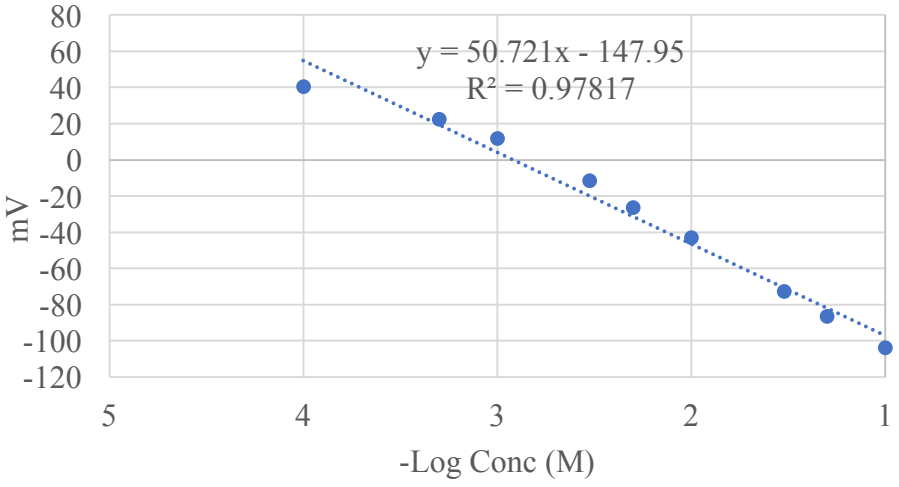

Figure 100 Initial Calibration Curve for NO_3^- electrode

B. Adsorption of 0.001M NO_3^- ions by MCM-41 and $ZnCl_2$-MCM-41

Table 54 shows the experimental data for adsorption of potassium by MCM-41 and $ZnCl_2$-MCM-41. Figure 101 shows the plot for concentration versus time after adsorption by MCM-41 and $ZnCl_2$-MCM-41. Tables 55 and 56, and Figure 102 show the mass adsorbed by these adsorbents. The adsorption capacities for MCM-41 and $ZnCl_2$-MCM-41 was calculated as 5.283 and 5.093 mg/g respectively. Both of these values are very low, and so the adsorbents don't see to be effective in case of 0.001M nitrate ions adsorption.

Table 54 Adsorption of 0.001M NO_3^- ions

	MCM-41		$ZnCl_2$-MCM-41	
Time (min)	**0.001M MCM-41 (mV)**	**Conc. after adsorption by MCM-41 (M)**	**0.001M $ZnCl_2$-MCM-41 (mV)**	**Conc. after adsorption by $ZnCl_2$MCM-41 (M)**
0	11.9	0.00073	11.8	0.00074
20	13.1	0.00069	12.9	0.00070
40	15.8	0.00061	15.9	0.00061
60	18.6	0.00053	17.3	0.00057
90	21.2	0.00047	21.3	0.00047
120	24.6	0.00040	24.8	0.00040
160	27.7	0.00035	27.3	0.00035
200	29.3	0.00032	29.6	0.00032
240	29.1	0.00032	29.9	0.00031
300	28.8	0.00033	30.1	0.00031
24 hours	24.8	0.0040	31.0	0.0040

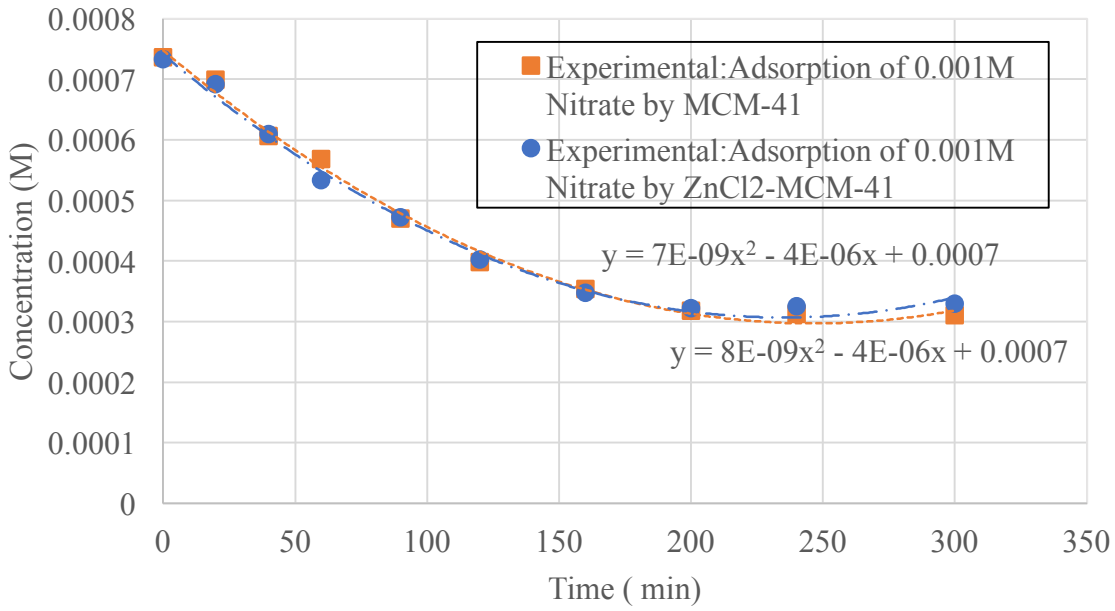

Figure 101 Experimental: Adsorption of 0.001M NO_3^- ions by MCM-41 and $ZnCl_2$-MCM-41

Table 55 Adsorption of 0.001M NO_3^- ions by MCM-41			
Time (min)	**Conc. after adsorption (M)**	**Mass adsorbed (m_i), mg**	**($\sum m_i$), (mg) in 0.15 g adsorbent**
0	0.00074		
20	0.00070	0.069	0.069
40	0.00061	0.172	0.241
60	0.00057	0.072	0.313
90	0.00047	0.182	0.495
120	0.00040	0.133	0.628
160	0.00035	0.083	0.711
200	0.00032	0.068	0.779
240	0.00031	0.008	0.787
300	0.00031	0.005	0.792
24 hours	0.00040		**$\sum m_i$=0.792**
Adsorption = $\sum m_i$=0.792 mg /0.15g =5.283 mg/g			

Table 56 Adsorption of 0.001M NO_3^- ions by $ZnCl_2$-MCM-41			
Time (min)	**Conc. after adsorption (M)**	**Mass adsorbed (m_i), mg**	**($\sum m_i$), (mg) in 0.15 g adsorbent**
0	0.00073		
20	0.00069	0.075	0.075
40	0.00061	0.154	0.229
60	0.00053	0.140	0.370
90	0.00047	0.115	0.485
120	0.00040	0.130	0.615
160	0.00035	0.102	0.717
200	0.00032	0.047	0.764
240	0.00032	-0.006	0.764
300	0.00033	-0.009	0.764
24 hours	0.00040		**$\sum m_i$=0.764**
Adsorption = $\sum m_i$=0.764 mg /0.15g =5.092 mg/g			

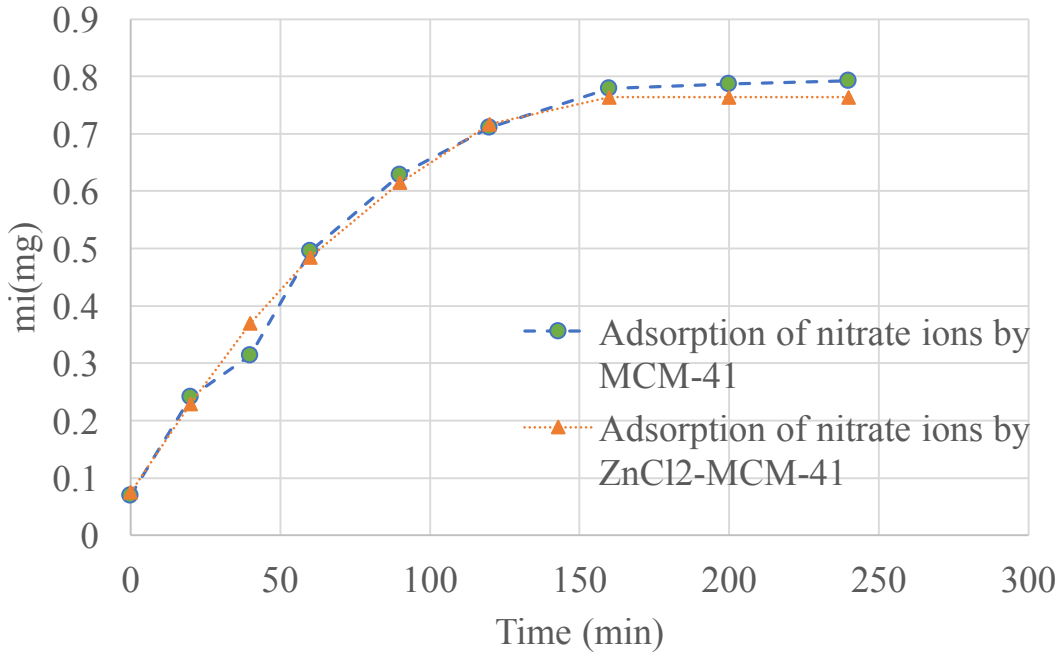

Figure 102 Mass of 0.001 NO_3^- ions adsorbed by MCM-41 and $ZnCl_2$-MCM-41

C. Adsorption of 0.01M NO_3^- ions by MCM-41 and $ZnCl_2$-MCM-41

Table 57 shows the experimental data for adsorption of potassium by MCM-41 and $ZnCl_2$-MCM-41. Figure 103 shows the plot for concentration versus time after adsorption by MCM-41 and $ZnCl_2$-MCM-41. Tables 58 and 59 show the mass adsorbed by these adsorbents. The adsorption capacities for MCM-41 and $ZnCl_2$-MCM-41 was calculated as 50.07 and 47.10 mg/g respectively. Both values are similar to each other.

Table 57 Adsorption of 0.01M NO_3^- ions

	MCM-41		$ZnCl_2$-MCM-41	
Time (min)	**0.01M MCM-41 (mV)**	**Conc. after adsorption by MCM-41 (M)**	**0.01M $ZnCl_2$-MCM-41 (mV)**	**Conc. after adsorption by $ZnCl_2$MCM-41 (M)**
0	-43	0.00982	-42	0.00937
20	-38	0.0078	-37.9	0.0077
40	-35.2	0.0068	-35.2	0.0068
60	-34.1	0.0064	-35	0.0067
90	-33.9	0.0064	-34.9	0.0067
120	-32.8	0.0061	-34.8	0.0067
160	-32.5	0.0060	-34	0.0064
200	-32.1	0.0059	-33.9	0.0064
240	-32.1	0.0059	-32.7	0.0060
300	-31.8	0.0058	-31	0.0056
24 hours	-28.6	0.0056	-30.9	0.0055

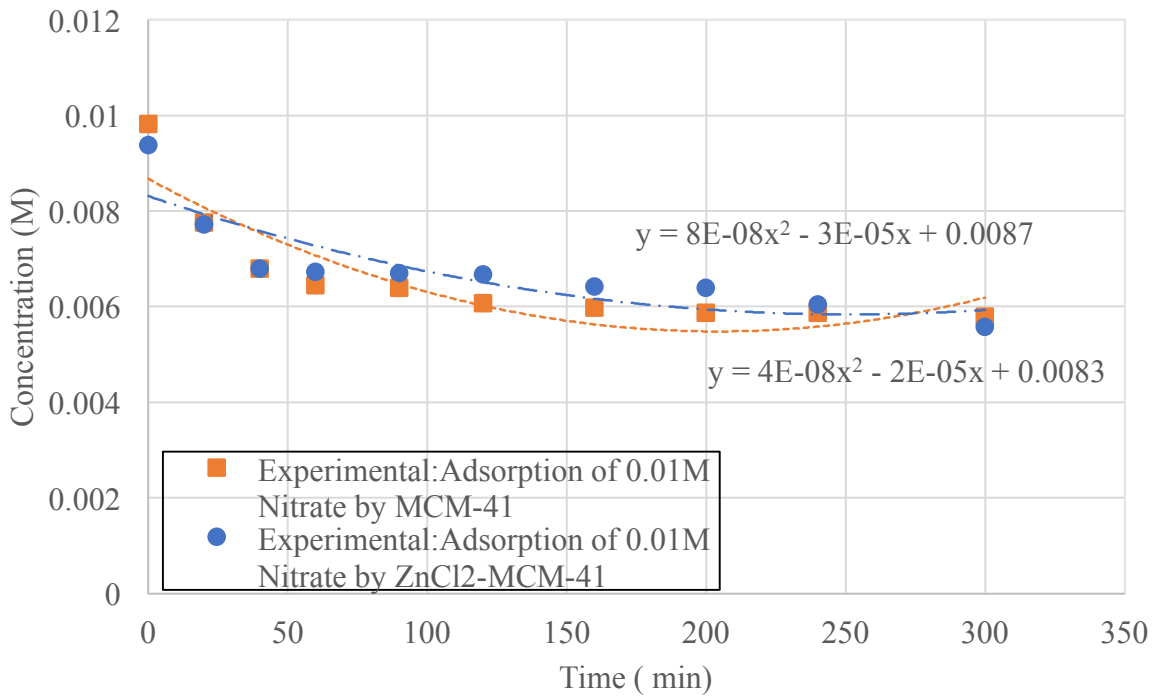

Figure 103 Experimental: Adsorption of 0.01M NO_3^- ions by MCM-41 and $ZnCl_2$-MCM-41

Table 58 Adsorption of 0.01M NO_3^- ions by MCM-41			
Time (min)	**Conc. after adsorption (M)**	**Mass adsorbed (m_i), mg**	**($\sum m_i$), (mg) in 0.15 g adsorbent**
0	0.00982		
20	0.0078	3.846	3.846
40	0.0068	1.788	5.634
60	0.0064	0.640	6.274
90	0.0064	0.113	6.387
120	0.0061	0.602	6.989
160	0.0060	0.159	7.148
200	0.0059	0.208	7.357
240	0.0059	0.000	7.357
300	0.0058	0.154	7.510
24 hours	0.0056		**$\sum m_i$=7.510**
Adsorption = $\sum m_i$=7.150 mg /0.15g =50.07 mg/g			

Table 59 Adsorption of 0.01M NO_3^- ions by $ZnCl_2$-MCM-41			
Time (min)	**Conc. after adsorption (M)**	**Mass adsorbed (m_i), mg**	**($\sum m_i$), (mg) in 0.15 g adsorbent**
0	0.00937		
20	0.0077	3.070	3.070
40	0.0068	1.720	4.791
60	0.0067	0.119	4.910
90	0.0067	0.059	4.969
120	0.0067	0.059	5.027
160	0.0064	0.460	5.487
200	0.0064	0.056	5.544
240	0.0060	0.655	6.199
300	0.0056	0.867	7.066
24 hours	0.0055		**$\sum m_i$=7.066**
Adsorption = $\sum m_i$=7.066 mg /0.15g =47.10 mg/g			

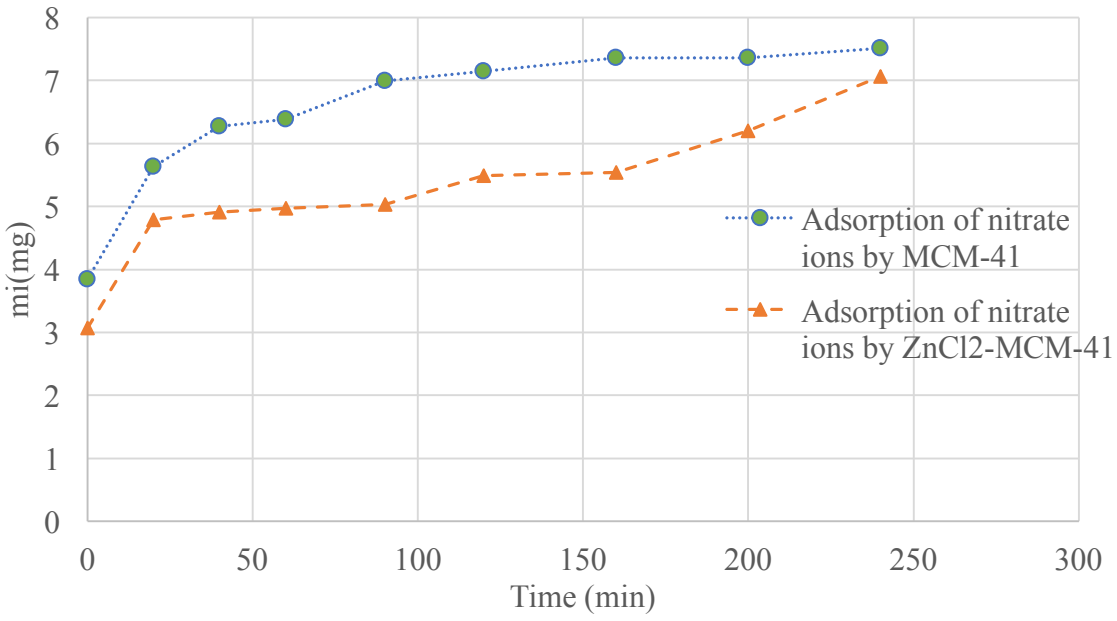

Figure 104 Mass of 0.01 NO_3^- ions adsorbed by MCM-41 and $ZnCl_2$-MCM-41

D. Adsorption of 0.1M NO_3^- ions by MCM-41 and $ZnCl_2$-MCM-41

Table 60 shows the experimental data for adsorption of potassium by MCM-41 and $ZnCl_2$-MCM-41. Figure 105 shows the plot for concentration versus time after adsorption by MCM-41 and $ZnCl_2$-MCM-41. Tables 61 and 62 show the mass adsorbed by these adsorbents. The adsorption capacities for MCM-41 and $ZnCl_2$-MCM-41 was calculated as 219.48 and 297.28 mg/g respectively, as shown in Figure 106. The adsorbents values were comparatively higher for the concentration of 0.1M than the other two concentrations for nitrate ions, suggesting the adsorption increased with the increase in concentration.

Table 60 Adsorption of 0.1M NO_3^- ions

	MCM-41		$ZnCl_2$-MCM-41	
Time (min)	**0.1M MCM-41 (mV)**	**Conc. after adsorption by MCM-41 (M)**	**0.1M $ZnCl_2$-MCM-41 (mV)**	**Conc. after adsorption by $ZnCl_2$MCM-41 (M)**
0	-99.6	0.143	-99	0.13873
20	-99.1	0.139	-98.4	0.13485
40	-99	0.139	-98.2	0.13358
60	-98.9	0.138	-98.1	0.13295
90	-98.8	0.137	-97.9	0.13170
120	-98.2	0.134	-97.4	0.12862
160	-97.6	0.130	-97.5	0.12923
200	-97.5	0.129	-97.1	0.12681
240	-97.1	0.127	-96.3	0.12210
300	-96.8	0.125	-95.1	0.11537
24 hours	-94	0.110	-93	0.10446

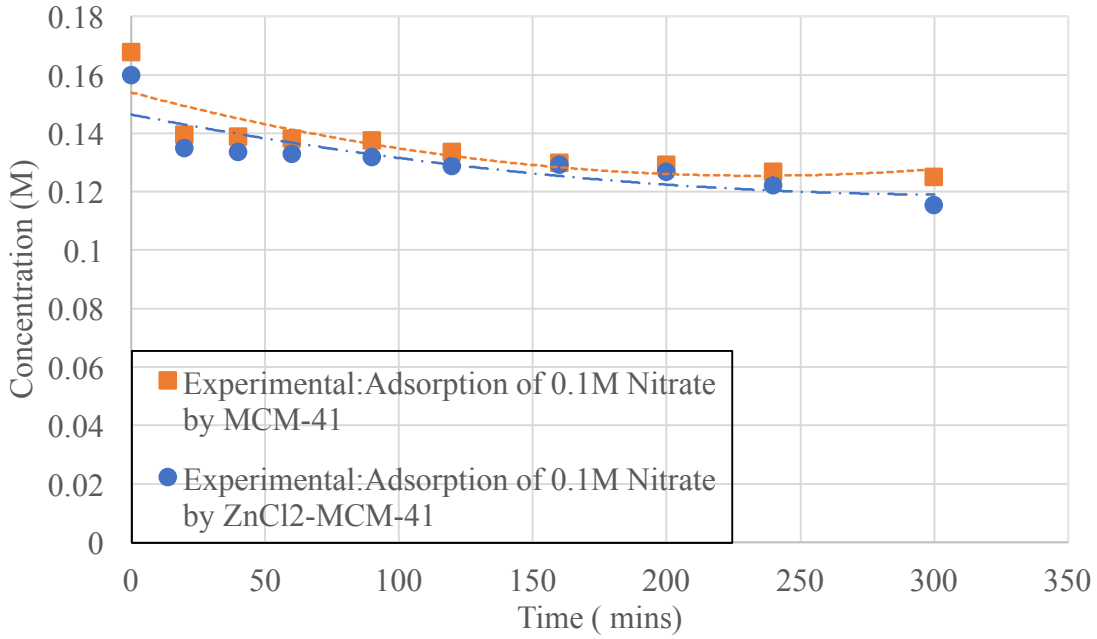

Figure 105 Experimental: Adsorption of 0.1M NO_3^- ions by MCM-41 and $ZnCl_2$-MCM-41

Table 61 Adsorption of 0.1M NO_3^- ions by MCM-41			
Time (min)	**Conc. after adsorption (M)**	**Mass adsorbed (m_i), mg**	**($\sum m_i$), (mg) in 0.15 g adsorbent**
0	0.143		
20	0.139	6.203	6.203
40	0.139	1.223	7.426
60	0.138	1.217	8.644
90	0.137	1.212	9.855
120	0.134	7.150	17.006
160	0.130	6.950	23.956
200	0.129	1.139	25.095
240	0.127	4.504	29.599
300	0.125	3.322	32.922
24 hours	0.110		**$\sum m_i$=32.922**
Adsorption = $\sum m_i$=32.922mg /0.15g =219.479 mg/g			

Table 62 Adsorption of 0.1M NO_3^- ions by $ZnCl_2$-MCM-41			
Time (min)	**Conc. after adsorption (M)**	**Mass adsorbed (m_i), mg**	**($\sum m_i$), (mg) in 0.15 g adsorbent**
0	0.13873		
20	0.13485	7.218	7.218
40	0.13358	2.361	9.579
60	0.13295	1.172	10.752
90	0.13170	2.328	13.079
120	0.12862	5.724	18.803
160	0.12923	-1.134	18.803
200	0.12681	4.504	23.307
240	0.12210	8.756	32.063
300	0.11537	12.529	44.592
24 hours	0.10446		**$\sum m_i$=44.592**
Adsorption = $\sum m_i$=44.592 mg /0.15g =297.28 mg/g			

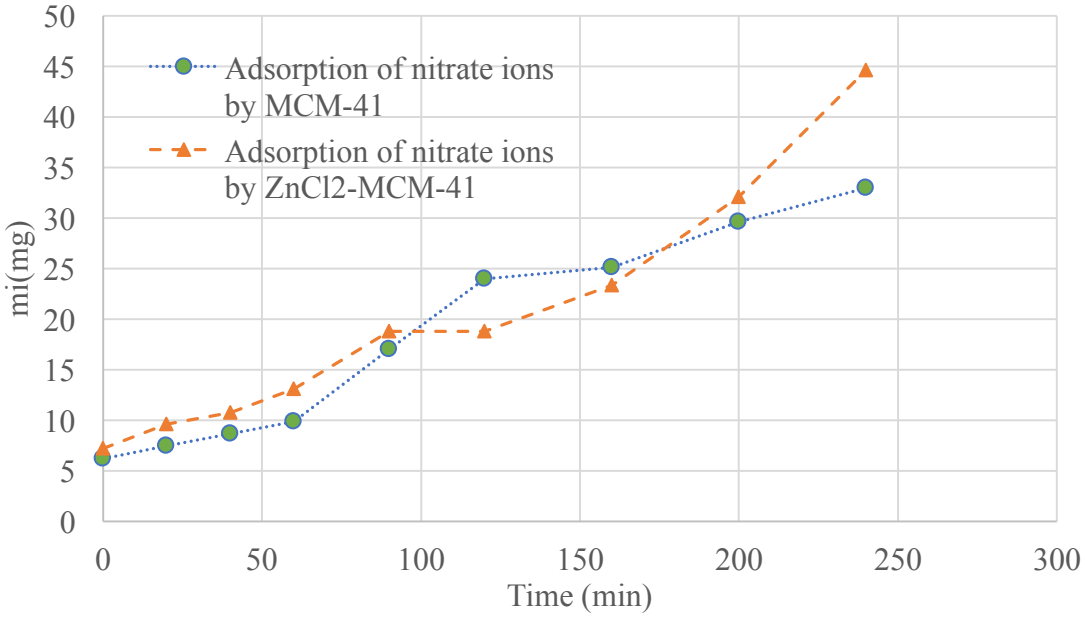

Figure 106 Mass of 0.1 NO_3^- ions adsorbed by MCM-41 and $ZnCl_2$-MCM-41

4.4.4 Activated Carbon Comparisons

For comparison of adsorption, activated carbon was also used for adsorbing calcium, potassium, and nitrate ions of concentrations 0.001M, 0.01M, and 0.1M, and for lead it was done with 0.1M lead.

A. Calibration of Calcium electrode

Table 63 shows the initial calibration data for calibration of calcium electrode. Figure 107 is the initial calibration curve with the equation used to calculate the concentration. The rest of the data is presented in the Appendix.

Table 63 Initial Calibration curve for Ca^{2+} ions

Original Concentration (M)	Log10 (Conc)	abs value of Conc	mV Reading
1.00E-01	-1.00	1.00	70.5
5.00E-02	-1.30	1.30	65.1
3.00E-02	-1.52	1.52	61.4
1.00E-02	-2.00	2.00	51.9
5.00E-03	-2.30	2.30	45.1
3.00E-03	-2.52	2.52	42.2
1.00E-03	-3.00	3.00	32.6
5.00E-04	-3.30	3.30	25.8
1.00E-04	-4.00	4.00	11.9

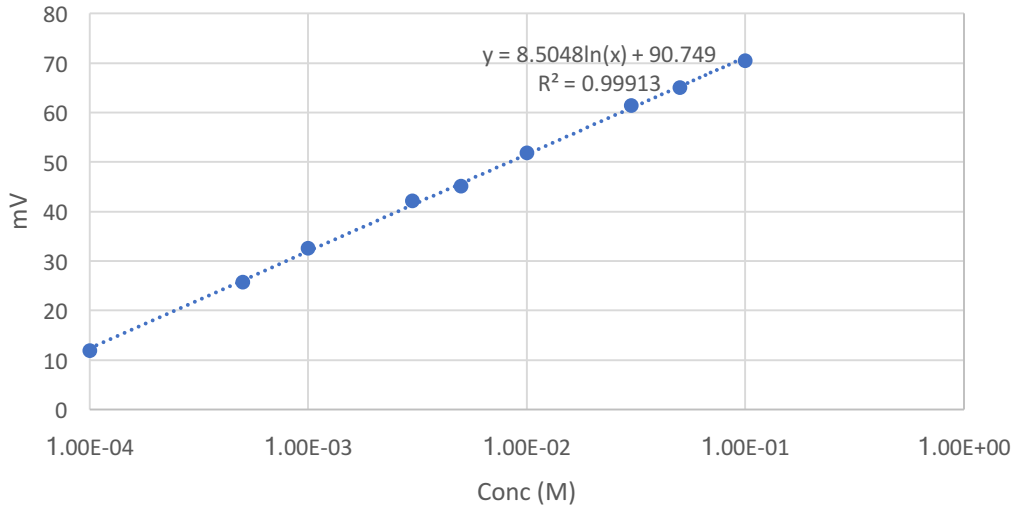

Figure 107 Calibration Curve for Calcium electrode

B. Adsorption of Lead ions by Activated carbon

For lead, the concentration tested was 0.1M. Table 64 and Figure 108 present the experimental data, and the calculated mass adsorbed by AC at specific interval of time. The adsorption capacity was calculated as 880.55 mg/g. This is lower than the capacities for MCM-41 & $ZnCl_2$-MCM-41.

Table 64 Adsorption of 0.1M Pb^{2+} ions by AC

Time (min)	Conc. after adsorption by AC (M)	Mass adsorbed (m_i), mg	($\sum m_i$), (mg)
0	0.100	-	-
20	0.1112	0	0
40	0.1101	7.260288	7.260
60	0.1096	2.896656	10.156
80	0.1086	5.923848	16.080
100	0.1078	5.19036	21.271
120	0.1063	9.156168	30.427
160	0.1043	12.630912	43.058
200	0.0883	99.7668	142.825
240	0.0741	87.931536	230.756
300	0.0723	11.393928	242.150
24 hours	0.0681		**$\sum m_i$=242.15**
Adsorption = $\sum m_i$=242.15/0.275=880.55			

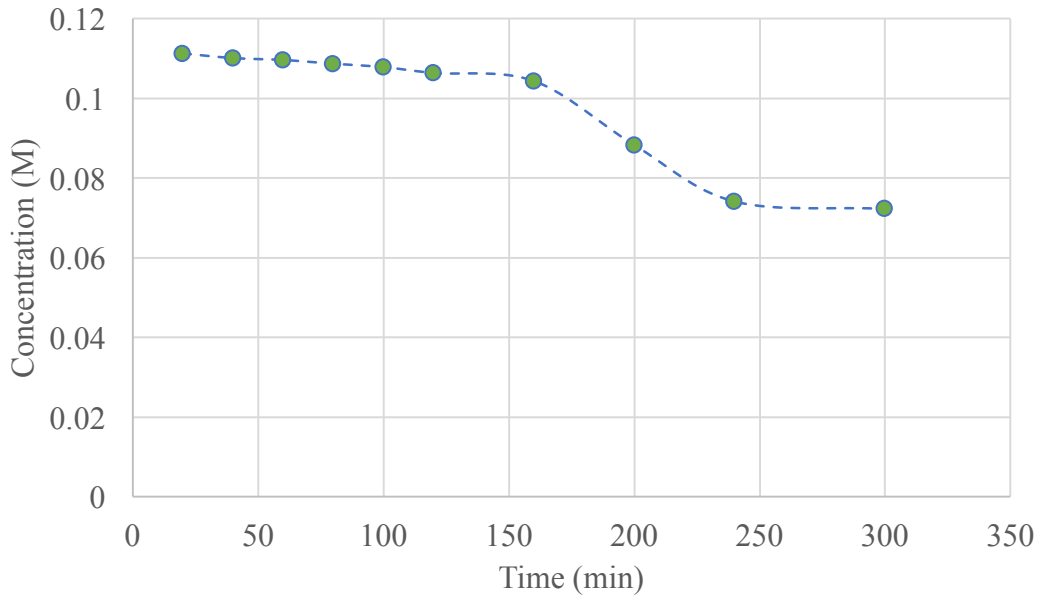

Figure 108 Adsorption of 0.1M lead by AC

C. Adsorption of 0.1M, 0.01M & 0.001M calcium ions by AC

The experimental values of concentration for 0.1M, 0.01M and 0.001M calcium ions are shown in Table 65. It also shows the mass adsorbed by AC after adsorption. The adsorption capacities of AC for 0.1M, 0.01M and 0.001M calcium are 88.70 mg/g, 39.62, and 7.98 mg/g respectively. It shows that the adsorption capacity of AC increases with increase in the initial concentration of the adsorbates. Figures 109 and 110 show the concentration versus time, and the mass adsorbed by AC respectively for all concentrations.

	Table 65 Adsorption of 0.1M Ca^{2+} ions by AC			
Time (min)	**mV**	**Conc. after adsorption by AC (M)**	**Mass adsorbed (m_i), mg**	**($\sum m_i$), (mg)**
0	71	0.0879	-	-
20	70.3	0.0814	7.866	7.866
40	70.5	0.0832	-2.186	7.866
60	70.3	0.0814	2.186	10.052
90	70.4	0.0823	-1.087	10.052
120	70.3	0.0814	1.087	11.139
160	70.4	0.0823	-1.087	11.139
200	70.2	0.0805	2.162	13.300
240	70.2	0.0805	0.000	13.300
300	70.2	0.0805	0.000	13.300
24 hrs	71.0	0.0879		
				$\sum m_i$=13.300
				Adsorption = $\sum m_i$=13.300/0.15=88.70 mg/g

Table 66 Adsorption of 0.01M Ca^{2+} ions by AC				
Time (min)	**mV**	**Conc. after adsorption by AC (M)**	**Mass adsorbed (m_i), mg**	**($\sum m_i$), (mg)**
0	51.9	0.0104	-	-
20	49	0.0074	3.599	3.599
40	48.6	0.0070	0.407	4.006
60	48.8	0.0072	-0.201	4.006
90	48.9	0.0073	-0.102	4.006
120	49.1	0.0075	-0.208	4.006
160	48.9	0.0073	0.208	4.214
200	49.2	0.0076	-0.314	4.214
240	49.1	0.0075	0.106	4.320
300	47.4	0.0061	1.624	5.944
24 hours	47.6	0.0063		
				$\sum m_i$=5.944
				Adsorption = $\sum m_i$=5.944/0.15=39.62 mg/g

Time (min)	Table 67 Adsorption of 0.001M Ca^{2+} ions by AC			
	mV	Conc. after adsorption by AC (M)	Mass adsorbed (m_i), mg	($\sum m_i$), (mg)
0	32.6	0.00107	-	-
20	26.2	0.00051	0.681	0.681
40	24.2	0.00040	0.127	0.808
60	25.2	0.00045	-0.060	0.808
90	25.7	0.00048	-0.033	0.808
120	25.3	0.00045	0.026	0.834
160	23.8	0.00038	0.088	0.923
200	23	0.00035	0.041	0.964
240	30	0.00079	-0.532	0.964
300	27.6	0.00060	0.233	1.197
24 hrs	32.2	0.00102		
				$\sum m_i$=1.197
	Adsorption = $\sum m_i$=1.197/0.15=7.98 mg/g			

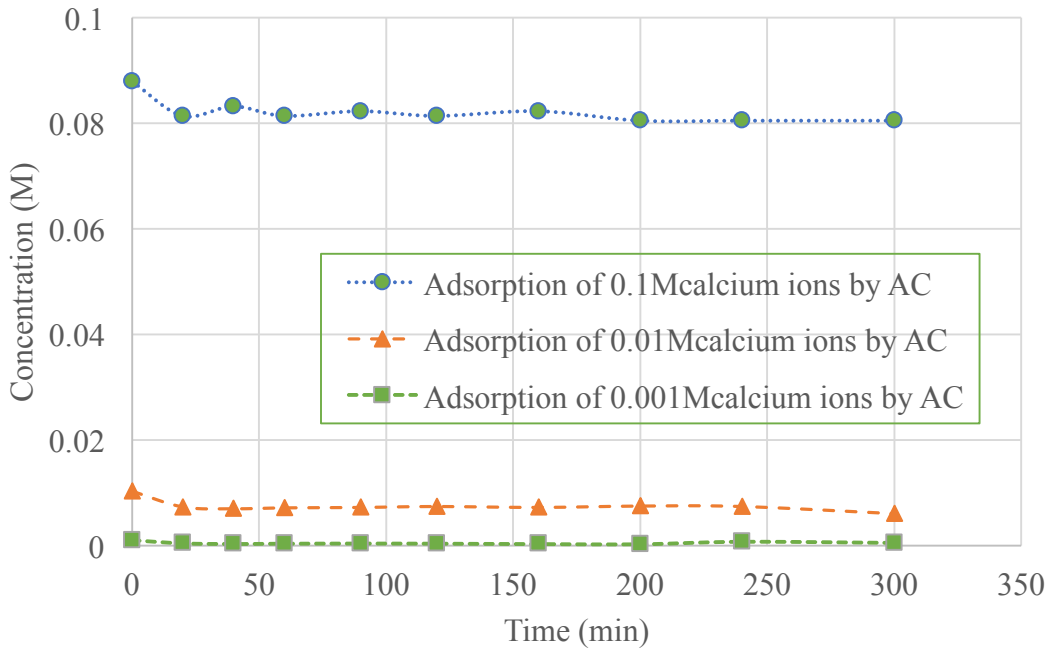

Figure 109 Experimental: Adsorption of Ca^{2+} ions by AC

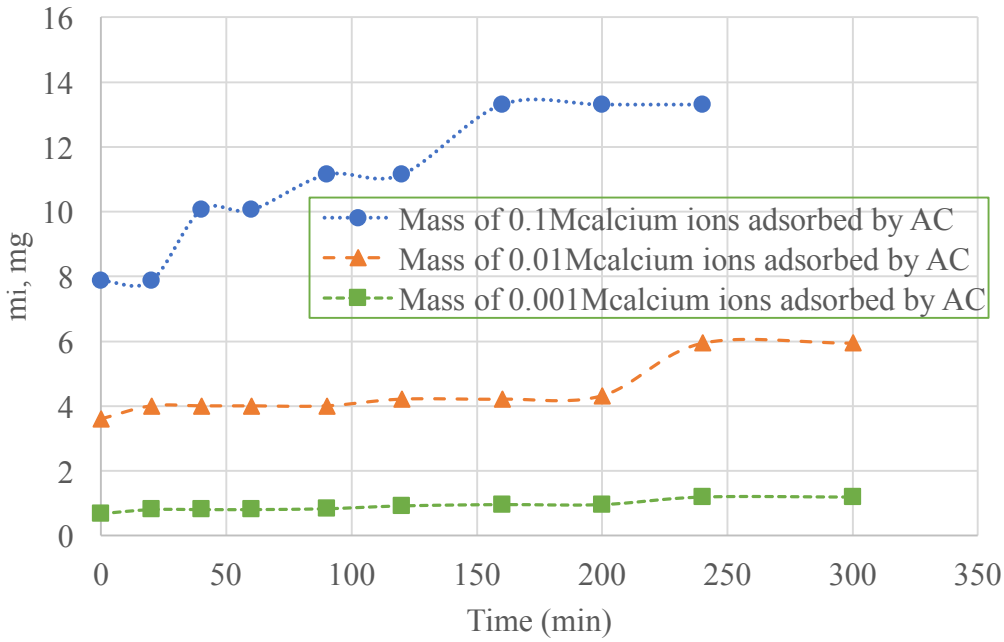

Figure 110 Mass of 0.1M Ca^{2+} ions adsorbed by AC

A. Adsorption of 0.1M, 0.01M & 0.001M nitrate ions by AC

The experimental values of concentration for 0.1M, 0.01M and 0.001M nitrate ions are shown in Table 68. It also shows the mass adsorbed by AC after adsorption. The adsorption capacities of AC for 0.1M, 0.01M and 0.001M nitrate are 116.63 mg/g, 3.281, and 0.166 mg/g respectively. It shows that the adsorption capacity of AC increases with increase in the initial concentration of the adsorbates. Figures 111 and 112 show the concentration versus time, and the mass adsorbed by AC respectively for all concentrations.

Table 68 Adsorption of 0.1M NO_3^- ions by AC				
Time (min)	**mV**	**Conc. after adsorption by AC (M)**	**Mass adsorbed (m_i), mg**	**($\sum m_i$), (mg)**
0	-100.0	0.145		
20	-100.0	0.145	2.571	2.571
40	-99.8	0.144	0.000	2.571
60	-99.1	0.139	2.547	5.117
90	-98.8	0.137	8.726	13.843
120	-99.0	0.139	3.652	17.495
160	-98.9	0.138	-2.429	15.066
200	-98.8	0.137	1.217	16.283
240	-98.9	0.138	1.212	17.495
300	-98.7	0.137	-1.212	17.495
24 hours	-100.0	0.145		
				$\sum m_i$=2.417
	Adsorption = $\sum m_i$=2.417 /0.15=116.63 mg/g			

Table 69 Adsorption of 0.01M NO_3^- ions by AC				
Time (min)	**mV**	**Conc. after adsorption by AC (M)**	**Mass adsorbed (m_i), mg**	**($\sum m_i$), (mg)**
0	-39.1	0.00817		
20	-39	0.00813	-12.727	0.000
40	-38.4	0.00790	0.423	0.423
60	-38.2	0.00783	0.138	0.561
90	-38.3	0.00786	-0.069	0.492
120	-38.4	0.00790	-0.069	0.423
160	-38.4	0.00790	0.000	0.423
200	-38.2	0.00783	0.138	0.561
240	-38.3	0.00786	-0.069	0.492
300	-38.3	0.00786	0.000	0.492
24 hours	-38.2	0.00783		
				$\sum m_i$=0.492
	Adsorption = $\sum m_i$=0.492 /0.15=3.281 mg/g			

Table 70 Adsorption of 0.001M NO_3^- ions by AC				
Time (min)	**mV**	**Conc. after adsorption by AC (M)**	**Mass adsorbed (m_i), mg**	**($\sum m_i$), (mg)**
0	-39.1	0.00817	-	
20	-39	0.00813	0.000	0.000
40	-38.4	0.00790	0.000	-0.019
60	-38.2	0.00783	-0.019	-0.019
90	-38.3	0.00786	0.000	0.019
120	-38.4	0.00790	0.019	0.025
160	-38.4	0.00790	0.006	0.025
200	-38.2	0.00783	-0.012	0.025
240	-38.3	0.00786	0.000	0.025
300	-38.3	0.00786	-0.006	0.025
24 hours	-38.2	0.00783		
				$\sum m_i$=0.025
	Adsorption = $\sum m_i$=0.025/0.15=0.166 mg/g			

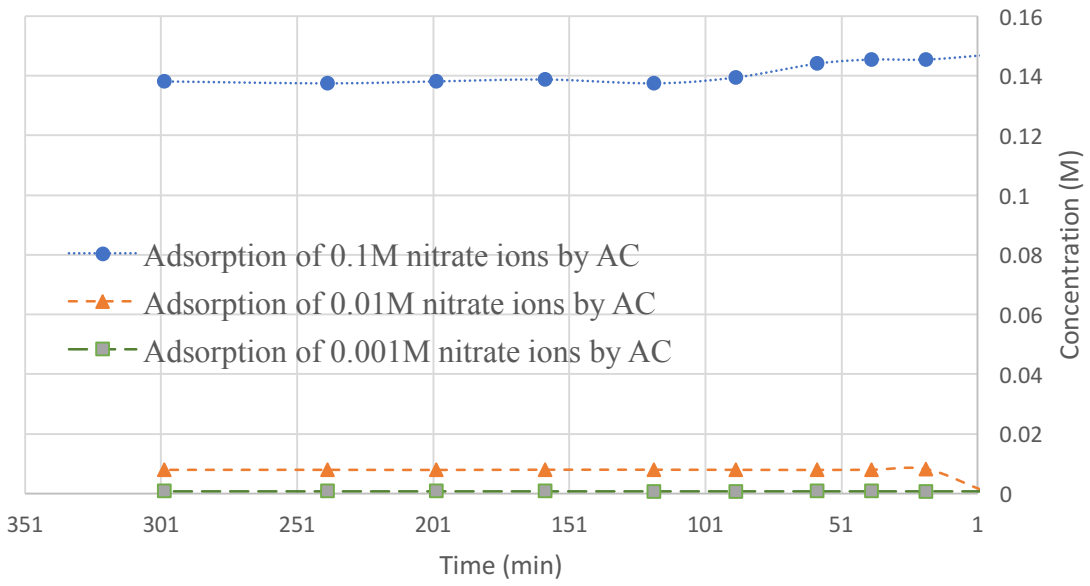

Figure 111 Adsorption of NO_3^- ions by AC

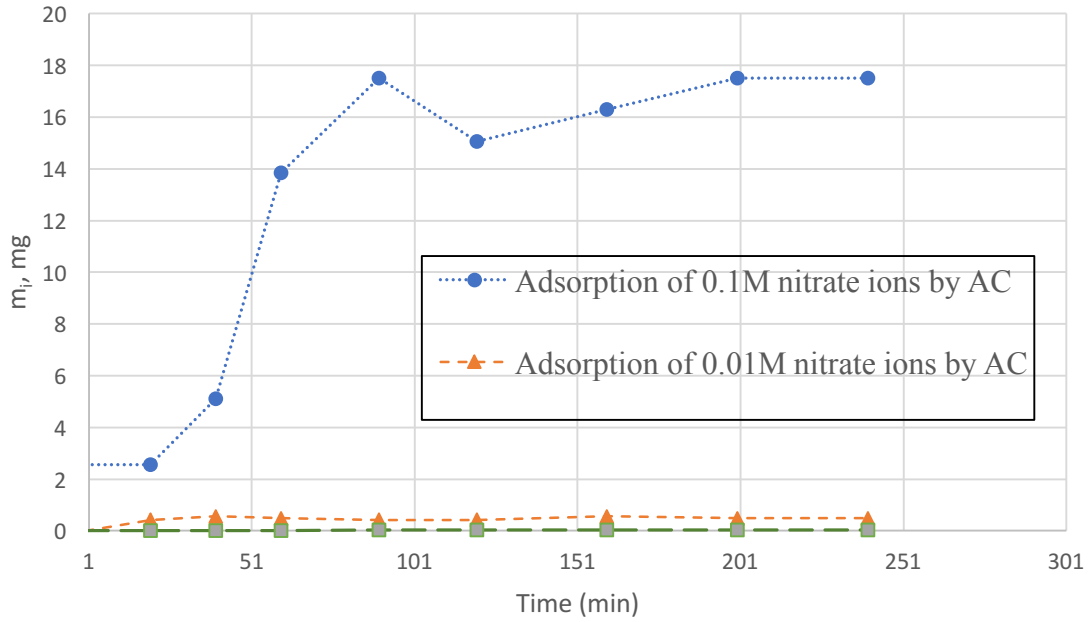

Figure 112 Mass of NO_3^- ions adsorbed by AC

B. Adsorption of 0.1M, 0.01M & 0.001M nitrate ions by AC

The experimental values of concentration for 0.1M, 0.01M and 0.001M potassium ions are shown in Table 71. It also shows the mass adsorbed by AC after adsorption. The adsorption capacities of AC for 0.1M, 0.01M and 0.001M potassium are 105.223 mg/g, 11.058, and 1.157 mg/g respectively. It shows that the adsorption capacity of AC increases with increase in the initial concentration of the adsorbates. Figures 113 and 114 show the concentration versus time, and the mass adsorbed by AC respectively, for all concentrations.

Table 71 Adsorption of 0.1M K^+ ions by AC				
Time (min)	**mV**	**Conc. after adsorption by AC (M)**	**Mass adsorbed (m_i), mg**	**($\sum m_i$), (mg)**
0	-38.8	0.105	-	-
20	-38.8	0.10583	-0.975	0.000
40	-41.1	0.09709	10.247	10.247
60	-41	0.09746	-0.427	10.247
90	-40.5	0.09930	-2.161	10.247
120	-41.2	0.09673	3.014	13.262
160	-41.3	0.09637	0.424	13.686
200	-41.5	0.09565	0.844	14.530
240	-41.8	0.09458	1.254	15.783
300	-41.7	0.09494	-0.416	15.783
24 hours	-42.3	0.09283	2.475	
				$\sum m_i$=15.783
	Adsorption = $\sum m_i$=15.783 /0.15=105.223 mg/g			

Table 72 Adsorption of 0.01M K^+ ions by AC				
Time (min)	**mV**	**Conc. after adsorption by AC (M)**	**Mass adsorbed (m_i), mg**	**($\sum m_i$), (mg)**
0		0.011		
20	-100	0.011	0.363	0.000
40	-102.7	0.010	1.206	1.206
60	-98.9	0.011	-1.734	1.206
90	-100.5	0.010	0.760	1.206
120	-100.7	0.010	0.092	1.298
160	-101.3	0.010	0.271	1.570
200	-100.3	0.011	-0.456	1.114
240	-101.5	0.010	0.545	1.659
300	-100.8	0.010	-0.315	1.659
24 hours	-101.3	0.010	0.226	
				$\sum m_i$=1.659
	Adsorption = $\sum m_i$=1.659 /0.15=11.058 mg/g			

Table 73 Adsorption of 0.001M K^+ ions by AC				
Time (min)	**mV**	**Conc. after adsorption by AC (M)**	**Mass adsorbed (m_i), mg**	**($\sum m_i$), (mg)**
0		0.001		
20	-161.7	0.0011	-0.070	0.000
40	-161	0.0011	-0.033	-0.033
60	-158.7	0.0012	-0.115	-0.033
90	-158.3	0.0012	-0.021	-0.033
120	-159.2	0.0012	0.047	0.047
160	-159.5	0.0012	0.015	0.062
200	-161.8	0.0011	0.111	0.173
240	-160.7	0.0011	-0.052	0.173
300	-157.6	0.0012	-0.159	0.173
24 hours	-153.5	0.0014	-0.241	0.173
				$\sum m_i$=0.173
	Adsorption = $\sum m_i$=0.173 /0.15=1.157 mg/g			

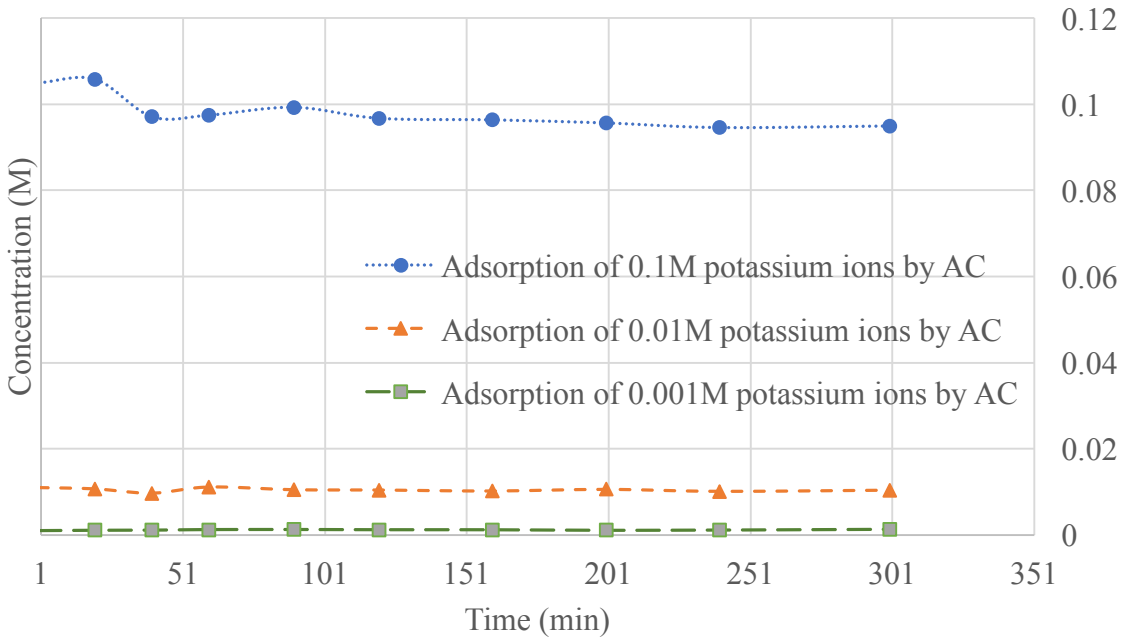

Figure 113 Adsorption of K^+ ions by AC

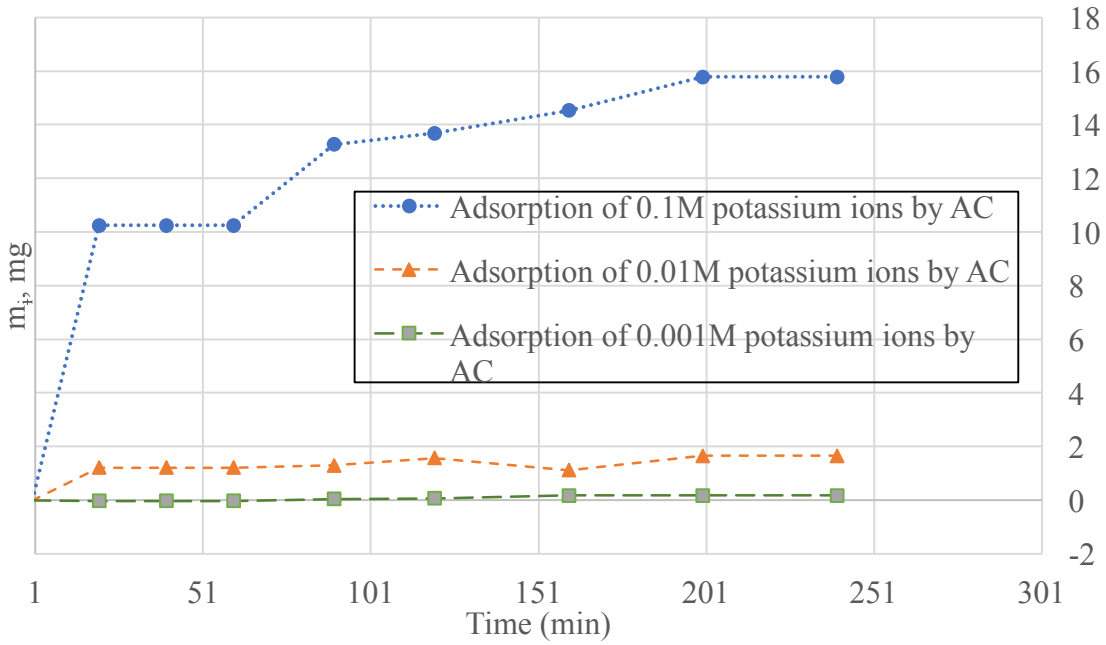

Figure 114 Mass of K^+ ions adsorbed by AC

CHAPTER 5- SUMMARY AND CONCLUSIONS

The objectives of this research were to a) synthesize and study the characteristics of MCM-41 and $ZnCl_2$-MCM-41, b) find their adsorption capacities for the removal of heavy metals (lead, mercury and chromium), and other ions (calcium, potassium, and nitrate) present in water, and c) compare the adsorption results with those of activated carbon.

In the introduction section, the need for removal of heavy metals from the environment, and MCM-41 as an adsorbent for removal of the heavy metals were presented in brief. MCM-41 is uniformly shaped mesoporous material, which can be confirmed by the TEM analysis shown in Figures 16 to 24. MCM-41, known for its large surface area, has been studied for its capacity as an adsorbent in the field of adsorption, catalysis, and as sensors. But pure MCM-41 has its limitations so MCM-41 has been functionalized with other organic and inorganic groups to enhance its adsorption capacity.

In the literature review portion in this paper, we discussed the synthesis, structure and characteristics of MCM-41, and its applications in different fields, as sensors and adsorbents. MCM-41 was synthesized using the method provided by Gaydhankar (2007) with the use of TMAOH, TEOS and CTAB. This pure MCM-41 was also functionalized by using zinc chloride by the use of microwave method.

The methodology shows the preparation of MCM-41, and $ZnCl_2$-MCM-41 as well as the batch adsorption studies done to calculate the adsorption capacities of MCM-41 and $ZnCl_2$-MCM-41 for the removal of heavy metals (lead, mercury, and chromium) as well as cations, calcium and potassium, and anion nitrate from water.

Comparison of data from literature and the experiments

The adsorption capacity of pure MCM-41 for the removal of lead was only 57.7 mg/g (Ghoohestani & Faghihian 2016), as shown in Table 1. But the adsorption capacity achieved by $ZnCl_2$-MCM-41 was as high as 479 mg/g (Raji et al. 2015), as shown in Table 1. The experimental adsorption capacity achieved in this study was 2846.4 mg/g for 0.1M lead (Pb^{2+}).

Similarly, for mercury, the highest adsorption capacity by MCM-41 was 538.9 mg/g (Mehdinia et al. 2015) by use of functionalized MCM-41 Di-thio-MCM-41(DT-MCM-41).

In this study, the highest adsorption capacity was 1302.74 mg/g for 0.1M mercury (Hg^{2+}).

For chromium, the highest adsorption capacity was 904 mg/g (Tian et al. 2011) as shown in Table 3. The adsorption capacities of $ZnCl_2$-MCM-41, achieved from batch studies, was as high as 139.27 mg/g and chromium (Cr^{3+}). These results show that the adsorption values were higher than the values from literature's values for mercury and lead, abut lower in case of chromium.

The capacities for removal of the cations and anions by $ZnCl_2$-MCM-41, were found to be 47.94 mg/g, 279.28 mg/g, and 219.48 mg/g for calcium (Ca^{2+}), potassium (K^+), and nitrate (NO_3^-) respectively.

Although some of the results from Table 74 seem much higher in capacity than those in the literature, other parameter determining this difference is the discrepancy in the concentration used in our experiments. We have used higher concentrations than the studies shown in the literature, thus that might be the cause of different results. The structure of MCM-41 is also different than the structure found from literature. Our results show the final product MCM-41 as amorphously packed material, rather than the crystalline structure found in literature. This might have changed the adsorption process itself, and thus affected the adsorption capacities.

Effects of initial concentration and contact time

Table 73 and 74 shows the adsorption capacities of MCM-41 and $ZnCl_2$-MCM-41 for the removal of different heavy metals tested as well as the cations, and anions. As it can be seen, the adsorption capacity increases with the increase of the concentration of the adsorbate in the solution. And the data further shows that $ZnCl_2$-MCM-41 has better adsorption capacity than MCM-41.

The adsorption is higher for higher concentration of 0.1M, and the other concentrations 0.01M and 0.001M do not show very significant adsorption in comparison to the 0.1M concentration.

The results for the removal percentage achieved by each adsorbent is also presented in Table 75. It shows that the percentage removal is higher for higher concentration. The removal percentage was highest for 0.1M mercury (91%), followed by lead (66% for 0.1M lead). The removal capacity seems to be different in case of the metals, and the cations and anions. In case of cations, and anions, the removal increased as the concentration decreased.

Another important factor that affected the adsorption process was contact time for adsorption. The sorption capacity increased with the increase in time, until it reached equilibrium for adsorption capacity. After a certain interval, the adsorption capacity was constant. As the heavy metals are adsorbed into the channels of adsorbents, it starts to saturate at a point, thus limiting the adsorption sites after a point.

Comparison with Activated Carbon

These results can also be compared with the activated carbon results, as shown in Table 75. It shows that MCM-41 and $ZnCl_2$-MCM-41 have better adsorption capacities for the adsorption of heavy metals. In most of the concentrations for calcium, nitrate, and potassium, all the

adsorbents did not show significantly high adsorption capacity, but still the results were better for MCM-41 and $ZnCl_2$-MCM-41 than for activated carbon.

Adsorption trend based on atomic radius and reactivity of metals

The adsorption capacity can be compared on the basis of the position of the heavy metals on the periodic table, their atomic radius and reactivity. Atomic radius for the 3 heavy metals lead, mercury, and chromium is in the order Pb> Hg>Cr. This trend can be seen in case of the adsorption of heavy metals in a solution, as seen on Table 74 and Table 75. In terms of competition of heavy metals in a solution, Tables 74, 75 and 76 show that lead is most favored by both MCM-41 and $ZnCl_2$-MCM-41 for all concentrations. Mercury is the second favored metal, chromium being the least adsorbed of all metals studied. This can also be seen on the basis of the reactivity of the metals. In case of reactive metals calcium and potassium, the adsorption is comparatively difficult. The less reactive metals lead and chromium are adsorbed significantly in comparison to calcium and potassium. Mercury being the least reactive of all the tested metals, is the most removed amongst all of the metals (adsorbed by 91%).

From these results, it can be concluded that MCM-41 and $ZnCl_2$-MCM-41 can be used as adsorbents for the removal of heavy metals as well as other cations and anions from a water solution. However, other factors such as pH and temperature also need to be studied in order to understand the adsorption nature better, and to use them as adsorbents in real-life applications.

Table 74 Summary Table for final concentration after 24 hours adsorption			
Initial conc. (M)	**Final conc. after adsorption by MCM-41 (M)**	**Final conc. after adsorption by $ZnCl_2$-MCM-41(M)**	**Final conc. after adsorption by AC (M)**
0.1M Pb	0.0945	0.034	0.0681
0.01M Pb	0.00897	0.00669	-
0.001M Pb	0.000574	0.000475	-
0.1M Hg	0.0715	0.00893	-
0.01M Hg	0.00787	0.00772	-
0.001M Hg	0.000803	0.000836	-
0.1M Cr	0.0821	0.05301	-
0.01M Cr	0.00645	0.00609	-
0.001M Cr	0.0005	0.000491	-
0.1M heavy metals (Cr, Hg and Pb)	0.065 Cr, 0.0661 Hg, 0.0416 Pb	0.0644 Cr, 0.06726 Hg, 0.0387 Pb	-
0.1M Ca^{2+}	0.051	0.056	0.0879
0.01M Ca^{2+}	0.00968	0.0087	0.0063
0.001M Ca^{2+}	0.0005	0.00062	0.00102
0.1M K^{+}	0.101	0.101	0.100
0.01M K^{+}	0.011	0.0104	0.00783
0.001M K^{+}	0.0008	0.0007	0.0928
0.1M NO_3^{-}	0.11	0.1045	0.100
0.01M NO_3^{-}	0.0056	0.0055	0.010
0.001M NO_3^{-}	0.0004	0.0004	0.0014

Table 75 Summary Table for Adsorption capacity (mg/g)

Adsorbate	MCM-41	$ZnCl_2$-MCM-41	AC
0.1M Pb	1657.6	2846.4	880.55
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 heavy metals (Cr, Hg and Pb)	95.6 (Cr), 223.06 (Hg) & 377.405 (Pb)	8.804 (Cr), 27.882 (Hg) & 644.77 (Pb)	-
0.1M Ca^{2+}	63.95	47.94	88.7
0.01M Ca^{2+}	10.56	12.62	39.62
0.001M Ca^{2+}	1.116	4.87	7.98
0.1M K^{+}	219.48	279.28	105.223
0.01M K^{+}	50.07	47.1	11.058
0.001M K^{+}	5.283	5.092	1.157
0.1M NO_3^{-}	297.28	219.479	116.63
0.01M NO_3^{-}	50.07	47.1	3.281
0.001M NO_3^{-}	5.283	5.092	0.166

Table 76 Summary Table for Removal percentage of adsorbents			
Adsorbate	**MCM-41 (%)**	**$ZnCl_2$-MCM-41 (%)**	**AC (%)**
0.1M Pb	5.5	66	31.9
0.01M Pb	10.3	33.1	-
0.001M Pb	42.6	52.5	-
0.1M Hg	27.87	91.07	-
0.01M Hg	21.3	22.8	-
0.001M Hg	19.7	16.4	-
0.1M Cr	17.9	46.99	-
0.01M Cr	35.5	39.1	-
0.001M Cr	50	50.9	-
0.1M heavy metals (Cr, Hg and Pb)	35% Cr, 34% Hg, 58.4% Pb	35.6% Cr, 32.74% Hg, 61% Pb	-
0.1M Ca^{2+}	49	44	12.1
0.01M Ca^{2+}	3.2	13	37
0.001M Ca^{2+}	50	38	0
0.1M K^{+}	0	0	0
0.01M K^{+}	0	0	21.7
0.001M K^{+}	20	30	0
0.1M NO_3^{-}	0	0	0
0.01M NO_3^{-}	44	45	0
0.001M NO_3^{-}	60	60	0

REFERENCES

Algarra, M., Jimenez, M. V., Rodriguez-Castellon, E., Jimenez-Lopez, A., & Jimenez-Jimenez, J. (2005). Heavy metals removal from electroplating wastewater by aminopropyl-Si MCM-41. *Chemosphere, 59*(6), 779-786. doi:10.1016/j.chemosphere.2004.11.023

Alothman, Z. A. (2012). A Review: Fundamental Aspects of Silicate Mesoporous Materials. *Materials, 5*(12), 2874-2902. doi:10.3390/ma5122874

Anbia, M., & Mohammadi, K. (2008). Removal of Copper-phthalocyanine from Aqueous Solution by Cationically Templated MCM-41 and MCM-48 Nanoporous Adsorbents. *Chinese Journal of Chemistry, 26*(11), 2051-2055. doi:10.1002/cjoc.200890366

Anbia, M., & Mohammadi, K. (2009). An Effective Method For Removal of Dichromate Ion and Furfural From Aqueous Solutions Using A Nanoporous Adsorbent. *Asian Journal of Chemistry, 21*(5), 3347-3354.

Bao, X. Y., Zhao, X. S., Qiao, S. Z., & Bhatia, S. K. (2004). Comparative analysis of structural and morphological properties of large-pore periodic mesoporous organosilicas and pure silicas. *Journal of Physical Chemistry B, 108*(42), 16441-16450. doi:10.1021/jp047479s

Bao, Y. X., Yan, X. M., Du, W., Xie, X. N., Pan, Z. Q., Zhou, J. L., & Li, L. S. (2015). Application of amine-functionalized MCM-41 modified ultrafiltration membrane to remove chromium (VI) and copper (II). *Chemical Engineering Journal, 281*, 460-467. doi:10.1016/j.cej.2015.06.094

Behbahani, M., Akbari, A. A., Amini, M. M., & Bagheri, A. (2014). Synthesis and characterization of pyridine-functionalized magnetic mesoporous silica and its application for preconcentration and trace detection of lead and copper ions in fuel products. *Analytical Methods, 6*(21), 8785-8792. doi:10.1039/c4ay01692k

Benhamou, A., Basly, J. P., Baudu, M., Derriche, Z., & Hamacha, R. (2013). Amino-functionalized MCM-41 and MCM-48 for the removal of chromate and arsenate. *Journal of Colloid and Interface Science, 404*, 135-139. doi:10.1016/j.jcis.2013.04.026

Cao, J. L., Wu, Y. H., Jin, Y. P., Yilihan, P., & Huang, W. F. (2014). Response surface methodology approach for optimization of the removal of chromium(VI) by NH2-MCM-41. *Journal of the Taiwan Institute of Chemical Engineers, 45*(3), 860-868. doi:10.1016/j.jtice.2013.09.011

Chen, C., Kim, J., & Ahn, W. S. (2014). CO2 capture by amine-functionalized nanoporous materials: A review. *Korean Journal of Chemical Engineering, 31*(11), 1919-1934. doi:10.1007/s11814-014-0257-2

Chen, F. Y., Hong, M. Z., You, W. J., Li, C., & Yu, Y. (2015). Simultaneous efficient adsorption of Pb2+ and MnO4- ions by MCM-41 functionalized with amine and nitrilotriacetic acid anhydride. *Applied Surface Science, 357*, 856-865. doi:10.1016/j.apsusc.2015.09.069

Chen, X. Q., Lam, K. F., & Yeung, K. L. (2011). Selective removal of chromium from different aqueous systems using magnetic MCM-41 nanosorbents. *Chemical Engineering Journal, 172*(2-3), 728-734. doi:10.1016/j.cej.2011.06.042

Chen, Y. T., & Mu, S. Y. (2014). Core-shell structured Fe3O4 nanoparticles functionalized with rhodamine derived probe for the detection, adsorption and removal of Hg(II): A sensing system with 'warning' signal. *Sensors and Actuators B-Chemical, 192*, 275-282. doi:10.1016/j.snb.2013.10.135

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. doi:10.1016/j.jssc.2016.04.003

Dai, X. X., Qiu, F. G., Zhou, X., Long, Y. M., Li, W. F., & Tu, Y. F. (2014). Amino-functionalized MCM-41 for the simultaneous electrochemical determination of trace lead and cadmium. *Electrochimica Acta, 144*, 161-167. doi:10.1016/j.electacta.2014.08.093

Dimos, K., Stathi, P., Karakassides, M. A., & Deligiannakis, Y. (2009). Synthesis and characterization of hybrid MCM-41 materials for heavy metal adsorption. *Microporous and Mesoporous Materials, 126*(1-2), 65-71. doi:10.1016/j.micromeso.2009.05.021

Egodawatte, S., Datt, A., Burns, E. A., & Larsen, S. C. (2015). Chemical Insight into the Adsorption of Chromium(III) on Iron Oxide/Mesoporous Silica Nanocomposites. *Langmuir, 31*(27), 7553-7562. doi:10.1021/acs.langmuir.5b01483

Etienne, M., Sayen, S., Lebeau, B., & Walcarius, A. (2002). Organically-modified mesoporous silica spheres with MCM-41 architecture as sorbents for heavy metals. *Nanoporous Materials Iii, 141*, 615-622.

Gaydhankar, T. R., Samuel, V., Jha, R. K., Kumar, R., & Joshi, P. N. (2007). Room temperature synthesis of Si-MCM-41 using polymeric version of ethyl silicate as a source of silica. *Materials Research Bulletin, 42*(8), 1473-1484. doi:10.1016/j.materresbull.2006.11.006

Ghoohestani, S., & Faghihian, H. (2016). Selective separation of Pb2+ from aqueous solutions by a novel imprinted adsorbent. *Desalination and Water Treatment, 57*(9), 4049-4058. doi:10.1080/19443994.2014.993718

Ghorbani, M., Nowee, S. M., Ramezanian, N., & Raji, F. (2016). A new nanostructured material amino functionalized mesoporous silica synthesized via co-condensation method for Pb(II) and Ni(II) ion sorption from aqueous solution. *Hydrometallurgy, 161*, 117-126. doi:10.1016/j.hydromet.2016.02.002

He, C. S., Ren, L., Zhu, W. P., Xu, Y. F., & Qian, X. H. (2015). Removal of mercury from aqueous solution using mesoporous silica nanoparticles modified with polyamide receptor. *Journal of Colloid and Interface Science, 458*, 229-234. doi:10.1016/j.jcis.2015.07.054

Heidari, A., Younesi, H., & Mehraban, Z. (2009). Removal of Ni(II), Cd(II), and Pb(II) from a ternary aqueous solution by amino functionalized mesoporous and nano mesoporous silica. *Chemical Engineering Journal, 153*(1-3), 70-79. doi:10.1016/j.cej.2009.06.016

Idris, S. A., Davidson, C. M., McManamon, C., Morris, M. A., Anderson, P., & Gibson, L. T. (2011). Large pore diameter MCM-41 and its application for lead removal from aqueous media. *Journal of Hazardous Materials, 185*(2-3), 898-904. doi:10.1016/j.jhazmat.2010.09.105

Kaewbuddee, C., Chanpiwat, P., Kidkhunthod, P., & Wantala, K. (2016). Lead Adsorption Behaviours on Nanoscale Zero Valent Irons (nZVI) Coupled with Rice Husk MCM-41. *Sains Malaysiana, 45*(7), 1155-1167.

Kaur, I., Mandiyal, D., Singh, B. P., Kumar, R., & Chawla, J. (2016). Amino-functionalized mesoporous MCM-41: an efficient adsorbent for the removal of chromium (III) ions from aqueous solution. *Journal of Water Supply Research and Technology-Aqua, 65*(6), 480-493. doi:10.2166/aqua.2016.118

Kuster, C., Reinhardt, B., Froba, M., & Enke, D. (2014). Silica-Based Nanoporous Materials. *Zeitschrift Fur Anorganische Und Allgemeine Chemie, 640*(3-4), 565-569. doi:10.1002/zaac.201300456

Lu, H. F., Qiao, X. L., Wang, W., Tan, F. T., Xiao, Z. Q., & Chen, J. G. (2016). Facile preparation of mesoporous silica/nano zero-valent iron composite for Pb(II) removal from aqueous solution. *Desalination and Water Treatment, 57*(23), 10745-10756. doi:10.1080/19443994.2015.1040851

Mathew, A., Parambadath, S., Kim, S. Y., Park, S. S., & Ha, C. S. (2015). Adsorption of Cr(III) ions using 2-(ureylenemethyl)pyridine functionalized MCM-41. *Journal of Porous Materials, 22*(3), 831-842. doi:10.1007/s10934-015-9956-2

Mehdinia, A., Akbari, M., Kayyal, T. B., & Azad, M. (2015). High-efficient mercury removal from environmental water samples using di-thio grafted on magnetic mesoporous silica

nanoparticles. *Environmental Science and Pollution Research, 22*(3), 2155-2165. doi:10.1007/s11356-014-3430-6

Melde, B. J., Johnson, B. J., & Charles, P. T. (2008). Mesoporous silicate materials in sensing. *Sensors, 8*(8), 5202-5228. doi:10.3390/s8085202

Parida, K., Mishra, K. G., & Dash, S. K. (2012). Adsorption of toxic metal ion Cr(VI) from aqueous state by TiO2-MCM-41: Equilibrium and kinetic studies. *Journal of Hazardous Materials, 241*, 395-403. doi:10.1016/j.jhazmat.2012.09.052

Prasomsri, T., Jiao, W. Q., Weng, S. Z., & Martinez, J. G. (2015). Mesostructured zeolites: bridging the gap between zeolites and MCM-41. *Chemical Communications, 51*(43), 8900-8911. doi:10.1039/c4cc10391b

Prelot, B., Einhorn, V., Marchandeau, F., Douillard, J. M., & Zajac, J. (2012). Bulk hydrolysis and solid-liquid sorption of heavy metals in multi-component aqueous suspensions containing porous inorganic solids: Are these mechanisms competitive or cooperative? *Journal of Colloid and Interface Science, 386*, 300-306. doi:10.1016/j.jcis.2012.07.045

Puanngam, M., & Unob, F. (2008). Preparation and use of chemically modified MCM-41 and silica gel as selective adsorbents for Hg(II) ions. *Journal of Hazardous Materials, 154*(1-3), 578-587. doi:10.1016/j.jhazmat.2007.10.090

Raji, F., & Pakizeh, M. (2013). Study of Hg(II) species removal from aqueous solution using hybrid $ZnCl_2$-MCM-41 adsorbent. *Applied Surface Science, 282*, 415-424. doi:10.1016/j.apsusc.2013.05.145

Raji, F., & Pakizeh, M. (2014). Kinetic and thermodynamic studies of Hg(II) adsorption onto MCM-41 modified by $ZnCl_2$. *Applied Surface Science, 301*, 568-575. doi:10.1016/j.apsusc.2014.02.136

Raji, F., Pakizeh, M., Saraeian, A., & Raji, M. (2016). A detailed study on adsorption isotherms of Hg(II) removal from aqueous solutions using nanostructured sorbent $ZnCl_2$-MCM-41. *Desalination and Water Treatment, 57*(40), 18694-18709. doi:10.1080/19443994.2015.1091997

Raji, F., Saraeian, A., Pakizeh, M., & Attarzadeh, F. (2015). Removal of Pb(II) from aqueous solution by mesoporous silica MCM-41 modified by $ZnCl_2$: kinetics, thermodynamics, and isotherms. *Rsc Advances, 5*(46), 37066-37077. doi:10.1039/c5ra01192b

Saad, A., Bakas, I., Piquemal, J. Y., Nowak, S., Abderrabba, M., & Chehimi, M. M. (2016). Mesoporous silica/polyacrylamide composite: Preparation by UV-graft

photopolymerization, characterization and use as Hg(II) adsorbent. *Applied Surface Science, 367*, 181-189. doi:10.1016/j.apsusc.2016.01.134

Saman, N., Johari, K., & Mat, H. (2014). Synthesis and characterization of sulfur-functionalized silica materials towards developing adsorbents for mercury removal from aqueous solutions. *Microporous and Mesoporous Materials, 194*, 38-45. doi:10.1016/j.micromeso.2014.03.036

Samiey, B., Cheng, C. H., & Wu, J. N. (2014). Organic-Inorganic Hybrid Polymers as Adsorbents for Removal of Heavy Metal Ions from Solutions: A Review. *Materials, 7*(2), 673-726. doi:10.3390/ma7020673

Sattari, E., Moazzen, E., Amini, M. M., Ebrahimzadeh, H., & Heravi, M. R. P. (2013). Chromate Removal Using Novel Modified MCM-41 Nanoporous Silica: Synthesis and Characterization of Novel Terpyridine-Modified MCM-41. *Acta Chimica Slovenica, 60*(1), 124-130.

Showkat, A. M., Zhang, Y. P., Kim, M. S., Gopalan, A. I., Reddy, K. R., & Lee, K. P. (2007). Analysis of heavy metal toxic ions by adsorption onto amino-functionalized ordered mesoporous silica. *Bulletin of the Korean Chemical Society, 28*(11), 1985-1992.

Tao, S. Y., Wang, C., Ma, W., Wu, S. O., & Meng, C. G. (2012). Designed multifunctionalized magnetic mesoporous microsphere for sequential sorption of organic and inorganic pollutants. *Microporous and Mesoporous Materials, 147*(1), 295-301. doi:10.1016/j.micromeso.2011.06.027

Tavakoli, H., Sepehrian, H., & Cheraghali, R. (2013). Encapsulation of nanoporous MCM-41 in biopolymeric matrix of calcium alginate and its use as effective adsorbent for lead ions: Equilibrium, kinetic and thermodynamic studies. *Journal of the Taiwan Institute of Chemical Engineers, 44*(3), 343-348. doi:10.1016/j.jtice.2012.11.019

Tian, L., Xie, G., Li, R. X., Yu, X. H., & Hou, Y. Q. (2011). Removal of Cr (VI) from aqueous solution using MCM-41. *Desalination and Water Treatment, 36*(1-3), 334-343. doi:10.5004/dwt.2011.2521

Wei, L. G., Zhang, H. S., Dong, Y. L., Song, W. N., Liu, X. X., & Zhao, Z. F. (2016). Synthesis and characterization of MCM-49/MCM-41 composite molecular sieve: an effective adsorbent for chromate from water. *Rsc Advances, 6*(75), 71375-71383. doi:10.1039/c6ra13100j

Wu, S. J., Li, F. T., Xu, R., Wei, S. H., & Li, G. T. (2010). Synthesis of thiol-functionalized MCM-41 mesoporous silicas and its application in Cu(II), Pb(II), Ag(I), and Cr(III) removal. *Journal of Nanoparticle Research, 12*(6), 2111-2124. doi:10.1007/s11051-009-9770-3

Wu, Y. H., Yang, S. X., Zhang, M. L., Aierken, A., & Wu, Y. Y. (2015). Abatement of Cr(VI) and As(III) by MnO2 loaded MCM-41 in wastewater treatment. *Korean Journal of Chemical Engineering, 32*(8), 1667-1677. doi:10.1007/s11814-014-0352-4

Zhai, Q. Z., Hu, W. H., & Guo, X. Y. (2016). ADSORPTIVE PERFORMANCE OF MCM-41 TOWARDS Hg(II) IN WATER. ADSORPTION AND DESORPTION STUDIES. *Environment Protection Engineering, 42*(1), 5-15. doi:10.5277/epe160101

Zhao, H. L., Hong, T., Lan, M. B., Wang, W. J., Zheng, S. J., & Liu, B. Z. (2013). Preparation and Characterization of Organic-Functionalized Mesoporous Silica as Heavy Metal Adsorbents. *Journal of Nanoscience and Nanotechnology, 13*(2), 1295-1299. doi:10.1166/jnn.2013.5971

APPENDIX

Pb Adsorption Experiment Data

Pb Calibration

The lead adsorption concentration was calculated by taking the initial concentration and the final concentration at definite time intervals using an ISE lead electrode. The electrode calibration was done before taking measurements of the voltage of the solutions by the electrode. The following data shows the calibration data, graphs and the concentration calculations from the respective calibration curve equations.

For solution concentration of 0.1M:

Molecular mass of (Pb $(NO3)_2$) = 331.2 grams/moles

a. Mass required to prepare 350 ml as final volume for 0.1M solution of lead from lead nitrate (Pb $(NO3)_2$)

   Molecular weight (M.W) of lead nitrate= 331.2 grams/moles

   For 0.1M Pb^{2+} solution (350 ml volume), lead nitrate required= M.W of Pb $(NO_3)_2$

   Molarity of the solution (M) x Total volume of the final solution in liters (V)

   =331.2 g/moles x 0.1M x 0.35 L

   =331.2 g/moles x 0.1 moles/L x 0.35 L = 11.592 grams Pb $(NO_3)_2$

b. Preparation of other dilutions for lead calibration

   Other standards for the calibration of ISE electrode was done by using series dilution from the prepared 0.1M standard of Pb (II) solution. Tables 77 shows the dilution of the standard for preparation of different concentrations of lead solutions using the formula $\mathbf{C_1V_1=C_2V_2}$.

Where,

C_1= Concentration of the standard solution 0.1M Pb (II)

V_1= Volume of the standard solution 0.1M Pb (II) used

C_2= Concentration of the final solution of Pb (II)

V_2= Volume of the final solution of Pb (II) to be prepared

To prepare 30 mL 0.01M Pb (II) solution, the volume required of 0.1M Pb (II) was calculated as:

$C_1V_1=C_2V_2$

(0.1M) * (V_1) = (0.01M) * (100 mL)

V_1= 10.0 mL of 0.1M Pb (II)

From this solution, solutions with lower concentrations were prepared.

Table 77 Series Dilution for lead solutions

Solutions #	Concentration (M) of final solution	Volume (V_1) of 0.01M Pb required (mL)
1	1.00E-02	30
2	7.00E-03	21
3	5.00E-03	15
4	4.00E-03	12
5	2.00E-03	6
6	1.00E-03	3
7	5.00E-04	1.5
8	2.00E-04	0.6
9	1.00E-04	0.3
10	5.00E-05	0.15
11	2.00E-05	0.06
12	1.00E-05	0.03

Calibration Data for lead electrode

Lead calibration reading for experiments with 0.001M Pb (II) adsorbed by MCM-41 and $ZnCl_2$-MCM-41 were taken at initially, and then at different time intervals for the goal of taking more accurate readings after a long interval. Tables 78 to 85 show the calibration data for lead electrode taken at different time intervals.

Calculation of the lead concentration from the linear equation in the graph

y = -24.248x - 157.41 from Figure 115 for initial calibration of lead electrode

where, y= milli-volt detected (mv) in electrode

and x= -Log of lead conc. (M)

so, for calculating the concentration for the first reading at 0 minutes in Table 79.

x = (-230+157.41)/ (-24.248)

-Log conc. (M) $_{\text{at 0 min}}$ = (-230+157.41)/ (-24.248)

so, Conc. (M) $_{\text{at 0 min}}$ = 10^- ((-230+157.41)/ (-24.248)) = **0.001015 M**

All the other calculations were done accordingly in MS Excel spreadsheet. The concentrations calculated from two samples for each sample were averaged, and presented in the results section.

Calibration for 0.001M Pb (II)

Table 78 Calibration data for lead electrode					
Solutions #	Molar Concentration (M)	-Log 10 of conc (M)	Initial Reading (mV)	Reading for 2 hours (mV)	Reading for 24 hours (mV)
1	1.00E-02	2.00	-207	-198	-204
2	7.00E-03	2.15	-211	-201	-207
3	5.00E-03	2.30	-213	-205	-211
4	4.00E-03	2.40	-215	-207	-213
5	2.00E-03	2.70	-222	-214	-220
6	1.00E-03	3.00	-228	-220	-228
7	5.00E-04	3.30	-237	-228	-233
8	2.00E-04	3.70	-247	-237	-244
9	1.00E-04	4.00	-255	-247	-252
10	5.00E-05	4.30	-264	-253	-262
11	2.00E-05	4.70	-271	-256	-268
12	1.00E-05	5.00	-278	-258	-274

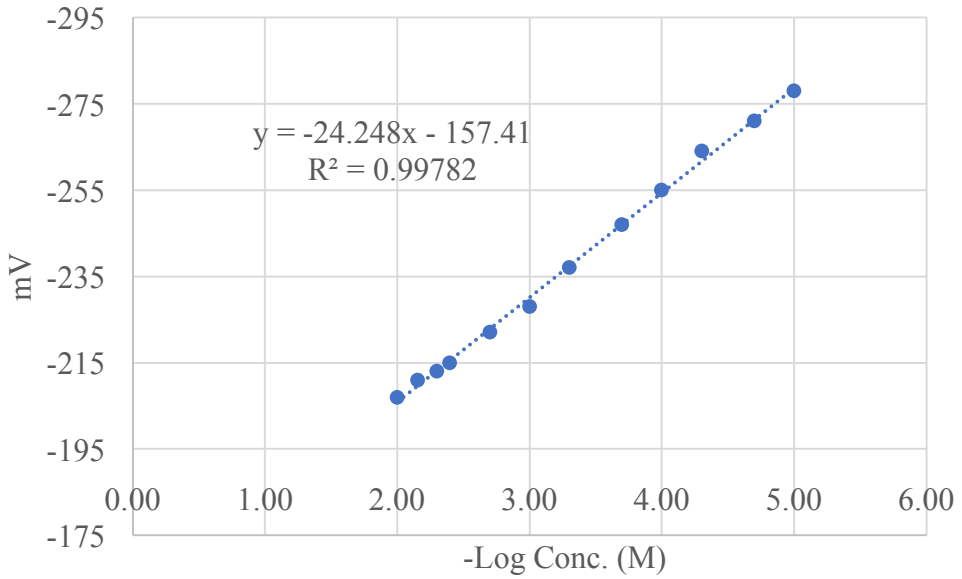

Figure 115 Initial Calibration curve for lead

Initial concentration of Lead= 0.001M; Adsorbent used= 0.15 mg/30 mL Pb (II)

Table 79 Sample 1: Electrode measurements for 0.001M Pb (II)				
Time (min)	Adsorption with MCM-41		Adsorption with $ZnCl_2$-MCM-41	
	mV Reading	Concentration (M)	mV Reading	Concentration (M)
0	-230	0.001015	-230	0.001015
10	-231	0.000923	-230	0.001015
20	-231	0.000923	-231	0.000923
30	-232	0.000839	-229	0.001116
40	-234	0.000694	-231	0.000923
50	-233	0.000763	-232	0.000839
60	-235	0.000631	-231	0.000923
120	-234	0.000694	-232	0.000839
180	-233	0.000763	-231	0.000923
300	-235	0.000631	-230	0.001015
24 hours	-236	0.000574	-231	0.000923
48 hours	-236	0.000574	-232	0.000839

Table 80 Sample 1: Electrode measurements for 0.001M Pb (II)

	Adsorption with MCM-41		Adsorption with $ZnCl_2$-MCM-41	
Time (min)	mV Reading	Concentration (M)	mV Reading	Concentration (M)
0	-230	0.001015	-230	0.001015
10	-231	0.000923	-230	0.001015
20	-231	0.000923	-231	0.000923
30	-232	0.000839	-231	0.000923
40	-234	0.000694	-232	0.000839
50	-233	0.000763	-232	0.000839
60	-235	0.000631	-233	0.000763
120	-234	0.000694	-232	0.000839
180	-233	0.000763	-235	0.000631
300	-235	0.000631	-235	0.000631
24 hours	-236	0.000574	-237	0.000522
48 hours	-236	0.000574	-238	0.000475

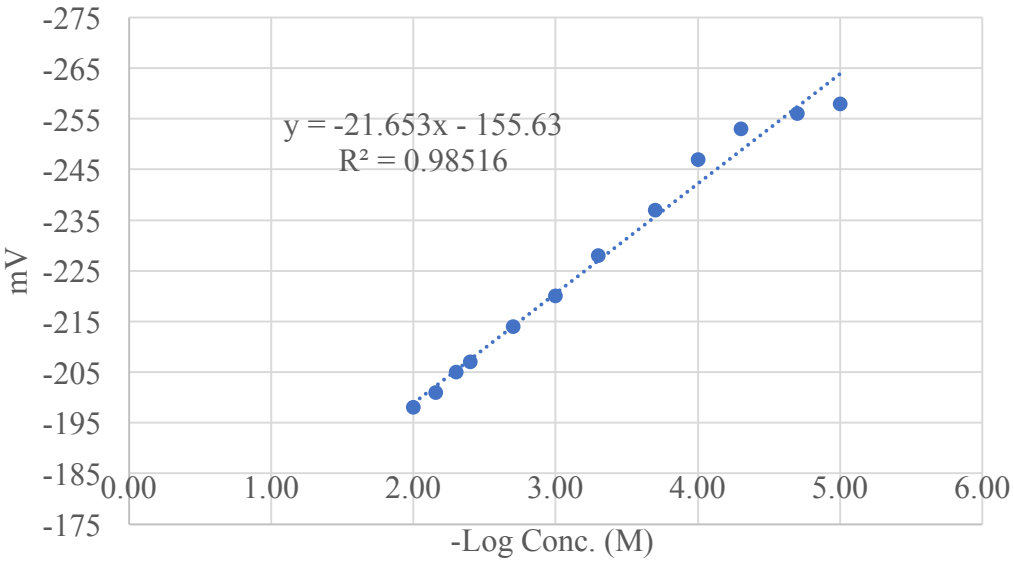

Figure 116 Initial Calibration curve for lead (taken before taking 2 hours reading)

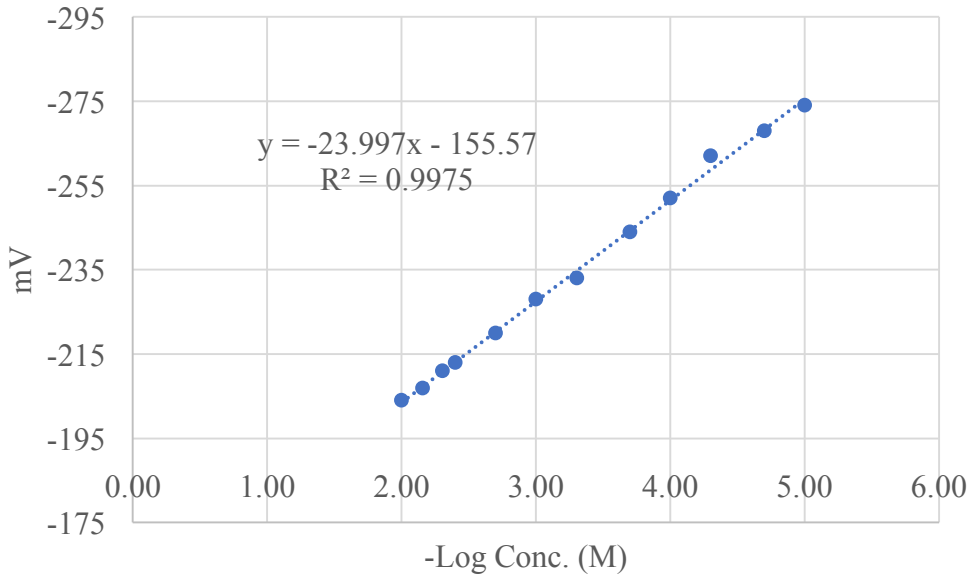

Figure 117 Initial Calibration curve for lead (taken before taking 24 hours reading)

For 0.01M Pb (II) calculations

Table 81 Sample 1: Lead electrode calibration for 0.01M Pb (II)

Molar Conc. (M)	Initial reading (mV)	LOG10	after 30 minutes to 1 hour (mV)	120 minutes (mV)	180 minutes (mV)	5 hours (mV)
1.00E-02	-202	-2.00	-202	-204	-204	-205
7.00E-03	-204	-2.15	-204	-207	-207	-208
5.00E-03	-207	-2.30	-207	-211	-210	-211
4.00E-03	-210	-2.40	-210	-214	-213	-214
2.00E-03	-216	-2.70	-216	-221	-220	-221
1.00E-03	-225	-3.00	-225	-229	-228	-229
5.00E-04	-231	-3.30	-231	-234	-233	-236
2.00E-04	-240	-3.70	-240	-244	-243	-246
1.00E-04	-248	-4.00	-249	-252	-251	-254
5.00E-05	-259	-4.30	-259	-263	-262	-264
2.00E-05	-264	-4.70	-265	-268	-265	-267
1.00E-05	-269	-5.00	-268	-273	-273	-276

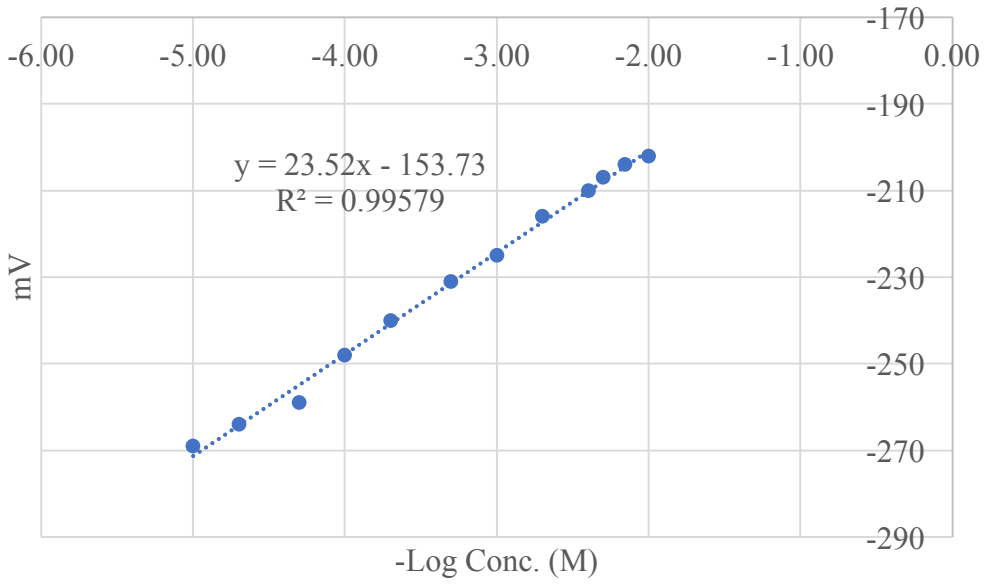

Figure 118 Initial Calibration curve for lead (taken before taking 30 minutes reading)

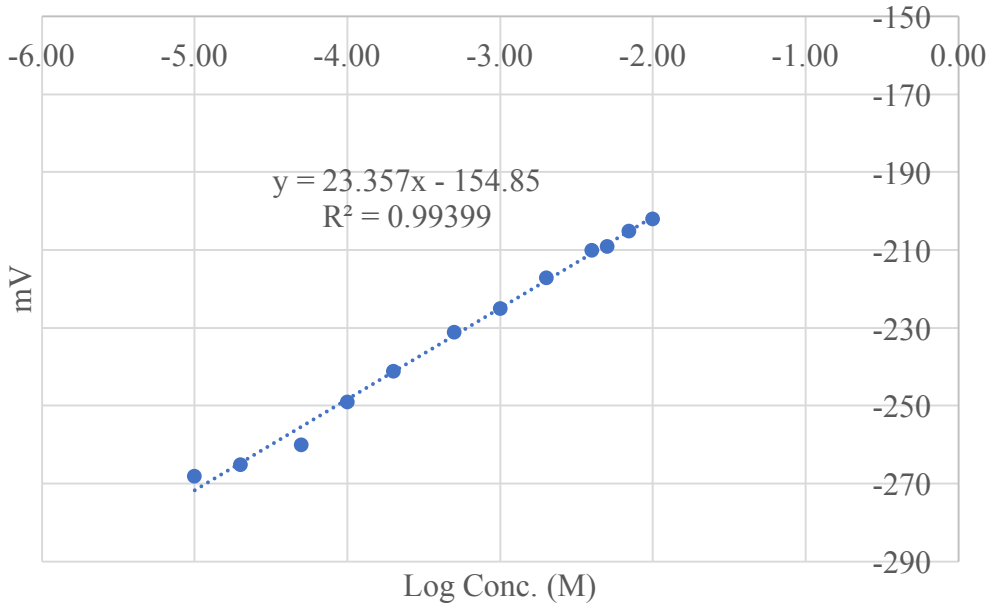

Figure 119 Initial Calibration curve for lead (taken before 1 hour reading)

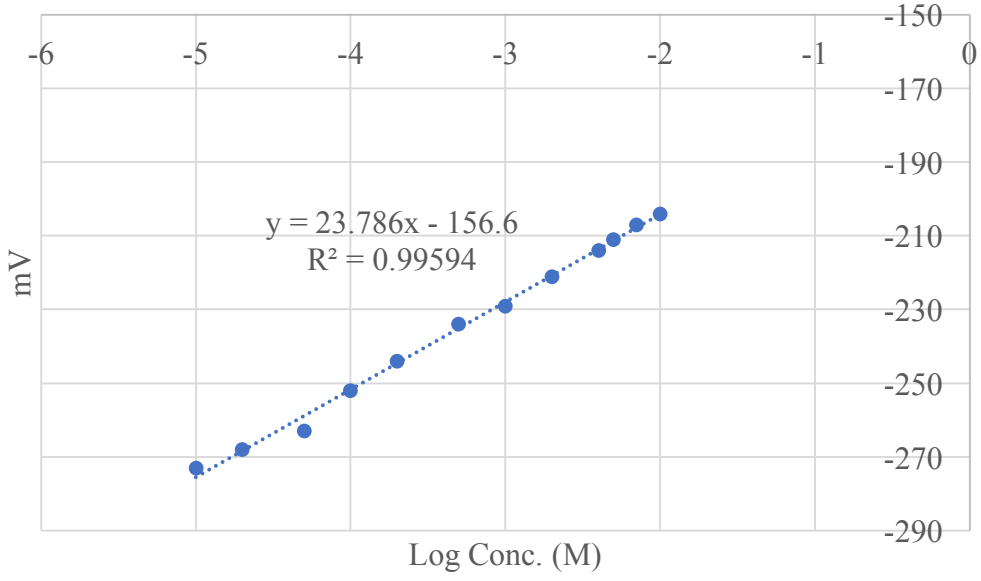

Figure 120 Initial Calibration curve for lead (taken before 120 minutes reading)

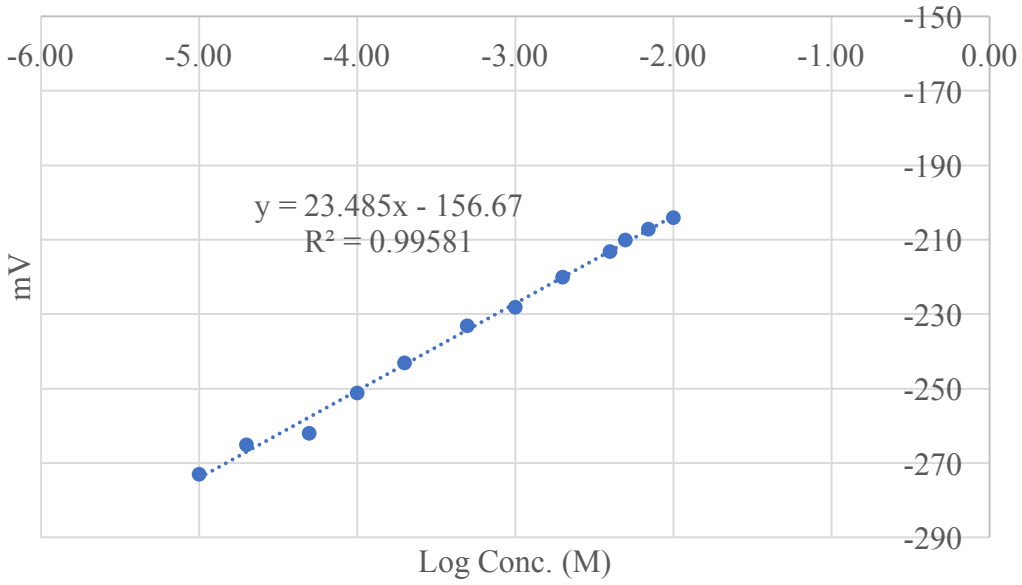

Figure 121 Initial Calibration curve for lead (taken before 180 minutes reading)

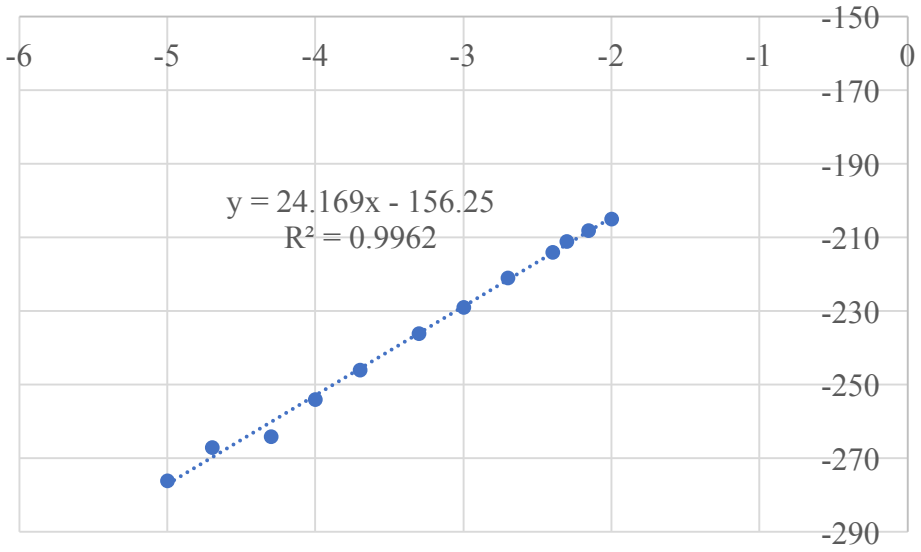

Figure 122 Initial Calibration curve for lead (taken before 300 minutes reading)

For 0.1M Pb (II) electrode measurements

Note: start time for MCM-41/Pb solution is different than $ZnCl_2$-MCM-41/Pb

MCM-41/Pb start time: 30 minutes later

Table 82 Calibration Reading (mV) for adsorption of 0.1M Pb (II) by $ZnCl_2$-MCM-41							
Conc. (M)	**LOG 10 of Conc (M)**	**Initial Reading (mV)**	**40 min (mV)**	**50 min reading (mV)**	**120 min (mV)**	**5 hours (mV)**	**24 hours (mV)**
1.00E-01	-1.00	-177	-172	-174	-173	-174	-174
9.00E-02	-1.05	-180	-175	-176	-177	-177	-177
8.00E-02	-1.10	-183	-176	-178	-179	-179	-179
6.00E-02	-1.22	-186	-179	-182	-183	-181	-181
4.00E-02	-1.40	-190	-183	-186	-188	-187	-187
2.00E-02	-1.70	-195	-189	-193	-192	-190	-191
1.00E-02	-2.00	-201	-194	-198	-196	-195	-195
5.00E-03	-2.30	-206	-198	-203	-201	-200	-201
2.00E-03	-2.70	-214	-208	-213	-209	-208	-208
1.00E-03	-3.00	-218	-211	-216	-211	-211	-211
5.00E-04	-3.30	-222	-217	-223	-216	-216	-216
2.00E-04	-3.70	-229	-232	-232	-222	-221	-221
1.00E-04	-4.00	-235	-235	-241	-225	-226	-226
Equation from graph		y = 18.292x - 162.72	y = 20.165x - 153.47	y = 20.98x - 155.22	y = 16.987x - 160.96	y = 16.639x - 160.88	y = 16.611x - 161.09

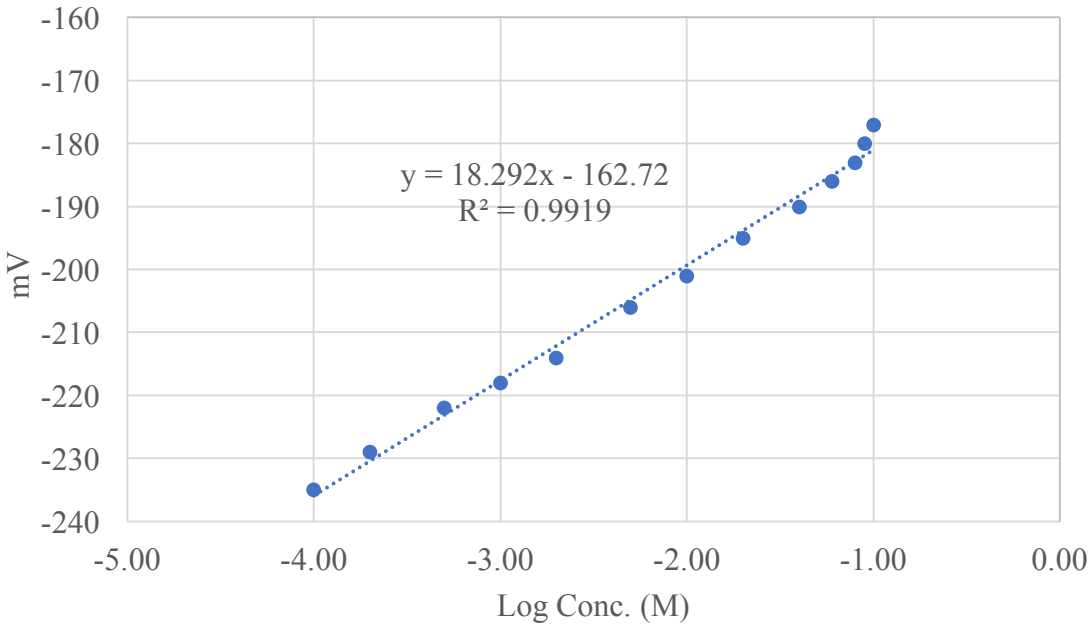

Figure 123 Initial Calibration curve for lead

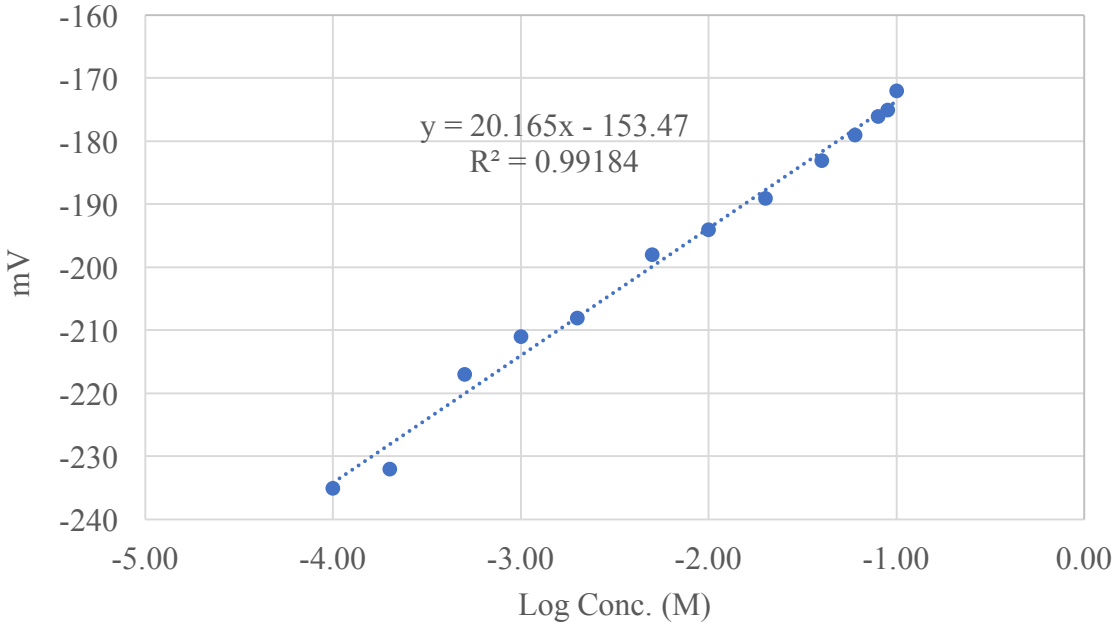

Figure 124 Calibration curve for lead (before taking 40 minutes reading)

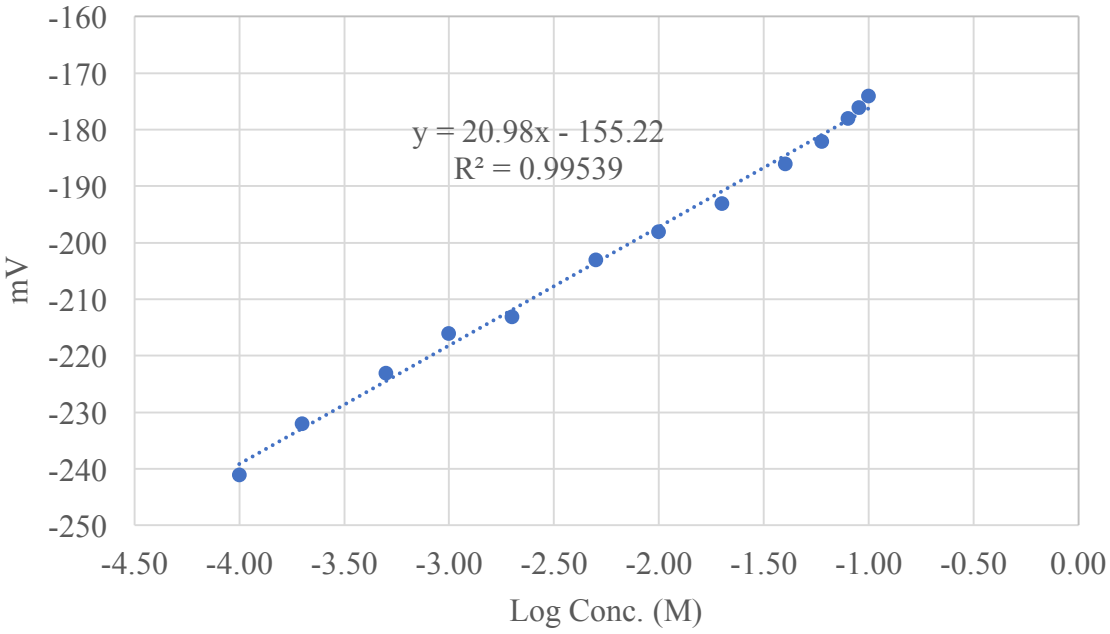

Figure 125 Calibration curve for lead (before taking 50 & 80 minutes reading)

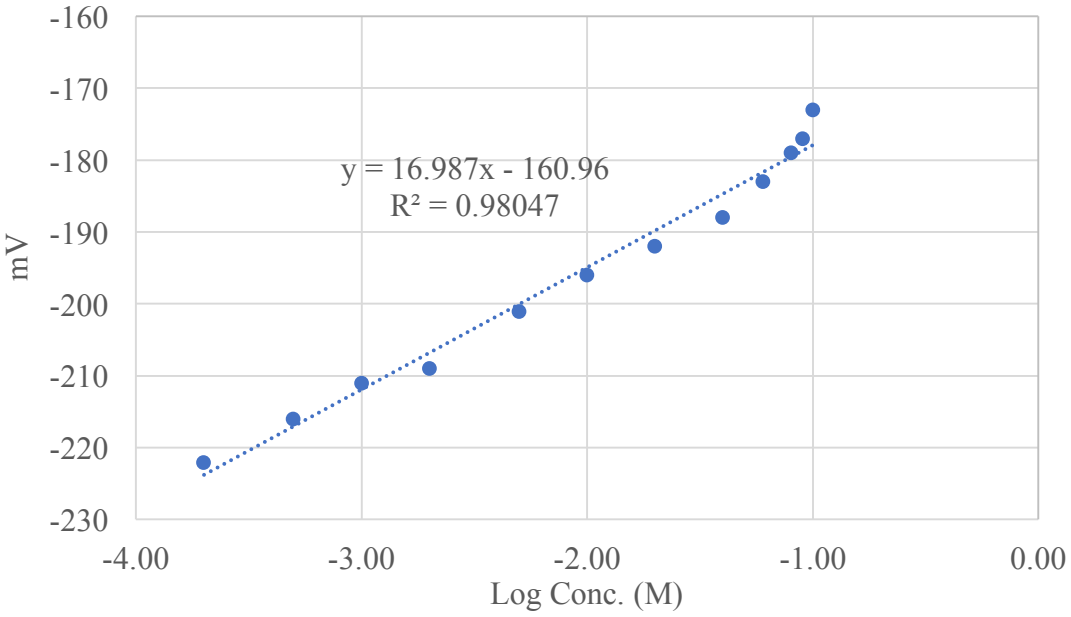

Figure 126 Calibration curve for lead (before taking 120 minutes reading)

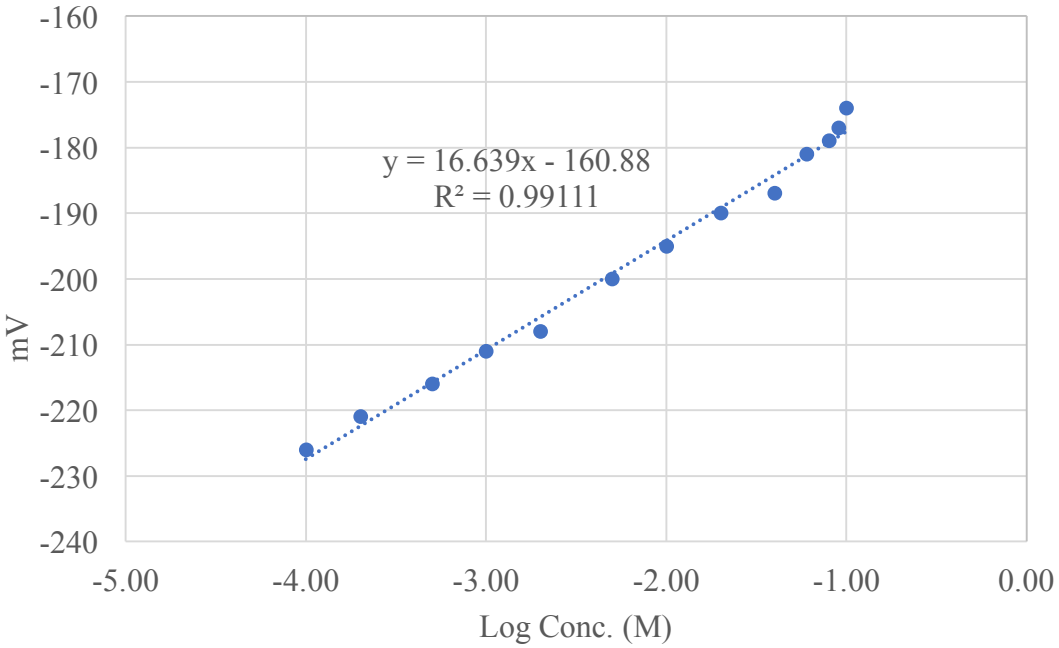

Figure 127 Calibration curve for lead (before taking 300 minutes reading)

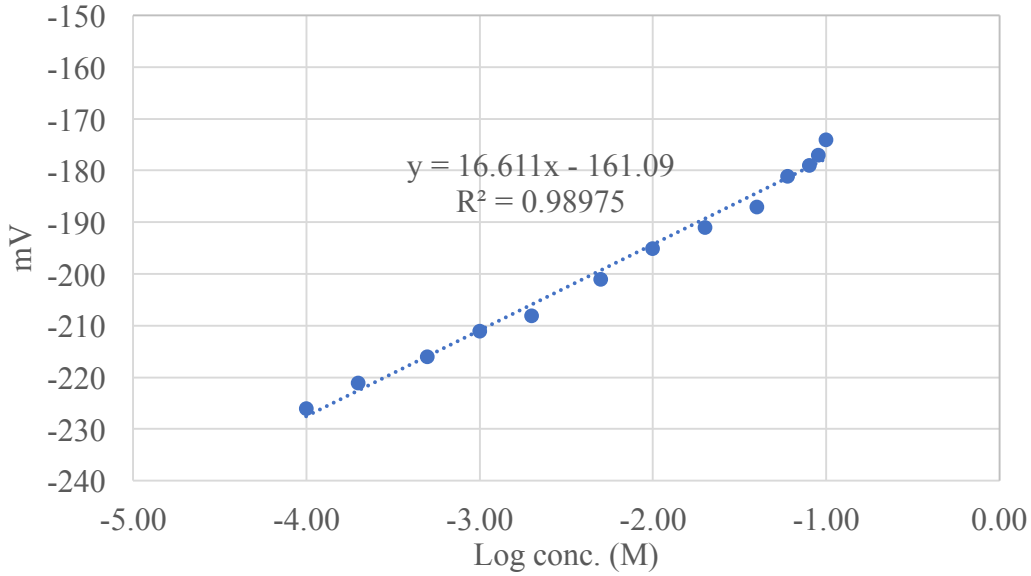

Figure 128 Calibration curve for lead (before taking 24 hours reading)

Table 83 Electrode measurement for adsorption of 0.1M Pb (II) by $ZnCl_2$-MCM-41					
Equations used from graphs	**Time (min)**	**mV reading**	**Conc. (M)**	**mV reading**	**Con. (M)**
		Sample 1		Sample 2	
y = 18.292x - 162.72	0	-181	1.002E-01	-180	1.14E-01
y = 18.292x - 162.72	10	-181	1.002E-01	-180	1.14E-01
y = 18.292x - 162.72	20	-183	7.786E-02	-183	7.79E-02
y = 18.292x - 162.72	30	-182	8.831E-02	-182	8.83E-02
y = 20.165x - 153.47	40	-175	8.557E-02	-176	7.63E-02
y = 17.789x - 157.05	50	-178	6.075E-02	-178	6.64E-02
y = 17.789x - 157.05	60	-179	5.836E-02	-179	5.84E-02
y = 17.789x - 157.05	80	-179	5.836E-02	-179	5.84E-02
y = 16.987x - 160.96	120	-179	8.670E-02	-180	7.57E-02
y = 16.639x - 160.88	300	-181	6.177E-02	-181	6.18E-02
y = 16.611x - 161.09	24 hrs	-182	5.511E-02	-182	5.511E-02

Table 84 Calibration of Lead electrode for adsorption of 0.1M Pb (II) by MCM-41					
Conc. (M)	**Log Conc (M)**	**0-50 min (mV)**	**60 & 80 min (mV)**	**120 min (mV)**	**300 min (mV)**
1.00E-01	-1.00	-171	-164	-174	-174
9.00E-02	-1.05	-175	-169	-177	-177
8.00E-02	-1.10	-176	-171	-179	-179
6.00E-02	-1.22	-179	-174	-181	-181
4.00E-02	-1.40	-183	-176	-187	-187
2.00E-02	-1.70	-189	-183	-190	-190
1.00E-02	-2.00	-194	-187	-195	-195
5.00E-03	-2.30	-198	-192	-200	-201
2.00E-03	-2.70	-208	-195	-208	-208
1.00E-03	-3.00	-211	-198	-211	-211
5.00E-04	-3.30	-217	-201	-216	-216
2.00E-04	-3.70	-232	-207	-221	-221
1.00E-04	-4.00	-235	-210	-226	-226
Equation		y = 20.253x - 153.2	y = 14.07x - 155.89	y = 16.639x - 160.88	y = 16.648x - 160.94

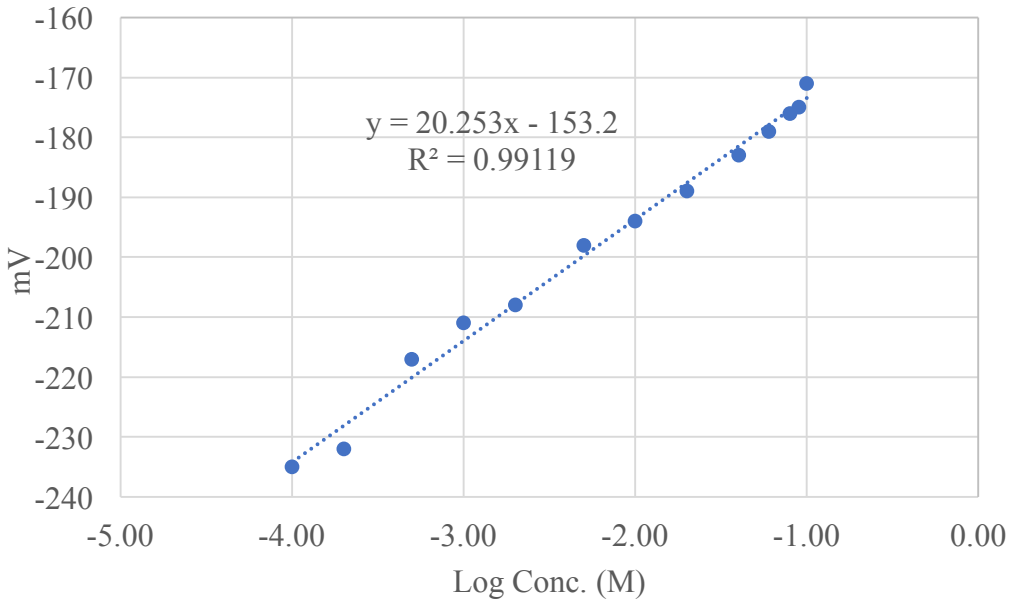

Figure 129 Initial Calibration curve for lead

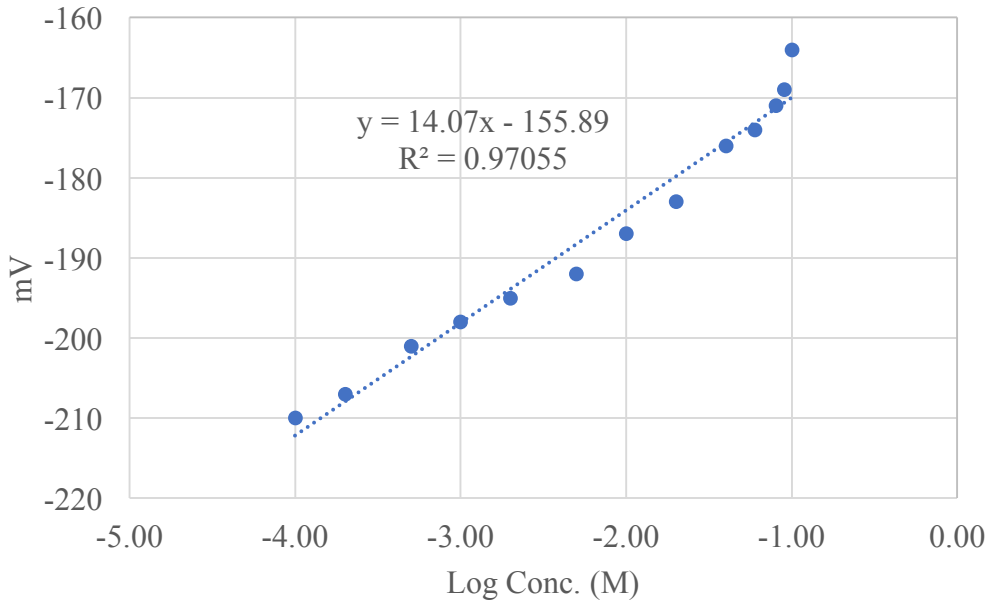

Figure 130 Calibration curve for lead (taken before 1 hour reading)

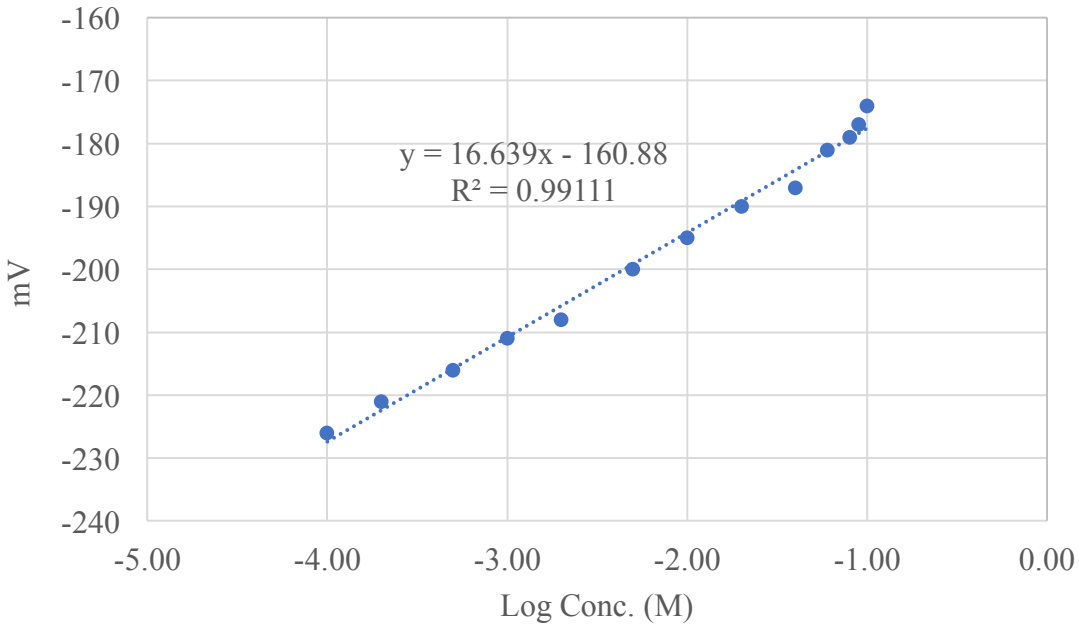

Figure 131 Calibration curve for lead (taken before 120 minutes reading)

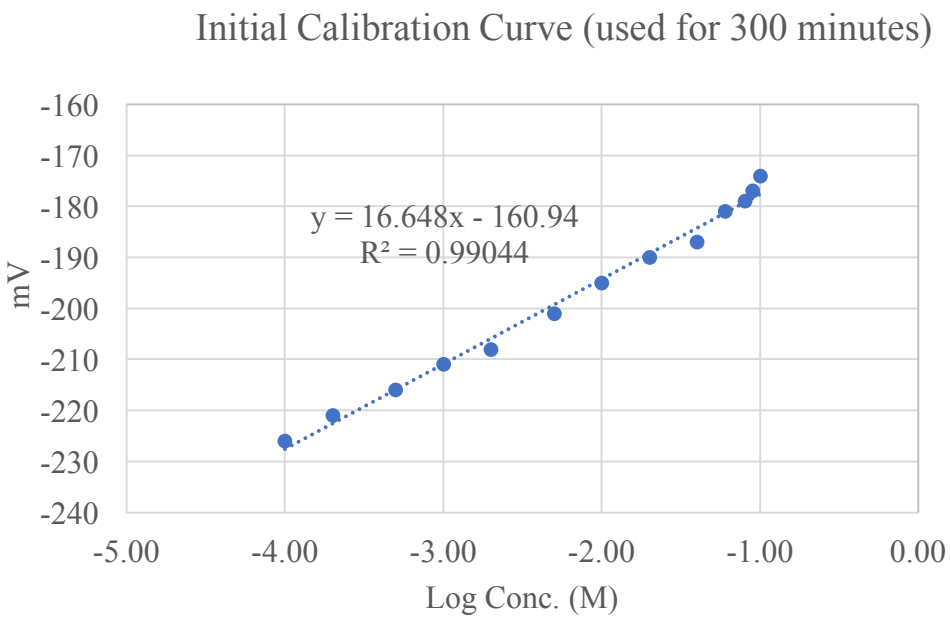

Figure 132 Calibration curve for lead (taken before 300 minutes reading)

Table 85 Electrode measurement for adsorption of 0.1M Pb (II) by MCM-41					
Equations used from graphs	**Time (min)**	**mV reading**	**Conc. (M)**	**mV reading**	**Con. (M)**
		Sample 1		Sample 2	
y= 20.253x - 153.2	0	-171	1.322E-01	-171	1.322E-01
y= 20.253x - 153.2	10	-172	1.180E-01	-172	1.180E-01
y= 20.253x - 153.2	20	-173	1.053E-01	-172	1.180E-01
y= 20.253x - 153.2	30	-177	6.681E-02	-176	7.486E-02
y= 20.253x - 153.2	40	-176	7.486E-02	-174	9.397E-02
y= 20.253x - 153.2	50	-176	7.486E-02	-175	8.387E-02
y = 14.07x - 155.89	60	-169	9.00E-02	-169	9.00E-02
y = 14.07x - 155.89	80	-170	9.935E-02	-170	9.935E-02
y = 16.639x - 160.88	120	-171	8.435E-02	-170	9.935E-02
y = 16.648x - 160.94	300	-177	1.085E-01	-176	1.267E-01
y= 20.253x - 153.2	24 hrs	-171	1.322E-01	-171	1.322E-01

Preparation of Calcium, potassium and nitrate solutions

Calcium solutions were made from calcium chloride, potassium solutions and nitrate solutions were prepared from potassium nitrate.

Molecular weight of $CaCl_2$ = 110.98 g/mole

Molecular weight of KNO_3^- = 101.1032 g/mole

a. Mass required to prepare 500 ml as final volume for 0.1M solution of calcium from calcium chloride $CaCl_2$,

   For 0.1M Ca^{2+} solution (500 ml volume), calcium chloride required= M.W of $CaCl_2$

   Molarity of the solution (M) x Total volume of the final solution in liters (V)

   =110.98 g/moles x 0.1M x 0.5 L

   =110.98 g/moles x 0.1 moles/L x 0.5 L = 5.549 grams $CaCl_2$

b. Mass required to prepare 500 ml as final volume for 0.1M solution of potassium and nitrate from potassium nitrate (KNO_3^-),

For 0.1M K^+ and NO_3^- solution (500 ml volume), potassium nitrate required= M.W of KNO_3^- * Molarity of the solution (M) x Total volume of the final solution in liters (V)

=101.1032 g/mole x 0.1M x 0.5 L

=101.1032 g/mole g x 0.1 moles/L x 0.5 L = 4.4044 grams KNO_3^-

The dilution of calcium standard is shown in Table 86. All the other calibration data are shown in Tables 87 to 89.

Table 86 Dilution of 0.1M standard solution for calibration standards to prepare 50 mL of each solution

S.N	Concentration (M)	Vol of 0.1M solution required (mL)	Volume of 0.1M solution in µl	Volume of water required (ml)
1	1.00E-01	50	50000	0
2	5.00E-02	25	25000	25
3	3.00E-02	15	15000	35
4	1.00E-02	5	5000	45
5	5.00E-03	2.5	2500	47.5
6	1.00E-03	1.5	1500	48.5
7	1.00E-03	0.5	500	49.5
8	5.00E-04	0.25	250	49.75
9	1.00E-04	0.05	50	49.95
	Total Volume of 0.1M	**99.8**		

Calibration data for Calcium electrode

Table 87 Calibration data for calcium electrode					
Solutions #	Molar Concentration (M)	-Log Conc. (M)	Initial Reading (mV)	5 hours reading (mV)	For 24 hours reading (mv)
1	1.00E-01	1.00	71.8	71.4	66.3
2	5.00E-02	1.30	66	66	61
3	3.00E-02	1.52	61.2	61.2	55.9
4	1.00E-02	2.00	51.6	51.6	45.9
5	5.00E-03	2.30	43.9	43.9	38.5
6	3.00E-03	2.52	40.1	40.1	35.2
7	1.00E-03	3.00	32.8	32.4	28.5
8	5.00E-04	3.30	25.6	25.6	20.5
9	1.00E-04	4.00	7.9	7.4	2.9

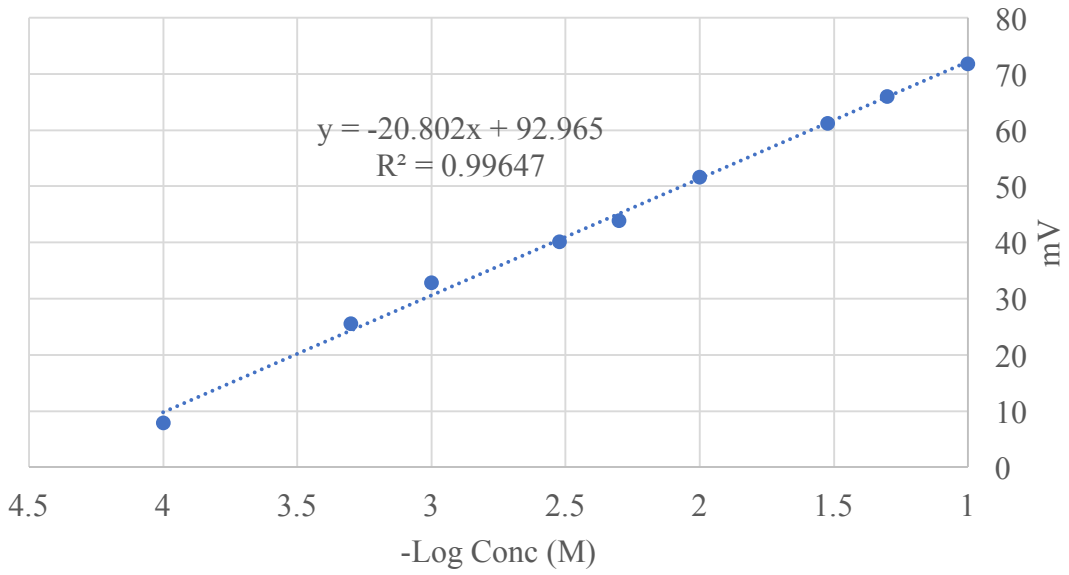

Figure 133 Initial Calibration curve for calcium

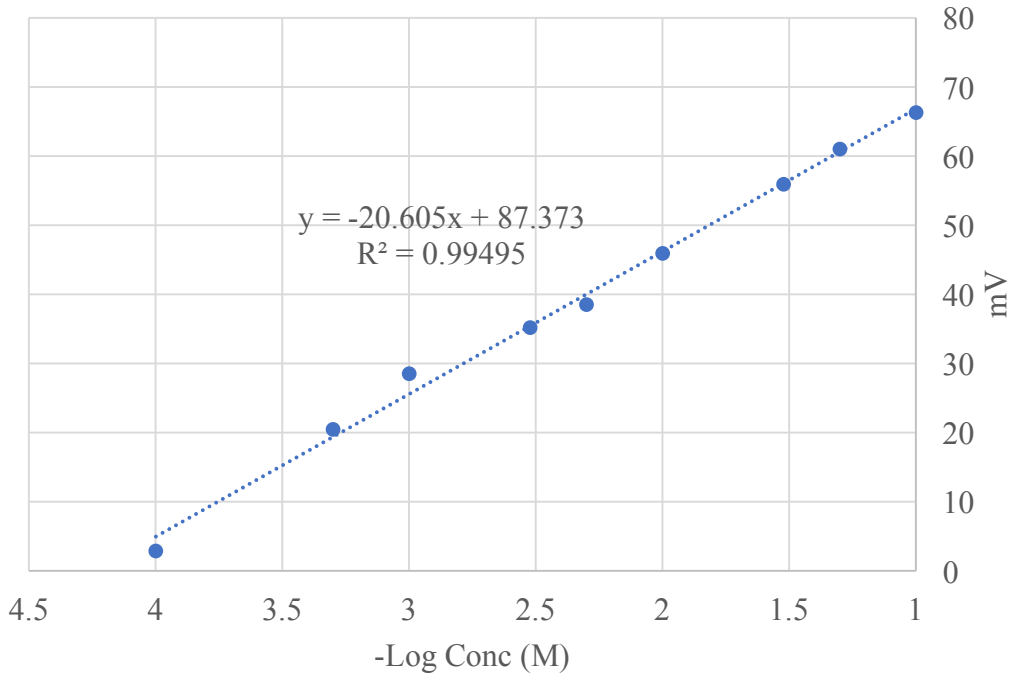

Figure 134 Calibration curve for calcium (for 24 hours)

Calibration reading for Potassium electrode

Table 88 Calibration data for potassium electrode

Solutions #	Molar Conc. (M)	-Log Conc. (M)	Initial Reading (mV)	For readings between 1 hour to 2 hours	5 hours reading (mV)	For 24 hours reading (mv)
1	1.00E-01	1.00	-38.9	-38.4	-37.1	-35.9
2	5.00E-02	1.30	-55.4	-55.4	-54.4	-53.3
3	3.00E-02	1.52	-69.4	-69.4	-69.2	-66.5
4	1.00E-02	2.00	-102.1	-103	-101.4	-99.9
5	5.00E-03	2.30	-122.7	-122.7	-122.2	-119.5
6	3.00E-03	2.52	-137.8	-137.8	-136.8	-133.9
7	1.00E-03	3.00	-166.1	-168.9	-162.4	-161.5
8	5.00E-04	3.30	-189.5	-189.5	-188.5	-183
9	1.00E-04	4.00	-213	-214	-213.1	-205

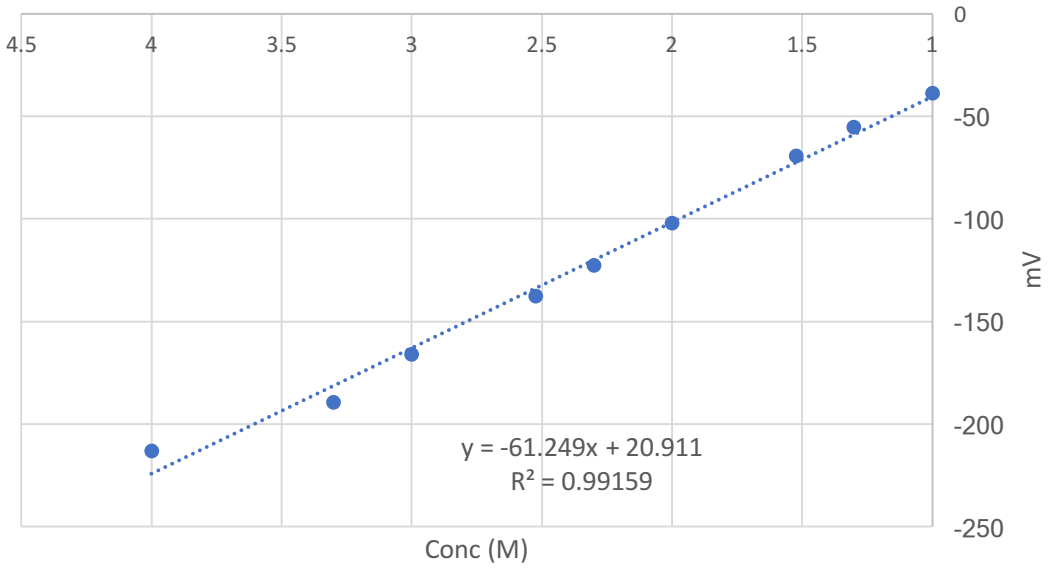

Figure 135 Initial Calibration curve for potassium

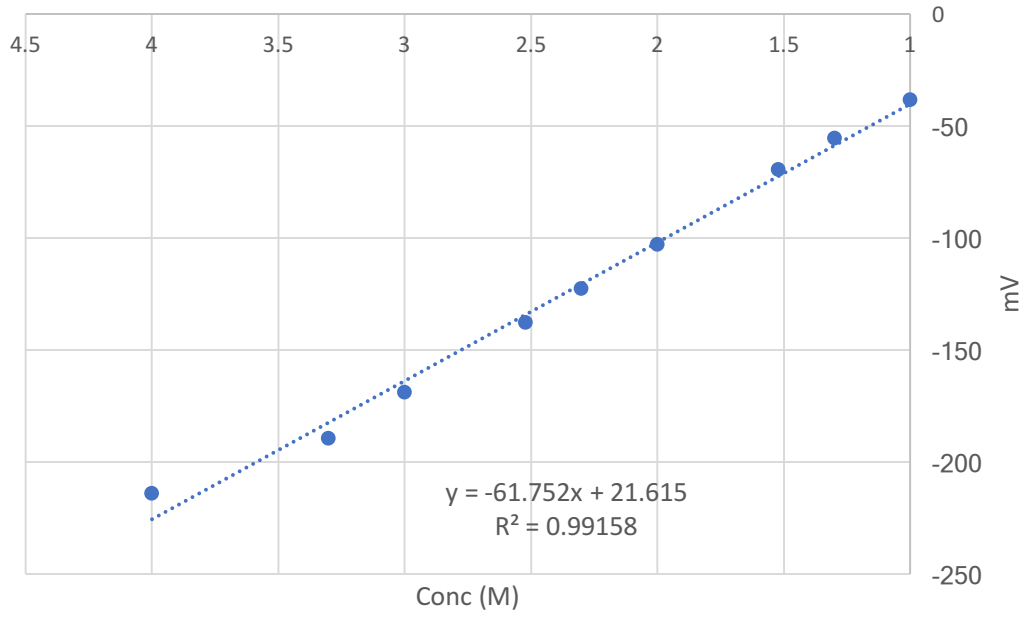

Figure 136 Calibration curve for potassium (for taking 1 hour reading)

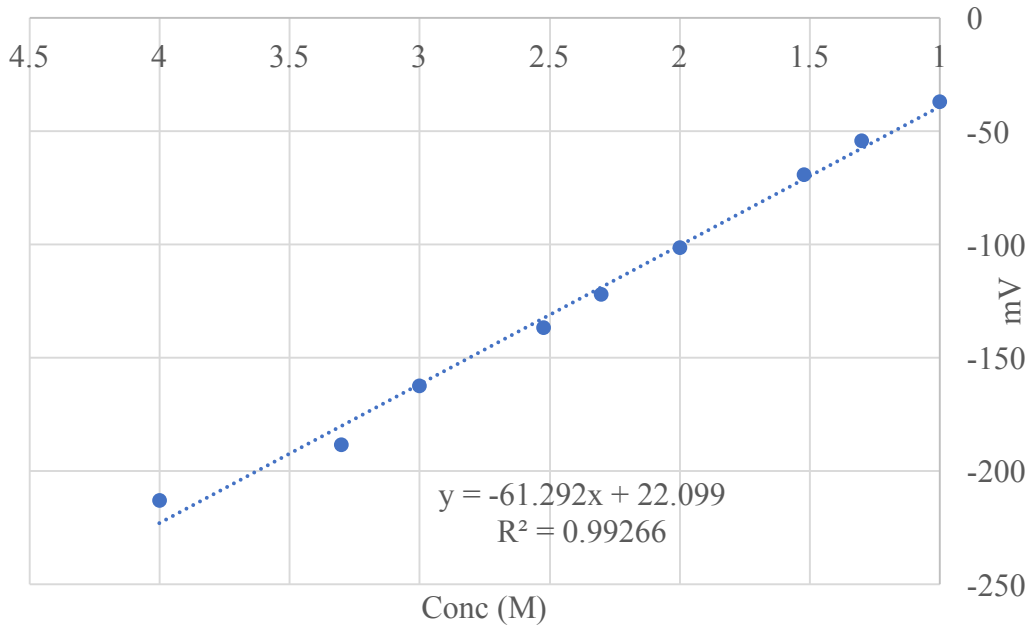

Figure 137 Calibration curve for potassium (for taking 5 hours reading)

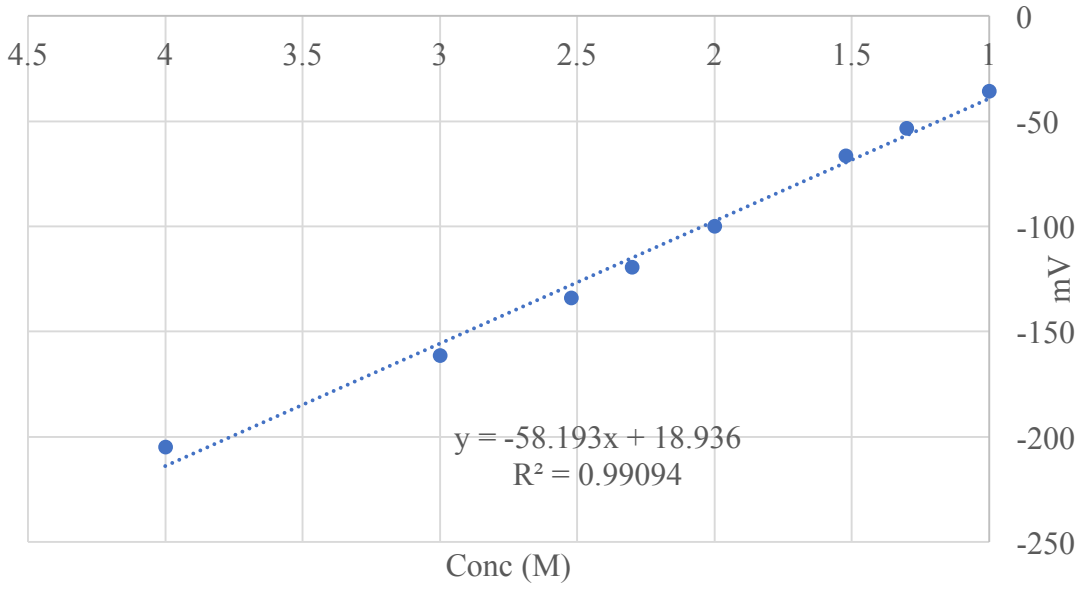

Figure 138 Calibration curve for potassium (for taking 24 hours reading)

Calibration for nitrate electrode

Table 89 Calibration data for nitrate electrode					
Solutions #	Molar Conc (M)	-Log Conc. (M)	Initial Reading (mV)	For 24 hours reading (AC) (mv)	For 24 hours reading (MCM-41) (mv)
1	1.00E-01	1.00	-104	-100.2	-96.3
2	5.00E-02	1.30	-86.4	-82.1	-78.1
3	3.00E-02	1.52	-72.9	-69.1	-64.6
4	1.00E-02	2.00	-43	-38.4	-33.9
5	5.00E-03	2.30	-26.2	-21.5	-16.4
6	3.00E-03	2.52	-11.6	-9.9	-4.3
7	1.00E-03	3.00	11.8	12.4	18.3
8	5.00E-04	3.30	22.6	22.7	24.1
9	1.00E-04	4.00	40.7	39.2	46.3

Calibration Curve graphs for nitrate

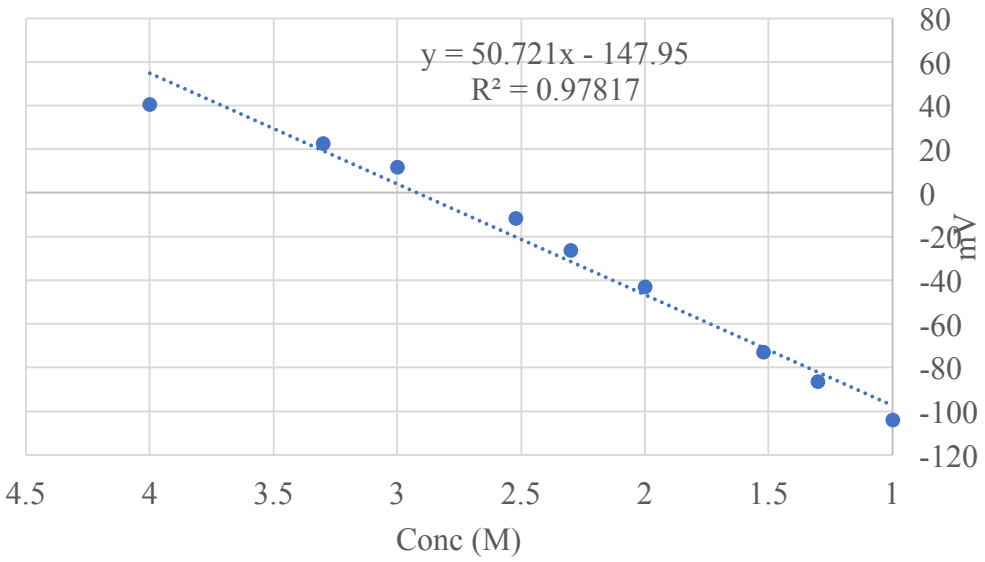

Figure 139 Initial Calibration curve for nitrate

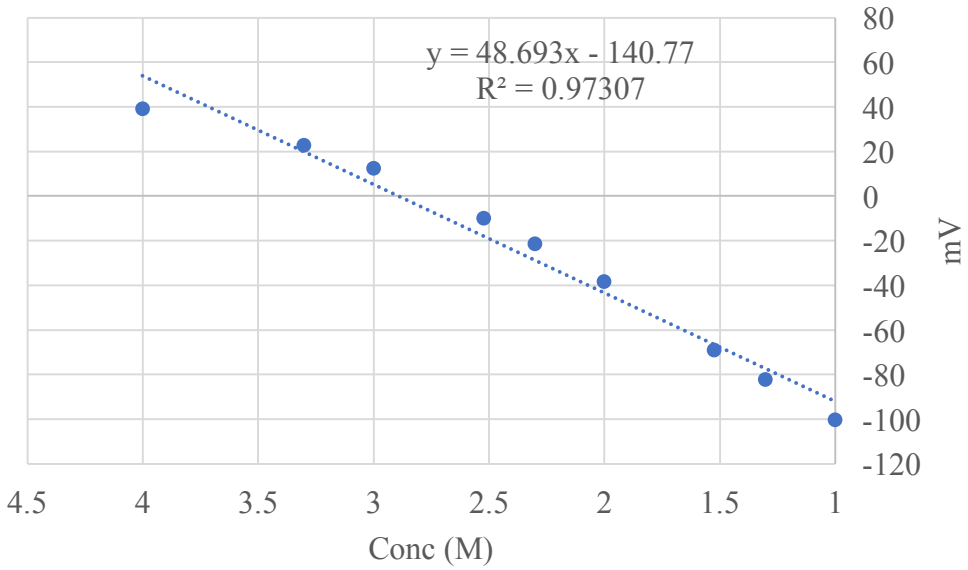

Figure 140 Initial Calibration curve for nitrate (before taking 24 hours reading for samples with MCM-41 & $ZnCl_2$-MCM-41)

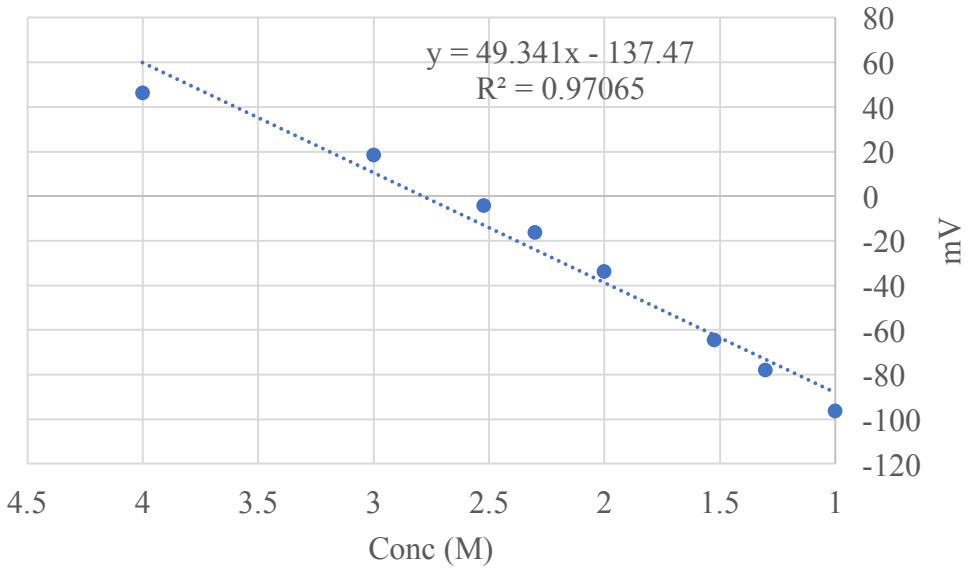

Figure 141 Initial Calibration curve for nitrate (before taking 24 hours reading for samples with AC)

FOR ICP-OES ANALYSIS

ICP-OES (Inductively coupled plasma optical emission spectroscopy) was used to analyze the concentration of different heavy metals after the adsorption.

Preparation of standards and blanks for calibration of ICP-OES

For calibrating the ICP-OES instrument, standard solutions of different heavy metals were prepared.

c. Mass required to prepare 350 ml as final volume for 0.1M solution of lead from lead nitrate ($Pb(NO3)_2$)

   Molecular weight (M.W) of lead nitrate= 331.2 grams/moles

   For 0.1M Pb^{2+} solution (350 ml volume), lead nitrate required= M.W of $Pb(NO_3)_2$ *

   Molarity of the solution (M) x Total volume of the final solution in liters (V)

   =331.2 g/moles x 0.1M x 0.35 L

   =331.2 g/moles x 0.1 moles/L x 0.35 L = 11.592 grams $Pb(NO_3)_2$

d. Mass required to prepare 350 ml for 0.1M solution of mercury from mercuric chloride ($HgCl_2$)

   Molecular weight (M.W) of mercuric chloride = 271.52 grams/moles

   For 0.1M Hg^{2+} solution (350 ml volume), $HgCl_2$ required= M.W of $HgCl_2$ x Molarity of the solution (M) x Total volume of the final solution in liters (V)

   =271.52 g/moles x 0.1M x 0.35 L

   =271.52 g/moles x 0.1 moles/L x 0.35 L = 9.5032 grams $HgCl_2$

e. Mass required to prepare 350 ml for 0.1M solution of chromium from chromium chloride hexahydrate ($CrCl_3$. 6 H_2O)

Molecular weight (M.W) of $CrCl_3$. 6 H_20 = 266.36 grams/moles

For 0.1M Cr^{3+} solution (350 ml volume), $CrCl_3$. 6 H_2O required=

M.W of $CrCl_3$. 6 H_2O x Molarity of the solution (M) x Total volume of the final solution in liters (V)

=266.36 g/moles x 0.1M x 0.35 L

=266.36 g/moles x 0.1 moles/L x 0.35 L = 9.3226 grams $CrCl_3$. 6 H_2O

To prepare a standard 0.1M solution, 11.592 grams of lead nitrate was placed in a 250 ml Erlenmeyer flask with 100 ml of DI water and stirred magnetically until completely dissolved. Similarly, 9.5032 grams of mercuric chloride was placed in a 250 ml Erlenmeyer flask with 100 ml of DI water and magnetically stirred until completely dissolved. And 9.323 grams of chromium chloride hexahydrate was placed in 250 ml Erlenmeyer flask containing 100 ml of DI water, and magnetically stirred until completely mixed. Then all three solutions were mixed together in a 500 ml Erlenmeyer flask and DI water added to the mark of 350 ml to make a 350 ml of 0.1M heavy metals standard solution. This solution was used for all the solutions required for the experiments using combined heavy metals experiment as well as to prepare a calibration standards for ICP-OES analysis, by using series dilution. Table 90 shows the calibration standards volume calculation for the series dilution.

Table 90 Dilution of 0.1M standard solution for calibration standards (50 mL final solution)				
S.N	**Concentration (M)**	**Vol of 0.1M solution required (mL)**	**Volume of 0.1M solution in µl**	**Volume of water required (ml)**
1	1.00E-01	50	50000	0
2	5.00E-02	25	25000	25
3	3.00E-02	15	15000	35
4	1.00E-02	5	5000	45
5	5.00E-03	2.5	2500	47.5
6	1.00E-03	0.5	500	49.5
	Total Volume of 0.1M	**98**		

Volume required for the experiment= 60 ml of 0.1M heavy metals solution x 4 samples = 240 ml 0.1M solution

Total volume required to be prepared= 98 ml +240 ml = 330 ml.

Volume prepared= 350 ml

Calculation of model concentration and normalized concentration of ions from experimental results

The experimental results were used to calculate the model concentration for each of the ions (heavy metals and other cations, and anions) in order to get a smoother graphical representation of the data. This was done by modeling the experimental data charts on a polynomial equation achieved from the experimental data itself. The equation was used to calculate the model concentration. This was then normalized by using a factor in order to achieve more normal curve for each concentration. The calculations were done as shown below:

For Model concentration:

For 0.1M lead (Pb) adsorption by $ZnCl_2$-MCM-41

The polynomial equation achieved from the graph is

$y = 1E\text{-}06x^2 - 0.0005x + 0.1267$

where, y = concentration of the ion being adsorbed in molar concentration (M) (Here: 0.1M lead)

and x = Time in minutes (min)

At time = 0 minutes,

y = 0.1267M

and, at time = 20 minutes,

$y = 1E\text{-}06 * (20)^2 - 0.0005 * (20) + 0.1267 =$ **0.1171 M**

Form this concentration, to normalize it, the factor of normalization was calculated as:

For time = 0 minutes,

Normalized concentration (M) =

Model Conc. (M)/ Initial model conc (M) * Original concentration

= (0.1267M/ 0.1267 M) * 0.1 M = **0.1 M**

For time = 20 minutes,

Model Conc. (M)/ Initial model conc (M) * Original concentration

= (0.1171M/ 0.1267 M) * 0.1 M = **0.092 M**

Calculation of Mass adsorbed, and cumulative mass adsorbed of the adsorbate by the used mass of adsorbent:

For mass of adsorbate, the equation used was:

$$\mathbf{m_i = \frac{(C_0 - Ce)V}{m}}$$

Here, m_i is the equilibrium Pb (II) concentration in mg/g; C_e and C_o are the equilibrium and initial concentrations respectively; V is the volume of the solution in liters (L); and m is the mass of the sorbent in grams (g).

Mass adsorbed was calculated using equation:

$$\mathbf{m_i = (Ce - Co) in \frac{moles}{L} * Molecular\ weight\ in \frac{g}{moles} * V\ in(L) * 1000 \frac{mg}{g}}$$

so, for calculation of mass of 0.1M lead, adsorbed by $ZnCl_2$-MCM-41 is calculated as:

m_i = (0.1267-0.1171) moles/L * (207.2 g Pb /moles) * 0.03 L * 1000 mg/g

m_i = 59.674 mg of 0.1M Pb adsorbed in a 30mL solution with 0.15 g of $ZnCl_2$-MCM-41

The adsorption capacity was calculated by dividing the total adsorbed mass by 0.15g of the adsorbate, so, for adsorption capacity of $ZnCl_2$-MCM-41 to adsorb 0.1M lead is = ∑mi / mass of the adsorbent = (387.88)/ 0.15 g = **2585.856 mg Pb/ g adsorbent**

All the other calculations were done similarly, except for the calculations with the ICP results, the volume was different for each concentration, as 5 mL of the solution was taken out for each time interval.

Calibration data for ICP-OES (Raw data directly from ICP-OES)

ICP-OES was calibrated at the beginning of the measurement, and the standards were fed in the instrument. Calibration data has been presented in Tables 91 to 99. The wavelengths selected for each metal are also shown in the Tables.

Table 91 Standard 1(0M)				
	Pb 220.353	Hg 194.164	Cr 267.716	Cr 205.560
Replicate 1	2	31	8	5
Replicate 2	4	27	6	6
Replicate 3	6	24	6	2
Mean intensity	4.013	27.448	6.3183	4.2819
Mean concentration	0	0	0	0
%RSD intensity	47.274	11.418	18.665	46.032

Table 92 Standard 2 (0.001M)				
	Pb 220.353	Hg 194.164	Cr 267.716	Cr 205.560
Replicate 1	424	482	384	80
Replicate 2	430	488	400	76
Replicate 3	429	489	406	78
Mean intensity	427.86	486.31	396.8	78.003
Mean concentration	0.001	0.001	0.001	0.001
%RSD intensity	0.69486	0.74108	2.8989	2.0858

Table 93 Standard 3 (0.005M)				
	Pb 220.353	Hg 194.164	Cr 267.716	Cr 205.560
Replicate 1	247	2087	2037	380
Replicate 2	261	2147	2100	394
Replicate 3	257	2131	2129	394
Mean intensity	255.1	2121.7	2088.6	389.33
Mean concentration	0.005	0.005	0.005	0.005
%RSD intensity	2.73	1.4591	2.2523	2.0477

Table 94 Standard 4 (0.01M)				
	Pb 220.353	Hg 194.164	Cr 267.716	Cr 205.560
Replicate 1	604	4370	4827	892
Replicate 2	665	4590	5261	971
Replicate 3	667	4606	5309	985
Mean intensity	645.54	4522.1	5132.4	949.33
Mean concentration	0.01	0.01	0.01	0.01
%RSD intensity	5.5802	2.9144	5.1798	5.27

Table 95 Standard 5 (0.03M)				
	Pb 220.353	Hg 194.164	Cr 267.716	Cr 205.560
Replicate 1	32146	14321	20116	3664
Replicate 2	32563	14387	20502	3664
Replicate 3	32909	14503	20572	3730
Mean intensity	32539	14403	20397	3686.2
Mean concentration	0.03	0.03	0.03	0.03
%RSD intensity	1.1738	0.64044	1.203	1.0312

Table 96 Standard 6 (0.05M)				
	Pb 220.353	Hg 194.164	Cr 267.716	Cr 205.560
Replicate 1	57398	23433	34339	6113
Replicate 2	56987	23625	33808	6141
Replicate 3	58892	23658	35156	6178
Mean intensity	57759	23572	34434	6144
Mean concentration	0.05	0.05	0.05	0.05
%RSD intensity	1.7357	0.51381	1.9733	0.52629

Table 97 Standard 7 (0.1M)				
	Pb 220.353	Hg 194.164	Cr 267.716	Cr 205.560
Replicate 1	101710	45587	70931	12074
Replicate 2	103987	46760	74236	12174
Replicate 3	98309	46233	71368	12209
Mean intensity	101340	46193	72178	12153
Mean concentration	0.1	0.1	0.1	0.1
%RSD intensity	2.8197	1.2717	2.4874	0.57678

Table 98 Calibration data for ICP-OES (Averaged)					
	Concentration (M)	Pb 220.353	Hg 194.164	Cr 267.716	Cr 205.560
1	0	4.013	27.448	6.3183	4.2819
2	0.001	427.86	486.31	396.8	78.003
3	0.005	255.1	2131	2129	394
4	0.01	645.54	4522.1	5132.4	949.33
5	0.03	32539	14403	20397	3686.2
6	0.05	57759	23572	34434	6144
7	0.1	101340	46193	72178	12153

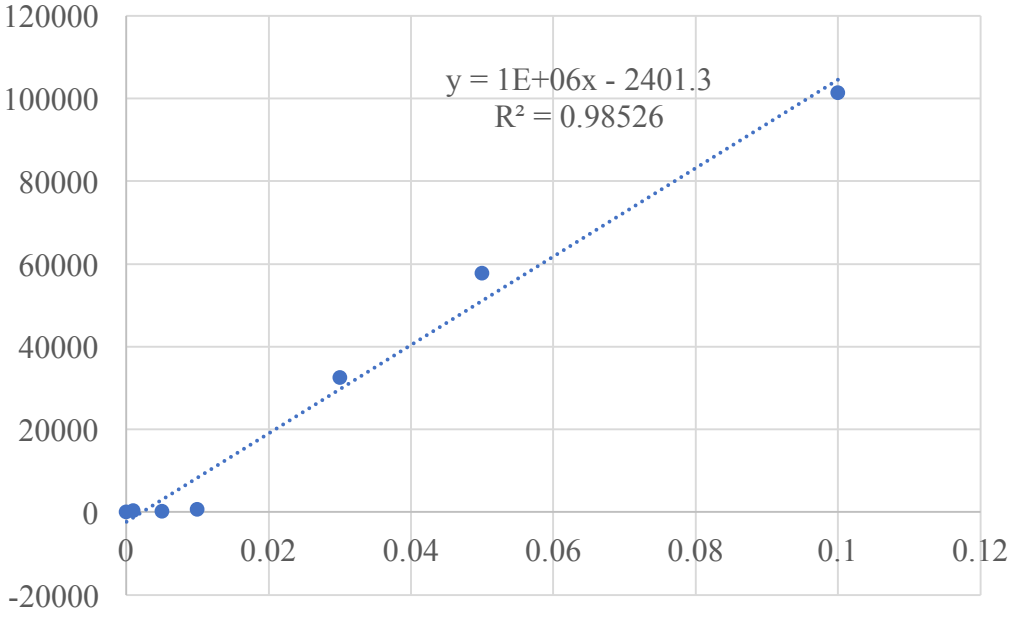

Figure 142 Calibration curve for Pb (with wavelength 220.53)

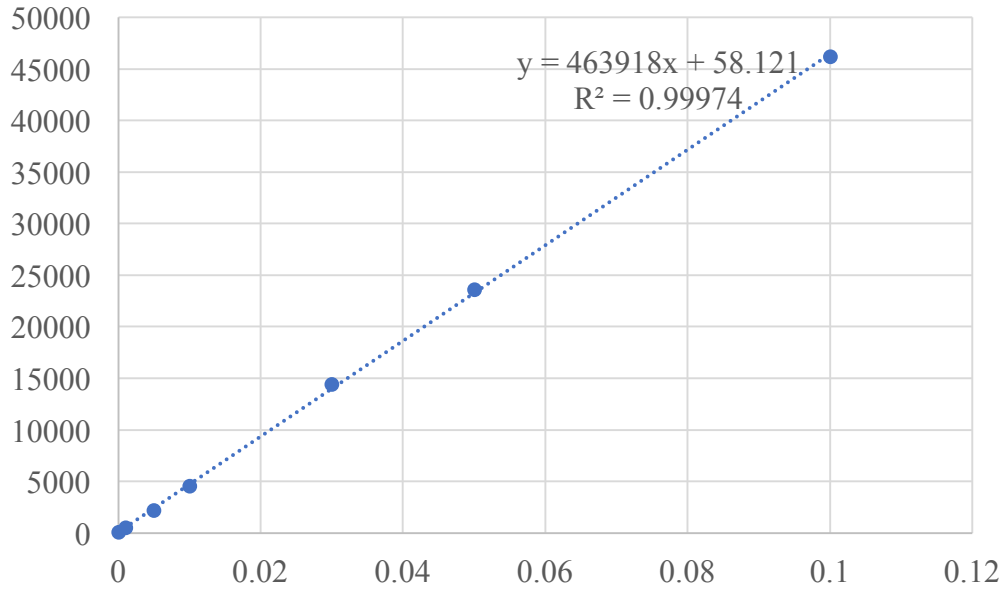

Figure 143 Calibration curve for Hg (with wavelength 194.164)

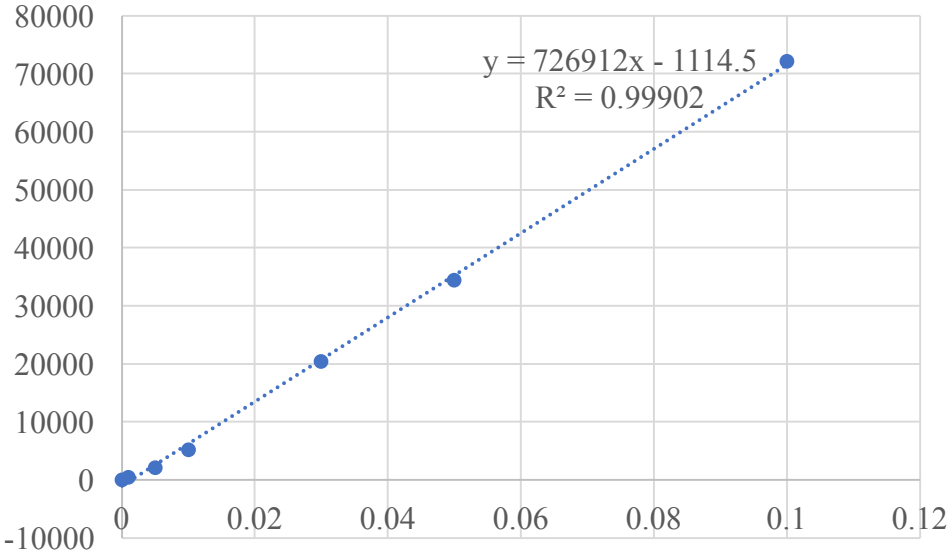

Figure 144 Calibration curve for Cr (with wavelength 267.716)

ICP-OES data of the samples

ICP-OES measurements for mercury

Table 99 ICP-OES raw data for mercury				
ADSORPTION OF 0.1M MERCURY BY MCM-41				
Sample	**Vol of the solution (mL)**	**Time (min)**	**Measured Conc. (M) for Hg 194.164 (S1)**	**Measured Conc. (M) for Hg 194.164 (S2)**
1	60	0	0.1	0.1
2	55	20	0.087758	0.130722
3	50	30	0.087758	0.087993
4	45	40	0.087618	0.087758
5	40	60	0.087473	0.087376
6	35	120	0.087371	0.087152
7	30	160	0.085656	0.086598
8	25	200	x	0.084808
9	20	240	x	0.080152
10	15	300	0.084884	0.059377
11	10	24 hours	0.084808	0.058204
ADSORPTION OF 0.1M MERCURY BY $ZnCl_2$-MCM-41				

Sample	Vol of the solution (mL)	Time (min)	Measured Conc. (M) for Hg 194.164 (S1)	Measured Conc. (M) for Hg 194.164 (S2)
1	60	0	0.1	0.100014
2	55	20	0.091723	0.130003
3	50	40	0.088969	0.129497
4	45	60	0.087436	0.12828
5	40	120	0.087425	0.088695
6	35	160	0.087061	0.087436
7	30	200	0.084225	0.086192
8	25	240	0.083336	0.059349
9	20	300	0.009135	0.059033
10	15	24 hours	0.008151	0.008933
11	10			
ADSORPTION OF 0.01M MERCURY BY MCM-41				
Sample	**Vol of the solution (mL)**	**Time (min)**	**Measured Conc. (M) for Hg 194.164 (S1)**	**Measured Conc. (M) for Hg 194.164 (S2)**
1	60	0	0.01	0.01
2	55	20	0.008874	0.013427
3	50	40	0.008839	0.013005
4	45	60	0.008734	0.00967
5	40	90	0.008394	0.009557
6	35	120	0.008385	0.009461
7	30	180	0.008381	0.008636
8	25	200	0.008366	0.006646
9	20	240	0.008313	0.006356
10	15	300	x	
11	10	24 hours	0.007874	
ADSORPTION OF 0.01M MERCURY BY $ZnCl_2$-MCM-41				
Sample	**Vol of the solution (mL)**	**Time (min)**	**Measured Conc. (M) for Hg 194.164 (S1)**	**Measured Conc. (M) for Hg 194.164 (S2)**
1	60	0	0.1	0.1
2	55	20	0.013211	0.01314
3	50	40	0.013165	0.012754
4	45	60	0.009224	0.008779
5	40	90	0.008858	0.008086

6	35	120	0.0087687	0.006613
7	30	180	0.008499	0.006388
8	25	240	0.00809	0.006333
9	20	300	0.008086	
10	15	24 hours	0.007723	
ADSORPTION OF 0.001M MERCURY BY MCM-41				
Sample	**Vol of the solution (mL)**	**Time (min)**	**Measured Conc. (M) for Hg 194.164 (S1)**	**Measured Conc. (M) for Hg 194.164 (S2)**
1	60	0	0.001058	0.001117
2	55	20	0.00088	0.001414
3	50	30	0.000842	0.001118
4	45	40	0.000809	0.001084
5	40	60	0.0007	0.001071
6	35	120	0.000679	0.000972
7	30	160	0.000557	0.000952
8	25	200	x	0.000927
9	20	240	0.000407	0.000857
10	15	300	0.000162	0.000841
11	10	24 hours	0.000066	0.000803
ADSORPTION OF 0.001 MERCURY BY $ZnCl_2$-MCM-41				
Sample	**Vol of the solution (mL)**	**Time (min)**	**Measured Conc. (M) for Hg 194.164 (S1)**	**Measured Conc. (M) for Hg 194.164 (S2)**
1	60	0	0.001129	0.001214
2	55	20	0.000755	0.001438
3	50	30	0.00068	0.001363
4	45	40	0.000473	0.001323
5	40	60	0.000473	0.001212
6	35	120	0.000436	0.001191
7	30	180	0.000285	0.001117
8	25	200	x	0.000957
9	20	240	0.000141	0.000956
10	15	300	0.00009	0.000901
11	10	24 hours	0.000042	0.000836

*Note: S1- Sample 1, S2- Sample 2, Vol-Volume, Conc.- Concentration.

ICP-OES for Chromium

For chromium, data for wavelength 267.716 was selected as optimal, and hence used for all the other calculation purposes. Table 100 shows the ICP-OES data for adsorption of chromium.

Table 100 ICP-OES raw data for chromium

SAMPLE 1: ADSORPTION OF CHROMIUM BY MCM-41					
Samples	**Volume of the solution (mL)**	**Time (min)**	**Original Concentration (M)**	**Measured Conc. (M) for Cr 205.560**	**Measured conc. (M) for Cr 267.716**
1	60	0	0.1	0.085835	0.087655
2	55	20	0.1	0.083973	0.087365
3	50	40	0.1	0.085472	0.086697
4	45	60	0.1	0.086017	0.086858
5	40	90	0.1	0.086996	0.089504
6	35	120	0.1	0.093458	0.096057
7	30	160	0.1	0.06331	0.063083
8	25	200	0.1	0.07093	0.069664
9	20	240	0.1	0.06281	0.062442
10	15	**24 hours**	0.1	**0.062026**	**0.060613**
SAMPLE 1: ADSORPTION OF CHROMIUM BY $ZnCl_2$-MCM-41					
Samples	**Volume of the solution (mL)**	**Time (min)**	**Original Concentration (M)**	**Measured Conc. (M) for Cr 205.560**	**Measured conc. (M) for Cr 267.716**
1	60	0	0.1	0.090807	0.10015
2	55	20	0.1	0.082446	0.08436
3	50	40	0.1	0.085857	0.086898
4	45	60	0.1	0.087822	0.089615
5	40	90	0.1	0.08761	0.088811
6	35	120	0.1	0.094396	0.095636
7	30	160	0.1	0.097532	0.100169
8	25	200	0.1	0.088223	0.089591
9	20	240	0.1	0.085532	0.086758
	15	**24 hours**		**0.088443**	**0.08955**

SAMPLE 2: ADSORPTION OF CHROMIUM BY MCM-41					
Samples	**Volume of the solution (mL)**	**Time (min)**	**Original Concentration (M)**	**Measured Conc. (M) for Cr 205.560**	**Measured conc. (M) for Cr 267.716**
1	55	0	0.1	0.09501	0.096107
2	50	20	0.1	0.090258	0.091956
3	45	40	0.1	0.090705	0.09204
4	40	60	0.1	0.094169	0.095369
5	35	90	0.1	0.08939	0.090807
6	30	120	0.1	0.0887	0.090222
7	25	160	0.1	0.079748	0.088691
8	20	200	0.1	0.08669	0.087291
9	15	240	0.1	0.043989	0.04434
10	10	24 hours	0.1	0.088925	0.090491
SAMPLE 2: ADSORPTION OF CHROMIUM BY $ZnCl_2$-MCM-41					
Samples	**Volume of the solution (mL)**	**Time (min)**	**Original Concentration (M)**	**Measured Conc. (M) for Cr 205.560**	**Measured conc. (M) for Cr 267.716**
2	50	20	0.1	0.095807	0.097874
3	45	40	0.1	0.090141	0.091193
4	40	60	0.1	0.093044	0.094954
5	35	90	0.1	0.087974	0.089599
6	30	120	0.1	0.090448	0.092825
7	25	160	0.1	0.088849	0.090705
8	20	200	0.1	0.088419	0.08981
9	15	240	0.1	0.094861	0.097602
10	10	24 hours	0.1	0.093835	0.094655
SAMPLE 1: ADSORPTION OF CHROMIUM BY MCM-41					
Samples	**Volume of the solution (mL)**	**Time (min)**	**Original Concentration (M)**	**Measured Conc. (M) for Cr 205.560**	**Measured conc. (M) for Cr 267.716**
1	60	0	0.01	0.006798	0.006976
2	55	20	0.01	0.006871	0.006654
3	50	40	0.01	0.006776	0.006312
4	45	60	0.01	0.006196	0.005666
5	40	90	0.01	0.00707	0.006569
6	35	120	0.01	0.006553	0.006096

7	30	180	0.01	0.006997	0.006482
8	25	240	0.01	0.006234	0.005868
9	20	300	0.01	0.006628	0.006109
10	15	24 hours	0.01	0.006308	0.005838
SAMPLE 1: ADSORPTION OF CHROMIUM BY $ZnCl_2$-MCM-41					
Samples	**Volume of the solution (mL)**	**Time (min)**	**Original Concentration (M)**	**Measured Conc. (M) for Cr 205.560**	**Measured conc. (M) for Cr 267.716**
1	60	0	0.01	0.006623	0.006316
2	55	20	0.01	0.006142	0.005722
3	50	40	0.01	0.006175	0.005721
4	45	60	0.01	0.006777	0.006323
5	40	90	0.01	0.006371	0.005864
6	35	120	0.01	0.006951	0.006457
7	30	180	0.01	0.006265	0.005893
8	25	240	0.01	0.006878	0.006316
9	20	300	0.01	0.006412	0.005902
10	15	24 hours	0.01	0.006195	0.005744
SAMPLE 2: ADSORPTION OF CHROMIUM BY MCM-41					
Samples	**Volume of the solution (mL)**	**Time (min)**	**Original Concentration (M)**	**Measured Conc. (M) for Cr 205.560**	**Measured conc. (M) for Cr 267.716**
1	55	0	0.01	0.089763	0.0078954
2	50	20	0.01	0.008039	0.007421
3	45	40	0.01	0.007085 uv	0.006564 uv
4	40	60	0.01	0.006636 uv	0.006153 uv
5	35	90	0.01	0.006916 uv	0.006365 uv
6	30	120	0.01	-0.000013 uv	-0.000010 uv
7	25	160	0.01	0.010418	0.009543
8	20	200	0.01	0.007375 uv	0.006823 uv
9	15	240	0.01	0.006616 uv	0.006072 uv
10	10	24 hours	0.01	0.006449 uv	0.005945 uv

SAMPLE 2: ADSORPTION OF CHROMIUM BY $ZnCl_2$-MCM-41					
Samples	**Volume of the solution (mL)**	**Time (min)**	**Original Concentration (M)**	**Measured Conc. (M) for Cr 205.560**	**Measured conc. (M) for Cr 267.716**
1	55	0	0.01		
2	50	20	0.01	0.006710 uv	0.006222 uv
3	45	40	0.01	0.006496 uv	0.005993 uv
4	40	60	0.01	0.006790 uv	0.006252 uv
5	35	90	0.01	0.006470 uv	0.005996 uv
6	30	120	0.01	0.007146 uv	0.006570 uv
7	25	160	0.01	0.006275 uv	0.005832 uv
8	20	200	0.01	0.006295 uv	0.005830 uv
9	15	240	0.01	0.006502 uv	0.006017 uv
10	10	24 hours	0.01	0.006089 uv	0.005562 uv
SAMPLE 1: ADSORPTION OF CHROMIUM BY MCM-41					
Samples	**Volume of the solution (mL)**	**Time (min)**	**Original Concentration (M)**	**Measured Conc. (M) for Cr 205.560**	**Measured conc. (M) for Cr 267.716**
1	60	0	0.001		
2	55	20	0.001	0.000004 uv	0.000027 uv
3	50	40	0.001	-0.000032 uv	0.000006 uv
4	45	60	0.001	0.000133 uv	0.000085 uv
5	40	90	0.001	0.000051 uv	0.000049 uv
6	35	120	0.001	0.000088 uv	0.000089 uv
7	30	180	0.001		
8	25	240	0.001		
9	20	300	0.001		
10	15	24 hours	0.001		
SAMPLE 1: ADSORPTION OF CHROMIUM BY $ZnCl_2$-MCM-41					
Samples	**Volume of the solution (mL)**	**Time (min)**	**Original Concentration (M)**	**Measured Conc. (M) for Cr 205.560**	**Measured conc. (M) for Cr 267.716**
1	60	0	0.001	0.000265 uv	0.000023 uv
2	55	20	0.001	0.000025 uv	0.000024 uv
3	50	40	0.001	0.000021 uv	0.000017 uv
4	45	60	0.001	0.000025 uv	0.000041 uv
5	40	90	0.001	0.000121 uv	0.000104 uv

6	35	120	0.001	0.000155 uv	0.000145 uv
7	30	180	0.001	0.000021 uv	0.000056 uv
8	25	240	0.001	0.000128 uv	0.000120 uv
9	20	300	0.001	0.000095 uv	0.000084 uv
10	15	24 hours	0.001	0.000047 uv	0.000058 uv
SAMPLE 2: ADSORPTION OF CHROMIUM BY MCM-41					
Samples	**Volume of the solution (mL)**	**Time (min)**	**Original Concentration (M)**	**Measured Conc. (M) for Cr 205.560**	**Measured conc. (M) for Cr 267.716**
1	60	0	0.001	0.0008941	0.0008726
2	55	20	0.001	0.0008803	0.0008963
3	50	40	0.001	0.000708	0.000621
4	45	60	0.001	0.000612	0.000563
5	40	90	0.001	0.000604	0.000543
6	35	120	0.001	0.005362	0.004955
7	30	160	0.001	0.000555	0.000524
8	25	200	0.001	0.000696	0.000624
9	20	240	0.001	0.000541	0.000612
10	15	24 hours	0.001	0.000497	0.000464
SAMPLE 2: ADSORPTION OF CHROMIUM BY $ZnCl_2$-MCM-41					
Samples	**Volume of the solution (mL)**	**Time (min)**	**Original Concentration (M)**	**Measured Conc. (M) for Cr 205.560**	**Measured conc. (M) for Cr 267.716**
1	60	0	0.001	0.000981	0.000763
2	55	20	0.001	0.000664	0.000614
3	50	40	0.001	0.000625	0.000572
4	45	60	0.001	0.000667	0.000603
5	40	90	0.001	0.000404	0.000385
6	35	120	0.001	0.000627	0.000584
7	30	160	0.001	0.000608	0.000562
8	25	200	0.001	0.000421	0.000387
9	20	240	0.001	0.000492	0.000442
10	15	24 hours	0.001	0.000491	0.000435

ICP-OES data for heavy metals solution measurement

Table 101 ICP-OES raw data for heavy metals combination solutions							
SAMPLE 1: ADSORPTION OF COMBINED HEAVY METALS BY MCM-41							
Sample	**Vol of the solution (mL)**	**Time (min)**	**Original Conc. (M)**	**Measured Conc. (M) for Cr 205.560**	**Measured conc. (M) for Cr 267.716**	**Measured Conc. (M) for 194.164 Hg^{2+}**	**Measured Conc. (M) for 220.353 Pb^{2+}**
1	60	0	0.1	0.10061	0.10105	0.100364	0.09876
2	55	20	0.1	0.09673	0.098298	0.100158	0.074465
3	50	40	0.1	0.097231	0.09874	0.100867	0.069205
4	45	60	0.1	0.099878	0.101936	0.103388	0.073486
5	40	90	0.1	0.099812	0.100696	0.102492	0.076003
6	35	120	0.1	0.099073	0.099749	0.101438	0.072428
7	30	160	0.1	0.098052	0.100592	0.102343	0.065163
8	20	200	0.1	0.097607	0.099791	0.100678	0.065634
9	15	240	0.1	0.098425	0.100254	0.102621	0.06373
10	10	300	0.1	0.097239	0.098712	0.100749	0.062608
		24 hours	0.1	0.061813	0.062226	0.065246	0.038162
SAMPLE 1: ADSORPTION OF COMBINED HEAVY METALS BY ZnCl2-MCM-41							
Sample	**Vol of the solution (mL)**	**Time (min)**	**Original Conc. (M)**	**Measured Conc. (M) for Cr 205.560**	**Measured conc. (M) for Cr 267.716**	**Measured Conc. (M) for 194.164 Hg^{2+}**	**Measured Conc. (M) for 220.353 Pb^{2+}**
1	60	0	0.1	0.10088	0.102071	0.104077	0.098419
2	55	20	0.1	0.096479	0.097963	0.100064	0.076158
3	50	40	0.1	0.10166	0.10312	0.103652	0.073749
4	45	60	0.1	0.097556	0.098884	0.100692	0.073013
5	40	90	0.1	0.102021	0.103841	0.103937	0.07561
6	35	120	0.1	0.098881	0.100253	0.101813	0.072228
7	30	160	0.1	0.096858	0.098458	0.100141	0.066617
8	20	200	0.1	0.097775	0.100319	0.101721	0.064974
9	15	240	0.1	0.098444	0.100372	0.102252	0.067935
10	10	300	0.1	0.096445	0.097511	0.098725	0.067048
		24 hours	0.1	0.064612	0.065581	0.06775	0.039137

SAMPLE 2: ADSORPTION OF COMBINED HEAVY METALS BY MCM-41							
Sample	**Vol of the solution (mL)**	**Time (min)**	**Original Conc. (M)**	**Measured Conc. (M) for Cr 205.560**	**Measured conc. (M) for Cr 267.716**	**Measured Conc. (M) for 194.164 Hg^{2+}**	**Measured Conc. (M) for 220.353 Pb^{2+}**
2	55	20	0.1	0.097961	0.099904	0.101508	0.077224
3	50	40	0.1	0.102086	0.104182	0.100168	0.07908
4	45	60	0.1	0.097884	0.099544	0.101464	0.078351
5	40	90	0.1	0.099669	0.102735	0.103577	0.076734
6	35	120	0.1	0.100692	0.101868	0.103037	0.074313
7	30	160	0.1	0.097806	0.099539	0.101087	0.064239
8	20	200	0.1	0.09683	0.098062	0.098306	0.065965
9	15	240	0.1	0.100338	0.101528	0.10289	0.070974
10	10	300	0.1	0.067214	0.069096	0.070332	0.041823
		24 hours	0.1	0.066079	0.066959	0.066977	0.045036
SAMPLE 2: ADSORPTION OF COMBINED HEAVY METALS BY ZnCl2-MCM-41							
Sample	**Vol of the solution (mL)**	**Time (min)**	**Original Conc. (M)**	**Measured Conc. (M) for Cr 205.560**	**Measured conc. (M) for Cr 267.716**	**Measured Conc. (M) for 194.164 Hg^{2+}**	**Measured Conc. (M) for 220.353 Pb^{2+}**
2	55	20	0.1	0.096364	0.098169	0.100236	0.075361
3	50	40	0.1	0.100724	0.102089	0.099039	0.079034
4	45	60	0.1	0.099364	0.100906	0.101937	0.076802
5	40	90	0.1	0.102612	0.10536	0.10492	0.078302
6	35	120	0.1	0.09792	0.099341	0.101202	0.072284
7	30	160	0.1	0.098026	0.10026	0.101864	0.071489
8	20	200	0.1	0.098499	0.101515	0.101728	0.067424
9	15	240	0.1	0.099223	0.101186	0.102744	0.065978
10	10	300	0.1	0.09941	0.101399	0.101894	0.070963
		24 hours	0.1	0.063225	0.064314	0.06677	0.038357