Adsorption of Heavy Metal using Mesoporous Silica

Elham O.S.J, Sabari N.A, Roslan A.A, Mohamad Zamri N.A.I

Faculty of Chemical Engineering, UiTM Pasir Gudang

Abstract

Heavy metals such as Pb, Zn, Ni, Cr are discharged into water from various industries which they can be toxic or carcinogenic in nature and can cause severe problems for humans and aquatic ecosystems. The pollution of water is now being an environmental problem of global concern and efforts are being made for their efficiency of removal using various natural and synthetic materials. To overcome the problems, the present study was undertaken to explore the efficiency of heavy metal adsorption by mesoporous silica at the concentration of 30 ppm of Zinc and Lead. Further experiments have been carried out by using Fourier Transform-Infrared spectroscopy (FTIR) and Inductively Coupled Plasma spectrometry (ICP-AES). The result obtained from the study shows that the ability adsorption of Pb^{2+} ion was significantly higher than others metal ions which heavy metal removal percentage was 74.93% compared to Zn^{2+} that was 74.36%. In addition, as the contact time increases and more dosage of adsorbent added, it shows the increment of percentage reduction of heavy metal by using mesoporous silica. Thus, it can be proved that adsorption process is widely used for the removal of heavy metals from wastewater because of its low cost, availability and eco-friendly nature.

Keywords: mesoporous silica, heavy metal, adsorption

1. Introduction

Water is a natural source that provides vital roles in life on earth. Water plays an important role in our daily life routine such as for cooking, washing and drinking but nowadays, our water sources have been contained of heavy metal on high level that it is in critical condition which is of major concern (P. Ajitha, et al., 2017). It is in-line as World Wide Fund Malaysia (WWF) CEO Datuk Dr Dionysius Sharma said the issue had become a serious problem in Malaysia and had led to negative impact on the sustainability of the country's water resources. In addition, according to the environment quality 2013 report by the Department of Environment, 5.3% of a total 473 rivers were polluted with 36.6% slightly polluted.

The term of heavy metals can be defined as metals which contain relatively high densities, atomic weights or atomic numbers. The increasing level of heavy metals in water contributes a high risk to human health and ecological system. Heavy metals are reported as being priority pollutants, due to their toxicity and mobility in natural water ecosystems (Demirbas, a 2008). Cr, Ni, Zn, Cu and Cd are the most abundant harmful metals in the water effluents (Mihaela mureseanu, et al., 2008). Furthermore, they are toxic substances which can be considered as persistent and bio accumulative contaminants as they cannot be destroyed nor degraded (Mihaela Mureseanu, et al., 2008). These pollutants presence in waste water from industrial applications including mining, refining, and production of textiles, paints and dyes (Demirbas, a 2008).

In addition, the presence of high heavy metals in water reduce the quality of water and it is not safe enough to be in use. Furthermore, the presence of heavy metal in aqueous solution creates a major problem as they are toxic even at a very low concentration. If the metals are ingested beyond the permitted concentration, they may cause serious health-related diseases (S.babel, & t.a.kurniawan, 2004). Exposure to some metals, such as zinc and lead, may also cause development of autoimmunity, in which a person's immune system attacks its own cells. This can lead to joint diseases such as rheumatoid arthritis, and diseases of the kidneys, circulatory system, nervous system, and damaging of the fatal brain.

A wide variety of techniques is found to be used to remove heavy metals from water such as ion exchange, reverse osmosis, nanofiltration precipitation and adsorption (Jose aguado, 2009). Nevertheless, these methods have their own limitations such as low efficiency, sensitive working environments and production of toxic slurry. Hence, researchers are now needing a more practical and environmental friendly technologies which adsorption is one of the option that has the most effective, economic and selective methods for heavy metal removal (Da'na, e., 2017). Moreover, with the new development of nanotechnology, nanosorbents have shown higher efficiency and faster adsorption rates for heavy metal removal compared with other conventional sorbents (Fang, l., liang, l., et al 2017). Furthermore, this process utilization for very small particles improves the mass transfer of molecules into or out of the pore system. This molecular functionalization in the large internal surface of these materials can extend the range of possible application, for example, toward selective adsorption or specific catalytic activity (Johannes kobler. 2008). Adsorption is widely used in the removal of heavy metals from waste water adsorptive compound like activated charcoal, zeolites and clay which are capable of capturing metal ions from dilute aqueous solutions. There are also natural materials have been evaluated as adsorbents for heavy metal removal such as corn cob, saw dust, plant biomass, rice bran and etc. However, these adsorbents possess low adsorption capacities, low efficiencies large cost of post-processing (P. ajitha, et al., 2017).

The problem of this pollution has encouraged the researcher to research the modest technology for removal of heavy metal in water treatment so that the supply of clean water is continuous for a long term. Therefore, this research is focusing one of the alternative method which is by using mesoporous silica in water treatment.

Nowadays, numerous researchers showed interest on the development of new method for the synthesis of mesoporous silica with an improvement in surface area, pore size and pore volume. The properties of mesoporous silica in physical and chemical are depending on the synthesis conditions such as pH of the medium, temperature, source of silica, templating agent which commonly used by surfactant to obtain the mesoporous materials having high surface area, tunable pore sizes, large pore volumes and rich morphology and also mesoporous silica depend on its concentrations (Lalchhingpuii, Tiwari, D, Lalhmunsiama,et al. 2017). Surfactant can show their unique properties which is contain two different chemical structure, hydrophobic and hydrophilic. Hydrophilic surfactant properties shown an important role by adsorbing contaminant particles in water.

In late 1970s, mesoporous silica has gain much attention due to their special characteristics in pore structures and consists a very large surface area. Besides that, it has range of morphologies that can be synthesized into three types such as sphere rods, disc and powder. Mesoporous silica is functionalized with various chelating agents as an adsorbent due to high selectivity for metal ion adsorption. However, heavy metal adsorption in water treatment by using mesoporous silica is not well-known yet in our industry. It is a good opportunity for researchers to use this method because it is environmental friendly and low cost.

Recently, various types of mesoporous silica were found to be efficient in heavy metal adsorption in aqueous solutions. In any cases, mesoporous silica can be modified chemically via the attachment of functional groups including carboxylic acid, sulfonic acid and amino-carbonyl. In previous research, mesoporous silica had been prepared as polyaniline, polypyrole or hexagonal types for cadmium (Cd) removal as it reported that the rate of removal reached at 99.2% at optimum Ph of 8 (Renu, mardhu agarwal,et al. 2017). Therefore, in this study, mesoporous silica can be synthesized by sodium silicate and sulphuric acid then using ethanol to wash the removal template. The heavy metal used are zinc (Zn) and lead (Pb) to identify the efficiency of mesoporous silica in removing heavy metal.

Therefore, the objective of this research is to study the ability of synthesis mesoporous silica as an adsorbent in heavy metal treatment. The efficiency of mesoporous silica acts for removal of heavy metal are going to be focused on Zn and Pb ion. The samples were analysed by Fourier Transform Infrared Spectrometer (FTIR) to identify the functional group in mesoporous silica and Inductively Coupled Plasma mass spectrometry (ICP) for heavy metal removal.

2. Methodology

2.1 Materials

Sodium silicate (Na_2O 3.4 SiO_2) and sulphuric acid (H_2SO_4) were used as main chemical for the preparation of mesoporous silica. Ethanol will be used to wash off the wet gel that formed by the reaction of sodium silica and sulphuric acid. Sources of metals for sorption experiments were Zinc (Zn) and Lead (Pb).

2.2 Preparation of mesoporous silica

Mesoporous silica was prepared by mixing 24% sodium silica and 76% sulphuric acid as in 100 ml in 1L conical flask and was stirred at room temperature for 7 hours using magnetic stirrer. Subsequently, the wet gel that was formed will be washed with ethanol in centrifuge, then, it will be filtered to remove excess water. The obtained white solution was collected in petri dish and will be left to dry in oven at 150°C overnight. Thereafter, the solution that has dried will be crushed with crusher until becomes white powder. The white powder will be going through calcination for 2 hours at 350°C. High temperature will be needed in this process to remove water contain in the mesoporous silica as it need to be in dried form.

2.3 Preparation of standard solution

The preparation of standard solution is prepared by calculation of m1v1 = m2v2 formula to calculate the volume of solution for zinc chloride and lead nitrate, respectively, to be added in 1000ml conical flask that contain distilled water. Before that, the calculation is made to calculate the amount of zinc chloride and lead nitrate which is 2.1g and 1.6g, respectively. Once both solution for zinc chloride and lead nitrate are put into 1000ml respectively, the concentration is fixed to 30ppm for each of the solution to be distributed into small conical flask of 50ml. The concentration of 30ppm is about 3ml of each solution to be put into 50 ml of conical flask and added distilled water before added different amount of dosage of mesoporous silica, 2g, 4g, 6g, 8g and 10 g. The standard solution is then can be analyzed by Inductively Coupled Plasma spectroscopy (ICP).

Fig 1. a) Mixture of sodium silicate with sulfuric acid before further experiment to become mesoporous silica

b) Final form of mesoporous silica

2.4 Characterization of synthesis mesoporous silica

The mesoporous silica analyzed by Fourier-Transform Infrared spectroscopy (FTIR) to identify functional group in mesoporous silica using Bruker model Vertex 70 model. Furthermore, the synthesis mesoporous silica being analyzed by Inductively Coupled Plasma spectroscopy (ICP) using Perkin Elmer Optima 8000 model to detect the percentage adsorption of heavy metals like Pb^{2+} and Zn^{2+} at different concentration.

2.5 Heavy metal adsorption experiments

In order to test the metal removal ability of the synthesized materials, a set of adsorption experiments were carried out by mixed the samples of mesoporous silica (2g, 4g, 6g, 8g and 10g) in 50mL of heavy metal

solution which contain two types of heavy metals that were lead (Pb) and zinc (Zn). The constant parameter used were concentration of heavy metal solution which is 30ppm and the contact time of loading with heavy metal solutions which were taken at 30 minutes, 60 minutes and 90 minutes. The adsorbent-solution mixture then filtered with a syringe filter to collect the final solutions. Metal concentration, both in the initial and final solutions, was determined by Inductively Coupled Plasma spectroscopy (ICP) using Perkin Elmer Optima 8000 model which the rate of heavy metal adsorption capacity was taken.

3. Results and discussion

3.1 FT-IR spectral analysis

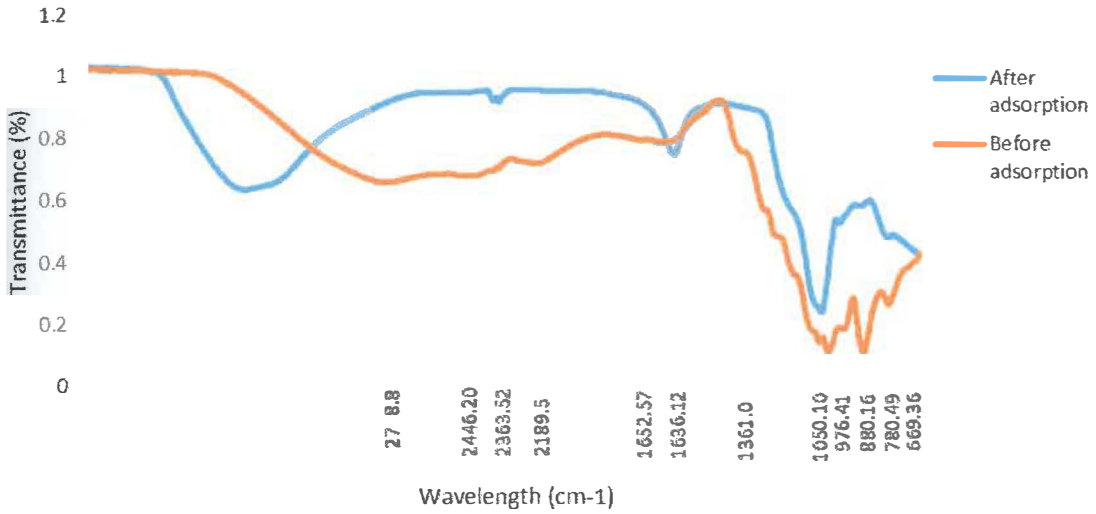

Figure 2

FT-IR spectroscopy is one of the most important and widely used analytical techniques which using by most of the scientists to identify organic, polymeric and in some cases, inorganic materials (P. ajitha, et al., 2017). In this study, FT-IR spectroscopy is to identify the functional group obtained in mesoporous silica.

The FT-IR spectrum of mesoporous silica before the adsorption of heavy metal presented in Figure 2 shows the exist of bending alkene bond which is C=O and C-H bending at 669.36 cm^{-1} and 780.49 cm^{-1}, 880.16 cm^{-1} (Vinod K. Gupta, 2012). The peaks which were observed at 960.24 cm^{-1}, 1020.91cm^{-1}, 1059.59cm^{-1} and 1361.01cm^{-1} show the presence of C=C bending in alkene bond, then the presence of Si-O-Si and O-H bending in alcohol. It is the same as previous research on mesoporous silica stated there was a presence of Si-O-Si and O-H in mesoporous sample (Ariffin, 2017). At the prominent peak, the wavenumber at 1652.57cm^{-1} shows that the C=C stretching in alkene bond while 2189.57cm^{-1} shows the C=C stretching in alkyne. The carbon dioxide bond, O=C=O had been observed stretching at the three peaks which were 2340.95cm^{-1}, 2363.52cm^{-1} and 2446.20cm^{-1}. At the last peak, the bond of aldehyde, C-H stretching at wavenumber of 2798.82cm^{-1}.

Furthermore, FT-IR spectrum of mesoporous silica after the adsorption with heavy metal solution which shows at 782.36cm^{-1}, the bond of C=C bending as cis alkene and same as well as at wavenumber 890.35cm^{-1} which C=C bending as alkene. Also, the bending of alkene bond, C=C occur at 976.41cm^{-1}. At the lowest peak of the graph, the wavenumber at 1050.10cm^{-1} shows that CO-O-CO stretching as anhydride. Next, at the prominent peak, at 1636.12cm^{-1} shows the C=O stretching as carbonyl group which adsorption known as "carbonyl stretch" (Anantha Ratna Kumari, 2016). Also, at the two highest peaks obtained, 2340.54cm^{-1} and 2360.47cm^{-1} showed C≡N a stretching symmetrical alkyne. The last peak at 3366.27cm^{-1} which the infrared peaks of alcohol bond (O-H)

broadened because of hydrogen bending which due to lattice OH and bound water stretching vibrations (Tushar Kantu Sen, 2011).

3.2 Adsorption on heavy metal by Lead (II)

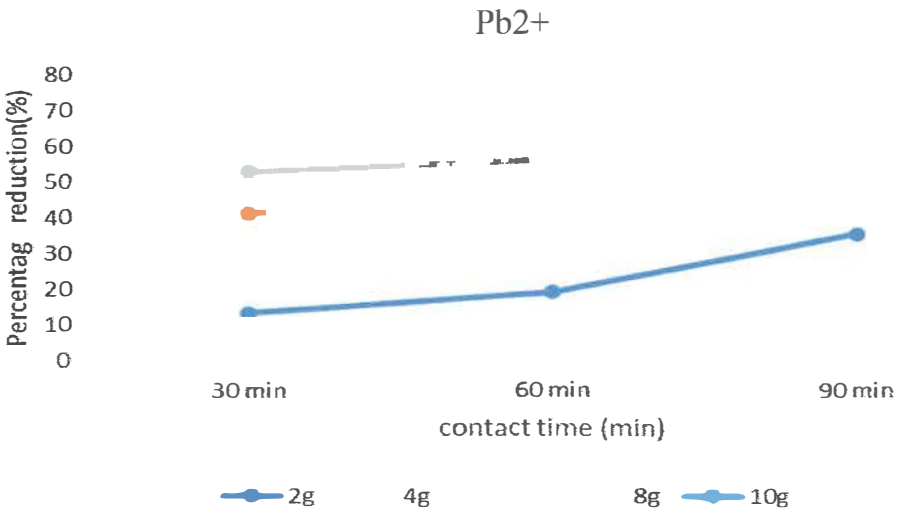

Fig 3(a) Effect of contact time and adsorbent dosage on adsorption of lead by mesoporous silica

3.2.1 Effect on contact time

The percentage removal of heavy metal Pb^{2+} are studied varying contact time starting from 30 min to 90 min and using 2g, 4g, 6g, 8g and 10 g as dosage shown in Fig 3(a). The fastest uptake of Pb^{2+} is occurred between 30 min to 60 min which increase until 90 min for 10g dosage. The adsorption of heavy metal Pb^{2+} are 61.67%, 71.47% and 74.93 respectively. For 2g loading, the percentage reduction is rising rapidly from 30 min to 60 min and up to 90 min which are 13.33%, 19.0% and 35.00%, respectively. According to (P.Ajitha, K.Vijayalaksmi, M.Saranya, 2017), the contact time is an effective factor in a batch process. The effect of contact time was evaluated by changing the contact time from 30 mins to 90 mins by keeping the parameters such as concentration of standard solution for the heavy metals constant at 30 ppm but different adsorbent dosage (2g, 4g, 6g, 8g, 10g). The effect of contact time on the adsorption of Pb^{2+} onto mesoporous silica was investigated using the batch technique and the obtained results was represented in Fig 3(a). Based on the graph in Fig 3(a), the adsorption curve for both at 4g and 6g loading are quite similar as adsorption of Pb^{2+} increases slightly from 30 min to 90 min at 49% and 58%, respectively. Meanwhile, the percentage reduction for 8g dosage is levelled out at 62.5% in 60 min and rapidly increase at 74.93% in 90 min.

3.2.2 Effect on dosage

The percentage of the amount on the removal of heavy metal Pb^{2+} by mesoporous silica are studied varying adsorbent doses of 2g, 4g, 6g, 8g and 10 g within 30 min, 60 min and 90 min of contact time as shown in Fig 3(a). From the observation, it can be clearly observed that the higher the amount of dosage, the higher the percentage reduction of heavy metal Pb^{2+} in the solution. Adsorbent dosage is an important factor to determine the amount of adsorbent required to remove heavy metal in the solution. The increase in adsorption efficiency is due to the accessibility of more number of adsorption active sites and functional groups for the adsorption of Pb^{2+} ion that have been stated in (Laleh Divband, Saeed Boroomand, Roya Mafi, 2015). Based on the graph in Fig 3(a), dosage of 2g rises at 35.00% at 90 min from 13.333% at 30 min followed by 4g of dosage, from 41.03% at 30 min to 49.00% at 90 min. At the dosage of 6g, the percentage removal of Pb^{2+} is 52.67% to 58% which does not give a big gap of percentage reduction. This is maybe due to the overlapping or aggregation of active sites in the dosage of mesoporous silica. Next, the adsorbent dose for 8g is levelled out at 58.07% of 30 min to 74.73% of 90 min. Afterwards, it can be seen that the amount of dosage 10g has the highest adsorption of heavy metal Pb^{2+} pointed at