Synthesis of Mesoporous Silica for Adsorption of Heavy Metal

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Abstract

In this study, synthesis of mesoporous silica was prepared for the adsorption of heavy metal which are Pb and Zn. The silica was prepared using sulfuric acid (H_2SO_4) and sodium silicate ($NaSiO_3$) by using sol-gel process. The effect of essential parameters on the removal efficiency including initial concentration and contact time were studied. Silica adsorb highest removal efficiency in Pb compared to Zn which was recorded at 88.64% at 50 ppm during 90 minutes. The percentage removal of Zn also increases as the initial concentration increases. The higher the concentration, the higher the percentage removal. The percentage removal of Pb was increased as the contact time increase while the percentage removal of Zn was decreased as the contact time increase. The selectivity of Pb was higher than Zn. This is because Pb was adsorb more on the surface of the adsorbent. Thus, it can be concluded that silica is suitable to be used as an adsorbent in our country because it has structural formula that has the ability to adsorb heavy metal in the wastewater in our country.

Keywords: Adsorption; Drinking water; Heavy metal; Mesoporous silica

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1. Introduction

Drinking water is one of the essential need for human being in everyday life. Human needs to drink at least 8 cups of water every day for healthy body. This is because a lot of water is needed for the metabolism processes in our body. Besides that, it has many applications and uses for example for food production and many more. In 2015, about 663 million people are still lacking of safe drinking water in 2015 (Molinos-Senante & Sala-Garrido, 2017). In fact, 89% of people had searching a suitable water for drinking in 2015. However, the amount of clean water available is continuously decrease annually. This is because water pollution in our country is serious due to the industrial sector. Most of the factories in Malaysia tend to dispose their waste to the water as it is the easiest way to dispose them. Hence, it might cause harmful and dangerous effect to the human and environment. Thus, water pollution and other environmental problems will occur if the disposal of waste into the water are continuously increase.

One of the problems that occur in the water is the existence of heavy metal. Heavy metal is defined as metallic element that have relatively high density compared to water. It is also a harmful chemicals and has a high degree of toxicity. Besides that, it is considered as hazardous materials and their toxicity to living organisms comes from their tendency to accumulate in living tissues because they are not biodegradable which can cause several health hazards like kidney problems, anemia, lung cancer and dyspnea (Abo-el-enein et al., 2017). These heavy metal can be found in water from various processes in industrial application such as mining, refining and production of textiles, paints and dyes (Gascón, et al., 2009). The industrial sector has been growing rapidly so, the heavy metal pollutant is continuously increase and can cause many environmental problem in the future. Examples of heavy metal are lead (Pb) and zinc (Zn). Lead (Pb) and zinc (Zn) can cause many problems in water.

The increasing quantity of zinc in water can lead to many health difficulties such as anemia, stomach cramps, vomiting, and skin irritations. Zinc also can lead to cancer if the concentration is higher. 5 ppm is the standard concentration of zinc that is safe and present in the water. So, if the concentration is higher than it, the quality and condition of water is dangerous. Lead (Pb) also has its harmful effects to the human and other living things. Some of the effects are cardiovascular effects, increased blood pressure and incidence of hypertension and decreased kidney function.

There are many ways to remove the heavy metal in the water. Some of the treatment process for removal of heavy metal are precipitation, membrane filtration, ion exchange, adsorption, and co-precipitation/adsorption (Hegazi, 2013). However, one of the most used process is adsorption process. Adsorption seems to be one of the most nonspecific processes adopted for the extraction of metals from water (Hadjal et al., 2004). This is because adsorption process requires low cost and has many other advantages. The other processes may produce toxic and harmful by-products that can bring harm to the environment. Thus, adsorption process can be categorized as ecofriendly treatment process as it does not damaging the environment.

In recent years, adsorption process has become one of the alternative treatments and the search for low-cost adsorbents that have metal-binding capacities has intensified (Barakat, 2011). Before this, carbon is used as adsorbent for the adsorption process. However, in this modern era, the researcher need to find a new alternative adsorbent that can replace carbon. Thus, a new hybrid organic-inorganic mesoporous ordered structures have been proposed as heavy metal adsorbents (Gascón et al., 2009). Adsorption process usually uses mesoporous silica as the adsorbent.

In this modern technology, mesoporous silica has been widely used in industrial application due to the development of industrial sector in this country. Mesoporous silica is basically a substance that has pores or holes and is usually small. There are many types of mesoporous silica present in our country. However, there are three main categories of porous materials which are microporous, mesoporous, and macroporous. By definition, microporous materials are the materials with pore diameters less than 2 nm while mesoporous materials are materials that have pore diameter between 2-50 nanometer ranges and lastly, macroporous materials are materials having pore diameter greater than 50 nanometer (Kumar, Malik, & Purohit, 2017).

Silica actually has already been recognized as a powerful water adsorbent (Lorrane et al., 2017). This is because mesoporous silica has high efficiency and low energy consumption compared to carbon which has been used as adsorbent in the past. There are many ways to synthesis mesoporous silica. Some of the examples are Sol-Gel processing, template assisted techniques, microwave assisted techniques, chemical etching technique (Kumar et al., 2017). The common process used is sol-gel processing. This is because the processes is easier and requires low cost. Thus, the main objectives of this study is to synthesis mesoporous silica for adsorption of heavy metal which are Pb and Zn and to determine adsorption efficiency of Pb and Zn.

2. Material and Methods

2.1 Materials

Sodium silicate (Na_2SiO_3) and sulfuric acid (H_2SO_4) were used in this study. Na_2SiO_3 and H_2SO_4 were used to synthesis mesoporous silica. 24 wt% of Na_2SiO_3 and 76 wt% of H_2SO_4 were used in this experiment. Ethanol (CH_3CH_2OH) was used to remove any water present in the mesoporous silica.

2.2 Synthesis of mesoporous silica

100 ml of both Na_2SiO_3 and H_2SO_4 were mixed together in a 1L conical flask and stirred using a magnetic stirrer at room temperature for 7 hours and produced wet gel. Then, it will produce wet gel. The wet gel was then washed by using ethanol (CH_3CH_2OH) and filtered to remove any water present in the mesoporous silica. The solution was collected in a crucible and dried using an oven. The solution was then heated overnight at temperature 150℃. Then,

the solution was dried and crushed using crusher until it becomes white powder. Lastly, the powder was then occur for calcification for two hours at temperature 350℃. The sample was placed in a clean glass bottle and labelled.

2.3 Heavy metal standard solution

Standard solution was prepared using lead nitrate $(PbNO_3)_2$ and zinc chloride ($ZnCl_2$). 1000 ppm was used as stock solution. $(PbNO_3)_2$ and $ZnCl_2$ were weighed and place in a 1000 ml volumetric flask and distilled water is added until it reached 1000 ml. Then, 1ml, 2ml, 3ml, 4 ml, and 5ml from the standard solution were taken to make different concentrations which were 10 ppm, 20 ppm, 30 ppm, 40 ppm and 50 ppm. The solution was dissolved with distilled water until it reached 100 ml.

2.4 Adsorption of heavy metal

5g of silica was weighed and were dissolved in different concentration of heavy metal standard solution which were 10 ppm, 20 ppm, 30 ppm, 40 ppm, and 50 ppm. The solution is then stirred in different contact times, which are 30 minutes, 60 minutes and 90 minutes. The solution was filtered using filter paper and further filtered using membrane filter.

2.5 Characterization of mesoporous silica and heavy metal

FTIR analy i was conducted to identify functional groups in the mesoporous silica. FTIR analysis was conducted in FTIR Bruker Vertex 70. Inductively coupled plasma mass spectrometry (ICP) was used to determine the concentration of the heavy metal adsorbed by the mesoporous silica in Inductive Coupled Plasma (Perkin Elmer, Optima 8000).

$$\text{Percentage removal} = \frac{\text{Initial concentration} - \text{Final concentration}}{\text{Initial concentration}} \times 100$$

3. Results and Discussion

3.1 Mesoporous silica characterization

FTIR spectroscopy was conducted to determine the functional groups in an element. The FTIR analysis of the mesoporous silica before and after the adsorption of heavy metal was shown in Fig. 1. The frequency of oscillation of any chemical bond is related to a quantity known as the wavenumber. The greater the frequency of oscillation of the chemical bond, the greater the wavenumber is. According to (A. Ahmad et al., 2016), the broad band that appeared around 3,200–3,600 cm was mainly ascribed to the free or hydrogen bond O–H and/or NH (amino) symmetrical stretching variations. For the pure mesoporous silica, the strong adsorption bands of the aromatic C-H bending was seen at the peak 880.16 cm^{-1}.The gap of the peak before and after the adsorption at that wavelength was far. Thus, it shows that the adsorption process at that time was strong. Then, the functional group of alkene (C=C) bond was present at the peak 1652.57 cm^{-1}, with weak intensity. This can be seen as the peak of before and after adsorption at that wavelength shows little difference compared to other wavelength. At that wavelength, the adsorption of heavy metal process was occurred slightly. Alkyne group also was present at the wavelength 2363.52 cm^{-1}. The intensity at this wavelength was also medium. Thus, we can see also the gap of the peak before and after the adsorption at that wavelength. Lastly, alkane (C-H) group was present at the wavelength 2798.82 cm^{-1} with medium to strong intensity. So, the gap of the peak before and after the adsorption was large.

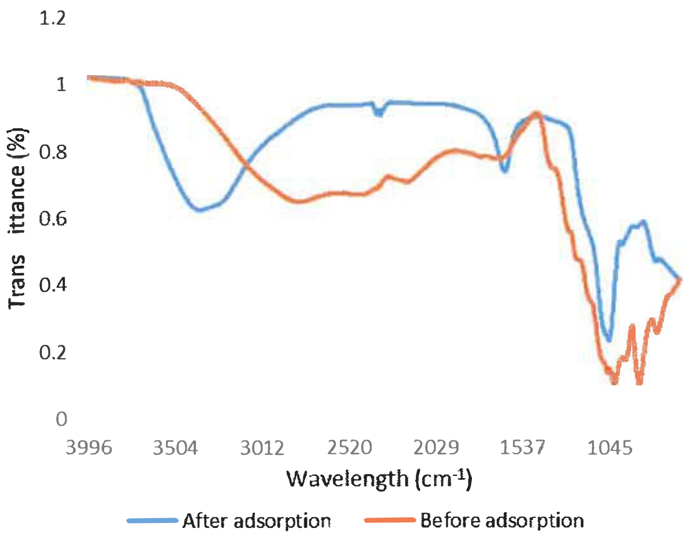

Fig. 1. FTIR spectra analysis of mesoporous silica before and after the adsorption process

3.2 Effects of contact time in Pb

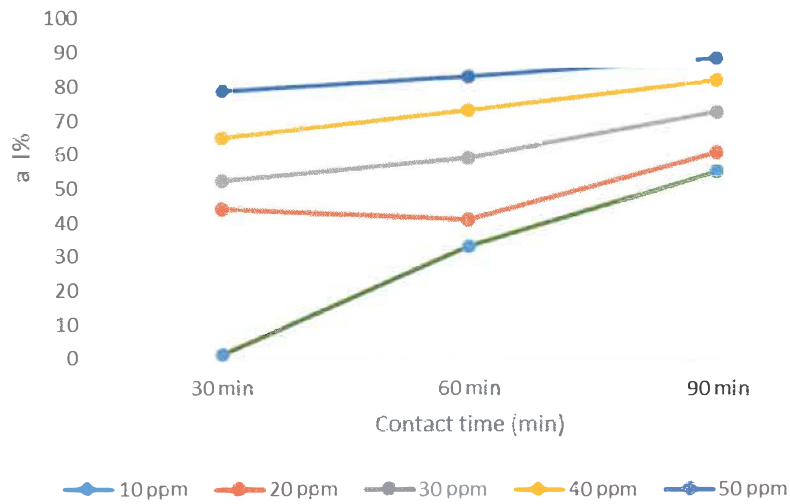

Fig. 2. Effect of contact time on the removal percentage of Pb (II) ion by mesoporous adsorbent.

In order to study the effects of contact time on the removal efficiency of Pb (II) ion using the mesoporous silica, the experiment was carried out using constant loading dose which is 5g and at vary concentrations (10 ppm – 50 ppm). From the experiment, it was observed that the percentage removal increases as the contact time increases. This is because the adsorbent adsorb more heavy metal as they filled the surface of the adsorbent as the contact time increases. This is due to the high amount of active sites available on the mesoporous adsorbent surface and high solute gradient of concentration (Vojoudi et al., 2017). So, the higher the concentration and contact time, the larger the amount of heavy metal adsorb on the active sites of the adsorbent. The percentage removal of Pb (II) ion at 20 ppm was slightly decreases from 44.35% to 41.20% at 60 minutes. The rate of percentage removal of Pb (II) ion at 10 ppm was quite rapid which was levelled out from 1.50% at 30 minutes to 33.18% at 60 minutes. This shows that at lower concentration, the attractive force of Pb (II) ion with the binding site of the adsorbent was greater compared to the other concentrations. The highest percentage removal was on 50 ppm at 90 minutes which was recorded at 88.64%. It was clearly shown that the higher the concentration, the higher the percentage removal of Pb (II) ion. Higher concentration of the heavy metal has greater ability to bind on the surface of the adsorbent because it has higher strength to be adsorb by the adsorbent. The adsorbent at lower concentration tend to adsorb little amount of the heavy metal because it has smaller surface area in order to attract the heavy metal on its surface. Thus, it cannot afford to adsorb large amount of heavy metal in the aqueous solution as its surface area is smaller. According to Abdelhadi et al. (2017), all OMSW biochar experiment that they carried out were effective at removal of higher than 80% of lead and copper. It was true as our results for the highest percentage removal obtained was recorded at 88.64%. Thus, it shows nearly 90% of the Pb (II) ion was adsorbed on the surface of the adsorbent. According to (Karami, 2013), magnetite nanorods adsorbent was used for the removal of Fe^{2+}, Pb^{2+}, Zn^{2+}, Ni^{2+}, Cd^{2+} and Cu^{2+} ions was recorded that the efficiencies was more than 90% during 20 minutes. This shows that magnetite nanorods adsorb heavy metal faster compared to mesoporous silica adsorbent because silica adsorbent adsorb highest percentage removal starting at 90 minutes. However, the adsorption efficiency of Pb (II) ion will increase if the contact time is prolonged. This is because the higher the contact time, the larger the amount of heavy metal will be adsorbed on the surface of the adsorbent.

3.3 Effects of contact time in Zn

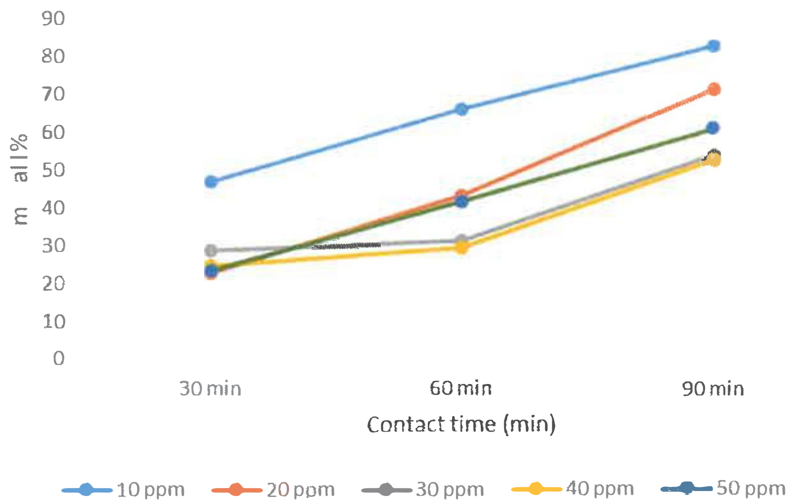

Fig. 3. Effect of contact time on the removal percentage of Zn (II) ion by mesoporous adsorbent.

To study the effects of contact time on the removal percentage of Zn (II) ion by mesoporous adsorbent, the experiments were carried out using constant loading dose which is 5g and different initial concentration varying from 10 ppm to 50 ppm. Based on the graph, it was observed that the percentage removal of Zn (II) ion was increases with the increases of contact times. This is because the longer the contact time, the adsorbent get to adsorb more heavy metal on its surface. This is because the ions easily interact with available binding sites as interaction initiated between adsorbent and the heavy metal (Ali et al., 2018). It was also recorded that the highest percentage removal on Zn (II) ion was at 10 ppm. Thus, the lower the concentration, the higher the percentage removal. The highest percentage removal was recorded at 82.99% at 10 ppm during 90 minutes. The trend of this results showed an increasing of the percentage removal as the contact time increases. However, the trend for the lowest percentage removal of Zn (II) ion was recorded at 40 ppm which was recorded at 24.58% at 30 minutes and 53.03% at 90 minutes. The percentage removal of the heavy metal at concentration 50 ppm was higher than at concentration 40 ppm. Thus, it shows that at concentration 50 ppm, the adsorbent adsorb more heavy metal compared to the