Valorization of Okara biosorbent for Heavy Metal Removal

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Abstract

Many of the industry has caused several damages to the water due to release of toxic heavy metals. Heavy metals that discharge in the wastewater from industries such as lead, copper, zinc, cadmium, manganese which are very harmful to organisms and environment. In the present study, okara was used as the material for adsorption of Pb^{2+} and Zn^{2+} from simulated wastewater. The experiment was tested by using different parameters such as adsorbent dose and contact time. The treated and untreated okara was used to evaluate their potential as heavy metal removal. For the treated okara (TO), it undergoes ultrasonic-assisted alkaline as the pretreatment. Pretreatment of okara with NaOH increased the capacity of heavy metals adsorption compared to untreated okara (UTO) for both parameters. For Pb^{2+} solution, the highest adsorption percentage of treated okara for adsorbent dose is at 5g and the highest adsorption percentage of TO for contact time is at 40 min. However, for Zn^{2+} solution, the highest adsorption percentage of TO for adsorbent dose is at 20 g whereas the highest adsorption percentages of treated okara for contact time is at 140 min. Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) analysis was used to analyse the present of Pb^{2+} and Zn^{2+} and also to measure the quantity of heavy metals adsorption from the simulated wastewater. The most influence of parameters is contact time. The results showed that the adsorption capacity increases as the contact time increases.

Keywords: Soybean waste; Adsorption; Biosorbent; Metals; Lead; Zinc

1. Introduction

Excessive release of heavy metal into the environment due to industrialization and urbanization has caused a great problem worldwide. Heavy metals will discharge in the wastewater from industries such as lead, copper, zinc, cadmium, manganese which are very harmful to organisms and environment (Tripathi & Rawat Ranjan, 2015). Many heavy metals are essential trace elements for humans, animals, and plants in a small amount. But in larger amounts can cause acute and chronic toxicity and linked to learning disabilities, cancers and even death.

Therefore, treating the wastewater before discharge is the best way to solve the problems. Several conventional methods have been used in removing of heavy metal in wastewater to solve these problems such as membrane filtration, chemical precipitation, adsorption, ion-exchange, filtration, flotation, coagulation-flocculation and electrochemical (Etorki et al., 2014). But, the common treatment that normally used to remove heavy metals is adsorption using agricultural waste or also known as low-cost adsorbent because this method is less expensive compared to another method.

There are several types of agricultural waste normally used as an adsorbent such as peanut husk, charcoal, natural zeolite, fly ash and rice husk (Abdel Salam et al., 2011). All of these wastes gave an effective result as an adsorbent. But, based on the researched that have been conducted, soybean waste also known as okara can also be categorized as one of the low-cost adsorbents because its availability is enough for the large-scale production. In addition, fresh okara degrades quickly so it does not give a bad impact on the environment.

Okara is a pulp consist of insoluble parts of the soybean which remain after pure soybean are filtered in the production of soy milk and tofu. Okara contains 50% carbohydrate, cellulose, hemicellulose, and lignin which may help the process of adsorption (Choi et al., 2015). The composition of okara exhibited good sorption abilities to heavy metals, organochlorine, and anion.

In this study, okara is used to remove Zinc Zn^{2+} ion and Lead Pb^{2+} ion. On the other part, okara has been categorized in two which are treated Okara (TO) and untreated Okara (UTO). Treated Okara (TO) undergoes pretreatment combining alkali and ultrasound treatment. Pretreatment of okara by alkali-assisted ultra-sonication is conducted in this study. This is because the alkali pretreatment is found to be effective in removing heavy metals from aqueous solution (Wan Ngah & Hanafiah, 2008a). According to the studies, most are using sodium hydroxide for the pretreatment of their adsorbent which are cottonseed hulls and soybean hulls. They found that the heavy metal adsorption is increasing up to 79% for zinc metal. Next, based on the studies shows that treatment of spent grain with NaOH enhanced the adsorption of Pb^{2+} ions (Low et al., 2000). This shows that the alkali pretreatment

of the adsorbent gives an advantage to the adsorption of heavy metal by increase the negative charge sites or greater number of metal adsorption sites, it will be resulting in greater metal adsorption capacity (Wan Ngah & Hanafiah, 2008)

In the present study, pretreatment was carried out by exposing okara to ultrasound irradiation for 1 hour, using an ultrasonicc bath with the power of 100W and 37kHz frequency. Based on few studies, ultra-sonication pretreatment will increase the adsorption of heavy metals from the aqueous solution. According to the studies stated that treated sample of cotton gin waste by ultra-sonication was found to have a better performance since its resulted in higher metal removal percentages and higher adsorption capacity compared to untreated cotton gin waste (Pellera et al., 2017). Ultra-sonication provides significant speeding up for metal extraction (Bendicho & Lavilla, 2013) So, pretreatment alkali-assisted ultra-sonication of okara is conducted to investigate how it assists the metal adsorption from the simulated wastewater.

For the treated okara (TO), the raw okara need to immerse in sodium hydroxide solution (Viraraghavan & Kapoor, 1996). The reason why alkali ultra-sonication was chosen as the process of pretreatment because it increases the adsorption capacity of heavy metals (Hu et al., 2015). It has been studied that, contact time of adsorbent towards the heavy metals, adsorbent dosage, pH, and temperature are factors affecting heavy metals adsorption (Ojedokun & Bello, 2016). The parameters (adsorbent dosage and contact time of adsorbent towards heavy metals) gave the significant effect of okara towards the adsorption of heavy metals (Nguyen et al., 2013).

The objective of this study is to investigate the potential of low-cost adsorbent which is the raw and pretreated okara for the elimination of heavy metals from the simulated wastewater. This study is to clean the water of the environment from hazardous material such as the Pb^{2+} and Zn^{2+}. The results of the adsorption capacity of these materials have been evaluated by using ICP-OES.

2. Methodology

2.1 Preparation of okara

Okara was selected as biosorbent in this study. It was acquired from a local factory in Kota Tinggi, Johor. Treated and untreated okara will be used in this experiment. To prepare the okara, it was dried in the oven at 85°C to avoid from getting burned and the duration was 24 h. Then, it was left cooled for 15 minutes at room temperature. Next, the okara was grind into powder form and were stored in containers before it was used for the next steps.

2.2 Pretreatment of okara

A portion of the okara was treated by dissolving it in 0.1 M of sodium hydroxide (NaOH) solution. Then, the sample was immersed in the ultrasonic bath (Elmasonic P series – Elma Ultrasonic Cleaner) which contains distilled water. They were immersed for 60 min at 30°C and the frequency was 37 kHz at 100% of power percentage. After sonication, the okara was rinsed with distilled water to ensure that the NaOH concentration was washed away from the okara itself. This process was repeated until the color of the distilled water that washed the okara turn from murky to a clear solution. Lastly, the okara was dried for 24 h and stored in containers for the next process after it was crushed to powder form.

2.3 Effect of adsorbent dose.

This experiment was conducted to evaluate the effect of adsorbent dose towards the adsorption of heavy metals of okara. Firstly, varying doses of okara (5g, 10g, and 20g) of both TO and UTO were weighed and insert into respective conical flasks. Next, 100 mL of 50 ppm of lead (II) nitrate ($Pb(NO_3)_2$) solutions were prepared and dissolved into different conical flasks containing different doses of okara. The procedure was repeated using 100 mL of zinc chloride ($ZnCl_2$) solutions with the concentration of 50 ppm. Then, the samples then were put in the incubator shaker (New Brunswick™ Innova® 44/44R) for 60 minutes at room temperature for mixing process. After the contact time was over, the samples were filtered, and the solutions were kept for the next step which was analysis.

2.4 Effect of contact time.

The contact time effect was evaluated to determine the optimum time for TO and UTO to adsorb the heavy metals. The contact time for the okara to adsorb the heavy metals were 20 min, 40 min, 120 min, and 140 min. 4 samples of both TO and UTO for each contact time were needed for $Pb(NO_3)_2$ solutions and another 4 samples of TO and UTO also for each contact time for $ZnCl_2$ solutions to proceed with this experiment. Next, all of the samples were brought into the incubator shaker (New Brunswick™ Innova® 44/44R) for mixing purpose and will be taken out when the contact times of respective samples were over. Finally, the samples were filtered, and the solutions were stored for analysis.

2.5 Determination of okara adsorption capacity.

To analyze the amount of heavy metals has been adsorbed by the okara, all of the samples were analyzed by using inductively coupled plasma optical emission spectrometry (Perkin Elmer – Optima 8000 ICP-OES). The adsorption capacity percentage was determined using equation (1), as:

$$\text{Adsorption capacity (\%)} = \frac{C_i - C_f}{C_f} \times 100\% \quad (1)$$

Where C_i is the initial concentration of sample solution (mg/L), and C_f is the final concentration of sample solution. The results were presented in bar chart.

3. Results and discussion

In this study, Okara was chosen as the low-cost adsorbent to remove heavy metal ions such as Pb^{2+} and Zn^{2+} in simulated waste water. Okara was categorized into two which are treated okara (TO) and untreated Okara (UTO). TO undergoes alkali-assisted ultra-sonication in this study. The parameters such as adsorbent dose and contact time were investigated in this study for the process optimization. For the adsorbent dose, different doses have been used which were 5g, 10g, and 20g. For contact time, the results were calculated for the respective minutes which are 20 min, 40 min, 120 min and 140 min. The results and discussion are shown below.

3.1 Effect of adsorbent dose on Pb2+ adsorption

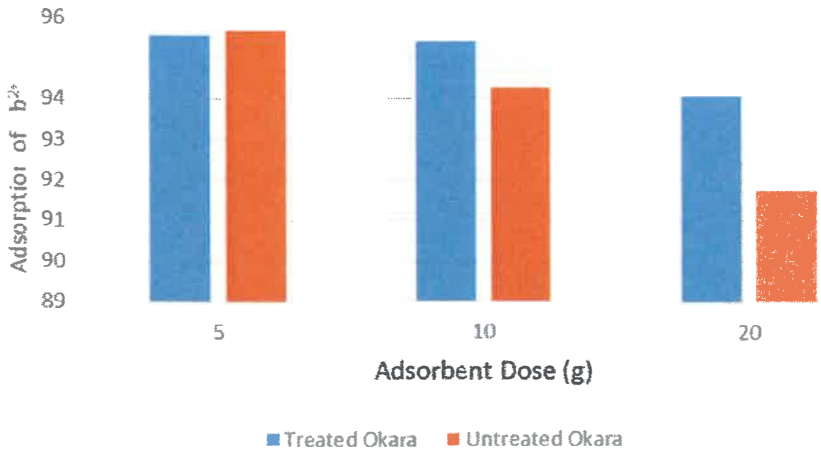

Figure 1: Adsorption capacity of Pb^{2+} VS Adsorbent Dose

The effect of adsorbent amount on metal ion adsorption was studied by preparing 50 mg/L solution of Pb^{2+} containing different doses adsorbent which are 5g, 10g, and 20g as shown in Figure 1 and there are two types of okara which are untreated okara and ultrasonic-assisted alkali pretreated okara were observed. According to the results, adsorption capacity of Pb^{2+} ions for treated okara the range is 93.5% to 95.5%. For adsorbent dose 5g, 10g, and 20g, the removal percentage resulted are 95.50%, 95.39%, and 94.06% respectively. The results of this study show that the increasing in adsorbent dose from 5g to 20g resulting in decrease of

adsorption percentage of Pb^{2+}. In contrast, other studies show that the increasing of adsorbent dose resulting in increase of adsorption percentage Pb^{2+} (Georgescu et al., 2017). Furthermore, the alkali pretreatment can enhance the adsorption of Pb^{2+} ions. Based on the studies shows that treatment of NaOH enhanced the adsorption ions (Low et al., 2000). Moreover, low adsorbent dose can fully increase the size of pores compared to higher adsorbent dose which are 10g, and 20g. This is because higher adsorbent dose may lead to incompletely treat of alkali because less surface area exposed to the alkali which was conducted the alkali with the same volume of sodium hydroxide for each different amount of adsorbent dose.

Next, for the results of untreated okara, it was found that the adsorption capacity of Pb^{2+} was constantly decrease as the adsorbent dose increase. The higher the surface area, the bigger the size of pores. So, the optimal dose for adsorption of Pb^{2+} was 5g. Based on (Etorki et al., 2014) studies, they found that the optimal adsorbent dose to absorb Pb^{2+} also 5g but they were using Fava Beans as the low cost adsorbent.

For the comparison of adsorption using treated and untreated okara, most of the adsorbent dose of treated okara has high adsorption capacity. This is because of the cavitation of bubbles (Pilli et al., 2011; Rastogi, 2011). When applied on liquid, ultrasound waves consist of a cyclic succession of expansion and compression phases imparted by mechanical vibration. Once a bubble is created, it will undergo expansion and compression cycles and the bubbles will grow slowly. It will lead to increasing the pores at the surface of okara with the alkali-assisted ultrasonication with sodium hydroxide.

3.2 Effect of contact time on Pb^{2+} adsorption

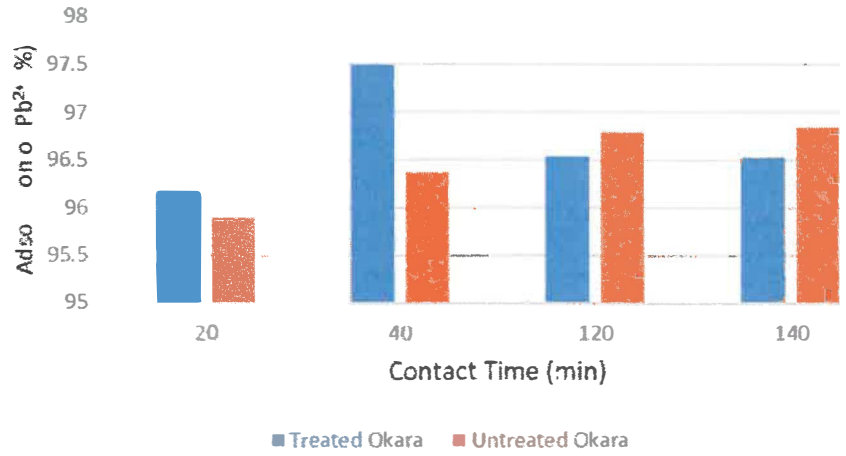

Figure 2: Adsorption of Pb^{2+} VS Contact Time

The experiment was conducted at fixed concentration of Pb^{2+} solution which is 50 mg/L and fixed adsorbent dose at 10 g of okara. The effect of contact time on the removal of Pb^{2+} ions by TO and UTO was recorded in Figure 2. The experiment was conducted at different contact time (20 min, 40 min, 120 min, 140 min). Based on the results, it shows that both TO and UTO with the increasing of contact time, can adsorb more Pb^{2+} ions. The adsorption percentage of Pb^{2+} for 20 min, 40 min, 120 min and 140 min were 96.17%, 97.49%, 96.53% and 96.52% respectively for TO. But, at the duration of 40 min it adsorbs the highest amount of Pb^{2+} ions which was 97.49% compared to others. Results showed that at first 40 min, the adsorption rate was very fast but after 40 min the adsorption rate was reduced. This is because due to the fact that all the adsorbent site was vacant at the beginning and capabilities were high due to adsorb ions (Hafshejani et al., 2015). After this time, the adsorption percentage slightly decrease at 120 min and 140 min. However, after 120 min, there is a small gap between the adsorption percentage at the time of 120 and 140 min because it already reached its equilibrium phase. The result achieve in the study are more or less similar with the experiment conducted to adsorbed phosphorous in aqueous solution by using iron loaded okara (Nguyen et al., 2013).

For the UTO at 20 min, 40 min, 120 min and 140 min, the results were 95.89%, 96.36%, 96.79% and 96.84% respectively. As the contact time between UTO and Pb^{2+} solution increase, the adsorption percentage of Pb^{2+} ions were increase. The highest percentage of heavy metal removal was at 140 min which is 96.848% and the lowest percentage of adsorption was at 20 min which is 95.897%. This is because the lower the contact time, the lower the surface area of okara to mix with Pb^{2+} solution hence resulting in lower adsorption percentage. The optimum contact time for UTO was at 140 min because the adsorbent percentage of UTO remain unchanged after this time. Same results were achieved by other studies (Basu et al., 2017; Hafshejani et al., 2015).

3.3 Effect of adsorbent dose on Zn^{2+} adsorption

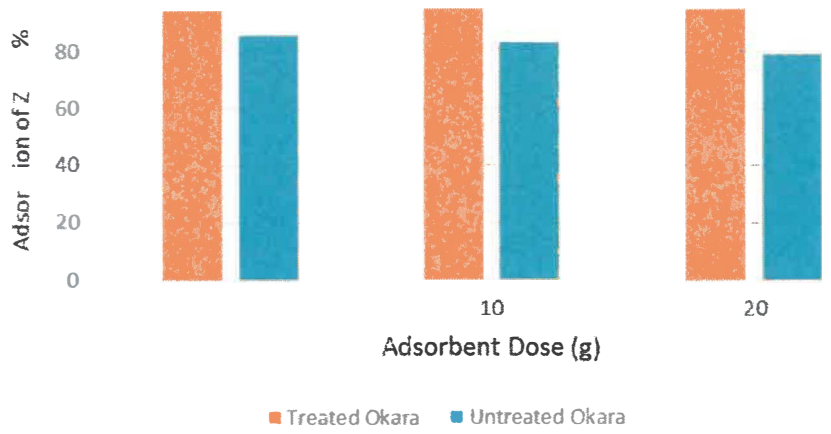

Figure 3: Adsorption of Zn^{2+} VS Adsorbent Dose

The effect of adsorbent amount on metal ion adsorption was studied by preparing 50 mg/L solution of Zn^{2+} containing different doses adsorbent which are 5g, 10g, and 20g as shown in Figure 3. Zn^{2+} ions removal using TO increase from 5g to 10g and decrease from 10g to 20g. The data achieved for adsorption of Zn^{2+} for 5g, 10g and 20g from this experiment were 94.35%, 94.72% and 94.55% respectively. The adsorption of Zn^{2+} ions for 5g of TO be the lowest (94.35%) compared to others. As the adsorbent increase to 10g, the adsorption percentage was increase. The increase in the removal percentage with change in adsorbent dose is due to increasing in active site on the adsorbent and which makes penetration of the metal ions to the removal site much easier and also attractive interaction increases between ions and adsorbent surface (Fakhre & Ibrahim, 2018) and also to the fact that the number of available active center from nanomaterial surface is even greater as the mass of used adsorbent is higher, thus favoring the adsorption of Zn^{2+} ions (A. M. Georgescu et al., 2017). But, the decreasing of adsorption percentage can be observed from 10g to 20g. This is because that less surface area of TO is exposed to the Zn^{2+} ions and the ions that have been adsorbed by TO were low.

Next, for the results of UTO for 5g, 10g and 20g, the adsorption percentage of Zn^{2+} ions were 85.68%, 83.09% and 78.86% respectively. The adsorption percentage of Zn^{2+} ions were decrease as the adsorbent dose were increase. The higher the amount of adsorbent dose, the lower the surface area of UTO resulting to small size of the pores. On the other hand, other studies found that as the adsorbent dose increase, the adsorption capacity increase (Bozbaş & Boz, 2016; Hegazi, 2013) by using different types of adsorbent which were rice husk, fly ash and anadara inaequivalvis shells as low-cost biosorbents.

3.4 Effect of contact time on Zn^{2+} adsorption

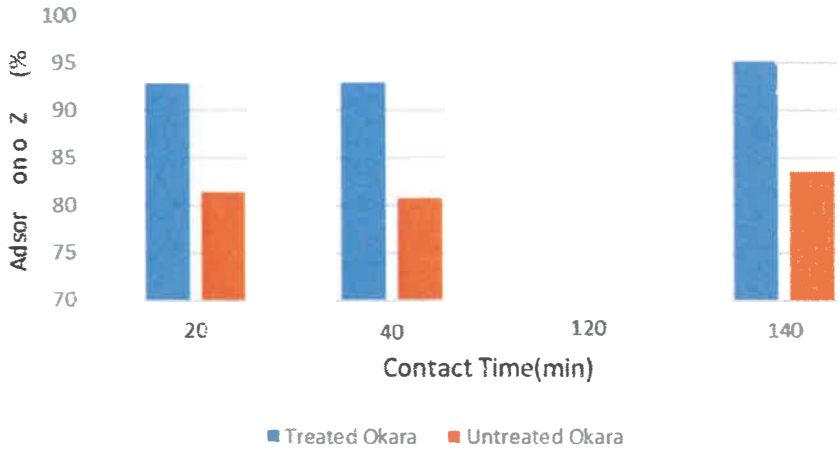

Figure 4: Adsorption capacity of Zn^{2+} VS contact time