Desorption of Zinc Heavy Metal Ion from Soybean Waste Biosorbent

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Abstract

The study was carried out to measure the effect of type of elution reagents, concentration of elution reagents and contact time with elution reagent on desorption of Zinc (II) heavy metal ions from soybean waste biosorbents. Organic waste like soybean waste contain several functional group like carboxyl, carbonyl, acetamido, amino and hydroxyl. These functional group are contained in natural polymers such as cellulose, hemi-cellulose, pectin and lignin which able to bind heavy metal ions present in aqueous solution. The biosorbent, soybean waste in this research were characterized with Fourier Transform Infrared (FTIR) to identify the characteristic of the soybean waste as an efficient biosorbent. Then, investigation and comparison of the effects of eluent type, eluent concentration and contact time was made for the desorption study of the soybean waste. Desorption experiment was conducted with three different elution with two different concentrations each. (The elution used in this study are HNO_3 (0.1M & 1.0M), NaOH (0.1M & 1.0M) and EDTA (0.05 M & 0.1M).) The sample after the desorption study is then tested by running the Inductively Couple Plasma – Optical Emission Spectrometry (ICP-OES) test. The results show that the maximum Zinc (II) ions desorption capacity was 88.43% with the elution of HNO_3 at 0.1 M. while the minimum Zinc (II) ions desorption capacity was NaOH at 1.0 M with 28.76% of heavy metal desorption. The results of this study imply that soybean waste is a suitable biomass to remove Zn and are able to under goes the desorption process for regeneration and reusability that is economically beneficial.
Keyword: Eluent; Desorption; Soybean Waste; Zinc(II); EDTA; FTIR

1.Introduction

Water pollution has now become one of the major problems in the environment as it widely occurs due to the abundant amount of heavy metals from waste that were disposed into water bodies such as rivers, ponds and lakes. This happens because of the increase in the sector of battery manufacture, mining and electroplating that releases heavy metals as their wastes (Hegazi, 2013). Many methods of heavy metal removal from water have been determined to reduce this problem such as precipitation (Barakat, 2011), membrane filtration (Bakalár et al., 2009), ion exchange (Dąbrowski et al., 2004) and adsorption (Sadeek et al., 2015). Studies have showed that adsorption using activated carbon is the best method in treatment of waste water. However, due to the high cost, there is a limitation on using this method as it is not suitable for wide industry range. To overcome this problem, many researches were held and it was found that agricultural waste can act as an adsorbent and can desorb heavy metals to be used once again. There are many advantages when we use agricultural waste as adsorbent such as lower costing, higher adsorption efficiency, minimization of chemical or biological sludge, no additional nutrient requirement, and regeneration of biosorbents and possibility of metal recovery (Sud et al., 2008).

The basic components of the agricultural waste are hemicellulose, lignin, extractives, lipids, proteins, simple sugars, water hydrocarbons and starch which contains a variety of functional groups that facilitates metal complexation which helps for the sequestering of heavy metals (Bailey et al, 1999). In this paper, we decided to use soybean curd residue, namely soja waste in Portugese as an adsorbent and also run a desorption study. This is because about 800,000 metric tonnes of soybean waste is disposed of annually as by-products of tofu production in Japan. The expense for soybean waste disposal costs around 16 billion yen per annum (Muroyama et al., 2006). Based on statistics that were recorded, about 1.9 million metric tonnes of soy bean meal waste produced in Malaysia. Due to that, we have to search for other alternatives in order to reduce the combustion of soy bean waste as it can release carbon dioxide which then can leads to Green House Effects.

It is well known that the consumption zinc contained water causes various health problems to living organisms. Approximately 2.3 g zinc is present in a human body and has a dietary value of a trace element. Its functions mainly involve enzymatic processes and DNA replication. The human hormone insulin contains zinc, and

it plays an important role in sexual development. Zinc toxicity can occur in both acute and chronic forms. Nausea, vomiting, loss of appetite, abdominal cramps, diarrhea, and headaches are the acute adverse effects of high zinc intake while the chronic form results in low copper status, altered iron function, reduced immune function, and reduced levels of high-density lipoproteins.

Even though research on adsorption and its potential agents, not many have concentrated their efforts in further improving the effectiveness of the adsorbents by recovering used adsorbents for further use. This matter becomes even more concerning due to the fact that spent biosorbents still containing heavy metals pose an immediate threat to humans and the environment thus, spent biosorbents must undergo heavy metal recovery before being disposed of (Lata et al., 2015). If the heavy metals could be recovered from spent biosorbents and the biosorbents can undergo biosorption again after recovery, its cost effectiveness is significantly improved attracting more usage of this method (Stirk & Staden, 2002).

The purpose of desorption is to remove the heavy metals from biosorbents for further use as recycled biosorbents which is economically benefiting. Acids like HCl, HNO_3, and H_2SO_4 desorbs all metal ions in most of the cases, except Cr(VI). PB^{2+} and Zn^{2+} can be removed using EDTA in addition to acids. Since Cr(VI) is present in anionic form, it can be eliminated from the loaded absorbent using bases like NaOH, Na_2CO_3, or $NaHCO_3$ (Mishra et al., 2013)

The aim of this study were to prepare adsorbents, characterize their properties to adsorb heavy metals and to evaluate the desorption effectiveness of different elution reagents and contact time of elution reagent. The desorption of Zn^{2+} from loaded soybean waste zinc were examined by desorption capacities using three different solutions with two different concentrations. The result for adsorption and desorption capacities were analyzed using ICP-OES.

1.Methodology

2.1 Sample Preparation

Soybean waste samples were collected from a local tofu factory located in Kota Tinggi, Johor. The soybean waste have been washed several times with tap water to remove impurities. Then, they were oven dried at 90°C for overnight. The dried soybean waste were milled and sieved to powder form. Soybean wastes were sieved at 250 μm.

2.2 Zinc (II) Ion Stock Solution and Eluent Preparation

Zn (II) ion stock solution was prepared in stock with concentration of 100 mgL^{-1} using $ZnCl_2$. It was further diluted to a fix concentration of 65 mgL^{-1} with distilled water. Then, solutions of 0.1M and 1.0M of HNO_3 was prepared by diluting it from 14M. The 0.1M NaOH solution is diluted from 1.0M of NaOH by adding it with distilled water. EDTA solutions of 0.05M and 0.1M were prepared from dissolving EDTA powder in distilled water.

2.3 Desorption Study

Prior to desorption studies, method of adsorption is done first where soybean waste samples of approximately 0.1g were gently agitated in 100mL of 65 mg/L Zn^{2+} solution for an hour at room temperature in an orbital shaker. Sample were immediately filtered through filter paper before ICP-OES measurement using Perkin Elmer (model) which was done to obtain final concentration of Zn^{2+} in solution (X) for reading in desorption study. The desorption study was done by immersing loaded soybean waste into different elution reagents (HNO_3 0.1M & 1.0M, NaOH 0.1M & 1.0M, EDTA 0.05M & 0.1M). The mixture was left for 60 mins and then filtered by filter paper to remove the adsorbents. Metal ion concentration in elution reagent is analyzed by using ICP – OES Perkin Elmer (model) to determine the presence of Zn^{2+} in the eluents after desorption. The desorption percentage is calculated using the following equation.

$$Desorption\ (\%) = \frac{Y}{X^{\circ} - X} \times 100\% \quad (1)$$

X^o= Initial concentration of Zn in heavy metal solution (mg/L), X= Final concentration of Zn in heavy metal solution (mg/L), Y= Concentration of Zn^{2+} in eluent reagent (mg/L)

2.4 Characterization of soybean waste

FTIR spectra raw soybean waste, loaded soybean and desorbed soybean was analyzed to investigate the changes of functional group characteristic absorption band behavior after adsorption and desorption. The FTIR spectra of soybean waste was determined by using FTIR spectrometer (Vertex 70, Bruker). Sample spectra was recorded between 4000 cm^{-1} and 650 cm^{-1} with an average of 32 scans per spectrum with resolution of $4cm^{-1}$.

2.Results and Discussion

3.1 Effect of type of elution and concentration in desorption of heavy metal (Zn^{2+})

Desorption study was carried to determine the regeneration and reusability of soybean waste for the interpretation of the efficiency and feasibility of metal removal process. Desorption study of metal ions that were bound to the soybean waste was conducted by immersing the loaded soybean waste samples in three different eluents, HNO_3, NaOH and EDTA at varying concentration.

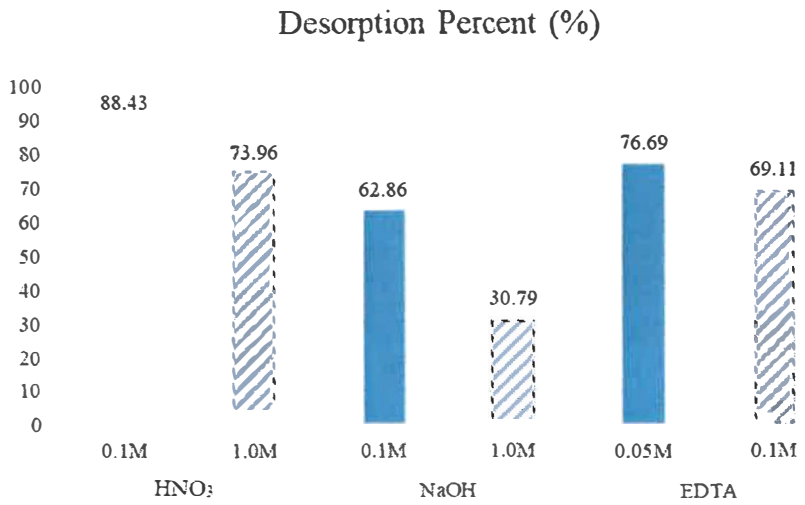

Figure 1. Type and concentration of elution reagent on desorption percentage.

From Figure 1, it is clearly observed that the biosorbent desorption was affected by the different type of eluents, for instance the desorption by HNO_3 and EDTA were visibly higher than NaOH. The highest desorption was achieved by HNO_3 at 0.1M with 88.43% while the lowest desorption was achieved by NaOH at 1.0M with 30.79%. The desorption study of Chromium (III) from aqueous solution by (Garcia-Reyes & Rangel-Mendez, 2008) shows that the highest desorption of chromium ions was achieved by NaOH at 0.1M with 89% while the lowest is 16% desorbed by HNO_3 at 0.1M.

These results can be explained by the ions Zn^{2+} which obviously a cation or metal ion is desorbed using acids like HNO_3 and EDTA. While for metal with anion like Cr(VI) can be eliminated by using bases like NaOH, Na_2CO_3 or $NaHCO_3$ (Mishra, et al., 2013). Thus, this explained the reason NaOH desorbed the least Zn^{2+} among all the other eluents used in the experiment. As for result of desorption efficiency for HNO_3 is slightly higher than that of EDTA is because HNO_3 is a stronger acid as compared to EDTA, so it can be concluded that HNO_3 is relatively more effective eluent for recovering metal ions from soybean waste biosorbent.

On the other hand, the desorption studies are also affected by the concentration of elution. Based on the Figure 1, it is clearly showed that HNO_3 of 0.1M is the optimum solution for desorption of zinc metal as its percentage of desorption is the highest which is 88.43% compared to HNO_3 of 1.0M which is 73.95% respectively. Same goes with concentration of NaOH and EDTA in 0.1M and 0.05 M is better in desorption than the concentration of NaOH and EDTA in 1.0M.

Basically, the result shown above illustrated that desorption capacity decreased with increasing of concentration. This observation is caused by an increase of acid concentration which making H^+ accumulating in the solution. This will make the concentration gradient of H^+ ions and Zn^{2+} ions increase which will then lead to the increasing of driving force of ion exchange thus advocate the desorption process. However, the increase of concentration in solution will make the H^+ increase too. This situation may cause repulsion of electrostatic between Zn^{2+}, and causing inhibition of Zn^{2+} desorption (Chandane & Singh, 2014).

3.2 Effect of contact time with elution reagent in desorption

The effect of contact time with elution reagent on desorption was investigated by immersing loaded soybean waste samples in EDTA 0.1M for 20 and 60 mins. The results obtained shows that 20 min contact time with EDTA 0.1M desorbed 97.99% of Zn^{2+} from loaded soybean waste while 60 min contact time had a lower desorption percentage of 66.68%. The results can be seen in Figure 2.

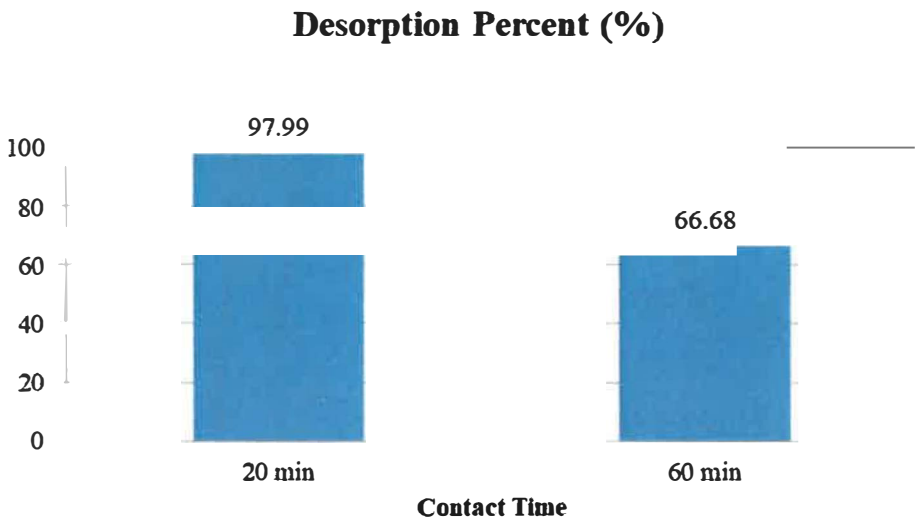

Figure 2. Contact time on desorption percentage.

These results are in agreement with a study by (Zhang & Wang, 2015) where they found out that the desorption of heavy metal ions can reach maximum desorption capacity at 30 mins thus causing the ions to be reabsorbed into the adsorbent. If absorbent remains in the eluent after eluent has achieved maximum desoprtion capacity, the absorbent will regenerate and reabsorb the Zinc (II) ions which explains why the results obtained show a decrease in desorption percentage at 60 mins. This proves that soja waste adsorbents can be potentially recovered and recycled for further use.

3.3 Fourier Transform Infrared (FTIR) Spectroscopy

To investigate primary functional groups present in soja waste that take part in adsorption of Zn^{2+}, FTIR spectra of raw soybean waste (RSW) samples, loaded soybean waste (LSW) samples and desorbed soybean waste (DSW) samples were analysed. By observing the change in behaviour of characteristic absorption band of the functional groups, the functional groups that are involved in adsorption can be determined.

The results obtained from the FTIR analysis shown in Figure 3, shows a drastic change in the characteristic absorption band of functional groups in soybean waste samples after adsorption and desorption. Adsorption bands at 3400 cm^{-1} represent the intramolecular O-H vibration absorption peak. After adsorption the peak greatly changed from 1.12949 transmittance to 0.71518 transmittance after adsorption and further decreased to 0.69274 transmittance. This indicates the increase of O-H bonds in sample after adsorption and desorption. At the wavenumber of 2900 cm^{-1} the peak represents the C-H bonding. After adsorption the peak is lowered to a transmittance of 0.86933 from 1.0154. However, the peak only changes slightly after desorption to transmittance of 0.8484. This indicates C-H bonds increase during adsorption and desorption. The peaks exhibited at wavenumber of 1700 cm^{-1} represens the bonding between C-O. The nature of change in transmittance after adsorption and desorption is similar to O-H and C-H bonds where there is significant change after adsorption and little change after desorption. The change in behaviour of these bonds indicate that they are involved in the adsorption of Zn^{2+}. Therefore the structures found in soybean waste which are involved in adsorption is cellulose which is represented by the functional group (O-H) and (C-H) and hemicellulose represented by the functional group (C=O) (Azizan, et al., 2016).

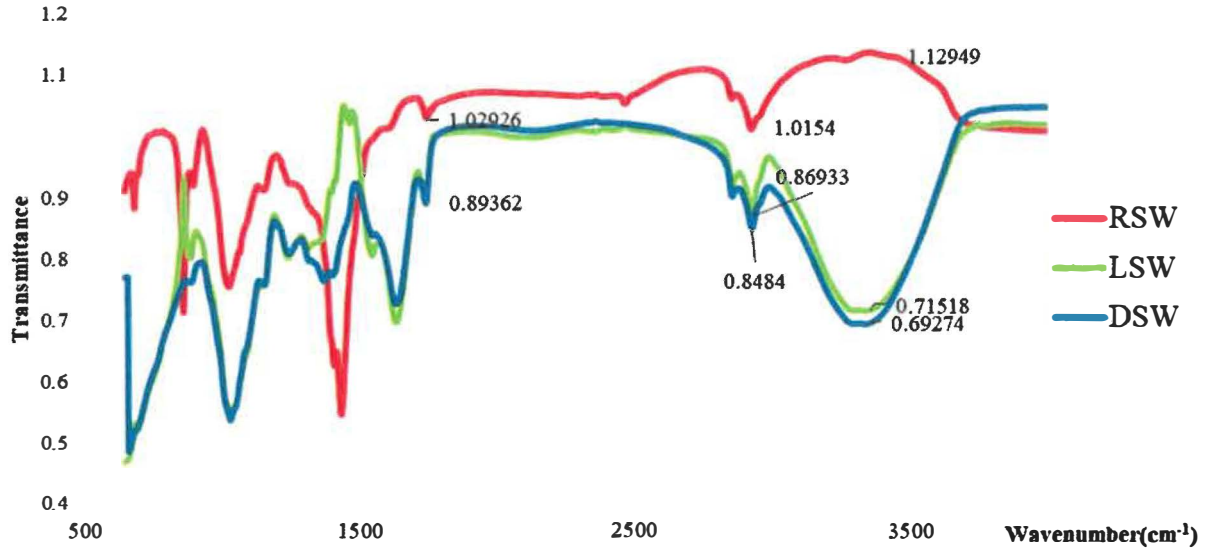

Figure 3. FTIR Spectra of Raw Soja Waste (RSW), Loaded Soja Waste (LSW) and Desorbed Soja Waste (DSW)

3.Conclusion

To conclude, the study of desorption of Zn^{2+} from soybean waste adsorbents by using elution reagents such as HNO_3, NaOH and EDTA at concentrations of 0.1M and 1.0M, 0.1M and 1.0M and 0.05M and 0.1M respectively was successful. Soybean waste can be recovered and reused for further adsorption cycles. The highest desorption percent achieved between type of elution reagents is 88.43% by 0.1M HNO_3. The desorption percent also varies with concentration where lower concentrations of elution reagents desorp Zn^{2+} more efficiently when compared to higher concentrations of correspondent elution reagent. The study of the effect of time on desorption percent was also successful in proving that desorption capacity of elution reagents has their limits and will not further desorp Zn^{2+} after a specific period of time. The main functional groups that are involved in adsorption were also identified to be cellulose and hemicellulose by interpreting the results from FTIR analysis.