Jurnal Teknologi

Full Paper

ZIRCONIUM LOADED BANANA STEM FIBERS AS ADSORBENT FOR RECOVERY OF HG(II)

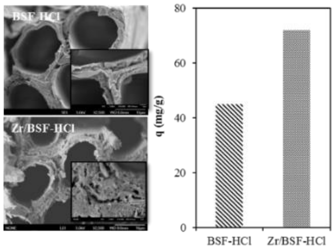
Nurrulhidayah Salamun[a], Sugeng Triwahyono[a,b*], Aishah Abdul Jalil[c,d]

[a]Department of Chemistry, Faculty of Science, UTM, 81310 UTM Johor Bahru, Johor, Malaysia
[b]Centre for Sustainable Nanomaterials, Ibnu Sina Institute for Scientific and Industrial Research, UTM, 81310 UTM Johor Bahru, Johor, Malaysia
[c]Department of Chemical Engineering, Faculty of Chemical and Energy Engineering, UTM, 81310 UTM Johor Bahru, Johor, Malaysia
[d]Centre of Hydrogen Energy, Institute of Future Energy, UTM, 81310 UTM Johor Bahru, Johor, Malaysia

Article history
Received
19 May 2015
Received in revised form
24 March 2016
Accepted
1 May 2016

*Corresponding author
sugeng@utm.my

Graphical abstract



Abstract

Mercury is one of the most toxic pollutants which pose a great threat to both human health and organism security. A great deal of research over recent decades has been motivated by the requirement to lower the concentration of these heavy metals in water and the need to develop low cost techniques which can be widely applied for heavy metals remediation. Adsorption is by far the most reliable technologies for removing mercury from water. In this study, banana stem fibers, a natural biomass was loaded with zirconium (IV) to investigate its feasibility for mercury removal from an aquatic environment. The XRD pattern for both BSF-HCl and Zr/BSF-HCl exhibited mainly the cellulose I structure which consists of two distinct crystal phases. The FESEM images illustrated the presence of relatively well organized, pronounced and uniform cavities distributed around the surface, indicated a good possibility for the metal ions to be adsorbed. The result shows that Hg (II) adsorption capacity increased from 45 to 72 mg/g after the immobilization of Zr due to increase in the active sites on the adsorbent.

Keywords: Banana stem fiber; cellulose; zirconium; adsorption; Hg(II)

Abstrak

Merkuri adalah salah satu daripada bahan pencemar yang paling toksik yang menimbulkan ancaman yang besar kepada kedua-dua kesihatan manusia dan keselamatan organisma. Beberapa dekad kebelakangan, banyak penyelidikan telah didorong oleh keperluan untuk menurunkan kepekatan logam berat di dalam air dan keperluan untuk membangunkan teknik kos rendah yang boleh digunakan secara meluas untuk pemulihan logam berat. Penjerapan adalah setakat ini teknologi yang paling dipercayai bagi penyingkiran merkuri dari air. Dalam kajian ini, serat batang pisang, satu biojisim asli telah dimasukkan dengan zirkonium(IV) untuk kajian kemungkinan untuk penyingkiran merkuri dari persekitaran akuatik. Corak XRD untuk kedua-dua BSF-HCl dan Zr/BSF-HCl mempamerkan struktur selulosa I yang terdiri daripada dua fasa kristal yang berbeza. Imej-imej FESEM menggambarkan kehadiran rongga yang agak teratur, jelas dan seragam di seluruh permukaan, menunjukkan kemungkinan yang baik bagi ion logam untuk terserap. Hasil kajian menunjukkan bahawa kapasiti penjerapan Hg (II) meningkat dari 45 ke 72 mg/g selepas kehadiran Zr disebabkan oleh peningkatan tapak aktif pada penjerap.

Kata kunci: Serat batang pisang; selulosa; zirkonium; penjerapan; Hg(II)

1.0 INTRODUCTION

Heavy metals in water refer to heavy, dense, metallic elements that occur in trace levels, but are very toxic and tend to accumulate. Heavy metals have been found in potentially harmful concentrations in numerous drinking water systems due to natural or industrial pollution sources. Among those heavy elements, mercury is the most toxic and non-biodegradable metal that brings no beneficial effects on human. In particular, the World Health Organization (WHO) reported that between 25,000 and 125,000 tons of mercury were released into the environment in 1976. Mercury can be entered to the environment by several sources, resulting in contamination of atmospheric and aquatic systems. In the last 50 years, largest part of the mercury contamination arise from gaseous emissions of fossil fuel combustion, industrial processes (mainly chloro-alkali productions, pharmaceutical and cosmetic preparations, electrical instruments) and municipal solid waste treatment plants [1,2]. As Hg(II) is a highly toxic element, the removal of Hg(II) from effluents has been a significant concern in most industrial branches, due to economic and environmental factors.

To date, many techniques have been used, including electrochemical degradation, membrane separation, ion exchange, reverse osmosis, precipitation, solvent extraction, and adsorption [3-4]. Among these techniques, adsorption appears to be the most promising method because of its cost effective, easy regeneration of adsorbents, and possibility of metal recovery [5].

Several inexpensive naturally occurring lignocellulosic materials such as coconut coir pith, rice straw, sugarcane bagasse and banana stem fibers have been studied as adsorbent for heavy metals removal [6-8]. Banana stem is another commonly available and abundant natural material where it is also an example of lignocellulosic biomass waste, which composed of cellulose, hemicellulose, and lignin. These biopolymers have abundant and specific functional group such as hydroxyl (OH) groups, which have affinities for heavy metal ions. Although shown to be effective adsorbent for a wide range of solutes, particularly divalent metals cations, crop residues suffer from at least two major drawbacks: low exchange or sorption capacity, and poor physical stability. In order to overcome these problems, chemical modification and/or activation of the raw adsorbents are required. Consequently, more active binding sites are provided, better ion-exchange properties are obtained, and new functional groups are formed.

From previous study, it was reported that inorganic metal ion exchanger such as hydrous zirconium oxide and zirconium phosphate is superior than the organic exchangers in terms of thermal stability and resistance to radiation and abrasion [9-10]. In this study, the introduction of Zr(IV) into the cellulose framework is expected to produce an enhancement of the active sites and will apparently increase the capacity to adsorb cationic toxic heavy metals.

2.0 METHODOLOGY

2.1 Preparation of Adsorbent

BSF (10 g) will be immersed in 1M acidic solution (150 mL) for 24 h under ambient temperature in order to remove solubilized hemicellulose for better cellulose accessible. After the treatment, the BSF are filtered, washed thoroughly with distilled water and dried at 353 K for 24 h (BSF-HCl). Then, the acid treated samples of BSF (5 g) were added to a solution of zirconium oxychloride and stirred for 24 h at 298 K. The resultant solids are also filtered, washed with distilled water and dried at 353 K (Zr/BSF-HCl).

2.2 Characterization of Adsorbent

The X-ray diffraction (XRD) patterns of the adsorbents were re-corded on a Bruker AXS D8 Automatic Powder Diffractometer using Cu Ka radiation with λ=1.5418 Å at 40 kV and 40 mA in the range of 2θ=20-60°. The Segal's empirical method [11] was used to obtain the crystallinity index of the samples X_c, as shown in Eq. (1):

$$X_c = I_{002} - I_{am} \big/ I_{002} \times 100 \qquad (1)$$

where, I_{002} and I_{am} are the peak intensities of crystalline and amorphous materials, respectively.

Field-emission scanning electron microscopy was conducted using an energy dispersion X-ray spectroscopy (FESEM-EDX, JEOL JSM-6701F) to determine the morphological properties as well as the elemental composition of the biosorbents. Prior to the analysis, the sample was coated with platinum to avoid charging.

Nitrogen physisorption was measured at 77 K with a SA 3100 Beckman Coulter. Prior to measurement, the sample was outgassed at 373 K for 1 h.

2.2 Adsorption Experiments

Batch adsorption experiment was conducted by adding 0.01 g adsorbent in a 200 mL of 10 mg/L Hg(II) solution. The Hg(II) solution was prepared by dissolving $HgCl_2$ (Merck) in double distilled water. Prior to the adsorption, the adsorbent was activated in a *vacuo* at 373 K for 1 h. The mixture was incubated with a constant stirring rate of 300 rpm at room temperature to reach equilibrium. The sampling was taken at appropriate time intervals and followed by centrifugation at 14,000 rpm for 15 min. The residual Hg(II) concentration was determined with an Agilent 4100 MP-AES spectrometer.

3.0 RESULTS AND DISCUSSION

3.1 Characterization of Adsorbent

The XRD patterns for BSF-HCl and Zr/BSF-HCl are shown in Figure 1. Both BSFs exhibited mainly the cellulose *I* structure which consists of two distinct crystal phases, namely I_α and I_β. The major peak at 2θ = 21.9˚ corresponds to the crystalline structure of cellulose *I*, whilst the amorphous background is characterized by the low diffracted intensity at a shoulder peak in the region 2θ = 14-16˚ [12]. The crystallinity indices of BSF-HCl and Zr-BSF-HCl were 64.4 and 60.2 %, respectively. A slight decrease in the crystallinity index and the intensity at both peaks indicated zirconium ions were successfully introduced into the cellulose framework.

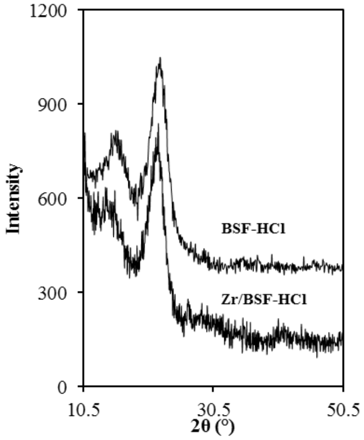


Figure 1 XRD patterns of BSF-HCl and Zr/BSF-HCl

The FESEM images for both BSFs illustrate relatively well organized, pronounced and uniform cavities distributed around the surface indicated a good possibility for the Hg(II) ions to be adsorbed (Figure 2) [13]. Apart from that, aggregations of metal particles were only observed on the surface of Zr/BSF-HCl and the presence of zirconium ions were confirmed by EDX analysis. Table 1 shows the quantitative elemental analysis data of Zr/BSF-HCl taken after adsorption, indicating that 28.8 % of Hg was detected. The platinum is subjected to the coating material which was coated on the surface of the Zr/BSF-HCl before the analysis.

Table 1 Quantitative elemental analysis data of Zr/BSF-HCl after Hg(II) adsorption

Element	Mass %
Pt	10.1
C	32.4
O	10.7
Zr	18.1
Hg	28.8
Total	100

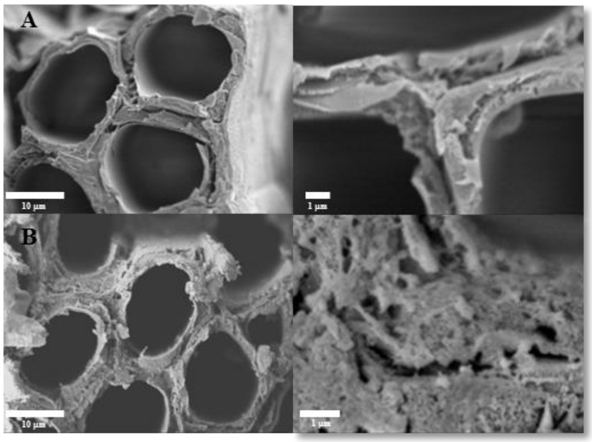


Figure 2 FESEM images of A) BSF-HCl and B) Zr/BSF-HCl

In EDX images (Hg mappings) as shown in Figure 3, the sites where Hg was adsorbed are homogeneously distributed on the surface of Zr/BSF-HCl. EDX was a useful tool to verify that Hg was adsorbed throughout the surface.

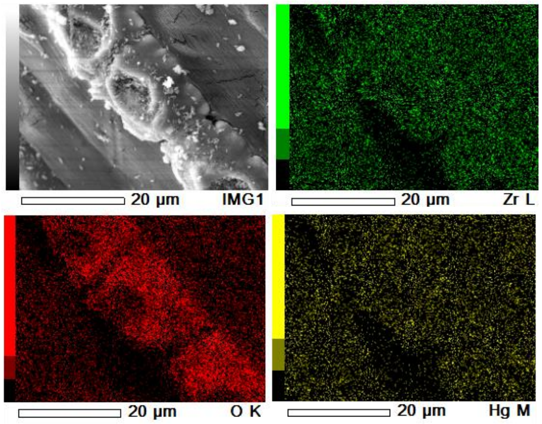


Figure 3 FESEM and Zr, O and Hg map of Zr/BSF-HCl

3.1 Adsorption Studies

3.1.1 Effect of modification on BSF-HCl

The compounds found in BSF are mainly cellulose, hemicellulose, lignin substances, and other low molecular weight compounds. It is believed that the adsorption characteristics of the material are mainly due to the presence of hydroxyl groups present on cellulose substances [14].

The adsorption capacity of Hg(II) on BSF and Zr/BSF-HCl are presented in Figure 4. It was observed that Hg(II) adsorption capacity increased from 45 to 72 mg/g after the immobilization of Zr due to increase in the active sites on the adsorbent [7]. It was believed that with the presence of zirconium ions, the adsorption rate should be increased as well owing to higher number of hydroxyl groups generated on the framework. Thus, more Hg(II) ions will be attracted to the surface of Zr/BSF-HCl. This value was higher than the adsorption capacity of other adsorbents reported in the literature (Table 2). Previously, Meena *et al.* (2008) reported that a chemically treated sawdust by NaOH and H_2SO_4 gave a maximum adsorption capacity, q_m of 20.62 mg/g. Meanwhile, Rocha *et al.* (2009) studied the ability of NaOH treated-rice straw to remove Hg(II) from water (22.1 mg/g). Both studies revealed the extent of chemical pre-treatment for enhancing the adsorption capacity, and the need to introduce other inorganic metal (such as Zr(IV)) to increase the amount of active sites on the adsorbent.

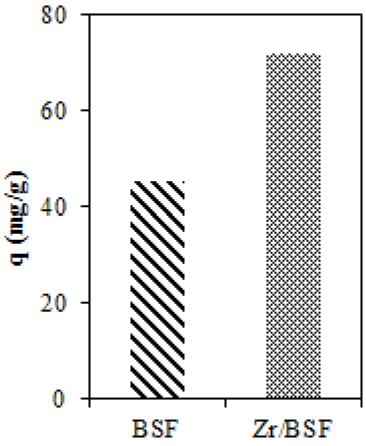


Figure 4 Adsorption capacity of Hg(II) on BSF-HCl and Zr/BSF-HCl

Table 2 Comparison with other adsorbents for Hg(II) adsorption

Adsorbent	q (mg/g)	Ref
Zr/BSF-HCl	72	This study
BSF-HCl	45	This study
Sawdust	20.62	15
Rice straw	22.1	6
Sago waste	5.6	3

3.1.2 Effect Of Contact Time

Contact time between the adsorbate and adsorbent to achieve a steady-state equilibrium time is an important factor in adsorption since it depends on the nature of the system used.

Figure 5 illustrates the Hg(II) adsorption uptake by Zr/BSF-HCl as a function of time at initial concentration of 20 mg/L and pH 6-7. It is observed that about 80 % of the maximum uptake of Hg(II) could be achieved within 30 min. The kinetic curve for Hg(II) ions showed that the adsorption was initially rapid, and reached equilibrium after approximately 90 min. This may be due to the saturation of Zr/BSF-HCl surface with Hg ions as well as adsorption and desorption processes that occur after the saturation.

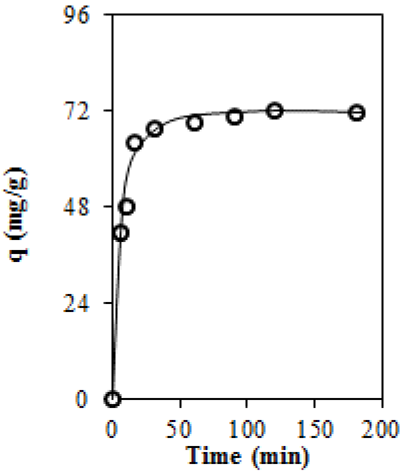


Figure 5 Effect of contact time on Hg(II) adsorption onto Zr/BSF-HCl

4.0 CONCLUSION

This study demonstrated the utilization of Zr/BSF-HCl for efficient adsorption of Hg(II). A slight decrease in the crystalline structure from XRD analysis indicated Zr was successfully introduced in the cellulose framework. This result was consistent with EDX analysis in which the presence of Zr was also observed. The adsorption capacity of Hg(II) on Zr/BSF-HCl increased from 45 to 72 mg/g. The modification of the cellulose framework with Zr apparently increases the number of active sites in the material, owing to higher number of hydroxyl groups generated on the framework. Low cost and availability of banana stem fibers, and significantly high adsorption capability of the Zr/BSF-HCl make it a promising and potentially attractive adsorbent for treating wastewater contaminated with heavy metals and consequently provides a step towards a sustainable society.

Acknowledgement

This work was supported by Ministry of Higher Education, Malaysia and Universiti Teknologi Malaysia through the Research University Grant (06H17) and awards of UTM Zamalah Scholarship (Nurrulhidayah Salamun).

References

[1] Ismaiel, A. A., Aroua, M.K., Yusoff, R. 2013. Palm Shell Activated Carbon Impregnated with Task-Specific Ionic-Liquids as a Novel Adsorbent for the Removal of Mercury from Contaminated Water. *Chemical Engineering Journal.* 225: 306-314.

[2] Kaghazchi, T., ShamsiJazeyi, H. 2011. Modification of Activated Carbon using a NO_x-Containing Gaseous by-Product For Enhanced Hg(II) Removal from Aqueous Phase. *Journal of Industrial and Engineering Chemistry.* 17: 608-614.

[3] Carlos, G.-R. 2006. Mercury (II) Removal from Aqueous Solutions by Nonviable *Bacillus Sp.* from a Tropical Estuary. *Bioresource Technology*. 97: 1907-1911

[4] Kadirvelu, K., Kavipriya, M., Karthika, C., Vennilamani, N., Pattabhi, S. 2004. Mercury (II) Adsorption by Activated Carbon made from Sago Waste. *Carbon*. 42: 745-752.

[5] Abidin, M.A.Z., Jalil, A.A., Triwahyono, S., Adam, S.H., Kamarudin, N.H.N. 2011. Recovery of Gold (III) from an Aqueous Solution onto a *Durio Zibethinus* Husk. *Biochemical Engineering Journal*. 54(2): 124-131.

[6] Anirudhan, T.S., Divya, L., Ramachandran, M. 2008. Mercury (II) Removal from Aqueous Solutions and Wastewaters using a Novel Cation Exchanger Derived from Coconut Coir Pith and its Recovery. *Journal of Hazardous Materials.* 157: 620-627.

[7] Rocha, C.G., Zaia, D.A.M., da Silva Alfaya, R.V., da Silva Alfaya, A.A. 2009. Use of Rice Straw as Biosorbent for Removal of Cu(II), Zn(II), Cd(II) and Hg(II) ions in Industrial Effluents. *Journal of Hazardous Materials*. 166: 383-388.

[8] Salamun, N., Triwahyono, S., Jalil, A.A., Matsuura, T., Salleh, N.F.M. 2015. Acid-*vacuo* Heat Treated Low Cost Banana Stems Fiber for Efficient Biosorption of Hg (II). *RSC Advances.* 5: 14129.

[9] Mishra, S.P., Singh, V.K., Tiwari, D. 1996. Radiotracer Technique in Adsorption Study: Part XIV. Efficient Removal of Mercury from Aqueous Solutions by Hydrous Zirconium Oxide. *Applied Radiation and Isotopes*. 47: 15-21.

[10] Zhang, Q.R., Du, W., Pan, B.C., Pan, B.J., Zhang, W.M., Zhang, Q.J., Xu, Z.W., Zhang, Q.X. 2008. A Comparative Study on Pb^{2+}, Zn^{2+} and Cd^{2+} Sorption onto Zirconium Phosphate Supported by a Cation Exchanger. *Journal of Hazardous Materials.* 152: 469-475.

[11] Segal, L., Creely, J.J., Martin, A.E., Conrad, C.M. 1959. An Empirical Method for Estimating the Degree of Crystallinity of Native Cellulose using the X-Ray Diffractometer. *Textile Research Journal.* 29: 786-794.

[12] Guimarães, J.L., Frollini, E., da Silva, C.G., Wypych, F., Satyanarayana, K.G. 2009. Characterization of Banana, Sugarcane Bagasse and Sponge Gourd Fibers of Brazil. *Industrial Crops and Products*. 30: 407-415.

[13] Foo, K.Y., Lee, L.K., Hameed, B.H. 2013. Preparation of Banana Frond Activated Carbon by Microwave Induced Activation for the Removal of Boron and Total Iron from Landfill Leachate. *Chemical Engineering Journal*. 223: 604-610.

[14] Albarelli, J. Q., Rabelo, R. B., Santos, D. T., Beppu, Meireles, M.A.A. 2011. Effects of Supercritical Carbon Dioxide on Waste Banana Peels for Heavy Metal Removal. The *Journal of Supercritical Fluids*. 58: 343-351.

[15] Meena, A.K., Kadirvelu, K., Mishra, G. K., Rajagopal, C., Nagar, P.N. 2008. Adsorptive Removal of Heavy Metals from Aqueous Solution by Treated Sawdust (*Acacia Arabica*). *The Journal of Hazardous Materials.* 150: 604-611.