Applied Mechanics and Materials Vol. 680 (2014) pp 146-149
Online available since 2014/Oct/20 at
© (2014) Trans Tech Publications, Switzerland
doi:10.4028/www.scientific.net/AMM.680.146

Submitted: 11.08.2014
Accepted: 16.08.2014

Watermelon rind: A Potential Adsorbent for zinc removal

N.Othman*, Y. S. Kueh, F.H. Azizul-Rahman, R. Hamdan

Micropollutant Research Centre,

Faculty of Civil and Environmental Engineering, University Tun Hussein Onn, Beg Berkunci 101, 86400 BatuPahat, Johor, Malaysia

norzila@uthm.edu.my

Keywords: Biosorbent, biosorption, heavy metal, zinc

Abstract. The industrial revolution has significantly increase the discharge of wastewater into water bodies with heavy metals. In this study, watermelon rind was used as a biosorbent. Wastewater from mosaic industry was characterized by using flame AAS and zinc was found to have concentration range of 350mg/L to 450mg/L. Watermelon rind was characterized by using XRF and SEM. The results from XRF before biosorption shows the presence of Si to enhance biosorption. Zinc present after biosorption. The optimum pH, biosorbent amount, zinc concentration and contact time were found to be pH8, 1.5g, 400mg/L, and 30minutes respectively. The watermelon rind was proven as an effective biosorbent for zinc removal from aqueous solution

Introduction

Wastewater threatens public health and the environment if untreated in proper ways. It contains inorganics and organics compound. The inorganics are referred as non degradable minerals and metals. Inorganic like heavy metals may end up into toxic compound for living organisms and environment. Continuous exposure of the heavy metals may increase the risk of lung damage, brain and nerve damage, cancer attack, coma, and death if serious [1]. Therefore, the wastewater must be treated before discharge into the receiving environment.

Currently, treatment methods for removing heavy metals are ion exchange, chemical precipitation, membrane filtration, coagulation and flocculation, and adsorption. However, these treatment methods are relatively expensive, generating large amounts of chemical sludge, and involving large energy [2]. An option of heavy metal removal using biosorption. Biosorption is defined as the removal of a metal from solution by biological material [3][4]. The process involves a solid phase of biosorbent and a liquid phase of solvent containing metal ions [5]. Biosorption utilizes the non-living microbial biomass to bind with heavy metal ions by physico-chemical pathways of uptake [6]. There are several advantages of biosorption over conventional treatment methods which are low cost, high efficiency, minimization of chemical and biological sludge, regeneration of biosorbent, and possibility of metal recovery [7]. The overall biosorption is determined by pH, temperature, initial heavy metal concentration, biosorbent dose, contact time, and biosorbent size through affecting the uptake rate, selectivity, and amount of heavy metals removed [8]. Biosorbent such as fruit rind consists of pectin, citrulline, cellulose, proteins, and carotenoids which have functional groups of hydroxyl, amine, and carboxylic. These functional groups can easily bind to metal ions by changing their hydrogen ions for metal ions or giving an electron pair to form complexes with the metal ions [9 – 10]. In addition, the silica (Si) contained in the structure of watermelon rind is believed can enhance the biosorption process [10]. In this research characterization and optimization study were conducted for wastewater and biosorbent.

Materials and method

Sampling of wastewater. The wastewater sampling using grab sampling. The sample was collected 8 times during high production and dry weather. The sample was collected and stored in a clean bottle which was then acidified with nitric acid to a pH below 2.0. The sample was stored in a refrigerator at approximately 4°C.

Digestion of wastewater. 0.2mL of the wastewater sample was mixed with 10mL of nitric acid (HNO_3) in a crucible dish. The mixture was then heated on the hotplate until the sample fully digested. The digested sample was cooled down and diluted to 100mL.

Preparation of biosorbent. The watermelon rind was collected from the local fruit stall and washed with tap water. The rind was dried at sunlight until dry. The biosorbent was then soaked in nitric acid (HNO_3) with concentration of 15% for 24 hours. and transferred to deionized water (H_2O) for 24 hours. The rind was dried in an oven at 60°C until constant dry. The rind was ground and sieved to uniform size of 150μm.

Optimization study. All experiments were conducted using batch method by varying the parameters namely, pH, biosorbent amount, concentration of wastewater, and contact time(as shown in Table 1). 100mL of prepared wastewater was mixed with the biosorbent and the mixture was shaked at 125rpm at room temperature. The mixture were then filtered. The biosorbent was analyse using XRF, SEM-EDX. The wastewater flame AAS.

Table 1 Working range for the parameters.

Parameters	pH	Biosorbent amount (g)	Concentration of wastewater (mg/L)	Contact time (mins)
Working range	6, 6.5, 7, 7.5, <u>8</u>, 8.5, 9	0.5, 1.0, <u>1.5</u>, 2.0, 2.5	100, 200, <u>400</u>, 600, 800	10, 20, <u>30</u>, 40, 50, 60

Note: <u>Underlines</u> *indicate the optimum value.*

Results and Discussion

Characterization of mosaic wastewater The results from FAAS shows that zinc, chromium and lead were found in the wastewater. Table 2 shows heavy metal concentration.

Table 2 Concentration range of heavy metals.

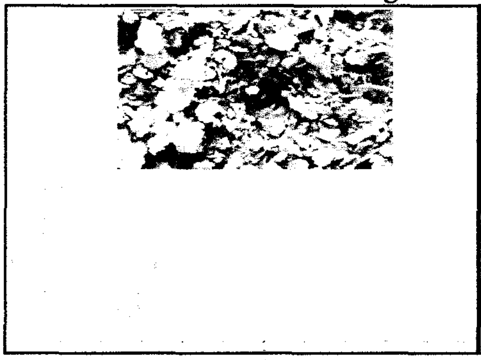
Heavy Metals	Concentration (mg/L)
Zinc (Zn)	350 – 450
Chromium (Cr)	150 – 250
Lead (Pb)	15 - 25

XRF analysis. The result from XRF before and after the biosorption is shown in Table 3 The concentration of silica oxide (SiO_2) was 83.70% which is the highest among the chemical composition. It shows loaded of Zn was 24.40% after biosorption.

Table 3 Result of XRF before and after biosorption.

Formula	Concentration before	Concentration after
ori-g	7	7
added-g	3	3
CO_2	0.10%	0.1
SiO_2	83.70%	1.18%
SO_3	8.32%	0.93%
CaO	2.18%	0.15%
Al_2O_3	1.61%	0.26%
Fe_2O_3	1.00%	1.34%
P_2O_5	0.99%	0 < LLD
K_2O	0.87%	ND
Cl	0.82%	ND
MoO_3	0.30%	ND
ZnO	ND	24.40%

SEM-EDX analysis. As presented in Figure 1, watermelon rind gave a porous surface texture which enables the adsorption of metal ions onto the surface. Besides, it also shows that the surface morphology of watermelon rind consisted of two kinds of colour tone which were lighter and darker [11]. The lighter shades represented inorganic component while the darker shades were organic components. From the spectrum of watermelon rind in Figure.1, Si was observed. After biosorption of Zn using watermelon rind, the morphology undergone a physical change. Lump-like deposits or shiny particle were formed as shown in Figure 2.



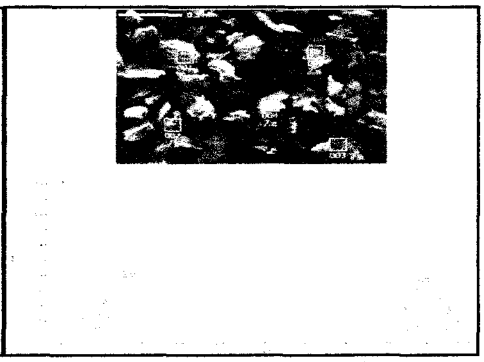
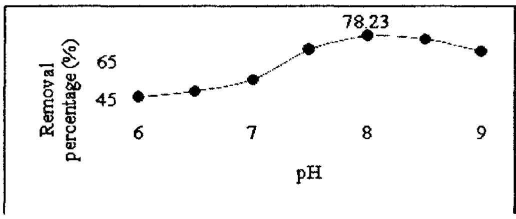


Figure 1 SEM-EDX before biosorption. **Figure 2** SEM-EDX after biosorption

Effect of pH. pH plays a significant role in biosorption process. Figure.3 shows pH8 had the highest removal with 78.23%. When the pH is low, the H^+ ions from the acid compete with the Zn ions for adsorption sites and hence decreased the removal and the capacity [12]. Besides, when the pH is too high, the biosorption decreased.This might be due to the formation of soluble hydroxyl complexes of Zn^{2+} ions and Zn^{2+} ions exists as predominant species. Furthermore, several hydroxides starts precipitating at high pH [13].

Effect of biosorbent amount. As shown in Figure.4, the highest removal occurred at 1.5g with 83.33%. The low removal at 0.5g can be explained by the low availability adsorption site on the biosorbent[26]. This is due to alot of biosorbent can overlap the adsorption sites on the biosorbent causing the decreasing of total surface area [14]. The uptake capacity decreased from 0.5g to 2.5g due to less collision between metal ions and the biosorbent.



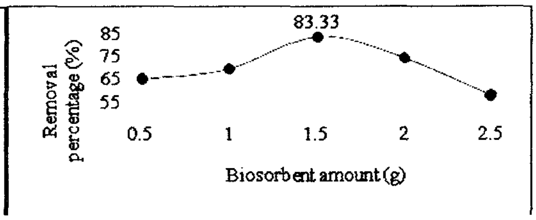
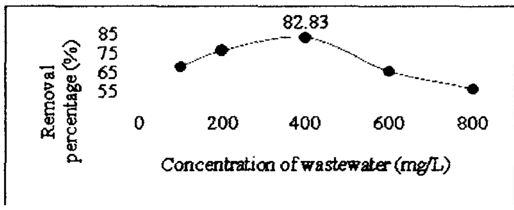


Figure 3 Zinc removal against pH; **Figure.4** Zinc removal against biosorbent

Effect of concentration of wastewater. The removal was at peak when the Zn concentration was 400mg/L as shown in Figure 5. The removal was low at 100mg/L because the ratio of biosorbent to metal ions is too large that the adsoption site of the biosorbent overlaps and decreases the total surface area exposed to the metal ions [11]. However, the removal was also low when the concentration was 800mg/L because the adsorption site is in low availability and causes the saturation of adsorption site]. The uptake capacity increased from 100mg/L to 800mg/L due to high collision between the metal ions and biosorbent surface. **Effect of contact time.**Figure 6 indicates that the rate of removal of Zn was higher from 10 mins to 30 mins. This might be due to more biosorption sites available at the beginning. After 30 mins, the removal decreased which can be explained by the exhaustion of the bisorption sites [13].



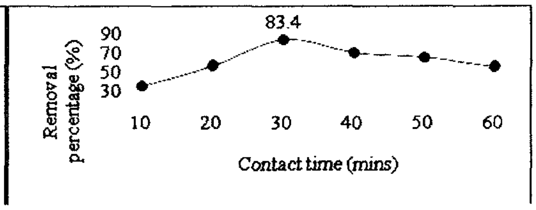


Figure 5 Zinc removal against wastewater conc; **Figure.6** Zinc removal against time

Conclusions. The optimum condition for zinc removal using watermelon rind was at pH8, 1.5g biosorbent, 400mg/L zinc metal ions, and 30mins of contact time with 80% zinc removal.

References

[1] Maczulak, A. (2010). 3. Environmental Toxins. *Pollution: Treating Environmental Toxins,* pp. 54-88. New York: Facts On File, Inc.

[2] Ahalya, N., Ramachandra, T. V. &Kanamadi, R. D. (2003). Biosorption of Heavy Metals. *Research Journal of Chemistry and Environment,* Vol. 7, pp. 71-79.

[3] Liu, C., Ngo, H. H. &Guo, W. S. (2012). Watermelon Rind: Agro-waste or Superior Biosorbent. *Appl. Biochem. Biotechnol.,*Vol. 167, pp. 1699-1715.

[4] Wang, J. & Chen, C. (2010). Research Advances in Heavy Metal Removal by Biosorption. *Acta Sci. Circumstantiae,* Vol. 30, pp.673-701.

[5] Fu, F. & Wang, Q. (2011). Removal of Heavy Metal Ions from Wastewaters: A Review. *Journal of Environment Management,* Vol. 92, pp. 407-418.

[6] Igwe, J. C., Ogunewe, D. N. &Abia, A. A. (2005). Competitive Adsorption of Zn(II), Cd(II), and Pb(II) Ions from Aqueous and Non-aqueous Solution by Maize Cob and Husk. *Afr. J. Biotechnol.,* Vol. 4(10), pp. 1113-1116.

[7] Das, N., Vimala, R. &Karthika, P. (2008b). Biosorption of Heavy Metals – An Overview. *Indian Journal of Biotechnology,* Vol. 7, pp. 159-169.

[8] Nguyen, T. A. H., Ngo, H. H., Guo, W. S., Zhang, J., Liang, S., Yue, Q. Y., Li, Q. & Nguyen, T. V. (2013). Applicability of Agricultural Waste and By-products for Adsorptive Removal of Heavy Metals from Wastewater. *Bioresource Technology,* Vol. 148, pp. 574-585

[9] Agnes, M. R. & Penelope, M. P. V. (2005). Determination of Citrulline in Watermelon Rind. *J. Chromatogr. A 1078,* pp. 196-200.

[10]Andrew, M., Zheng, Y., Qju, F., Nimtzc, M. & Bell-Eunice, G. (2008). Structure of Xylogalacturonan Fragments from Watermelon Cell-wall Pectin. Endopolygalacturonase can Accommodate a Xylosyl Residues on the Galacturonic Acid Just Following the Hydrolysis Site. *Carbohydr. Res.,* Vol. 343, pp. 1212-1221.

[11]Kumar, J., Balomajumder, C. &Mondal, C. (2011). Application of Agro-Based Biomasses for Zinc Removal from Wastewater – A Review. *Clean – Soil Air Water,* Vol. 39, pp. 641-652.

[12] Lakshmipathy, R. &Sarada, N. C. (2013). Application of Watermelon Rind as Sorbent for Removal of Nickel and Cobalt from Aqueous Solution. *International Journal of Mineral Processing,* Vol. 122, pp. 63-65.

[13]Osman, H. E., Badwy, R. K. & Ahmad, H. F. (2010). Usage of Some Agricultural By-products in the Removal of Some Heavy Metals from Industrial Wastewater. *J. Phytol,* Vol. 2, pp. 51-62

[14]Marin, A. B. P., Aguilar, M. I., Ortuna, J. F., Meseguer, V. F., Saez, J.&Florenz, M. (2010). Biosorpton of Zn(II) by Orange Waste in Batch and Packed Bed Syatems. *J. Chem. Technol. Biotechnol,* Vol. 85, pp. 1310-1318.