

Batch adsorption of activated coconut shell for the removal of zinc from palm oil mill effluent

Adeleke Abdulrahman Oyekanmi ^{a,*}, Ab Aziz Abdul Latiff ^b, Zawawi Daud ^b, Norli Ismail ^a, Mohammed Kabir Aliyu ^b, Mohd Arif Rosli ^c, Nazlizan Nasir ^a, Noorain Suhani ^a, Vicky Kumar ^a

^a School of Industrial Technology, Universiti Sains Malaysia, Pulau Pinang, Malaysia.

^b Department of Water and Environmental Engineering, Faculty of Civil and Environmental Engineering, Universiti Tun Hussein Onn Malaysia, 86400, Parit Raja Batu Pahat, Johor, Malaysia.

^c Department of Civil Engineering Technology, Faculty of Engineering Technology, Universiti Tun Hussein Onn Malaysia, Pagoh Educational Hub, 84600, Panchor, Muar, Johor, Malaysia.

* Corresponding author: adeleke@usm.my

Article history

Received 1 December 2018

Revised 20 February 2019

Accepted 30 Mac 2019

Published Online 15 October 2019

Abstract

Activated carbon from coconut shell was prepared to investigate the removal of zinc from palm oil mill effluent (POME). The reduction of zinc is significant to protect the ecosystem. The effect of temperature on the adsorbent was observed from the thermo gravimetric analysis while the decomposition of the lignocellulosic structure of the adsorbent was observed at 385 °C. A total mass loss of 38.87% was observed. The Fourier-transform infrared spectroscopy used for the chemical characterization illustrated that hydroxyl, carbonyl, ether and aromatic compounds were the major functional groups that contributed on the presence of oxygen at the available active sites on the adsorbent. This finding supported the result of the thermo gravimetric analysis of the lignocellulosic structure of the material. The adsorption equilibrium onto the coconut shell activated carbon was carried out to investigate the experimental data. The experimental data was fitted into the three isotherm models (Langmuir, Freundlich and Temkin) and from the findings, data was fitted most to the Temkin isotherm with a correlation coefficient of 0.9705. Adsorption efficiency of the activated coconut shell was obtained at 98.04%. This result explained the adsorbate –adsorbent interaction and the effect of heat energy on the adsorption process. The coconut shell activated carbon showed to be a very effective adsorbent for the removal of zinc from POME.

Keywords: Adsorption, isotherm, equilibrium, efficiency, coconut shell, zinc

© 2019 Penerbit UTM Press. All rights reserved

INTRODUCTION

The discharge of untreated wastewater to water bodies and the environment is a major practice in most of the developing countries in the world. The presence of heavy metals in the ecosystem is considered to be hazardous and imposed major health risks. The effect of discharge of this polluted water to the environment is the cause of diseases while the consumption by human and animal is of utmost concern to researchers (Gani *et al.*, 2017). The main challenge faced by researchers is the difficulty in effective treatment of high strength wastewater containing heavy metals at minimal effluent concentration due to both economic and technical deficiencies. Zinc is presented in POME and considered harmful by researchers if it is discharged to the environment without proper treatment.

Adsorption is a very effective mechanism of processing wastewater before discharge. The process of adsorption is efficient in terms of cost, very effective treatment and it produces high-quality effluent. Activated carbon is proven to be widely used for adsorption of wastewater. The cost of commercial activated carbon is very expensive and hence, it is not economically suitable for research activities (Abdul Rahman *et al.*, 2016). Therefore, the use of locally

made materials to serve the purpose of activated carbon have been used over the years for research. Some of the materials include maize cob (Satish Kumar *et al.*, 2009), banana peel (Lv *et al.*, 2012; Aziz *et al.*, 2018), rice husk (Dada *et al.*, 2012), wood (Ma *et al.*, 2014), cow bones (Latiff *et al.*, 2015; Adeleke *et al.*, 2016; Adeleke *et al.*, 2017) and peat (Rosli *et al.*, 2017).

These materials have been processed as activated carbon and used as effective replacement of commercial carbon either as single or composite adsorbents for wastewater treatment (Sekar *et al.*, 2004). Efforts have been made by using coconut shells for the treatment of wastewater (Amuda *et al.*, 2007; Shen *et al.*, 2010). The effectiveness of coconut shell carbon is due to its lignocellulosic characteristics and very viable functional groups such as carboxyl and hydroxyl groups that having high tendency for exchangeable ion (Katesa *et al.*, 2013). However, the use of coconut shell activated carbon for the treatment of heavy metal of palm oil mill effluent (POME) has rarely been reported in the literature. Therefore, the inclusion will enhance knowledge and offer an alternative treatment method of POME.

The objective of our present study was to investigate the removal of zinc as primary treatment from POME using low-cost coconut shell carbon as adsorbent.

EXPERIMENTAL

Adsorbate

Raw sample of POME was collected in a 20L plastic container and transported to the laboratory. The method of storage and preservation was referred to (APHA 2005; Mohamed *et al.*, 2018).

Adsorbent

Coconut shells were obtained at Klan Hoe plantation Kluang, Johor, Malaysia. The fruits were washed and dried at 110°C for two days. The dried samples were heated in the furnace at 250°C for 2h. The char produced was activated at 850°C for 2h. The carbon obtained was dried at 110°C for 24h. The activated carbon produced was stored in a tightly packed container.

Batch adsorption study

A batch study was conducted to determine the extent of reduction of zinc ion from POME by using the prepared adsorbent. The experiment was conducted using 250ml conical flasks; 100ml of the adsorbate was placed in the flasks at different adsorbent dosages (5-30g/100ml) of adsorbate at 30°C. The pre-determined conditions used for the investigation were pH 7, 105 minutes contact time, 150 rpm shaking speed and 150 µm particle size. Each of the conical flasks was removed after the end of each contact time. The mixture was separated using 0.45 µm membrane filter.

The investigation of the sorption of the zinc ion was achieved by using the atomic absorption spectroscopy Aanalyst Perkin Elmer. The amount removed was calculated as following:

$$q_e = \left(\frac{C_0 - C_e}{C_0} \right) \times 100\% \quad (1)$$

Where q_e is the equilibrium uptake (mg/g), V is the volume of solution (L), C_0 is the initial concentration of zinc ion in adsorbate (mg/L) and C_e is the final equilibrium concentration (mg/L).

Isotherm studies

The application of adsorption isotherm models was to determine the interaction between the adsorbate and adsorbent. This process is very useful to determine the sorption mechanism and the surface characteristics of the prepared adsorbent. In this study, the Langmuir, Freundlich and Temkin Isotherms were used. An expression of Langmuir isotherm was given by adsorbate. The expression of Langmuir model was given by:

$$q_e = \frac{q_{max} K_L C_e}{1 + K_L C_e} \quad (2)$$

Where q_e is the quantity of adsorbate adsorbed per unit mass of adsorbent (mg/L), C_e is the equilibrium liquid phase concentration of the adsorbate (mg/L), q_{max} is the Langmuir constant that expresses maximum mono layer adsorption capacity (mg/g) and K_L is the Langmuir constant that expresses the rate of adsorption.

The expression of the Freundlich model was given by:

$$q_e = K_f C_e^{1/n} \quad (3)$$

Where q_e is the quantity of adsorbate per unit mass of the adsorbent adsorbed (mg/L), K_f is the coefficient of the distribution of the adsorbent adsorbed per unit equilibrium concentration expressed as (mg/g (L/mg)) and n describes whether the adsorption n process is favourable.

Also, the Temkin isotherm was expressed as:

$$q_e = B \ln K_T + B \ln C_e \quad (4)$$

Where q_e is the quantity of adsorbate per unit mass of the adsorbent adsorbed (mg/L), K_T is expressed as L/g, $B \ln (K_T)$ as the intercept and C_e is the equilibrium liquid phase concentration of the adsorbate (mg/L).

A linear plot of $1/C_e$ versus $1/q_e$ was used to express Langmuir isotherm where q_{max} is the maximum adsorption capacity (mg/g) while b is the Langmuir constant known as the energy of adsorption (L/g). Also plot of $\ln q_e$ against $\ln C_e$ was expressed as the Freundlich isotherm while K_f and n are constants of intercept and slope, respectively. The Temkin isotherm expresses variation of the adsorption energy in J/mol , KT is the Temkin constant in L/g, while R is the universal gas constant in $J/mol/K$.

Analytical methods

The effect of temperature to determine the thermal decomposition of the prepared activated carbon was investigated using the thermogravimetric analysis Leinseis L81. This was achieved at 5°C and held at temperature for 120 minutes under stable atmospheric condition. The surface morphology and the chemical characterization were investigated using Fourier- transform infrared spectroscopy (FT-IR) Perkin Elmer S100.

RESULTS AND DISCUSSION

The batch study was conducted using different adsorbent dosages at 30 °C under fixed conditions of pH, shaking speed, contact time and particle size. The result of the characterization of the adsorbent was used to determine the effectiveness of the adsorption process.

Batch study

The result of the batch study was determined by the removal efficiency of the sorption of zinc ion onto the adsorbent under the fixed condition of 150 rpm shaking speed, pH 7, and 105 minutes contact time. The result in Fig. 1 shows that the sorption of zinc onto coconut shells carbon was very effective at different adsorbent dosages used. The sorption yield was observed to increase along with increasing dosage. The optimum reduction was observed at 30g/L of applied dosage with removal efficiency of 98.04% and the least dosage applied achieved 88.9% removal efficiency. The large surface area provides the availability of active sites on the surface that attributed to the sorption of the metal ion.

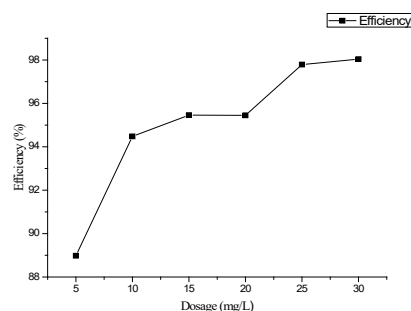


Fig. 1 Removal efficiency of adsorbent at different dosages.

Isotherm studies

The Langmuir and Freundlich isotherms are two parameter models that widely used to investigate the adsorption capacity and constants relating to the activated energy. The Temkin model is used to determine the heat of adsorption as it decreases linearly over the surface. The model establishes further relationship between the adsorbent and the adsorbate. The Langmuir model assumes a homogeneous surface with the formation of a monolayer of adsorbate onto the adsorbent. According to the results in Table 1, the q_{max} and R^2 values obtained for the Langmuir Isotherm were 0.04094 mg/g and 0.92525, respectively. The value of q_m has close similarity with the work of Tsai *et al.* (2009) in which Oyster shell, hard clam shell, and short-neck clam shell have q_{max} values of 0.084, 0.060 and 0.893 mg/g, respectively.

The Freundlich model assumes a heterogeneous surface of the sorption of the adsorbate onto the adsorbent. In accordance with Freundlich theory, the heterogeneity factor of a value of $1/n < 1$ illustrates a normal Langmuir isotherm, when $1/n > 1$, it shows a case of cooperative adsorption (Liu, 2015). Adsorption process is linear if $n=1$, chemical if $n < 1$ and physical if $n > 1$. In Table 2, the value of $n = 1.0219$ indicated that physical adsorption process was occurred and the data was fitted to the Langmuir isotherm. The close fitted values of the correlation coefficient of Langmuir and Freundlich isotherm showed that both homogeneous and heterogeneous surfaces were existed in terms of the experimental conditions (Hamdaoui, 2006).

The Temkin isotherm also demonstrated the physical nature of the adsorption process, where the positive slope and intercept of the linear regression were a demonstration of exothermic reaction of the adsorption process. The result of the fitted data to the adsorption isotherms is illustrated in Fig. 2.

Table 1 Isotherm models.

Adsorbent	Langmuir		
	R^2	K_L	q_{max}
Coconut shell carbon	0.92525	4.34185	0.04094
	Temkin		
	R^2	$b(J/molK)$	$KT (L/g)$
	0.97057	15504.2	0.9950
	Freundlich		
	R^2	K_F	n
0.94318	5.8579	1.0219	

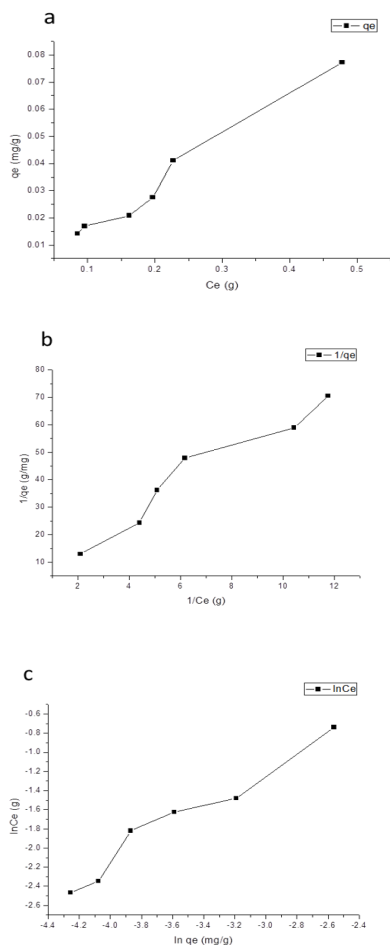


Fig. 2 (a) Temkin isotherm, (b) Langmuir isotherm and (c) Freundlich model for zinc removal from POME.

Thermo gravimetric analysis

The thermal analysis in Fig. 3 revealed that as the temperature was increased between 0-90°C, no obvious mass loss was observed. At further elevated temperature, decomposition of lignin began at 160°C. According to Katesa et al. (2013), decomposition of lignin occurs within the temperature range of 160-900°C. The pyrolysis of the lignocellulosic structure occurs at temperature of 385°C. The decomposition of lignocellulose usually happens within 200-400°C, hemicellulose at 200-380°C and cellulose at 250-400°C (Gašparovič et al., 2010). The total mass loss was evaluated to be 32.87%.

Chemical surface characterization

The Fourier transform infrared spectroscopy (FT-IR) spectra was obtained and shown in Fig. 4. The FT-IR spectra of the material illustrated the presence of different functional groups. The band at 3600 cm^{-1} was attributed to hydroxyl groups. The band at 3314 cm^{-1} was indicated for CH stretching vibrations. The region of the spectrum around 2970-2831 cm^{-1} was attributed to C-H stretching vibrations. The stretching vibration at 1404.25 cm^{-1} could be attributed to C=C bonds typical of aromatic rings. The band at 1023.01 cm^{-1} was attributed to C-O-C vibration in ethers as a result of angular deformation of ethers (Liu, 2015). The lignocellulosic structure of coconut shell could be affirmed as a result of the presence of hydroxyl, carbonyl, ethers and aromatic compounds (Cazetta et al., 2011).

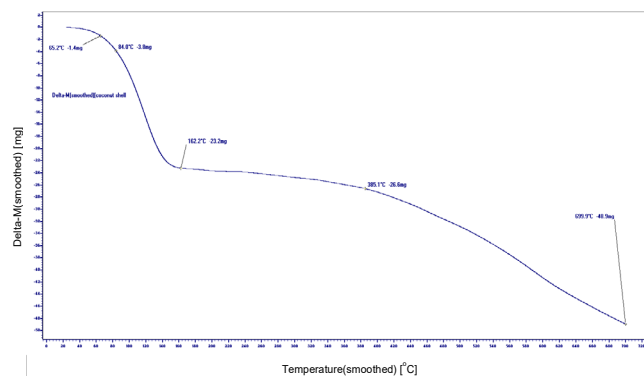


Fig. 3 Decomposition analysis of coconut shell carbon.

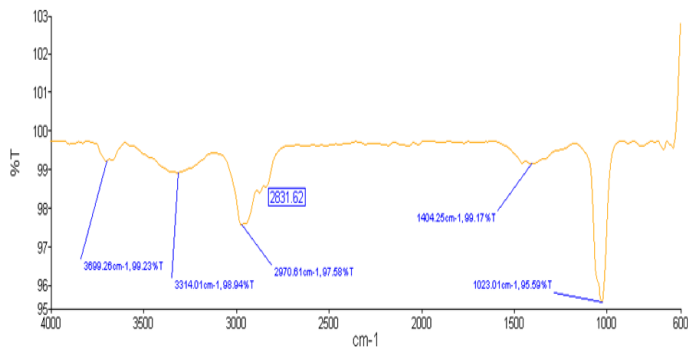


Fig. 4 FT-IR spectra for the coconut shell carbon.

CONCLUSION

The prepared coconut shell activated carbon was confirmed to possess C=C, OH, and C-OC from carbonyl, hydroxyl, ethers and aromatic functional groups. The pyrolysis was achieved at 385°C with a total mass loss of 32.87% This structure has greatly influenced the removal of zinc from the POME. The adsorption potential was further investigated using isotherm models. The equilibrium data was fitted well to Langmuir, Freundlich and Temkin isotherms. Due to the textural and chemical characteristics of the coconut shell carbon, the result tested on POME for the removal of zinc metal showed great potential of the adsorbent for the treatment of wastewater containing organic matters.

ACKNOWLEDGEMENT

Authors would like to appreciate the Ministry of Higher Education Malaysia for the full support given to this work under the fundamental research grant scheme. “Grant Vot 1571” and “Ministry of science Technology and innovation S029”.

REFERENCES

- Abdul Rahman, A., Latiff, A. A. A., Daud, Z., Ridzuan, M. B., Jagaba, A. H. 2016. Preparation and characterization of activated cow bone powder for the adsorption of cadmium from palm oil mill effluent. *IOP Conference Series: Materials Science and Engineering*, 136(1), 012045.
- Adeleke, A. R. O., Latiff, A., Aziz, A., Daud, Z., Ridzuan, B., Daud, M., Falilah, N. 2016. Remediation of raw wastewater of palm oil mill using activated cow bone powder through batch adsorption. *Key Engineering Materials*, 705, 380-384.
- Adeleke, A. O., Al-Gheethi, A. A., Daud, Z. 2017. Optimization of operating parameters of novel composite adsorbent for organic pollutants removal from POME using response surface methodology. *Chemosphere*, 174, 232-242.
- Amuda, O. S., Giwa, A., Bello, I. A. 2007. Removal of heavy metal from industrial wastewater using modified activated coconut shell carbon. *Biochemical Engineering Journal*, 36(2), 174-181.
- American Public Health Association., Eaton, A. D., American Water Works Association., Water Environment Federation. (2005). *Standard methods for the examination of water and wastewater*. Washington, D.C: APHA-AWWA-WEF.
- Cazetta A. L., Vargas A. M., Nogami E., Kunita M. H., Guilherme M. G., Martins A. C., Silva T. S., Moraes J. C., Almeida. V. C. 2011. NaOH-activated carbon of high surface area produced from coconut shell: Kinetics and equilibrium studies from the methylene blue adsorption. *Chemical Engineering Journal*, 174(1), 117-125.
- Dada, A. O., Olalekan, A. P., Olatunya, A. M., Dada, O. 2012. Langmuir, Freundlich, Temkin and Dubinin–Radushkevich isotherms studies of equilibrium sorption of Zn²⁺ onto phosphoric acid modified rice husk. *IOSR Journal of Applied Chemistry*, 3(1), 38-45.
- Gani, P., Sunar, N. M., Matias-Peralta, H., Parjo, U. K., Oyekanmi, A. A. 2017. Green approach in the bio-removal of heavy metals from wastewaters. *MATEC Web of Conferences*, 103, 06007. https://www.matec-conferences.org/articles/mateconf/pdf/2017/17/mateconf_iscee_2017_06007.pdf
- Hamdaoui, O. 2006. Batch study of liquid-phase adsorption of methylene blue using cedar sawdust and crushed brick. *Journal of Hazardous Material*, 135(1), 264–273.
- Katesa, J., Junpiromand, S., Tangsathitkulchai, C. 2013. Effect of carbonization temperature on properties of char and activated carbon from coconut shell. *Qingdao Daxue Shifanxueyuan Xuebao/Journal of Teachers College Qingdao University*, 20(4), 269-278.
- Koreňová, Z., and Jelemenský, L. 2010. Kinetic study of wood chips decomposition by TGA. *Chemical Papers*, 54(2), 174-181.
- Latiff, A., Aziz, A. O., Rahman, O. A. A., Daud, Z., Ridzuan, M. B., Daud, M., Falilah, N. 2015. Batch adsorption of manganese from palm oil mill effluent onto activated cow bone powder. *ARPN Journal of Engineering and Applied Sciences*, 11(4), 2627-2629.
- Liu, S. 2015. Cooperative adsorption on solid surfaces. *Journal of colloid and interface science*, 450, 224-238.
- Lv, Y., Gan, L., Liu, M., Xiong, W., Xu, Z., Zhu, D., Wright, D. S. 2012. A self-template synthesis of hierarchical porous carbon foams based on banana peel for supercapacitor electrodes. *Journal of Power Sources*, 209, 152-157.
- Ma, X., Zhang, F., Zhu, J., Yu, L., Liu, X. 2014. Preparation of highly developed mesoporous activated carbon fiber from liquefied wood using wood charcoal as additive and its adsorption of methylene blue from solution. *Bioresource Technology*, 164, 1-6.
- Mohamed, R., Al-Gheethi, A., Abdulrahman, A., Sainudin, M. S., Bakar, S. A., Kassim, A. H. M. (2018). Optimization of ceramic waste filter for bathroom greywater treatment using central composite design (CCD). *Journal of Environmental Chemical Engineering*, 6(2), 1578-1588.
- Rosli, M. A., Daud, Z., Latiff, A. A. A., A Rahman, S. E., Rahman, O. A. A., Zainorabidin, A., Awang, H., Halim, A. A. (2017). The effectiveness of Peat-AC composite adsorbent in removing color and Fe from landfill Leachate. *International Journal of Integrated Engineering*, 9(3), 35-38.
- kumar, M. S., Binupriya, A. R., Kavitha, D., Kumar, R. S., Jayabalan, R., Choi, J. G., Yun, S. E. 2009. Adsorption potential of maize cob carbon for 2, 4-dichlorophenol removal from aqueous solutions: equilibrium, kinetics and thermodynamics modeling. *Chemical Engineering Journal*, 147(2), 265-271.
- Sekar, M., Sakthi, V., Rengaraj, S. 2004. Kinetics and equilibrium adsorption study of lead (II) onto activated carbon prepared from coconut shell. *Journal of colloid and interface science*, 279(2), 307-313.
- Shen, Y. S., Wang, S. L., Huang, S. T., Tzou, Y. M., Huang, J. H. 2010. Biosorption of Cr (VI) by coconut coir: Spectroscopic investigation on the reaction mechanism of Cr (VI) with lignocellulosic material. *Journal of Hazardous Materials*, 179(1), 160-165.
- Tsai, W. T., Chen, H. R., Kuo, K. C., Lai, C. Y., Su, T. C., Chang, Y. M., Yang, J. M. 2009. The adsorption of methylene blue from aqueous solution using waste agriculture shell powders. *Journal of Environmental Engineering Management*, 19(3), 165-172.