International Journal of Chemical Engineering– IJCE
Volume 2: Issue 1 [ISSN 2475-2711]
Publication Date: 30 October, 2015

Synthesis of magnetic biochar from Garcinia Mangostana peel using muffle furnace for adsorption of Zn^{2+} ions from aqueous solution.

M.Ruthiraan[1], E.C. Abdullah[1*], K.R. Thines[1], N.M. Mubarak[2],

Abstract— **Synthesis of mangosteen peel based magnetic biochar was carried out in Muffle Furnace at zero oxygen condition at 700°C heating temperature for 20 minutes. The biomass for pyrolysis was prepared through oxidation process with Iron Oxide ions mixed with 0.4M $KMnO_4$ and 0.4M HNO_3 acid. The process optimization was determine by manipulating agitation speed (rpm), time (min) and pH value by using Design Expert software version 7.0. The statistical analysis revealed that the optimum condition for removal of Zn^{2+} ions were at adsorbent dosage of 0.5 g, pH 9.0, agitation speed and time were 125 rpm and 45 min respectively. The maximum adsorption capacity opted for the adsorbent with surface area 730 m^2/g was 86.33 mg/g. For the initial concentration of 30 mg/L, the maximum removal percentage obtained was 93%. The surface adsorption characteristics were determined by Langmuir and Freundlich constant which were 0.0461 L/mg and 12.283 L/mg respectively. The research outcome indicates that the Mangosteen peel based magnetic biochar is a promising adsorbent for removal of Zn^{2+} ions from aqueous solution.**

Keywords—Magnetic biochar, Zinc, Adsorption, Mangosteen Peel, Wastewater

I. Introduction

Ever since industrial revolution took place, it became the starting point for environmental quality deterioration. Maintaining a balanced ecosystem has been a hassle for most of the environmentalist across the world. Human activities for betterment of life lead to various types of pollution. Water pollution gave a drastic impact on both flora and fauna. Nevertheless, humans are being the victims too. Discharge of untreated wastewater from industries lead to extinction of aqua life. Heavy metals are non-biodegradable and moreover intake of metal ions contained food beyond the permissible level could lead to chronic diseases[1] such as such as shortage of red blood cells, chromosomal damages and malfunction of immune system, cancer, liver damage, urination problems and breathlessness problems[2]. Among the heavy metal ions, Zn^{2+} is to be found in large quantity in industrial effluent due to its wide range of use. According to World Health Organization (WHO), to permissible level of Zn^{2+} in both natural surface water and ground water should be below 10mg/L and 40mg/L respectively[3]. Therefore, it is necessary to minimize the Zn^{2+} content in wastewater in order to prevent health risk associate to presence of this pollutant in wastewater. A range of methods have been adopted to treat heavy metal contaminated industrial effluent such as biodegradation, oxidation, solvent extraction, ion exchange and adsorption[4]. However, adsorption is being a promising method due to its high adsorption capability and cost efficiency[5]. Besides, low consumption of reagent and regeneration of adsorbent added value to opt this treatment method[6, 7]. Carbon rich adsorbents are the best medium to be used in removal pollutant particles from wastewater such as activated carbon, biochar, carbon fibre and granular carbon. Recently, magnetic biochar has attracted the interest of researchers to employ this low cost adsorbent due to its fascinating properties such as high surface area, high porosity which enhances the adsorption capacity compared to activated carbon and other adsorbents. The magnetic property of this versatile adsorbent has lower down the hassle in removing the adsorbent upon completion of adsorption process [8, 9]. The magnetic biochar used in this study was derived from mangosteen peel by attaching Iron Oxide ions onto the surface mangosteen peel and underwent pyrolysis process at minimal oxygen supply.

In this research work, statistical optimization on removal of Zn^{2+} ions from analytical grade aqueous solution by using mangosteen peel derived magnetic biochar was carried out. The contribution of each operating parameters such pH, agitation speed and contact time on removal of the blue dye was investigated. The adsorption behaviour of both adsorbent and adsorbate were further investigated by employing Langmuir and Freundlich isotherm model.

[1]M.Ruthiraan, E.C.Abdullah*, K.R. Thines
Malaysia-Japan International Institute of Technology, University Technology Malaysia (UTM)
Malaysia

[2]N.M.Mubarak
UCSI University
Malaysia

II. Material and methods

A. Material

The garcinia mangostana peels used to produce magnetic biochar were opted from local market in Klang Valley. The analytical grade Iron (III) Oxide powder and Zn^{2+} solution purchased from Friendemann Schmidt were used as purchased.

B. Synthesis of magnetic biochar

The raw material was washed and oven dry at 105^{0}C for 3 days to minimize the moist content (6%-8%) then crushed and sieved to obtain particle size less than 20μm. The biomass was sonicated using sonicator (model: Elmasonic

P) by mixing with 400 ml of 1.0M of Iron (III) Oxide solution together 0.4M HNO_3 and 0.4M $KMnO_4$ solution at volume ratio of 3:1 for 3h at 45ºC (70% frequency). The slurry was dried in oven at 70ºC for 5 days and converted into magnetic biochar by pyrolysis using muffle furnace (model: WiseTherm, FP-03, 1000ºC, 3.L) with limited oxygen. The synthesis of magnetic biochar was carried out 700ºC for 20 min. The produced sample was thoroughly washed with distilled water until the pH became neutral.

C. *Characterization*

The physical structure and morphology of Garcinia mangostana peel derived magnetic biochar were analysed by using (Brand: Zeiss Model: Auriga) the field emission scanning electron microscope (FESEM) technique. The total surface area of the produced adsorbent was determined by using Quanta Chrome Autosorb 1 6B BET surface analyser. The sample was degassed at 200ºC for 3h prior to N_2 gas adsorption was conducted at 77K. The Fourier transform infrared (FTIR) spectroscope (Brand: Bruker, Model: IFS66v/S) was used to study the surface chemistry of the adsorbent before and after adsorption study was conducted. All pH measurements were done by using Mettler Toledo type (MP220 model, USA) and the adsorption capacity was analysed using (Model: Perkin Elmer Aanalyst 400) Atomic Adsorption Spectroscopy (AAS).

D. *Adsorption Study*

All batch adsorption studies were conducted at room temperature by adding 0.5g of magnetic biochar into 100ml of 30 mg/L concentrated analytical grade Zn^{2+} solution. The design of experiment was obtained employing Design Expert 7.0 software with Response Surface Method. The operating parameters such adsorbate pH, agitation time and speed were altered to determine optimum adsorption capacity using Central Composite Design (CCD). The adsorption pH was varied from 3.0 – 9.0 by adding 1.0M HCl or 1.0M NaOH. The agitation time and speed were varied from 30 – 60min and 100 – 150 rpm respectively. The adsorption capacity of magnetic biochar was computed by calculating the difference between initial concentration and final concentration. The adsorption capacity was calculated by using the mass balance equation as below:-

$$q_e = \frac{(C_o - C_e)V}{m} \quad (1)$$

Where q_e is the adsorption capacity (mg/g) at equilibrium, C_o and C_e are the initial concentration and the equilibrium concentration (mg/L), respectively. V is the volume (L) of solution and m is the mass (g) of adsorbent used.

III. Result and Discussion

A. *Characterization of magnetic biochar*

Fig. 1(a) and (b) exhibit the field emission scanning electron microscopy (FESEM) (Zeiss, Auriga) images of both raw biomass and magnetic biochar respectively at 1µm scale. These FESEM images exhibits the surface topography. The magnetic biochar shows the macro porosity but no any pores observed on the raw biomass at same magnification scale. These pores play a vital role in enhancing the liquid–solid adsorption processes. The formations of pores occur due to chemical decomposition of water and other organic substances which full down the synthesis yield [10, 11]. The presence of acid and alkaline substance during the preparation of precursor for synthesis of magnetic biochar enhances the development of pores.

The physical characterization which influence the highest adsorption capacity of the produced iron oxide based magnetic biochar was determined by using BET (Brand: Quanta Chrome Model: Autosorb 6B). The analysis revealed that conducting pyrolysis process at temperature of 700ºC for 20 min gave specific BET surface area of 730 m^2g^{-1} which proved that carbonization process will demonstrate minimum specific surface of 350 m^2g^{-1} at high temperature. This development was reported previously in other studies and explained that the activation not only widens the size of the existing pores but also forms a new pores [12].

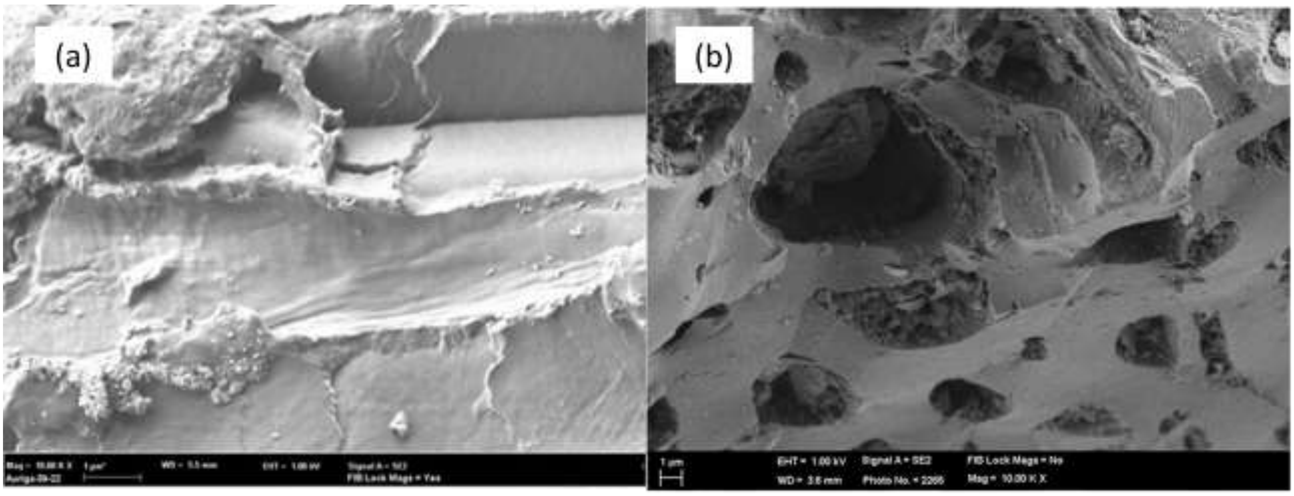

Figure 1. (a) FESEM image of raw mangosteen, (b) FESEM image of magnetic biochar

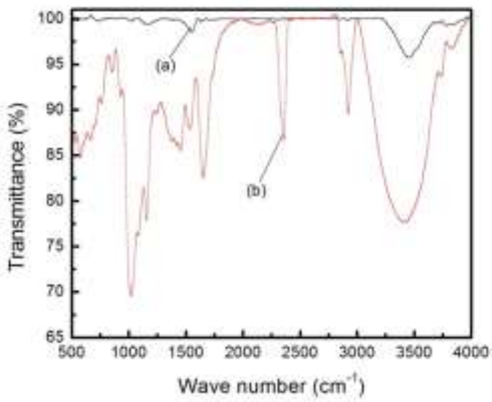

Figure 2. (a) FTIR image of raw biomass, (b) FTIR image of magnetic biochar

FTIR analysis was carried out to obtain the information on the presence of various bands represent vibration of functional groups on surface of adsorbent. The oxidation method in the pre-synthesis work lead to formation of various functional groups on the surface of mangosteen peel magnetic biochar can be identified based on the peak formed in Fig. 2(b). The raw mangosteen particle shows only one peak at approximately 3400cm^{-1} which indicates the stretching vibration of -OH groups of polymeric compounds predominantly due to the presence of cellulose and a small peak at approximately 1600cm^{-1} indicates the presence of aromatic C=C and C=O [13]. A range of broad peaks can be observed as illustrated in Fig. 2(b), where the peak at 560 cm^{-1} is assigned to attachment of Iron Oxide (Fe-O). The other broad peaks represent respective functional groups: C-O-C (1000cm^{-1}), CH_2 (2900cm^{-1}, 1450cm^{-1}), ester C=O (1680cm^{-1}), 2400cm^{-1} and -OH (3400cm^{-1})[14]. These functional groups give an idea of enhancing the formation of pores on the surface of char.

B. *Sorption studies*

The optimum adsorption condition of Zn^{2+} ions onto the surface of magnetic biochar was determine by aiding Central Composition Design by interacting 3 parameters. The effect of each operating parameter was examined to determine the best combination to attain highest removal percentage of Zn^{2+} ions. Fig.3 (a) – (c) represent 3D plot obtained from DOE program. All the batch experiments were conducted at room temperature. Fig. 3(a) denotes at increasing speed and contact time, the Zn^{2+} removal percentage increased. Moreover, the image obtained revealed that agitating at higher speed with lower contact time does not promote adsorption process due to dispersion of adsorbent particle which was favoring for adsorption. It can be concluded that the physisorption required moderate agitation speed with optimum contact time in order to enhance adsorption process. The effect of pH value and agitation speed was illustrated in Fig. 3(b). Based on this 3D plot, it is clear shown that adsorption capacity maximized at alkaline medium compared to either acidic or neutral conditions with increasing in shaking speed. Fig. 3 (c) demonstrates as the adsorbent–adsorbate contact time increased at alkaline adsorption condition, the removal percentage increased. The analysis of the 3D plots indicate that the Zn^{2+} ions attained maximum removal of 93% from wastewater at pH 9.0 with 45min contact time and moderate agitation speed of 125 rpm. The manipulation between operating parameters were based on by other researcher using EFB magnetic biochar [3].

C. *Isotherm Studies*

The Langmuir isotherm model was chosen to determine the maximum adsorption capacity corresponding to homogeneous monolayer adsorption of Zn^{2+} ion onto magnetic biochar produced in this research work. The linearized form of Langmuir model is expressed as below:-

$$\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{C_e}{q_m} \qquad (2)$$

A plot (C_e/q_e) versus C_e (Fig. 4) was constructed to compute the Langmuir constant related to the affinity of

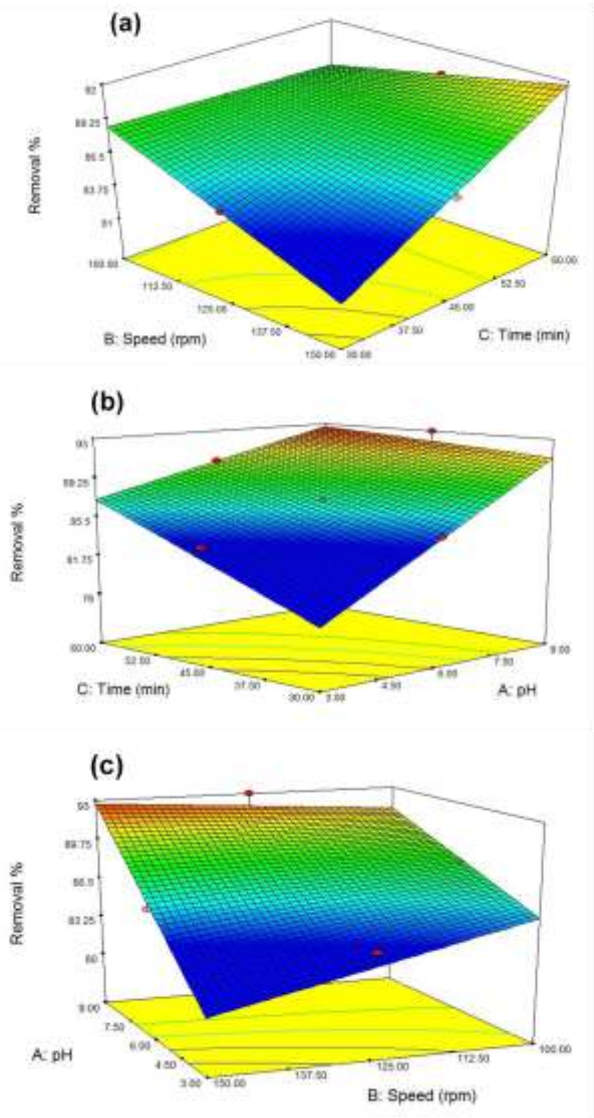

Figure 3. (a) 3D plot interaction of agitation speed (rpm) and agitation time (min), (b) 3D plot interaction of pH and agitation time (min), (c) 3D plot interaction of agitation speed(rpm) and pH

TABLE I. ISOTHERM PARAMETERS FOR ZN^{2+} REMOVAL USING MAGNETIC BIOCHAR

Isotherm Model	Parameters	
Langmuir	K_L	0.0461
	q_m	86.33
	R^2	0.9982
Freundlich	K_F	12.283
	n	5.208
	R^2	0.9632

binding sites, K_L (L/mg) and maximum adsorption capacity of adsorbent, q_m (mg/g). The other variables involved in the Langmuir model were, C_e (mg/L), the equilibrium concentration and q_e (mg/g) represent the amount of adsorbed Zn^{2+} concentration per unit weight. The calculated data were presented in Table 1. The high correlation value (R^2) of 0.995 obtained from Fig. 4 denotes that a good agreement between the parameters and confirms the monolayer adsorption has took place.

The characteristic of heterogeneous surface was analysed by employing the Freundlich isotherm model and the linearized form of Freundlich model is expressed as below:-

$$log q_e = log K_F + \left(\frac{1}{n}\right) log C_e \qquad (3)$$

Where q_e (mg/g) denotes the amount adsorbed metal ion per unit mass of the adsorbent, C_e (mg/L) is the equilibrium concentration, K_F and n were the Freundlich constants determine the effectiveness of heterogeneous surface adsorption by the adsorbent. The 1/n value obtained less than 1 (1/n= 0.192) based on the plot log q_e versus log C_e as shown in Fig. 5 indicates favorable sorption and confirms the heterogeneity of the adsorbent. The Langmuir (4) and Freundlich (5) equations were developed to fit the Zn^{2+} equilibrium adsorption capacity, q_e and the concentration of unabsorbed metal ions were computed as below:-

$$q_e = \frac{0.0461 C_e}{1 + 86.33 C_e} \qquad (4)$$

$$q_e = 12.283 C_e^{5.208} \qquad (5)$$

IV. Conclusion

This research work indicate that mangosteen peel derived magnetic biochar produced at vacuum condition could be an effective adsorbent to be used in removal of Zn^{2+} ions from wastewater . The oxidation process carried out to prepare biomass for pyrolysis process gave an idea in enhancing the surface area of the adsorbent. The presence of organic functional groups has belief to help in formation of surface pore. The pyrolysis process carried out 700ºC for 20 min is an optimum condition to obtain higher surface area of 730 m^2/g. The maximum removal percentage of 93% was obtained at alkaline condition (pH 9.0) by agitating at moderate speed. Higher shaking speed has created lesser adsorbent-adsorbate contact time due to fast particle dispersion in the aqueous solution. Besides, longer contact time has led to desorption process where as optimum adsorption was determined at 45 min. The experimental results were analysed using both Langmuir and Freundlich isotherm models. The models have presented a favouring adsorption trait which was determined by the calculated R^2 correlation values of 0.9982 and 0.9632 respectively.

Acknowledgment

This work is fully supported by Malaysia-Japan International Institute of Technology under FRGS/2/2013/TK05/UTM/01/5.

References

[1] Bhattacharya, A.K., S.N. Mandal, and S.K. Das, Adsorption of Zn(II) from aqueous solution by using different adsorbents. Chemical Engineering Journal, 2006. 123(1–2): p. 43-51.

[2] MUBARAK, N.M., et al., Adsorption and kinetic study on sn2+ removal using modified carbon nanotube and magnetic biochar. International Journal of Nanoscience, 2013. 12(06): p. 1350044.

[3] Mubarak, N.M., et al., Statistical optimization and kinetic studies on removal of Zn2+ using functionalized carbon nanotubes and magnetic biochar. Journal of Environmental Chemical Engineering, 2013. 1(3): p. 486-495.

[4] Acharya, J., et al., Removal of lead(II) from wastewater by activated carbon developed from Tamarind wood by zinc chloride activation. Chemical Engineering Journal, 2009. 149(1–3): p. 249-262.

[5] Bhattacharya, A.K. and C. Venkobachar, Removal of cadmium (II) by low cost adsorbents. Journal of Environmental Engineering, 1984. 110(1): p. 110-122.

[6] Igwe, J. and A. Abia, A bioseparation process for removing heavy metals from waste water using biosorbents. African Journal of Biotechnology, 2006. 5(11).

[7] Abdel-Ghani, N., M. Hefny, and G.A. El-Chaghaby, Removal of lead from aqueous solution using low cost abundantly available adsorbents. International Journal of Environmental Science & Technology, 2007. 4(1): p. 67-73.

[8] Zhang, G., et al., CuFe2O4/activated carbon composite: A novel magnetic adsorbent for the removal of acid orange II and catalytic regeneration. Chemosphere, 2007. 68(6): p. 1058-1066.

[9] Wiatrowski, H.A., et al., Reduction of Hg(II) to Hg(0) by Magnetite. Environmental Science & Technology, 2009. 43(14): p. 5307-5313.

[10] Mohan, D., et al., Modeling and evaluation of chromium remediation from water using low cost bio-char, a green adsorbent. Journal of Hazardous Materials, 2011. 188(1–3): p. 319-333.

[11] Mohan, D., et al., Cadmium and lead remediation using magnetic oak wood and oak bark fast pyrolysis bio-chars. Chemical Engineering Journal, 2014. 236: p. 513-528.

[12] Mubarak, N.M., et al., Synthesis of palm oil empty fruit bunch magnetic pyrolytic char impregnating with FeCl3 by microwave heating technique. Biomass and Bioenergy, 2014. 61: p. 265-275.

[13] Harikishore Kumar Reddy, D. and S.-M. Lee, Magnetic biochar composite: Facile synthesis, characterization, and application for heavy metal removal. Colloids and Surfaces A: Physicochemical and Engineering Aspects, 2014. 454: p. 96-103.

[14] Chen, B., Z. Chen, and S. Lv, A novel magnetic biochar efficiently sorbs organic pollutants and phosphate. Bioresource Technology, 2011. 102(2): p. 716-723.