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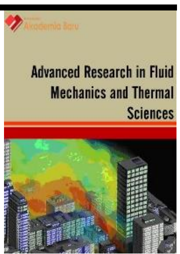

Heavy Metal Ions Adsorption from Aqueous Solution by Jackfruit Peel as Activated Biochar Low-Cost Adsorbent

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ABSTRACT

This study investigates the viability of using jackfruit peel, an amply available solid waste in Malaysia, to adsorb heavy metals by synthesizing it to remove metal ions from water. The JPB was synthesized by carbonizing it at 500^{o}C for 2 hours under air atmosphere flow. To determine its physic-chemical properties, the JPB was characterized using several techniques including XRD, FTIR, SEM, and EDX. The study was carried out in batches to determine the effects of the contact time, initial concentration (5–100 mg/L), pH (4–9) and temperature (25 -45 ◦C) on the removal of heavy metals at a prescribed amount of 0.1 g. The analysis of the experimental data was initially carried out using various types of linearized Langmuir isotherm and Freundlich isotherm, but it was eventually apparent that the data was better suited to the Langmuir model which indicated a higher determination coefficient (ranging from 0.448 to 0.9966). Resultantly, it was found that JPB is highly effective in adsorbing heavy metals from aqueous solutions.

Keywords:
Adsorption; heavy metals; jackfruit peel; characterization; isotherm models

1. Introduction

The contamination of heavy metals in water caused by manufacturing and mining activities has now become a critical global issue. Contaminated industrial wastewater contains non-biodegradable properties with high levels of toxicity which pose serious threats to the environment and living beings alike [1]. Among the toxic properties are lead, cadmium, mercury, arsenic, copper, zinc, and chromium [2]. Such heavy metals can be removed from wastewater using traditional techniques such as ion exchange, membrane filtration, chemical precipitation, solvent extraction and electrochemical treatment [3]. Nevertheless, there are several drawbacks to these methods including the incurrence of high operational costs, the setting-off of secondary contamination following the usage of more chemicals during the treatment process, and poor effectiveness [4]. On the other hand, the use of Biochar for soil/water treatment offers better potentials and benefits such as allowing the waste to be reused, the incurrence of lower carbon footprint, and better cost-savings [5-7] Biochar is the

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resulting product of heating biomass (typically agricultural and industrial wastes) via the process of pyrolysis which entails air-limited conditions. Initially, it is deemed as a carbon-storing material that facilitates mitigating global warming [8]. In this current study, the biochar was produced by synthesizing a jackfruit peel via the carbonization method and subsequently undergoing acid activation. Biochar has been used as an option to treat heavy metal

contamination in soil and water [9]. Numerous characterization techniques were used to examine the physicochemical properties of the synthesized biochar. It was then applied to adsorb heavy metals from wastewater and the result showed its excellent capacity for removing lead and cadmium metal ions. The advantages of using the biochar synthesized from jackfruit peel it was Disposal of agricultural waste that often creates a serious problem of disposal for environments. Also, it helps to reduce the cost of waste disposal.

2. Methodology

2.1 Materials

The jackfruit peel was sourced from a local store in Tanjung Malim, Malaysia. The concentrated phosphoric acid H3PO4 (98%) and Acetone (99.0%) were attained from Merck Malaysia while the Lead (II) nitrate, Copper (II) nitrate, Iron (II) chloride, Manganese (II) chloride, and Cadmium chloride were acquired from Merck Germany. The preparation of the deionized water was carried out in the chemistry laboratory at University Pendidikan Sultan Idris (UPSI). The jackfruit peel was carbonized using a 2-Zone Tube furnace. 2ZTF-1100-2035. The Atomic Absorption Spectroscopy (AAS) was used to determine the adsorption of the heavy metals from the wastewater. No further treatments were imposed on all the solvents and reagents.

2.2 Synthesis of Biochar

The jackfruit peel underwent several rounds of cleansing using deionized water to eliminate contaminants (dirt) and then oven-dried at a temperature of 80 oC for 48 hours. Using a miller, the dried jackfruit peel was then crushed into powder. The powdered form was then saturated with concentrated H3PO4 to activate it and subsequently carbonized in a furnace (a 2-Zone Tube furnace. 2ZTF-1100-2035) under air atmosphere flow at a temperature of 500 oC for 2 hours. Before removing it from the furnace, the activated and carbonized material was left to cool down. Next, the biochar's pH was neutralized by washing it several times with deionized water. After filtering, the biochar was again dried in an oven at 80 oC for 24 hours before moving on to the next step.

2.3 Physic-chemical Characterizations of Biochar

2.3.1 Scanning electron microscopy (SEM)

The Scanning Electron Microscope (SEM) (Hitachi S-3400 Japanese model) was used to examine the surface morphology of the synthesized biochar samples. Prior to the analysis, a Sputter Coater was used to coat the biochar samples with gold.

2.3.2 X-ray diffraction analysis

The X-ray Diffraction (XRD) technique – performed using the Shimadzu XRD 6000 power X-ray diffractometer – was carried out to examine the structure and crystallography of the synthesized biochar. During the sample analysis, the Cu, Kα radiation electrons were accelerated at 27.7 kW and

30 mA in an evacuated X-ray tube with Ni filter over a range of 0° to 80° with a step of 0.04° at screening speed of 2θ min^{-1}.

2.3.3 Fourier transform infrared

The Fourier transform infrared spectroscopy (FTIR) (Thermo Scientific Nicolet TM iS10) was used to examine the relative surface functional groups of the synthesized biochar, logged in between the range of 400–4000 cm^{-1} in wavenumber. Prior to analysis, the biochar pellet was prepared by combining the biochar sample (0.1 mg each) with KBr (100 mg) in a mortar pestle. The mixture was then pressed into the hydraulic pump. Under infrared light, the pellet was scanned and the resulting spectra were documented.

2.4 Isotherm Models

Adsorption isotherm models have been used to describe the distribution of metal ions between the solid phase (adsorbent) and liquid phase (solution) when equilibrium was reached (Table 1). The Freundlich and Langmuir isotherm models have been widely used to describe the interaction between metal ions in solution and adsorbents. Freundlich isotherm model is an empirical equation based on adsorption on a multilayer heterogeneous surface [10].

Table 1
Mathematical Equations Applied in adsorption isotherm study of metal ions on the various adsorbents

Model	Linear equation	plot	Calculated coefficient
Langmuir	$\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{C_e}{q_m}$ $q_e = C_o - C_e$	$\frac{C_e}{q_e}\ vs\ C_e$	K_L= slop/intercept q_m = 1/slope $R_L = \frac{1}{1+K_L C_0*}$
Freundlich	$\text{In}q_e = \text{In}K_F + \left(\frac{1}{n}\right)\text{In}C_e$	$\text{In}q_e\ vs\ InC_e$	$K_F = e^{\text{intercept}}$ n = 1/slope

R_L calculated at optimum concentration of ions, Co*= 100 mg/L

2.5 Batch Adsorption Studies

Experiments on batch adsorption were conducted by mixing 0.1 g of biochar to 250 mL of metal ion solution in a conical flask. Using an incubator shaker, the combination was shaken at 160 rpm for 24 hours. The pH level for the solution was set in the range of 4-9, which was adjusted using 0.1 mol/L HCl or 0.1 mol/L NaOH. The effect of initial metal concentration was examined within the range of 5-100 mg/L whilst the effect of temperature on the adsorption capacity of the adsorbents was studied within the range of 25-45 °C. Meanwhile, the AAS 400 Perkin Elmer Atomic Absorption Spectrometer was used to determine the concentration of a metal ion in the supernatant. Eq. (1) below was used to calculate the amount of metal ion adsorbed into the biochar where *q* is the amount of metal ion adsorbed, *C*o is the initial metal ion concentration, *C*e is the equilibrium metal ion concentration, *w* is the weight of biochar, and *V* is the volume of metal ion solution. The adsorption study was conducted using triplicate experiments.

$$(q) = \frac{(Co-Ce)V}{M} \tag{1}$$

where Co and Ce represent the initial and equilibrium concentrations (mg/L), V is the volume of metal solution used and M is the weight of the adsorbent used (g).

3. Results and Discussion

3.1. Adsorption Studies

3.1.1. Effect of solution pH

Metal removal relies on pH condition which directly affects the solution's metal chemistry and the ionization of several functional groups thus affecting the presence of the binding sites [11]. The capacity of the biochar to adsorb the ions was studied under the pH range of 4-9. The finding as presented in Figure 1 indicates that the pH range of 4-9 has a significant effect in removing the ions, the adsorption capacity decreases for pH values more than 7. The finding can be explained that between the pH range of 4 and 6, lead and cadmium ions are mainly present as M(II) ions. Low adsorption at pH 4 and below may be caused by the higher concentration and mobility of the hydronium ions (H^+) in comparison to the M(II) ions. Additionally, these metal salts are also highly soluble and easily ionized in an acidic range. Hence, at lower pH values, the biochar surface is enclosed by an abundance of H^+ ions which are competing with metal ions to access the binding sites. With the higher concentration of H^+, the adsorbent's surface is positively charged hence preventing the adsorbents and metal cations from attaching. With the increase in pH, the adsorbent's surface becomes more negatively charged thus allowing for more metal adsorption. The subsequent studies were hence carried out at pH 7.

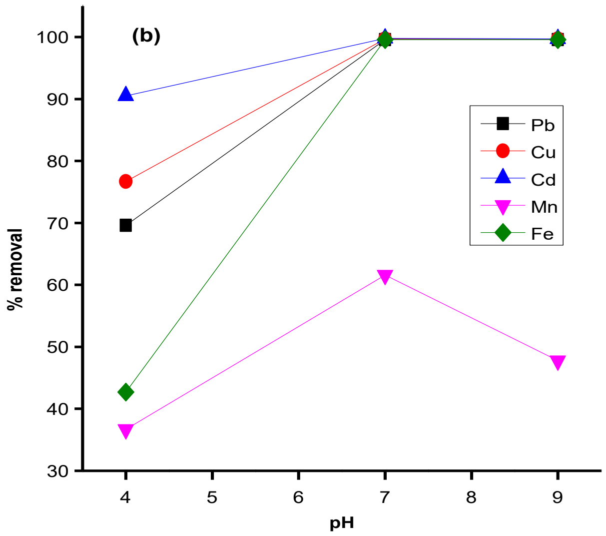

Fig. 1. Effects of initial solution pH on Pb (II), Cu (II), Fe (II), Cd (II) and Mn (II) adsorption onto Peel (ads. dosage = 0.1 g/40 mL; metal ion concentration. = 100 mg/L)

3.1.2 Effect of contact time

The capacity of the biochar to adsorb the metal ions was studied under a fixed initial metal concentration of 100 mg/l and adsorbent dosage of 0.1 g in a time range of between 15 minutes to 24 hours. The finding as presented in Figure 2, indicates that adsorption was rapid during the first 1 hour of contact but gradually decreases up to the point where equilibrium is achieved. The rapidity of adsorption during the initial stage may be caused by the presence of the binding sites which become the push factor for the accelerated metal ion transfer to the biochar's surfaces. The gradual decrease in intake was caused by the saturated surface that became congested with the metal ions hence slowing down the adsorption process. Equilibrium was achieved during the first 2-3 hours.

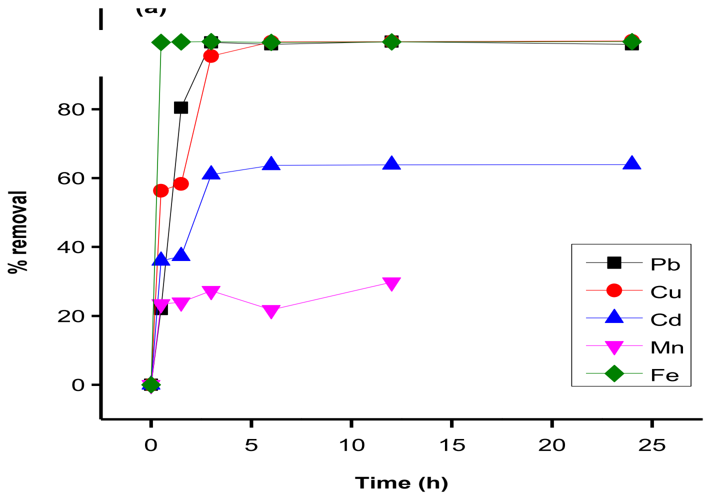

Fig. 2. Effect of contact time on the removal of Pb (II), Cu (II), Fe (II), Cd (II) and Mn (II) by Peel (Initial ion pH = 7; metal in concentration = 100mg/L; ads. dosage = 0.1 g/40 mL; time = 24 h)

3.1.3 Effect of solution temperature

The capacity of the biochar to adsorb Pb (II), Fe (II), Cu (II), Cd (II) and Mn (II) ions was studied under varying temperatures between 25 °C – 45 °C. The finding as indicated in Figure 3 shows that the number of ions adsorbed into the biochar surges with increased temperature, with the maximum number of adsorbed ions obtained at 45 °C. This indicates that the biochar's adsorption is endothermic. Hence, subsequent experiments were conducted at the respective optimum temperatures of 25 and 45 °C.

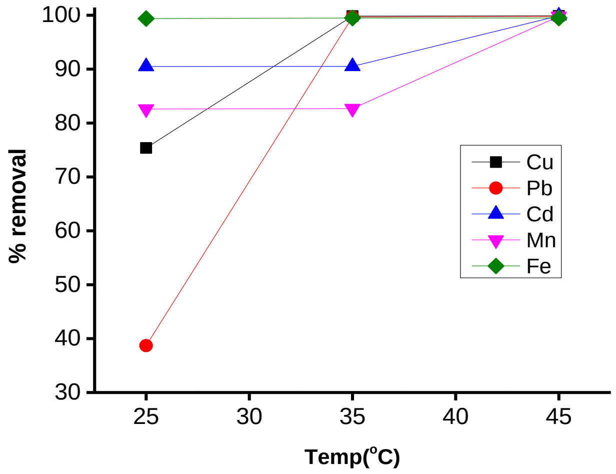

Fig. 3. Effect of Temperature on the removal of Pb (II), Cu (II), Fe (II), Cd (II) and Mn (II) ions on peel biochar (pH=7, dosage = 0.1 g/40 mL; metal conc. = 100 mg/L; time = 24 h and temp = 25 to 45 ± 1°C)

3.1.4 Adsorption isotherm models

The most common isotherm models used for characterizing adsorbents are the Langmuir and Freundlich isotherms [12]. This current study used both isotherms with initial metal concentrations ranging from 5 to 100 mg/L at 45 °C and 25 °C under a pH of 7.0 to evaluate the activated biochar's equilibrium adsorption capacity in removing the Pb (II), Cu (II), Fe (II), Cd (II) and Mn (II) ions. As shown in Figure 4, the metal ion uptake (q_e) of Pb (II), Cu (II), Fe (II), Cd (II) and Mn (II) using the activated biochar surges with increased Pb (II) equilibrium concentrations (C_e). This is because higher initial concentrations give the needed push factor to overcome the metal ions' resistance between the aqueous and solid phases [13].

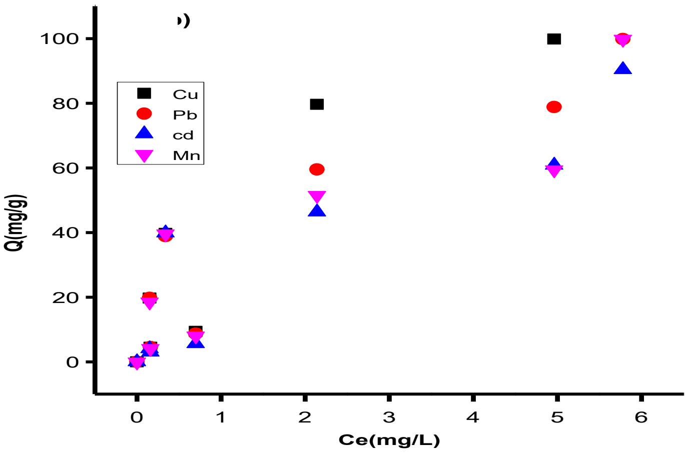

Fig. 4. Adsorption isotherms of Pb (II), Cu (II), Cd (II) and Mn (II) ions on Peel biochar (temp = 25 ± 1°C)

The coefficient of determination (R^2) enables the models to visualize the experimental data. As shown in Table 2, the adsorption data is more suited to the Langmuir model as indicated by the higher R^2 (i.e. between 0.448 and 0.9966) than the Freundlich isotherm (i.e. with R^2 between 0.1276 and 0.5935), which signifies monolayer adsorption i.e. zero occurrence of subsequent adsorptions ensuing the presence of heavy metals in the active sites. However, the Freundlich model had indicated an *n* value larger than 1. The data is in line with the model where there is an occurrence of multilayer adsorption on the adsorbent surface. This result is somewhat anticipated considering the intricacy of the biosorbent material [14]. Figures 5 and 6 show the adsorption isotherm of the ions on the biochars based on the Langmuir and Freundlich models, respectively.

Table 2
Langmuir and Freundlich isotherm constants and coefficients of determination for Pb (II), Cu (II), Cd (II) and Mn (II) adsorption onto the peel

Adsorbent/Metals	Langmuir Isotherm				Freundlich Isotherm		
	Q_{max} (mg/g)	K_L (L/mg)	R_L	R^2	K_F (mg/g) (L /mg)^n	n	R^2
			Peel				
Pb	10.1	0.206	0.046	0.7038	0.0864	0.065	0.4442
Cu	17.5	0.11	0.083	0.9966	0.825	1.058	0.368
Cd	20.0	0.469	0.021	0.8757	0.07	0.894	0.4593
Mn	76.9	5.083	0.0019	0.6567	1.517	0.07	0.1276
Fe	4.40	2.719	0.0036	0.6416	5.067	0.007	0.9599

*Calculated value at an optimum concentration of Pb (II), Cu (II), Fe (II), Cd (II) and Mn (II)

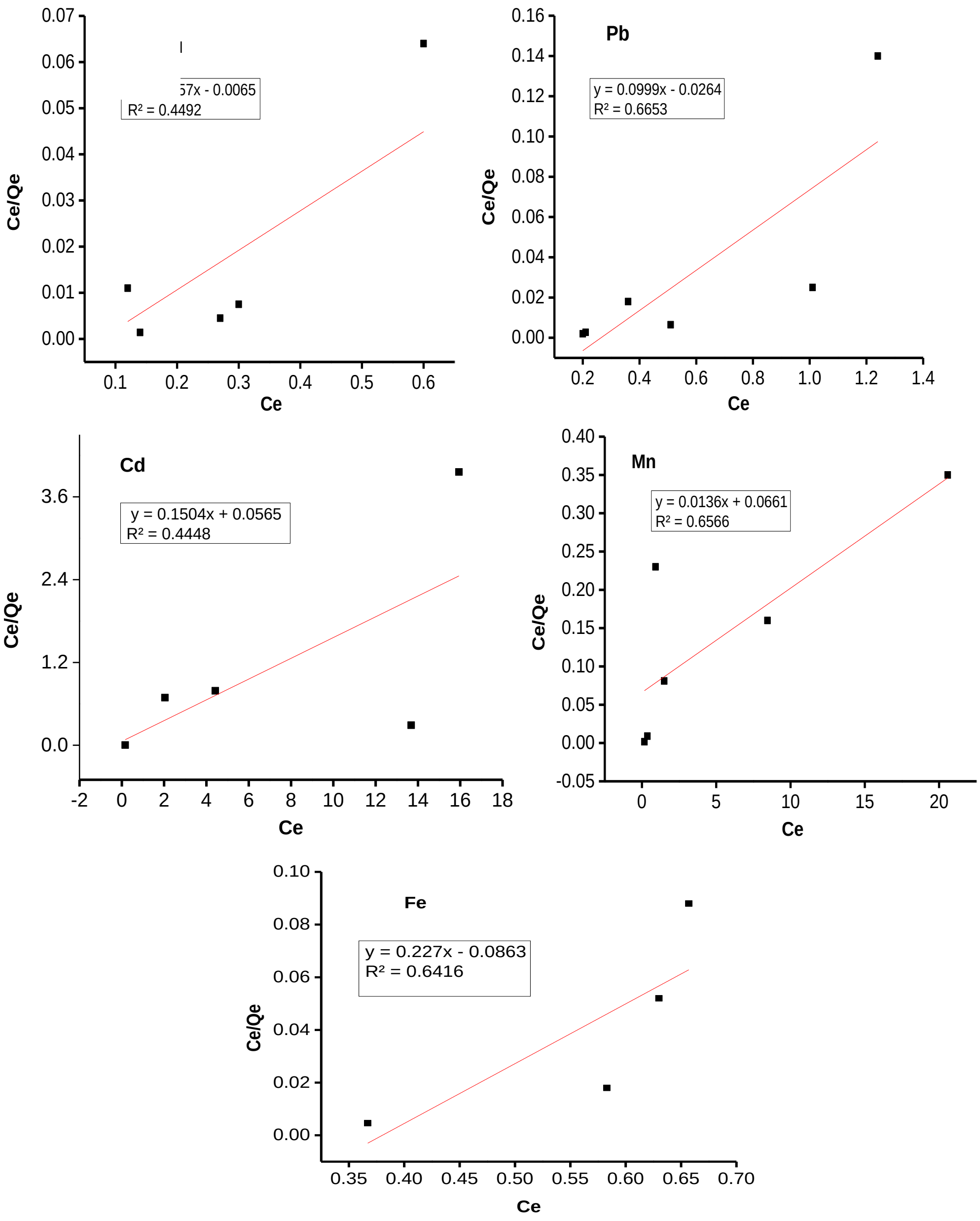

Fig. 5. Adsorption isotherm of Pb (II), Cu (II), Cd (II) and Mn (II) ions on Peel linearized according to Langmuir

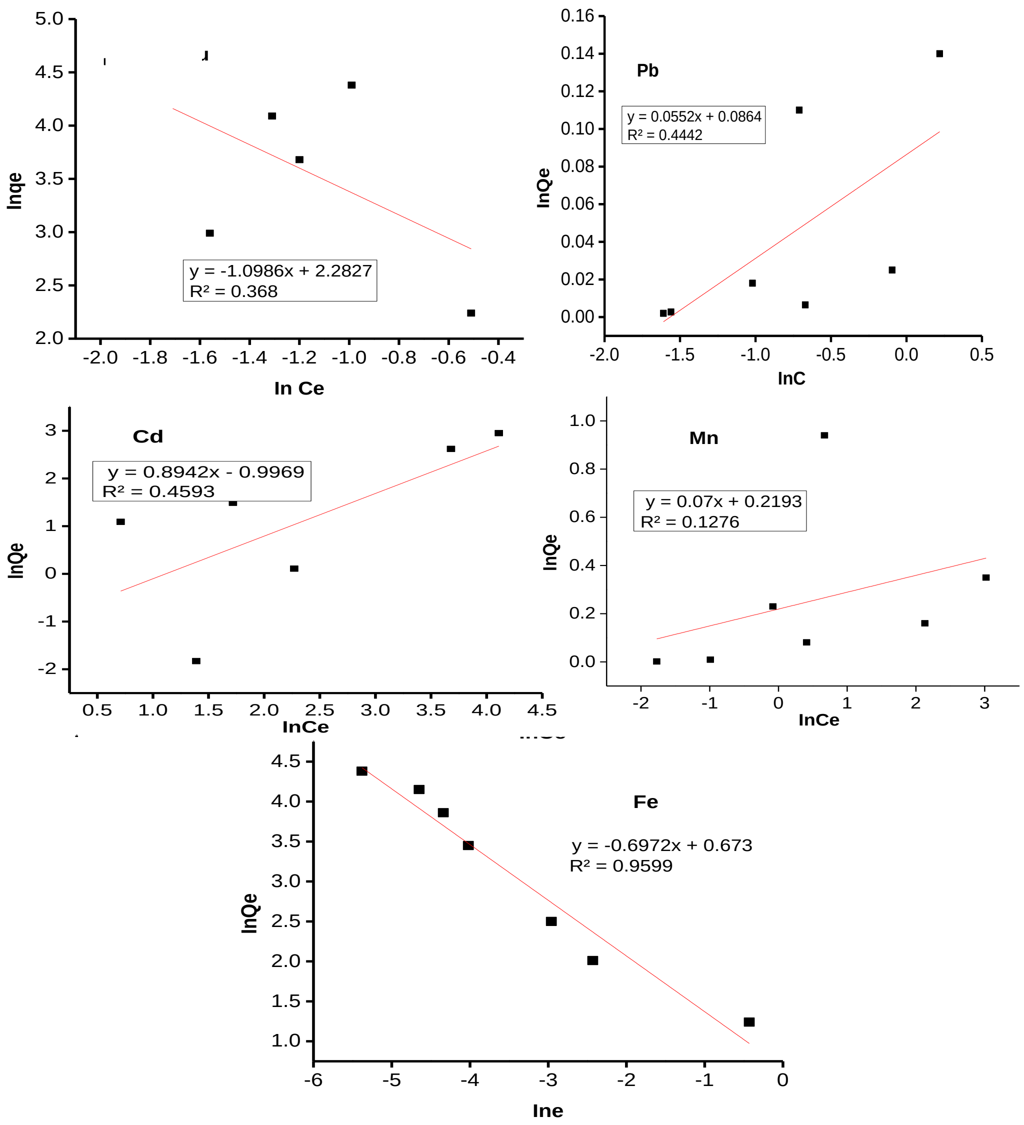

Fig. 6. Adsorption isotherm of Pb (II), Cu (II), Cd (II) and Mn (II) ions on Peel, linearized according to Freundlich

3.2. Characterization Studies

3.2.1 Morphology studies field emission scanning electron microscope (FESEM)

Figure 7 shows the FESEM images of the biochar samples prepared at 500 °C. The pyrolyzed – biochar materials exhibited various micropores to mesopores. Based on the morphology, the external surfaces of the chars are shown to be filled with cavities and somewhat uneven due to the activation of the H_3PO_4 and its interaction with the agricultural residues during carbonization. The difference between other raw agricultural wastes and the jackfruit peel is indicated by the abundance of micropores and mesopores in the latter. The different structures of the micropores and mesopores act as channels for removing metal ions and allow an effective adsorption process; hence, this indicates the high significance of the micropores and mesopores for eliminating heavy metals [15].

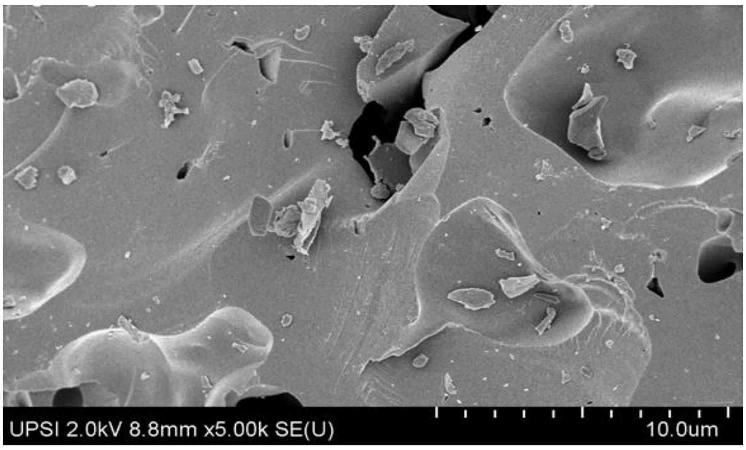

Fig. 7. FESEM images of the peel biochar

3.2.2 Functional surface groups (FTIR analysis adsorption)

Figure 8 shows the FTIR spectra of the biochar prior to adsorption as well as the spectra of the biochar samples prepared using H_3PO_4 which showed these bands: i) 1721-1728 cm−1 due to C=O stretching in carboxylic acids or isolated carbonyl moieties [16], ii) the peak of 1614 cm^{-1} (aromatic C=C) due to skeletal vibrations of un-oxidized graphitic domains, iii) 1506 cm^{-1} due to C=C stretching in aromatic rings [16], and iv) 680-610 cm^{-1} and 1155 cm^{-1} due to deformation vibrations of the O=S=O groups and S-O bends (sulfates). This indicates the effectiveness of the activated carbon preparation as there is a reaction between the precursor and the activation. The biochar's oxygen functional groups consisted of carboxylic acids (or carboxylic anhydrides), phenols, and carbonyl groups (isolated or arranged in quinone manner).

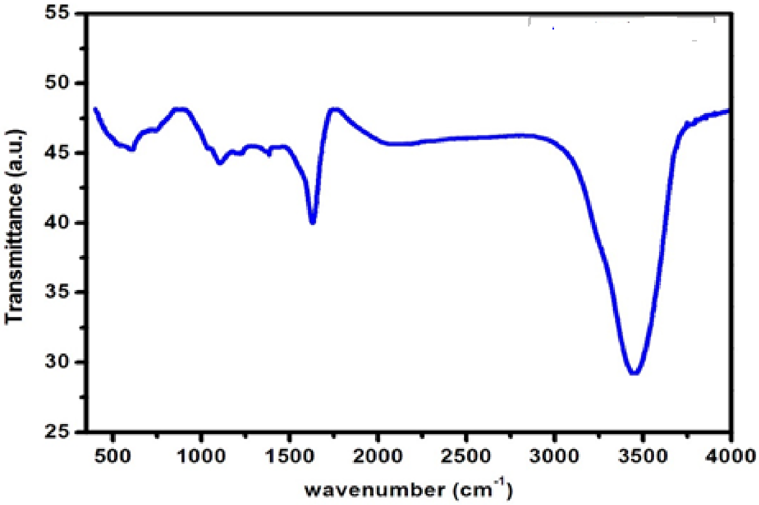

Fig. 8. FTIR spectra of the peel biochar

3.2.3 X-ray diffraction studies

Figure 9 shows the biochar's XRD pattern at an activated temperature of 500°C, peaking at 2θ = 27° in parallel with the peak of the graphite. The broadest maxima were exhibited by the peaks of the biochar carbon, indicating that biochar is characteristically amorphous. In both instances, a major hump was shown to be present between the 2ɵ = 10 to 2ɵ = 27. The hump in this region range between C (002) and C (101) shows the existence of an amorphous carbon material comprising randomly-oriented aromatic carbon sheets [17]. The XRD spectra for the biochar in this study are in line with the characterizations of biochar and activated carbon XRD in other studies such as that of [18].

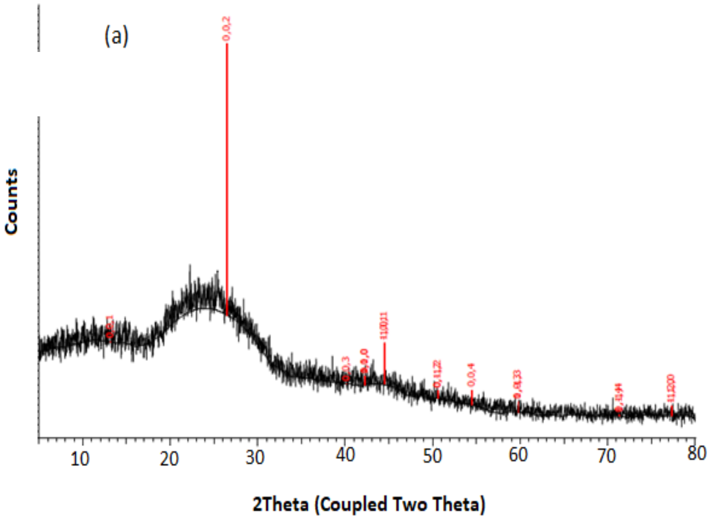

Fig. 9. XRD pattern of peel

3.2.4 Elemental content of biochar (EDX analysis)

The surface elements of the activated biochar samples were identified using the EDX analysis. As shown in Figure 10, the resultant activated biochar is made up of elemental carbon, hydrogen, nitrogen, calcium, magnesium, aluminum, silicon, phosphorus, and potassium. The weighted average of the biochar elements are as follows: Carbon (C, 63.99), Potassium (K, 4.61), Calcium (Ca, 0.32), Oxygen (O, 19.13), Magnesium (Mg, 0.12), Aluminium (Al, 0.15), Silicon (Si, 0.36), Phosphorus (P, 0.17), and Sulphur (S, 11.16).

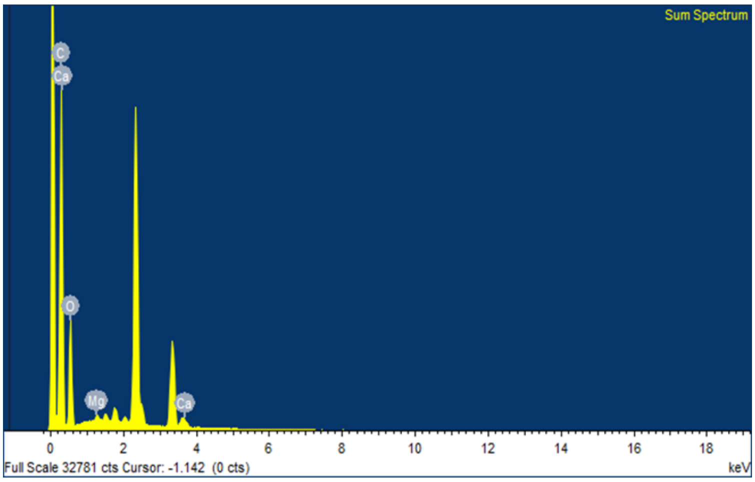

Fig. 10. Elemental content of peel biochar

4. Conclusion

The findings of this study confirmed the viability of using jackfruit peel as a cost-effective adsorbent of heavy metals specifically Cd, Pb, Cu, Fe, and Mn from aqueous solutions. The functional groups present in the biochar support metal ion binding. Nevertheless, this study only provided basic estimates of the usage of jackfruit peel-based biochar for water treatment. There is a need to examine the biochar's efficacy in treating actual industrial wastewater. The use of jackfruit peels is advantageous as they are readily available in large quantities and at a low-cost; furthermore, their re-usage for water treatment will be a practical solution to their poor disposal. The heavy metals adsorption capacity of these extracted biochars from the contaminated river water was tested. The optimum experimental conditions for the batch adsorption were carried out with 0.1g and 100 mg/L of metal ions, pH 7 and 45 oC for the peel. The removal of Mn (II), Cu (II), Pb (II), Cd (II) and Fe (II) was shown to be strongly dependent on the adsorption parameters such as pH, temperature, initial ion concentration and contact time.

References

[1] Kampalanonwat, Pimolpun, and Pitt Supaphol. "The study of competitive adsorption of heavy metal ions from aqueous solution by aminated polyacrylonitrile nanofiber mats." *Energy Procedia* 56 (2014): 142-151.

[2] Sulaymon, Abbas H., Ahmed A. Mohammed, and Tariq J. Al-Musawi. "Competitive biosorption of lead, cadmium, copper, and arsenic ions using algae." *Environmental Science and Pollution Research* 20, no. 5 (2013): 3011-3023.

[3] Mohammadnezhad, Gholamhossein, Roozbeh Soltani, Saeed Abad, and Mohammad Dinari. "A novel porous nanocomposite of aminated silica MCM-41 and nylon-6: Isotherm, kinetic, and thermodynamic studies on adsorption of Cu (II) and Cd (II)." *Journal of Applied Polymer Science* 134, no. 40 (2017): 45383.

[4] Ding, Yang, Yunguo Liu, Shaobo Liu, Zhongwu Li, Xiaofei Tan, Xixian Huang, Guangming Zeng, Yaoyu Zhou, Bohong Zheng, and Xiaoxi Cai. "Competitive removal of Cd (II) and Pb (II) by biochars produced from water hyacinths: performance and mechanism." *RSC advances* 6, no. 7 (2016): 5223-5232.

[5] Beiyuan, Jingzi, Daniel CW Tsang, Yong Sik Ok, Weihua Zhang, Xin Yang, Kitae Baek, and Xiang-Dong Li. "Integrating EDDS-enhanced washing with low-cost stabilization of metal-contaminated soil from an e-waste recycling site." *Chemosphere* 159 (2016): 426-432.

[6] El-Naggar, Ali, Sang Soo Lee, Jörg Rinklebe, Muhammad Farooq, Hocheol Song, Ajit K. Sarmah, Andrew R. Zimmerman, Mahtab Ahmad, Sabry M. Shaheen, and Yong Sik Ok. "Biochar application to low fertility soils: a review of current status, and future prospects." *Geoderma* 337 (2019): 536-554.

[7] El-Naggar, Ali, Sabry M. Shaheen, Yong Sik Ok, and Jörg Rinklebe. "Biochar affects the dissolved and colloidal concentrations of Cd, Cu, Ni, and Zn and their phytoavailability and potential mobility in a mining soil under dynamic redox-conditions." *Science of the total environment* 624 (2018): 1059-1071.

[8] Lehmann, Johannes, Jan Skjemstad, Saran Sohi, John Carter, Michele Barson, Pete Falloon, Kevin Coleman, Peter Woodbury, and Evelyn Krull. "Australian climate–carbon cycle feedback reduced by soil black carbon." *Nature Geoscience* 1, no. 12 (2008): 832-835.

[9] Kosolsaksakul, Peerapat, Ian W. Oliver, and Margaret C. Graham. "Evaluating cadmium bioavailability in contaminated rice paddy soils and assessing potential for contaminant immobilisation with biochar." *Journal of environmental management* 215 (2018): 49-56.

[10] Freundlich, H. M. "F.(1906). Uber die adsorption in lasungen [J]." *Journal of Physical Chemistry* 57: 385.

[11] Farghali, A. A., M. Bahgat, A. Enaiet Allah, and M. H. Khedr. "Adsorption of Pb (II) ions from aqueous solutions using copper oxide nanostructures." *Beni-Suef University Journal of Basic and Applied Sciences* 2, no. 2 (2013): 61-71.

[12] Mehrabi, Novin, Mansooreh Soleimani, Mina Madadi Yeganeh, and Hakimeh Sharififard. "Parameter optimization for nitrate removal from water using activated carbon and composite of activated carbon and Fe 2 O 3 nanoparticles." *RSC advances* 5, no. 64 (2015): 51470-51482.

[13] Patrulea, Viorica, Anamaria Negrulescu, Manuela M. Mincea, Laura D. Pitulice, Otilia Bizerea Spiridon, and Vasile Ostafe. "Optimization of the removal of copper (ii) ions from aqueous solution on chitosan and cross-linked chitosan beads." *BioResources* 8, no. 1 (2013): 1147-1165.

[14] De Souza, João Valdir Tadioto Miranda, Kristiany Moreira Diniz, Cristina Lorena Massocatto, César Ricado Teixeira Tarley, Josiane Caetano, and Douglas Cardoso Dragunski. "Removal of Pb (II) from aqueous solution with orange sub-products chemically modified as biosorbent." *BioResources* 7, no. 2 (2012): 2300-2318.

[15] Ok, Yong Sik, Sophie M. Uchimiya, Scott X. Chang, and Nanthi Bolan. *Biochar: Production, characterization, and applications*. CRC press, 2015.

[16] Wang, Xianze, Zhongmou Liu, Zhian Ying, Mingxin Huo, and Wu Yang. "Adsorption of trace estrogens in ultrapure and wastewater treatment plant effluent by magnetic graphene oxide." *International journal of environmental research and public health* 15, no. 7 (2018): 1454.

[17] Lokman, Ibrahim M., Umer Rashid, and Yun Hin Taufiq-Yap. "Microwave-Assisted Methyl Ester Production from Palm Fatty Acid Distillate over a Heterogeneous Carbon-Based Solid Acid Catalyst." *Chemical Engineering & Technology* 38, no. 10 (2015): 1837-1844.

[18] Xie, Zhigang, Wei Guan, Fangying Ji, Zhongrong Song, and Yanling Zhao. "Production of biologically activated carbon from orange peel and landfill leachate subsequent treatment technology." *Journal of Chemistry* 2014 (2014).