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Activated carbon from honeydew rind as an adsorbent in zinc removal from aqueous solutions.

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Abstract. This study focusing in producing activated carbon (AC) from honeydew rind, a low-cost agricultural by-product, by chemical activation using H_2SO_4 used as an adsorbent for the removal of zinc ions from aqueous solutions. Preparation method on the effect of surface morphology at different carbonization temperatures 450^{o}C, 470^{o}C, 490^{o}C and 510^{o}C was studied. The AC was characterized using FEM-SEM, FTIR and TG. Batch adsorptions were carried out to optimize different variables such as zinc concentration, contact time, pH and biosorbent amount. AAS analysis showed that the maximum adsorption of zinc onto honeydew rind AC was achieved at the conditions of pH 7.5, 1.5g biosorbent amount, 1000mg/L initial zn concentration and 45min contact time. The maximum metal uptake and maximum removal were 66.55mg/g and 99.79% respectively.

Introduction

The persistent and non biodegradable of heavy metals had triggered in depth study on removal of heavy metals in the receiving environmental. Zinc (Zn) is one of heavy metals residues from various massive chemical industries such as batteries, tanneries, metal plating, agrochemicals, petrochemicals and mining [1, 2]. Daily recommended dose of Zn for men, women, children and infant is 15mg, 12mg, 10mg and 5mg respectively [3]. The residue of Zn enters the environment mainly through water stream as untreated wastewater. People who live near waste sites containing are likely to be exposed to zinc through breathing, drinking contaminated drinking water and the polluted water. There is therefore essential to remove this metal from wastewater in order to prevent from entering natural water bodies by polluted water containing the harmful metal [4, 5].

At present, a list of technologies have been designed and employed for heavy metal removal purpose namely precipitation, biological treatment, membrane-filtration process, fenton reagent and adsorption [6, 7]. Despite of the efficiency in pollutants removal these methods have significant disadvantages, such as high chemical and energy requirements, hazardous sludge formation, low efficiency at low concentration of pollutants and high cost at large scale [8]. Nevertheless, despite of high cost of operational, adsorption using AC as adsorbent is the most efficient technique and produces the least drawbacks. Hence there is a new interest among researchers on exploring alternative precursor to produce a low cost adsorbent for wastewater treatment.

Activated carbons (AC) are principally amorphous solids with large internal surface areas and pore volumes. This characteristic fit to many applications such as separation and purification technologies, catalytic processes, decolorization and wastewater treament [9, 10]. To date, due to their adsorptive capacity, AC has been well known in the sorption of chemical species from aqueous solutions as adsorbent [11]. In spite of the fact that charcoal has been the oldest adsorbent known in wastewater treatment but the cost of operational of commercial ACs from this material is still high at US$20/kg [12]. Therefore alternative adsorbents with economical feaseble factor; cost effective and efficiency have been the main target of recent research in this area. ACs used in

wastewater treatment are traditionally obtained from precursors such as wood, palm kernel and animal bones [13]. However, the interest for the application of alternative and value added raw materials from crop waste has increased during last years. These non wooden materials have been utilized in many research in this area as they have potential to become an alternative biosorbent with economical feasible factors. In addition, AC derived from crop waste remains as a natural substance in ecosysytem [14-18].

This study was aimed to produce AC from non-economical honeydew rind for Zn removal in aqueous solutions. Prior to the chemical activation process, pre-treatment and optimization of the duration of soaking the rind in the nitric acid were studied as well as impregnation time. The surface morphology and pore surface diameter of the ACs were determined. The adsorption of Zn was studied with respect to the initial pH, contact time, initial metal ion concentration and biodsorbent dose.

Experimental

Raw material and preparation condition

Honeydew rind was sorted and washed with tap water, pretreated with 5% nitric acid (HNO_3) for 4h, soaked in distilled water and oven dried at 60^{o}C. Impregnation step used 20% sulfuric acid (H_2SO_4) for 6 h and oven dryied at 110^{o}C. Carbonization was done at 450^{o}C, 470^{o}C, 490^{o}C or 510^{o}C for 30 min. The AC was washed with hot distilled water for several times followed by cold water until pH nuetral then dried at 110^{o}C. The AC was kept in tight container for further uses.

Batch adsorption study

Batch adsorption studies [**Table 1**] were carried out by orbital shaking 0.1g of granular AC in 100mL of aqueous solutions of Zn ion at 125rpm for 30 min at room temperature.

Table 1 : Experimental conditions

Parameters	Range	Parameters	Range
Zn initial concentration (mg/l)	100, 500, 1000, 1500	pH	6.0, 6.5, 7.0, 7.5
Contact Time (min)	15, 30, 45, 60	Biosorbent amount (g)	0.1, 0.5, 1.0, 1.5, 1.8

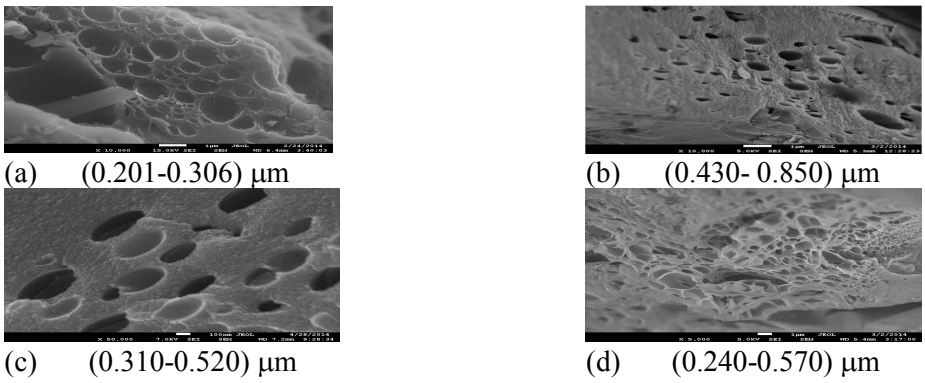
Characterization

Surface functional groups were determined by fourier transform infrared spectra (FTIR) using SHIMADZU IR Prestige 21. Thermogravimetric (TG) analysis was performed by using a LINSEIS THERMOBALANCE with simultaneous recording of TG and differential thermogravimetric analysis (DTG) curves in relation to temperature and time. Field emission-scanning electron microscope (FE-SEM) images of AC before and after adsorption were recorded using JEOL JSM-7600F Field Emission Scanning Electron Microscope (USA).

Result and discussion

FE-SEM, TG and FTIR analysis

The pore surface diameter of AC produced at different carbonization temperature of 20% H_2SO_4 impregnated shown in **Fig. 1** at 1000x magnification. It is proposed that H_2SO_4 provokes the pyrolytic decomposition of the precursor and the arrangemnet of the crosslinked structure [17]. All diamaters were in μm. At 450^{o}C, diameter was observed in the range of 0.201- 0.306. The undeveloped porosity on the surface changed to well-developed porosity as the temperature increased to 470^{o}C. The surface was observed clearer due to the decomposition removing impurities from the material [15]. Direct measurement from the micrograph showed that the average pore diameter was in the range of 0.430 - 0.850. Darker area spotted compared to the images of 450^{o}C may be theorize higher carbonization temperature elevate the depth of porosity development. Further observation indicated the diamaters have become larger as temperature increased to 490^{o}C and 510^{o}C speculated the damage of the walls' structure [16] consequently lead to pores ruptures and reduce adsorption ability. Besides, higher temperature and duration of



(a) (0.201-0.306) µm (b) (0.430- 0.850) µm

(c) (0.310-0.520) µm (d) (0.240-0.570) µm

Fig 1. The changes of surface morphology of the AC and their width ranges (µm) at different carbonization temperature (a) 450°C, (b) 470°C, (c) 490°C and (d) 510°C.

carbonization induced more carbon to involve hence gasification occured. As the result, ash content increases resultant more carbon to be consumed and lowered carbon yield [13, 14]. Thus AC with pore surface diameter of (0.430-0.850) µm impregnated with 20% H_2SO_4 and carbonized at 470°C was selected for batch adsorption study.

TG analysis was done to investigate thermal degradation of honeydew rind against temperature and time [**Fig. 2**]. The initial stage, ranging from 30°C-100°C, involves the loss of moisture contain in the sample with approximately of 9 wt.%. Approximately of 7 wt.% loss occurred at 100°C-200°C related to the elemination of volatiles resulting from the decomposition of hemicellulose in the rind. The stage of 300–480°C was believed by the decomposition of cellulose and lignin with the maximum weight loss of 46 wt.%. This is due to breakage of chemical bonded water, bioplymer composites to carbon [16]. The weight loss was observed come to end above 475°C suggesting 470°C is suitable for preparation of the AC. The total of weight loss was 89%.

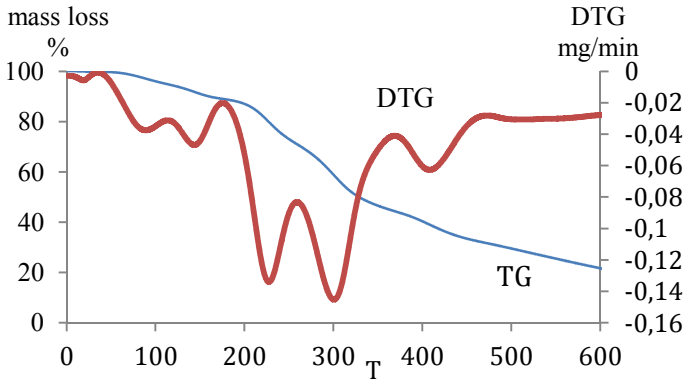


Fig. 2. TG and DTG curves of dried honeydew rind 5% HNO_3 pretreatment.

FTIR result showed [**Table 2**] the existance of carboxyl, hydroxyl and alcoholic functional groups. This result proved that honeydew rind AC consists same functional groups as the common plant base AC [4, 17]. A strong and broad adsorption broad peak detected at 3307.28 cm^{-1} on loaded-AC (LAC) which corresponds to the stretching of O-H and the amine N-H groups show the existance of bonded hydroxide in the raw sample. C-O stretch appeared at 1099.21 cm^{-1} for unloaded-AC (ULAC) represents primary hydroxyl and secondary hydroxyl at 1110.75 cm^{-1} for LAC. These results indicated complexation of functional groups with Zn ion has changed the chemical environment of the functional groups and led to a shift of the AC functional groups in the FTIR-loaded spectra. The FE-SEM micrograph in **Fig. 3(b)** of LAC indicated disappearance

Table 2: Comparisons of FT-IR results from UL-AC and LAC biosorption.

ULAC biosorption (cm^{-1})	Identified Groups	LAC biosorption (cm^{-1})	Identified Groups
671.10	Alkynes; -C≡C-H: C-H bend	686.52	Alkynes; -C≡C-H: C-H bend
1099.21	Primary hydroxyl; stretching C-O	1110.75	Secondary hydroxyl, stretching C-O
1577.46	Aromatic structure; stretching C=C	1623.75	Aromatic structures, stretching C=C
2360.41	Alkyne triple bond, nitrile triple bonds	3307.28	Hydroxyl, carboxylic acid; stretching O-H, N-H

of pores surface in **Fig. 3(a)**. It is due to adsorbed Zn bound with the AC and most expected resultant from the process Zn removal from aqueous solution through biosorption process.

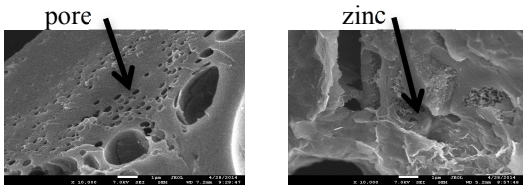


Fig. 3. Micrograph **(a)** ULAC and **(b)** LAC.

Batch adsorption

Table 3 showed maximum removal and uptake capacity for each parameters tested. In general zn removal increase for all parameters. Meanwhile Zn uptake capacity trend increasing and started to decrease above 7.5 pH and 1000mg/L zn concentration. This is due to at higher pH ionizatian of compounds on the sorbent surface produces negatively charged oxygen (O−). The condition enhances the cation exchange capacity thus leads to repulsion of the positively charged Zn from the sorbent surface [12]. At high Zn ion concentrations, the ratio of surface active sites to the total metal ions in the solution was low hence not all metal ions interacted with the adsorbent and removed from the solution [13]. In contrast the uptake capacity for contact time and biosorbent amount showed a decreasing trend above 45 minutes and 1.5g respectively. This could be due to higher biosorbent dose causes electrostatic interactions with the medium and interference between the bindings sites [14-15].

Table 3: Maximum Zn removal percentage and Zn uptake capacity at paramaters tested.

Item/value	pH	Initial zn concentration	Contact time	Biosorbent amount
	7.5	1000mg/L	45 min	1.5 g
Zn removal (%)	98.5	99.5	99.0	98.8
Zn uptake (mg/g)	98.9	97.2	66.8	79.4

Conclusion

ACs with developed porosity and excellent zinc adsorption performance have been prepared from the honeydew rind pretreated with 5% HNO_3, impregnated with 20% H_2SO_4 and carbonization temperature of 470^{o}C. This study has convinced that the honeydew rind has fully converted to AC after carbonization temperature of 470^{o}C. The AC prepared from the honeydew rind has shown good adsorption capacity for zinc removal in aqueous solution. Maximum percentage removal of Zn is 99.78% and Zn uptake is 99.79 mg/g at optimized paramaters values.

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