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Honeydew Rind Activated Carbon as an Adsorbent for Zn(II) and Cr(III) Removal from Aqueous Solution: An Optimization Study

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ABSTRACT

A combination of phosphoric acid (H_3PO_4) 20% v/v impregnation and carbonization method was employed to convert honeydew rind into activated carbons (ACPHDR) for Zn(II) and Cr(III) removal aqueous solution. The characterization of ACPDHR by N2 sorption, iodine number and Boehm analysis result 1272 m^2/g surface area, 1174 mg/g and 1.13 mmol/g total acidic functional groups respectively. Fourier transform infrared (FTIR) and Field emission scanning electron microscopy-electron dispersed microscopy (FESEM-EDX) analysis of unloaded and metal-loaded carbon showed shifted of significance peaks and the changes of surface morphology of the sorbent. The adsorption was optimized at pH, shaking duration, initial metal concentration and mass of adsorbent of 5.5, 40 min and 500 mg/L, 0.4 g for Zn(II) and 4, 40 min, 1000 mg/L, 0.1 g for Cr(III) removal. It is concluded that the metal removal was influenced by pH solution, contact time, initial metal concentration and mass of adsorbent. The highest removal of Zn(II) and Cr(III) was observed at 84.24% and 90.10% respectively. Waste from honeydew will be benefited from this research which offer a cheaper alternative precursor to coal based activated carbons.

Keywords: Heavy metals, honeydew rind, impregnated, low cost adsorbent, phosphoric acid

INTRODUCTION

Heavy metals removal from polluted water has become one of the most imperative environmental issues due to their acute toxicity towards aquatic, human and other forms of life. Zn(II) is a harmful metal toxin and frequent contaminant found in industrial discharge. Types of industrial discharge

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contains Zn(II) are chemicals, petroleum refinery, pulp and paper mills plants (Moreno-Barbosa et al., 2013). Cr(III) in effluents commonly originated from textile mills, batteries, fertilizers, air craft plating and finishing (Sharma et al., 2011). Unlike other toxins, heavy metals are non-biodegradable and remain serious potential hazard to human lives (Hegazi, 2013). Therefore, sufficient remediation of the industrial wastewater before it is discharged into public water bodies is of essential for human health and environmental nature.

Method of the industrial effluents remediation commonly used are precipitation, coagulation, ion exchange, adsorption and electroplating. Although these conventional methods have been in use over the years for the elimination of excess concentration of heavy metals from polluted water, they are usually expensive and sometimes resulted to incomplete removal of pollutant issue (Zhao et al., 2016). Adsorption is known as the most practical method of wastewater treatment. However the use of activated carbon (AC) such as economical-coal-based adsorbent and palm kernel activated charcoal spikes the operational cost (Abdullah et al., 2010). Therefore there is the need to develop more potent and economical method of treatment for the elimination of heavy metals from effluents specifically to new precursor of AC (Nowicki et al., 2015).

Rice husk (Suhas et al., 2016), soybean hulls, waste tea leaves (Wankhade & Ganvir, 2013), peanut shells, and langsat (Foo & Hameed, 2012) are among of fruit waste contain carboxyl and hydroxyl functional groups which can be involved in metal binding and have been studied as a potential AC precursors (Chen et al., 2013). To date, little research works have been done to investigate honeydew rind (HDR) for its potential as activated carbon. This work is therefore to contribute to the search and the possibility of utilizing HDR, which are found in abundance locally. The objectives are to produce activated carbon form honeydew rind by chemical activation, to study the optimization of Zn(II) and Cr(III) removal in batch adsorption using ACPHD and to study the isotherm and equilibrium adsorption.

MATERIALS AND METHODS

Preparation of Impregnated HDR

Honeydew rinds were collected from fruit juice stalls and restaurants in Batu Pahat, Johor. They were washed with tap water and soaked in nitric acid 5% for 6 h to remove earthy impurities. After the acid was drained the rinds was immersed in distilled water in order to discard excess acid. The rinds was next rinsed and oven-dried at 60°C, kept in dry storage for the use as precursor material in activated carbon production (Yunus et al., 2015).

Impregnation

The purpose of impregnation step is to improve pores development on the surface of the rind. Phosphoric acid has been preferred in agricultural base-AC production in previous work (Birbas, 2011; Humpola et al., 2016). The superiority of H_3PO_4 is its environmental character (Birbas, 2011). The dried HDR was soaked with H_3PO_4 of 20% v/v for 6 h. The chemical was drained off and the impregnated HDR and oven dried at 110°C.

Carbonization

All the impregnated HDR were carbonized in muffle furnace (Protherm PLF, Turkey). The sample was placed in crucible and the furnace was run at the following temperature program; the muffle was heated at 5°C/min up to 300°C. At this temperature, it was held for 15 min to release any volatile organic compounds from the sample. The heating was continued up to 490°C at 5°C/min and soaked for 30 min (Kalijadis et al., 2011). The carbon was allowed to cool down in desiccator. The low temperature-ramp rate was applied to lessen the internal temperature acclivity of the sample. Specific temperature range was subjected to the sample for to get desirable carbonization extent (Nurdin et al., 2015).

Characterization

FTIR spectrometer (PE Spectrum 100 USA) was employed to determine the presence of surface functional groups in ACPHDR with the range of 4000–400 cm^{-1}, FESEM-EDX (JEOL JSM-6335F, USA) for surface morphology observations, atomic absorption spectrometer (PE AAnalyst 800, USA) for metal ions concentration determination, Brunauer, Emmet and Teller (BET) for surface area determination (SA 3100 Surface Analyser (Beckman Coulter)) at 77 K, Iodine number test ASTM D4607-94 (ASTM 2006) and Boehm (Boehm, 2002).

Adsorption Optimization Study

The optimization of metal adsorption parameter was investigated. The parameters were pH of solution, shaking duration and initial metal concentration. Table 1 shows the adsorption parameters for optimization study.

Table 1
The conditions used for the Zn(II) and Cr(III) adsorption onto ACPHDR optimization experiments

Parameter	Range	
	Zn(II)	Cr(III)
pH	4.0, 4.5, 5.0, 5.5, 6.0, 6.5, 7.0	2.5, 3.0, 3.5, 4.0, 4.5, 5.0, 5.5
Shaking duration (min)	10, 20, 40, 60, 90, 110	10, 20, 40, 60, 90, 110
Initial metal concentration (mg/L)	200, 300, 400, 500, 600	700, 800, 900, 1000, 1100
Mass of adsorbent (g)	0.1, 0.2, 0.3, 0.5, 0.7, 1.0	0.1, 0.2, 0.3, 0.5, 0.7, 1.0

RESULTS AND DISCUSSION

FTIR Spectra and SEM Micrographs

The band assignments of native and metal-bounded carbons, the shifted peaks are presented in Table 2. The metal-loaded adsorbent performed shifted peak as the effect of metal bound. The bands at around 3200 cm^{-1} representing bonded OH functional groups for all AC. The presence of C=C and C–O–C groups were marked by the bands at 1221.83 cm^{-1} for native ACPHDR and shifted to 1219.83 cm^{-1} for Zn(II) loaded AC and 1219.02 cm^{-1} for Cr(III) loaded AC due to metal adsorption. These peaks were the acclaimed potential adsorption sites for the metal ions (Humpola et al., 2013).

Table 2
FTIR assignments for native ACPHDR and metal bound ACPHDR

Unloaded ACPHDR	Wavenumber (cm^{-1})				Assignment
	Zn(II)-loaded ACPHDR	Difference	Cr(III)-loaded ACPHDR	Difference	
1033.97	1057.04	+23.07	1060.58	+26.61	hydrogen-bonded P=O to O–C
1221.84	1219.83	-2.01	1219.02	-2.82	C-O-C bond
1237.61	1242.38	+4.77	1243.53	+10.92	C-N amine group
1580.94	1581.75	+0.81	1587.03	+6.09	Secondary amine group
2910.58	2893.53	-17.05	2891.49	-19.09	C-H aliphatic group
3205.31	3224.79	+19.48	3231.04	+25.73	Bonded –OH groups

Surface Textural and Surface Morphology Analysis

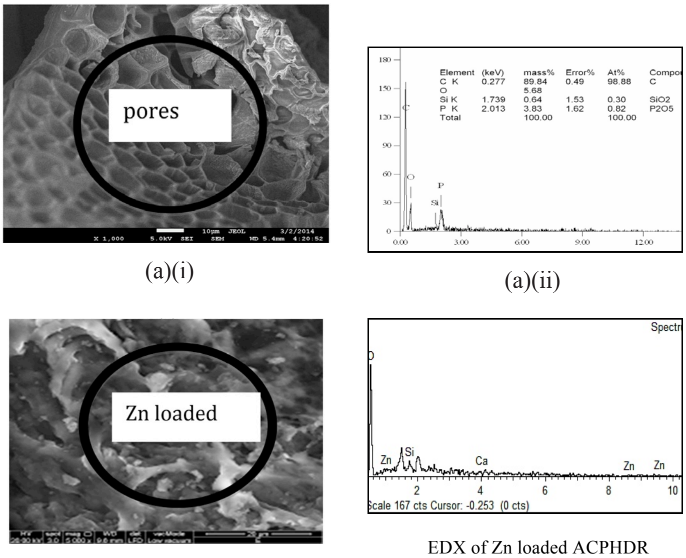
The observation from FESEM micrograph reveals that native ACPHDR of the group were highly porous with honeycomb-like or tunnel shaped surface structures (Figure 1a(i)). The surface morphology of metal bound ACPHDR (Figure 1(b)(i) and (c)(i)) appeared differently whereby the pores have been covered with Zn and Cr that appears as shiny particle due to adsorption process. EDX spectra of bounded sorbent indicates of metal adsorption has occurred on the sorbent surface (Figure 1(a)(ii) and (b)(ii)) which did not exist on native adsorbent (Figure 1(a)(ii)). The surface textural analysis, iodine number and Boehm analysis has resulted as follows; 1272 m^2/g surface, 1174 mg/g and 1.13 mmol/g respectively. In comparison, the iodine number of commercial AC has in average of 800-1200 mg/g (Higazi, 2015). The analysis demonstrated ACPHDR has high porosity surface and acidic in nature. The acidic functional groups was complex with Zn(II) and Cr(III) and thus increased metal adsorption by the carbons (Ibrahim et al., 2016; Zhou et al., 2016).

The Effect of pH

In aqueous system, solubility and polarity of sorbate influenced by pH solution thus impact the adsorption capacity of adsorbent (Sharma et al., 2011). It is observed an increase of Zn(II) removal with increasing of pH solution from the initial pH to the higher pH value (Figure 2(a)). The optimum pH solution was found at 5.5, which showed 87.23% removal before it decreased consistently at the higher pH until the maximum pH value was reached. The best Cr(III) removal percentage was obtained at pH 4; 90.14% meanwhile the adsorption capacity was 900.02 mg/g.

The Effect of Shaking Time

The adsorption rate of both metals were observed as rapid in the initial shaking duration succeeded by a gradual ascending with time until equilibrium adsorption (Zn(II) 339.25 mg/g; Cr(III) 888.06 mg/g) was noticed at 40 min (Figure 2(b)). Additional increment in shaking time did not demonstrate obvious change in equilibrium concentration. The behavior is common as a result of the surfeit of the available adsorption sites (Hegazi, 2013). The metals rapid adsorption at the early stage was probably as the effect of the initial concentration gradient as the removal value decreased to (Zn(II) 54.14%, Cr(III) 79.87%) at the final pH.



Element	(keV)	mass%	Error%	At%	Compo
C K	0.277	89.84	0.49	98.88	C
O		5.68			
Si K	1.739	0.64	1.53	0.30	SiO2
P K	2.013	3.83	1.62	0.82	P2O5
Total		100.00		100.00	

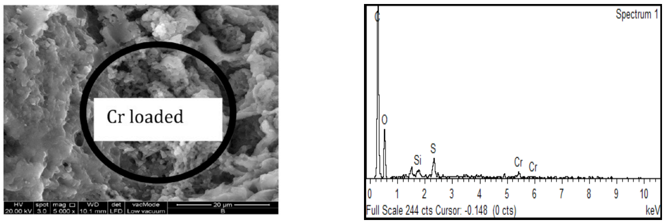
(a)(i)

(a)(ii)

(b)(i)

EDX of Zn loaded ACPHDR

(b)(ii)



EDX of Cr-loaded ACPHDR

(c)(i)

(c)(ii)

Figure 1. FESEM micrograph of adsorbent surface and EDX Diagram: (a) Native ACPHDR. (1000x magnification); (b) Zn-loaded ACP; and (c) Cr-loaded ACP (marked as in the circle) (5000x magnification)

The Effect of Initial Metal Concentration

Both metals uptake and percentage removal lessen at higher solution concentrations (Figure 2(c)). Lower concentrations resulted low metal ions binding due to the small number of available sorption sites and consequently the initial concentration affect the constituent adsorption until it reached equilibrium pH. At higher concentrations, however, the binding sites of adsorption become less available concluded the initial concentration is a significant factor in metals removal (Wahi et al., 2011).

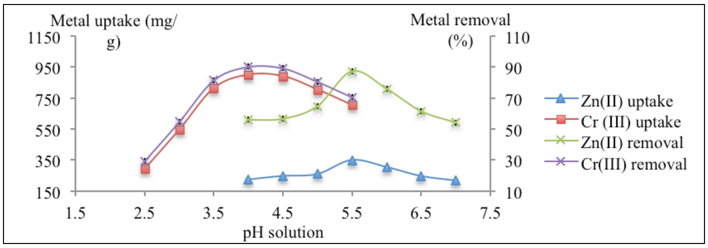


Figure 2. (a) The effect of pH solution Zn(II) and Cr(III) adsorption

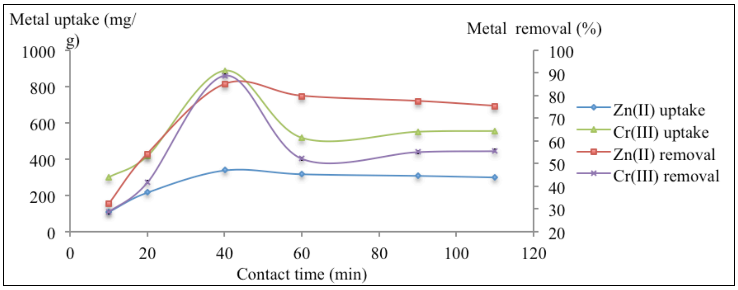


Figure 2. (b) The effect of contact time and on Zn(II) and Cr(III) adsorption

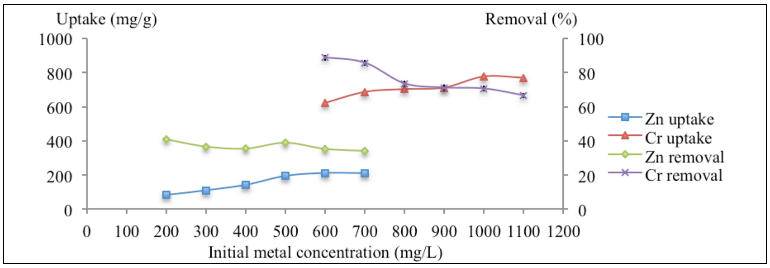


Figure 2. (c) The effect of initial metal concentration on Zn(II) and Cr(III) adsorption

The Effect of Mass of Adsorbent

Result indicated that both metals uptake decrease with an increase in adsorbent mass (Figure 2(d)). Metal uptake of Zn(II) and Cr(III) showed a decrease from 305.93 mg/g to 64.31 mg/g and 859.36 mg/g to 281.57 mg/g respectively when the mass of adsorbent rose from 0.1 g to 1.0 g. The removal of Zn(II) increased from 74% to 82.90% at (0.1-0.5 g) of ACHDR and however decrease until the final mass of adsorbent. Cr(II) removal was observed continual decrease (85.94 - 50.13%) until the final mass of ACPHR. The optimum ACPDHR mass was found at 0.4 g and 0.1 g for Cr(III) and Zn(II) respectively.

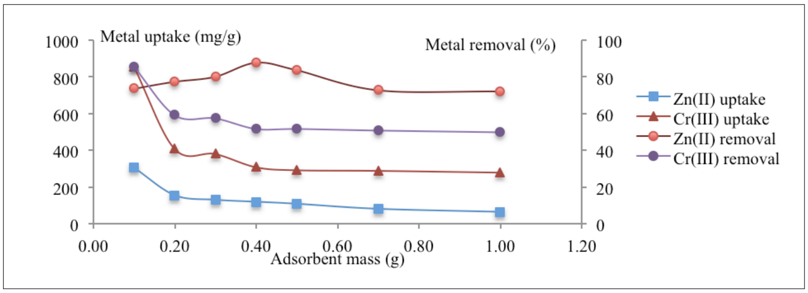


Figure 2. (d) The Effect of Mass Adsorbent on Zn(II) and Cr(III) adsorption

CONCLUSION

According form the present work, activated carbon generated from honeydew rind demonstrates as being a good adsorbent for wastewater treatment. Adsorption study concluded that the metals removal was influenced by pH solution, contact time, initial metal concentration and mass of ACPHDR. The highest removal of Zn(II) and Cr(III) was investigated at 84.24% and 90.10% respectively at optimized adsorption condition. It is concluded that the waste from honeydew will be benefited from this research because offers a cheaper alternative precursor to coal based activated carbons. Thus, the study convinces that ACPHDR could be promising material as adsorbent for the removal of Zn(II) and Cr(III) from aqueous solution.

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