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The Use of Microwave Derived Activated Carbon for Removal of Heavy Metal in Aqueous Solution

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Abstract

Palm oil processing waste which is palm oil kernel shell (POKS) was converted to activated carbon (POKS AC) through 7 min microwave pyrolysis at temperature 270 °C followed by chemical activation using NaOH and HCl. The adsorption study on Ni(II), Cu(II) and Cr(IV) was conducted to evaluate the efficiency of the prepared activated carbon to remove heavy metal. The adsorption capacity was determined as a function of adsorbate initial concentration and adsorbent dosage. Based on Langmuir isotherm, Ni(II) showed highest adsorption capacity of 40.98 mg/g, followed by Cr(IV) and Cu(II) with adsorption capacity of 40.60 mg/g and 13.69 mg/g, respectively. Cr(IV) and Cu(II) showed better fitting to Freundlich isotherm model with high correlation regression indicating the applicability of heterogeneous adsorption. Ni(II) show better fitting with Langmuir isotherm that indicate monolayer coverage. The use of POKS AC is not only effective for adsorption of Cr(IV), Ni(II) and Cu(II) in aqueous solution but also helps to overcome the over abundance of POKS waste problem.

Keywords: Palm oil kernel shell, activated carbon, microwave pyrolysis, heavy metal.

1.   INTRODUCTION

Heavy metal in water bodies has become major issues in many countries. Considerable amount of heavy metal such as lead, mercury, nickel, copper and chromium are polluting fresh waters due to anthropogenic activities. Main sources are from urban and agricultural run-off, farms, industrial effluents, sewage treatment plants, domestic discharges, constructions and earthworks [1]. Heavy metals such as nickel (Ni(II)), copper (Cu(II)) and chromium (Cr(IV)) are known to be hazardous to human health, and major concerns is on the ability of these metals to bio-accumulate in biological systems [2]. Ni(II) affects human skin and respiratory system, and has acute inflammatory effects on the nasal membrane [3]. Ingestion of Cu(II) in food, in severe cases may produce fatal hepatic and renal damage [4]. Human exposed to Cr(IV) compounds are prone to diseases such as asthma, lung, nose cancer and skin allergy [1]. The maximum permissible limit set by Malaysian Environmental Quality Act (1974) for Ni(II), Cu(II) and Cr(IV) in Standard B water is 1.0 mg/l, 1.0 mg/l and 0.05 mg/l, respectively.

At present, a number of technologies are used to remove heavy metals from water bodies such as filtration, chemical precipitation, and ion ex-change. However, these techniques are either inefficient or very costly [5]. Adsorption by activated carbon has advantages over other methods due to the simple and sludge free design and relatively low preparation cost [6]. Conventionally, activated carbon is prepared conventional carbonization, where samples are heated externally. However, long-hour carbonization leads to inefficient energy use. To overcome this problem, microwave pyrolysis is proposed as an alternative to conventional activated carbon preparation technique. The nature of microwave that heats materials internally makes it an ideal solution for carbonizing samples faster. The electrical consumption and size of material being heat was also shown to be inversely proportional [7], giving microwave pyrolysis an advantage over conventional carbonization.

In this study, attempts were made to prepare activated carbon through microwave pyrolysis followed by chemical activation. Taking advantage on the abundance of palm oil kernel shells (POKS) in Malaysia, this material was used as precursor. The effectiveness of the activated carbon prepared on removal of Ni(II), Cu(II) and Cr(IV) from aqueous solution were also studied.

2. MATERIAL AND METHOD

Activated carbon preparation: POKS sample were collected at SALCRA Palm Oil Mill, Serian, Sarawak. POKS sample were washed, dried and grinded to particle size range of 0.5-1.0 mm prior to 7 min microwave pyrolysis (input power: 1000 W, frequency: 2.45 MHz, nitrogen gas flow: 100 ml/min). To create an inert atmosphere, nitrogen gas was flowed through the system for 30 min pripor to pyrolysis. Temperature during pyrolysis was measured using infra-red thermometer (Therma CAM P65). Chemical activation of the pyrolysed char was carried out by soaking the char in 20% NaOH for 2 h, drying (105 °C, 24 h), mixing with HCl (5 ml, 5 M), washing with distilled water until activated carbon of pH4.5 was obtained and finally drying [5].

Chemical characterization: To test the moisture content, the activated carbon prepared was weighed, oven dried (100 °C, 24 h), and reweighed. The ash content was determined by igniting the moisture free activated carbon in furnace (500 °C, 1 h) followed by second ignition (700 °C, 4 h), and weighing. Surface area was estimated according to Alzaydien (2009). The surface morphology test was conducted using scanning electron microscope (SEM) (JOEL, JSM-6390LA). Perkin Elmer Fourier Transform Infrared (FTIR) spectrometer was used for functional group analysis and Atomic Absorption Spectrometer (AAS) (Shimadzu) for heavy metal analysis.

Metal ion solution preparation: Analytical grade chemicals were used. 10 ml of Cu, Cr, and Ni aliquot were homogenously mixed with 1000 ml of distilled water and 4.5 ml of 70% HNO_3. Dilution of Cu, Cr, and Ni stock solution was carried out to prepare metal ion solutions with concentrations 5, 10, 15, 20, 25, 30, and 35 mg/l.

Adsorption study: (a) Effect of adsorbent dosage: Five different adsorbent dosages (0.2, 0.4, 0.6, 0.8, and 1.0 g) were mixed with metal ion solutions prepared (100 ml, 10 mg/l). The mixture was agitated on a rotary shaker (150 rpm, 1 h), gravity filtered, and the filtrate was analyzed using AAS. Control experiment is flask consists of 100 ml metal ion solution. (b) Effect of metal initial concentration: Seven different initial concentrations metal ion solutions (5, 10, 15, 20, 25, 30, and 35 mg/L) were prepared in separate flasks. 1.0 g of adsorbent at pH 4.5 was added with each flask, agitated on rotary shaker (150 rpm, 1 h), gravity filtered, and filtrate was analyzed using AAS.

Adsorption isotherms: Langmuir and Fruendlich isotherm can be used to estimate the adsorption capacity Q_m of the activated carbon from palm oil fruits

shell on the adsorption of Cu(II), Ni(II) and Cr(II). The relative coefficients of this model are calculated using linear least-square fitting. The Langmuir model assumes that uptake of metal ions occurs on a homogenous surface by monolayer adsorption without any interaction between adsorbed ions (Rao *et al.*, 2009) and can be written in linear form as:

$$\frac{C_e}{q_e} = \frac{C_e}{Q_m} + 1/(Q_m b) \quad \text{......[1]}$$

where q_e and C_e are metal equilibrium concentration in adsorbed and liquid phase in mmol/g and mmol/L, respectively. Q_m and b are Langmuir constants representing the sorption capacity (in mg/g) and energy of sorption, respectively. These constants can be calculated from the intercept and slope of the linear plot,

$$\frac{C_e}{q_e} \ vs \ C_e \quad \text{......[2]}$$

The Freundlich equation is an empirical equation based on adsorption on a heterogeneous surface (Rao *et al.*, 2009) and can be written in the linear form as;

$$logq_e = logk_f + \frac{1}{n} \ logC_e \quad \text{.........[3]}$$

where k_f and n are indicator of sorption capacity (in mg/g) and intensity respectively.

These Fruendlich constant can be calculated from the slop and intercept of linear plot, with

$$logq_e \ vs \ logC_e \text{ .... [4]}$$

3.   RESULTS AND DISCUSSION

Characteristics of adsorbent: Table 1 shows the chemical characteristics of the raw material, palm oil kernel shell activated carbon (POKS AC) and commercial activated carbon (Commercial AC). The activated carbon prepared has lower moisture and ash content compare to the raw material, implying that significant amount of moisture and inorganic matter has been removed after 7 minutes microwave treatment. However, the values were higher than commercial AC, showing that longer treatment time might be needed to enhance the quality activated carbon. Low ash content is desirable as presence of ash inhibits surface area development due to inorganics that may block the micro pore volume, and normally this type of activated carbon will exhibit low surface area [8].

Table 1: Chemical characterization of raw POKS, POKS AC and commercial AC

	Raw POKS	POKS AC	Commercial AC
Moisture content (wt%)	10.94	6.10	2.00
Ash content (wt%)	8.50	3.06	1.53
Surface area (m²/g)	109.4	192.6	96.6

Surface area plays important role for activated carbon adsorbent for adsorption capacity, where larger surface area results in larger adsorption capacity [8]. POKS AC has large surface area compare to raw material, indicating that microwave pyrolysis and chemical activation has successfully increased the surface area off the activated carbon. This is due to promotion of the formation of pore structures in POKS AC [9]. The low surface area of commercial AC is probably due to difference in raw material and preparation method.

Pore structure plays important role due to increase surface area for adsorption. Increase in surface area means more active sites for adsorption of heavy metal which increase the efficiency of the activated carbon [8]. SEM analysis results showed that microwave pyrolysis has successfully improved pores structure of POKS after 7 min treatment (Figure 1(a) and (b)). The formation of pore structures was further enhanced by chemical activation (Figure 1(c)). Results also showed that the pore structures in POKS AC are comparable to that of commercial AC.
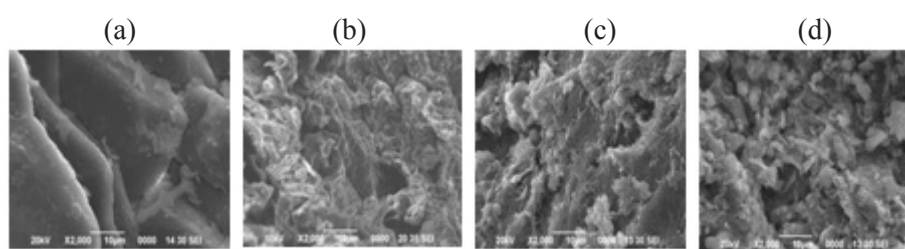
(a)　　　　　(b)　　　　　(c)　　　　　(d)

Figure 1: Surface morphology of (a) raw POKS (b) POKS char
(c) POKS AC (d) commercial AC

The IR absorption spectra of the raw material of POKS, POKS AC and commercial AC are shown in Figure 2. For the three samples, shown are broad bands in 3300-3500 cm^{-1} region, which could be assigned to OH stretching mode from hydroxyl and phenolic group [8]. Broad band at 1300-1000cm^{-1} in these samples could be assigned to C−O stretching in alcohols and phenols that

confirming the OH groups present in all three samples. The absorption peak at 1270 cm^{-1} and 1044 cm^{-1} for raw material, 1023 cm^{-1} for POKS AC and 1034 cm^{-1} for commercial AC shows similar C−O stretching. All of the sample show presence of –OH and C=O functional group. This type of functional group has responsibility for adsorption sites [5].

POKS AC show the presence of S=O functional group at 1116 cm^{-1}. This group appears after the chemical activation process. Presence of S=O functional group in POKS AC implies better absorption ability compare to the raw material [8].

Overall, the IR absorption spectra of the raw material of POKS, POKS AC and commercial AC are shown in Figure 2. All samples show presence of –OH and C=O functional group, which is responsible for adsorption in activated carbons [5]. POKS AC show the presence of S=O functional group at 1116 cm-1, which could potentially increase its adsorption ability [10].
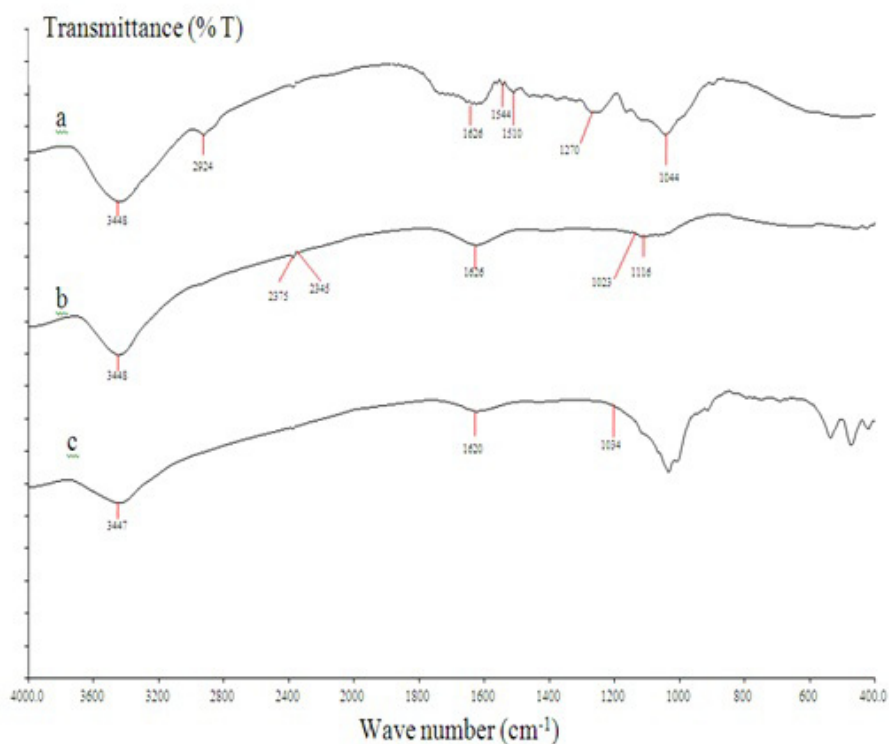

Figure 2: FT-IR spectrum of (a) raw POKS, (b) POKS AC, and (c) commercial AC

Adsorption study: Results indicated that with increasing adsorbent dosage, percentage removal of heavy metal from aqueous solution increased (Figure 3). Highest removal of Ni(Ii), Cu(II) and Cr(IV) in the experiment was 4%, 27%, and 21%, respectively, at adsorbent dosage of 1.0 g. In general, metal adsorption capacity increased with increasing activated carbon quantity, due to increase in quantity of active sites [8,11]. Low Ni(II) removal is due to homogenous adsorption of the metal on POKS AC. This result is confirmed by high regression coefficient of Langmuir isotherm model for adsorption of Ni(II).
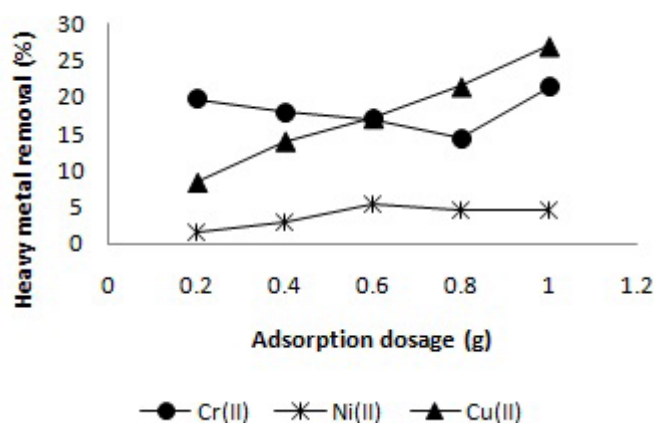

Figure 3: Effect on adsorbent dosage on removal of Ni(II), Cu(II) and Cr(IV)

Adsorption density is an important parameter in order to determine the adsorption capacity for unit mass of the adsorbent (POKS AC). Results showed that there was a decrease in adsorption density as higher adsorbent dosages were introduced (Figure 4). Ni(II), Cu(II) and Cr(IV) showed a decrease in adsorption density from 0.81mg/g to 0.44mg/g, 4.19mg/g to 3.19mg/g, and 9.88mg/g to 3.60mg/g, respectively. This situation was related to the fact that the availability of metals in solution phase decrease with an increase in adsorbent dosage per unit adsorbent and the adsorption sites remain unsaturated during adsorption reaction [5,8]. Result for adsorbent density is inversely proportional for the initial metals concentrations.
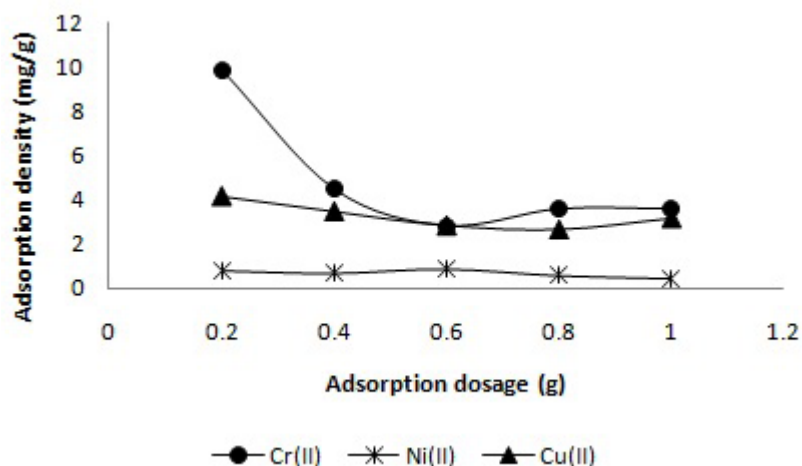
Figure 4: Effect on adsorbents dosage on the removal efficiency of Ni(II), Cu(II) and Cr(IV) based on adsorption density

Results also showed that the percentage of metal removal increased with the increase in metal initial concentration (Figure 5). At lower metal initial concentration (5 mg/l), Ni(II), Cu(II), and Cr(IV) removal were 12%, 26% and 10% respectively. Significant increase in Cr(IV) was shown where 48% Cr(IV) was removed at 35 mg/l. In fact, at higher concentrations, more metal ions are left unadsorbed in solutions, and energetically less favorable sites become involved with increasing concentration in the aqueous solution [12].
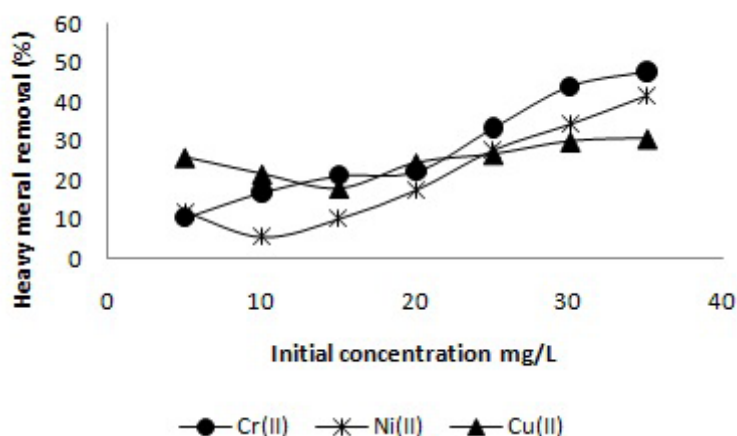

Figure 5: Effect on initial concentration on removal of Ni(II), Cu(II) and Cr(IV)

Adsorption Isotherm: The experimenting data related to the adsorption of Cr(IV), Ni(II) and Cu(II) onto the POKS AC are interpreted by Langmuir and Fruendlich adsorption model and the isotherm are shown in Figure 6 and Figure 7. Figure illustrate the comparative adsorption between Ni(II), Cu(II) and Cr(IV). The parameters of adsorption are calculated by the linear line method and constant related to each isotherm were calculate and summarized in Table 3.
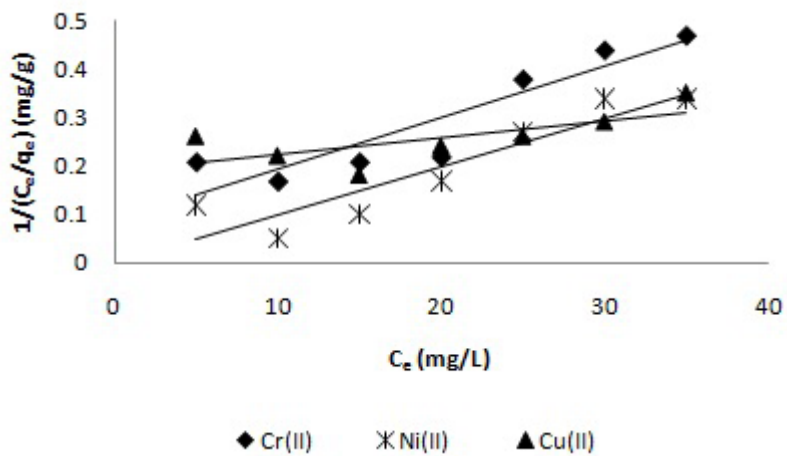

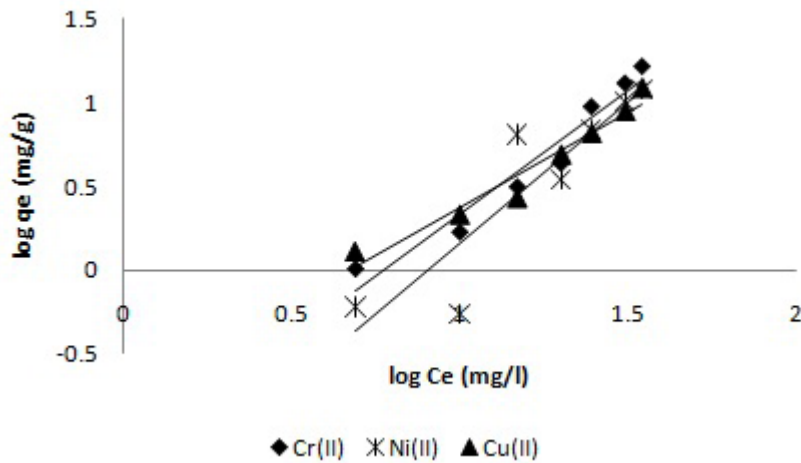**Figure 6**: Langmuir adsorption isotherm of Ni(II), Cu(II) and Cr(IV)

Figure 7: Freundlich adsorption isotherm of Ni(II), Cu(II) and Cr(IV)

Results in Table 2 conclude that adsorption of Cu(II) and Cr(IV) are best explained by Freundlich model due to high value of regression coefficient which is 0.947 and 0.943 respectively, indicating heterogeneous adsorption of these metals on POKS AC [12]. Adsorption of these metals on heterogeneous surface leads to greater adsorption of the metals [12]. This explains the higher adsorption for Cu(II) and Cr(IV) which are up to 30.74 and 47.80 % removal respectively.

Table 2: Langmuir and Freundlich constant for Ni(II), Cu(II) and Cr(IV) adsorption

		Langmuir constant			Freundlich constant	
	Q_m (mg/g)	b	R^2	K_f	1/n	R^2
Cr(II)	40.60	0.28	0.839	5.32	1.65	0.943
Ni(II)	40.98	0.24	0.846	7.42	1.30	0.817
Cu(II)	13.69	0.04	0.494	3.61	1.12	0.947

Ni(II) show high regression coefficient value of 0.846 for Langmuir adsorption model, and 0.817 for Freundlich isotherm. This indicates that uptake of Ni(II) occurs effectively through heterogenous adsorption [12], explaining the high removal of heavy metal, up to 41.79%. From the calculation based on Langmuir isotherm, Ni(II) show the highest absorption capacity of 40.98 mg/g, followed by Cr(IV) and Cu(II) with adsorption capacity of 40.60 mg/g and 13.69 mg/g, respectively.

4. CONCLUSION

Palm oil kernel shell can be effectively converted to activated carbon (POKS AC) through microwave pyrolysis followed by chemical activation. Adsorption study concludes that the adsorption capacity of POKS AC on Ni(II), Cu(II) and Cr(IV) was considerably good, between 13.7 – 41 mg/g. The use of microwave pyrolysis in carbonization of POKS found to be effective, time saving alternative compared to the time and energy consuming by conventional carbonization.

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