Rock Melon Activated Carbon (RMAC) for Removal of Cd(II), Ni(II) and Cu(II) from Wastewater: Kinetics and Adsorption Equilibrium

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Abstract—The use of effective adsorbents has been investigating as a replacement of current costly methods for heavy metals removal. The present work evaluates the potential of rock melon shell waste as alternative adsorbent for cadmium, nickel and copper ions in aqueous solution. The rock melon shells were dried, ground and separated based on the sizes through sieve shaker. Then, the rock melon shell powder was activated at temperature range of 400 °C - 650 °C. FESEM and BET were used for adsorbent morphology and surface area analysis. The prepared adsorbent and adsorbate were applied for testing and manipulating the process parameter effects. The results were analyzed by using the Atomic Absorption Spectroscopy (AAS). The optimal process conditions were used for adsorption equilibrium and kinetics justification. The removal of the heavy metals improved as the pH, contact time and adsorbent dosage increased. However, it tended to achieve equilibrium state once the active sites of the adsorbent were fully occupied. The highest removal of Cd(II), Ni(II) and Cu(II) ions equilibrated within 120 min, at pH of 8 and adsorbent dosage was 0.3 g which was exceed 99%. The second order kinetics model best fits the obtained data while the mecahanism indicates surface adsorption and intraparticle diffusion. The adsorption equilibrium accompanies the Freundlich isotherm for cadmium and nickel, but the Langmuir for copper ion.

Index Terms—Rock melon shells, heavy metals, kinetics and adsorption equilibrium.

I. INTRODUCTION

The ineffective-adsorption of heavy metals, such as cadmium, nickel and copper ions from industrial wastewater present challenging problems for industry and environment, whereas the rock melon shells waste was discarded without any processing for added-value components. The rock melon shells offers an alternative feedstock for activated carbon synthesis due to the rock melon plantations has been developing in Malaysia (Perak, Terengganu, Pahang, etc.), but the rock melon shells were casted out from the beverage industries, restaurants, etc. as agricultural waste.

There are a few methods for removal of heavy metals, such as ion exchange, reverse osmosis, chemical precipitation etc., but these mehods take considerable time, extensive set up and needs to high cost, thus this work aim is to solve this issues by using rock melon shells waste based potential activated carbon (RMAC) as high efficiency adsorbent for removal of Cd(II), Ni(II) and Cu(II) ions in aqueous solution, isotherm Langmuir and Freundlich, and adsorption kinetics. The adsorption using rock melon shells waste based potential activated carbon has many advantages such as higher activity, short time, effective and low cost.

Adsorption is one of alternative methods for effective purification and separation techniques which used in the water and industrial wastewater treatment. It is tendency of molecules from an ambient fluid phase to adhere the surface of solid [1]. Conventional treatment technologies for the removal of these toxic heavy metals are not economical and further generate huge quantity of toxic chemical sludge. Biosorption or biological method has proven to be a low cost technology for the removal of heavy metals [2]. Nowadays, many low cost adsorbents from calcareous shells, bentonite, agricultural waste residue such as hazelnut shell, rice husk, pecan and jackfruit shells, maize cob or husk, etc. [3]-[5] have been used as the adsorbent, and the rock melon shell was used as another waste material for the adsorbent development.

The coal-activated carbon is widely used as adsorbent in the industry for heavy metals removal from wastewater [6]. Even though the use of activated carbon is efficient and well establish but it was expensive compared to other adsorbents, so, many researchers investigated a way to reduce the cost of activated carbon by add additives to the activated carbon such as alginate, tannic acid, magnesium and many more. Activated carbon has excellent adsorption properties which have been characterized by high specific area [7]. In spite of that, the activated carbon has been using extremely due to its ability to remove various types and amounts of heavy metals. It is confirmed that the activated carbon is to be more efficient in term of heavy metals removal but less efficient in the cost consumption compared to the agriculture waste adsorbents. Heavy metals in wastewater exhibit a global concern of environment due to its toxicity characteristics to many organisms. The use of low-cost adsorbents from agriculture waste has been investigating as a replacement for current costly processing of heavy metals removal from solution. The cellulosic agricultural waste materials are an abundant source for significant metals biosorption. On the other hand, rock melon shells could be good adsorbents for the removal of heavy metals instead of being an agricultural waste that may increase the environment pollution.

II. MATERIALS AND METHODS

A. Materials

The rock melon shells waste was collected from restaurants and beverages industries, Kuantan, Pahang. The chemicals of cadmium(II) sulphate, nickel(II) sulphate, copper(II) sulphate, hydrochloric acid and sodium hydroxide were procured from Sigma Aldrich Sdn Bhd, Kuala Lumpur, Malaysia.

B. Methods

Rock melon shells (RMS) waste was used as the main raw material in this work. The RMS was dried, crushed in a mill to get a grain size of 2mm. Sodium hydroxide was added to the crushed shells at a ratio of 1:1 (g RMS/g NaOH) to prepare the impregnate samples. These samples were carbonized at 400–650°C for 1.12 h under nitrogen (N2) flow of 120 mL min-1 at a heating rate of 10 °C min-1. The carbonized sample (activated carbon) then washed several times with distilled water to remove the phosphoric acid, and then the activated rock melon shell were dried in an oven at 80 °C for 24 h. FESEM and BET were used for adsorbent morphology and surface area analysis. The prepared adsorbent and adsorbate were applied for testing and manipulating the parameters effect of solution pH, contact time and adsorbent dosage. In the same time, the adsorbate solutions were performed at 25°C by the various pH of 2, 4, 6, 8 and 10, and put in a rotary shaker which operated by150 rpm for 2 hours. The sample was filtered using Whatman filter paper 125 mm before analyzed with Atomic Adsorption Spectroscopy. For the adsorption isotherm investigation, the initial adsorbate solution concentration was varied from 20 mg/L, 40 mg/L, 60 mg/L, 80 mg/L and 100 mg/L. Next, the effect of initial concentration was conducted using constant solution with the optimum pH, 0.3g of adsorbent dosage and sample contact time of 120 min. The solution was shaken also on a rotary shaker. In order to evaluate the various contact time of 40 – 120 min and adsorbent dosage of 0.1 – 05 g effect on the heavy metals removal, the adsorbate solution was mixed with 0.3g of activated rock melon shells powder. The mixture was shaken on a rotary shaker. The results were analyzed by using the Atomic Absorption Spectroscopy (AAS). The optimal process conditions were used for adsorption equilibrium and kinetics justification. Next, the effect of process parameter, like pH solution, adsorbent dosage and contact time on the removal efficiency was determined using the following formula (refer to "(1)"):

$$Removal\ Efficiency\ (\%) = \frac{C_o - C_e}{C_e} \times 100 \qquad (1)$$

where C_0 = heavy metal concentration (mg/L) at the initial time and C_e = heavy metal concentration (mg/L) at the equilibrium condition.

III. RESULTS AND DISCUSSION

A. Field Emission Scanning Electron Microscopy (FESEM) of Rock Melon Shells

The surface morphology of adsorbent from rock melon shell were analyzed by FESEM. Fig. 1(a) shows that the surface of adsorbent before activated is rough, compact and disordered surface with low porosity structure compared after activation process. Otherwise, Fig. 1(b) illustrates an relatively smooth with spherical particles of porous structure that confirming the thermal decomposition. It should allow the diffusion of heavy metals by the pore of the adsorbent.
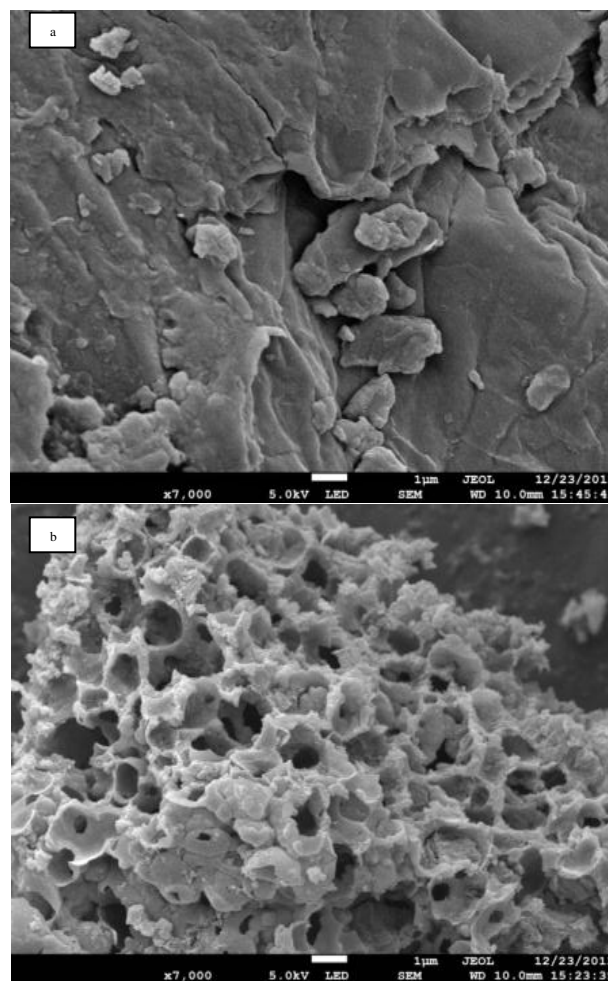

Fig. 1. FESEM micrograph of *rock melon* shells powder at 7,000×, before activation (a), after activation (b).

B. Brunauer-Emmett-Teller (BET) of Rock Melon Shell

The major roles in the adsorbent activity are the specific surface area and active sites. The BET analysis gave the surface area of rock melon shell post-activation increased to 38.776 m^2g^{-1} with a molecular area of 16.2 $Å^2$. It was reported that the surface area of tea waste was 0.79 m^2/g and wooden charcoal was 30 m^2g^{-1} [8]. These surface areas of both adsorbents were lower than activated rock melon shells. Therefore, the results proved that the activation process increased the sites of adsorbent activity.

C. Effect of pH Solution on Cd(II), Ni(II) and Cu(II) Removal

The pH of solution gives the important impact on the heavy metals removal, since it determines the surface charge of the adsorbent which means the degree of ionization and speciation of the adsorbate. Fig. 2 appears to be the effect of pH on the adsorption of cadmium (II), nickel (II) and copper (II). The pH optimum condition of 8 was achieved. As the increasing pH, adsorption of the heavy metals also improved,

and otherwise. The removal efficiency is highest at the optimal pH. Next, the adsorption decreases at low pH, and it might be predicted due to the competitiveness of hydrogen and heavy metal ions on the sorption sites. The equilibrium adsorption (q_e) was found also by the increase of pH [9].
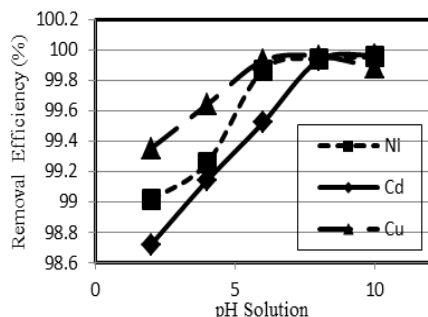

Fig. 2. Effect of pH on Cd(II), Ni(II) and Cu(II) removal.

D. Effect of Adsorbent Dosage on Cd(II), Ni(II) and Cu(II) Removal

The adsorbent dosage can be illustrated as the mass of activated carbon (g) in the fixed volume of the aqueous solution (mL). As shown in Fig. 3 below, the influence of adsorbent dosage (g) on the heavy metals removal. As the additional amount of adsorbent increased, the removal efficiency which became higher. This achieves up to the equilibrium condition. The equilibrium is reached at the adsorbent dosage of 0.3 g. The adsorptive capacity of the available activated carbon is not fully utilized at the higher adsorbent. This possibility occurs due to the different concentration. It could be described by the fact that a fixed mass of adsorbent may only adsorb a certain amount of metals. The low driving force for adsorption at higher adsorbent dosage also takes place [10].
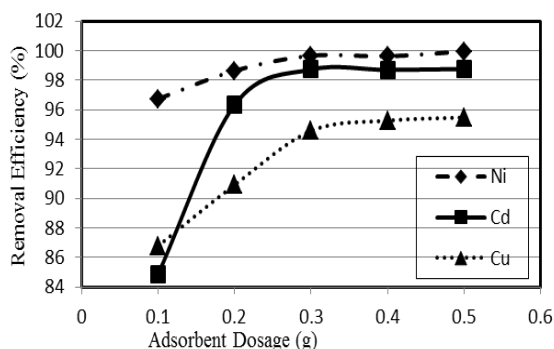

Fig. 3. Effect of adsorbent dosage on Cd(II), Ni(II) and Cu(II) removal.

E. Effect of Contact Time on Cd(II), Ni(II) and Cu(II) Removal

As shown in Fig. 4, it gives the effect of contact time on the heavy metal removal efficiency. Based on the graph plotted, it demonstrates the contact time longer, the percentage of metal adsorption also increased. It indicates that more heavy metals could be adsorbed by the activated rock melon shells. The reduction of copper, nickel and cadmium is rapidly for the first 80 min, and the equilibrium is nearly reached after 120 min. The reduction rate of heavy metal ions is faster in the beginning due to the larger surface area of the adsorbent is being available for the adsorption of the metals. As the surface adsorption sites are being exhausted, the rate of heavy

metals uptake is controlled by the rate of transport phenomenon from the exterior to the interior sites of the adsorbent particles. It can be estimated that a large number of vacant surface sites are available for adsorption during the initial stage of the treatment time, and after a lapse of time causes less remaining vacant surface sites on hand. The uptake of adsorbate species is fast in the initial stages of the contact period, and thereafter it became slower near the equilibrium [11].
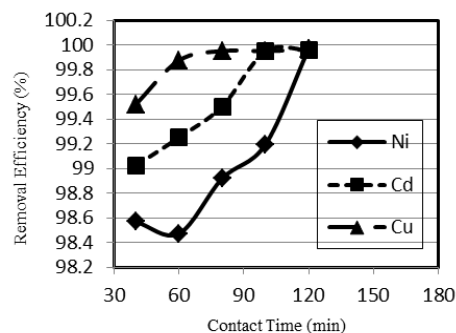

Fig. 4. Effect of contact time on Cd(II), Ni(II) and Cu(II) removal.

F. Effect of Initial Concentration on Cd(II), Ni(II) and Cu(II) Removal

The adsorption of copper, nickel and cadmium by the rock melon shells waste was observed at the different initial concentration from 20 to 100 mg/L, pH solution of 8, contact time of 120 minutes and 0.3 g of adsorbent. This invention is important in order to determine the adsorption isotherm. Fig. 5 shows the results of various initial metal concentration relates with Cd(II), Ni(II) and Cu(II) reduction. Generally, all metals give rapid increase of removal at first 60 mg/L, while the metal removal achieves equilibrium slowly at 60 mg/L forward. Besides that, it is also clear that with the increasing of initial concentrations influence the metal removal, and it would be equilibrium condition faster. The initial concentration provides an important driving force to overcome all mass transfer resistance of metal ions between the liquid and solid phases, hence a higher initial concentration of metal ions may increase the adsorption capacity. It believes that at low concentrations, the metals are adsorbed by the specific sites, while with the increase of concentrations, the specific sites undergo saturation and the exchange sites filled [12].
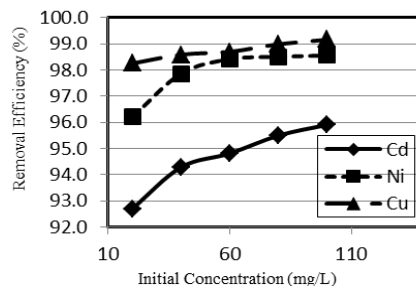

Fig. 5. Effect of initial concentration on Cd(II), Ni(II) and Cu(II) removal.

G. Langmuir Isotherm

In this experiment, the Langmuir and Freundlich isotherm were used to describe the relationship between the amount of

heavy metals adsorbed and its concentration of equilibrium in solutions. Langmuir isotherm assumed that the adsorption process took place at specific homogenous sites between the adsorbent [13]. The following equation is used for the Langmuir isotherm fitting (refer to "(2)"):

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

where q_e is the amount of metal reduction over specific amount of adsorbent (mg/g), C_e is equilibrium concentration of the solution (mg/L), and qm is the maximum amount of metal ions required (mg/g). The Langmuir equation can be rearranged to linear form for the accessibility of plotting and defining the Langmuir constants (K_L) and maximum adsorption capacity of rock melon shells waste (q_m). The values of q_m and K_L can be determined from the linear plot of $1/q_e$ versus $1/C_e$ (refer to "(3)"):

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{q_m K_L C_e} \qquad (3)$$

where q_m is the maximum adsorption capacity for cadmium, nickel and copper ions uptake, mg/g and K_L the Langmuir adsorption constant in L/mg. The graph $1/q_e$ of plotted against $1/C_e$ yielding the value of ranging from 3.38 mg/g to 14.28 mg/g. The Langmuir isotherm fits well with the correlation coefficient of 0.989 (Fig. 6).
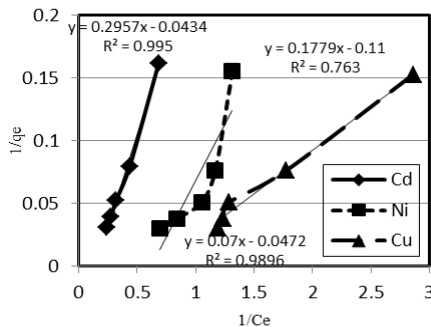

Fig. 6. Langmuir Isotherm of Cd(II), Ni(II) and Cu(II) removal.

H. Freundlich Isotherm

Freundlich Isotherm is a multilayer adsorption model which considers the interaction between adsorbate molecules are given by the following equation (refer to "(4)"):

$$q_e = K_f C_e^{1/n} \qquad (4)$$

where K_f and $1/n$ are the Freundlich constants relates to adsorption capacity and intensity. Similar to the Langmuir isotherm, the Freundlich equilibrium constant also is evaluated from the intercept and the slope. The Freundlich equation can be linearized in logarithmic form for the constant determination as shown below (refer to "(5)"):

$$\log q_e = \log K_f + 1/n \log C_e \qquad (5)$$

where K_f and n are the Freundlich adsorption isotherm constants. The adsorption isotherm, K_f is as the indicators of

the adsorption capacity and n is the heterogeneity factor representing the deviation from linearity of adsorption and is also known as Freundlich coefficient [14].
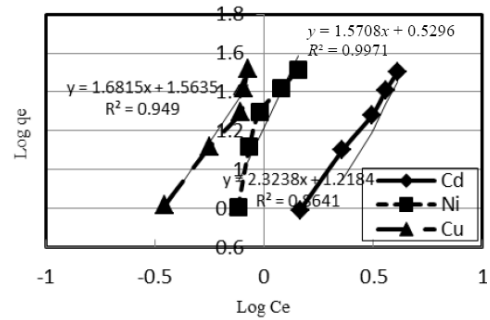

Fig. 7. Freundlich Isotherm of Cd (II), Ni (II) and Cu (II) removal.

The ability of Freundlich model for the experimental data fitting was examined from the graph plotted belows. The graph was plotted by log C_e vs. log q_e for the intercept value of K_f and the slope of n construction. From Fig. 7, the Freundlich constants K_f values ranging from 0.085 to 0.64 and n are found to be 0.60 to 0.82. The Freundlich isotherm best fits with the correlation coefficient of 0.997. Thus, the Langmuir isotherm fits well of this adsorption case. The Langmuir and Freundlich isotherms adsorption constants with the correlation coefficients are given in Table I below:

TABLE I: LANGMUIR AND FREUNDLICH ADSORPTIONS

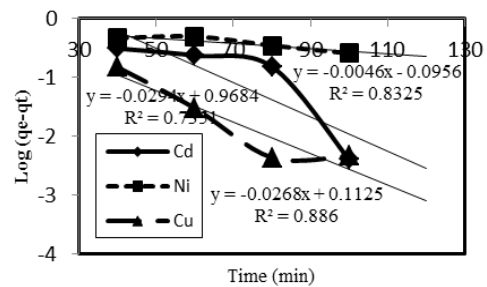| Heavy metals	Langmuir			Freundlich		
	q_{max}, mg/g	K_c, 1/mg	R^2	K_f, (mg/g) (1/mg) ^(1/n)	n	R^2
Cd	3.38	0.18	0.995	0.19	0.64	0.997
Ni	5.62	0.21	0.763	0.09	0.82	0.864
Cu	14.28	2.67	0.989	0.19	0.59	0.949

Fig. 8. Pseudo-first order kinetic for Cd(II), Ni(II) and Cu(II) removal.

I. Adsorption Kinetics

A linear form of pseudo-first-order model was described in the equation as follows (refer to "(6)"):

$$\log q_e - q_t = \log q_e - k_{1\,ads} / 2.303\, t \qquad (6)$$

where q_e and q_t are the amount of adsorption at equilibrium and time t, respectively, and $k_{1\,ads}$ is the rate constant of the pseudo-first order adsorption process. The adsorption data provides a straight line pseudo-first order graph and the value of adsorption rate constant, $k_{1\,ads}$ can be computed. All three Cd(II), Ni(II) and Cu(II) heavy metals ions are observed in the

Fig. 8. As the plot is found to be linear with good correlation coefficient, indicates that the pseudo first order equation is appropriate to Cd(II), Ni(II) and Cu(II) ions sorption on the prepared activate carbon. So, the adsorption process is a pseudo-first-order process. The curve illustrates the pseudo-first-order model does not fit well and not to be in the linear form.

The pseudo-second order kinetic can be expressed in a linear form based the equation below (refer to "(7)"):

$$\frac{t}{q_t} = \frac{1}{h} + \frac{1}{q_e}t \qquad (7)$$

where $h = k\, q_e^2$ (mg g-1 min-1) which can be known as the initial adsorption rate and k is the rate constant of pseudo-second order adsorption (g mg-1 min-1). The graph of t/q_t versus t should give a straight line (Fig. 9). In addition, k and h can be determined from the slope and the intercept of the curve.
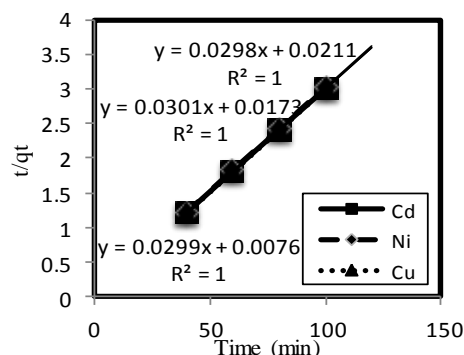

Fig. 9. Pseudo-second order kinetic for Cd(II), Ni(II) and Cu(II) removal.

The pseudo-first and second order adsorption constants including correlation coefficients are shown in Table II below:

TABLE II: PSEUDO-FIRST AND SECOND ORDER KINETICS

Heavy Metals	Pseudo 1st Order		Pseudo 2nd Order	
	$k1ads$, L/min	R^2	$k2ads$, g/mg. min	R^2
Cd(II)	0.0677082	0.7351	0.0420872	1
Ni(II)	0.0105938	0.8325	0.0523705	1
Cu(II)	0.0617204	0.886	0.1176329	1

IV. CONCLUSION

Rock melon shells waste based activated carbon (RMAC) has been successfully approved to act as an potential low cost adsorbent for removal of heavy metals from aqueous solution as wastewater model. The highest adsorption for removal of Cd(II), Ni(II) and Cu(II) is > 99 % and equilibriates by the time of 2 h, pH of 8 and adsorbent dosages of 0.3 g with the adsorption isotherm types are favourable. The Freundlich and Langmuir isotherm ($R^2 = 0.997$ and 0.995) for Cd(II), and it was found to describe the process better than Langmuir and Freundlich isotherm ($R^2 = 0.990$ and $R^2 = 0.950$) for Cu(II)

and ($R^2 = 0.763$ and $R^2 = 0.864$) for Ni(II) with the maximum adsorption capacity is highest for Cu(II) of 14.29 mg/g. The adsorption kinetics of wastewater containing Cd(II), Ni(II) and Cu(II) are approved by the pseudo-first and second order, and the second-order kinetics results R^2 good values of 1.00 and k of 0.0781 - 0.1776.

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