

ADSORPTION OF COPPER FROM AQUEOUS SOLUTION BY *ELAIS GUINEENSIS* KERNEL ACTIVATED CARBON

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Abstract

In this study, a series of batch laboratory experiments were conducted in order to investigate the feasibility of *Elais Guineensis* kernel or known as palm kernel shell (PKS)-based activated carbon for the removal of copper from aqueous solution by the adsorption process. Investigation was carried out by studying the influence of initial solution pH, adsorbent dosage and initial concentration of copper. The particle size of PKS used was categorized as PKS-M. All batch experiments were carried out at a constant temperature of 30°C (±2°C) using mechanical shaker that operated at 100 rpm. The single component equilibrium data was analyzed using Langmuir, Freundlich, Redlich-Peterson, Temkin and Toth adsorption isotherms.

Keywords: *Elais Guineensis*, copper removal, adsorption and isotherms.

1. Introduction

Pollution from heavy metals is a major concern in developing countries. The discharge of heavy metals into water-courses is a serious pollution problem which may affect the quality of water supply. Increasing concentrations of these metals in the water constitute a severe health hazard mainly due to their non-degradability and toxicity. Numerous metals such as chromium Cr (III) and Cr (VI), copper (Cu), lead (Pb), manganese (Mn), mercury (Hg), cadmium (Cd), etc are known to be significantly toxic.

Cu, the metal considered in this project, is a widely used material. Copper metal contamination exists in aqueous waste streams from many industries such as electronic and electrical, metal plating, mining, manufacture of computer heat sinks, Cu plumbing, as well as biostatic surface, as a component in ceramic glazing and glass colouring. Unfortunately, Cu is a persistent, bioaccumulative and toxic chemical that does not readily break down in the environment and is not easily metabolized. It may accumulate in the human or ecological food chain through consumption or uptake and may be hazardous to human health or the environment. Drinking water that contains higher than normal levels of Cu may cause vomiting, diarrhea, stomach cramp and nausea. The chronic effects of consumption of high levels of copper are liver and kidney damage. The suggested safe level of Cu in drinking water for humans varies depending on the sources, but tends to be pegged at 1.5 to 2.0 mg/L. Hence, removal of copper from water and wastewater assumes important. Table 1 shows the Environmental Quality Act 1974, Environmental Quality (Sewage and Industrial Effluents) Regulations, 1979, in Malaysia with selected parameter limits of effluent of heavy metals.

Table 1. Environmental Quality Act 1974, Environmental Quality (Sewage and Industrial Effluents) Regulations, 1979, Malaysia: Selected parameter limits of effluent of Standards A and B (Department of Environment, DOE, Malaysia).

Parameter, mg/L	Standard	
	A ^a	B
Mercury	0.005	0.05
Cadmium	0.01	0.02
Arsenic	0.05	0.10
Lead	0.10	0.50
Chromium, trivalent	0.20	1.0
Copper	0.20	1.0
Nickel	0.20	1.0
Zinc	1.0	1.0
Iron	1.0	5.0

^a This standard applies to the industrial and development projects which are located within the catchments areas (areas upstream of surface or above sub-surface water supply intakes, for the purpose of human consumption including drinking).

Respectively, among the unit operations in water and wastewater treatment, adsorption occupies an important position. It is recommended that the adsorbent is available in large quantities, of free or very low cost and easily regenerable. In the midst of a large variety of adsorbent available, activated carbon is the most important and cheapest adsorbent used in the current method of pollution control. In Malaysia, the palm oil industry generates huge amounts of palm shell. Some of this solid waste is usually used as fuel to produce process steam and/or electricity in palm oil mills. However, a large portion of it is either burned in open air or dumped

in area adjacent to the mill, which creates huge environmental and disposal problems. Therefore, application of palm shell activated carbon as an adsorbent offers highly effective technological means in dealing with the heavy metals pollution of the aqua-environment with the minimum investment requirement.

2. Materials and Method

2.1. Instrumentations

Three equipments were used in this research:

- An atomic absorption spectrometer (AAS) with copper hollow cathode lamp and air acetylene flame was used to determine the copper concentrations.
- A pH meter was used for pH measurement. The meter was standardized using buffer solutions with pH values: 2 to 8.
- A mechanical shaker was used for agitating the samples.

2.2. Adsorbents

Palm kernel shell (PKS) – based activated carbon used as adsorbent was that of granular form, and the mesh size is listed in Table 2. Activated carbon was that of laboratory grade and was used directly as received from the supplier (KD Technology, Malaysia).

Table 2. Properties of PKS–Based Activated Carbon.

PKS AC	Particle size (mm)	S_{BET} (m^2/g)	V_{micro} (cm^3/g)	V_{meso} (cm^3/g)	V_{total} (cm^3/g)	D_{micro} (Å)	D_{meso} (Å)	Ash content
PKS – M	0.25 – 0.60	1146	0.43	0.12	0.582	5.3	26.1	<5%

2.3. Synthetic effluent preparation

An accurate weight of 1.000 g (± 0.0005) $CuSO_4$ was dissolved in 1 L of distilled water to produce the stock solutions of synthetic effluent. These stock solutions were then diluted into the required concentrations using distilled water whenever necessary. Every time the stock and standard solution have been prepared, the solution was shaken for about 2 hours using orbital incubator shaker at 30°C and 100rpm to ensure that each solution was homogeneous.

2.4. Experimentations

Batch adsorption experiments were carried out in a series of stoppered reagent bottles. 30 mL of $CuSO_4$ solution with predetermined initial concentration of 10, 20, 30, 40 and 50 mg/L was put inside the 30 mL stoppered reagent bottles, which contained 0.5 g of activated carbon. Prior to that, the pH solution was adjusted to the desired values by adding HNO_3 or $NaOH$. The reagent bottles with activated

carbon–CuSO₄ mixture were shaken using an orbital incubator shaker, which operated at 100 rpm and 30°C (±2°C) for 6 hours to attain the equilibrium condition. Blank solutions were treated similarly without the adsorbent, and the recorded concentrations at the end of each operation were taken as the initial. The final concentrations of the solution were then determined from a calibration curve.

3. Results and Discussion

3.1. Effect of initial pH

The acidity of solution pH is one of the most important parameters controlling the uptake of heavy metals from wastewater and aqueous solutions. The uptake and percentage removal of copper from the aqueous solution are strongly affected by the pH of the solution as illustrated in Fig. 1. The uptake of copper increases from 0.11 mg/g to 1.20 mg/g when the pH increases from pH 2 to pH 6. Copper sorption is noted to increase significantly at pH 4 with 0.96 mg/g and 1.07 mg/g adsorption capacity at pH 5 respectively. After that the capacity of adsorption decreases slightly in pH range of 6 to 9.

The minimum adsorption observed at low pH (pH 2) may be due to the fact that the higher concentration and higher mobility of H⁺ ions present favoured the preferential adsorption of hydrogen ions compared to Cu (II) ions [1]. It would be plausible to suggest that at lower pH value, the surface of the adsorbent is surrounded by hydronium ions (H⁺), thereby preventing the metal ions from approaching the binding sites of the sorbent [2]. This means that at higher H⁺ concentration, the biosorbent surface becomes more positively charged such that the attraction between biomass and metal cations is reduced [3]. In contrast, as the pH increases, more negatively charged surface becomes available thus facilitating greater copper removal. It is commonly agreed that the sorption of metal cations increases with increasing pH as the metal ionic species become less stable in the solution.

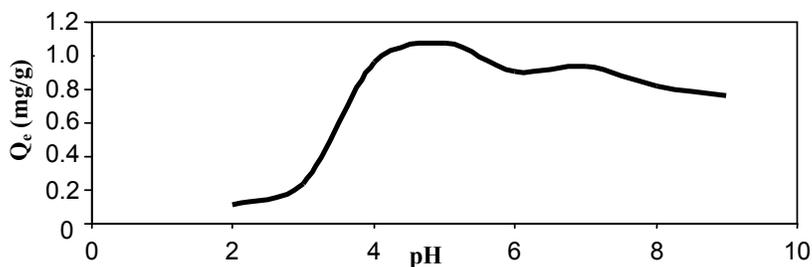


Fig. 1. Effect of pH on Copper Adsorption Capacity, Q_e (mg/g) by 1 g Adsorbent Mixed in 30 mL of Initial Concentration 50 mg/L, Orbital Shaking of 2 Hours at 100 rpm, Incubated at 30 ± 2°C.

However, at higher pH values (pH 6, pH 7, pH 8 and pH 9) there is a decrease in the adsorption capacity. This is due to the occurrence of copper precipitation. At pH 6 there are three species present in solution as suggested by Elliot and Huang [4], Cu²⁺ in very small quantities and Cu(OH)⁺ and Cu(OH)₂ in large quantities. Three species are adsorbed at the surface of adsorbent by ion exchange mechanism with the functional groups present in adsorbent or by hydrogen bonding.

3.2. Effect of adsorbent dosage

The adsorbent dosage is another important parameter, which influences the extent of metal uptake from the solution and thus the effect as shown in Fig. 2. It was evident that the amount of metal uptake increases from 0.86 mg/g with 0.5 g adsorbent up to 1.08 mg/g with 1.0 g adsorbent.

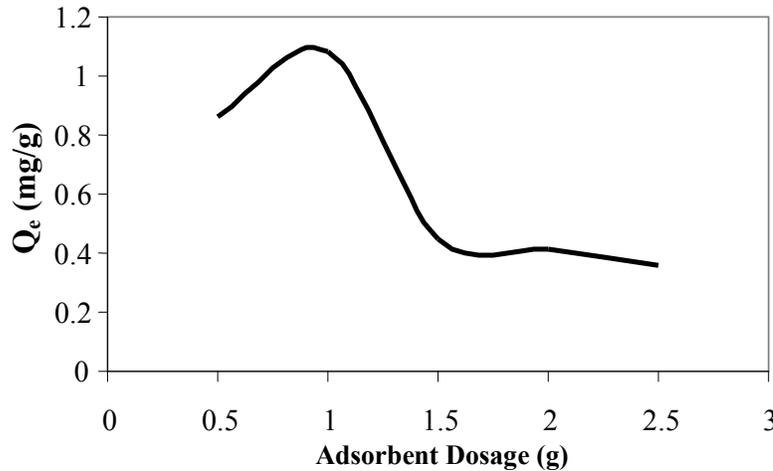


Fig. 2. Effect of adsorbent dosage (g) on copper adsorption capacity, Q_e (mg/g) in 30 mL of initial concentration 50 mg/L at pH 5, orbital shaking of 2 hours at 100rpm, incubated at $30 \pm 2^\circ\text{C}$.

Prior to that, it is apparent that the percent removal of copper increases as the adsorbent dosage increases from 0.5 g up to 1.0 g due to the limited availability of the number of adsorbing species for a relatively larger number of surface sites on the adsorbent at higher dosage of adsorbent. It is plausible that with higher dosage of adsorbent there would be greater availability of exchangeable sites from metal ions [5]. Besides, Fourest and Roux [6] suggested that the reduction in adsorbent dosage in the suspension at a given metal concentration enhances the metal/adsorbent ratio, and thus increases the metal uptake per unit adsorbent, as long as the latter is not saturated. Similar observation has been reported by Mashitah et al [7] for the adsorption of copper ions onto *Pycnoporous sanguineus* biomass.

However, the adsorption capacity decreased sharply with the increasing of adsorbent dosage at value 1.5 g. The copper adsorption capacity decreases gradually at adsorbent dosage 2.0 g with 0.41 mg/g adsorption capacity and at 2.5 g with 0.34 mg/g. These results may be due to the overlapping of the adsorption sites as a result of overcrowding of adsorbent particles [8]. Moreover, the high adsorbent dosage could impose a screening effect of the dense outer layer of the cells, thereby shielding the binding sites from metal [9].

3.3. Effect of initial adsorbate concentration

Figure 3 shows that adsorption capacity increasing from 0.23 to 1.09 mg/g as the metal concentration increases from 10 to 50 mg/L. The trend is that of the result of the progressive increase in the electrostatic interaction between the copper ions and the adsorbent active sites. Moreover, this can be explained by the fact that more adsorption sites were being covered as the metal ions concentration increases [10]. Besides, higher initial concentrations lead to an increase in the affinity of the copper ions towards the active sites [11].

The decline in the adsorption capacity is due to the availability of smaller number of surface sites on the adsorbent for a relatively larger number of adsorbing species at higher concentrations [12]. Similar results were observed by Han et al. [13] for the adsorption of copper (II) and lead (II) on chaff.

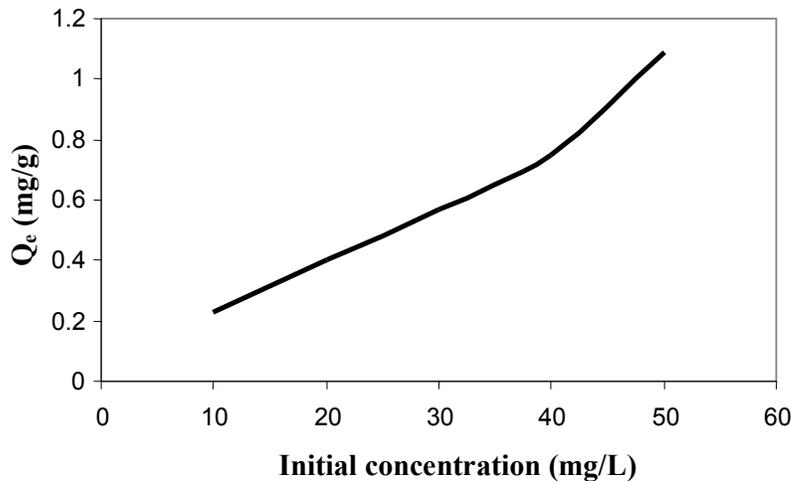


Fig. 3. Effect of Initial Concentration (mg/L) on Copper Adsorption Capacity, Q_e (mg/g) by 1 g Adsorbent Mixed in 30 mL Solution at pH 5, Orbital Shaking of 2 Hours at 100 rpm, Incubated at $30 \pm 2^\circ\text{C}$.

3.4. Adsorption isotherm

The capacity of the adsorption isotherm is fundamental, and plays an important role in the determination of the maximum capacity of adsorption. It also provides a panorama of the course taken by the system under study in a concise form, indicating how efficiently a carbon will adsorb and allows an estimate of the economic viability of the carbons commercial applications for the specified solute. In order to adapt for the considered system, an adequate model that can reproduce the experimental results obtained, equations of Langmuir, Freundlich, Redlich-Peterson, Toth and Temkin have been considered.

Langmuir model is the most widely used isotherm equation, as follows,

$$Q_e = \frac{x}{m} = \frac{K_L C_e}{(1 + a C_e)} \quad (1)$$

Freundlich isotherm equation is given as:

$$Q_e = K_F C_e^{1/n} \quad (2)$$

The Redlich-Peterson isotherm is a combination of Langmuir-Freundlich model. It approaches the Freundlich model at high concentration and is in accord with the low concentration limit of the Langmuir equation. The equation is given as:

$$Q_e = \frac{k_j C_e}{1 + \alpha_L C_e^\beta} \quad (3)$$

The equation of Toth combines the characteristics of Langmuir and Freundlich model, which can be presented as:

$$Q_e = \frac{a C_e}{[b + (C_e)^d]^{1/d}} \quad (4)$$

Besides that, the Temkin isotherm also used in this study to fit with the experimental data, and it can be represented as,

$$Q_e = K_1 \ln C + K_2 \quad (5)$$

The experimental data on the effect of an initial concentration of metal on the carbon of the test medium were fitted to the isotherm models and graphical representations of these models are presented in Fig. 4. All of the constants are presented in Table 3.

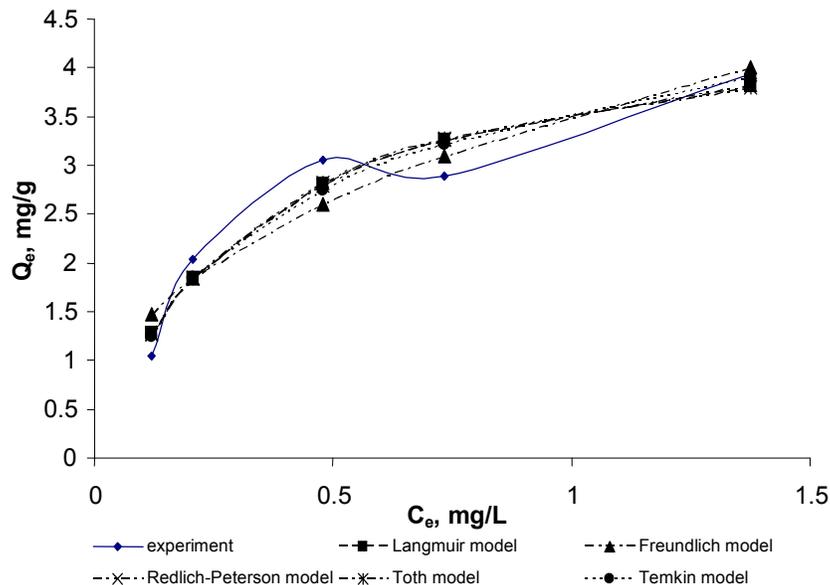


Fig. 4. Langmuir Isotherm for Adsorption Process.

Table 3. The Value of Parameters for Each Isotherm Model Used in The Studies.

Isotherm Model	Parameter	R^2
Langmuir	$K_L=14.6454$	0.9371
	$\alpha=3.1192$	
Freundlich	$K_f=3.5129$	0.9019
	$1/n=0.4089$	
Redlich-Peterson	$k_p=15.1699$	0.9373
	$\beta=0.9757$	
	$\alpha_1=3.2688$	
Toth	$a=4.5488$	0.9373
	$b=0.3025$	
	$d=1.0725$	
Temkin	$K_1=1.0871$	0.9432
	$K_2=3.557$	

Since the value of R^2 (non linear correlation coefficient) nearer to one indicates that the respective equation better fits the experimental data. The representations of the experimental data by all models equation results in non-linear curve with R^2 values of a least 0.9 as tabulated in Table 4. Temkin isotherm was concluded to be preferred model for the adsorption process. The observations confirm the capacity of PKS to adsorb copper fit: the Temkin model fits well with R^2 value of 0.9432. The maximum adsorption capacity obtained from the test is 3.9293 mg/g. The plotted equations obtained from the graph are presented in Table 4 below.

Table 4. The Adsorption Isotherm Equations Used in the Studies.

Isotherm model	Equation
Langmuir	$q_e = \frac{14.6454C_e}{1 + 3.1192C_e}$
Freundlich	$q_e = 3.5129C_e^{0.4089}$
Redlich-Peterson	$q_e = \frac{15.1699C_e}{1 + 3.2688C_e^{0.9757}}$
Temkin	$q_e = K_1 \ln C_e + K_2$
Toth	$q_e = \frac{4.5488}{(0.3025 + C_e^{1.0725})^{0.9324}}$

4. Conclusion

The study indicates that activated carbon prepared from *Elais Guineensis* kernel or known as palm kernel shell could be used as an effective adsorbent material for the treatment of copper aqueous wastewater. The adsorption of copper on activated carbon is found to be pH, initial concentration and dose dependent. The optimum conditions of copper uptake obtained from this study are: pH 5.0, initial

concentration 50 mg/L and biomass loading of 1.0 g. In addition, the correlation of Temkin adsorption isotherm fits the experimental data most accurately. It was determined that the maximum adsorption capacity is 3.9293 mg/g.

The material (*Elais Guineensis* kernel) is not only economical, but also is an agricultural waste product. Hence activated carbon derived from *Elais Guineensis* kernel would be useful for the economic treatment of wastewater containing copper metal.

Acknowledgement

We would like to thank the Department of Chemical Engineering Technology, UniKL MICET and the Department of Chemical and Environmental Engineering, Universiti Putra Malaysia for providing the research facilities and constant encouragement; and K.D. Technology, Malaysia for the generous provision of palm shell activated carbon for our research.

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