

Equilibrium Kinetics and Isotherm Studies of Cu (II) Adsorption from Waste Water onto Alkali Activated Oil Palm Ash

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Abstract: Problem statement: Heavy metal accumulation in waste water could affect aquatic life, human health and overall ecosystem adversely. Therefore, in recent years much emphasis has been given for the use of industrial waste material as low cost adsorbents for removal of metallic contaminants from waste water. **Approach:** Present study deals with the adsorption equilibrium and kinetics of Cu (II) cation using sodium hydroxide activated Oil Palm Ash (OPA). Adsorption was investigated in a batch system with respect to various parameters such as initial metal ion concentration, contact time and pH of the solution. Surface characterization of the prepared adsorbent was done by using surface area analyzer, Scanning Electron Microscope (SEM) and X-ray Fluorescence and compared with natural oil palm ash. The adsorption equilibrium data were best represented by Langmuir, Freundlich and Temkin model. Equilibrium kinetics studies were performed by Pseudo first order, Pseudo second order and Intra-particle diffusion. **Results:** Maximum monolayer adsorption capacity observed at 30°C was 18.86 mg g⁻¹. Kinetic data correlated well with the pseudo second order model, suggesting that the adsorption process might be chemical sorption. The linear plots of intra particle diffusion revealed that the adsorption process was mainly governed by pore diffusion. Equilibrium uptake was increased with increase of initial concentration and contact time. Experimental data showed that about 96.03% of copper can be removed at pH 5.5. **Conclusion:** The research concluded that activation by alkali treatment of natural OPA would produce sufficient porosities and surface area and it has got good potential to remove Cu (II) from waste water.

Key words: Oil Palm Ash (OPA), Scanning Electron Microscope (SEM), World Health Organization (WHO), Empty Fruit Bunch (EFB), Palm Shell (PS), Langmuir equation, equilibrium data, Empty Fruit Bunch (EFB), sodium hydroxide

INTRODUCTION

Aqueous effluents emanating from many industries contain heavy metals dissolved in it. If these discharges are emitted without purification, they may have severe impact on environment (Krim *et al.*, 2006). Primarily some anthropogenic activities, such as weathering of rocks and volcanic activities play a vital role for enriching the water reservoirs with heavy metals (Yisa, 2010; Ong and Kamruzzaman, 2009). Numerous metals such as manganese (Mn), mercury (Hg), lead (Pb), cadmium (Cd), arsenic (As), copper (Cu). are known to be significantly toxic due to their non-biodegradability and toxicity (Ghaly *et al.*, 2008; Omar and Al-Itawi, 2007). Among these heavy metals, copper is considered

as one of the most toxic one. The potential source of copper in industrial effluents includes paper and pulp, fertilizer, wood preservatives, refineries, metal cleaning and plating bath etc. The excessive intake of copper may cause renal and hepatic damage, severe mucosal irritation, wide spread capillary damage, gastrointestinal irritation and possibly necrotic changes in kidney and liver. World Health Organization (WHO) has recommended that maximum acceptable limit for Cu (II) concentration in drinking water should be 1.5 mg L⁻¹. Consequently, it is essential that the potable water should be given some treatment before domestic supply.

Many conventional methods including oxidation, membrane filtration, coagulation, reverse osmosis, adsorption, ion exchange, precipitation. have been

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reported in the literature to remove copper along with other heavy metals from waste water. These methods may be ineffective or extremely expensive especially when the waste stream contains relatively low concentration of metal (1-100ppm) dissolved in large volume. However, adsorption can be regarded as one of the most popular method for the removal of heavy metals from the wastewater due to its low cost, easy availability, biodegradability, simplicity of design and high removal efficiency (Azhar *et al.*, 2005; Esmaeili *et al.*, 2005; Shaker, 2007). Moreover, it does not produce harmful substances. Therefore, adsorptive removal of heavy metals including copper from aqueous streams by using agricultural and industrial waste products which are abundant in nature and requires little processing has received much attention in recent years (Zuorro and Lavecchia, 2010). Several adsorbent derived from low cost material such as agarose, *zea mays* Tassel (Caliphs *et al.*, 2010), sea mussel and white clay, *Spirogyra neglecta* (Modher *et al.*, 2009), dried activated sludge (Soltani *et al.*, 2009), tea waste (Amarasinghe and Williams, 2007; Mahvi *et al.*, 2005) volcanic tuff (Mihaly-Cozmuta *et al.*, 2005). for treating waste water at the solid-solution interface have been reported.

Above perusal of the literature reflects that several types of adsorbents have been used for removal of heavy metals from waste water. Activated oil palm ash possesses some unique properties due to its extended surface area, porosities and oxide content on its surface. These properties significantly can contribute for its enhanced uptake capacity.

Therefore, oil palm ash was taken for the preparation of adsorbent and its applicability for the removal of copper ion from waste water was evaluated. Malaysia has huge supply of agro-based waste biomass-generated from oil palm industries which consists of Empty Fruit Bunch (EFB), Palm Shell (PS) and mesocarp fiber. This biomass is burnt in boiler to produce steam for electricity generation which produces a lot of solid waste- oil palm ash. The utilization of palm ash provides two-fold advantage with respect to environmental contamination. In that case, solid waste disposal problem can be partly reduced and simultaneously it can be converted to value added, easily available, eco-friendly adsorbent.

Present research aims to remove Cu (II) from waste water by using chemically treated palm oil ash and to investigate the influence of all the physicochemical parameters involved during the sorption process. The research focuses on adsorption kinetics and isotherm studies of the prepared adsorbent. We are reporting here

an improved activation strategy for oil palm ash by using sodium hydroxide which can enhance its surface area significantly and consequently increase its adsorption capability.

MATERIALS AND METHODS

Chemicals: Copper (II) sulfate, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, sodium hydroxide (NaOH) and Hydrochloric Acid (HCl) were purchased from Merck, Germany. Stock solution of Copper (II) sulfate having concentration of about 1000 mg L^{-1} was prepared by using double distilled water. Various concentrations of test solution of Cu (II) ranging from 50-100 mg L^{-1} were prepared by subsequent dilution of the stock solution while the initial pH was adjusted to 5.5 using a pH meter (Mettles Toledo, Model: Ross FE 20, USA). Fresh dilution of the stock solution was done for each sorption study. All reagents used here were of AR grade chemicals.

Oil Palm Ash (OPA) activation: The palm oil fuel ash used here was taken from the middle of the flue tower and was collected from East oil Mill, Golden Hope Plantation Sdn. Bhd, Pulau Carey, Selangor. The adsorbent thus obtained was sieved through sieve no 200 μm . It was washed with deionized water for several times to remove foreign particles and oven dried at 110°C over night. The ratio of oil palm ash with caustic soda was kept 5:1 that is 50 grams of oil palm ash were added with 10 gm of NaOH in 250 mL distilled water. Then the mixture was refluxed at 160°C for 8 h in a round bottom flask with a magnetic stirrer placed inside it. The slurry was allowed to cool at room temperature and filtered. The filter cake was repeatedly washed with deionized water until neutral pH of the filtrate was observed. Then it was dried in an oven at 110°C for 12 h before use and stored in desiccators over fresh silica gel for further application.

Surface characterizations: Scanning Electron Microscope (SEM) was used to study the morphological changes of untreated and treated oil palm ash. X-ray fluorescence (XRF, Rigaku RIX, 3000, Japan) was used to identify the chemical composition of the activated adsorbent. Surface area, pore volume and pore diameter of the prepared adsorbent was measured by Autosorb1, Quantachrome Autosorb Automated gas sorption system supplied by Quantachrome. Before performing the nitrogen gas adsorption, the activated OPA was outgassed under vacuum at temperature 300°C for 4 h. to remove any moisture content from the solid surface. Surface area and pore volume were calculated by

Brunaure Emmett Teller (BET). Above mentioned procedure was automatically performed by software (Micropore version 2.26) available with the instrument.

Equilibrium studies: Each of the batch experiment was carried out by adding 0.2 gm of OPA with 50 mL of different concentration of Cu (II) solution at 150 rpm. The residual concentration of Cu (II) was analyzed after predetermined interval of time until the system reached equilibrium by using atomic absorption spectrophotometer (Perkin-Elmer Model 3100).

Isotherm studies: For isotherm generation each experiment was conducted at 30°C in a thermoregulated water bath (Haake Wia Model, Japan) with shaker cover in order to prevent heat loss to the surroundings. The equilibrium adsorption amount (q_e) is calculated according to Eq. 1:

$$q_e = \frac{(c_i - c_e)V}{w} \quad (1)$$

Here, q_e is the adsorption amount of metal ion (mg g^{-1}) at equilibrium contact time, W is the weight of adsorbent (g), V is the volume of solution (mL). The removal efficiency of the metal ion was calculated by using Eq. 2:

$$\text{Removal \%} = \frac{c_i - c_e}{c_i} \times 100 \quad (2)$$

RESULTS

SEM was used to study the changes in morphology of untreated OPA and chemically treated sample of OPA which was shown by Fig. 1a and b. The figure clearly reveals that surface morphologies of both the sample were different. It was observed that natural palm ash had rough structure without any cracks and crevices. However significant number of pores with different structure was observed after activation of the sample. Due to this well developed porosities created by sodium hydroxide, activated oil palm ash had high surface area and adsorption capacity.

After activation, the major chemical constituent of modified oil palm ash (wt%) observed was: SiO_2 (51.70), Al_2O_3 (5.50), Fe_2O_3 (5.77), Na_2O (2.00), K_2O (5.69), MgO (11.20), CaO (10.90), P_2O_5 (5.95), SO_3 (0.10), TiO_2 (0.41) and MnO (0.44). The high oxide content of silica along with other oxide has given the structure of palm ash to be used as good adsorbent for metal.

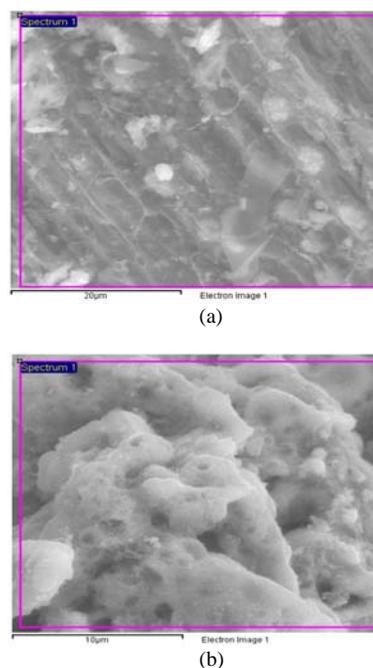


Fig. 1: (a) Natural oil palm ash (b) Activated oil palm ash

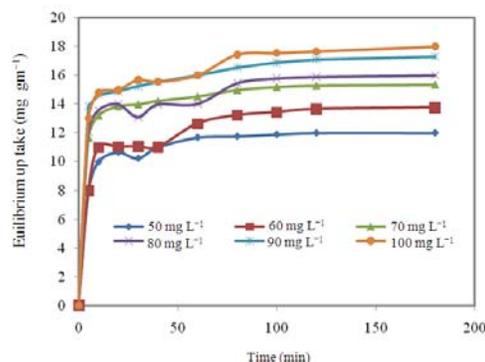


Fig. 2: Effect of initial metal ion concentration with equilibrium contact time

The phenomenon of adsorption is mainly dependent on surface area and pore structure. The calculated BET surface area for the natural sample was $3.774 \text{ m}^2 \text{ g}^{-1}$, but it increased to $467.1 \text{ m}^2 \text{ g}^{-1}$ after activation. This enlargement of surface area is probably due to increase in micro pore volume and micro pore surface area. The micro pore volume and micro pore surface area of natural sample of OPA observed was 0.0014 cm^3 and $4.057 \text{ m}^2 \text{ g}^{-1}$ respectively which were increased to $0.199 \text{ cm}^3 \text{ g}^{-1}$ and $561.9 \text{ m}^2 \text{ g}^{-1}$ after chemical treatment.

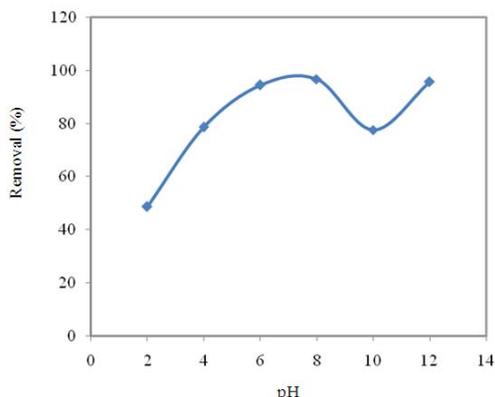


Fig. 3: Effect of pH on removal % of copper

Figure 2 shows the effect of initial metal ion concentration and uptake with equilibrium contact time. It is clear from the graph that amount of uptake q_t (mg gm^{-1}) increased with increased agitation time and after certain period of time; it reached to a constant value beyond which no further adsorption took place. The results showed that, the adsorption was fast at initial stage of contact period and after that near the equilibrium it became slower. The rate of uptake was initially high due to the availability of larger surface area of modified oil palm ash for adsorption. With the lapse of time, the surface adsorption sites were exhausted. The remaining vacant sites were difficult to be occupied by the cation due to repulsive forces between adsorbate present in solid and bulk phases. As the concentration of the metal ion is increasing, the sorption capacity by the sorbent is also increasing. Similar trend was observed for phenol adsorption onto rice husk and rice husk ash (Mahvi *et al*, 2004). The plot reveals that within 80 min the system reached equilibrium and after that the adsorption became more or less same. However, here experimental data were measured for 3 h to ensure that full equilibrium was attained.

In order to study the effect of pH, the solution pH was varied from 2-8 while keeping the other variable constant. Figure 3 depicts the effect of pH on removal% of copper. It was found that adsorption of Cu (II) ion from the solution was strongly pH dependent. At pH 2-3 range the adsorption was low and rapidly increased between pH 4-7 resulting greater removal efficiency. This phenomenon can be explained by the presence of H^+ and H_3O^+ ions in the solution at lower pH. At pH less than 4, hydrogen protons may compete with metal ions for active binding sites on the surface of palm oil ash, which leads to fewer binding sites being

available to bind metal ions, so the adsorption amount of Cu (II) was very little. As the pH increases, the adsorption surface became less positive and therefore electrostatic attraction between metal ions and the surface of palm oil ash was increased resulting greater removal efficiency between pH 4-8. The result depicts that removal% was increased steadily up to pH 8, attains maximum value of about 94.56%.

However, after pH 8, there is a sharp decrease in adsorption. This decrease is may be due to formation of soluble hydroxyl complexes. After pH 8, there is again increase of removal % which results S-like adsorption curve. This S-like curve reflects cumulative effect of adsorption and precipitation. Therefore the adsorption of Cu (II) ion onto oil palm ash was studied at pH 5.5 for subsequent experiments at equilibrium.

To design the sorption systems, chemical kinetics is very important as it explains how slow and fast the rate of chemical reaction occurs and the factors which affect the reaction rate. In order to gain some insight into the sorption process of Cu (II) ions onto the surface activated palm oil fuel ash, pseudo first order and pseudo second order kinetic models were implemented.

The pseudo first order equation (Ong *et al*, 2010) based on based on equilibrium adsorption is expressed as:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t \quad (3)$$

Where, q_e and q_t are the amount of adsorbed (mg g^{-1}) at equilibrium and at any time t , k_1 is the first order rate constant (min^{-1}).

The plot of $\log(q_e - q_t)$ versus t (Fig not shown) gave the slope k_1 and intercept of $\log q_e$.

Table-1 shows the co-relation coefficient R^2 and rate constant k_1 for different initial concentration at 30°C . Pseudo second order equation (Ho and McKay, 1999) can be given by:

$$\frac{t}{qt} = \frac{k_1}{k_2 \cdot q_2^2} + \frac{1}{q_2}t \quad (4)$$

Here, k_2 is the rate constant of second order adsorption. The linear plot of $\frac{t}{q_t}$ versus t gave $\frac{t}{q_e}$ as slope and $\frac{1}{k_2 \cdot q_2^2}$ as intercept. This model is more likely to predict the behavior over the whole range of adsorption. The linear plots of pseudo second order model is shown in Fig. 4 and the model parameters are listed in Table 1.

Table 1: Comparison of pseudo-first order and pseudo-second order adsorption rate constant for different initial concentration

C ₀ (mgL ⁻¹)	Pseudo-first order kinetics			Pseudo-second order Kinetics			
	q _e (exp) (mg g ⁻¹)	q _e (cal) (mg g ⁻¹)	K ₁ (min ⁻¹)	R ²	q _e (cal) (mg g ⁻¹)	K ₂ (min ⁻¹)	R ²
50	12.0033	5.3951	0.0484	0.894	12.3457	0.0233	0.999
60	13.7777	6.0395	0.0299	0.952	14.2857	0.011	0.998
70	15.371	3.7411	0.0299	0.964	15.625	0.0234	0.999
80	15.9987	5.035	0.0276	0.894	16.3934	0.013	0.997
90	17.3053	4.0458	0.023	0.97	17.5439	0.0158	0.999
100	17.9989	5.0816	0.023	0.939	18.5185	0.0117	0.998

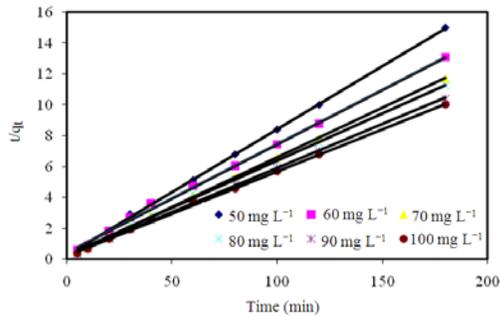


Fig. 4: Pseudo Second order Kinetics for adsorption of Cu (II) onto Activated Palm Ash at 30°C Temperature at pH 5.5

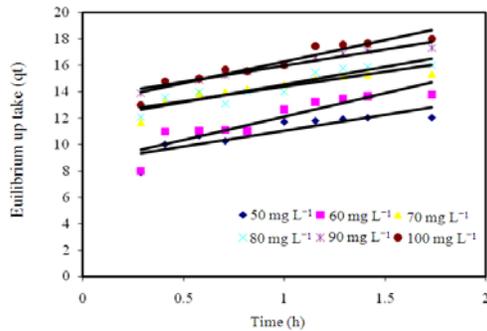


Fig. 5 : Intra-Particle diffusion for adsorption of Cu (II) onto Activated Palm Ash at 30°C Temperature at pH 5.5

The prediction of the rate-limiting step is a key factor to be determined in the adsorption process. The most commonly used technique for identifying the mechanism involved in the adsorption process is by fitting an intraparticle diffusion plot. An intraparticle diffusion coefficient K_{id} is given by the equation:

$$q_t = k_{id}t^{0.5} \tag{5}$$

The plot of q_t versus $t^{0.5}$ as shown by Fig. 5. The slope of the plot has been defined to yield the intraparticle diffusion parameter K_{id} (mg⁻¹ min^{-0.5}). On the other hand, the intercept of the plot reflects C, the boundary layer effect. The larger the intercept, the greater the contribution of the surface sorption in the rate-controlling step.

The calculated intraparticle diffusion coefficient K_{id} values are listed in Table 2.

The salient features of isotherm studies are essential for the adsorption process to be interpreted adequately. Many models have been proposed by the researchers to explain adsorption equilibrium. The most commonly used isotherm models for solid-liquid adsorption are the Langmuir, Freundlich and Temkin isotherms.

The Langmuir isotherm is based on monolayer adsorption (constant heat of adsorption for all sites) on the active sites of the adsorbent and it is expressed by following equation:

$$q_e = \frac{k_L C_e}{1 + a_L C_e} \tag{6}$$

The linear form of the Langmuir isotherm is given by:

$$\frac{C_e}{q_e} = \frac{1}{q_{max} K_L} + \frac{1}{q_{max}} C_e \tag{7}$$

Where:

- q_e = The equilibrium cation on the adsorbent (mg g⁻¹)
- C_e = The equilibrium cation concentration in solution (mg L⁻¹)
- q_{max} = The maximum monolayer adsorption capacity of the adsorbent (mg g⁻¹) and K_L = The Langmuir adsorption constant (L mg⁻¹)

Table 2: Intra particle rate constant for different initial concentration

Initial concentration (mg L ⁻¹)	C	K _{dir} (mg/gh ^{0.5})	Correlation coefficient, R ²
50	8.650	2.406	0.738
60	8.564	3.538	0.814
70	12.140	2.237	0.817
80	11.910	2.637	0.844
90	13.510	2.446	0.961
100	13.00	3.266	0.898

Table 3: Essential characteristics of langmuir isotherm

Value of R _L	Type of Isotherm
R _L >1	Unfavorable
R _L = 1	Linear
0<R _L <1	Favorable
R _L = 1	Irreversible

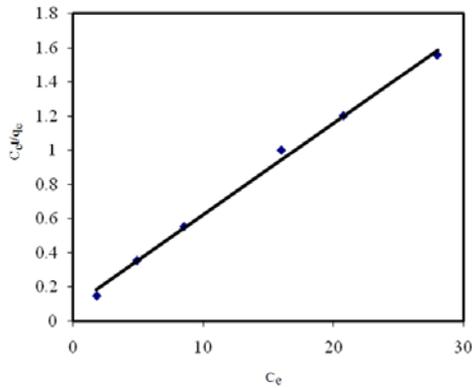


Fig. 6: Langmuir Isotherm at onto activated palm ash at 30°C Temperature at pH 5.5

When C_e/q_e is plotted against C_e, a straight line with slope 1/q_{max} and intercept of 1/q_{max}K_L is obtained.

The essential characteristics of the Langmuir equation (ALzaydien, 2009) can be expressed in terms of a dimensionless factor, R_L which is given below:

$$R_L = \frac{1}{1 + K_L C_o} \quad (8)$$

C_o is the highest initial cation concentration (mg L⁻¹). The value of separation factor R_L, can be represented by following Table 3.

The linear plot of Langmuir Isotherm at 30°C temperature is shown on Fig. 6 and the model parameters at 30°C are listed in Table 4.

Freundlich isotherm gives the relationship between equilibrium liquid and solid phase capacity based on the multilayer adsorption (heterogeneous surface) properties. This isotherm is derived from the assumption that the adsorption sites are distributed exponentially with respect to the heat of adsorption and is given by:

Table 4: Isotherm model parameters and correlation coefficient at 30°C Temperature

Isotherm model	Parameters	values	R ²
Langmuir	q _m , maximum monolayer adsorption capacities(mg g ⁻¹)	18.8600	0.996
	R _L , separation factor	0.0163	
	K _L , Langmuir constant	0.6025	
Freundlich	K _F , Affinity Factor (mg/gm(L mg ⁻¹) ^{1/n})	11.3700	0.966
	1/n, Freundlich exponent	0.1210	
Temkin	K _T , (l mg ⁻¹)	137.1300	0.979
	B	2.1500	

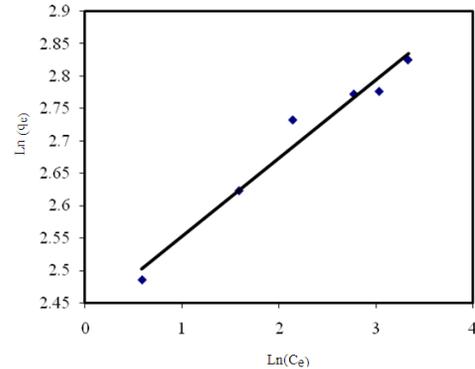


Fig. 7: Freundlich Isotherm at onto activated palm ash at 30°C Temperature at pH 5.5

$$q_e = k_f C_e^{1/n} \quad (9)$$

And can be linearized as:

$$\ln q_e = \ln k_f + \frac{1}{n} \ln C_e \quad (10)$$

where, K_f (mg g⁻¹) and $\frac{1}{n}$ relates the multilayer adsorption capacity and intensity of adsorption. The linear plot of Freundlich Isotherm at 30°C temperature is shown on Fig. 7 and the model parameters at 30°C are listed in Table 4.

Temkin isotherm, which considers the effects of the heat of adsorption of all molecules in the layer would decrease linearly with coverage due to the adsorbate and adsorbent interactions and is given by:

$$q_e = \frac{RT}{b} \ln A C_e \quad (11)$$

Equation 11 can be linearized as:

$$\ln q_e = \left(\frac{RT}{b}\right) \ln A + \left(\frac{RT}{b}\right) \ln C_e \quad (12)$$

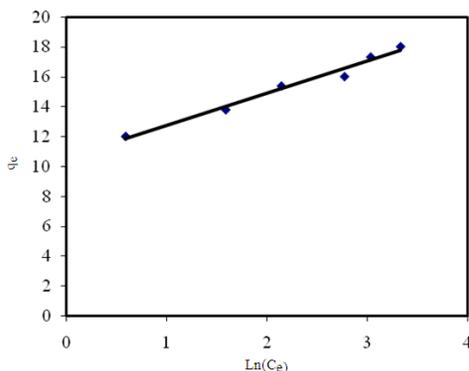


Fig. 8: Temkin Isotherm onto activated palm ash at 30°C Temperature at pH 5.5

Here $RT/b = B$ (J mol^{-1}), which is Temkin constant related to heat of sorption whereas a (L g^{-1}) is the equilibrium binding constant corresponding to the maximum binding energy. R ($8.314 \text{ J mol}^{-1} \text{ K}$) is universal; gas constant and $T(\text{K})$ is absolute solution temperature. Figure 8 depicts Temkin model under the concentration range studied here.

DISCUSSION

The results from the experiments described in this study show that copper ions can be adsorbed efficiently on activated oil palm ash. However, the ability of activated oil palm ash is the result of a number of mechanisms, including surface adsorption, chemisorptions, complexation, ion exchange, microprecipitation and metal hydroxide complexation. In order to understand the detailed mechanism by which copper ion has been removed from the solution by adsorption, it is essential to identify the chemical constituent present on the adsorbent. The high percentage of SiO_2 may also be involved in the adsorption phenomena through SiO bond with copper (II) ions, as presented by following scheme:



The results obtained from Pseudo first order kinetics demonstrated that the experimental q_e (mg g^{-1}) values did not agree well with the calculated values obtained from the linear plots. The correlation

coefficient, R^2 of pseudo first order kinetics are between 0.894-0.970. This confirms that it is not appropriate to use the Lagergren first order kinetic model to predict the adsorption kinetics for Cu (II) onto activated palm oil ash for the entire sorption period.

On the contrary, the correlation coefficient, R^2 for the second order kinetic model were almost equal to unity for all copper concentrations indicating the applicability of the model. Thus it appeared that the system under study is more appropriately described by pseudo second order kinetics which was based on the assumption that the rate limiting step may be chemisorptions involving valency forces through sharing and exchange of electrons.

From the plot of intra-particle diffusion, it is observed that the lines did not pass through the origin. This indicated that the rate limiting process is not only governed by intra particle diffusion. Some other mechanism along with intraparticle diffusion was involved.

The validity of the Langmuir model here suggested that the adsorption process was monolayer and adsorption of each molecule had equal activation energy. The R_L value obtained is between 0-1 indicating that the adsorption of copper onto activated oil palm ash is favorable. The Langmuir model was found to fit the data significantly better than Freundlich model, which showed the more homogeneous nature of activated palm ash. Freundlich exponent, $1/n$ ranging between 0 and 1 is a measure of adsorption intensity or surface heterogeneity. The value $1/n$ below one indicates favorable adsorption of copper onto activated oil palm ash. The Temkin isotherm showed a higher regression coefficient, which may be due to the linear dependence of heat of adsorption at low or medium coverage. This linearity may be due to repulsion between adsorbate species or to intrinsic surface heterogeneity. The regression coefficient of these models showed a strong affinity for the adsorption of Cu (II) onto activated palm ash.

CONCLUSION

This study investigated the adsorption of Cu (II) from aqueous solution using surface modified palm oil fuel ash at initial pH of 5.5 of the solution. The adsorption was found to be strongly dependent on pH, contact time and initial metal ion concentration. Pseudo second order gave better R^2 values confirming chemisorptions onto the surface. Equilibrium was attained within 3 h. Both Freundlich and Langmuir model can be used to fit the data and estimate model parameters but the overall data is slightly better fitted

by Langmuir isotherm. The result indicates that, sodium hydroxide modified oil palm ash is economically viable, environmentally friendly and promising material which can be used successfully for separation of Cu (II) from waste water.

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