Kinetic Modeling and Isotherm Studies for Copper(II) Adsorption onto Palm Oil Boiler Mill Fly Ash (POFA) as a Natural Low-Cost Adsorbent

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Adsorption characteristics of palm oil boiler mill fly ash (POFA) for the removal of Cu(II) from aqueous solution were investigated using batch adsorption studies. The effects of relevant parameters such as contact time, solution pH, adsorbent dosage, and initial concentration of copper were examined. Fundamental batch investigations indicated that 90% of the Cu(II) was removed in the first 30 min, achieving equilibration after only 270 min of agitation. The Cu(II) uptake mechanism is particularly pH- and concentration-dependant, favoring a pH value of 6.0. A decrease in adsorption capacity (q_e) with an increase in Cu(II) removal efficiency (RE %) was obtained as the adsorbent dosage increased. The adsorption behavior of Cu(II) fit well to the Langmuir isotherm, with a monolayer adsorption capacity of 17 mg/g. The applicability of the Langmuir isotherm suggested the formation of monolayer coverage of Cu(II) ions onto equivalent sites of the adsorbent. Kinetics experimental data followed the trend of pseudo second-order kinetics, which is consistent with chemisorption with intraparticle diffusion as one of the rate-determining steps. Therefore, this study indicates that POFA could be used successfully as a natural low-cost adsorbent for Cu(II) removal from aqueous solutions.

Keywords: Adsorption isotherm; Adsorption mechanism; Copper; Kinetics studies; Palm oil boiler mill fly ash (POFA)

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INTRODUCTION

Environmental degradation due to contamination by heavy metals has become a severe public health problem in this modern age (Bayat 2002). The increasing use of heavy metals over the past few decades has inevitably led to an increased flux of metallic substances in the environment (Wang *et al.* 2010). The increasing concentration of heavy metals is a severe health hazard due to their toxicity even at very low concentrations, their non-biodegradable nature, and their persistence in the environment. Heavy metal ions are of particular concern when the concentrations exceed the permissible limits (Naiya *et al.* 2009). Despite being one of the most toxic substances and having adverse effects on human health and the environment, copper (Cu) is still widely used in various industries (Demirbas *et al.* 2009). It has been reported that excessive intake of Cu by humans may lead to severe mucosal irritation, hepatic and renal damage, widespread capillary damage, and central nervous system problems (Larous *et al.* 2005). The World

Health Organization recommends a maximum acceptable concentration of Cu(II) in drinking water of 1.5 mg/L (Rao *et al.* 2006).

At present, different wastewater treatment technologies are available, including conventional methods such as chemical precipitation, coagulation, reverse osmosis, ion exchange, membrane filtration, oxidation, air stripping, sedimentation, and adsorption (Foo and Hameed 2009; Naiya *et al.* 2009; Salam *et al.* 2011; Wang *et al.* 2010). Among these methods, adsorption is recognized as the most efficient and promising fundamental approach to the wastewater treatment processes. Basically, adsorption is a surface phenomenon whereby atoms or molecules bind to the solid surface of a substrate, called the adsorbent, and form attachments via physical or chemical bonds (Foo and Hameed 2009). Adsorption has been proposed as a promising technique for the removal of diverse contaminants, as it is simple, easy to operate, and highly effective in removing heavy metals from effluents with either high solute loadings or dilute concentrations (Popuri *et al.* 2009; Wang *et al.* 2010).

Adsorption of heavy metals using commercialized activated carbon has been widely used in many applications due to its high surface area and adsorption capacity. However, the high cost of the activation process limits its use in the wastewater treatment applications (Babel and Kurniawan 2003; Demirbas 2008; Sud *et al.* 2008). Realizing the complications of the situation, a large number of agricultural lignocellulosic by-products have been utilized in order to develop cheaper and more effective adsorbents for the removal of various pollutants from wastewater (Demirbas 2008; Han *et al.* 2010). These lignocellulosic by-products possess various advantages, such as eco-friendly nature, renewability, low cost, and abundant availability, as compared to commercial adsorbents (Han *et al.* 2010).

According to Yoshizaki *et al*. (2012), 80% of waste material from oil palm cultivation, such as empty fruit bunch (EFB), palm mesocarp fiber (PMF), and palm kernel shell (PKS), are either utilized for plantation nutrients recycling or burnt inefficiently in the mills. In Malaysia alone, the potential palm oil ash production is considered to be four million tons/year (Mohamed *et al.* 2005). Generally the huge quantities of biomass generated from the oil palm industry can cause a severe environmental problem if the materials are not properly utilized (Ahmad *et al.* 2011). Meanwhile, the combustion of palm mesocarp fiber (PMF) and palm kernel shell (PKS) as boiler fuel will inevitably produce oil palm fly ash as a by-product (Chowdhurry *et al.* 2011). Research by Ofomaja (2010) reported that palm kernel fibre can be utilized effectively in removing copper ions from wastewater. The sorption process is endothermic in nature and there is high affinity of the adsorbent towards the sorbate.

However, the application of oil palm biomass as commercialized adsorbents is still in research stage. Therefore in order to enhance the value of this material, palm oil boiler mill fly ash (POFA) could be developed into a natural low-cost absorbent for the removal of heavy metals in the industrial wastewater needed be explored and further investigated. On top of that, the abundant and cheap supply of the biomass materials will further justify its use in the wastewater industry (Ahmad *et al.* 2011; Chowdhurry *et al.* 2011; Foo and Hameed 2009). The objective of this study is to investigate the performance and characteristics of POFA as a natural low-cost adsorbent for removal of Cu(II) from aqueous solutions. Batch adsorption experiments were conducted to further investigate the adsorption isotherm and kinetics modeling of Cu(II) onto POFA under varying experimental conditions, such as contact time, solution pH, dosage level, and initial metal ion concentration.

EXPERIMENTAL

Preparation of Solutions

All chemicals utilized in the study were of analytical grade and supplied by Acros Organics (USA). Synthetic wastewater solutions were prepared by dissolving analytical-grade copper sulfate pentahydrate, $CuSO_4.5H_2O$, in deionized water to obtain 1000 mg/L stock solution. The Cu(II) was diluted with deionized water to obtain working solutions from 10 to 200 mg/L Cu(II) by making fresh dilutions for each batch experiment. For the pH studies, the pH of solutions was adjusted using 0.1 M NaOH and HNO_3.

Batch Adsorption Studies

The adsorption of Cu(II) from aqueous solution using POFA was investigated in a series of batch adsorption experiments. All experiments were performed at room temperature (30 ± 2 °C) using an orbital shaker (Model: Stuart, USA 301) at 200 rpm to keep the media in suspension. The goal of the first experiment was to investigate the effect of contact time. A 0.5 g sample of POFA was added into the conical flasks containing Cu(II) solutions with an initial solution pH of 5.10. Afterward, the Cu(II) solutions (50 mL, 150 mg/L) were agitated at 200 rpm for different interval contact periods ranging from 30 to 330 min. The goal of the second experiment was to study the effect of pH and was determined using a pH meter (Model: Orion 2 star bench top pH meter). The pH values of Cu(II) solution were adjusted manually, ranging from 2.0 to 7.0 with the aid of 0.1 M HNO_3 or NaOH. Then, the Cu(II) solutions (50 mL, 150 mg/L) and 0.5 g of POFA were added into the conical flasks and agitated at 200 rpm for a pre-determined contact time based on the first experiment.

The objective of the third experiment was to investigate the effect of different adsorbent dosages. Different dosages of POFA ranging from 0.1 to 5.0 g were added into the conical flasks containing Cu(II) solutions (50 mL, 150 mg/L) and then agitated at 200 rpm for a pre-determined contact duration and pH. The fourth experiment was aimed at studying the isotherm and the effect of initial Cu(II) concentration. Solutions of Cu(II) at concentrations of 10, 50, 100, 150, and 200 mg/L were prepared, and the procedures used in the previous experiments were replicated. All solution samples were separated from the adsorbent using a syringe and filtered using a 0.45-μm nylon syringe filter. Cu(II) residual was analyzed using an inductively coupled plasma mass spectrometer (Perkin-Elmer, ICP-MS ELAN DRC-e). All methods were adapted from the Standard Methods for the Examination of Water and Wastewater (APHA 1998). All tests were conducted in duplicate.

Removal Efficiency and Capacity

The removal efficiency (RE %), the amount of adsorbate adsorbed per unit mass of adsorbent at time (q_t, mg/g), and the amount of adsorbate adsorbed per unit mass of adsorbent at equilibrium (q_e, mg/g), were calculated from the following equations,

$$RE\ \% = \frac{C_o - C_e}{C_o}\ x\ 100 \tag{1}$$

$$q_t = \frac{C_0 - C_t}{m}\ x\ V \tag{2}$$

$$q_e = \frac{C_0 - C_e}{m} \, x \, V \tag{3}$$

where C_o and C_e (mg/L) are the adsorbate concentrations of Cu(II) initially and at equilibrium, respectively, and C_t (mg/L) is the concentration of adsorbates at time t. V is the volume of the solution (L), and m is the mass of dry adsorbent used (g).

Adsorption Isotherm Models

The purpose of an adsorption isotherm is to reveal the specific relation between the equilibrium concentration of the adsorbate in bulk and the adsorbed amount at the surface. The equilibrium data for Cu(II) adsorption onto POFA were analyzed in terms of the Langmuir, Freundlich, and Temkin isotherm models. The Langmuir adsorption model (Langmuir 1916) is based on the assumption that maximum adsorption corresponds to a saturated monolayer of solute molecules on the adsorbent surface, with no lateral interaction between the adsorbed molecules. The linear form of the Langmuir isotherm model is given by the following equation:

$$\frac{C_e}{q_e} = \frac{1}{q_m b} + \frac{C_e}{q_m} \tag{4}$$

Here, q_e (mg/g) is the amount of equilibrium uptake, C_e is the equilibrium cation concentration in solution (mg/L), q_m is the monolayer adsorption capacity of the adsorbent (mg/g), and b is the Langmuir adsorption constant (L/mg), which is related to the rate of adsorption. The Langmuir constants q_m and b can be calculated from the slope and intercept of the linear plot of C_e/q_e versus C_e.

The effect of isotherm shape on the favorability of a Langmuir-type adsorption process can also be expressed in terms of a dimensionless constant separation factor or equilibrium parameter, R_L, which can be calculated using the following equation,

$$R_L = \frac{1}{1 + bC_0}, \tag{5}$$

where b is the Langmuir isotherm constant and C_o is the initial concentration of Cu(II) ions. The value of R_L indicates the isotherm to be either unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$), or irreversible ($R_L = 0$).

The Freundlich isotherm (Freundlich 1906) can be applied for non-ideal adsorption on heterogeneous surfaces and multilayer adsorption. The Freundlich isotherm equation can be written in linear form as given below,

$$\log q_e = logk + \frac{1}{n} \, logC_e \,, \tag{6}$$

where k and n are Freundlich constants, with k (mg/g $(\text{L/mg})^{1/n}$) being the adsorption capacity of the adsorbent and n giving an indication the favorability of the adsorption process. Values of $n > 1$ represent favorable adsorption conditions. The Freundlich constants k and n can be calculated from the slope and intercept of the linear plot of log q_e versus log C_e.

The Temkin isotherm model involves the effects of indirect adsorption or adsorbate interaction. This isotherm assumes that the heat of adsorption of all the molecules in the layer decreases linearly with coverage because of adsorbent–adsorbate interactions and that the adsorption is characterized by a uniform distribution of binding energies, up to some maximum binding energy (Temkin and Pyzhev 1940). The linear form of the Temkin isotherm can be expressed as,

$$q_e = B\, log\, k_t + B\, log\, C_e \,, \qquad (7)$$

where $B = RT/b$, b is the Temkin constant related to heat of adsorption (J/mol), R is the universal gas constant (8.314 J/mol K), and T is the absolute temperature (K). The inverse quantity $1/b$ indicates the adsorption potential of the adsorbent, while k_t (L/mg) is the equilibrium binding constant corresponding to the maximum binding energy. The plot of q_e versus log C_e enables the determination of the isotherm constants k_t and B.

Kinetic Studies

Kinetics studies are essential in an adsorption process because they reveal the uptake rate of the adsorbate, which controls the residual time for the entire adsorption process (Demirbas *et al.* 2009). The adsorption kinetics of Cu(II) on POFA was determined using similar procedures to those used in the batch adsorption studies. The Lagergren's pseudo first-order, pseudo second-order, and intraparticle diffusion kinetic models were selected in this study to describe the adsorption process. Lagergren's pseudo first-order model states that adsorption is preceded by diffusion through a boundary layer (Lagergren 1898). The Lagergren's equation for first-order kinetics can be written as follows,

$$log\,(q_e - q_t) = log(q_e) - \frac{k_1}{2.303} t \,, \qquad (8)$$

where q_t is the amount of adsorbate adsorbed (mg/g) at time t, and k_1 is the rate constant (min^{-1}). The Lagergren's first-order rate constant k_1 and q_e are calculated from the intercept and slope by plotting log (q_e - q_t) versus t (min). The pseudo second-order chemisorption kinetics can be written as (Ho and McKay 1998),

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \;, \qquad (9)$$

where k_2 (min.mg/g) is the rate constant of the pseudo-second order adsorption and can be determined experimentally from the slope and intercept of a plot of t/q_t versus t (min). The initial adsorption rate, h (mg/g.min), can be calculated from the pseudo second-order model using the following equation:

$$h = k_2 q_e^2 \qquad (10)$$

The rate of intraparticle diffusion or pore diffusion is characterized by the relationship between the amount of metal ions adsorbed at time q_t (mg/g) and the square root of time ($t^{0.5}$). The intraparticle diffusion model is based on the theory proposed by (Weber and Morris 1963). The linear form of the equation can be expressed as,

$$q_t = k_{id} t^{0.5} + C, \qquad (11)$$

where k_{id} is the intraparticle diffusion rate constant (mg/g.min$^{0.5}$), and the values of intercept C are associated to the boundary layer thickness. The intraparticle diffusion rate constant (k_{id}) is calculated from the intercept and slope by plotting q_t (mg/g) versus $t^{0.5}$ (min$^{0.5}$).

Preparation and Characterization of Palm Oil Boiler Mill Fly Ash (POFA)

In this study, palm oil boiler mill fly ash (POFA) was selected as a natural low-cost adsorbent for the removal of Cu(II) from aqueous solution. The POFA was provided by LCSB Lepar Oil Palm Mill and later was oven dried (using a Memmert UFE 500 oven) at 250 °C for 24 h and stored in desiccators prior to usage. For determination of the physical surface characteristic of POFA, Brunauer-Emmette-Teller (BET), and Barrett-Joyner-Halenda (BJH) method analysis was employed in determining the specific surface area and pore size distribution using Quantachrome instruments version 2.01 (Demirbas 2009; Naiya *et al.* 2009). A scanning electron microscope (Hitachi model S-3400N) coupled with an energy dispersive X-ray (EDX) analyzer was used to obtain the surface images and to identify the elemental composition of POFA before and after the adsorption (Han *et al.* 2010; Wang *et al.* 2010).

RESULTS AND DISCUSSION

Palm Oil Boiler Mill Fly Ash (POFA) Characteristics

The incineration of EFB to obtain its ash is currently a common practice in numerous oil palm mills. Ash often is available as an under-utilized waste product of the combustion of lignocellulosic materials (Hubbe *et al.* 2011). Generally, all fly ash contains the same basic chemical elements, but only in different proportions (Cho *et al.* 2005). Palm oil boiler mill fly ash (POFA) has been found to contain high amounts of alumina, calcium, potassium, and silica that could be utilized to synthesize active compounds that are responsible for sorption of pollutant gasses into the absorbent (Mohamed *et al.* 2006; Zainudin *et al.* 2005). Thus it is possible to assume that these similar compounds could also be used for the adsorption of heavy metals in aqueous solution. According to Foo and Hameed (2009), oil palm ash is characterized by a spongy and porous structure that has a large surface area and pore volume.

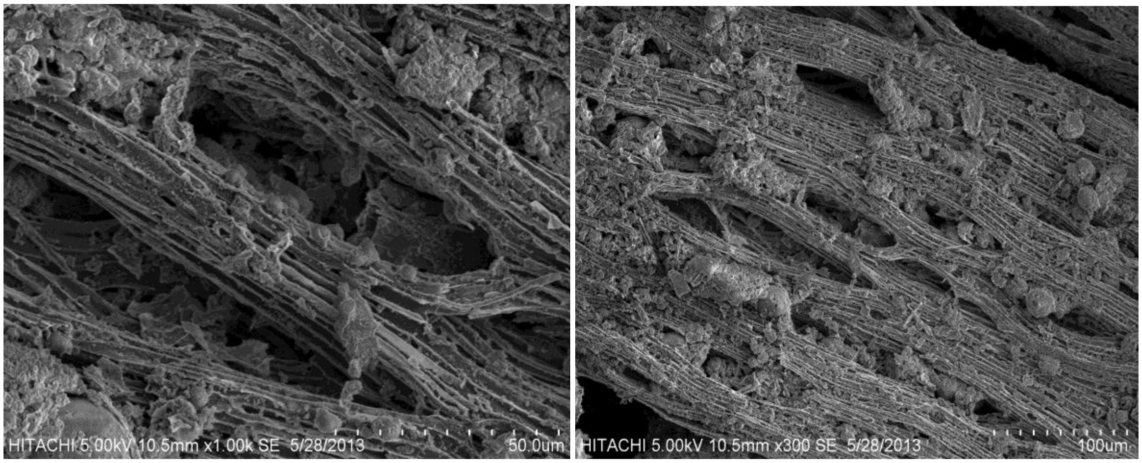

Fig. 1. SEM micrograph of the morphological structure of POFA

In this study, the results obtained from multipoint BET analysis showed that the specific surface area of POFA was found to be 206.6 m^2/g. The results from BJH pore size distribution adsorption analysis for total surface area and pore volume of POFA were 24.8 m^2/g and 0.112 cc/g, respectively. Figure 1 shows SEM micrographs of POFA morphological structure. The SEM analysis confirmed that the morphological structure of POFA was porous in nature. A possible explanation for this is that cellulosic materials of biological origin have systems of interconnecting pores, thus providing a relatively high surface area (Hubbe *et al.* 2011).

EDX analysis was performed in order to identify the major elemental constituents present on the structural surface of POFA. Based on Table 1, the main constituents in POFA were carbon, oxygen, and silicone. Once again, high carbon (26.96 %) and oxygen (49.11 %) contents can be observed, indicating that the POFA itself consists of porous carbon. Apart from that, the high amounts of aluminosilicate compounds in the presence of calcium oxide could assist in providing adequate negatively charged sites for cation exchange reactions to take place with toxic heavy metals present in the aqueous solution during treatment. In addition, the alkaline nature of fly ash itself makes it a good neutralizing agent (Ahmaruzzaman 2010; Bayat 2002; Visa *et al.* 2012). According to Wang *et al.* (2010), the adsorption process and capacity are closely associated with the adsorbent's physical and chemical characteristics such as particles size, pore diameter and quantity, specific surface area, and surface chemical characteristics.

Table 1. Elemental Analysis Before and After Adsorption of Cu(II) onto POFA

Elemental Component	Initial wt. (%)	Final wt. (%)
C	26.96	32.8
O	49.11	42.86
Mg	1.1	1.79
Al	1.41	2.94
Si	12.05	5.16
P	0.82	1.4
Cl	0.38	Null
K	3.41	Null
Ca	4.06	5.68
Fe	0.7	1.8
Cu	Null	5.18
Ta	Null	0.38
Total	100	100

Figure 2 shows the EDX spectrum analysis of POFA before and after the adsorption of Cu(II). The absence of Cu(II) ions was confirmed by EDX spectra before the adsorption of Cu(II) onto POFA (Fig. 2a); however the presence of Cu(II) ions (Fig. 2b) was detected after the adsorption took place. Also, some of the metal cations such as K^+ and Cl^- disappeared from the EDX spectra. It is plausible to suggest that ion exchange mechanism had taken place in the course of the adsorption of Cu(II) onto POFA. These observations indicate that ion exchange may be one of the mechanisms responsible for Cu(II) adsorption by POFA, most likely in combination with other mechanism such as chemisorption, surface adsorption, and diffusion through pores (Demirbas 2008).

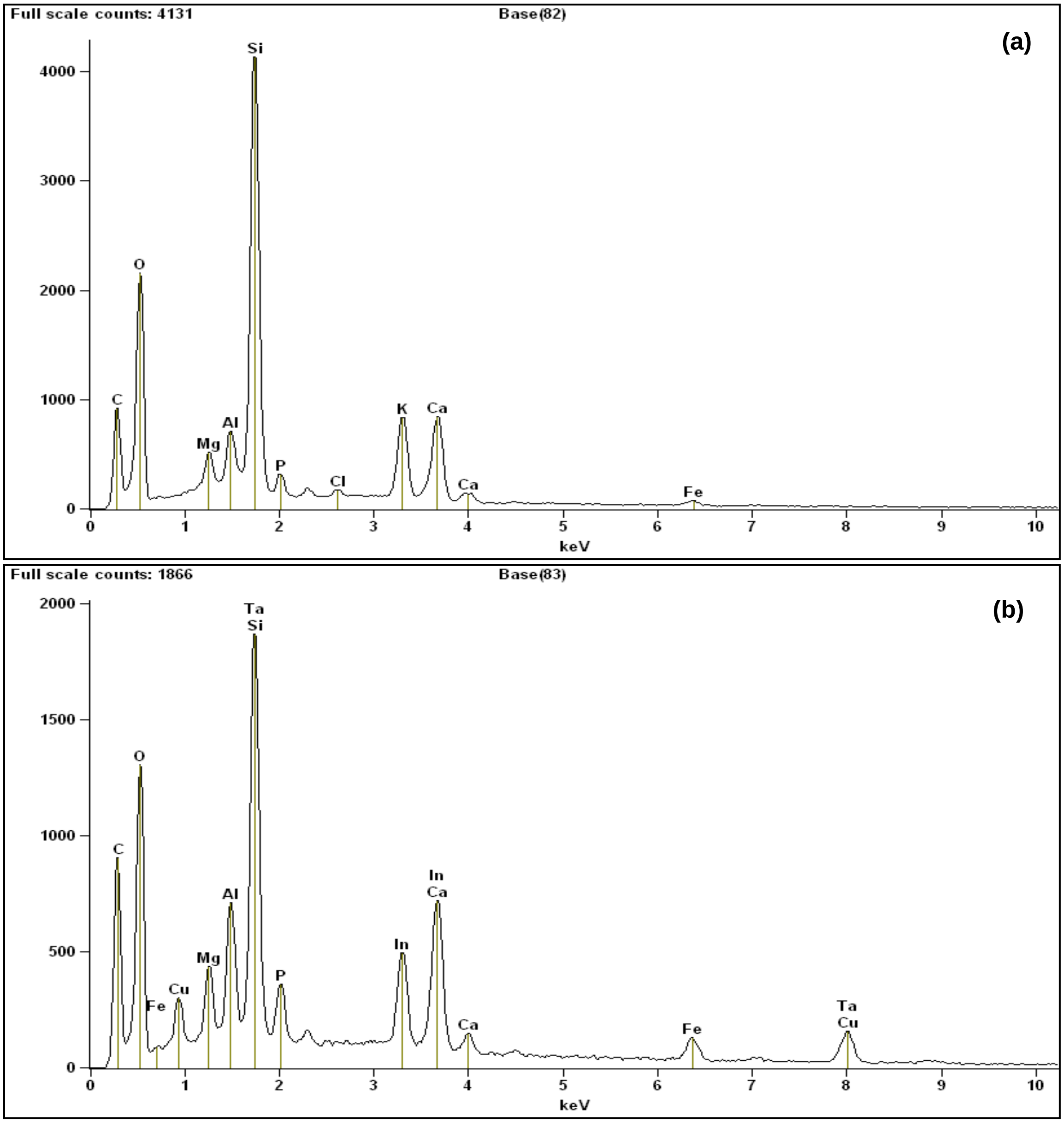

Fig. 2. Energy dispersive X-ray (EDX) spectrum analysis of POFA before (a) and after (b) the adsorption of Cu(II)

Effect of Contact Time

The effect of contact time was evaluated to identify the efficiency of POFA for the removal of Cu(II). It is essential to evaluate the effect of contact time required to reach equilibrium, as a prior stage to the kinetics study of heavy metal adsorption, because in most cases it aids in determining the nature of the process and the required retention time. Moreover, the development of charge on the surface of the adsorbent is usually governed and greatly influenced by contact time. Figure 3 illustrates the effect of contact time on the adsorption capacity and rate of Cu(II) uptake onto POFA.

The majority of the Cu(II) was rapidly removed within the first 30 min of the experiment. Following that, the removal adsorption rate increased at a slower pace corresponding to the contact time, before reaching a plateau value at 270 min; the adsorbed amount can be considered to be constant from that point onwards. From the figure, it is readily apparent that significant removal of the adsorbent occurred within 270 min, and no appreciable changes in terms of removal were noticeable afterwards. Thus, the equilibration time is considered to be 270 min, which is sufficient for the removal of Cu(II) using POFA. The concentration of Cu(II) was reduced from 150 mg/L to 0.192 mg/L after a 270-min contact time. Meanwhile, the amount of Cu(II) adsorbed by POFA from an initial concentration of 150 mg/L after a 270-min equilibration time was 14.98 mg/g.

The adsorption rate was initially high at the beginning of the experiment due to the large number of sites available for the adsorption process. The changes in the rate of removal can be attributed to the decreasing availability of vacant sites on the adsorbent. As a result of Cu II) adsorption onto the adsorbent's binding sites, the vacant sites become occupied, and as contact time increases, more and more functional groups participate in the adsorption of Cu(II), until it reaches equilibrium (Lalhruaitluanga *et al.* 2010). Therefore the equilibration time was set to 270 min in the subsequent experiments, and the data obtained were further used to determine the kinetics of Cu(II) adsorption.

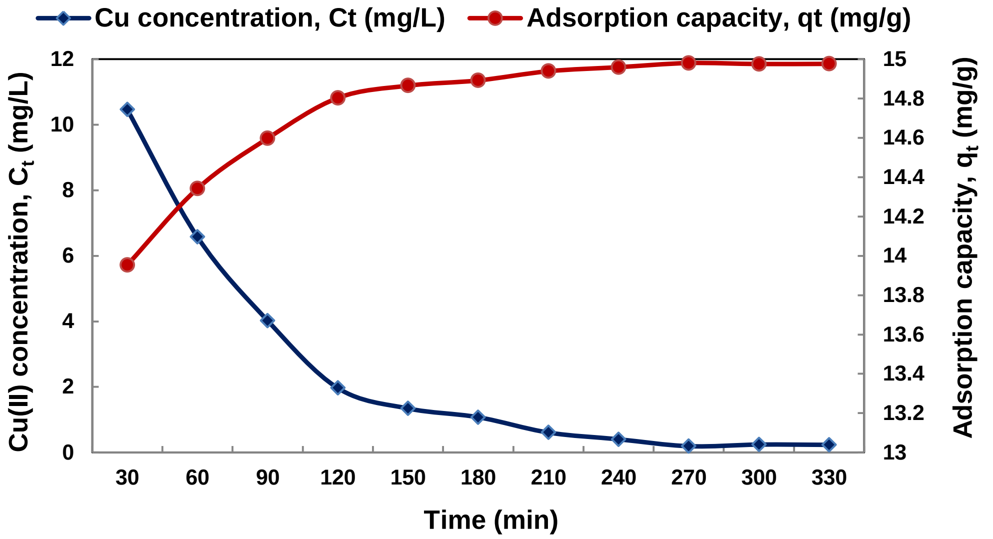

Fig. 3. Effect of contact time on the adsorption of Cu(II) onto POFA

Effect of Solution pH

The removal of Cu(II) from aqueous solution through adsorption is highly dependent on the initial solution pH, which determines the surface charge of the adsorbent, the degree of ionization, and the adsorbate speciation (Cho *et al.* 2005; Pehlivan and Cetin 2008). The effect of pH on the adsorption of Cu(II) onto POFA is shown in Fig. 4 (a). It can be observed that the adsorption capacity increased significantly with the increasing solution pH from 2 to 3. Afterward, the adsorption capacity of POFA increased gradually as the solution pH increased from 3 to 6 and finally a plateau value was obtained between pH value of 6 and 7. The decrease in adsorption rate at very low pH values (2 to 3) can be attributed to the presence of H_3O^+ at high concentration that competes with the Cu(II) ions for negatively charged sites on the adsorbent surface (Ofomaja 2010; Rao *et al.* 2008; Visa *et al.* 2012).

In fact, at the very low pH values, the preferential adsorption favours H_3O^+ over Cu(II) ions, resulting in a reduced of uptake (Ajmal *et al.* 2000). Nevertheless, as the solution pH increases, the electrostatic repulsion between cations and adsorbent surface charge decreases and fewer H_3O^+ ions are available to compete with the Cu(II) ions for active binding sites, allowing the Cu(II) uptake to increase (Khormaei *et al.* 2007; Ofomaja 2010). Similar findings were also reported by Ofomaja (2010) and Demirbas (2009) for the adsorption of copper ion onto palm kernel fibre and hazelnut shell activated carbon, respectively. However, at higher pH value (≥ 6) the adsorption capacity became constant, since copper started to precipitate from solution as $Cu(OH)_2$. This is further justified by the speciation diagram illustrated in Fig. 4(b) (Demirbas 2009). Observation from the diagram shows that the dominant copper species at (pH ≤ 6) is in the form of ionic (Cu^{2+}), which is mainly involved in the adsorption process, causing an increase in the amount of Cu(II) adsorbed (Demirbas 2009).

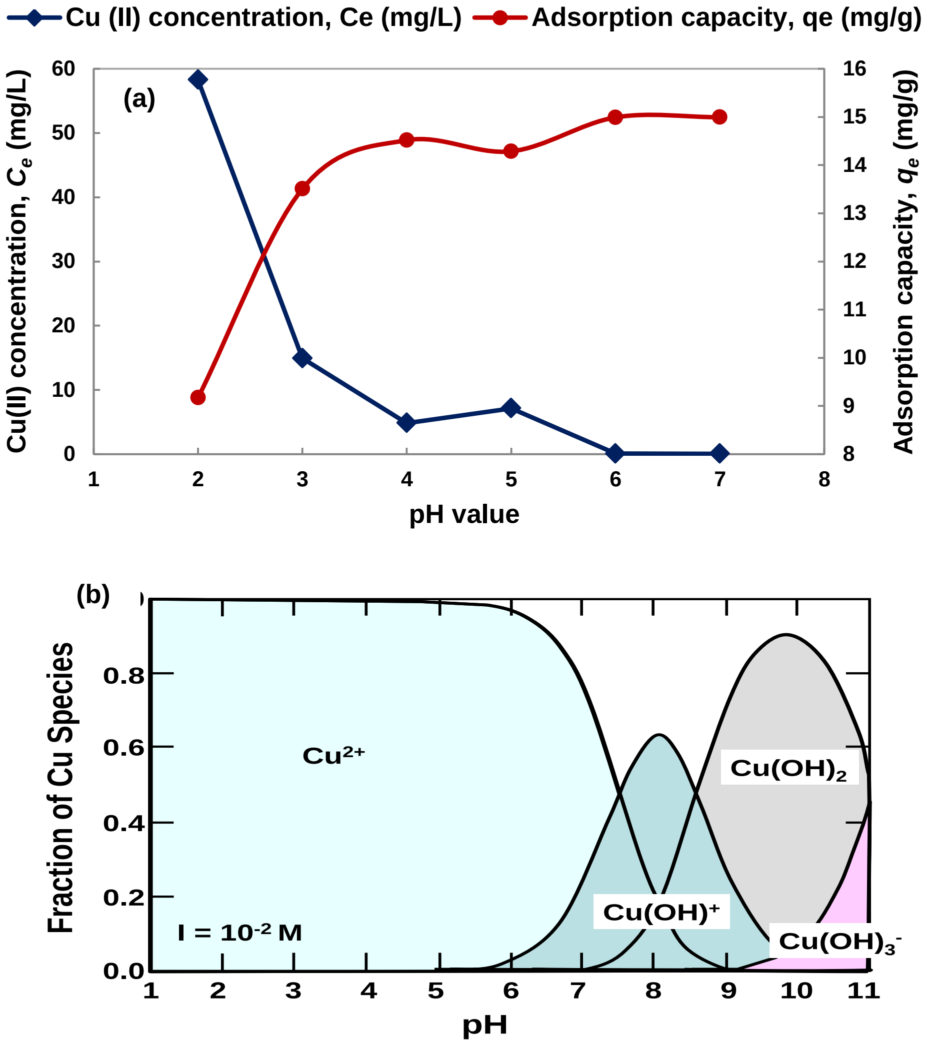

Fig. 4. (a) Effect of pH on the adsorption of Cu(II) onto POFA; and (b) speciation diagram of copper species in aqueous solution as a function of pH (redrawn from Demirbas 2009)

Since POFA also contains abundant alkaline materials such as CaO and MgO, the hydroxide ion (−OH) is eventually liberated during the use of POFA, thus increasing the solution pH during the adsorption process; at sufficiently high pH, this results in the formation of $Cu(OH)_2$ (Pehlivan and Cetin 2008). In spite of that, the main constituents of POFA are metal oxides, mainly of Al, Fe, Mg, and Si. These metal oxides form metal-hydroxide complexes in the solution. The acidic or basic dissociation of these complexes at the solid-solution interface will apparently result in the development of a positive or negative charge on the adsorbent surface that contributed to the increasing of Cu(II) ions uptake (Pehlivan and Cetin 2008). Generally, the interaction mechanisms between Cu(II) ions and POFA are a function of pH that involved adsorption, precipitation, and ion exchange. Therefore, the optimum pH for the removal of Cu(II) using POFA is obtained at pH 6.0, and the subsequent experiments were carried out at this pH value.

Effect of adsorbent dosage

Dosage is an essential parameter in adsorption studies because it determines the capacity of the adsorbent for a given initial concentration of the metal ion solution. Figure 5 shows the effect of adsorbent dosage variation on the removal and adsorption of Cu(II) onto POFA. An increasing trend in the removal efficiency (*RE %*) corresponding to adsorbent dosage was observed. As the adsorbent dosage increased, so did the *RE %*, until it reached a certain dosage, at which the *RE %* became constant and a plateau value was obtained. The *RE %* increased from 0.1 to 1.0 g of dosage; however, a slower removal pace was observed as the adsorbent dosage increased above 1.0 g. The explanation for this is that with a higher adsorbent dosage, there is a greater availability of exchangeable sites for the adsorbate, which exposes more active sites for Cu(II) binding (Babel and Kurniawan 2003).

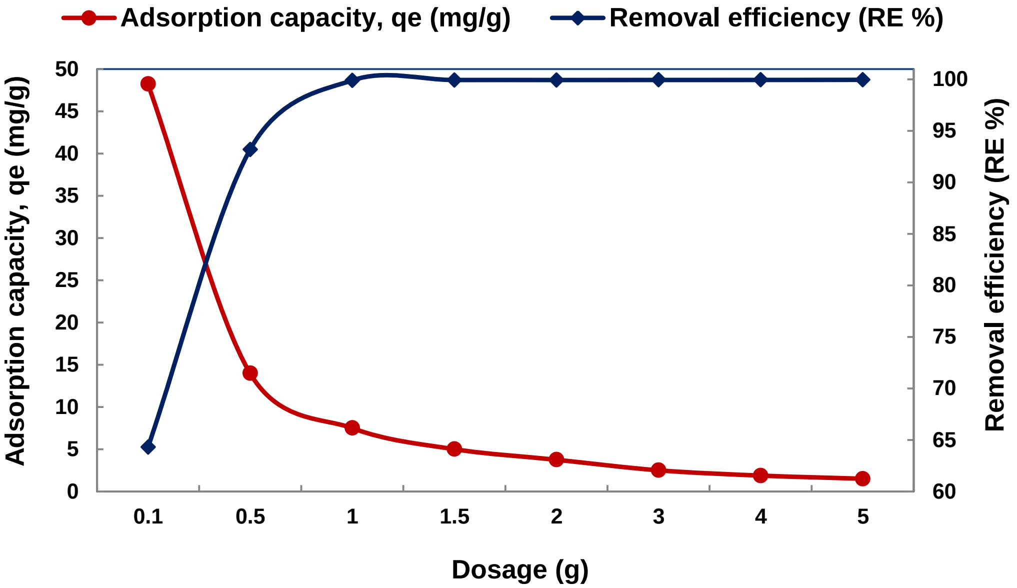

Fig. 5. Effect of adsorbent dosage on the adsorption of Cu(II) onto POFA

Nevertheless, at dosages > 1.0 g, the shift in Cu(II) removal became very low as the surface Cu(II) concentration and the solution Cu(II) concentration reached equilibrium with each other (Naiya *et al.* 2009; Wang *et al.* 2010), resulting in a slower uptake onto POFA. Meanwhile, q_e decreased because the ratio of Cu(II)/POFA decreased with increasing of adsorbent amount. Another reason may be due to particle interactions, such as aggregation, resulting from high adsorbent concentration. Such aggregation could lead to a decrease in the available surface area of the adsorbent (Rao *et al.* 2008; Wang *et al.* 2010).

Effect of Initial Cu(II) Concentration

The effect of initial concentration on the adsorption of Cu(II) onto POFA was investigated with varying solution concentrations (10, 50, 100, 150, and 200 mg/L) using a 0.5 g adsorbent dosage. As expected, based on Fig. 6, the amount of Cu(II) adsorbed at equilibration time and optimum pH shows that with increasing solution concentration, q_e increased while *RE %* decreased. It is apparent from the figure that the removal of Cu(II) was highly concentration-dependent. This is because all adsorbents have a limited number of active sites, which would have become saturated at a certain concentration. The initial Cu(II) concentration provides the driving force to overcome the mass-transfer barrier between the adsorbent and adsorbate medium; hence, a higher initial concentration of metal ions may increase the adsorption capacity.

Similar results were also reported for adsorption of cadmium from aqueous solution (Papandreou *et al.* 2007; Srivastava *et al.* 2008; Wang *et al.* 2010). The Cu(II) uptake mechanism is particularly dependent on the initial concentration; at low initial solution concentrations, the surface area and the availability of adsorption binding sites are relatively high, and the Cu(II) is easily adsorbed and removed. Meanwhile, at higher initial solution concentrations, the total available active sites are limited, thus resulting in a decrease in Cu(II) uptake (Wang *et al.* 2010). The increase in q_e at higher initial concentrations can be attributed to the enhancement of the driving force. The data obtained from investigation of the effects of initial concentration were further used to determine the isotherms of Cu(II) adsorption.

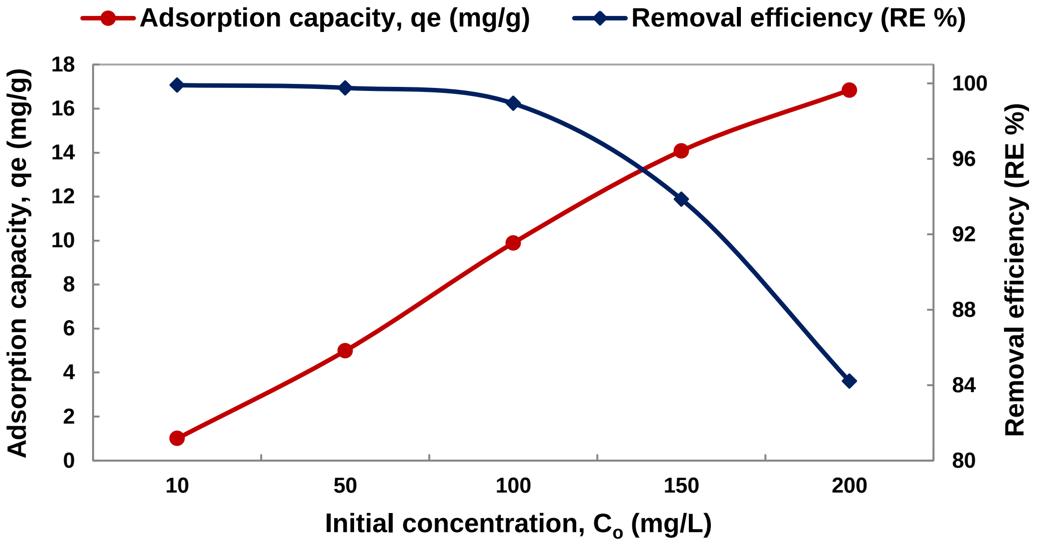

Fig. 6. Effect of initial concentration on the adsorption of Cu(II) onto POFA

Adsorption Isotherms

The equilibrium data were analyzed using Langmuir, Freundlich, and Temkin isotherm models to obtain the most fitting isotherm. The parameters obtained from the isotherm models can be used to explain the structural properties of the adsorbent and the adsorption behavior. The adsorption isotherms of POFA are shown graphically in Fig. 7, and the isotherm parameters are listed in Table 2. All graph plots show a straight line, indicating that the adsorption of Cu(II) could be fit well with all of the isotherm models. However, coefficient of determination (R^2) comparison indicates that the Langmuir isotherm achieved more satisfactory results (R^2 = 0.9971) compared to the Freundlich isotherm (R^2 = 0.9119) and comparable results relative to the Temkin isotherm (R^2 = 0.9961) for adsorption of Cu(II) onto POFA.

The fact that the Langmuir isotherm fit the experimental data very well may be due to the homogeneous distribution of active sites on the POFA surface, as the Langmuir isotherm model assumes monolayer coverage of the adsorbate over a homogenous adsorbent surface. Apart from that, the Langmuir adsorption model is based on the assumption that maximum adsorption corresponds to a saturated monolayer of solute molecules on the adsorbent surface, with no lateral interaction between the adsorbed molecules (Nadeem *et al.* 2006; Wang *et al.* 2010). Meanwhile, Fig. 8 shows that the variation of separation factor (R_L) values fell within the range of 0 to 1, indicating that the adsorption of Cu(II) onto POFA was favorable under the conditions of testing. Also, the fact that the R_L value approached zero with the increasing of C_o demonstrates that the adsorption of Cu(II) onto POFA was less favorable at high initial concentrations. Therefore, the Langmuir isotherm is considered to be adequate for describing the adsorption of Cu(II) onto POFA.

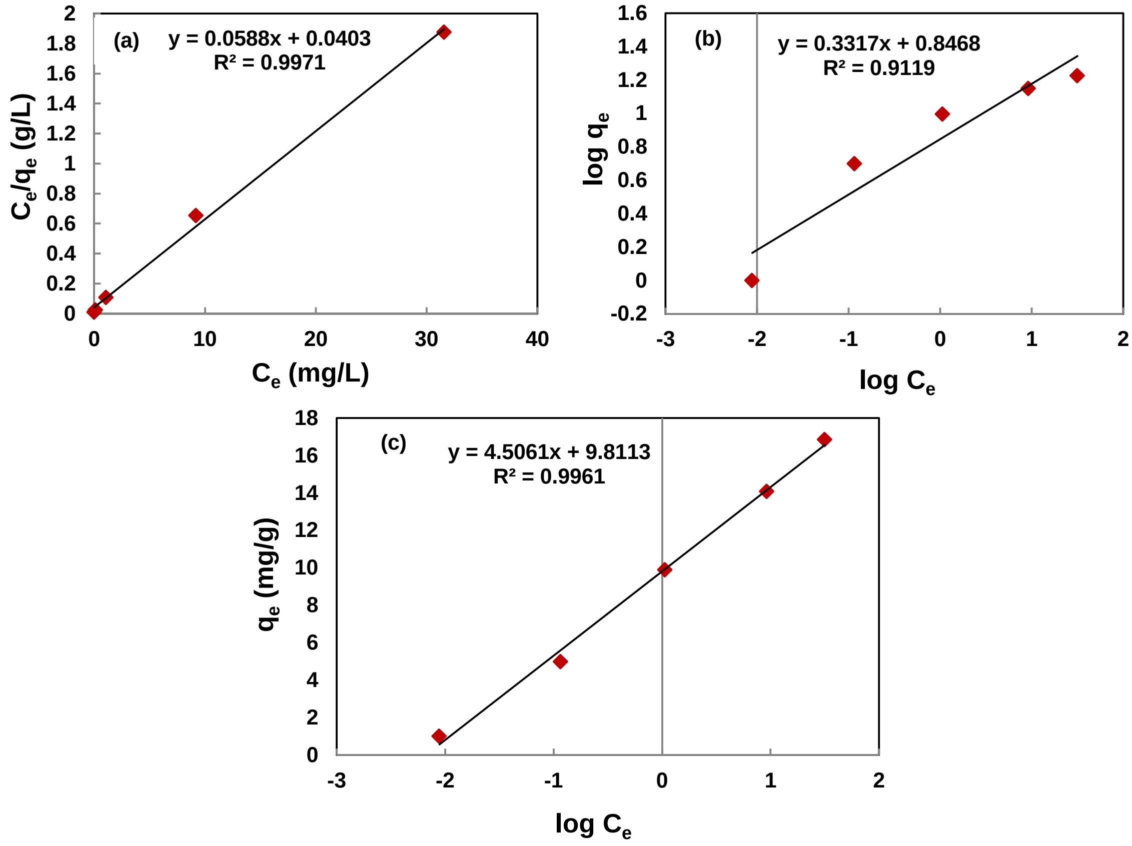

Fig. 7. Linear isotherms for the adsorption of Cu(II) onto POFA: (a) Langmuir, (b) Freundlich, and (c) Temkin

Table 2. Isotherm Model Constants for Adsorption of Cu(II) onto POFA

Isotherm model	Parameters	Values
Langmuir isotherm	q_m (mg/g)	17.0068
	b (L/mg)	1.4591
	R^2	0.9971
Freundlich isotherm	k (mg/g (L/mg)$^{1/n}$)	7.0275
	$1/n$	0.3317
	R^2	0.9119
Temkin isotherm	B (L/mg)	4.5061
	b (J/mol)	559.0515
	k_t (L/mg)	150.431
	R^2	0.9961

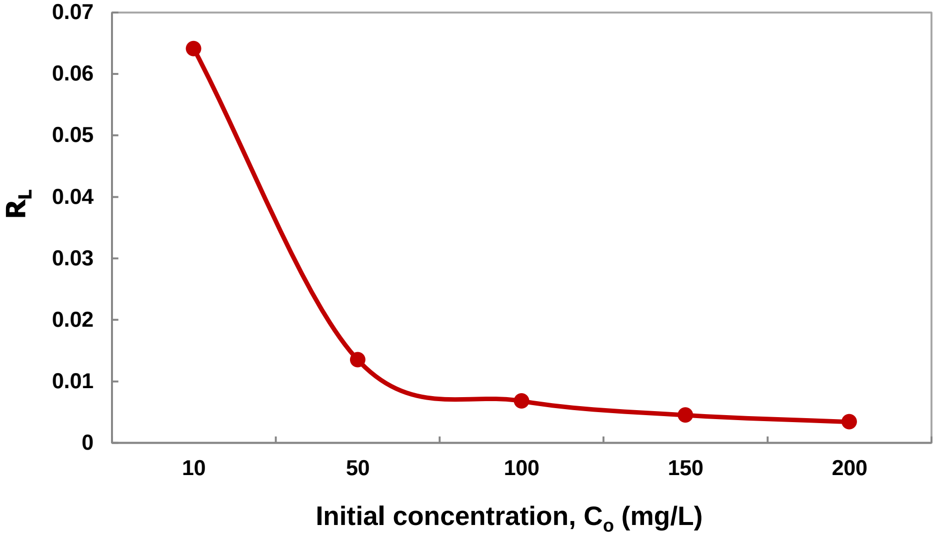

Fig. 8. Plot of R_L against initial Cu(II) concentration

Adsorption Kinetics

The Lagergren's pseudo first-order, the pseudo second-order, and the intraparticle diffusion models were employed to describe the adsorption mechanism of POFA, as illustrated in Fig. 9. The kinetic model rate constants and parameters are listed in Table 3. When the theoretical q_e values obtained from the first-order plots were compared with the experimental q_e values, there were large differences between them, resulting in an almost total rejection of the first-order kinetics. The pseudo second-order model showed better agreement for the theoretical q_e values, with less deviation from the experimental values compared to the pseudo first-order and intraparticle diffusion model. Additionally, the coefficients of determination (R^2) were also closer to satisfactory for the pseudo second-order kinetics (≥ 0.9967) for all initial concentrations compared to the pseudo first-order kinetics (≥ 0.7139) and intraparticle diffusion (≥ 0.7606), which indicates that the adsorption of Cu(II) onto POFA fit the pseudo second-order equation more precisely. From Fig. 10, it can be observed that there was a parallel increase in the variation of the initial adsorption rate at lower initial concentrations ($C_0 \leq 50$ mg/L), but as the initial concentrations increased the adsorption rate decreased to a more stable value. As can be observed from Table 3, it was found that the rate constant, k_2 (min.mg/g) decreased proportionately with the increasing of the initial concentration, which shows very good agreement of the pseudo second-order model at lower Cu(II) concentrations.

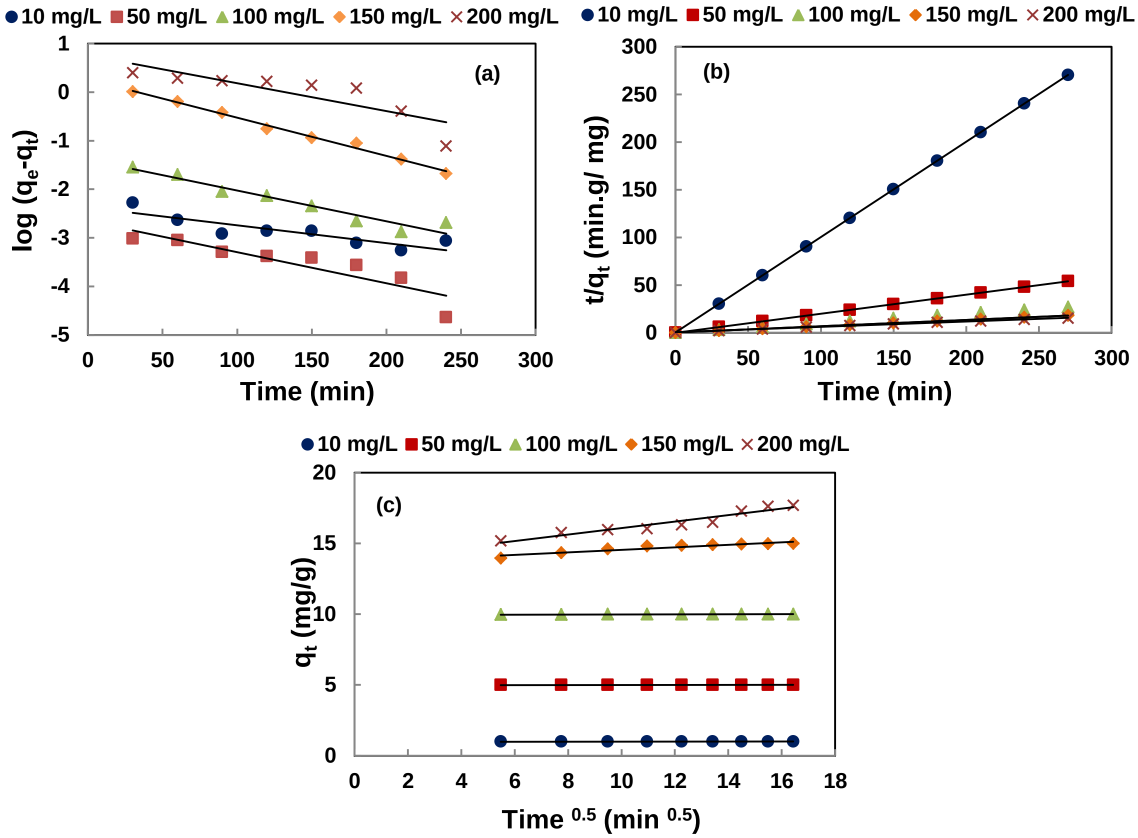

Fig. 9. Kinetics models for the adsorption of Cu(II) onto POFA: (a) Lagergren's pseudo first-order, (b) pseudo second-order, and (c) intraparticle diffusion

Nevertheless, the results obtained through the pseudo second-order model alone are insufficient to predict the diffusion mechanism (Akar *et al.* 2008). Therefore the intraparticle diffusion model was also employed to analyze the adsorption kinetic data. It is well known that the diffusivity of adsorbate is essential in determining the overall adsorption rate. Mainly there are two main types of diffusions processes that are the film diffusion and intraparticle diffusion. The intraparticle diffusion plots may represent multi-linearity in the adsorption process, indicating that two or more steps are operational. The first stage involves the diffusion of the adsorbate through the solution to the external surface of the POFA or also known as the instantaneous adsorption stage. The second stage is the gradual adsorption stage that involves intraparticle diffusion as the rate-controlling parameter due to low solute concentration in the solution (Kumar *et al.* 2007; Zheng *et al.* 2009).

It is plausible to suggest that during the adsorption process, Cu(II) may be initially transported to the macro-, meso-, and then, finally, slowly diffused into the micropores. Similar results were also reported by Kumar *et al.* (2007) for the adsorption of 4-nitrophenol onto activated carbon and by Ofomaja *et al.* (2010) for the biosorption of Pb(II) onto mansonia wood sawdust. Meanwhile, the calculated values of the intraparticle diffusion rate constant (k_{id}) shown in Table 3 indicated that the intraparticle diffusion rate increased in parallel with the initial Cu(II) concentration.

Table 3. Lagergren's Pseudo First-Order, Second-Order, and Intraparticle Diffusion Rate Constants and Parameters at Different Initial Cu(II) Concentrations

C_o (mg/L)	$q_{e,exp}$ (mg/g)	Pseudo 1st order kinetic model			Pseudo 2nd order kinetic model			Intraparticle diffusion model		
		k_1 (min^{-1})	$q_{e,\,calc}$ (mg/g)	R^2	k_2 (min.mg/g)	$q_{e,\,calc}$ (mg/g)	R^2	k_{id} ($\text{mg/g.min}^{1/2}$)	$q_{e,\,calc}$ (mg/g)	R^2
10	0.9985	0.0085	0.0042	0.7705	8.6260	0.9984	1.0000	0.00040	0.9926	0.7606
50	4.9972	0.0147	0.0022	0.8091	25.025	4.9975	1.0000	0.00009	4.9957	0.9668
100	9.9950	0.0145	0.0404	0.9360	1.2500	10.0000	1.0000	0.00250	9.9573	0.8833
150	14.9808	0.0182	1.8323	0.9918	0.0341	15.0602	0.9999	0.08930	13.655	0.8810
200	17.6878	0.0131	5.7346	0.7139	0.0075	17.7936	0.9967	0.22850	13.793	0.9228

An increase in initial concentration produced a higher concentration gradient, which eventually caused the adsorption and diffusion process to become faster (Ofomaja *et al.* 2010). As can be observed from Fig. 9 (c), the plots of q_t versus $t^{0.5}$ yielded a linear relationship that did not pass through the origin. According to Weber and Morris (1963), if the controlling step is intraparticle diffusion, then a plot of solute adsorbed (q_t) against the square root of the contact time ($t^{0.5}$) should yield a straight line passing through the origin.

However, since the intraparticle lines have non-zero intercept, the intraparticle diffusion mechanism is not the sole controlling adsorption mechanism. The adsorption process may also involve some other mechanisms along with the intraparticle diffusion. Therefore, it appears that the system under consideration is more appropriately described by the pseudo second-order model, based on the assumption that the rate-limiting step may be chemical sorption or chemisorption involving valence forces through sharing or exchange of electrons between the adsorbent and the adsorbate with intraparticle diffusion mechanism involve as one of the rate-determining steps (Chowdhury *et al.* 2011; Ofomaja *et al.* 2010; Wang *et al.* 2010).

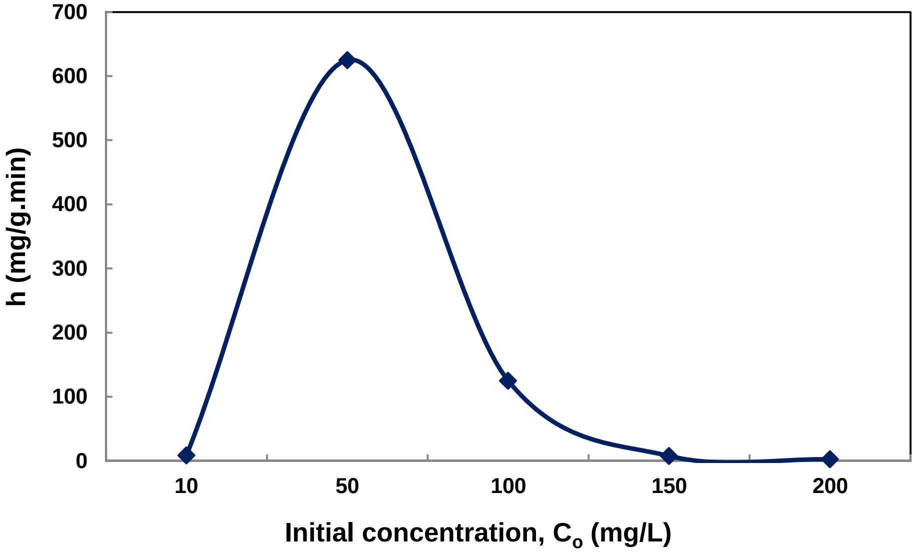

Fig. 10. The variation of the initial adsorption rate with the initial Cu(II) concentration

CONCLUSIONS

1. There was rapid uptake of Cu(II) by palm oil boiler mill fly ash (POFA) in the first 30 min of the adsorption process, and more than 90% of Cu(II) was removed within that period.
2. The adsorption capacity increased slowly with contact time, reaching a plateau value after a contact time of 270 min. Thus, the equilibration time was considered to be 270 min, which was sufficient for the removal of Cu(II) using POFA.

3. The results revealed that the Cu(II) uptake mechanism was highly pH-dependent and adsorption capacity increased with increasing solution pH. The optimum pH for the removal of Cu(II) using POFA was obtained at pH 6.0.

4. A higher dosage of POFA led to an increase in Cu(II) removal efficiency but a decrease in adsorption capacity.

5. It was also found that the Cu(II) uptake mechanism was particularly concentration-dependant.

6. The Langmuir isotherm model fit well for Cu(II) adsorption onto POFA, with maximum adsorption capacity of 17 mg/g.

7. Kinetic models for adsorption onto POFA were best described as pseudo second-order, which was also found to be consistent with chemisorption with intraparticle diffusions mechanism involved in the rate-determining step.

8. In conclusion, fundamental batch adsorption study indicates that POFA has an excellent potential for effective removal of Cu(II) from aqueous solutions. The rapid uptake and high adsorption capacity along with its freely abundant availability of POFA is potentially attractive for use in future practical applications.

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REFERENCES CITED

Ahmad, T., Rafatullah, M., Ghazali, A., Sulaiman, O., and Hashim R. (2011). "Oil palm biomass-based adsorbents for the removal of water pollutants - A review," *Journal of Environmental Science and Health, Part C: Environmental Carcinogenesis and Ecotoxicology Reviews* 29(3), 177-222.

Ahmaruzzaman, M. (2010). "A review on the utilization of fly ash," *Progress in Energy and Combustion Science* 36(3), 327-363.

Ajmal, M., Rao, R. A. K., Ahmad, R., and Ahmad, J. (2000). "Adsorption studies on Citrus reticulate (fruit peel of orange): Removal and recovery of Ni (II) from electroplating wastewater," *Journal of Hazardous Materials* 79(1-2), 117-131.

Akar, T., Ozcan, A. S., Tunali, S., and Ozcan, A. (2008). "Biosorption of a textile dye (Acid Blue 40) by cone biomass of *Thuja orientalis*: Estimation of equilibrium, thermodynamic and kinetic parameters," *Bioresour. Technol.* 99(8), 3057-3065.

APHA, AWWA, WEF (1998). *Standard Methods for the Examination of Water and Wastewater*, 20th ed., American Public Health Association, Washington, DC.

Babel, S., and Kurniawan, T. A. (2003). "Low-cost adsorbents for heavy metals uptake from contaminated water: A review," *Journal of Hazardous Materials* 97(1-3), 219-243.

Bayat, B. (2002). "Combined removal of zinc (II) and cadmium (II) from aqueous solution by adsorption onto high-calcium Turkish fly ash," *Water, Air, and Soil Pollution* 136(1-4), 69-92.

Cho, H., Oh, D., and Kim K. (2005). "A study on removal characteristics of heavy metals from aqueous solution by fly ash," *Journal of Hazardous Materials* 127(1-3), 187-195.

Chowdhury, Z. Z., Zain, S. M., and Rashid, A. K. (2011). "Equilibrium isotherm modeling, kinetics and thermodynamics study for removal of lead from waste water," *E-journal of Chemistry* 8(1), 333-339.

Demirbas, A. (2008). "Heavy metal adsorption onto agro-based waste materials: A review," *Journal of Hazardous Materials* 157(2-3), 220-229.

Demirbas, E., Dizge, N., Sulak, M. T., and Kobya, M. (2009). "Adsorption kinetics and equilibrium of copper from aqueous solutions using hazelnut shell activated carbon," *Chemical Engineering Journal* 148(2), 480-487.

Foo, K. Y., and Hameed, B. H. (2009). "Value-added utilization of oil palm ash: A superior recycling of the industrial agricultural waste," *Journal of Hazardous Materials* 172(2-3), 523-531.

Freundlich, H. M. F. (1906). "Over the adsorption in solution," *J. Phys. Chem*. 57A, 385-470.

Han, R., Zhang, L., Song, C., Zhang, M., Zhu, H., and Zhang, L. (2010). "Characterization of modified wheat straw, kinetic and equilibrium study about copper ion and methylene blue adsorption in batch mode," *Carbohydr. Polym.* 79(4), 1140-1149.

Ho, Y. S., and McKay, G. (1998). "A comparison of chemisorption kinetic models applied to pollutant removal on various sorbents," *Process Saf. Environ. Prot.* 76(4), 332-340.

Hubbe, M. A., Hasan, S. H., and Ducoste, J. J. (2011). "Metal ion sorption: Review," *BioResources* 6(2), 2161-2287.

Khormaei, M., Nasernejad, B., Edrisi, M., and Eslamzadeh, T. (2007). "Copper biosorption from aqueous solutions by sour orange residue," *Journal of Hazardous Materials* 149(2), 269-274.

Kumar, A., Kumar, S., Kumar, S., and Gupta, D. V. (2007). "Adsorption of phenol and 4-nitrophenol on granular activated carbon in basal salt medium: Equilibrium and kinetics," *Journal of Hazardous Materials* 147(1-2), 155-166.

Lagergren, S. (1898). "About the theory of so called adsorption of soluble substances, kungliga svenska vetenskapsakademiens," *Handlingar, Band*. 24(4), 1-39.

Langmuir, I. (1916). "The constitution and fundamental properties of solids and liquid," *Journal of the American Chemical Society* 38(11), 2221-2295.

Larous, S., Meniai, A. H., and Lehocine, M. B. (2005). "Experimental study of the removal of copper from aqueous solutions by adsorption using sawdust," *Desalination* 185(1-3), 483-490.

Lalhruaitluanga, H., Jayaram, K., Prasad, M. N. V., and Kumar, K. K. (2010). "Lead (II) adsorption from aqueous solutions by raw and activated charcoals of *Melocanna baccifera* Roxburgh (bamboo) - A comparative study," *Journal of Hazardous Materials* 175(1-3), 311-318.

Mohamed, A. R., Lee, K. T., Noor, N. M., and Zainudi, N. F. (2005). "Oil palm ash $Ca(OH)_2CaSO_4$ absorbent for flue gas desulfurization," *Chem. Eng. Technol.* 28(8), 939-945.

Mohamed, A. R., Zainudin, N. F., Lee, K. T., and Kamaruddin, A. H. (2006). "Reactivity of absorbent prepared from oil palm ash for flue gas desulfurization: Effect of SO_2 concentration and reaction temperature," *Stud Surf Sci Catal* 159, 449-452.

Nadeem, M., Mahmood, A., Shahid, S. A., Shah, S. S., Khalid, A. M., and McKay, G. (2006). "Sorption of lead from aqueous solution by chemically modified carbon adsorbents," *Journal of Hazardous Materials* 138(3), 604-613.

Naiya, T. K., Bhattacharya, A. K., and Das, S. K. (2009). "Adsorption of Cd (II) and Pb (II) from aqueous solutions on activated alumina," *Journal of Colloid and Interface Science* 333(1), 14-26.

Ofomaja, A. E. (2010). "Equilibrium studies of copper ion adsorption onto palm kernel fibre," *Journal of Environmental Management* 91(7), 1491-1499.

Ofomaja, A. E. (2010). "Intraparticle diffusion process for lead (II) biosorption onto mansonia wood sawdust," *Bioresour. Technol.* 101(15), 5868-5876.

Papandreou, A., Stournaras, C. J., and Panias, D. (2007). "Copper and cadmium adsorption on pellets made from fired coal fly ash," *Journal of Hazardous Materials* 148(3), 538-547.

Pehlivan, E., and Cetin, S. (2008). "Application of fly ash and activated carbon in the removal of Cu^{2+} and Ni^{2+} ions from aqueous solutions," *Energy Sources, Part A: Recovery, Utilization, and Environmental Effects* 30(13), 1153-1165.

Popuri, S. R., Vijaya, Y., Boddu, V. M., and Abburi, K. (2009). "Adsorptive removal of copper and nickel ions from water using chitosan-coated PVC beads," *Bioresour. Technol.* 100(1), 194-199.

Rao, M. M., Ramesh, A., Rao, G. P. C., and Seshaiah, K. (2006). "Removal of copper and cadmium from the aqueous solutions by activated carbon derived from *Ceiba pentandra* hulls," *Journal of Hazardous Materials* 129(1-3), 123-129.

Rao, M. M., Rao, G. P., Seshaiah, K., Choudary, N. V., and Wang, M. C. (2008). "Activated carbon from *Ceiba pentandra* hulls, an agricultural waste, as an adsorbent in the removal of lead and zinc from aqueous solution," *Waste Management* 28(5), 849-858.

Salam, O. E. A., Reiad, N. A., and ElShafei, M. M. (2011). "A study of the removal characteristics of heavy metals from wastewater by low-cost adsorbents," *Journal of Advanced Research* 2(4), 297-303.

Sud, D., Mahajan, G. and Kaur, M. P. (2008). "Agricultural waste material as potential adsorbent for sequestering heavy metal ions from aqueous solutions - A review," *Bioresour. Technol.* 99(14), 6017-6027.

Srivastava, V. C., Mall, I. D., and Mishra, I. M. (2008). "Removal of cadmium(II) and zinc(II) metal ions from binary aqueous solution by rice husk ash," *Colloids Surf A: Physicochem Eng. Aspects* 312(2-3), 172-184.

Temkin, M. J., and Pyzhev, V. (1940) "Recent modifications to Langmuir isotherms," *Acta Physiochim USSR.* 12, 217-222.

Visa, M., Isac, L., and Duta, A. (2012). "Fly ash adsorbents for multi-cation wastewater treatment," *Applied Surface Sciences* 258(17), 6345-6352.

Wang, F. Y., Wang, H., and Ma, J. W. (2010). "Adsorption of cadmium (II) ions from aqueous solution by a new low-cost adsorbent - Bamboo charcoal," *Journal of Hazardous Materials* 177(1-3), 300-306.

Weber, W. J., and Morris, J. C. (1963). "Kinetics of adsorption on carbon from solution," *J. Sanit. Eng. ASCE* 89(SA2), 31-59.

Yoshizaki, T., Shirai, Y., Hassan, M. A., Baharuddin, A. S., Abdullah N. M. R, Sulaiman A., and Busu, Z. (2012). “Economic analysis of biogas and compost projects in a palm oil mill with clean development mechanism in Malaysia,” *Environment, Development and Sustainability* 14(6), 1065-1079.

Zainudin, N. F., Lee, K. T., Kamaruddin, A. H., Bhatia, S., and Mohamed, A. R. (2005). “Study of adsorbent prepared from oil palm ash (OPA) for flue gas desulfurization,” *Separ Purif Technol* 45(1), 50-60.

Zheng, H., Liu, D., Zheng, Y., Liang, S., and Liu, Z. (2009). “Sorption isotherm and kinetic modeling of aniline on Cr-bentonite,” *Journal of Hazardous Materials* 167(1-3), 141-147.

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