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Equilibrium studies and dynamic behavior of cadmium adsorption by palm oil boiler mill fly ash (POFA) as a natural low-cost adsorbent

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ABSTRACT

The highlight of this study is the adsorption properties and characterization of palm oil boiler mill fly ash (POFA) as a natural low-cost adsorbent for the removal of Cd(II) from aqueous solution. An array of batch adsorption studies has been done with the effects demonstrated by relevant parameters such as contact times, solution pH, adsorbent dosage, and initial Cd(II) concentration to investigate POFA performance. Energy-dispersive X-ray (EDX) analysis has shown that the structural surface of POFA containing porous carbon and revealing ion exchange may serve as one of the major mechanisms accountable for Cd (II) adsorption onto POFA. Fundamental batch investigations have implied that 80% of Cd (II) was removed in the first 30 min reaching equilibration, after only going through the process of agitation for 210 min. The Cd(II) uptake mechanism is specifically pH and concentration dependant with pH 7 being the optimum reading. A decreased adsorption capacity with an increased Cd(II) removal efficiency was obtained as the adsorbent dose increased. The experimental data adhered to the pseudo-second-order kinetics, which further confirms chemisorptions. The adsorption behavior of Cd(II) fits appropriately and accurately with the Langmuir isotherm model with maximum monolayer adsorption capacity of 15.82 mg/g. Therefore, it is illustrated by this study that POFA could be used effectively as a natural low-cost adsorbent for Cd(II) removal from aqueous solutions.

Keywords: Adsorption mechanism; Cadmium; Dynamic behavior; Energy-dispersive X-ray (EDX) analysis; Kinetic studies; Palm oil boiler mill fly ash (POFA)

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1. Introduction

Pollutants which are considered to be responsible for the most severe health problem to the public are inappropriately discharged heavy metals [1]. It is established that the higher concentration of heavy metals can pose severe health detriment due to their toxic levels, non-biodegradable, and persistent nature, particularly when their amount has surpassed the permissible limits [2]. Cadmium (Cd) is a type of metal known to be toxic as it contains carcinogenic characteristics and unidentified biological function to human health [3]. Cd is found extensively in the municipal sewage, other than in the

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effluents of battery fluid discharge, fertilizers, electronic components, and cadmium-containing piping systems. The limit allowed for Cd in drinking water is 0.005 mg/L in line with the guideline value recommended by the World Health Organization [4]. Research on toxic indicates that in the long run, the effects from Cd poisoning can damage the kidney and alter the constitution of the bone, liver, and blood, whereas the short-term effects include nausea, vomiting, diarrhea, and cramps [2,5].

To date, different technologies of treatment are available for the removal of metals, which contain effluents. More common methods namely chemical precipitation, coagulation, reverse osmosis, ion exchange, membrane filtration, oxidation, air stripping, and adsorption have been adopted in various wastewater treatments [2,6,7]. Nonetheless, of these numerous cleanup techniques, adsorption techniques become prominent as a more superior and promising technique due to the fact that they require low energy, the design is simple and that they are very effective in treating effluents, either with high solute loadings or dilute concentrations [3,8]. Heavy metal adsorption using conventional adsorbents such as commercialized activated carbon has been very popularly used in many applications as an effective adsorbent. Nevertheless, the costly activation process is undeniably a major drawback and thus restraining its usage [9–11].

Therefore, a change to natural low-cost adsorbents particularly using agricultural lignocellulosic by-products serves as an innovative solution, which is efficient and economical in nature. These lignocellulosics by-products would be the most practical, since these materials are cheap, not dangerous, easy to be found, and come in abundance in its natural environment [10]. Oil palm, or scientifically named *Elaeis guineensis,* is the most significant species in *Elaeis* genus, which belongs to the Palmae family [12]. While traditionally being indigenous to West Africa, now this plant can be located in tropical areas throughout the world. Through time, it thrives as the most important industrial crops especially in South East Asia countries namely Malaysia, Indonesia, and Thailand. In 2006, Malaysia was named the second largest producer of palm oil with 15.88 million tonnes or 43% of the total world supply [13].

In general, the large quantities of biomass generated from the oil palm industry can explain a severe environmental problem if the materials fail to be utilized properly [14]. Malaysia itself produces approximately four million tons potential palm oil ash [15] annually. Palm oil boiler mill fly ash (POFA) is produced after the oil palm fiber combustion and shell as boiler fuel to generate steam for palm oil mill consumption [16]. As another approach, the material's added value, POFA could be transformed into a natural low-cost absorbent for the removal of heavy metals to be used in diverse industrial applications [6,14,16]. To add, the abundant and cheap supply of the biomass materials will further bring justification to its usage.

This current work will shed light on the POFA utilized to remove Cd(II) from aqueous solutions. Here, no modification was made to the adsorbent for mitigating the cost and energy consumption for the whole treatment process. This paper carries the objective of examining the performance and adsorption mechanism of POFA as a natural low-cost adsorbent. Fundamental batch adsorption experiments were carried out to characterize and model the adsorption equilibrium of Cd(II) onto POFA under different experimental conditions, namely contact time, solution pH, adsorbent dosage, and initial Cd(II) concentrations. Also, the kinetic and experimental data for the adsorption studies and the Energy dispersive X-ray (EDX) analyses were applied to establish and further describe the adsorption mechanism and dynamic behavior of Cd(II) onto the POFA.

2. Materials and methods

2.1. Preparation and characterization of POFA

POFA was chosen in this study, as a natural low-cost adsorbent for the removal of Cd(II) from aqueous solution. The POFA was supplied by LCSB Lepar Oil Palm Mill and later was oven dried using (Memmert UFE 500 oven) at 250°C for 24 h and stored in desiccators before being used. To ascertain the physical surface characteristic of POFA, the Brunauer–Emmette–Teller (BET) and Barrett–Joyner–Halenda (BJH) method analysis was employed to determine the specific surface area and pore size distribution using Quantachrome instruments version 2.01. A scanning electron microscopy (Hitachi model S-3400N) together with an EDX analyzer was used to retrieve the morphological surface images and distinguish the elemental composition in the POFA, pre- and post-adsorption.

2.2. Chemicals and reagents preparations

The entire chemicals used in the study were of analytical grade and supplied by Fisher Scientific (Malaysia) and Merck (India). Stock solution of Cd(II) with a concentration of 1000 mg/L was prepared by dissolving cadmium nitrate tetrahydrate $Cd(NO_3)_2{\cdot}4H_2O$, in deionized water (water resistivity > 18.2 Mohms cm at 27°C; Millipore Corp, USA). The preferred range of Cd(II) was diluted with deionized water to get working solutions from 10 to 200 mg/L Cd (II) concentrations by making fresh dilutions for each experiment batch. Nitric acid (0.1 M HNO_3) and sodium hydroxide (0.1 M NaOH) were used to adjust the desired pH values throughout the experiments.

2.3. Batch adsorption studies

The adsorption mechanism of Cd(II) was determined through several batch adsorption experiments. All the experiments were equilibrated using an orbital shaker (Model: Stuart, USA 301) at 200 rpm to attain homogenous mixing, and the experiments had been carried out at constant room temperature (30 ± 1℃). Several batch experiments with a variation of target variables were carried out to delineate the mechanism and optimum conditions of Cd(II) adsorption using POFA. The first experiment was to analyze the effect of adsorbent equilibrium contact time. Cd(II) solution (50 mL, 150 mg/L) and 0.5 g of POFA were added into the conical flasks and then agitated at 200 rpm with different interval contact times between 30 and 300 min.

Determination of the effect of solution pH using a pH meter is the aim of the second experiment (Model: Orion 2 star bench top pH meter). The pH values of Cd(II) solutions were adjusted manually from 3.0 to 8.0 assisted by HNO_3 (0.1 M) or NaOH (0.1 M) solutions. Then, Cd(II) solutions (50 mL, 150 mg/L) and 0.5 g of POFA were added into the conical flasks and then agitated at 200 rpm for a pre-determined equilibrium contact time. The third experiment was to study the usage of multiple adsorbent dosages. Different dosages of POFA ranging from 0.1 to 5.0 g were added into the conical flasks containing Cd(II) solution (50 mL, 150 mg/L) and then agitated at 200 rpm at a pre-determined contact time and pH.

The fourth experiment seeks to look into the isotherm and the effect of initial Cd(II) concentrations. Cd(II) solution at concentrations of 10, 50, 100, 150, and 200 mg/L was prepared, and the procedures adopted in the experiment done earlier were replicated. All solution samples were separated from the adsorbent using a 0.45-μm nylon syringe filter. Cd (II) concentration was analyzed using an inductively coupled plasma mass spectrometry (PerkinElmer, ICP-MS ELAN DRC-e). Each solution was preserved via acidification using concentrated HNO_3 and stored at 4℃ before the analysis. Control experiments were also done using similar procedures without the POFA being existent. All methods were modified from the standard methods for examining both water and wastewater [17], and the batch experiments were conducted in triplicate to ensure that the findings are precise and consistent.

2.4. Removal efficiency and adsorption 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 based on the equations that follow,

$$\text{RE}\ \% = \frac{C_0 - C_e}{c_o} \times 100 \tag{1}$$

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

$$q_e = \frac{C_0 - C_t}{m} \times V \tag{3}$$

where C_0 and C_e (mg/L) are the adsorbate concentrations of Cd(II) initially and at equilibrium, respectively, and C_t (mg/L) is the concentrations of adsorbates at time. V is the volume of the solution (L) and m is the mass of dry adsorbent used (g).

2.5. Kinetic studies

In an adsorption process, kinetic study is vital because it dwells into the uptake rate of adsorbate and controls the residual time for the entire adsorption process [18]. The adsorption kinetics of Cd(II) onto POFA was determined using identical procedures that were adopted in the batch adsorption studies. The Lagergren's pseudo-first-order and pseudo-second-order kinetic models have been chosen in this study to describe the adsorption process. Lagergren's pseudo-first order dictates that adsorption is preceded by diffusion through a boundary [19]. The Lagergren's equation for first-order kinetics can be expressed as such:

$$\log\,(q_e - q_t) = \log\,(q_e) - \frac{k_1}{2.303}t \tag{4}$$

where q_t is the amount of adsorbate adsorbed (mg/g) at time (min) and k_1 is the rate constant (min^{-1}). The Lagergren's first-order rate constants k_1 and q_e are calculated from the intercept and slope by plotting log ($q_e - q_t$) vs. t (min). In the meantime, the pseudo-second-order kinetics can be written as [20]:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{5}$$

where k_2 (min mg/g) is the rate constant of the pseudo-second-order adsorption and can be determined in an experimental manner from the slope and intercept of plot t/q_t vs. t (min).

2.6. Sorption isotherm models

It is the aim of adsorption isotherms to reveal the specific relation between the equilibrium concentration of adsorbate in bulk and adsorbed amount at the surface. The adsorption equilibrium data of Cd(II) onto POFA were analyzed with respect to Langmuir, Freundlich and Temkin isotherm models. The Langmuir adsorption model [21] assumes that maximum adsorption corresponds to a saturated monolayer of solute molecules on the adsorbent surface, with no lateral interaction formed between the adsorbed molecules. The linear form of Langmuir isotherm model is obtained from the following equation:

$$\frac{C_e}{q_e} = \frac{1}{q_m b} + \frac{C_e}{q_m} \tag{6}$$

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) in relation to the adsorption rate. The Langmuir constants q_m and b can be calculated from the slope and intercept of the linear plot, with C_e/q_e vs. C_e.

The effect of isotherm shape whether or not it is favorable, for a Langmuir type adsorption process, can also be expressed in terms of a dimensionless constant separation factor or equilibrium parameter, R_{L}, which was calculated using the following equation:

$$R_{\mathrm{L}} = \frac{1}{1 + bC_0} \tag{7}$$

where b is the Langmuir isotherm constant and C_0 is the initial concentration of Cd(II). The value of R_{L} indicates the type of the isotherm to be either unfavorable ($R_{\mathrm{L}} > 1$), linear ($R_{\mathrm{L}} = 1$), favorable ($0 < R_{\mathrm{L}} < 1$), or irreversible ($R_{\mathrm{L}} = 0$).

The Freundlich isotherm [22] can be applied for non-ideal adsorption on heterogeneous surfaces and multilayer adsorption. The Freundlich isotherm equation can be written in the linear form as follows:

$$\log q_e = \log k + \frac{1}{n} \log C_e \tag{8}$$

whereas k and n are Freundlich constants with k [(mg/g (L/mg)$^{1/n}$] being the adsorption capacity of the adsorbent, and n indicates the favorability of the adsorption process. Values of $n > 1$ represent a favorable adsorption condition. The Freundlich constants k and n could be calculated from the slope and intercept of the linear plot, with $\log q_e$ vs. $\log C_e$.

Temkin isotherm model also deals with the consequences of certain indirect adsorbate or adsorbate interaction. It is assumed by this isotherm that the adsorption heat of all the molecules in the layer decreases linearly with coverage, owing to the interactions between adsorbent and adsorbate and that the adsorption is characterized by a uniform distribution of binding energies, up to some maximum binding energy [23]. The linear form of Temkin isotherm can be expressed as:

$$q_e = B \log k_t + B \log C_e \tag{9}$$

where $B = RT/b$, b is the Temkin constant related to the heat of adsorption (J/mol), R is the universal gas constant (8.314 J/mol K), and T is the absolute temperature (273.15 K). $1/b$ indicates the adsorption potential of the adsorbent while k_t (L/mg) is the equilibrium binding constant that corresponds to the maximum binding energy. The intercept of q_e vs. $\log C_e$ from the graph allows for the determination of isotherm constants k_t and B.

3. Results and discussion

3.1. POFA characteristics

The palm oil empty fruit bunch (EFB) incineration to obtain its ash is a common practice in various oil palm mills nowadays. Ash is often available as an underutilized waste product of the combustion of lignocellulosic materials [24]. In general, all fly ash has the same fundamental chemical elements, but only in varying proportions [25]. Research highlights that oil palm ash evidently contains high level of alumina, calcium, potassium, and silica that could be utilized to synthesize active compounds, which are responsible for the sorption of pollutant gasses into the absorbent [15,26]. Thus, it is possible to believe that these similar compounds could also be useful for the adsorption of heavy metals in aqueous solution.

In this study, the results derived from the multipoint BET analysis have shown that the specific surface area of POFA was found to be 206.577 m^2/g. Meanwhile, the results from the BJH pore size distribution adsorption analysis for the total surface area and pore volume of POFA were to be 24.726 m^2/g and 0.112 mL/g, respectively. By way of explanation, the cellulosic materials of the biological origin contain pore interconnecting systems, thus giving a relatively high surface area [24]. Fig. 1 graphically illustrates the SEM images of the POFA morphological structure, which confirms its porosity. Meanwhile, the spectral imaging distribution of carbon (Fig. 2(a)), oxygen (Fig. 2(b)), and silicone (Fig. 2(c)) on the structural surface of POFA and also signals of Cd(II) distribution can be observed in the Cd-loaded POFA post-adsorption (Fig. 2(d)).

An EDX analysis was conducted to identify the presence of the major elemental constituent on the structural surface of the POFA. Based on Table 1, the main constituents in POFA are carbon, oxygen, and silicone. Again, high carbon (26.96%) and oxygen (49.11%) contents can be observed, hinting at the fact that the structure of POFA itself consists of porous carbon. Also, the high amounts of aluminosilicates compounds in the presence of calcium oxide could facilitate in the provision of sufficient negatively charged sites for cation exchange reactions to take place, with toxic heavy metals present in aqueous solution as the treatment takes place. Moreover, the alkaline nature of fly ash has rendered itself a good neutralizing agent [27]. Wang et al. point out that the adsorption process and capacity are closely linked with adsorbents' physical and chemical characteristics such as particles size, pore diameter and quantity, specific surface area, and surface chemical characteristics [3].

The EDX spectrum analyses of POFA before and after the adsorption of Cd (II) can be referred in Fig. 3.

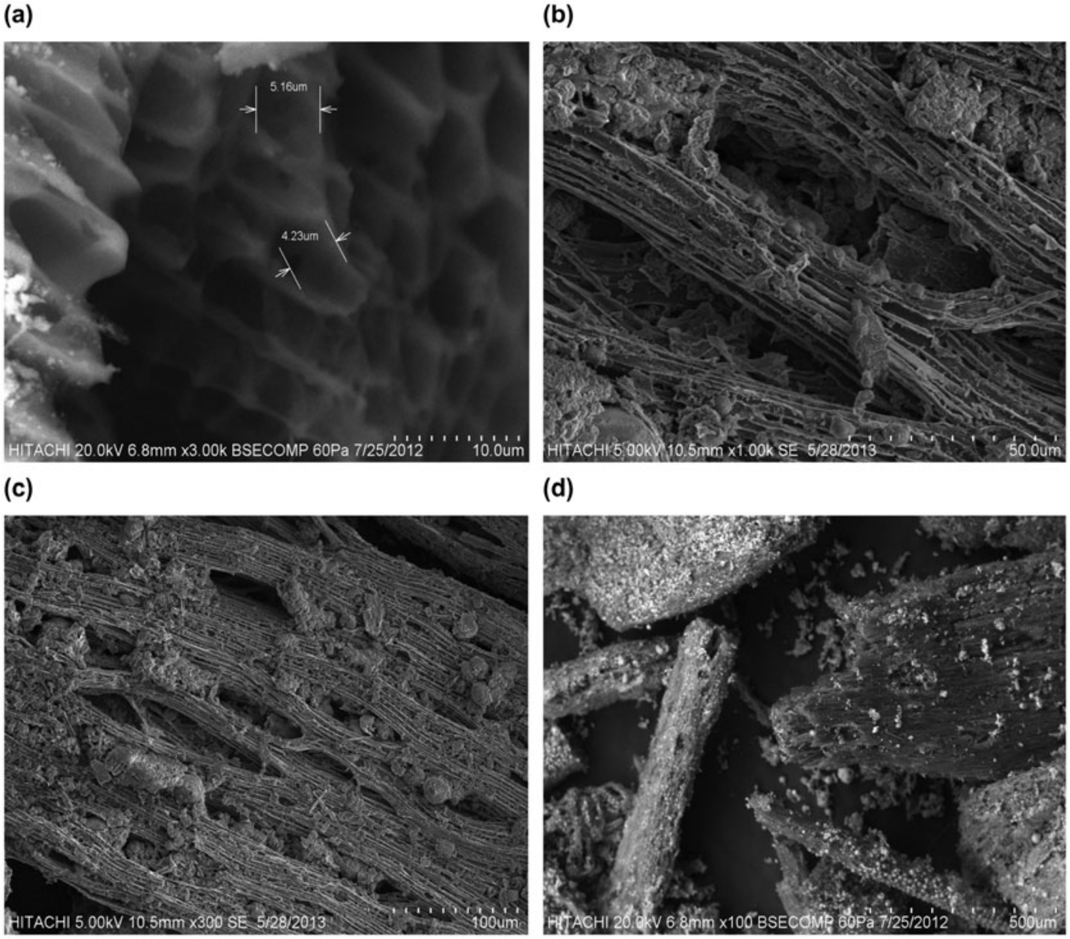

Fig. 1. Scanning electron micrographs of the POFA morphological structure at different spatial resolutions: 10 μm (a), 50 μm (b), 100 μm (c), and 500 μm (d).

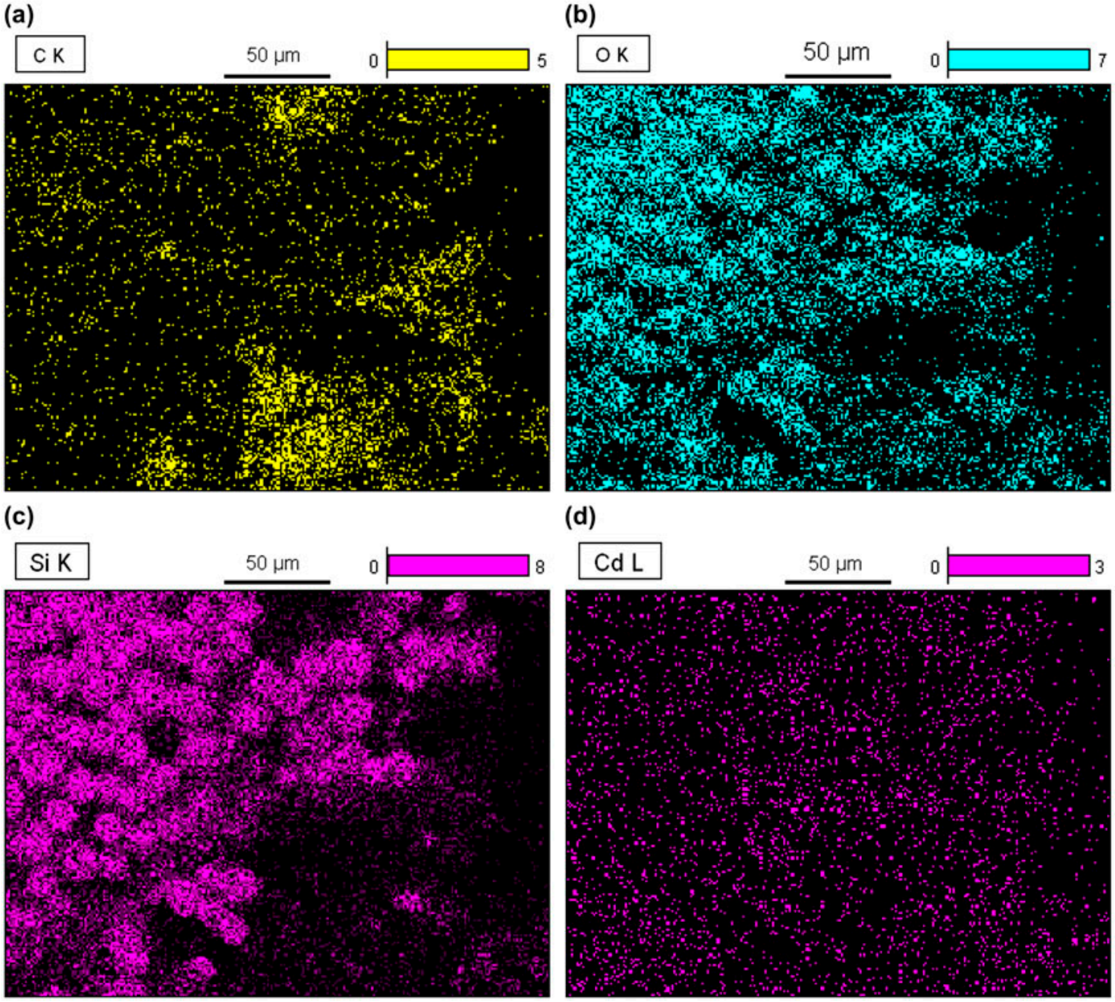

Fig. 2. Spectral imaging distribution of carbon (a), oxygen (b), silicone (c), and cadmium (d) on the structural surface of POFA after the adsorption of Cd(II).

Table 1
Elemental analysis before and after the adsorption of Cd (II) onto POFA

Elemental component	Initial wt. (%)	Final wt. (%)
C	26.96	23.82
O	49.11	52.26
Mg	1.1	1.17
Al	1.41	1.05
Si	12.05	14.67
P	0.82	1.29
Cl	0.38	Null
K	3.41	Null
Ca	4.06	3.7
Fe	0.7	Null
Cd	Null	2.06
Total	100	100

The non-appearance of Cd(II) ions was confirmed by the EDX spectra before the adsorption of Cd(II) onto POFA; yet, the presence of Cd(II) was detected after the adsorption had taken place. Also, some metal cations such as K^+ and Fe^{2+} had gone from the EDX spectra. We can thus reasonably suggest that the ion exchange mechanism had taken place throughout the Cd(II) adsorption onto POFA. A clear indication is that the ion exchange is a potential mechanism responsible for Cd (II) adsorption by POFA, superior to other mechanisms such as chemisorption, surface adsorption, and diffusion through pores [10].

3.2. Effect of contact time

The effect of different contact times was assessed for identifying the efficiency of POFA for its use in

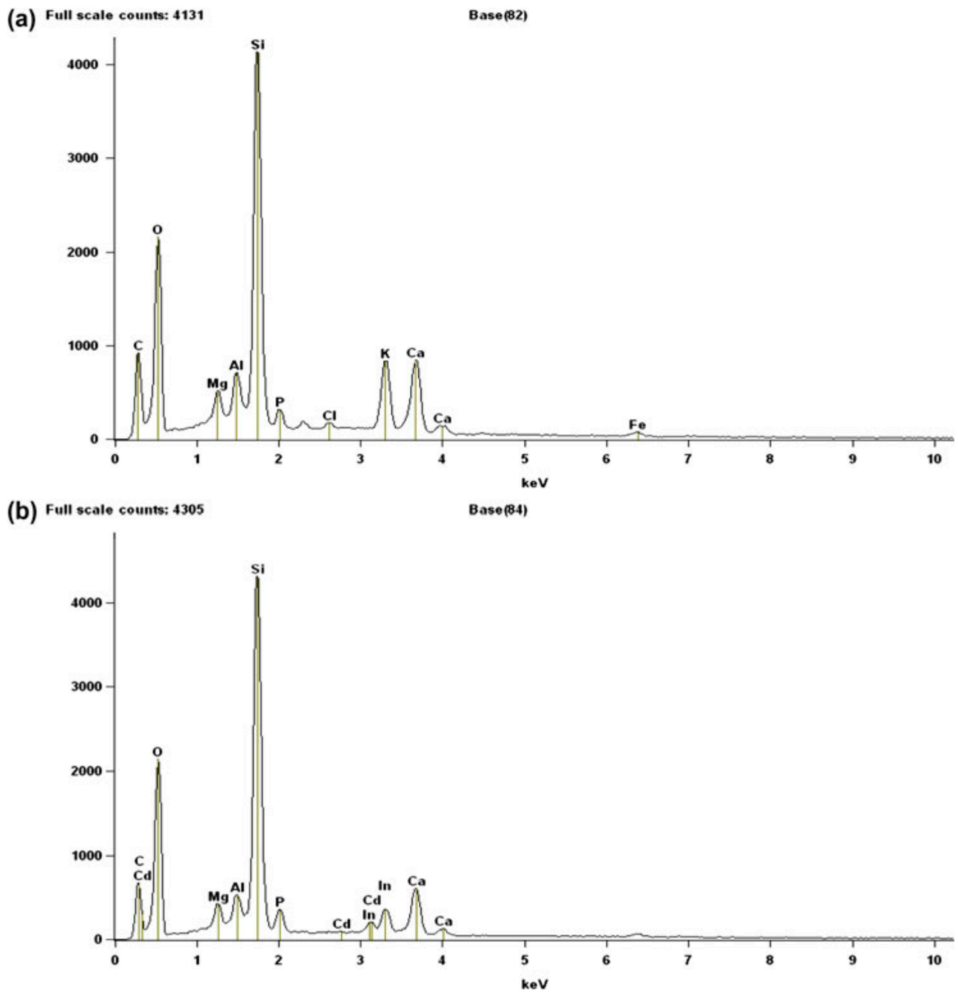

Fig. 3. Energy-dispersive X-ray (EDX) spectrum analysis of POFA before (a) and after (b) the adsorption of Cd(II).

Cd(II) removal. The evaluation of the effect of contact time required to reach equilibrium is essential, as one stage before the kinetic study of heavy metals adsorption is carried out. Most cases would suggest that the development of charge on the surface of adsorbent is usually governed and very much influenced by the contact time [28]. Fig. 4 illustrates the effect of contact time on the rate of Cd(II) uptake and adsorption capacity onto POFA. The rate of Cd(II) uptake increased fast during the first 30 min of the experiment and took much slower pace corresponding to the contact time before reaching a plateau value at the 210th min.

Thus, it is derived from Fig. 4 that significant Cd(II) uptake is shown to occur in 210 mins, and no changes were noticed from that point onwards, where the removal is concerned. Thus, equilibration time was noted at 210 min, which was regarded as enough for the removal of Cd(II) using POFA. The concentration of Cd(II) was lowered from 150 mg/L to 7.332 mg/L

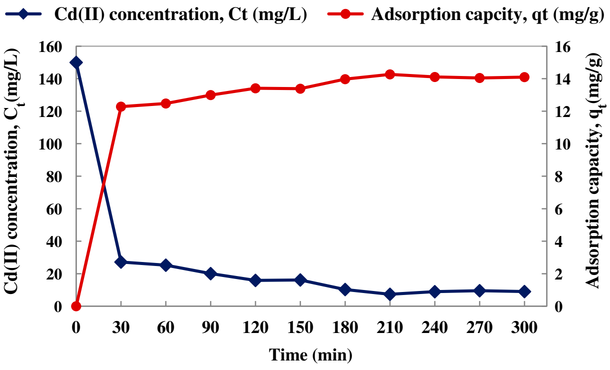

Fig. 4. Effect of contact time on the adsorption of Cd(II) onto POFA ($C_0 = 150$ mg/L, dosage = 0.5 g, and initial solution pH = 6.7).

after the 210 min contact time. Meanwhile, the amount of Cd(II) adsorbed by POFA from an early concentration of 150 mg/L after a 210 min equilibration time was found to be 14.267 mg/g.

From the observation, adsorptions rates were at first, high at the start of the experiment due to the abundant free binding sites. The significant changes noted in the removal rate are influenced by the binding of Cd(II) onto a vacant site of the adsorbent, causing it to be occupied. At the beginning of the adsorption process, the meso-pores had demonstrated their almost-saturated state with Cd(II) and continuous agitation will further lead to pore diffusion onto the inner surface of adsorbent particles through the monolayer film. As the adsorption process came to be completed, the Cd(II) had to traverse deeper into the micropores, encountering greater resistance that resulted in the deteriorating driving force and adsorption rate [3]. Therefore, the contact time was set to 210 min in the next experiments to ensure that the adsorption can reach equilibrium.

3.3. Effect of solution pH

The solution pH carries an essential variable in governing the metal adsorption of an adsorbent [1]. It is already established to affect the degree of ionization, speciation of the adsorbate, and surface charge of the adsorbent in the reaction process [25,29]. In this study, the effect of solution pH on the adsorption of Cd(II) onto POFA was assessed within the pH range of 3 to 8 (this can be seen in Fig. 5). It is observable that at high acidic medium, the adsorption capacity is rather low with the solution pH increasing from 3 to 4. Afterwards, the adsorption capacity of POFA increased remarkably as the solution pH heightened from 4 to 5, followed by a slow increase at solution pH from 5 to 7, and finally, a plateau value noted between pH value of 7 and 8. It is noticeable that the adsorption capacity increases parallel as a function of pH.

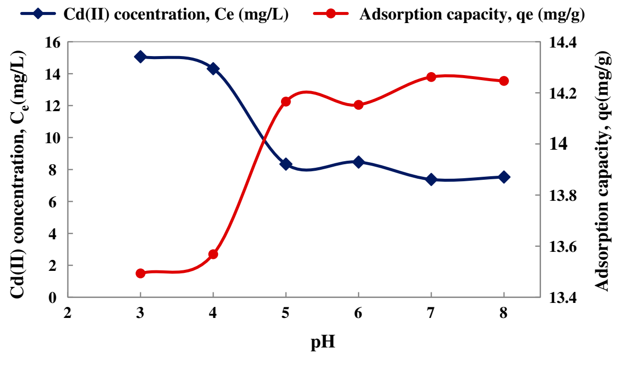

Fig. 5. Effect of solution pH on the adsorption of Cd(II) onto POFA ($C_o = 150$ mg/L, dosage = 0.5 g, and contact time = 210 min).

This phenomenon has given proof that the ion exchange mechanism may be engaged in the adsorption of Cd(II) onto POFA [30]. The adsorption rate is low under the acidic condition due to the existing H_3O^+ ions at higher concentration that stays in competition with Cd^{2+} ions for active binding sites onto the POFA surface [31,32]. In actuality, at pH value (≤5.0), a significant electrostatic repulsion exists between the positively charged surface and the cationic Cd(II), which hampers the adsorption of Cd(II) onto POFA. Similar trend has also been reported by Bayat on the adsorption of Zn(II) and Cd(II) onto high-calcium Turkish fly ash and Wang et al. over the adsorption of Cd(II) onto bamboo charcoal [1,3].

Nevertheless, as the solution pH escalated from 5 to 7, the electrostatic repulsion became lower due to the reduced density of positive charge of proton on the adsorbent surface and fewer H_3O^+ ions available to compete with the Cd^{2+} ions, thus resulting in an enhanced metal adsorption [25]. However, at higher pH value (>7), the adsorption capacity became constant, as Cd(II) was hydrolyzed into $Cd(OH)^+$ species and also started precipitating, as $Cd(OH)_2$ [32]. This fact has been affirmed by the speciation diagram established by Elliot and Denneny [33]. To add, the main constituents of POFA are metal oxides comprising of Al, Fe, Mg, and Si. These metal oxides have generated metal-hydroxide complexes in the aqueous solution.

It is confirmed that the tendency of metal cations to adsorb to oxide surfaces is very much associated with their tendency in the solution to be subjected to some hydrolysis reactions [34]. The hydrolysis of metal cations in aqueous solution leans on the generalized equation for divalent metal ions written as [25] that follows:

$$M^{2+} + nH_2O = M(OH)^{2-n} + nH^+ \tag{10}$$

Additionally, metal-hydroxide complexes adsorb at higher affinity because of the formation of hydroxide ion (−OH) on the metal that reduces the free energy requirement for the adsorption process [33]. Other than that, the adsorption of Cd(II) by POFA is highly pH-dependant as explained by the variable charge surfaces of the adsorbent metal oxides [1,29]. This is added by Cho et al. who assert that at pH values from 5 to 8, the influence of precipitation is unimportant and the removal of Cd(II) onto POFA is caused by the adsorption and ion exchange [25]. Therefore, the adsorption of Cd(II) onto POFA was examined at pH 7.0, and the following experiments were carried out at this pH value.

3.4. Effect of adsorbent dosage

A crucial parameter in the adsorption process would be the effect of various adsorbent dosages. It establishes the capacity of the adsorbent for a given initial concentration of metal ion solution. Fig. 6 shows that there was an accretion in the removal efficiency (RE %) as the adsorbent dosage increased until it came to a certain dosage where the RE % became constant or when a plateau value was obtained. Observation has proven that the RE % increased from the use of dosage ranging from 0.1 to 3.0 g, but a slower removal pace was reported as the adsorbent dose exceeded 3.0 g. There is a reason to suggest that with higher adsorbent dose, there would be more availability of exchangeable sites for the adsorbate, which shows off more active sites for the purpose of Cd(II) binding [9].

However, no significant changes had been observed with higher dosage > 3.0 g, as the surface Cd (II) concentration and the solution Cd(II) concentration come to be in equilibrium with each other [2,3] causing a slower uptake onto POFA. Meanwhile, the decrease in q_e with an increase in adsorbent dosage is largely explained by the unsaturation of adsorption sites through the reaction process. It is also caused by particle interactions, such as aggregation caused by the high adsorbent concentration that leads to a decrease in the total surface area of the adsorbent [3,31].

3.5. Effect of initial Cd(II) concentration

The effect of initial concentration on the removal of Cd(II) by POFA was explored with varying solution concentrations from 10 to 200 mg/L with 0.5 g adsorbent dosage. Expectedly, based on Fig. 7 the amount of Cd(II) adsorbed at equilibrium time and optimum solution pH demonstrates that with the increased solution concentration, q_e had increased, whereas RE % had decreased. Obviously, in Fig. 7, the removal of Cd(II) is highly reliant on concentration. It is self-explanatory that there is a scarcity of active sites in all adsorbents, which would have become saturated at a given concentration. The initial metal ion concentration acts as the driving force to overcome the mass-transfer barrier between the adsorbent and adsorbate medium. Similar results have also been reported by Papandreou et al. and Srivastava et al. [35,36].

The Cd(II) uptake mechanism depends a great deal on the initial concentration; at low initial solution concentration, the surface area and the availability of adsorption binding sites were relatively high; thus Cd (II) was conveniently adsorbed and removed. On the other hand, at higher initial solution concentration, the total available active sites are scarce, thus bringing about a decrease in the RE % of Cd(II) [3]. The increase in q_e at higher initial concentration can be attributed from the enhanced driving force that allows the ionic transfer between the solid-aqueous phases. Also, the experimental data were further used for ascertaining the adsorption isotherms of Cd(II) onto POFA.

3.6. Adsorption kinetics

The kinetics models rate both the constants and parameters for the Lagergren pseudo-first order, and pseudo-second order at different Cd(II) initial

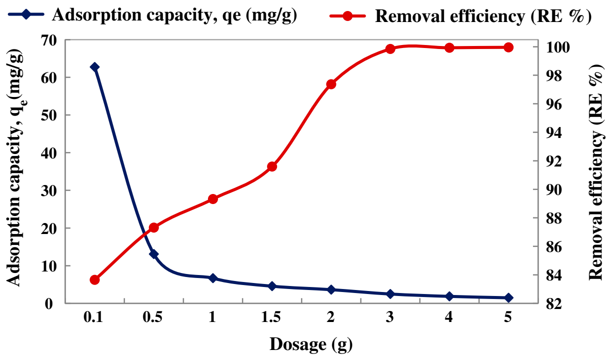

Fig. 6. Effect of adsorbent dosage variation on the adsorption of Cd(II) onto POFA (C_o = 150 mg/L, contact time = 210 min, and initial solution pH = 7.0).

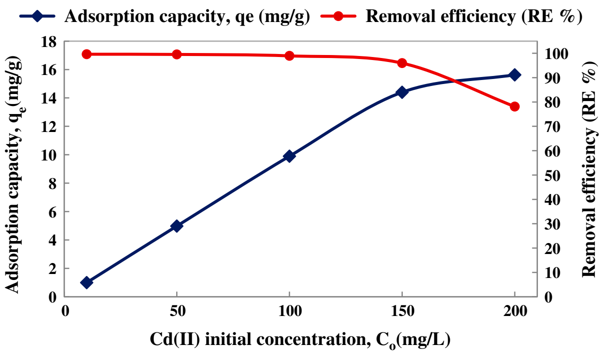

Fig. 7. Effect of initial concentration on the removal of Cd(II) onto POFA (contact time = 210 min, initial solution pH = 7.0, and dosage = 0.5 g).

Table 2
Lagergren's pseudo-first and second-order adsorption rate constants and parameters at different initial Cd(II) concentrations

		Lagergren's pseudo-first-order kinetic model			Pseudo-second-order kinetic model		
C_o (mg/L)	$q_{e,\exp}$ (mg/g)	k_1 ($\min^{-1}$)	$q_{e,\text{calc}}$ (mg/g)	R^2	k_2 (min·mg/g)	$q_{e,\text{calc}}$ (mg/g)	R^2
10	0.99850	0.00759	0.00104	0.9602	30.49856	0.9983	1.0000
50	4.99720	0.01036	0.01970	0.9444	1.938490	4.9800	1.0000
100	9.99500	0.01198	3.47136	0.9510	0.009540	9.4607	0.9971
150	14.9808	0.01198	3.46258	0.9483	0.010270	13.5501	0.9987
200	17.6878	0.01451	11.51065	0.8884	0.003430	18.0832	0.9933

concentrations as listed in Table 2 and which are illustrated in Fig. 8. It was noted that when the q_e values obtained from the first-order plots were compared with the experimental q_e values, a remarkable difference was noticed between the experimental q_e values and those obtained from the calculated q_e values, resulting in the first-order kinetics being rejected entirely. The pseudo-second-order model demonstrates a better agreement for the q_e values with less deviation shown from the experimental values. The coefficients of determination (R^2) were closer to satisfactory for the pseudo-second-order kinetics (>0.99) for all initial concentrations, as compared to the pseudo-first-order kinetics which indicates that the adsorption of Cd(II) onto POFA has a more precise fitting towards the pseudo-second-order equation.

Also, based on Table 2, the R^2 increased with the decreasing initial Cd(II) concentration, which shows very good agreement of the pseudo-second-order model at lower Cd(II) concentrations. Hence, seemingly, the system being considered is more appropriately described by the pseudo-second-order model, which works based on the assumption that the rate limiting step may be chemical sorption or chemisorptions involving valence forces through either the sharing or exchange of electrons between the adsorbent and the adsorbate [16,20,31].

3.7. Adsorption isotherms

The equilibrium adsorption isotherms are prominent as the basis of this study and as the design of an adsorption system [37]. In the present study, the equilibrium data had been used in an analysis using Langmuir, Freundlich, and Temkin isotherm models as to obtain the best fitting isotherm. The adsorption isotherms using POFA are graphically shown in Fig. 9, and the isotherm parameters are listed in Table 3. All plots show a straight line, indicating that the adsorption of Cd(II) adheres well to all the isotherms. Coefficients of determination (R^2) comparison indicate that the Langmuir model achieved satisfactory ($R^2 = 1.0$) compared to Freundlich ($R^2 = 0.8184$) and Temkin ($R^2 = 0.9576$) for the adsorption of Cd(II) onto POFA.

The fact that Langmuir model fits the experimental data well, where this may be due to the homogeneous distribution of active sites on the POFA surface, since the Langmuir equation makes an assumption that the surface is homogeneous. The Langmuir model is also based on the assumption that monolayer adsorption

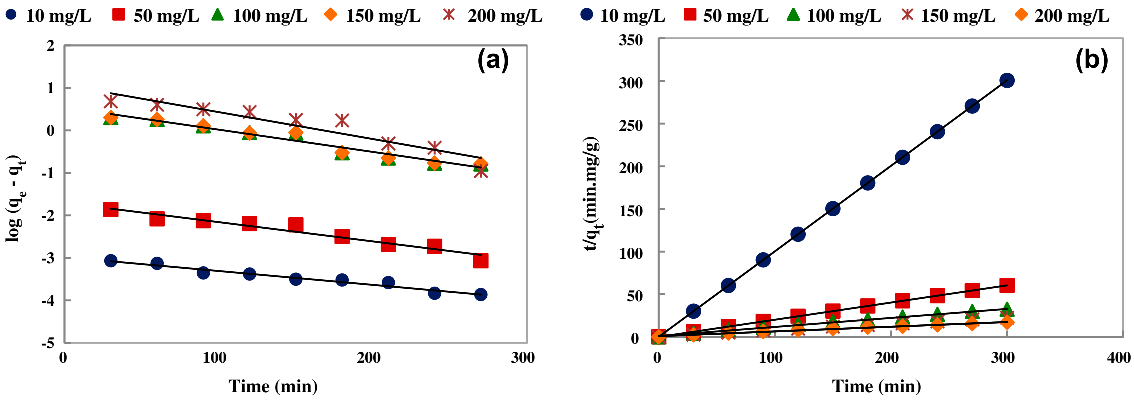

Fig. 8. Kinetics models for the adsorption of Cd(II) onto POFA pseudo-first order (a) and pseudo-second order (b).

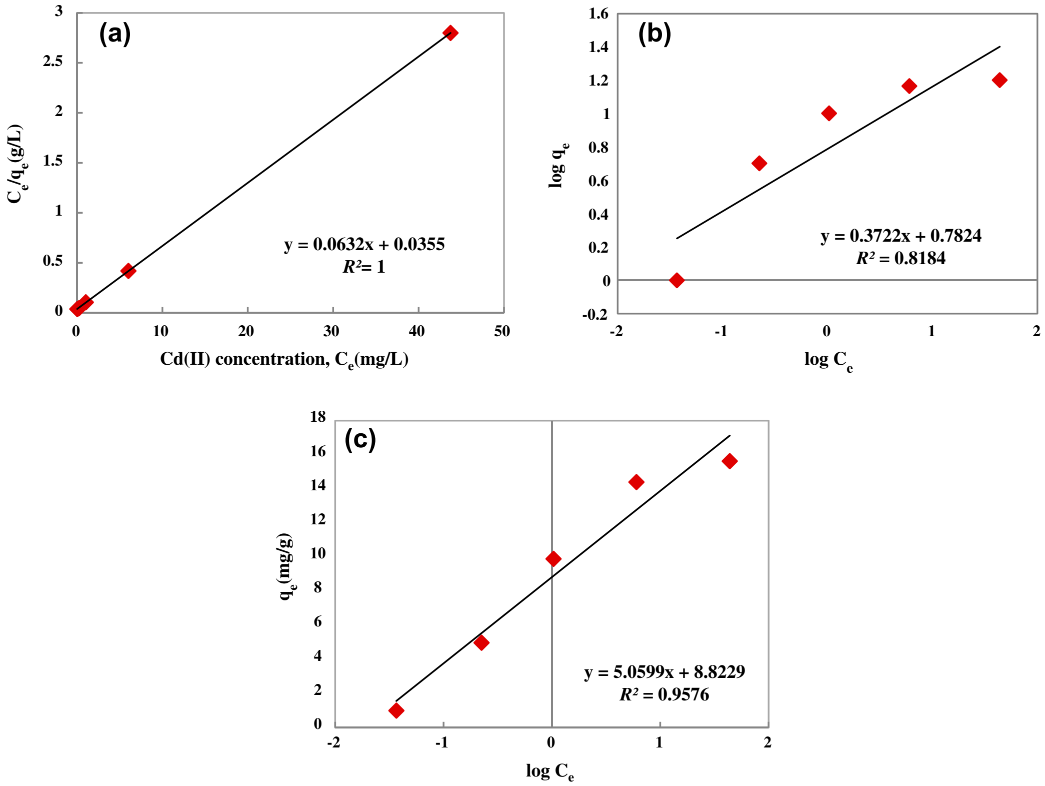

Fig. 9. Langmuir (a), Freundlich, (b) and Temkin (c) linear adsorption isotherms of Cd(II) onto POFA.

Table 3
Isotherm model constants for the adsorption of Cd(II) onto POFA

Isotherm model	Parameters	Values
Langmuir isotherm	q_m (mg/g)	15.8230
	b (L/mg)	1.7803
	R^2	1.0000
Freundlich isotherm	k	6.0589
	$1/n$	0.3722
	R^2	0.8184
Temkin isotherm	B (L/mg)	5.0599
	b (J/mol)	498.1105
	k_t (L/mg)	55.4231
	R^2	0.9576

corresponds to a saturated monolayer of solute molecules on the adsorbent surface, with nonexistent lateral interaction between the adsorbed molecules [38,39]. Meanwhile, Fig. 10 shows the variation of separation factor (R_L) values which fell within the range of 0 to 1, indicating that the adsorption of Cd(II) onto POFA was very much favored. Also, the R_L value approached zero with the increase of C_0 demonstrating that the adsorption of Cd(II) onto POFA is in favor towards lower initial concentration. Therefore, the Langmuir isotherm model is considered to be compatible in elaborating on Cd(II) adsorption onto POFA.

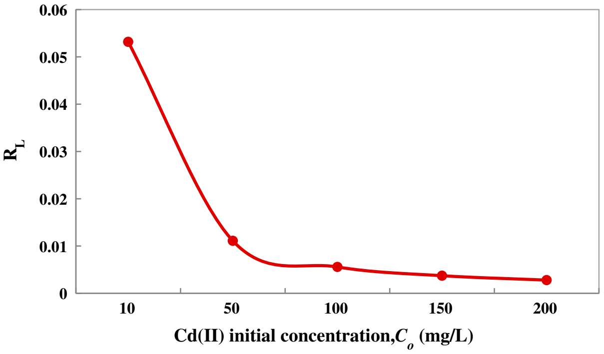

Fig. 10. Plot of R_L against Cd(II)—the initial concentration.

3.8. Comparison of adsorption capacity for the removal of heavy metals using various low-cost adsorbents as reported in literature

Ample literature concerning the use of low-cost adsorbent for the removal of heavy metals has been established for a number of years now. The adsorption

Table 4
Comparison of maximum monolayer adsorption capacities of metal ions onto various low-cost adsorbents

Type of adsorbent	q_{max} (mg/g)	Heavy metals	Reference
Activated Alumina	35.06	Cd(II)	[2]
Bamboo charcoal	12.08	Cd(II)	[3]
Palm oil fuel ash	16.39	Pb(II)	[16]
Activated carbon derived from *Ceiba pentandra* hulls	19.50	Cd(II)	[31]
Fired coal fly ash	18.98	Cd(II)	[35]
Alkali activated oil palm ash	18.86	Cu(II)	[40]
Palm oil fruit shells	32.46	Cu(II)	[41]
Oil palm fuel ash	16.12	Cr(III)	[42]
Palm oil boiler mill fly ash	17.00	Cu(II)	[43]
Palm oil boiler mill fly ash	15.82	Cd (II)	Present study

capacities of different types of low-cost adsorbents used for heavy metal removal are presented in Table 4, in which the results from this study were also drawn in comparison. The values are presented in monolayer adsorption capacity. The table shows that POFA illustrates a comparable adsorption capacity in lieu of other low-cost adsorbents, suggesting its potential to be used as a natural low-cost adsorbent for the removal of Cd(II) from aqueous solutions, explained by its relatively high adsorption capacity.

4. Conclusions

This current work has shed light on several batch adsorption experiments for the adsorption of Cd(II) from aqueous solution that have been carried out using POFA as a natural low-cost adsorbent. The results have clearly shown that the adsorption rate of Cd(II) was initially very rapid in the first 30 min, and in which period already more than 80% of total Cd(II) was removed. Meanwhile, the adsorption capacity had increased slowly corresponding to contact time before arriving at a plateau value after 210 min of agitation. Thus, equilibration time was considered to be 210 min and thus deemed sufficient for the removal of Cd(II) using POFA. The optimum pH value for Cd(II) removal using POFA was obtained at pH 7.0.

All in all, the adsorption capacity increased as the pH of the adsorbate increased. A higher dosage of adsorbent led to an increase of Cd(II) removal but the decrease in the adsorption capacity. The Cd(II) uptake mechanism is particularly dependent on both the pH and concentration. Kinetic modeling for Cd(II) adsorption onto POFA is best described through the pseudo-second-order model, which later on accepted the notion of chemisorptions. Langmuir isotherm model is compatible with the Cd(II) adsorption onto POFA with monolayer adsorption capacity of 15.823 mg/g at equilibrium time of 210 min and optimum pH of 7.0. Conclusively, fundamental batch adsorption studies imply that POFA has an excellent potential for removing Cd(II) from aqueous solution. The rapid uptake and high adsorption capacity, coupled with its natural abundance in the environment, are representative of its attractiveness as a low-cost adsorbent, which can be used in versatility in the industrial applications.

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