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Removal of Hexavalent Chromium from Aqueous Solution by Adsorption on Palm Oil Fuel Ash (POFA)

Nurulhana Nordin[1], Nur Amirah Ahmad Asmadi[1], Mohan Kumar Manikam[1], Azhar Abdul Halim[1*], Marlia Mohd Hanafiah[1,2], Sarah Nadira Hurairah[1]

[1]Center for Earth Sciences and Environment, Faculty of Science and Technology, Universiti Kebangsaan Malaysia, Bangi, Selangor, Malaysia
[2]Centre for Tropical Climate Change System, Institute of Climate Change, Universiti Kebangsaan Malaysia, Bangi, Selangor, Malaysia
Email: *azharhalim@ukm.edu.my

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Abstract

This study investigated the removal of hexavalent chromium, Cr(VI) from aqueous solution by adsorption using palm oil fuel ash (POFA), an agricultural waste from the palm oil industry. POFA adsorbent was characterized by X-ray diffraction (XRD) analysis. Batch adsorption study revealed that the optimum conditions for the removal were as follows: pH 2, adsorbent dosage 80 g/L and contact time of 6 min, which resulted in 92% removal and 0.464 mg/g maximum adsorption capacity. Adsorption isotherm and kinetic studies showed that Freundlich isotherm and pseudo-second-order kinetic models fitted best to the experimental data. Column adsorption study at 5 mL/min of flow rate showed that 90% removal was obtained at 2 min of contact time which represented its breakthrough point. The column reached saturation at 30 min and the maximum column adsorption capacity recorded was 0.412 mg/g. The column adsorption behavior showed good fit with both Thomas and Yoon-Nelson kinetic models. These findings suggested that the utilization of POFA as a low-cost adsorbent to remove Cr(VI) from wastewater, either in batch or fixed bed adsorption system is not only effective, but concurrently will help to reduce wastes from the palm oil industry.

Keywords

Hexavalent Chromium, Palm Oil Fuel Ash (POFA), Low Cost Adsorbent, Adsorption Isotherms, Adsorption Kinetics

1. Introduction

Chromium in the form of hexavalent is a pollutant that has a significant impact on the environment and health due to its toxic, carcinogenic and mutagenic properties. Anthropogenic activities such as skin processing, electroplating, pigment industry and metal mining-based industry had the potential to be a source of chromium contamination in soil and natural water sources (Bibi et al., 2016; Choppala et al., 2013). Generally, chromium exists in the environment as hexavalent, Cr(VI) and trivalent, Cr(III) species. Trivalent chromium is less toxic compared to hexavalent chromium, and it also functioned as a major micronutrient for glucose metabolism in the human body (Gheju et al., 2016; Shahid et al., 2017). However, trivalent chromium can be oxidized into hexavalent chromium, causing serious environmental concern and danger to human health. Lung cancer, dermatitis, kidney and liver failure are examples of human toxicity upon inhalation, ingestion or dermal absorption of the hexavalent chromium exposure from soils and water bodies or wastewater.

There are many chemical and physical treatment processes which have been carried out to remove hexavalent chromium, Cr(VI) from wastewater, including chemical precipitation, ion exchange, coagulation, reverse osmosis, electrolysis, chemical reduction, and adsorption (Halim & Ahmad, 2013). Due to its effectiveness and simple operation, adsorption method becomes the most preferable treatment for heavy metals removal from wastewater. However, conventional use of commercially available adsorbent like activated carbon involving high cost for industrial application. Thus, raising need for many recent studies to develop a low-cost adsorbent from readily available materials such as agricultural wastes. Agricultural wastes which are abundant in source are mainly consisting of cellulosic structure, which makes them an effective adsorbent for heavy metal ions (Guiza, 2017). Several recent studies involving agricultural wastes as adsorbent for Cr(VI) removal included usage of bamboo (Dula et al., 2014), rice straw (Kumar et al., 2017), coffee husk (Berihun, 2017), tea wastes, coconut shell and orange peel (Amir et al., 2017). In this study, palm oil wastes in the form of ash were used for Cr(VI) removal.

Palm oil fuel ash (POFA) is the by-product from burning process of oil palm shells, fibres and empty fruit bunches, which used as a fuel in the boiler to produce steam for electricity generation of milling processes. In Malaysia, it has been reported that more than 4 million tonnes of POFA were generated annually, and these numbers are expected to be increased due to increasing global demand for palm oil (Abdul Khalil et al., 2011). In common practice, POFA was simply disposed in landfill due to its limited usage and difficulties to be managed. Consequently, this huge amount of wastes has raised the environmental concerns in terms of increasing potential source of toxic pollutants in the landfill and its possible danger to human health. Therefore, as an approach to reduce the wastes from palm oil mill, there is little number of previous studies that have utilized POFA which is high in carbon and silica content (Utama et al., 2018) as the adsorbent material for treating wastewater (Manikam et al., 2019). To date, there is very limited research has been conducted involving usage of POFA for heavy metals removal from wastewater. Recent study by Imla Syafiqah & Yussof, 2018 has revealed that POFA was an effective and suitable adsorbent for mercury removal. However, fixed bed adsorption analysis was not conducted in the mentioned study. Thus, this present paper includes the column adsorption study to illustrate the design of continuous flow of adsorption.

The purpose of this study was to determine the effectiveness of POFA as a low-cost adsorbent for Cr(VI) removal from aqueous solution. Effects of pH, adsorbent dosage and contact time to the adsorption performance were also studied through batch and column adsorption method. Adsorption isotherms and kinetics of this study were also explained based on the related models. Characterization of POFA using X-ray diffraction (XRD) instrument was also conducted to identify the crystalline phase of the adsorbent.

2. Materials and Methods

2.1. Preparation of Palm Oil Fuel Ash (POFA) Adsorbent

The POFA which collected from local palm oil estate was washed with distilled water and then dried at 105˚C in oven for 24 h. It was then ground to powder and sieved to obtain an average particle size of less than 250 µm.

2.2. Characterization of POFA Adsorbent

In order to perform characterization of POFA adsorbent, X-ray diffraction (XRD) test was conducted using XRD instrument (Brand: Bruker, Model: D8 Advance). X-ray diffractogram of powdered POFA was obtained and later studied to identify the crystalline phase of the adsorbent.

2.3. Preparation of Hexavalent Chromium [Cr(VI)] Aqueous Solution

A total of 0.28 g potassium dichromate ($K_2Cr_2O_7$) powder (AR grade) was used to prepare a 100 mg/L Cr(VI) stock solution in a 1000 mL volumetric flask, by dissolving the powder with de-ionized water. The concentration of Cr(VI) in the solution was determined based on the standard method by APHA (2005), using the test method by HACH (2014)—Method 1,5 Diphenylcarbohydrazide (Method 8023). The concentration measurement was taken using HACH DR 2700 spectrophotometer.

2.4. Batch Adsorption Experiments

Batch adsorption experiments of this study involved three main analyses which were determination of optimum parameters, adsorption isotherms and adsorption kinetics studies. The optimum parameters studied were pH, adsorbent dosage and contact time. To study the Cr(VI) removal from aqueous solution by adsorption on POFA adsorbent, series of 250 mL conical flasks were filled with 100 mL of Cr(VI) solution. Different pH of Cr(VI) solution (pH 2.0, 2.5, 3.5, 4.0, 4.5 and 5.0) were used to determine its optimum pH, where the pH of the solution was adjusted by using sulfuric acid or sodium hydroxide. Then, to determine the optimum adsorbent dosage, different mass of POFA adsorbent were used for making up to the adsorbent dosage of 5, 10, 20, 40, 60, 80, 100 and 150 g/L. All the conical flasks were sealed with parafilm, placed on an orbital shaker and agitated at 200 rpm shaking speed for predetermined contact time (1, 2, 4, 6, 10, 15, 20 and 30 min). These different contact times assigned to the adsorption process in order to determine its optimum contact time for the Cr(VI) removal. Upon the completion of adsorption process, the solution was filtered by 0.45 µm nylon membrane filter, and the concentration of residual Cr(VI) in the solution was analyzed spectrophotometrically as mentioned in Section 2.3. The following batch adsorption experiment was conducted only at optimum parameters condition, in order to obtain the optimum Cr(VI) removal and maximum adsorption capacity of POFA adsorbent. For adsorption isotherms study, data from the determination of optimum adsorbent dosage experiment were used to plot the linear graph based on two adsorption isotherm models namely Langmuir and Freundlich. Meanwhile, adsorption kinetic of this study was identified using the data from determination of optimum contact time experiment. The data were used to plot the linear graph based on pseudo-first order and pseudo-second order adsorption kinetic models. Figure 1(a) shows the schematic diagram of batch adsorption experiment.

2.5. Fixed Bed Column Adsorption Experiments

Fixed bed column adsorption experiments were conducted using a column with 30 cm height and 2.5 cm diameter. A total of 36.4 g of powdered POFA adsorbent were placed in the column, layered with glass wool as supporting layers to form the adsorption media. By using peristaltic pump (Brand: Longer), 100 mg/L Cr(VI) aqueous solution was streamed in up-flow mode into the column and through the adsorption media at 5 mL/min of flow rate. Effluent samples were collected at the predetermined contact time of 2, 10, 20, 30, 40, and 50 min. These samples were then analyzed using spectrophotometer to obtain the final concentration of Cr(VI) in the solution as mentioned in section 2.3. Thomas and Yoon-Nelson kinetic models were then used to investigate the mechanism of the column adsorption of Cr(VI) on POFA adsorbent. Figure 1(b) shows the schematic diagram of fixed bed column adsorption experiment.

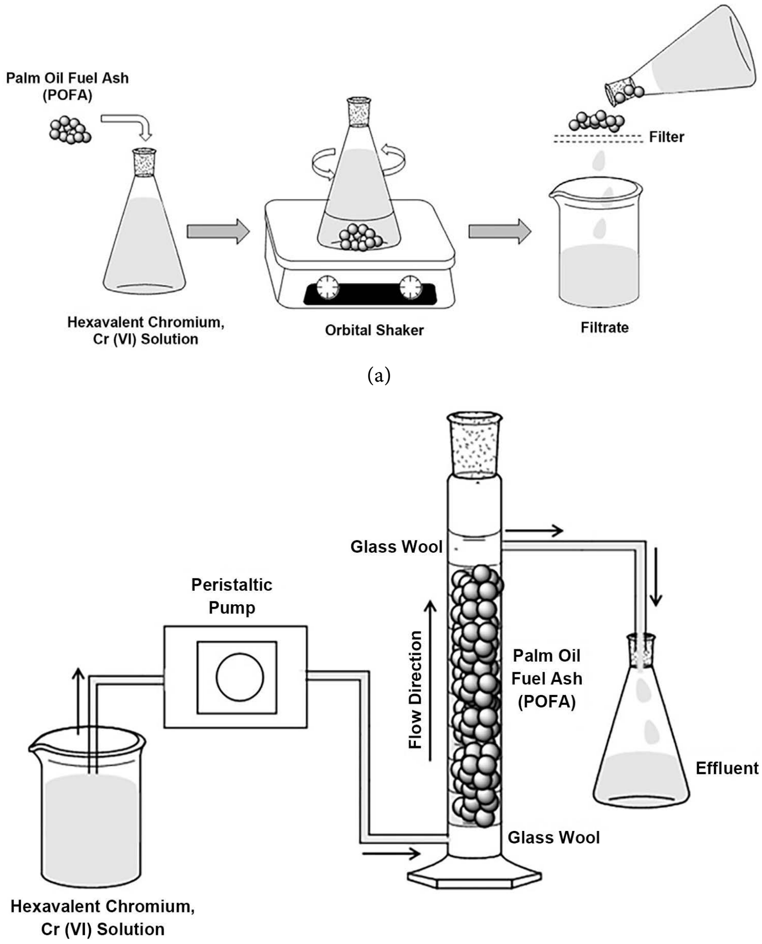
2.6. Calculation of Cr(VI) Adsorption

By using the spectrophotometer and method as mentioned in Section 2.3, the percentage of Cr(VI) removal, R (%) was calculated using the Equation (1):

$$R(\%) = \frac{C_i - C_f}{C_i} \times 100 \tag{1}$$

where C_i and C_f are the initial and final concentration of Cr(VI) in aqueous solution before and after adsorption (mg/L) respectively.

Meanwhile, the amount of Cr(VI) adsorbed on POFA adsorbent at equilibrium, q_e (mg/g) was calculated using the Equation (2):



(a)

(b)

Figure 1. (a) Schematic diagram of batch adsorption experiment. (b) Schematic diagram of fixed bed adsorption experiment.

$$q_e = \frac{\left(C_0 - C_e\right)V}{W} \tag{2}$$

where C_0 and C_e are the initial and equilibrium concentration of Cr(VI) in aqueous solution (mg/L) respectively, V is the volume of solution (L) and W is the mass of POFA adsorbent (g).

3. Results and Discussion

3.1. Characterization of POFA Adsorbent

Crystalline phase of POFA adsorbent was identified by XRD analysis over a scanning interval at 2 theta (2θ) and angle ranging from 16˚ to 52˚. Figure 2 shows the XRD spectrum of POFA adsorbent. The peaks observed from the diffractogram indicate crystalline phase of POFA adsorbent, which determined as quartz (silica, SiO_2) with 89.7 wt% and calcium silicate, Ca_2SiO_4 with 10.3 wt%. Strong and sharp peak observed at 26˚ represents good crystallinity of the adsorbent.

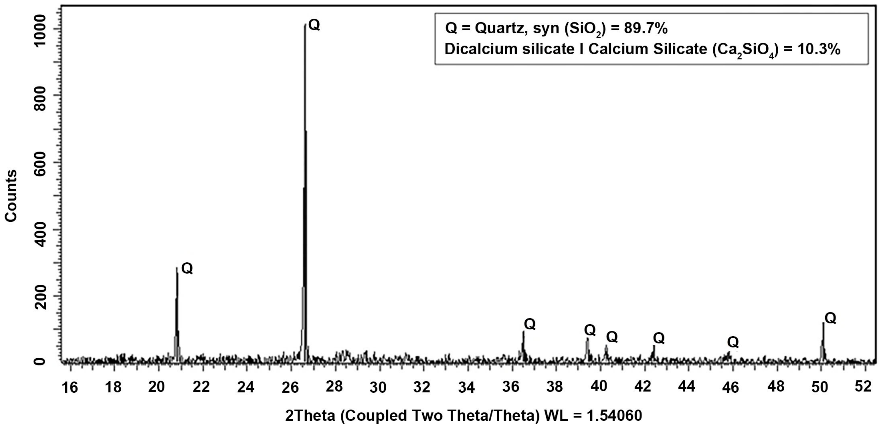


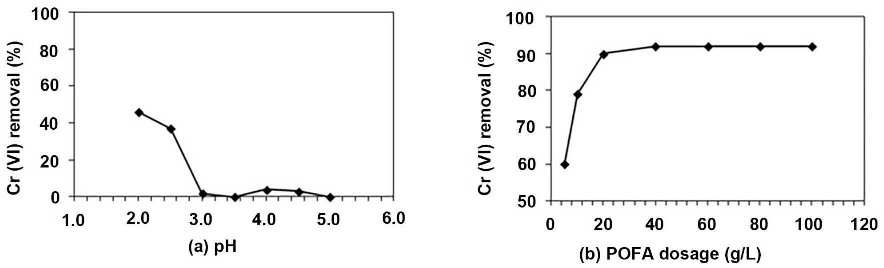
Figure 2. XRD spectrum of POFA adsorbent.

3.2. Batch Adsorption Studies

3.2.1. Effect of pH, Dosage and Contact Time

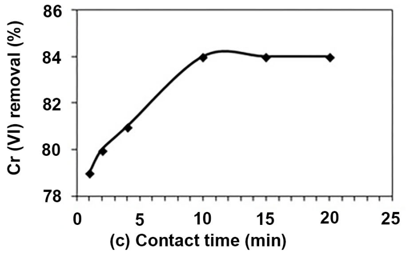
Surface properties of the adsorbent and active form of metal ions are influenced by the pH of the solution, thus it is an important parameter for adsorption study. Experiment conducted at pH ranging from 2.0 to 5.0 showed that the optimum pH for Cr(VI) removal was pH 2.0 of which 46% of removal were achieved. As the pH of the solution increased, the adsorption performance decreased, with a little fluctuation observed during pH 3.0 to 5.0 (**Figure 3(a)**), which represented by low percentage of Cr(VI) removal. This trend indicates that the adsorption of Cr(VI) by POFA adsorbent was strongly dependent by pH and favourable in lower pH. In acidic condition, the surface of POFA adsorbent was protonated and the dominant species of Cr(VI) in the solution was hydrogen chromate, $HCrO_4^-$ ion. Hence, allowing strong electrostatic attraction between the positive charge of the adsorbent surface and negative charge of the metal ion. The concentration of $HCrO_4^-$ ion was high at lower pH, resulted higher chromium adsorption capacity on the POFA adsorbent. While pH increased, this ion concentration decreased, lead to lower chromium uptake. Recent studies by Berihun (2017) and Rai et al. (2016) had reported similar trend for Cr(VI) removal using other adsorbents. The fluctuation observed which is similar to the previous study by Song et al. (2016) was due to unstable repulsive force between POFA adsorbent and chromium ions caused by abundance of OH^- ions when the pH was slightly increased, resulted in little fluctuation of Cr(VI) removal.

Figure 3(b) shows the effect of the POFA adsorbent dosage ranging from 5 to 150 g/L to the efficiency of Cr(VI) removal by adsorption. Initially, the percentage of Cr(VI) removal increased proportionally with adsorbent dosage, until it reached the equilibrium. Highest removal of Cr(VI) with 92% efficiency was achieved at the optimum adsorbent dosage of 80 g/L. The removal of Cr(VI) increased with the increasing adsorbent dosage due to more available binding sites from greater surface area of the adsorbent. After equilibrium was reached, further increased of adsorbent dosage did not affect the removal efficiency, as it might be attributed to shortage of Cr(VI) ion in the solution to occupy the



(Initial concentration: 100 mg/l,
Adsorbent dosage: 1.0 g/100 mL,
Agitation speed: 200 rpm,
Contact time: 30 min)

(Initial concentration: 100 mg/l,
pH: 2,
Agitation speed: 200 rpm,
Contact time: 30 min)



(Initial concentration: 100 mg/l,
Adsorbent dosage: 1.0 g/100 mL,
pH: 2
Agitation speed: 200 rpm)

Figure 3. Effect of pH (a), adsorbent dosage (b) and contact time (c) to Cr(VI) removal by adsorption on POFA.

binding sites on the POFA adsorbent. Hence the adsorption remained constant. Previous studies by Owalude & Tella (2016) and Dula et al. (2014) had reported similar behavior, where the Cr(VI) removal efficiency has increased with increasing dosage of adsorbent, which later has remained constant after equilibrium was achieved.

Effect of the contact time to Cr(VI) removal by adsorption on POFA adsorbent is illustrated in **Figure 3(c)**. The removal percentage of Cr(VI) increased from 1 to 6 min where the maximum removal with 85% efficiency was observed at optimum contact time of 6 min. During early stage of adsorption, greater number of available binding sites on POFA adsorbent allowed more chromium ions to be adsorbed resulted in higher percentage of Cr(VI) removal. As contact time increased, more binding sites were occupied and the surface of POFA adsorbent became exhausted, thus availability of more chromium ions to be adsorbed was reduced. Hence slightly decreasing of Cr(VI) removal efficiency was observed from 6 to 10 min, before it finally remained constant onwards until 30 min of contact time. Several researchers included Panda et al. (2017) and Ali et al. (2016) had reported similar trend where the percentage of Cr(VI) removal has rapidly increased with contact time at initial stage, and later it attained the saturation level.

3.2.2. Adsorption Isotherms

Adsorption isotherm studies interpret the adsorption process behavior based on the interaction between the adsorbent and adsorbed molecules, while optimizing the adsorbent dosage used. The most appropriate adsorption isotherm models for this study, Langmuir and Freundlich were used to relate the equilibrium data obtained.

The Langmuir model's assumption is that maximum adsorption is associated with the formation of the saturated monolayer of the adsorbed molecules on the homogenous surface of the adsorbent (Langmuir, 1918). It suggests that no further adsorption occurred once the adsorption sites on the adsorbent were occupied by the adsorbed molecules. The linear equation of the Langmuir adsorption isotherms is given as Equation (3):

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{K_L q_m C_e} \tag{3}$$

The value of Langmuir constant, K_L (L/mg) and the maximum adsorption capacity, q_m (mg/g) were calculated by the slope and y-intercept from the linear plot of $1/q_e$ against $1/C_e$, where q_e (mg/g) is the adsorption capacity at equilibrium and C_e (mg/L) is the concentration at equilibrium for each of the adsorbent dosage used.

Meanwhile, the Freundlich model assumes that multilayer adsorption takes place on heterogeneous surface of the adsorbent (Freundlich, 1906). The linear equation of Freundlich adsorption isotherm is given as Equation (4):

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \tag{4}$$

The value of Freundlich constant, K_F (mg/g) and adsorption intensity, n was determined by the y-intercept and the slope from the linear plot of log q_e against log C_e, where both q_e (mg/g) is the amount adsorbed and C_e (mg/L) is the concentration at equilibrium.

The isotherm parameters data including constants and regression values, R^2 for both models is shown in **Table 1**. The result showed that the adsorption of Cr(VI) on POFA adsorbent fitted best with the Freundlich model due to its closer R^2 value to 1. This concludes that the Cr(VI) removal in this study involved multilayer adsorption on heterogeneous surface of the POFA adsorbent. Recent studies by Yusuff (2018) using *Leucaena leucocephala* seed shell and Sugashini & Begum (2015) using rice husk, have reported similar observations where the

Table 1. Adsorption isotherm data of Cr(VI) removal by adsorption on POFA.

Adsorption Isotherm Model	Parameter	Cr(VI)
Langmuir	R^2	0.782
	q_m (mg/g)	0.464
	K_L (L/mg)	0.035
Freundlich	R^2	0.970
	n	0.416
	K_F (mg/g)	0.001

adsorption of Cr(VI) from aqueous solution has fitted closely to Freundlich adsorption isotherm model.

3.2.3. Adsorption Kinetics

Adsorption kinetics studies explain the adsorption mechanism of the absorbed material based on the results obtained at the time of equilibrium. In this study, the rate of Cr(VI) adsorption on POFA adsorbent was investigated using two adsorption kinetic models namely pseudo-first-order and pseudo-second-order. The linear equation of the pseudo-first-order adsorption kinetic is given as Equation (5) (Lagergren, 1898):

$$\ln\left(q_e - q_t\right) = \ln q_e - K_1 t \tag{5}$$

The value of pseudo-first-order constant, K_1 (min^{-1}) and the adsorption capacity at equilibrium, q_e (calculated) (mg/g) were determined from the slope and the y-intercept from the linear plot of ln($q_e - q_t$) against contact time, t (min), where q_e (experimental) (mg/g) is the amount adsorbed at equilibrium and q_t (mg/g) is the amount adsorbed at contact time.

Meanwhile, the linear equation of the pseudo-second-order adsorption kinetic is given as Equation (6) (Ho & McKay, 1999):

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e}\left(t\right) \tag{6}$$

The value of pseudo-second-order constant, K_2 ($\text{g}\cdot\text{mg}^{-1}\cdot\text{min}^{-1}$) and the adsorption capacity at equilibrium, q_e (calculated) (mg/g) were determined from the y-intercept and the slope from the linear plot of t/q_t against contact time, t (min), where q_t (mg/g) is the amount adsorbed at contact time.

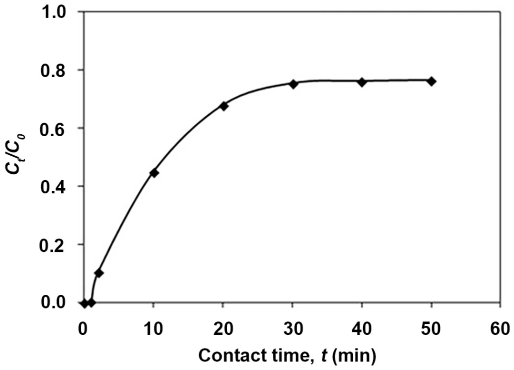
Table 2 shows the kinetic parameters data including constants, adsorption capacities and regression values, R^2 for both models. The results indicated that the experimental data represented best with pseudo-second-order kinetic model due to its R^2 value equals to 1 and its calculated adsorption capacity, q_e was 8.446 mg/g which agreed reasonably well to the experimental value of 8.417 mg/g. These finding suggest that the adsorption of Cr(VI) on POFA adsorbent involved chemisorptions or ion exchange process. Previous studies by Ali et al. (2016) using banana peel and Ghasemi et al. (2015) using walnut shell have reported similar results where the Cr(VI) adsorption mechanism has described best by pseudo-second-order kinetic model.

3.3. Column Adsorption Studies

Figure 4 illustrates the breakthrough curve of Cr(VI) column adsorption by POFA adsorbent. The breakthrough point was observed at 2 min of contact time, where the effluent concentration recorded was 10% of the inlet concentration, indicating 90% removal of Cr(VI). The steep curve from 2 until 20 min of contact time indicates rapid adsorption at initial stage. Then, from 20 to 30 min of contact time, the POFA adsorbent was started to be exhausted, resulted in less chromium ions uptake afterwards. After 30 min of contact time, the adsorbent

Table 2. Adsorption kinetic data of Cr(VI) removal by adsorption on POFA.

Adsorption Kinetic Model	Parameter	Cr(VI)
Pseudo-first-order	q_e (experimental) (mg/g)	8.417
	R^2	0.717
	q_e (calculated) (mg/g)	0.509
	K_1 (min^{-1})	0.074
Pseudo-second-order	R^2	1.000
	q_e (calculated) (mg/g)	8.446
	K_2 (g·mg^{-1}·min^{-1})	1.460



(C_0 and C_t: inlet and outlet Cr (VI) concentration respectively,
flow rate: 5 mL/min, mass of POFA adsorbent packed in the columm: 36.4 g, pH: 2)

Figure 4. Breakthrough curve for fixed bed column adsorption of Cr(VI) on POFA.

became exhausted and the saturation has been achieved, represented by the plateau of the breakthrough curve. The adsorption capacities at breakthrough point, q_b (mg/g) and at exhaustion time, q_e (mg/g) were calculated using the equation adapted from Taty-Costodes et al. (2005) given as Equation (7):

$$q_b = \frac{Q t_b C_0}{m} \tag{7}$$

where Q (L/min) is the volumetric flow rate, t_b (min) is the breakthrough time, C_0 (mg/L) is the inlet Cr(VI) concentration and m (g) is the amount of POFA adsorbent packed in the column. Table 3 shows adsorption breakthrough analysis data of this study. The experimental exhaustion adsorption capacity, q_e for the column adsorption analysis, 0.412 mg/g was slightly lower than the maximum adsorption capacity, q_m recorded from earlier batch adsorption analysis, which was 0.464 mg/g. This is attributed to less effective surface area for the interaction between chromium ions and POFA adsorbent in fixed bed column system compared to the continuous stirred batch flasks.

In order to predict the dynamic behavior of the column adsorption of Cr(VI) on POFA adsorbent, the most common and widely used kinetic models, Thomas and Yoon-Nelson models were used to fit the experimental data.

Table 3. Breakthrough analysis data of Cr(VI) column adsorption by POFA.

Adsorbent mass, m (g)	36.4
Breakthrough time, t_b (min)	2.0
Breakthrough adsorption capacity, q_b (mg/g)	0.028
Exhaustion time, t_e (min)	30.0
Exhaustion adsorption capacity, q_e (mg/g)	0.412

Thomas model relates the adsorption process with Langmuir adsorption-desorption kinetics without axial dispersion. It suggests that the rate driving force of the adsorption follows second-order reversible reaction of kinetics (Thomas, 1944). The linear equation of the Thomas column adsorption kinetic model is given as Equation (8):

$$\ln\left(\frac{C_0}{C_t}-1\right)=\frac{k_T q_{0(T)} m}{Q}-\frac{k_T C_0}{Q}V \tag{8}$$

where C_0 (mg/L) is the inlet Cr(VI) concentration in the solution, C_t (mg/L) is the outlet Cr(VI) concentration at time, m (g) is the amount of POFA adsorbent packed in the column, Q (L/min) is the volumetric flow rate and V (L) is the volume of effluent. The value of Thomas constant, k_T (L·min^{-1}·mg^{-1}) and maximum column adsorption capacity for this model, $q_{0(T)}$ (mg/g) were calculated by the slope and y-intercept from the linear plot of $\ln[(C_0/C_t)-1]$ against V (**Figure 5**)

Meanwhile, the Yoon–Nelson model assumes that the rate of decrease in the probability of adsorption of each adsorbate molecule is proportional to the probability of the adsorbate breakthrough on the adsorbent (Yoon & Nelson, 1984). The linear equation of the Yoon-Nelson column adsorption kinetic model is given as Equation (9):

$$\ln\left(\frac{C_t}{C_0-C_t}\right)=k_{YN}t-\tau k_{YN} \tag{9}$$

where C_0 (mg/L) is the inlet Cr(VI) concentration in the solution and C_t (mg/L) is the outlet Cr(VI) concentration at time, t (min). The value of Yoon-Nelson constant, k_{YN} (min^{-1}) and the time required for 50% adsorbate breakthrough, τ (min) were determined by the slope and y-intercept from the linear plot of $\ln[(C_t/C_0-C_t)]$ against t (**Figure 6**). Then, the maximum column adsorption capacity for this model, $q_{0(YN)}$ (mg/g) was calculated using Equation (10):

$$q_{0YN}=\frac{q_{\text{total}}}{m}=\frac{\frac{1}{2}C_0\left(\frac{Q}{100}\times 2\tau\right)}{m}=\frac{C_0 Q\tau}{1000m} \tag{10}$$

where Q (L/min) is the volumetric flow rate and m (g) is the amount of POFA adsorbent packed in the column.

Table 4 shows the column adsorption kinetic parameters data including constants, adsorption capacities and regression values, R^2 for these models. It was observed that the experimental data fitted reasonably with both Thomas and Yoon-Nelson models due to similar R^2 values > 0.7. The calculated values of

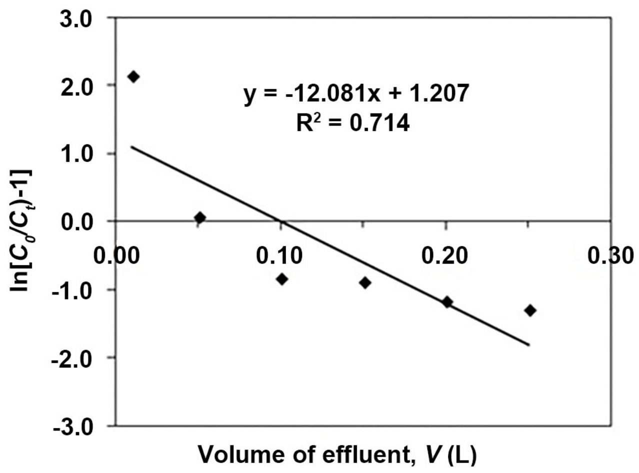


Figure 5. Thomas fixed bed adsorption kinetic model linear plots for Cr(VI) removal on POFA.

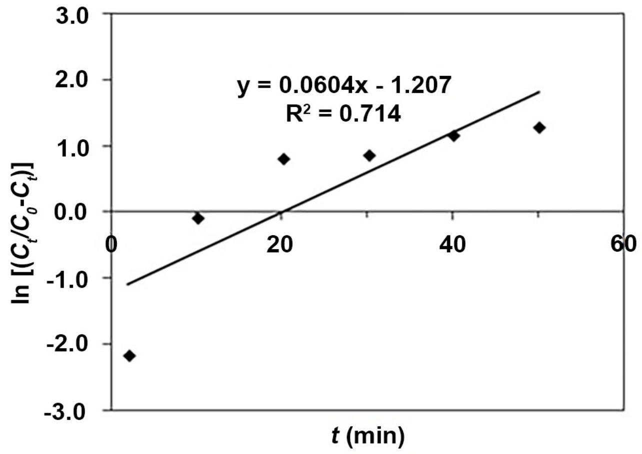


Figure 6. Yoon-Nelson fixed bed adsorption kinetic model linear plots for Cr(VI) removal on POFA.

Table 4. Column adsorption kinetic data of Cr(VI) removal by adsorption on POFA.

Column Adsorption Kinetic Model	Parameter	Cr(VI)
Thomas	q_e (experimental) (mg/g)	0.412
	R^2	0.714
	k_T (L·min^{-1}·mg^{-1})	0.001
	$q_{0(T)}$ (mg/g)	0.275
Yoon-Nelson	R^2	0.714
	k_{YN} (min^{-1})	0.060
	τ (min)	20.0
	$q_{0(YN)}$ (mg/g)	0.275

maximum adsorption capacities, q_0 were also similar for both models, which were 0.275 mg/g and it was comparable with the value of experimental exhaustion adsorption capacity, q_e of 0.412 mg/g.

Thus, it can be concluded that Cr(VI) removal by adsorption on POFA adsorbent in this study obeys Freundlich isotherm, pseudo-second-order, Thomas and Yoon-Nelson kinetic models. Recent study by Rodrigues et al. (2019) has reported similar findings of Cr(VI) adsorption on hydrotalcite adsorbent, where the adsorption behaviour has fitted well with the Freundlich isotherm and pseudo-second-order kinetic, which later confirmed by the agreement with Thomas model.

4. Conclusion

This study has shown that POFA is an effective low cost and readily available adsorbent for Cr(VI) removal from aqueous solution. From the batch adsorption study, the maximum removal of Cr(VI) has achieved at 92% efficiency with maximum adsorption capacity of 0.464 mg/g. The adsorption performance of POFA adsorbent was strongly dependent on the parameters that have been studied. The optimum parameters observed for the Cr(VI) removal were pH 2 of the solution, 80 g/L of adsorbent dosage and 6 min of contact time. The adsorption isotherm was compliant with the Freundlich model which indicated that multilayer adsorption has occurred on heterogeneous surface of the adsorbent. The adsorption behavior also fitted best with pseudo-second-order kinetic model which suggested that the adsorption of Cr(VI) on POFA adsorbent has involved chemisorptions or ion exchange process. From the column adsorption study, maximum 90% of Cr(VI) removal has obtained at 2 min of contact time which represented its breakthrough point. The maximum column adsorption capacity was 0.412 mg/g and the column adsorption behavior has shown a good fit with both Thomas and Yoon-Nelson kinetic models.

In conclusion, utilization of POFA as adsorbent to remove Cr(VI) from wastewater not only will be cost effective, but concurrently will tackle the issue of huge wastes from palm oil industry by reducing the cost of the wastes management and disposal. This study also gives a market value for POFA which is originally a waste, to be sold commercially as a low-cost biodegradable adsorbent. These positive findings strongly suggest that the usage of POFA for further research involving water treatment analysis of other kinds of pollutants from various sources such as industrial wastewater will be potentially effective and economical.

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Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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