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Removal of chromium from aqueous solutions using a palm kernel shell adsorbent

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ABSTRACT

The presence of chromium (VI) or its compounds in water is a result of its uses in modern society. The presence of toxic chromium (VI) in large quantities will adversely affect and interfere with many beneficial uses of water. Adsorption is an effective approach used to remove chromium (VI). Chemical characteristics of the palm kernel shell (PKS) were optimized by hydroxyl pretreatment followed by quaternization for the adsorption of chromium (VI). It was observed that the chemically modified palm kernel shell (CMPKS) showed an effective adsorption property, with a maximum capacity of 19 mg/g at pH 2 and 17 mg/g at pH 6 and 4. The kinetics model with pseudo-first and pseudo-second orders were studied, along with Langmuir and Freundlich isotherms. The Langmuir model and the pseudo-second-order model were observed to be a better fit for this process. Scanning electron microscopy analysis showed significant changes in the surface morphology of CMPKS, with changes in the projection and porous surfaces.

Keywords: Chromium hexavalent; Palm kernel shell; Adsorption; Biomaterial; Mercerization and quaternization

1. Introduction

The large amount of waste that comes from industrial manufacturing, agriculture and urbanization leads to unsafe underground and surface waters being consumed by humans and other living organisms [1]. Pollutants from wastes, especially heavy metals, can remain for decades in the environment, increasing the likelihood of human exposure since they cannot be degraded or destroyed. Increased worldwide manufacturing and urbanization largely destroy the environment through the disposal of industrial and household wastes. These wastewaters are frequently contaminated with nutrient substances or toxic heavy metals in which large amounts are accumulated in the natural aquatic and terrestrial ecosystems [2]. The wastes originating from industry, such as pigment, electroplating, metal cleaning, mining and leather processing, contain large quantities of heavy metals, especially chromium metal that commonly occurs in the environment [3,4].

In spite of the negative effects of chromium (VI) on health and the environment, there are many benefits and ongoing needs in agriculture and industry. Therefore, the development of facilities and methods of treating the chromium from contaminated water are crucial. There are many chemical and physical processes that are available to remove chromium (VI) from water, such as electrochemical reduction, chemical precipitation, supplied precipitation, solvent extraction, cementation, electrodialysis and reverse osmosis [5].

However, due to problems and high operational costs, these methods are not widely practised. Conversely, the

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biomaterials used in adsorption methods are economical and inexpensive adsorbents, which are considered feasible alternatives for chromium (VI) removal due to their low operational costs, efficiency and clean operation [6]. Rapid urbanization, overpopulation and industrial and technological advancement, as well as increased energy utilization and waste generation from domestic and industrial sources, have rendered many surfaces and underground waters unsafe for humans and other living resources [1]. Some of these wastes, especially heavy metals, can remain in the environment for decades, increasing the likelihood of human exposure since they cannot be degraded or destroyed.

Heavy metals or their compounds have been extensively released to the environment due to anthropogenic activities. This release has led to a sharp increase in the contamination of water. Because of their toxicity, the presence of any of these metals in excessive quantities will interfere with many environmental issues related to water. Different physical and chemical processes are available for the removal of heavy metals from wastewater, such as coprecipitation, coagulation, recovery, ultrafiltration, ion exchange, reverse osmosis and activated carbon, but they are not economically appealing because of high operational costs [7–10]. Therefore, there is a need to explore alternative materials with low cost as well as renewable techniques that could be used to remove heavy metals.

2. Materials and methodology

Fig. 1 illustrates the experimental design of this study. Palm kernel shell (PKS), an agricultural waste, is the basic material used in this research, and it was evaluated based on its adsorption efficiency of chromium.

2.1. Adsorbent preparation

Raw PKS was obtained from MINSAWI Industries (K.K.) Sdn Bhd, Kuala Kangsar, Perak, Malaysia. The raw PKS was cleaned and washed with hot water and was then dried and ground into small particles of approximately 0.125–1 mm. The process of drying was carried out at 105°C to ensure the complete removal of moisture content.

The PKS was mercerized with 30% potassium hydroxide (KOH) for the swelling of the particles. It was shown in previous studies that NaOH is able to swell the fibres of cotton yarn, along with a change in the chemical composition [11,12]. The mercerization process in this study was conducted in a temperature room for approximately 2 h. The mercerized

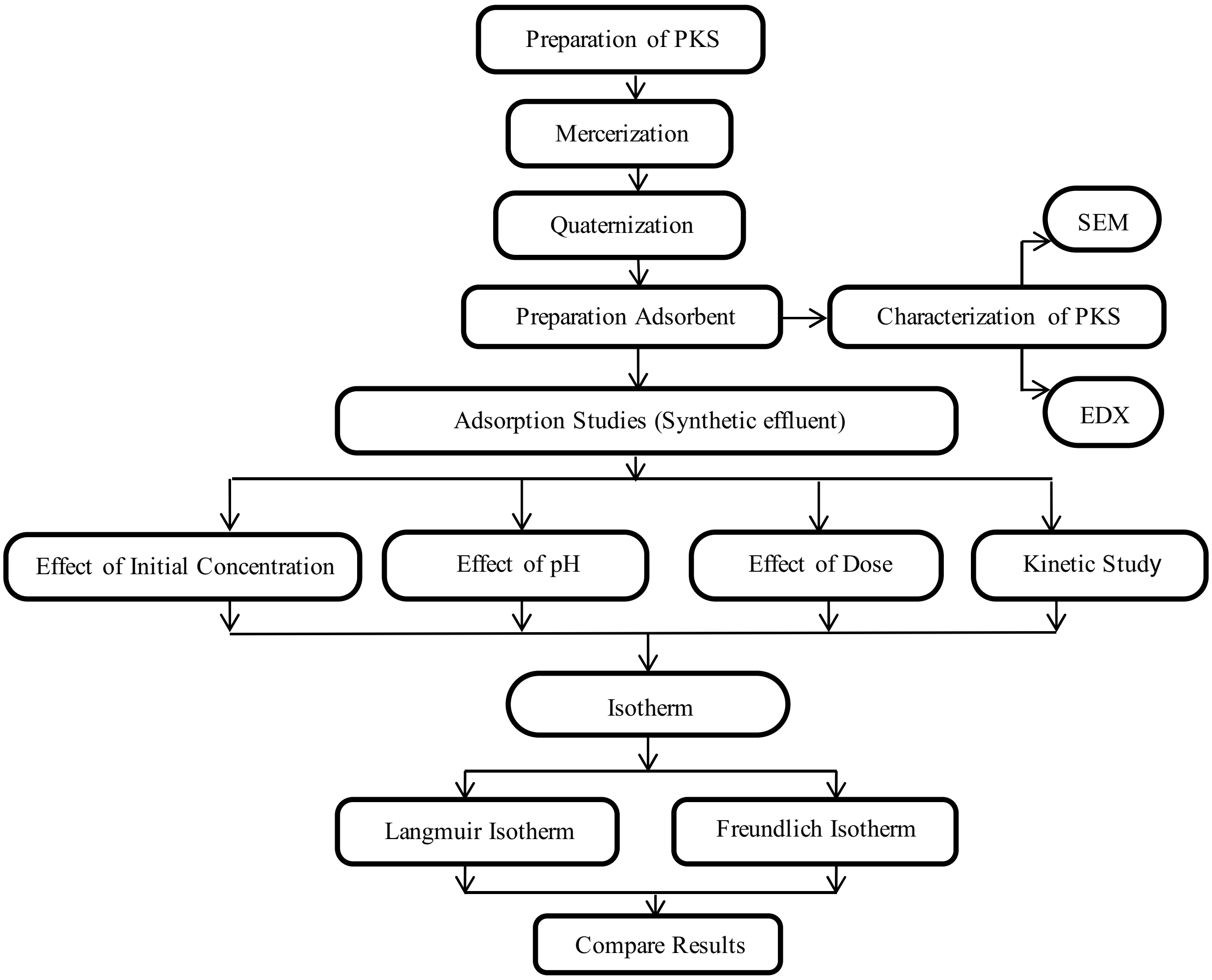

Fig. 1. Experimental design of the study.

PKS was washed with distilled water, followed by a 5% acetic acid bath and drying at 60°C.

The quaternization was conducted in a batch process, with 40 g of mercerized PKS. Mercerized PKS was reacted in a 500 mL mixture at the ratio 1:1.5 (v/v), containing 5 M KOH and 60% *N*-(3 chloro-2 hydroxypropyl) trimethylammonium chloride at 70°C for 18–20 h. This process was carried out to create positive charges on the resins under alkaline conditions by grafting amine groups. The resins of the chemically modified palm kernel shell (CMPKS) were washed repeatedly with adequate quantities of deionized water with stirring. After improving a transparent supernatant, the pH of the mixture was adjusted using 1 M HCl and 1 M NaOH. All the batches of CMPKS were dried at 105°C and were sieved to obtain resin size ranges of 0.125–0.25, 0.25–0.5 and 0.5–1 mm.

2.2. Preparation of chromium solution

The stock solution of chromium (VI) (1,000 mg/L) was prepared by dissolving 2.8 g of potassium dichromate ($K_2Cr_2O_7$) in 1,000 mL of distilled water. To achieve a viscous solution, different concentrations were prepared by diluting the stock solution with suitable quantities of distilled water. Final concentrations were verified with a DR-900 spectrophotometer (Hatch).

2.3. Chromium batch study

The chromium batch study was conducted to optimize the basic parameters, which are pH (2–9), initial concentration of chromium (25–150 mg/L), CMPKS dosages (0.1–0.6 g) and contact time. A chromium concentration of 50 mg/L was selected to determine the parameters since chromium frequently exists at this concentration in wastewater sources [13].The obtained data from this study were used to investigate a kinetics study with pseudo-first- and pseudo-second-order models, as well as Langmuir and Freundlich isotherm models. Batch studies were prepared by placing 100 mL of the sample in 250 mL conical flasks, followed by shaking at ±28°C. Each test was performed in triplicate to reduce the error.

2.4. Effect of pH

Chromium removal by bioadsorbent is largely dependent on the pH of the aqueous phase [14,15]. Biomass-based bioadsorbents include biomacromolecules such as thiol, amino, carboxyl groups and phenol. The biosorption process simply depends on the deprotonation and protonation of the functional groups [13,16].

2.5. Effect of chromium initial concentration

To investigate the initial chromium concentrations effect on the efficiency of removal, each sample was put into 0.4 g of the adsorbent in the different chromium concentrations. Essentially, concentrations of 20, 40, 60, 80, 100, 120 and 140 mg/L were used. This experiment was done at specified contact times, that is, 1–180 min, and shaking speeds of 100, 120 and 150 RPM were used. The solution was then filtered and collected in glass tubes. The concentration of Cr in the filtrate was measured.

2.6. Biosorption isotherm

A biosorption isotherm describes the essential uniqueness of the adsorbate, which includes the molecular structure, molecular weight, solubility, polarity and hydrocarbon saturation. In a nutshell, the adsorption of adsorbate on the surface of the adsorbent at a constant temperature and pressure is referred to as the adsorption isotherm. To obtain the equilibrium isotherm, a graph of the solid phase concentration is plotted against the liquid phase.

There are models that are usually used to analyse the fitness of adsorption isotherms. These models are the Langmuir, Freundlich, Redlich–Peterson, Brunauer–Emmett–Teller, Temkin and Dubinin–Radushkevich (D–R) isotherm models. Moreover, kinetic studies of biosorption are very important in the determination of the equilibrium time and in the rate of adsorption that can be developed, and they are used in predictive models. Furthermore, the results obtained can also be used in understanding the variables that influence the sorption of a solution. Generally, the main purpose for studying the adsorption isotherm is to evaluate the efficiency of a produced adsorbent to develop a suitable industrial system design by fitting to the best isotherm [17].

2.7. Langmuir isotherm

The Langmuir isotherm model assumes that the maximum adsorption corresponds to a saturated monolayer of solution molecules on the adsorbent surface. Once the molecule is concentrated on the adsorbent, there will be no transmigration of the solution or adsorbate on the plane of the surface [18]. The adsorption energy will be uniform throughout the surface area; otherwise, the pollutant will have uniform adsorption or attractive forces.

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

where q_e = adsorbate equilibrium concentration (mg/g); K_L = efficiency constant of solute adsorption (L/mg); α_L = energy constant of adsorption (L/mg) and C_e = adsorbate in solution equilibrium concentration (mg/g).

Eq. (1) is termed as a nonlinear form of Langmuir and can be linearized to form equation as follows:

$$\frac{C_e}{q_e} = \frac{1}{K_L} + \frac{\alpha_L C_e}{K_L} \tag{2}$$

The K_L Langmuir isotherm constant can be obtained from plotting C_e against C_e/q_e. The slope of the graph is the constant value of α_L/K_L, while the slope of this equation is $1/K_L$. The monolayer assumptions of Langmuir over an adsorbent surface between adsorbed molecules can be expressed as follows:

$$q_e = \frac{q_{\max K_L C_e}}{1+\alpha_L C_e} \tag{3}$$

The value of $q_{\max}$ (mg/g) is the maximum value of the adsorption capacity to form a complete monolayer on the surface. The essential characteristic of the Langmuir isotherm can be expressed by a separation or equilibrium parameter (R_L), a dimensionless constant and can be defined as follows:

$$R_L = \frac{1}{1 + bC_0} \quad (4)$$

The value of R_L indicates the nature of adsorption. If the separation factor is greater than one ($R_L < 1$), it means that the adsorption of chromium is unfavourable. When the range is between 0 and 1, that is, $0 > R_L < 1$, this indicates that the biosorption of chromium is favourable. However, if the value of R_L is equal to unity, the adsorption process is linear, and if it is equal to zero ($R_L = 0$), then it is an indication of an irreversible process.

2.8. Freundlich isotherm

The Freundlich isotherm process assumes heterogeneous surface energy. In this assumption, the adsorbent has many functional groups. Depending upon the pollutants, each functional group will have different kinetic energies or different preferences for the pollutant. Hence, uniform energy cannot be assumed in all cases, unless the adsorbent has uniformity or the same type of functional group. Perhaps, the Freundlich isotherm is more feasible when considering heterogeneous surface energy, especially in natural systems. For example, if soil or some natural adsorbents are used, many functional groups will be present on the surface of absorbents, and at the same time, that functional group will have a different energy of attraction or energy of adsorption. The functional expression can be written as follows:

$$q_e = K_f C_e^{1/n} \quad (5)$$

where q_e = adsorbate equilibrium concentration (mg/g); C_e = adsorbate on solution equilibrium concentration (mg/g) and K_f = the constant that indicates the sorption capacity of sorbate (mg/g).

The unit is given as $(\text{L/g})^{(1/n)}$, and n is a constant indicating the intensity of adsorption. This constant can be one or any integer or decimal number, where $n = 1$ is linear, $n > 1$ is a chemisorption process and $n > 1$ is a physisorption process [19]. The linear expression of this model can be obtained by the logarithm of the equation on both sides and is given as follows:

$$\log\frac{x}{m} = \log K_f + \frac{1}{n}\log C_e \quad (6)$$

where x = mass of adsorbate and m = mass of adsorbent.

2.9. Biosorption kinetics

A kinetic adsorption model is proposed to describe the solution uptake rate and the pseudo-second feasibility for scaled-up operation [20]. The pseudo-first-order, pseudo-second-order and Elovich models are the common models applied to kinetic studies [21]. The pseudo-first-order model can be mathematically expressed as follows:

$$\frac{dq_t}{dt} = k_1\left(q_e - q_t\right) \quad (7)$$

where k_1 = pseudo-first-order rate constant (min^{-1}); q_e = amount of adsorbate at equilibrium (mg/g) and q_t = biosorption capacities at equilibrium with respect to time t (mg/g).

The boundary condition $t = 0–t$ and $q_t = 0–q_t$ yields.

$$\ln\left(q_e - q_t\right) = \ln q_e - k_1 t \quad (8)$$

If the pseudo-first-order kinetic model is applicable to the system, then the plot of ln $(q_e - q_t)$ versus t will give a linear relationship, with $k_1 t$ and ln q_e as the slope and the intersect, respectively, that is, the linear plot of $(q_e - q_t)$ versus t gives the value of k_1. If the graph is linearly plotted with a good correlation coefficient, it shows that adsorption using this model is appropriate. The pseudo-second-order model can be expressed as:

$$\frac{dq_t}{dt} = k_2\left(q_e - q_t\right)^2 \quad (9)$$

The linear form of the equation is as follows:

$$\frac{t}{q_t} = \frac{1}{h} + \frac{1}{q_e}t \quad (10)$$

$$h = k_2 q_e^2 \quad (11)$$

where k_2 (g/mg min) is the pseudo-second-order rate constant and h (mg/g min) is the initial biosorption rate. The Elovich equation is shown as follows:

$$q_t = \left(\frac{1}{\beta}\right)\ln\left(1 + \alpha\beta t\right) \quad (12)$$

Eq. (12) is further simplified into a linear form as:

$$q_t = \frac{1}{\beta}\ln\left(\alpha\beta\right) + \frac{1}{\beta}\ln t \quad (13)$$

where α (mg/g-min) is the initial biosorption rate, β (g/mg) is related to the surface treatment and the activation energy for chemisorption.

3. Results and discussion

3.1. Effect of pH

pH was tested in studying the effect of pH on the removal of chromium, with a range of 2–9. As the pH increased, the electrostatic force attraction between the (cationic) chromium species and the surface of the adsorbent decreased, causing a lower removal efficiency. Moreover, hexavalent chromium may partially be converted into trivalent chromium (Cr^{+3}), which reacted with hydroxyl ions present on the surface of CMPKS [23]. Similar observations were made by other researchers [22]. The effect of pH on chromium removal was studied with a 0.1 g/100 mL adsorbent dose and with 120 min of contact time. The maximum adsorption capacity was 19 mg/g at pH 2, and it was close to 17 mg/g at pH 6 and 4, as observed (Fig. 2). The capacity decreased with increasing pH.

3.2. Effect of chromium initial concentration

To determine the effect of initial chromium concentrations on removal efficiency, the CMPKS dose of 0.4 g was added to 25, 50, 75, 100, 125 and 150 mg/L chromium concentrations at pH 6 (Fig. 3(a)). It was found that the increase in the initial chromium concentration from 25 to 150 mg/L resulted in a decrease in chromium removal efficiency from 88% to 52.67% due to the limited adsorbent material capacity, which directly decreased as the initial chromium concentration increased. Furthermore, this result is due to the increase in the number of ions competing for available binding sites and to the lack of binding sites for the complexions at higher initial chromium concentrations.

In addition, this study showed that the amount of chromium adsorbed was directly increased in the initial concentrations of chromium, which was 5.5–19.75 mg/g in constant adsorbent dose (Fig. 3(b)).

3.3. Effect of adsorbent dose

The study also determined the effect of dose on chromium adsorption. The amount of PKS used to remove chromium varied from 0.1 to 0.6 g. The condition was at pH 6 with a contact time of 120 min. This study explained that increases in the doses of the adsorbent resulted in the corresponding increase in chromium removal from 18% to 96% but was slightly different in corresponding doses of 0.5 and 0.6 g. The increase in the removal efficiency occurred because the availability of the surface also increases the pore size that is available for adsorption. Beyond the dose of 0.4 g, the removal rate increased slightly as the adsorbent dose continually increased (Fig. 4). This finding is similar to the previously reported study for rice husk, sawdust, wheat straw and other bioadsorbents [23].

3.4. Effect of contact time

The final parameter that was considered in this study was the contact time. The effect of contact time on the chromium removal efficiency while maintaining the pH, adsorbent dose and concentration constant using chromium solution is illustrated in Fig. 4. The contact time was noted to be proportional to the rate of the removal of chromium. From Fig. 5 it can be observed that there were three stages in this process. The first phase was the preliminary peak section, in which the adsorbent cured out chromium ions at the highest rate, at pH 6. During the second phase, the turnout was slowly referred to the consumption of all the active sites throughout the surface of the adsorbent, and it also provided a hint that the equilibrium phase was in view. The third stage was the equilibrium

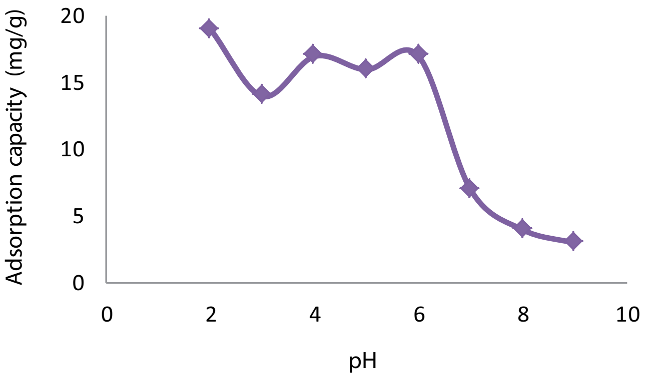

Fig. 2. Effect of pH on chromium removal.

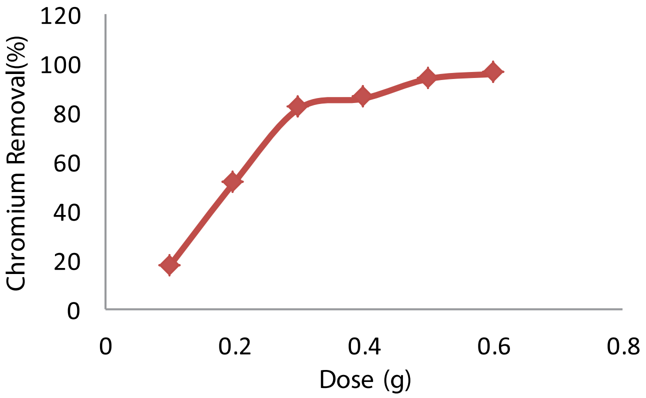

Fig. 4. Effect of different dosages of CMPKS on chromium removal %.

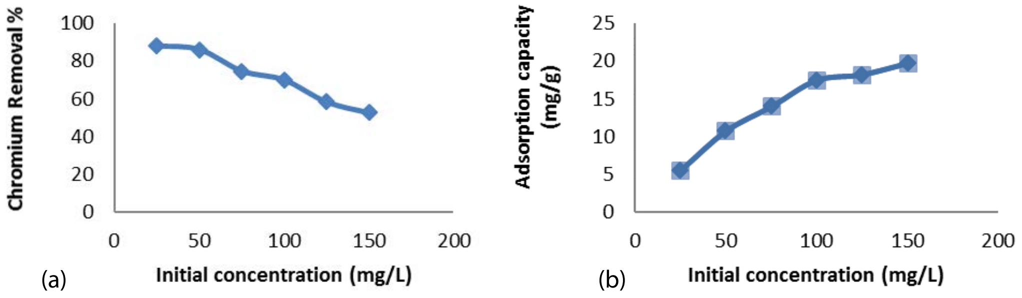

Fig. 3. (a) Effect of initial concentration on chromium removal and (b) Adsorption capacity (mg/g) at different initial concentrations of chromium.

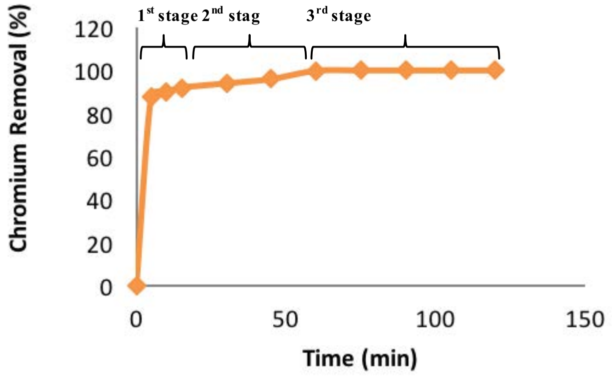

Fig. 5. Effect of contact time on chromium removal.

stage, observable after 60 min. During this phase, only very small uptake occurred, bringing the accumulated chromium removal to more than 86%.

3.5. Characterization of adsorbent

3.5.1. Scanning electron microscopy analysis

Scanning electron microscopy (SEM) was conducted on the surface morphology at 5.00 kV, and the enlargement sect between 1,000× and 1 K was used to monitor the surface structure and the pores present in raw PKS and CMPKS. The SEM images of PKS showed an irregular surface. The chemical modification made radical changes in surface morphology (Fig. 6(a)) and CMPKS expectations, having a smooth surface with some pores (Figs. 6(b) and (c)). CMPKS that is loaded with chromium leads to multiple attachments on the rough surface as well as occupation pores (Fig. 6(d)). Pores in adsorbents may have shape, location, connectivity and surface properties chemistry. Perhaps, one of the properties of a pore of CMPKS that makes it easy to observe is its size and dimensions. This property may likely be one of the reasons why size is often the first or main spatial property used to characterize the pore. High removal of chromium with limited pores indicates the suitability of the outer surface for adsorption.

3.5.2. Energy dispersive X-ray analysis

Energy dispersive X-ray spectrometry is a quantitative analysis that is used to understand the chemical composition of the PKS. The chemical-modified PKS after adsorption showed the presence of Cr, K, Cl, carbon and oxygen with values of 2.94, 1.54, 0.29, 25.91 and 69.33, respectively. The Cr confirmed the presence of adsorbed chromium, and K referred to the chemical-modified PKS that was able to adsorb it from aqueous solution that was already prepared in the laboratory, and it was also able to observe Cl, which came from the adjustment of pH. The CMPKS was efficient in not only removing chromium but also removing K and Cl.

3.6. Adsorption isotherm study

3.6.1. Langmuir isotherm

The Langmuir model assumes that adsorption occurs at specific homogeneous sites within the biosorbent [24].

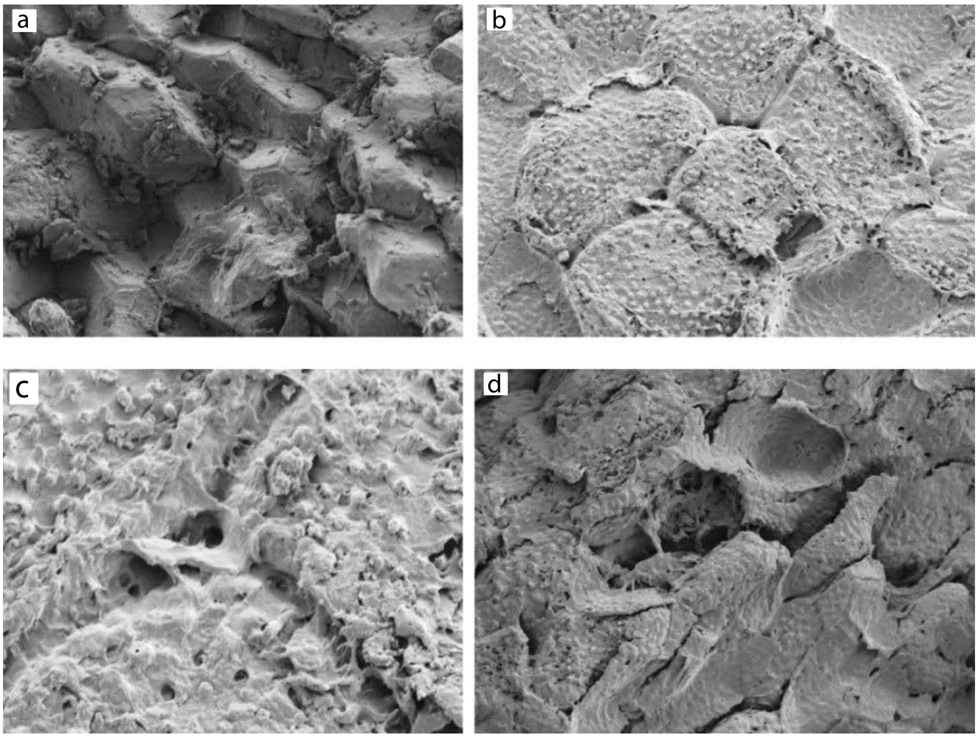

Fig. 6. SEM images of palm kernel shell: (a) Raw PKS, (b) CMPKS at resolution 1 K, (c) CMPKS at resolution 3 K and (d) chromium exhausted CMPKS.

The linearized formula of the Langmuir isotherm was used to characterize the adsorption process of chromium onto CMPKS, where Q_0 symbolizes the maximum monolayer capacity (mg/g), b is the constant of the Langmuir isotherm model, C_e is the equilibrium concentration (mg/L) and q_e is the amount of solute adsorbed (mg/g) [25]. A Langmuir isotherm plot of $1/q_e$ against $1/C_e$ is shown in Fig. 7.

From the plot, the obtained correlation coefficient R^2 value for Langmuir was 0.9896, which shows a good adsorption. The value of b was 0.1122 L/mg and Q_0 was 22.22 mg/g. This result suggested that the Langmuir isotherm might be a suitable model for CMPKS adsorption data. Thus, the process of chromium adsorption showed monolayer biosorption.

3.6.2. Freundlich isotherm

Fig. 8 shows that the adsorption of chromium onto PKSs is well characterized by the Freundlich isotherm model. The R_L values in the Freundlich isotherm model were found to be less than 1 for all concentrations, implying monolayer adsorption onto a surface. In this experiment, the value of the overall adsorption capacity K_f was found to be 4.304, referring to the ease of separation of chromium from aqueous solution, which is high. However, $1/n$ was observed to be less than 1, indicating that the adsorption is good. In this study, $1/n$ was 0.381 and R^2 was 0.923, showing that the intensity of the adsorption process is favourable over the entire range of concentrations studied. The results of adsorption isotherm analysis indicate that the adsorption of chromium on CMPKS favours the Freundlich isotherm model.

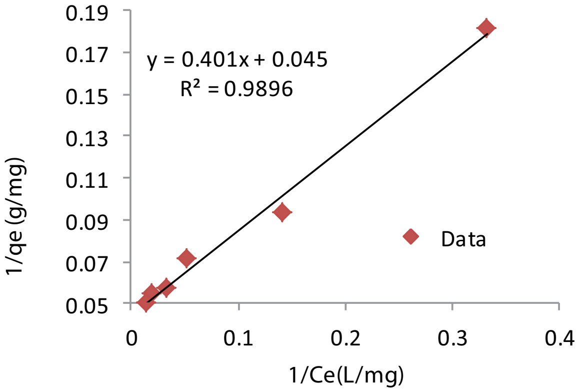

Fig. 7. Langmuir isotherm for the adsorption of chromium on palm kernel shell adsorbent.

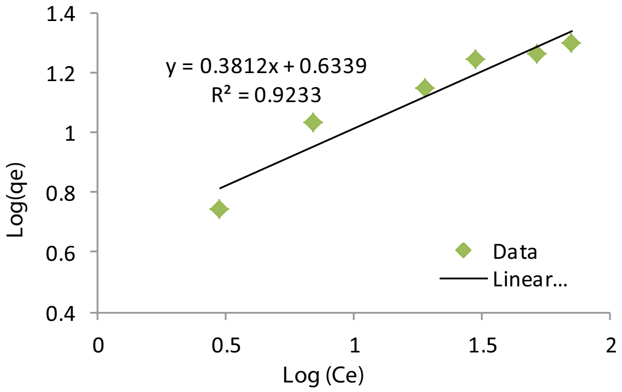

Fig. 8. Freundlich isotherm for the adsorption of chromium on palm kernel shell adsorbent.

3.7. Adsorption kinetics

The kinetic adsorption process that is involved in the chromium adsorption on the adsorbent is a dynamic adsorption process in terms of the order of the rate constant [26,27]. The adsorption experiment was carried out at concentrations of 25–150 mg/L, at pH 6, at an adsorbent dose of 0.4 g/100 mL and at a contact time varying from 5 to 120 min. Here, two kinetic models were used to fit the experimental data: pseudo-first-order and pseudo-second-order kinetic models.

3.7.1. Pseudo-first-order model

The Lagergren rate equation was used to investigate the pseudo-first-order reaction by plotting a straight line graph of ln $(q_e - q_t)$ against t, as shown in Fig. 9. The constant value of the first-order k_1 was obtained to be 0.0741 per minute. The correlation coefficient R^2 value was found to be 0.802. The q_e value obtained in the pseudo-first-order model was 0.425 mg/g. Based on the observed, calculated and experimental values, it can be seen that the adsorption of chromium does not follow the pseudo-first-order kinetic model.

3.7.2. Pseudo-second-order model

The pseudo-second-order model equation was used to obtain the constant rate of chromium by plotting the relation between t/q_t against t to show the trend of this model, which appears as a linear form at a 50 mg/L chromium concentration (Fig. 10). The k_2 for the second-order value was 0.054 g/mg min. The correlation coefficient R^2 value was found to be 0.99. The q_e value obtained in the pseudo-second-order model was 12.674 mg/g. Moreover, the likelihood of chemisorption largely constitutes chromium adsorption onto CMPKS.

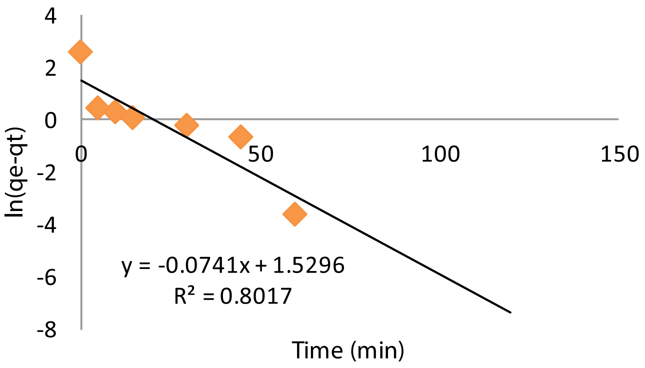

Fig. 9. Pseudo-first-order model for the adsorption of chromium on CMPKS.

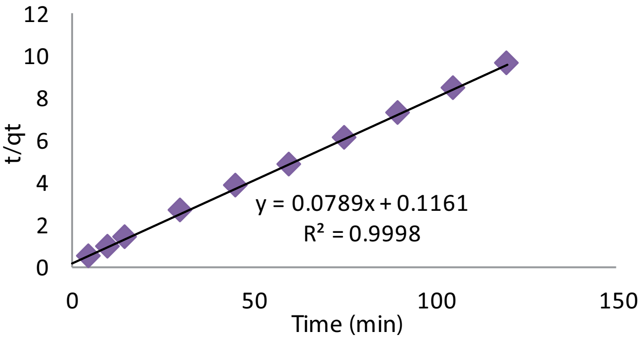

Fig. 10. Pseudo-second-order model for the adsorption of chromium on CMPKS.

Thus, the results showed that the pseudo-second-order model is the best for the biosorption process of the PKS.

4. Conclusion

In this experiment, chromium was removed by a chemical modification of PKSs. The result of this study suggested that CMPKS can be a potential adsorbent for the removal of chromium hexavalent from aqueous solutions. CMPKS can effectively remove chromium at pH 6. Conclusions can be drawn from the effect of four parameters, such as initial chromium concentration, adsorbent dose, contact time in minutes and pH of the aqueous solution. In addition, the result shows that the maximum adsorbent was found at 96% for the removal of chromium at a 0.6 g dose and the removal of chromium concentration of 50 mg/L in 120 min, and was found at 86% at the initial chromium concentration of 50 mg/L and at a dose of 0.4 g in 120 min of contact time.

The optimum removal for this study was 86% to provide an economic and low-cost removal option. Moreover, the Langmuir isotherm model was found to be the best model for the adsorption process, while the Freundlich isotherm model also indicates its active adsorption capability. The heterogeneous surfaces and adsorption capacity are related to the concentration of adsorbate at equilibrium. The pseudo-second-order kinetic model proved adsorption effectiveness, with a high correlation coefficient, almost reaching a unit value (0.99). This result indicates that electrostatic interactions or an effective chemisorption interaction is dominant.

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