Adsorption Kinetic Study for Removal of Heavy Metal from Aqueous Solution by Natural Adsorbent

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ABSTRACT

This paper deals with studying the removal of toxic heavy metals ions, such as Chromium (VI) and Manganese (II) from wastewater using activated carbon obtained from palm kernel at different conditions as contact time, amount of adsorbent, temperature, initial concentration and pH. In order to find out thermodynamic and kinetic parameters, equilibrium adsorption models were applied. The experimental data was confirmed with both Langmuir and Freundlich isotherm models. Adsorption rate constant was determined from Lagergren equation and pseudo-second order equations. The sorption ions of Chromium (VI) and Manganese (II) onto palm kernel was strongly adsorbed dependent on contact time, initial Chromium (VI) and Manganese (II) concentration, adsorbent dosage, temperature and pH value. thermodynamic parameters can be stated as, negative value of ΔG° and positive value of ΔS° show that the adsorption of Cr (VI) and Mn (II) ions onto palm kernel is a spontaneous process and positive value of ΔH° indicates that the adsorption is endothermic in nature. Finally, it can be seen that the pseudo-second order equation provided the best correlation coefficient (R²) for the adsorption data.

Keywords: Adsorption, palm Kernel, carbon, and heavy metals.

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1. INTRODUCTION

Palm kernels are the hard-protecting coverings of grains of rice. The husk is made of hard materials, including silica and lignin in order to protect the seed during the growing season. The husk is mostly indigestible to humans. During the milling process, the husks are removed from the grain to create brown rice; the brown rice is then milled further to remove the bran layer to become white rice. Palm kernels are an insulating material because they are difficult to burn and less likely to allow moisture to propagate mold or fungi. When burned, palm kernel produces significant amounts of silica element. The very high content in amorphous silica of the husks confer to them and to their ash (SiO₂~ 20 wt.%) after combustion are very valuable properties
for excellent thermal insulation. Besides, palm kernel contains abundant floristic fiber, protein and some functional groups such as carboxyl and amidogen \[1\].

The worldwide annual palm kernel output is about 80 million tones and over 97% of the husk is generated in the developing countries. Egypt is one of them. Generally, farmers and rice processor often burn the palm kernel as wastes, and this which release carbon dioxide (CO\(_2\)) into the atmosphere. CO\(_2\) is a well-known greenhouse gas. The increasing in volume of CO\(_2\) gas in the atmosphere is believed to cause global warming commonly known as greenhouse effect. The CO\(_2\) gas does not only elevate global temperature; it also gives negative impact to human health because its higher concentrations can effect on respiratory function. Large volume of CO\(_2\) displaces oxygen in the air, resulting in lower oxygen concentrations for breathing \[2\]. Contamination of ground and surface water by different organic and inorganic pollutants are a major factor of environmental problems for the numbers of years. The pollutants are usually discharged by the industries into natural water streams and could have contaminated the ground water.

The presence of toxic compounds in different industrial effluents often represents a risk to the environment. Different methods such as chemical oxidation, coagulation, chlorination, solvent attraction, liquid membrane permeation and adsorption, have previously been employed to remove pollutant in the wastewater. However, these treatment methods involve expensing materials and operating cost \[3\]. There has been a great deal of research into finding the cost-effective methods for the removal of contaminants from waste water. The abundance and availability of agricultural by-products such as palm kernel make them good sources of cheap raw material for natural adsorbents. Many carbonaceous materials such as fly ash, hen feathers and deoiled soya are used as an absorbance. Palm kernel (contains about 20% silica) has been reported as a good adsorbent for many metals and basic dyes \[3,4\].

In recent years, attention has been focused on the utilization of unmodified or modified palm kernel as a sorbent for the removal of pollutants (industrial wastewater). Some researchers (Nakbanpote, et al., 2000) found that the modified palm kernel exhibited higher adsorption capacities than unmodified palm kernel \[5\]. The major components of palm kernel which may be responsible for sorption are carbon and silica. Note that silica is composed of SiO\(_4\).4H\(_2\)O in which each oxygen atom is shared between two adjacent tetrahedrons. The Si-O bond is about 50% ionic owing to the large difference in the electronegativity of oxygen and silicon. Palm kernel as a sorbent in removing dyes, heavy metals and some other chemicals have been reported. Its application to absorb lead, cadmium, selenium, copper, zinc, mercury, reactive blue, reactive orange 16, reactive yellow 2 and 2,4-dichlorophenol have been reported. The capability or the rate of absorption of modified or unmodified palm kernel is depend on few factors such as the effect of pH, initial concentration, agitation rate, sorbent dosage, temperature which could be further researched for more efficient applications.

The aim of the present study to investigate the possibility of using low cost agriculture waste such as activated carbon obtained from palm kernel to remove Chromium (VI) and Manganese (II) ions from wastewater at different conditions.

2. EXPERIMENTAL

2.1. Preparation of adsorbent

The husk was washed with hot distilled water to remove water soluble impurities and dried in sun. Then it was impregnated with H\(_3\)PO\(_4\) (40%) and carbonized at 450
6°C in muffle furnace for 3 hours. For impregnation, the ratio of acid volume to weight of palm kernel carbon was used as 2:1. This palm kernel carbon was then washed with demineralized water and dried in a hot air at 100 °C. The Prepared activated carbon from palm kernel (ACs) were ground and sieved to 170 – 200 mesh before utilizing it as activated palm kernel carbon. The Preparation of activated carbon from palm kernel shows in Flow Chart below.

Flow Chart (1): Preparation of activated carbon from palm kernel

1- Palm kernel samples were cut into pieces of 1 to 3 cm.

2- The palm kernel was washed with hot distilled water to remove water soluble impurities.

3- The washed palm kernel dried in sun to remove the moistures content.

4- The dried palm kernel was impregnated with H$_3$PO$_4$ (40%) the ratio of acid volume to weight of palm kernel used as 2:1

5- The treated palm kernel with H$_3$PO$_4$ (40%) carbonized at 450 °C in muffle furnace for 3 hours.

6- The Prepared activated carbon palm kernel (ACs) was cooled at room temperature.

7- This palm kernel carbon was then washed with demineralized water.

8- This washed palm kernel carbon was dried in a hot air at 100 °C in an oven.

9- The dried ACs samples were sieved to 170 – 200 mesh before utilizing it as activated carbon palm kernel.
The physicochemical characteristic of palm kernel is shown in Table 1.

Table 1: Physicochemical characteristic of palm kernel. [2]

| Characteristic        | Unit  | Value  |
|-----------------------|-------|--------|
| Bulk density          | g/ml  | 0.73   |
| Solid density         | g/ml  | 1.5    |
| Moisture content      | %     | 6.62   |
| Ash content           | %     | 45.97  |
| Particle size         | mesh  | 200.16 |
| Surface area          | M²/g  | 272.5  |
| Surface acidity       | meq/gm| 0.1    |
| Surface basicity      | meq/gm| 0.45   |

2.2. Measures and analysis

The experiments were done by using digital magnetic stirrer MS-H-Pro with temperature sensor PT 1000. Samples (0.25ml) are withdrawn in the storage tank. Perkin-Elmer 2380 atomic absorption spectrophotometer was used to analyze concentrations of the dissolved Chromium (VI) and Manganese (II) ions. Crison GLP 21 pH-meter was used to adjust pH of solutions.

2.3. Procedure

The continuous techniques used due to large size of palm kernel. Therefore, it has not affected the continuous sample taking with time intervals. These experiments were performed by stirring palm kernel and 200 ml of potassium dichromate and Manganese sulphate solutions. Different pH values of the solution ranged from 1-4 was studied. pH was adjusted by using sulphric acid and sodium hydroxide. Experiments were carried out at different variables of temperature 301, 303, 308 and 313K, stirring speed 100, 250, 400, and 500 rpm, initial Chromium (IV) and Manganese (II) ions concentration 50, 100, 150, 200, and 300 mg/l and Palm kernel dosage 0.1, 0.2, 0.3 and 0.4 g/200ml. 0.25 ml of the sample was taken from the solution of the reaction at different time intervals for analysis. The samples were taken at regular time intervals. Then, they were analyzed by using atomic absorption spectrophotometer.

3. RESULTS AND DISCUSSIONS

3.1. Effect of pH

The pH of the solution is one of the most critical parameters of adsorption of metal ions from aqueous solutions which affects surface charge of the adsorbent, the
degree of ionization and specification of adsorbate \[6\]. The initial concentration of \(\text{Cr}^{6+}\) and \(\text{Mn}^{2+}\) were 100 mg/l and the contact time for adsorption was kept at 90 min to ensure the complete equilibrium.

In order to establish the effect of pH on the adsorption of Chromium and Manganese ions, the equilibrium studies at different pH values have been carried and in the range of 1 to 4 for Chromium and Manganese. The effect of initial pH on the adsorption process is presented in Figs. (3.1- 3.4). It is shown the adsorbed amount of Chromium and Manganese against increasing pH and maximum adsorption are obtained at pH 2 for \(\text{Cr}^{6+}\) and pH 4 for \(\text{Mn}^{2+}\).

For Chromium
The graph reveals that the adsorption of \(\text{Cr}^{6+}\) on palm kernel carbon increases with the decreased pH of the solution. It is evident from the plots that optimum pH is 2.0. Improved adsorption at low pH may be explained on the basis of assumption that the large number of \(\text{H}^+\) ions present in solution at low pH can neutralize the negatively charged palm kernel carbon surface or convert the neutral groups to the positively charged groups. Hence high degree of adsorption of \(\text{Cr}^{6+}\) may be attributed due to the electrostatic force of attraction between the adsorbent and adsorbate.

For Manganese
The adsorption capacities of \(\text{Mn}^{2+}\) ions onto adsorbents increased significantly with increasing pH value. At low pH the higher concentration of \(\text{H}^+\) ions in the solution compete with \(\text{Mn}^{2+}\) for the adsorption site of adsorbents. Generally, the positive charge of adsorbent surface decreases with increasing pH to value 6 leading to the decrease in the repulsion between adsorbent and \(\text{Mn}^{2+}\), thus improving the adsorption capacity.

Fig. 3.1: Effect of pH for the adsorption of Chromium (VI) onto palm kernel carbon (The initial concentration = 100 mg/l, palm kernel dose = 0.1g/200ml, stirring speed = 500 rpm T= 301K and time = 90 min).
Fig. 3.2: Effect of pH for the adsorption of Manganese (II) onto palm kernel carbon
(The initial concentration = 100 mg/l, palm kernel dose = 0.1g/ 200ml,
stirring speed = 500 rpm T= 301K and time = 90 min).

Fig.3.3. Effect of pH against %adsorption of Chromium (VI) onto palm kernel carbon
(The initial concentration = 100 mg/l, palm kernel dose = 0.1g/ 200ml,
stirring speed = 500 rpm T= 301°K and time = 90 min).
Fig. 3.4. Effect of pH against % adsorption of Manganese (II) onto palm kernel carbon
(The initial concentration = 100 mg/l, palm kernel dose = 0.1g/200ml, stirring speed = 500 rpm T= 301 K and time = 90 min).

3.2 Effect of contact time

The efficiency of Chromium and Manganese adsorption from aqueous solutions with five different initial concentrations (50, 100, 150, 200, 300 mg/l) on 0.1 g/200ml of Palm kernel was observed depending on contact time up to 90 min as shown in Figs. (3.5 and 3.6). Based on the change in metal concentration in the aqueous solution before and after achieving equilibrium absorption, the adsorption efficiency was calculated $q_e$. The removal increases with time and reaches a maximum at 90 min. This indicates that the concentration of Chromium and Manganese in the solution decreased rapidly within the first 30 min and the removal was virtually completed within 90 min. It is clear that the removal of metal ions can be derived into two stages: one in which the removal rate is very high. It is very important to determine the equilibrium time that is the contact time characterized by unchanging Cr$^{6+}$ and Mn$^{2+}$ concentration in the solution was achieved after 30 min for all used concentrations of solutions, this period is denoted as second stage of the adsorption.

This was explained by the fact that adsorption sites were vacant at first stage, and Cr$^{6+}$ and Mn$^{2+}$ could easily interact with these sites [7]. The adsorption capacity was almost constant for all the studied concentrations and such it was considered as the equilibrium time for Cr$^{6+}$ and Mn$^{2+}$ onto Palm kernel carbon.
Fig. 3.5: Effect of contact time on the % adsorption of Chromium (VI) onto Palm kernel carbon (The initial concentration = 50 to 300 mg/l, Palm kernel dose = 0.1 g/200 ml, pH = 2, stirring speed 500 rpm, contact time = 90 min and T = 301°C).

Fig. 3.6: Effect of contact time on the % adsorption of Manganese (II) onto Palm kernel (The initial concentration = 50 to 300 mg/l, palm kernel carbon dose = 0.1 g/ 200 ml, pH = 4, stirring speed 500 rpm, contact time = 90 min and T = 301°C).
High adsorption rate at the beginning of the adsorption process is due to the numerous readily available active adsorbing sites on the adsorbent surface that is the large uncovered surface area of palm kernel which was provided by high amount of palm kernel. Additionally, the driving force for the adsorption is the difference between concentration of Chromium and Manganese ions in the solution and solid/liquid interface which has the highest value at the beginning of the process, resulting in fast adsorption. Lower slopes of the curves confirm that the second stage was a bit lower due to lower diffusion velocity of metal ions within the pores of the palm kernel structure. It can be observed that the best adsorption efficiency was achieved in the case of initial solution with the lowest metal ions concentration (50 mg/l).

3.3 Effect of adsorbent dose

The palm kernel carbon concentration is an important parameter because it determines the capacity of palm kernel for a given initial metal ions concentration. The effect of adsorbent dose on the adsorption of heavy metal was studied at contact time of 90 min for initial heavy metal concentration of 100 mg/l at 301K. Fig.3.7 and 3.8, show that the removal percentage of Cr (VI) and Mn (II) ions increase as the adsorbent amount increases. Adsorption increases from 68.4 to 77.3 % with increase in adsorbent dose from 0.1 to 0.4 g/ 200 ml in case of Chromium ions and from 69.4 to 79.4 % in the case of Manganese ions after 90 min. The number of adsorption sites or surface area increases with the weight of adsorbent and hence results in a higher percent of metal ions removal at a high dose.

However, the amount of metal ions adsorbed per unit weight of adsorbent (q) decreases with the adsorbent dose Fig.3.7 and Fig.3.8 This is due to the fact that at higher adsorbent dose the solution ions concentration drops to a lower value and the system reaches equilibrium at a lower values of q indicating the adsorption sites remain unsaturated (It may be due to the overlapping of active sites at higher dosage causing a decrease in the effective surface area resulting in the conglomeration of exchanger particles).
Fig. 3.7: Effect of adsorbent dose of Palm kernel carbon on % Adsorption and q_e, initial concentration [Cr^{6+}] = 100 mg/l, pH= 2, stirring speed= 500 rpm, temperature= 301K.

Fig. 3.8: Effect of adsorbent dose of Palm kernel carbon on % Adsorption and q_e, initial concentration [Mn^{2+}] = 100 mg/l, pH = 4, stirring speed = 500 rpm, temperature = 301K.

3.4 Effect of initial concentration on Chromium and Manganese removal

At the initial stage of adsorption of metal ions from aqueous solution, the surface of the adsorbent is free of these metal ions and large amounts of Cr^{6+} or Mn^{2+} ions species move across from the solution to the palm kernel surface. It is necessary
to highlight that the adsorption capacity depends on the concentration of metal ions \cite{8}. The adsorption of Cr\textsuperscript{6+} or Mn\textsuperscript{2+} ions was carried out at different initial concentrations ranging from 50 to 300 mg/l at pH 2, 4 for Chromium and Manganese respectively, 90 min of contact time, 301K, 500 rpm and 0.1 g/ 200 ml of palm kernel. The amount of metal ions, q\textsubscript{e} (mg/g), increased with increasing initial concentration as shown in Fig.3.9 and Fig. 3.10, for Cr\textsuperscript{6+} and Mn\textsuperscript{2+} respectively. Furthermore, the results presented in Fig. 3.9 and 3.10, showed that the amount of the adsorbed Cr\textsuperscript{6+} or Mn\textsuperscript{2+} ions decrease with the increase of the initial concentration. This decrease in Chromium and Manganese removal percentage could be due to lack of sufficient active sites on palm kernel to adsorbed more metal ions available in the solution (i.e. saturation of black cumin sites at higher concentrations of copper or lead ions) \cite{9,10}. So, the percentage removal depended upon the initial metal ions concentration. This indicates the possible mono layer formation of metal ions on the outer surface of Palm kernel carbon.

Fig. 3.9: Effect of q\textsubscript{e} (mg/g) on initial concentration C\textsubscript{0} (mg/l) for Chromium using activated carbon palm kernel.
Fig. 3.10: Effect of $q_e$ (mg/g) on initial concentration $C_0$ (mg/l) for Manganese using activated carbon palm kernel.

3.5 Effect of speed of rotation on uptake of metal

Experimental results for the effect of speed of rotation (100, 250, 400, 500 rpm) are presented in Figs. 3.11 and 3.12. The removal of Cr$^{6+}$ and Mn$^{2+}$ using palm kernel carbon reaches 83.67% for Cr$^{6+}$ at 500 rpm and 92.35% for Mn$^{2+}$ at 500 rpm. It is obvious that speed of rotation helps metal removal from aqueous solutions. This is because metal ions, through their transportation to solid phase, meet resistance at the liquid phase, through the boundary layer. Rotation during experiments has led to a decrease of the boundary layer and a decrease to the resistance of transportation of metal ions. This increases the transfer rate of the ions.
Fig. 3.11: Effect of agitation on percentage adsorption of Chromium using activated carbon prepared from palm kernel carbon [Cr(VI) conc. = 100 mg/l; pH = 2.0; m/V = 0.1 g/200 ml; temperature = 301 K.]

Fig. 3.12: Effect of agitation on percentage adsorption of Manganese using activated carbon prepared from palm kernel [Mn(II) conc. = 100 mg/l; pH = 2.0; m/V = 0.1 g/200 ml; temperature = 301 K.]
3.6. Temperature Studies

3.6.1. Effect of Temperature

Temperature has a pronounced effect on the adsorption capacity the adsorbent. The continuous adsorption experiments were performed at different temperatures of 301K, 303K, 308K and 313K. The effect of temperature on the adsorption capacity of palm kernel was studied at constant initial concentration of 100 mg/l and 500 rpm for Chromium and Manganese, optimum pH values of 2 for Chromium and 4 for Manganese, and 0.1 g/ 200ml of palm kernel. The Figs.3.13 and 3.14 show that the removal efficiency increases by increasing the temperature for both chromium and Manganese.

Fig. 3.13: Effect of \( q_e \) on temperature at constant initial concentration of chromium of 100 mg/l, 0.1g/200 ml dose of activated carbon palm kernel and 500 rpm.
Fig. 3.14: Effect of $q_e$ on temperature at constant initial concentration of Manganese of 100 mg/l, 0.1g/ 200 ml dose of activated carbon palm kernel and 500 rpm. An increase in temperature involves increasing the mobility of Chromium and Manganese ions and decreasing in the retarding forces acting on the diffusing ions. these result enhancement the sorptive capacity of the adsorbent, increasing the chemical interaction between adsorbate-adsorbent and creation of active surface centers or by an enhanced rate of intra-particle diffusion of Cr$^{6+}$ and Mn$^{2+}$ ions into the pores of the adsorbent at higher temperature. This increase indicates that the adsorption is an endothermic process $^{[11-13]}$.

3.6.2. Thermodynamics parameters

The temperature dependence of the adsorption process is associated with changes in several thermodynamic parameters. The adsorption equilibrium data obtained for different temperatures were used to calculate the important thermodynamic properties such as standard Gibbs free energy ($\Delta G^o$), standard enthalpy change ($\Delta H^o$) and standard entropy change ($\Delta S^o$). These parameters were estimated using the following equations:

$$K_e = \frac{q_e}{C_e}$$  \hspace{1cm} (3.1)

$$\Delta G^o = -RT \ln K_e$$  \hspace{1cm} (3.2)

$$\Delta G^o = \Delta H^o - T \Delta S^o$$  \hspace{1cm} (3.3)

$$\ln K_e = \frac{\Delta S^o}{R} - \frac{\Delta H^o}{RT}$$  \hspace{1cm} (3.4)

where $q_e$(mg/g) is the amount of Cr$^{6+}$ or Mn$^{2+}$ ions adsorbed onto the palm kernel from the solution at equilibrium, $C_e$ (mg/l) the equilibrium concentration of Cr$^{6+}$ or Mn$^{2+}$ ions solution, R (J/mol.K) the gas constant 8.314, T(K) the absolute temperature, and $K_e$ (l/g) the adsorption equilibrium constant. $\Delta H^o$and $\Delta S^o$ were obtained from the slope and intercept of the Van’t Hoff’s plot of ln ($K_e$) versus 1/T as
shown in Figs. 3.15 and 3.16 and the values of $\Delta G^0$, $\Delta H^0$ and $\Delta S^0$ were collected in Table 2.

![Graph](image1)

Fig. 3.15: Effect of ln ($K_e$) on reciprocal of temperature, at constant initial concentration of 100 mg/l, 0.1 g/200ml of palm kernel and 500 rpm for Chromium.

![Graph](image2)

Fig. 3.16: Effect of ln ($K_e$) on reciprocal of temperature, at constant initial concentration of 100 mg/l, 0.1 g/200ml of palm kernel and 500 rpm for Manganese.

From Table 2, The Positive values of $\Delta H^0$ obtained indicated the endothermic nature of the process. The negative $\Delta G^0$ value confirmed the feasibility of the sorption process and the spontaneous nature of adsorption, and the degree of spontaneity of the reaction increases with increasing temperature. The positive $\Delta S^0$ suggests the increased randomness at solid/liquid interface during the adsorption of Cr (VI) and Mn (II). Also, during the adsorption of chromium and Manganese, the adsorbed solvent molecules, which are displaced by the chromium and Manganese ions, gain
more translational entropy than that is lost by the adsorbate ions, thus allowing for the prevalence of randomness in the system [11, 13, 14].

Table (2): Thermodynamic parameters of Chromium and Manganese onto palm kernel carbon at constant initial concentration of 100 mg/l.

| Heavy metal | T (K) | $\Delta G^o$ (kJ/mol) | $\Delta H^o$ (kJ/mol) | $\Delta S^o$ (J/mol.K) |
|-------------|-------|------------------------|------------------------|------------------------|
| Chromium    | 301   | -23.66879              | 19.51                  | 78.7                   |
|             | 303   | -23.82618              |                        |                        |
|             | 308   | -24.21968              |                        |                        |
|             | 313   | -24.61317              |                        |                        |
| Manganese   | 301   | -18.31967              |                        |                        |
|             | 303   | -18.44149              | 13.82                  | 60.91                  |
|             | 308   | -18.74603              |                        |                        |
|             | 313   | -19.05058              |                        |                        |

3.7: Kinetics of Adsorption

Kinetics is the study of the rates of chemical processes to understand the factors that influence the rates. Study of chemical kinetics includes careful monitoring of the experimental conditions which influence the speed of a chemical reaction and hence, help attaining equilibrium in a reasonable length of time such studies yield information about the possible mechanism of adsorption and the different transition states on the way to the formation of the final adsorbate-adsorbent complex and help develop appropriate mathematical models to describe the interactions.

Various kinetics models [14] namely pseudo first-order and pseudo second-order, have been used for their validity with the experimental adsorption data for Cr$^{6+}$ and Mn$^{2+}$ onto palm kernel carbon.

The study of adsorption kinetics describes the solute uptake rate and evidently this rate controls the residence time of adsorbate uptake at the solid-solution interface including the diffusion process. The mechanism of adsorption depends on the physical and chemical characteristics of the adsorbent as well as on the mass transfer process. The results obtained from the experiments were used to study the kinetics of metal ion adsorption. The rate kinetics of Cr$^{6+}$ and Mn$^{2+}$ adsorption onto palm kernel was analyzed using pseudo first-order [13, 15, 16] and pseudo second-order.

3.7.1 The pseudo first-order kinetic model

The pseudo first-order reaction equation of lagergren [17] was widely used for the adsorption of liquid/solid system on the basis of solid capacity. Its linear form is generally expressed as the following [14]:

$$\ln(q_e - q_t) = \ln(q_e) - k_1 t$$ (3.5)
where $q_e$ (mg/g) and $q_t$ (mg/g) are the values of amount adsorbed per unit mass at equilibrium and at any time respectively, $t$ (min) is time, $k_1$ ($\text{min}^{-1}$) is the pseudo first order adsorption rate coefficient. The values of $k_1$ and $q_e$ can be obtained from the slope and intercept of the linear plot of $\ln(q_e-q_t)$ vs. $t$, and showed in Fig.3.17, Fig.3.18 and listed Table 3.

It is necessary to know the value of $q_e$ for fitting the experimental data to the equation (3.5). The real test of the validity of equation (3.5) arises from a comparison of the experimentally determined $q_e$ values and those obtained from the plots of $\ln(q_e-q_t)$ vs. $t$ [14,17]. The correlation coefficients for the pseudo first-order kinetic model are low and a difference of equilibrium adsorption capacity ($q_e$) between the experimental and the calculated data was observed, indicating a poor pseudo first-order fit to the experimental data.

![Pseudo-first order kinetic fit for adsorption of Chromium onto palm kernel at different initial concentrations, 0.1 g/200ml palm kernel, 500 rpm and 301°K.](image-url)
3.7.2. The pseudo second-order kinetic model

The kinetic data were further analyzed using Ho and Mckay \cite{18,19}, which is based on the assumption that the adsorption follows second-order. The linear form can be written as follows:

\[
\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (3.6)
\]

where, \( k_2 \) (g/mg.min) is the rate constant of adsorption. By plotting a curve of \( t/q_t \) against \( t \), \( q_e \) and \( k_2 \) can be evaluated. The dependence of \( t/q_t \) versus \( t \), gives an excellent straight line relation for all the experimental concentrations Figs. 3.19 and 3.20. The values of \( q_e \), \( k_2 \) and \( R^2 \) are listed in Table 3 and all the \( R^2 \) values are very high in this study and close to 1 Table 3.

It was also noted that the values of the calculated pseudo second-order capacities, \( q_e \) were close to the experimentally determined capacities signifying the ability of the model to predict the experimental data. It can also be seen in Table 3 that, with an increase in initial metal concentration, the rate constant of adsorption \( k_2 \) decreases. A similar observation was also reported by the earlier researchers \cite{20,21}. The reason for this behavior can be attributed to the lower competition for the sorption surface sites at lower concentrations. At high concentrations, the competition for the surface active sites will be high and consequently lower sorption rates are obtained. The values for pseudo second-order index \( k_2q_e \) were determined for all samples and displayed in Table 3. The results show that the values of the index \( k_2q_e \) increased with reducing initial concentration of Chromium (VI) and Manganese (II).
The half-life of the adsorption process is shown in Table 3. The results shown revealed that that the half-life reduces with decreasing initial concentrations of Chromium (VI) and Manganese (II) in solution. This means that, as the initial concentration of Chromium (VI) and Manganese (II) in solution reduces, less time is needed to reduce the initial concentration by half its original value.

![Graph](image1)

**Fig. 3.19:** Pseudo-second order kinetic fit for adsorption of chromium onto palm kernel at different initial concentrations, 0.1 g/200ml palm kernel carbon dose, 500 rpm and 301 K.

![Graph](image2)

**Fig. 3.20:** Pseudo-second order kinetic fit for adsorption of Manganese onto palm kernel at different initial concentrations, 0.1 g/200ml palm kernel carbon dose, 500 rpm and 301K.
Table (3): Kinetic models and other parameters for adsorption of a) Chromium and b) Manganese onto palm kernel at different initial concentrations of metal ions, 0.1g/ 200 ml dose, 500 rpm and 301K.

(a)

| Kinetic models | Parameters | Concentration of Chromium(VI) solution |
|----------------|-----------|----------------------------------------|
|                |           | 50 (mg/l)  | 75(mg/l)  | 100(mg/l) | 150(mg/l) | 200(mg/l) |
| Pseudo-first order equation | $q_e$ (Exp) (mg/g) | 79.776 | 157.976 | 227.85 | 290.658 | 429.52 |
|                | $q_e$ (Calc.) (mg/g) | 39.97 | 81.59 | 137.14 | 201.17 | 284.06 |
|                | $k_1$ (min$^{-1}$) | 0.0390 | 0.0323 | 0.0360 | 0.0362 | 0.0379 |
|                | $R^2$ | 0.9435 | 0.9927 | 0.9881 | 0.999 | 0.9976 |
| Pseudo-second order equation | $q_e$ (Calc.) (mg/g) | 77.06 | 153.92 | 228.46 | 307.17 | 431.64 |
|                | $k_2$ (g/mg.min) | 0.00247 | 0.00104 | 0.00059 | 0.00036 | 0.00026 |
|                | $k_2q_e^2$ (mg/g.min) | 14.66 | 24.55 | 30.72 | 33.68 | 47.64 |
|                | $k_2q_e$ | 0.1902 | 0.1595 | 0.1345 | 0.1097 | 0.1104 |
|                | $t_{0.5}$ | 5.26 | 6.27 | 7.44 | 9.12 | 9.06 |
|                | $R^2$ | 0.999 | 0.992 | 0.996 | 0.9829 | 0.9826 |

(b)

| Kinetic models | Parameters | Concentration of Manganese (II) solution |
|----------------|-----------|----------------------------------------|
|                |           | 50 (mg/l)  | 100(mg/l) | 150(mg/l) | 200(mg/l) | 300(mg/l) |
| Pseudo-first order equation | $q_e$ (Exp) (mg/g) | 79.776 | 157.976 | 227.85 | 290.658 | 429.52 |
|                | $q_e$ (Calc.) (mg/g) | 23.83 | 49.83 | 72.25 | 99.13 | 155.8 |
|                | $k_1$ (min$^{-1}$) | 0.0314 | 0.0286 | 0.0296 | 0.0332 | 0.0372 |
|                | $R^2$ | 0.9923 | 0.9741 | 0.962 | 0.9798 | 0.9785 |
| Pseudo-second order equation | $q_e$ (Calc.) (mg/g) | 80.71 | 159.63 | 230.28 | 295.06 | 437.83 |
|                | $k_2$ (g/mg.min) | 0.00475 | 0.00214 | 0.00152 | 0.00115 | 0.00076 |
|                | $k_2q_e^2$ (mg/g.min) | 30.9411 | 54.4906 | 80.83809 | 100.3066 | 145.8732 |
|                | $k_2q_e$ | 0.383384 | 0.341366 | 0.351041 | 0.339953 | 0.333174 |
|                | $t_{0.5}$ | 2.61 | 2.93 | 2.85 | 2.94 | 3.00 |
|                | $R^2$ | 0.998 | 0.9984 | 0.998 | 0.9976 | 0.9984 |
3.8 Equilibrium Adsorption isotherm

The equilibrium adsorption isotherms are one of the most important data to understand the mechanism of the adsorption. They indicate how the adsorbate molecules distribute between the liquid phase and the solid phase at equilibrium. The analysis of the isotherm data by fitting them to different isotherm models is an important step to find the suitable model that can be used for design purpose. The Langmuir and Freundlich isotherm models are selected in this study [20-24].

3.8.1 Langmuir model

The Langmuir model is obtained under the ideal assumption of a totally homogenous adsorption, which each molecule possesses constant enthalpies and sorption activation energy (all sites possess equal affinity for the adsorbate) and represented as following: equation 3.7

\[
\frac{C_e}{q_e} = \frac{1}{q_{\text{max}} b} + \frac{C_e}{q_{\text{max}}} \quad (3.7)
\]

Where, \( q_e \) is the equilibrium metal ion concentration on the adsorbent (mg/g), \( C_e \) the equilibrium metal ion concentration in the solution, \( q_{\text{max}} \) the monolayer adsorption saturation capacity of the adsorbent and \( b \) is the Langmuir constant. Figs. (3.21 a,b) shows linear plots of \( C_e/q_e \) Vs. \( C_e \) was used to calculate the parameters of the Langmuir isotherm, by means of linear regression equation. From this regression equation and the linear plot, the value of the Langmuir constant was calculated and was tabulated in Table 4. The \( b \) and \( q_{\text{max}} \) were obtained from the slope and intercept of the plots respectively. High \( R^2 \) values for metal ions reveal the extremely good application of Langmuir model to these adsorptions.

The essential features of the Langmuir isotherm can be expressed in term of a dimensionless constant separation factor (\( R_L \)) which is defined as:

\[
R_L = \frac{1}{1 + b C_o} \quad (3.8)
\]

Where, \( C_o \) is the initial concentration of the metal ion. The values of \( R_L \) indicate the type of isotherm to be either unfavorable (\( R_L > 1 \)), linear (\( R_L = 1 \)), favorable (\( 0 < R_L < 1 \)) or irreversible (\( R_L = 0 \)). From this study \( R_L \) values for \( \text{Cr}^{6+} \) ions adsorption ranged from 0.725 to 0.305 and \( \text{Mn}^{2+} \) ions adsorption ranged from 0.608 to 0.205 are listed in table 4 indicate that the adsorption process is favorable [21-24].

3.8.2 Freundlich model

The Freundlich isotherm is the earliest known relationship describing the non-ideal and reversible adsorption not restricted to the formation of monolayer. This empirical model can be applied to multilayer adsorption, with non-uniform distribution of adsorption heat and affinities over the heterogeneous surface and expressed by the following equation:

\[
\log q_e = \log K_f + \frac{1}{n} \log C_e \quad (3.9)
\]
where $K_F$ and $1/n$ are the Freundlich constant denoting the adsorption capacity and intensity, respectively. Fig. (3.22 a,b) shows the linear plot of log $q_e$ versus log $C_e$, and the constants $1/n$ and $K_F$ were calculated from the slope and intercept respectively, and then collected in Table 4. The value of $1/n$ less than 1 represent of favorable adsorption and confirmed the heterogeneity of the adsorbent. Also, it indicates that the bond between heavy metal ions and palm kernel are strong $^{[25-28]}$.

![Graph](image)

Fig. 3.21: The linear Langmuir adsorption isotherm for a) chromium (VI) ions b) Manganese (II) ions with palm kernel carbon at 301 K.
Fig. 3.22: The linear Freundlich adsorption isotherm for a) chromium (VI) ions b) Manganese (II) ions with palm kernel carbon at 301 K.

Table 4: Adsorption isotherm constants for the adsorption of chromium (VI) and Manganese (II) onto activated carbon Palm kernel at 301K.

|                | Chromium |                           |                        |                         |                        |                         |                          |
|----------------|-----------|-----------------------------|------------------------|-------------------------|-------------------------|--------------------------|
|                | Langmuir  |                            |                        |                         |                         |                          |
|                | C_o (mg/l)| q_max (mg/g) | R^2     | R_L | 1/n | K_f | R^2 |
| 50             | 956.1     | 0.0076                  | 0.9946     | 0.725 | 0.78936 | 11.64 | 0.9942 |
| 100            |           |                         |                        | 0.568 | 0.9156 | 17.86 | 0.9984 |
| 150            |           |                         |                        | 0.467 |           |      |        |
| 200            |           |                         |                        | 0.397 |           |      |        |
| 300            |           |                         |                        | 0.305 |           |      |        |
|                |           |                           |                        |                         |                        |                          |
| Manganese      | Langmuir  |                            |                        |                         |                        |                          |
|                | C_o (mg/l)| q_max (mg/g) | R^2     | R_L | 1/n | K_f | R^2 |
| 50             | 803.98    | 0.0129                  | 0.9156     | 0.608 | 0.7264 | 17.86 | 0.9984 |
| 100            |           |                         |                        | 0.437 |           |      |        |
| 150            |           |                         |                        | 0.341 |           |      |        |
| 200            |           |                         |                        | 0.279 |           |      |        |
| 300            |           |                         |                        | 0.205 |           |      |        |
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