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Article

Kinetics and Thermodynamics Studies of the Biosorption of Pb(II), Cd(II) and Zn(II) Ions from Aqueous Solution by Sweet Orange (*Citrus sinensis*) Seeds

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Abstract: Kinetics and thermodynamics studies of the biosorption of Pb(II), Cd(II) and Zn(II) ions from aqueous solution by sweet orange (*Citrus sinensis)* seeds was investigated using batch adsorption experiment at 32 ^{o}C. The effect of pH, contact time, metal ion concentration and temperature were evaluated. The residual concentrations of the metal ions were determined by atomic absorption spectrophotometer. The results showed that maximum removal of Pb(II) and Zn(II) ions occurred at pH 6 with 98.69% and 99.82% respectively and Cd(II) ion was found to be 98.61% at pH 7. The equilibrium data fitted to Freundlich and Temkin adsorption isotherms. The order of fitness of the equilibrium data was in Temkin < Freundlich. Thermodynamics investigation showed that standard Gibb's free energy change (ΔG^o) was negative indicating that the adsorption of Pb(II), Cd(II) and Zn(II) ions by orange seeds *(Citrus sinensis)* were feasible and spontaneous. The negative value of standard enthalpy change (ΔH^o) implies that the reaction was exothermic and physical in nature while positive value of standard entropy change (ΔS^o) implies an irregular increase in the randomness at the solid/solution interface of the adsorbent during the adsorption process. The kinetics study revealed that the sorption of Pb(II), Cd(II) and Zn(II) ions could be best described by pseudo-second order kinetics models. This study demonstrated that orange seeds ***(Citrus sinensis)*** could be efficiently and effectively used as an alternative adsorbent to commercial activated carbon in the removal of Pb(II), Cd(II) and Zn(II) ions from aqueous solution.

Keywords: kinetics; thermodynamics; heavy metals; orange seeds; lead; cadmium; zinc.

1. Introduction

The increase in use of potentially toxic elements over the past few decades has unavoidably resulted in the flux of metallic substances in the aquatic and terrestrial environment [1,2]. These metals once released through anthropogenic activities cannot be destroyed or degraded and thus persist indefinitely in the environment, accumulate in living tissues throughout the food chain and pose a serious menace to human and public health [3].

Numerous concerted efforts has been made to remedy this occurrence, which includes the use of conventional methods such as ion exchange, membrane processing, electrolytic methods, chemical oxidation or chemical reduction, filtration, chemical precipitation and electrochemical treatment [4]. However, most of these methods are not economically feasible for small and medium size industries, they also suffered from high operational and maintenance costs, generation of toxic sludge and elaborated procedure involved in the wastewater treatment. Even commercial activated carbon is unequivocally accepted as universal adsorbent for wastewater treatment, but due to its higher cost, developing country like Nigeria cannot avoid this treatment technique as consequence of low income per capital [5].

In addition, adsorption technique was considered better in wastewater treatment because of simplicity of design, convenience and ease of operation. From last decades, biosorption process has emerged as a cost effective and efficient alternative method for wastewater treatment utilizing naturally occurring and agricultural waste materials as biosorbents. A large variety of agricultural wastes and by-products have been examined for their capability to remove pollutants from wastewater [2,6-11]. Agricultural wastes are widely available, affordable, environmental friendliness and presence of large amount of surface functional groups make agricultural wastes good alternatives to expensive synthetic adsorbents. Therefore, the search to develop efficient adsorbents is still on going.

Citrus Sinensis (sweet orange seeds) has become the most commonly grown tree fruit in the world and is employed commercially as a food, soft-drinks and candy flavor and for other purposes and it also protect the environment. These fruits are produced in large quantities and at times rubbish the environment. This built a requirement for the transformation of these wastes to valuable, hopeful, improved products which would promote the environment and the scientific community in the search for more cost effective adsorbent materials than the use of conventional adsorbents such as activated carbon. Literature review revealed that work had been done using orange peel for Ni(II) ions removal from simulated wastewater [12], but there is little or no information on the efficient use of orange seeds *(Citrus sinensis)* to adsorb Pb(II), Cd(II) and Zn(II) ions from aqueous solution. It is on this background information that this research was carried out.

2. Materials and Methods

2.1. Sample Collection and Pre-treatment

The *Citrus sinensis* (sweet orange seeds) were collected randomly within Minna metropolis of Niger state around April, 2012. The collected biomaterials were thoroughly washed with de-ionized water to remove dirt and other particulate matter. The fresh orange seeds were sun dried for two weeks and were pounded using mortar and pestle. It was re-pounded several times in order to get the smaller particles, and then soaked with n-hexane for three days to remove the fats in the adsorbents. After which, it was thoroughly washed again with distilled de-ionized water to remove the color in the adsorbents. Modification was done with 1 M HNO_3 for about six hours and then rinsed with de-ionized water and sun dried. The modification was done to increase the binding capacity of the adsorbent. The washed sample was once again subjected to a further treatment by pounding and sieving with a 300 μm size mesh to get a very fine powder and was weighed and stored in an air tight container.

2.2. Preparation of Aqueous Solution

The 1000 ppm of Pb(II), Cd(II) and Zn(II) were prepared accordingly by weighing and dissolving 1.6 g of $Pb(NO_3)_2$, 6.9 g of $CdSO_4.8H_2O$, and 4.6 g of $Zn(NO_3)_2.6H_2O$ in 1.0 liter volumetric flasks and they were made to the mark with more de-ionized water. Other concentrations were prepared from the stock solution by serial dilution.

2.3. Batch Adsorption Experiments

2.3.1. Effect of pH

The effect of pH on the adsorption uptake of each metal ions were studied by varying the pH from 1.0 - 8.0 at room temperature (32 ^{o}C). The 25 cm^3 of the prepared aqueous solution was measured and transferred into the beaker, followed by the addition of 0.5 g of the adsorbent. The pH of working solutions was adjusted to the desired values by the addition of either 0.1 M HCl or 0.1 M NaOH solution. After taking the pH value using pH meter, the mixture was well corked and were shaken using multi-purpose flask shaker for the 60 min. And thereafter the adsorbent was separated from metal ions solution using Whatman No. 42 filter paper and the final concentration of each of the metal ions remaining in the solution was determined using an atomic absorption spectrophotometer (Perkin Elmer; Analyst 200)

2.3.2. Effect of contact time

The effect of contact time with time intervals of was determined by using initial concentration of 10 ppm. The 25 cm^3 of the prepared aqueous solution was measured into a 250 mL conical flask with the aid of a measuring cylinder and 0.5 g of the adsorbent was weighed and added to the prepared aqueous solution in the conical flask, well corked and the mixture was shaken constantly for a time intervals of 10, 20, 30, 40, 50 and 60 min on a multi-purpose flask shaker at a speed of 350 rpm. The mixture was then filtered using Whatman No. 42 filter paper after each contact time and kept in plastic bottles. The final concentration of each of the metal ions was determined using atomic absorption spectrophotometer (Perkin Elmer; Analyst 200).

2.3.3. Effect of initial metal ions concentration

The effect of initial metal ion concentration on adsorption of Pb (II), Cd (II) and Zn (II) ions was determined using the equilibrium time for each of them at temperature 32 ^oC. The 25 cm^3 of the prepared aqueous solution were measured using measuring cylinder. The 0.5 g of the adsorbent was added and the flasks were corked. The mixture was vigorously shaken on a multi-purpose flask shaker for the equilibrium time for each of the metals ions. After the contact time intervals, the mixture was then separated using What man No 42 filter paper and the final concentration of each of the metal ions remaining in the solution was determined using an atomic absorption spectrophotometer (Perkin Elmer; Analyst 200).

2.3.4. Effect of temperature

The effect of temperature on the adsorption rate by orange seeds *(Citrus sinensis)* was determined for Pb(II), Cd(II) and Zn(II) ions using initial metal concentration of 10 ppm. The 25 cm^3 of aqueous solution was measured from the prepared 10 ppm and was transferred into 100 cm^3 beaker followed by the addition of 0.5 g of the adsorbent, and the mixture was then placed on a water bath and was stirred using a stirring rod. The temperatures considered were 20, 40, 60, 80 and 100 ^oC. After the contact time intervals, the mixture was filtered using Whatman No. 42 filter paper and the concentration of each of the metal ions remaining in the solution was determined using atomic absorption spectrophotometer (Perkin Elmer; Analyst 200).

2.4. Data Analysis

2.4.1. Calculation of metal uptake

The amount of metal ion adsorbed by the biosorbent was calculated by using the following equation

$$q = \frac{(C_o - C_e)V}{M} \qquad (1)$$

Where q is the amount of Pb(II), Cd(II) and Zn(II) adsorbed per gram adsorbent in mg^{-1}; C_o is the initial Pb(II), Cd(II) and Zn(II) concentration in mg/L; c_e is the concentration of Pb(II), Cd(II) and Zn(II) ions at equilibrium with the solid phase in mg/L; V is the volume of metal ion solution in litres (L); M is the mass of the orange seeds *(Citrus sinensis)* in gram.

The percentage removal of the metal ion was also calculated using the formula given below

$$X\% = \left(\frac{C_o - C_e}{C_o}\right) \times 100 \qquad (2)$$

Where $X\%$ is the percentage of metal ions removed.

2.4.2. Kinetic study profile

In analysis the kinetics profile of this sorbent material, pseudo-first and pseudo-second order kinetics model were employed and the equations are stated as follows.

2.4.2.1. Pseudo-first order kinetics

The rate law is given below:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \qquad (3)$$

Where, q_e and q_t are the amount of each of Pb(II), Cd(II) and Zn(II) adsorbed at equilibrium and time t, respectively. K_1 is the rate constant for the pseudo first order adsorption. The integrated law is given as follows

$$\mathrm{Log}(q_e - q_t) = \mathrm{Log}q_e - \frac{k_1}{2.303}t \qquad (4)$$

A plot of $\mathrm{Log}(q_e - q_t)$ against t was made and the values of k_1 and q_e were obtained from the slope and intercept, respectively.

2.4.2.2. Pseudo-second order kinetics

The second order kinetics rate law is given below:

$$\left({dq_t}/{dt}\right) = k_2(q_e - q_t)^2 \qquad (5)$$

Where k_2 is the rate law for pseudo second order biosorption.

On integrating between the boundary condition of $t = 0, t = t$ and $q = 0,\ q_e = q_t$

$$\frac{q_t}{q_{e(q_e - q_t)}} = k_2 t \qquad (6)$$

On linearizing, the following equation was gotten

$$t/q_t = \left(\frac{1}{k_2 q_e^2}\right) + \left(t/q_e\right) \quad (7)$$

A plot of $\left(\frac{t}{q_t}\right)$ against t gives $\left(\frac{1}{q_e}\right)$ as the slope and $\left(\frac{1}{k_2 q_e^2}\right)$ as intercept from which k_2 can be obtained. Both models are examined for suitability using their correlation coefficient, R^2 [13].

2.5. Adsorption Isotherms

Two adsorption isotherms were employed in this research and their respective formula are given below.

2.5.1. Freundlich adsorption isotherm

Freundlich isotherm is the earliest known relationship describing the adsorption equation and is often expressed as:

$$Q_e = K_f C_e^{1/n}$$

Where Q_e is the quantity of solute adsorbed at equilibrium (adsorption density: mg of adsorbate per g of adsorbent). C_e is the concentration of adsorbate at equilibrium K_f and n are the empirical constants dependent on several factors and n is greater than one [14].

2.5.2. Temkim isotherm

Temkim isotherm is given by the following equation:

$$Q_e = \frac{RT}{b} \ln(K_T C_e)$$

Equation above can be linearized into the following:

$$Q_e = B_1 \ln K_T + B_1 \ln C_e$$

Where $B_1 = \frac{RT}{b}$

Regression of q_e against $\ln C_e$ enables the determination of isotherm constant K_T and B_1. K_T is the equilibrium binding constant (L/mg) corresponding to maximum binding energy and constant B_1 is related to the heat of adsorption.

2.6. Thermodynamics Studies

The thermodynamics parameters such as standard Gibbs free energy change (ΔG^o), standard enthalpy change (ΔH^o) and standard entropy change (ΔS^o) were also studied in order to understand better the effect of temperature on the adsorption of Pb(II), Cd(II) and Zn(II) ions. This was achieved by carrying out equilibrium studies at different temperatures to obtain corresponding values of C_{ad} and C_e [13]. From these values, equilibrium constant, (K_c) was calculated using the following relationship:

$$K_c = {}^{C_{ad}}/_{C_e}$$

Where C_{ad} is the amount of Pb(II), Cd(II) and Zn(II) ions adsorbed at equilibrium in mg/L; C_e is the initial concentration of metal ions in mg/L; K_c is the thermodynamics equilibrium constant [15,16].

The standard Gibb's free energy change (ΔG^o) is related to the thermodynamics equilibrium constant by the following equation:

$$\Delta G = -RTlnK_c$$

Where, ΔG^o is the standard Gibb's free energy change in J/mol; R is the ideal gas constant whose value is 8.314 J/mol K ; K_c is the thermodynamics equilibrium constant; T is temperature in Kelvin.

3. Results and Discussion

3.1. The Results from Adsorption Experiments

3.1.1. Effect of pH on adsorption

The pH of the aqueous solution is one of the important parameters controlling the adsorption of toxic metal according to Wasewar *et al.* [9]. In this study, the function of hydrogen ions was determined at various pH covering the range 1 - 8 and the amount of metal ions adsorbed by the adsorbent was determined and the results of the investigation is illustrated in Fig. 1. At low pH value of 1 to 4, the amount of metal ions adsorbed was minimal. This could be explained in terms of the interaction between the charge of the adsorbent and the H^+ ions present in the solution [17]. For Pb(II) and Zn(II) ions, it was found that the metal ions removal from aqueous solution increased as the pH values increased from 1 to 4. The removal efficiency was higher at pH 6.0 with percentage removal of 98.69% and 99.82 % respectively. And as the pH increases further i.e. from 7 to 8, the metal ions removal decreases. This may be attributed to the fact that the hydroxyl groups of orange seeds formed stable complexes by coordination. Also, the surface charge of the adsorbent became more saturated leading to low adsorption of the metal ions. Conversely, for Cd(II) ions, the maximum adsorption (q_{max}) was attained at a pH value of 7.0 with percentage removal of 98.61% and low removal at pH value less than 3.0. This could also be due to the fact that H^+ ions compete with Cd(II) ions for the surface of the adsorbent which prevent Cd(II) ions from reaching the binding sites of the adsorbent caused by the repulsive forces resulted to low adsorption or it might also be due to the lower stability of chelates formed in extremely acidic media. Since toxic metals cations are totally released under highly acidic conditions [18]. At pH > 7.0 the adsorption of Cd(II) ions by the adsorbent reduces as a result of precipitation on the surface of the adsorbents due to formation of a hydroxide anions (cadmium hydroxide) precipitate. This result was in line with that reported by Amarasinghe and Williams [8] who studied the adsorption of Pb and Cu onto tea factory waste (TFW) in the pH range 2 to 7.

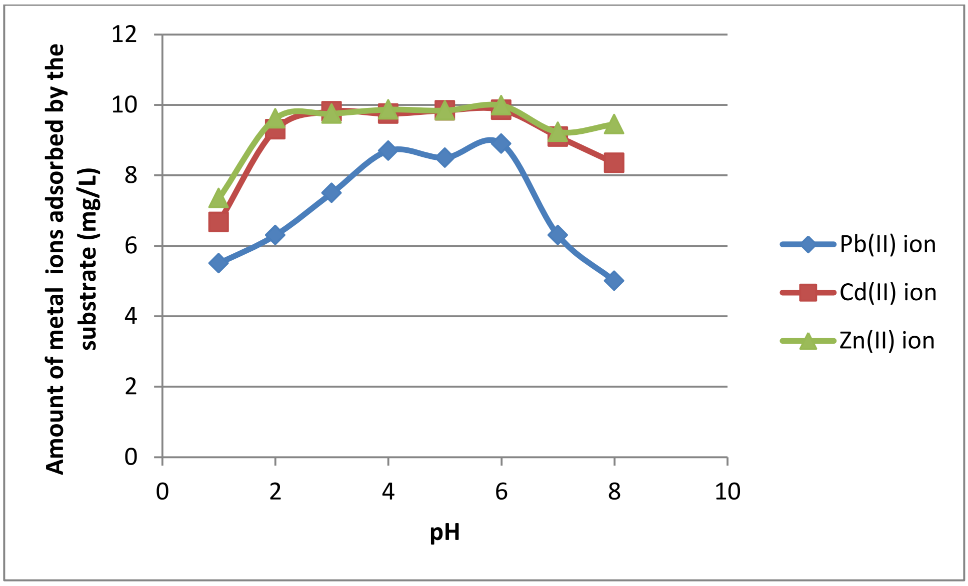

Figure 1. Effect of pH on the removal of the metal ions by orange seeds

3.1.2. Effect of contact time on adsorption

The biosorption of metal ions from aqueous solution is controlled by the rate of reaction which determines the equilibrium time. It is one of the important characteristics defining the efficiency of an adsorbent [19]. The kinetics of metal ions removal by orange seeds *(Citrus senensis)* was relatively fast within the first 30 min for Zn (II) ions as shown in Fig. 2. Then adsorption rate gradually decreases and removal of metal ion reaches equilibrium around 40 min with maximum percentage removal of 99.62%. Therefore, the percentage removal of Zn(II) ions increases with increase in contact time till equilibrium attained in 40 min which may be attributed to availability of enough active sites on the substrate. For Pb(II) ion, metal uptake increased with increase in contact time up to 20 min, after which equilibrium was attained at 30 min which may be due to large number of vacant sites available, which later slowed down and may be attributed to exhaustion of remaining surface sites and repulsive force between the adsorbent and metal ions. For Cd(II) ion, the equilibrium was reached at 20 min and the metal uptake of 97.9% was achieved, after which there was a decrease in the metal uptake and percentage removal. The initial faster rate of removal of Cd(II) ion may be due to the availability of the uncovered surface area of the adsorbents, since, the adsorption kinetics depends upon the surface area of the adsorbent [20]. The equilibrium time that was attained at 20, 30 and 40 min for Cd(II), Pb(II) and Zn(II) ions respectively may signifies the efficiency of the adsorbent for the removal of Cd(II), Pb(II) and Zn(II) ions from aqueous solution. This may also be attributed to the increase in the number of functional groups on the adsorbent introduced by 1.0 M HNO_3, since chemical modification of an adsorbent tends to increase the adsorption capacity of the adsorbent [21]. This study shows that the kinetic of Zn(II) ions biosorption was faster than those of Pb(II) and Cd(II) ions. This may be explained in terms of ionic radii, the ionic radius of the three metals; Zn(II) (0.74Å), Pb(II) (1.33Å) and Cd(II) (0.97Å). Since Zn(II) ions has a smaller ionic radius, it obvious that it was able to diffuse through the adsorbent pores faster than the heavier Pb(II) and Cd(II) ions. According to Oboh and Aluyor [22] during adsorption of metal ions, the ion of smaller ionic radii tends to move faster to potential adsorption sites than the heavier ones. This result was in conformation with that reported by Wasewar *et al*. [9] who studied the effect of contact time on the adsorption of Zn onto tea factory waste within various experimental conditions.

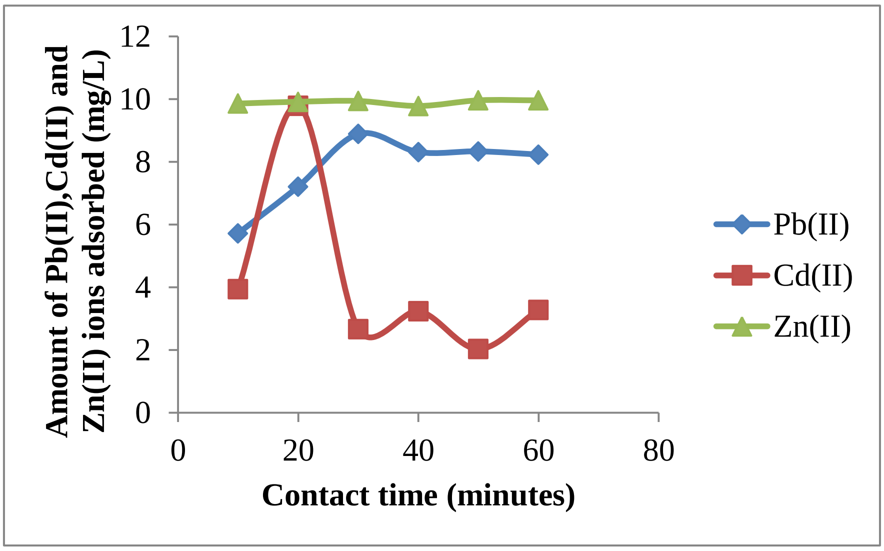

Figure 2. Effect of contact time on the sorption of Pb(II), Cd(II) and Zn(II) ions by orange seeds *(Citrus sinensis)*

3.1.3. Effect of initial metal ions concentration

The effect of initial metal ions concentration on the adsorption of Pb(II), Cd(II) and Zn(II) ions is shown in the Fig. 3. The amount of metal ions uptake for Pb(II), Cd(II) and Zn(II) ions, increases as the initial metal ions concentration increases. The rapid increase in the rate of adsorption may be due to the sufficient surface area to accommodate much more metal available in the solution. For Cd(II) ions, it was observed that adsorption of Cd(II) ions decreased from 98.74% to 97.12% with increased in metal ion concentration from 10 – 50 mg/L. At higher concentration most of the Cd(II) ions are left unabsorbed due to saturation of adsorption sites, and at low concentration of metal ions, more binding sites are available. But as the concentration increases, the number of ions competing for available binding sites in the biosorbent increased. For Zn(II) and Pb(II) ions, there was gradual increase in the rate of adsorption as the concentration of metal ions increases. This may be as a result of decrease in resistance for the uptake of solute from solution when the concentration of metal ions increases. The trend of adsorption was Zn(II) > Pb(II) > Cd(II) ion. The results obtained corroborated the findings of Okeimen and Onyenkpa [23] and Elaigwu *et al.* [24] that as the concentration of the adsorbate increases, the metal ions removed also increase.

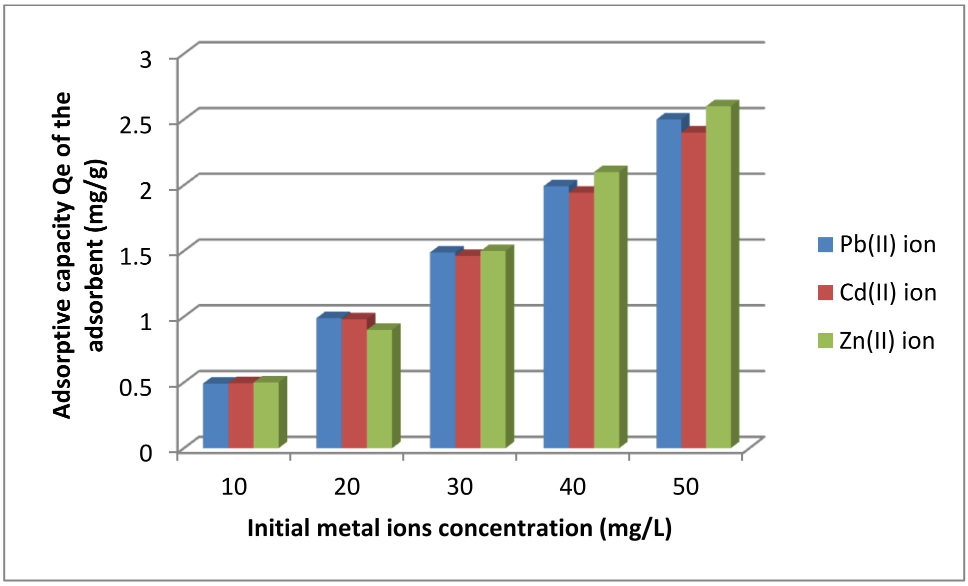

Figure 3. Effect of initial metal ions concentration on the adsorption of Pb(II), Cd(II) and Zn(II) ion by orange seeds.

3.1.4. Effect of temperature on adsorption

From the Fig. 4, it showed that there was gradual increase in the percentage removal for all the three metal ions as temperature increases from 20 to 100 ^{o}C. The maximum metal uptake by the adsorbent was determined as 9.935, 9.298 and 9.992 mg/L at 100 ^{o}C respectively. The increase in the amount of metal ions adsorbed as temperature increases might be attributed to the fact that the adsorption by orange seeds *(Citrus sinensis)* may involve not only be physical but also chemical adsorption, and sometimes involve bond rupture. The increasing temperatures had a remarkable action on swelling effect within the internal structure of the orange seeds enabling metal cation to penetrate further thereby increasing the adsorption rate.

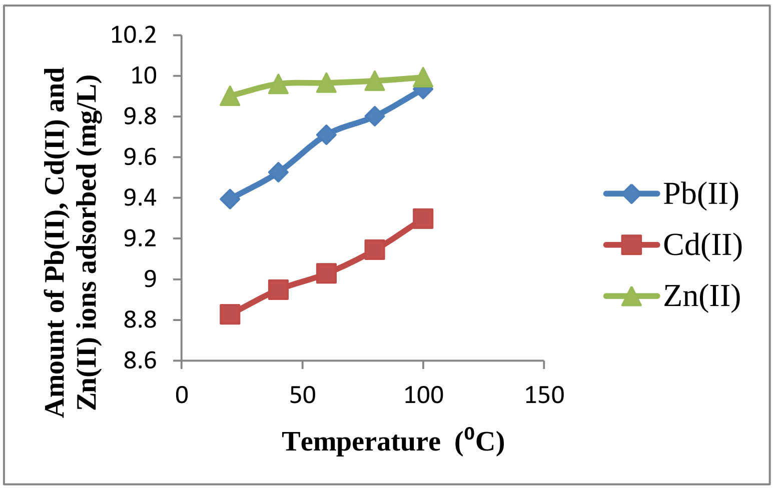

Figure 4. The effect of temperature for sorption of Pb(II), Cd(II) and Zn(II) ions by orange seeds *(Citrus sinensis).*

3.2. Adsorption Isotherms

Freundlich and Temkim isotherms were used to describe experimental data obtained. The Freundlich and Temkim isotherm plots are presented in Figs. 5-10. The various parameters are shown in Tables 1 and 2. From Table 1, the adsorption of Pb(II), Cd(II) and Zn(II) ions onto orange seeds *(Citrus sinensis)* can best be described by Freundlich isotherm based on the correlation coefficient values obtained. This means that the adsorption of the metal ions onto orange seeds *(Citrus sinensis)* was physical, heterogenous and multilayer in nature. Comparative examination of the data as shown in Tables 1 and 2 indicated that Freundlich model better described the adsorption of metal ions than Temkin model. The order of fitness was Freundlich > Temkin. These results were confirmed by the negative standard Gibb's free energy change (ΔG^0) value in (Table 5) which means the spontaneity of the adsorption process [14]. This is similar to the obtained results by Jimoh *et al.* [2] and Wasewar *et al.* [9].

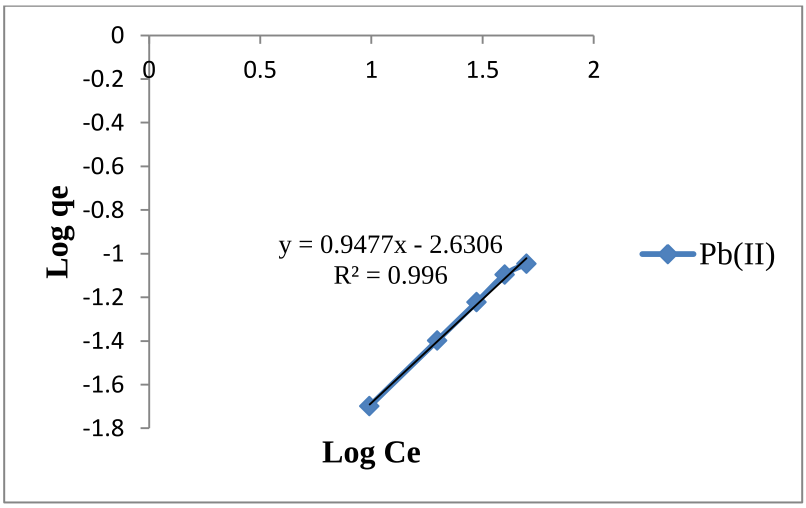

Figure 5. Freundlich isotherm plot for sorption of Pb (II) ions by orange seeds (*Citrus sinensis)*

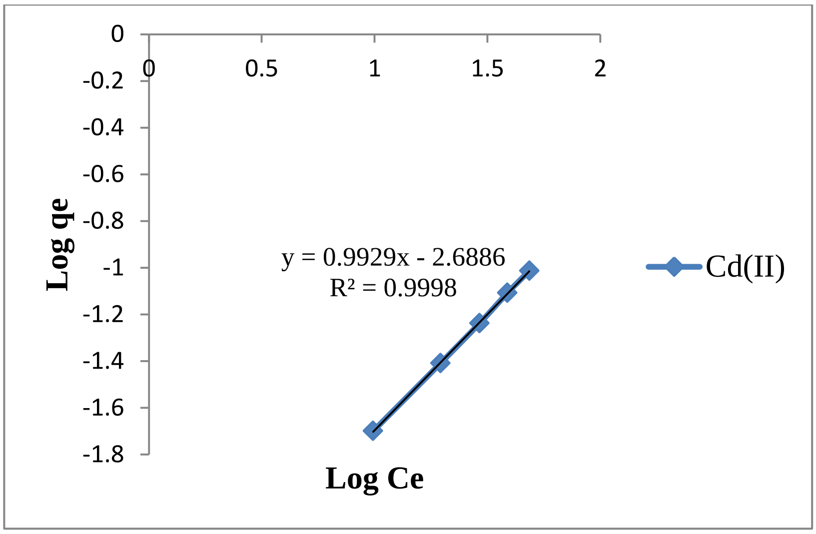

Figure 6. Freundlich isotherm plot for sorption of Cd(II) ion by orange seeds *(Citrus sinensis)*

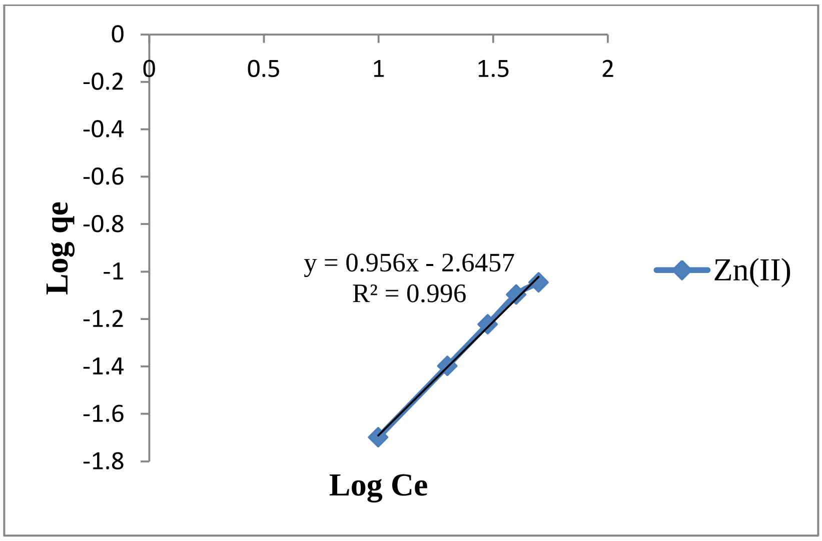

Figure 7. Freundlich isotherm plot for sorption of Zn(II) ion by orange seeds *(Citrus sinensis)*

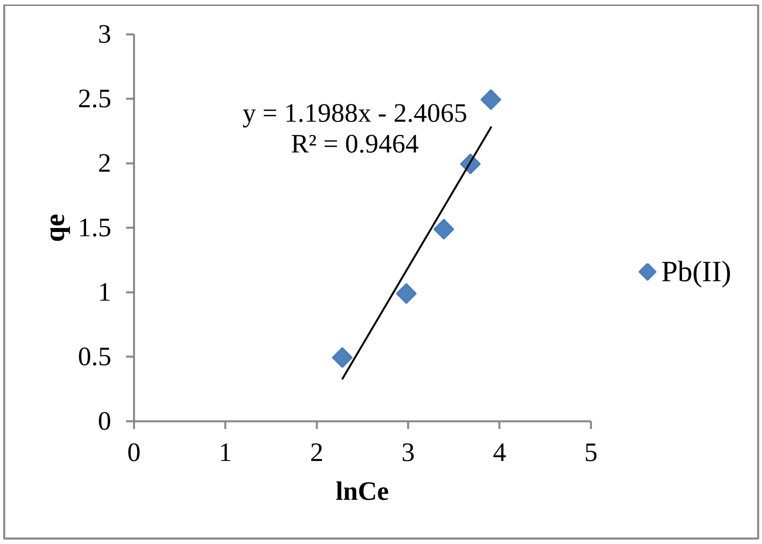

Figure 8. Temkin isotherm for the adsorption of Pb(II) ion by orange seeds *(Citrus sinensis).*

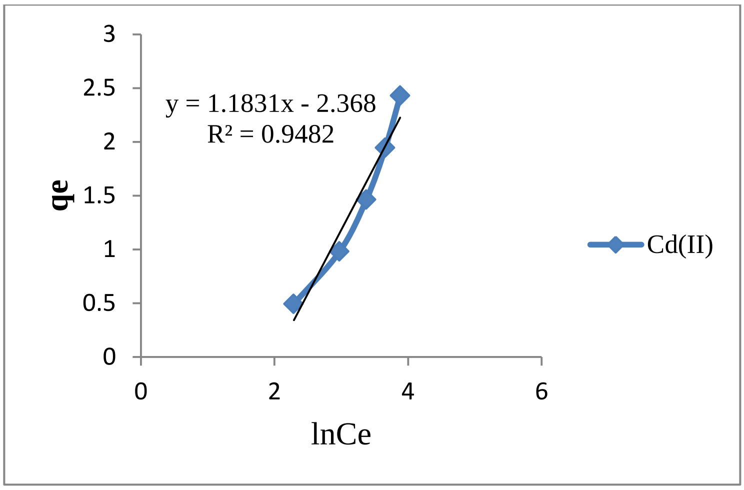

Figure 9. Temkin isotherm for the adsorption of Cd(II) ion by orange seeds *(Citrus sinensis)*

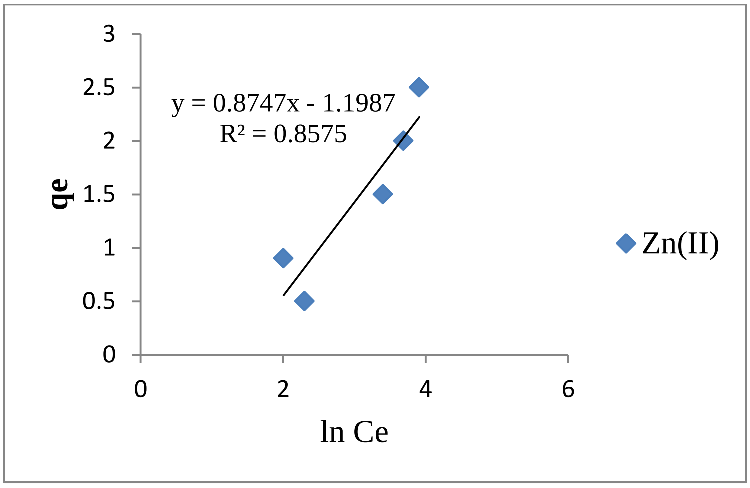

Figure 10. Temkin isotherm for the adsorption of Zn(II) ion by orange seeds *(Citrus sinensis)*

Table 1. Freundlich adsorption isotherm parameters for the removal of Pb(II), Cd(II) and Zn(II) ions by orange seeds *(Citrus sinensis)*

Metal	K_f **(mg/g)**	$\frac{1}{n}$ **(L/mg)**	**N**	R^2
Pb(II)	2.3×10^{-3}	0.947	1.056	0.996
Cd(II)	2.1×10^{-3}	0.992	1.008	0.999
Zn(II)	2.3×10^{-3}	0.956	1.046	0.996

Table 2. Temkin isotherm Parameters for the adsorption of Pb(II), Cd(II) and Zn(II) ions by orange seeds *(Citrus sinensis)*

Metal	K_T **(L/mg)**	B_1**(kj/mol)**	R^2
Pb(II)	3.313	-2.406	0.946
Cd(II)	3.264	-2.368	0.948
Zn(II)	2.396	-1.198	0.857

3.3. Adsorption Kinetics

The kinetics model plots are indicated in Figs. 11-16 and the various constant are displayed in Tables 3 and 4. Comparison of the two tables revealed that the adsorption of the metal ions could be explained using the pseudo-second order. This was due to the higher correlation regression coefficient R^2 value. Also correlation regression coefficient R^2 for Zn(II) ion was greater than the value obtained for Pb(II) and Cd(II) ion. This might also be ascribed to differences in atomic weight and ionic sizes. This might also be ascribed to the differences in ionic radius of the three metals, Zn(II) (0.74Å), Pb(II) (1.33Å) and Cd(II) (0.97Å). Since Zn(II) ions have a smaller ionic radius, it was able to diffuse through the adsorbent pores faster than the heavier ones such as Pb(II) and Cd(II) ions. According to Oboh and Aluyor [22] during adsorption of metal ions, the ion of smaller ionic radii tends to move faster to potential adsorption sites.

Table 3. Pseudo-first order constants for the biosorption of Pb(II), Cd(II) and Zn(II) ions by orange seeds *(Citrus sinensis)*

Metal	K_1 **(min^{-1})**	q_e **Calc (mg/g)**	R^2
Pb(II)	0.023	0.096	0.180
Cd(II)	0.037	20.51	0.057
Zn(II)	0.134	0.00019	0.674

Table 4. Pseudo-second order constants for the biosorption of Pb(II), Cd(II) and Zn(II) ions by orange seeds *(Citrus sinensis)*

Metal	K_2 **(g/mg min)**	q_e **Calc (mg/g)**	R^2
Pb(II)	0.441	0.451	0.988
Cd(II)	1.222	0.119	0.804
Zn(II)	11.834	0.498	0.999

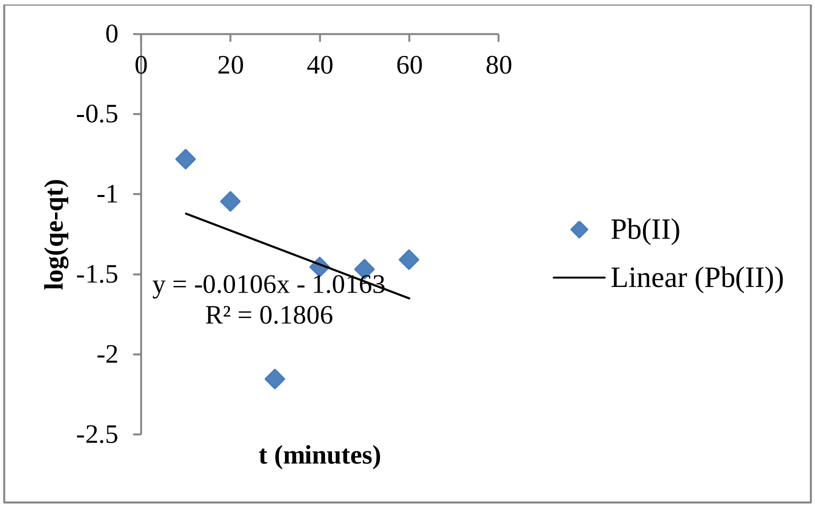

Figure 11. Pseudo-first order for adsorption of Pb(II) ion by orange seeds *(Citrus sinensis)*

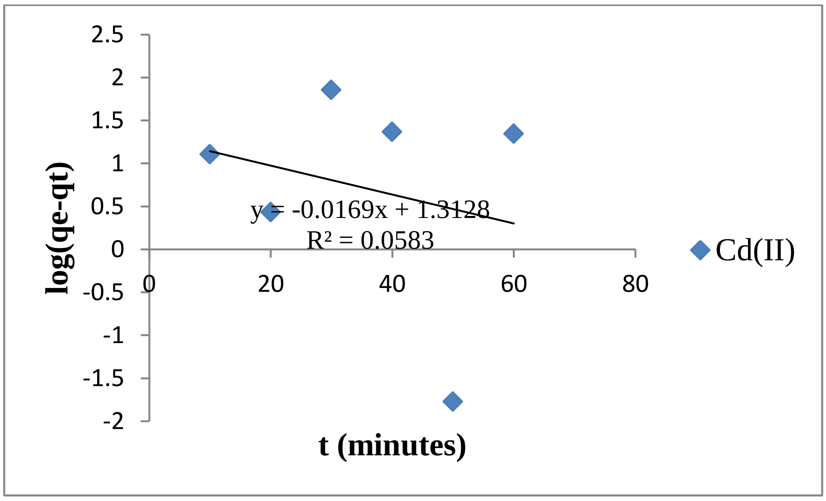

Figure 12. Pseudo-first order for adsorption of Cd(II) ion by orange seeds *(Citrus sinensis)*

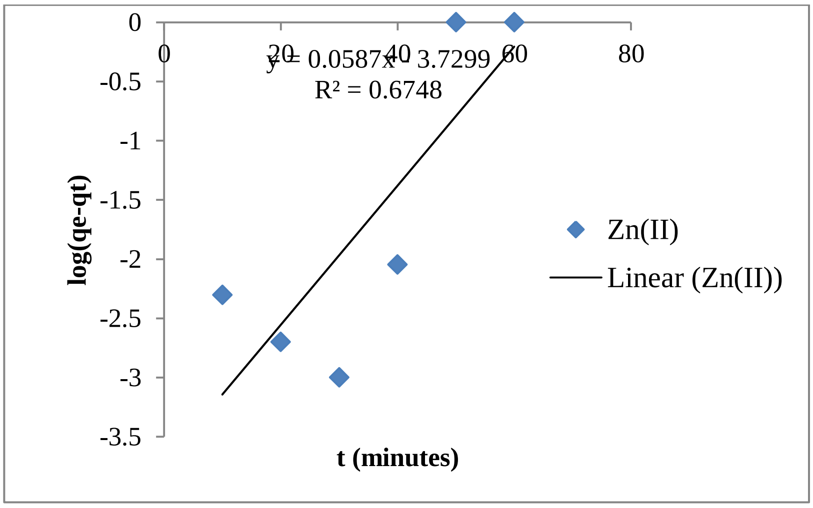

Figure 13. Pseudo-first order for adsorption of Zn(II) ion by orange seeds *(Citrus sinensis)*

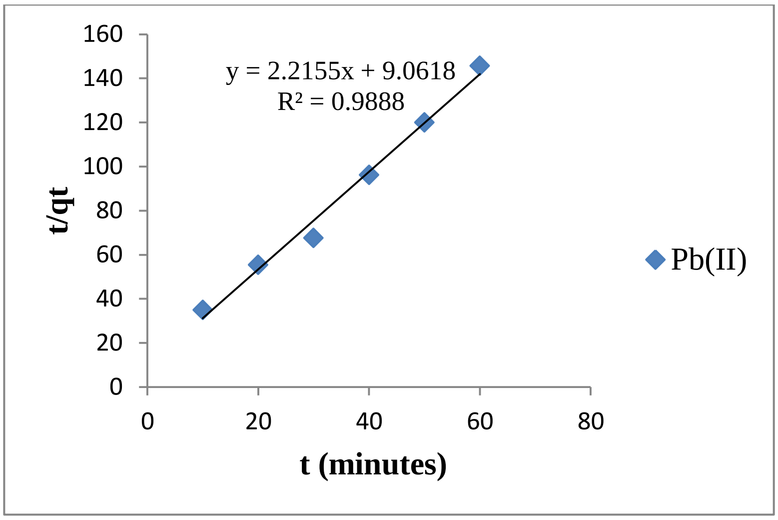

Figure 14. Pseudo-second order for adsorption of Pb(II) ion by orange seeds *(Citrus sinensis)*

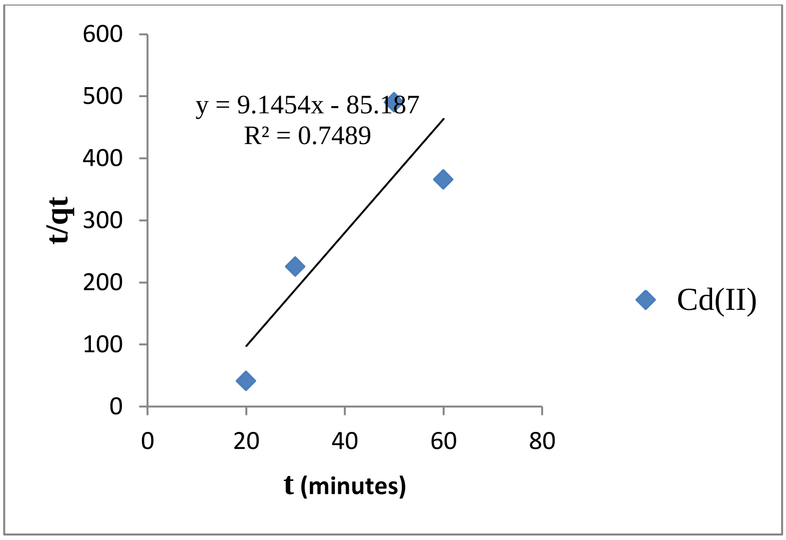

Figure 15. Pseudo-second order for adsorption of Cd(II) ion by orange seeds *(Citrus sinensis)*

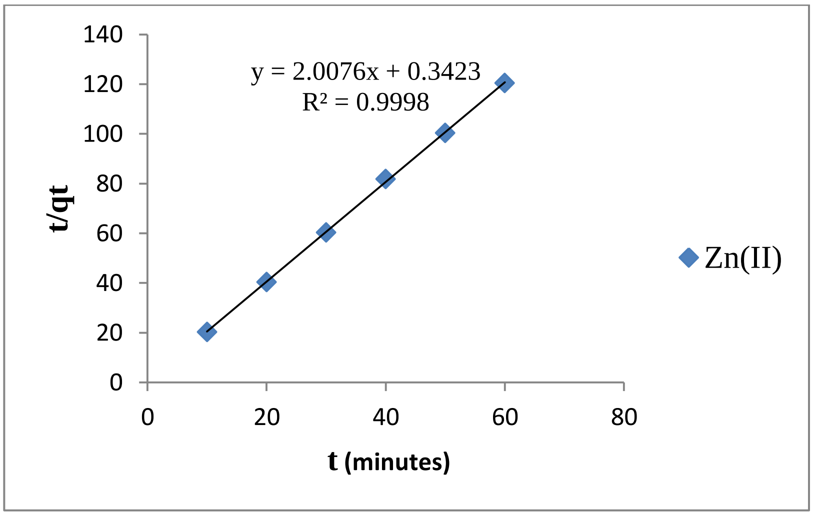

Figure 16. Pseudo-second order for adsorption of Zn(II) ion by orange seeds *(Citrus sinensis)*

3.4. Thermodynamics Studies

The values of standard enthalpy change (ΔH^o) and standard entropy change (ΔS^o) were obtained from the slopes and intercepts respectively, from the graph of ΔG^o against T in (^oC). From Table 5, it could be observed that standard enthalpy change (ΔH^o) and standard Gibb's free energy change (ΔG^o) were negative for all the metals ions while standard entropy change (ΔS^o) was positive in the same way. The negative values of standard Gibb's free energy change (ΔG^o) at all temperatures examined indicates that the adsorption of Pb(II), Cd(II) and Zn(II) ions by orange seeds *(Citrus sinensis)* was feasible and correspond to a spontaneous physical adsorption of the metal ions, which indicate that this biosorption process does not gain external energy [25,26]. The negative values of standard enthalpy change (ΔH^o) revealed that the adsorption process was exothermic and physical in nature. Furthermore, a positive value of standard entropy change (ΔS^o) was an indication of an irregular increase in the degree of the randomness at the adsorbent-adsorbate interface during the adsorption. The decrease in ΔG^o as shown in Table 5 despite increase in temperature indicates more efficient biosorption at higher temperature. The order of spontaneity of the biosorption process was found to be Cd(II) < Zn(II) < Pb(II) which was contrary to the findings reported for the biosorption of these metal ions with banana leaf by Babarinde *et al.* [27].

Table 5. Thermodynamics parameters of Pb(II), Cd(II) and Zn(II) ions adsorption onto orange seeds *(Citrus sinensis)*

Metal	ΔS^o (kj/k mol)	ΔH^o (kJ/mol)	ΔG^o (J/mol)	R^2
Pb (II)	187.900	-1.679	-57.311	0.991
Cd (II)	325.500	-0.880	-99.278	0.902
Zn (II)	24.520	-0.235	-7.479	0.811

4. Conclusions

Based on the above study the following conclusions were drawn: (1) pH, contact time, metal ions concentration and temperature had a remarkable effect on the metal uptake level by the substrate. (2) The biosorption process of the metal ions was best described by a pseudo-second order. (3) The equilibrium data could be explained by Freundlich than Temkin isotherm. (4) Thermodynamics investigation showed that standard Gibb's free energy change (ΔG^o) was negative indicating that the adsorption of Pb(II), Cd(II) and Zn(II) ions by orange seeds *(Citrus sinensis)* were feasible and spontaneous. The negative value of standard enthalpy change (ΔH^o) implies that the reaction was exothermic and physical in nature while positive value of standard entropy change (ΔS^o) implies an irregular increase in the randomness at the solid/solution interface of the adsorbent during the adsorption process.

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