

Research Article

Remediation of Cadmium (II) from Simulated Seawater: Kinetics, Equilibrium and Thermodynamic studies

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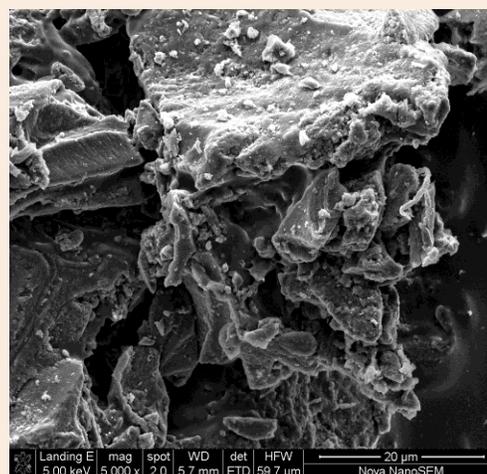
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Abstract

The presence of cadmium (Cd) in the marine environment is a serious pollution problem. The ability of activated carbon (AC) as an adsorbent for Cd removal from Cd – contaminated simulated seawater was studied. Experiments were carried out as function of the effect of adsorbent dose, contact time, stirring speed, initial Cd concentration and temperature. The pH was kept constant for all the experiment. The study has shown that AC is capable of removing Cd from contaminated seawater. The equilibrium and kinetic data agreed very well with the Freundlich isotherm and pseudo second-order kinetic models, respectively. Cd adsorption was endothermic. ΔS° and ΔH° was $73.43 \text{ JK}^{-1}\text{mol}^{-1}$ and 6.63 KJmol^{-1} , respectively. The maximum percentage removal of Cd achieved was 99.85 % and the Freundlich adsorption equilibrium constant was $5.52 \times 10^6 \text{ (mg/g (L/mg)}^{1/n})$.

Keywords: cadmium, remediation, adsorption, activated carbon, seawater.

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Introduction

Cadmium (Cd) is considered as one of the most toxic heavy metals and is often detected in industrial wastewaters originating from metal plating, smelting, battery manufacture, petroleum refining, pesticides, pigment manufactures, photographic industries, etc [1, 2]. Cd from these sources is released to the environment and distributed in the water and finds its way into human system. Cd can be released into the atmosphere through metal production activities, fossil fuel combustion, and waste incineration. The Cd in the atmosphere thus deposit onto surface soils and water [3]. Cd also occurs naturally in geological ores and is found at background levels in the marine environment. It is liable to bioaccumulate and thus is a contaminant of concern both for the marine environment and for human consumption of fish and other seafoods [4]. Concentrations of Cd in the marine environment have generally decreased over the period 1990 to 2007 where trends can be detected, but have not been consistently upwards or downwards over the period 1998 – 2007. However, concentrations remain above background in many areas and in some areas are still at levels where there is potential for significant adverse effects to the environment, or to human health [5].

Cd is carcinogenic; the World Health Organisation (WHO) has thus set a maximum guideline concentration of $0,003 \text{ mg L}^{-1}$ for Cd in drinking water [2, 6]. In aquatic systems, Cd is most readily absorbed by organisms directly from the water in its free ionic form Cd^{2+} [3, 7]. The acute toxicity of Cd to aquatic organisms is variable, even between closely related species, and is related to the free ionic concentration of the metal. Cd interacts with the

calcium metabolism of animals. In fish it causes lack of calcium (hypocalcaemia), probably by inhibiting calcium uptake from the water. However, high calcium concentrations in the water protect fish from Cd uptake by competing at uptake sites. Effects of long-term exposure can include larval mortality and temporary reduction in growth [7]. In animals, Cd concentrates in the internal organs rather than in muscle or fat. It is typically higher in kidney than in liver, and higher in liver than in muscle. Cd levels usually increase with age. Cd is not essential for plant or animal life.

There is considerable interest on the development of techniques to remove Cd from contaminated water such as: precipitation, extraction, coagulation, sedimentation, ion-exchange and electrochemical techniques. These conventional methods do not seem to be economically feasible. They are expensive or ineffective, especially when the metal concentrations are very low in the order of 1 to 100 mg L⁻¹. Adsorption is thus the most effective and widely used method of all, furthermore, it is also considered as an economical method. There are various adsorption studies of Cd, examples are; the kinetics and thermodynamics of Cd ion removal by adsorption onto nano zerovalent ion particles by Boparai et al. [2]. They reported that nano zerovalent ion (nZVI) is a good adsorbent for removing various organic and inorganic contaminants. The adsorption of Cd ions onto chitosan membranes was reported by Zielinska et al. [1], their report has shown that chitosan is also capable of removing Cd from aqueous solution. The kinetics and equilibrium studies of the removal of Cd from aqueous solutions by adsorption were also reported by Okasha et al. [8].

However, the kinetic, equilibrium and thermodynamic studies of the sorption of Cd in seawater matrixes (i.e Cd adsorption from Cd - contaminated seawater to adsorbents) have not been reported. The objective of the research is therefore to investigate the kinetics, equilibrium and thermodynamics of the adsorption of Cd (II) onto activated carbon (AC) under simulated seawater condition. Kinetics data were used to predict the rate at which the target contaminant is removed from aqueous solutions and equilibrium adsorption isotherms were used to quantify the adsorptive capacity of Cd onto AC. Results from this study can be used to assess the utility of AC for Cd (II) removal at the field scale.

Experimental

AC and CdCl₂.H₂O were obtained from Sigma Aldrich. Simulated seawater was prepared in the laboratory using the method by Ayanda et al. [9]. The simulated seawater was spiked with stock Cd (II) solution and adsorption study was carried out on the Cd – contaminated simulated seawater. Inductively coupled plasma-Mass Spectroscopy (ICP-MS) was used for the determination of Cd (II) concentration and scanning electron microscopy (SEM) was used for the morphology characterization of the adsorbents before and after the adsorption process.

Adsorption procedures

The effect of adsorption dose was performed at 20 °C in Erlenmeyer flasks, stirred on an Orbital shaker (Orbita Shake Labotec) for 60 min. Different masses of AC (0.0625 g – 1.0 g) thoroughly mixed in 50 mL of Cd – contaminated simulated seawater. The reaction mixtures were filtered and the filtrate analysed.

The effect of contact time was performed at 20 °C in Erlenmeyer flasks containing 0.5 g of the AC and 50 mL of Cd – contaminated simulated seawater. The flasks were stirred at a contact time of between 30 min to 3 h. The reaction mixtures were filtered and the filtrate analysed.

The effect of stirring speed was also performed at 20 °C in Erlenmeyer flasks containing 0.5 g of the AC and 50 mL of the Cd – contaminated simulated seawater. The flasks were stirred at 170, 180, 190 and 200 rpm (revolution per minute). The reaction mixtures were then filtered and the filtrate analysed.

Equilibrium experiments were performed in 100 mL Erlenmeyer flasks, containing 50 mL of Cd (II) solution in simulated seawater with initial concentration of Cd (II) from 50 to 100 mg L⁻¹. The adsorption behaviours of Cd (II) were investigated at 20 °C and pH 8. After shaking the flasks containing the Cd – contaminated simulated seawater and 0.5 g of AC for 60 min, the reaction mixtures were filtered to remove the particulates and the filtrates were analysed. The results obtained were used for the adsorption isotherms studies.

The effect of temperature was performed at different temperatures, 40 °C, 50 °C, 60 °C, 70 °C and 80 °C in Erlenmeyer flasks containing 0.5 g of the AC and 50 mL of the Cd – contaminated simulated seawater. The reaction mixtures were filtered and the filtrate analysed.

Adsorption kinetic models

The amount of Cd (II) adsorbed q (mg Cd ion per g AC) was determined by the mass balance presented in Equation 1 [10]:

$$q = (C_o - C_t) \times \frac{V}{m} \quad (1)$$

where C_o and C_t are Cd (II) concentrations (mg L⁻¹) at time 0 and t, respectively, V is the volume of the solution (mL), and m is the mass of the AC (g).

The pseudo first-order and pseudo second-order, were fitted to experimental data to investigate the adsorption kinetics of Cd uptake by the AC.

The linear form of pseudo first order model can be expressed as:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (2)$$

where q_e and q_t (mg g⁻¹) are the adsorption capacities at equilibrium and at time t (min), respectively. k_1 is the pseudo first order rate constant (min⁻¹).

The pseudo second-order rate expression is linearly represented as:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (3)$$

where k_2 is the rate constant for pseudo second-order adsorption (g mg⁻¹ min⁻¹) and $k_2 q_e^2$ or h (mg g⁻¹ min⁻¹) is the initial adsorption rate.

Adsorption isotherm models

The adsorption of Cd (II) by AC was modelled using the Langmuir and Freundlich adsorption isotherms. The Langmuir isotherm assumes monolayer adsorption on a uniform surface with a finite number of adsorption sites. Once a site is filled, no further sorption can take place at that site. The linear form of the Langmuir isotherm model is designated as:

$$\frac{C_e}{q_e} = \frac{1}{k_L q_m} + \frac{C_e}{q_m} \quad (4)$$

where k_L is the Langmuir constant related to the energy of adsorption and q_m is the maximum adsorption capacity (mg g⁻¹).

The Freundlich isotherm is based on the assumption that the adsorbate adsorbs onto the heterogeneous surface of an adsorbent. The linear form of Freundlich equation is expressed as:

$$\log q_e = \log k_F + \frac{1}{n} \log C_e \quad (5)$$

where k_F and n are Freundlich isotherm constants related to adsorption capacity and adsorption intensity, respectively and C_e is the equilibrium concentration (mg L⁻¹).

Thermodynamic parameters

The thermodynamic parameters can be determined from the thermodynamic distribution coefficient, K_c (Equation 6). The standard Gibbs free energy ΔG° (kJ mol⁻¹), standard enthalpy change ΔH° (kJ mol⁻¹), and standard entropy change ΔS° (J mol⁻¹ K⁻¹) was calculated using the Equations 7 and 8:

$$K_c = \frac{C_e}{C_a} \quad (6)$$

$$\Delta G^o = -RT \ln K_c \quad (7)$$

$$\log K_c = \frac{\Delta S^o}{R} - \frac{\Delta H^o}{R} \cdot \frac{1}{T} \quad (8)$$

where C_a (mg L^{-1}) is the amount of Cd (mg) adsorbed on the AC per liter of the solution at equilibrium, C_e (mg L^{-1}) is the equilibrium concentration of Cd in the solution, R is the universal gas constant, $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$; T is absolute temperature.

Results and Discussions

Effect of adsorbent dose

Adsorption dosage is one of the vital parameter in the study. The adsorbent dosage was varied from 0.0625 – 1.0 g, to study the effect on the adsorption of Cd (II). To study this effect, the concentration of Cd (II) was taken as 100 mg L^{-1} and other parameters were kept constant. The results (Fig. 1) obtained showed that as the amount of AC was increased from 0.0625 to 0.5 g, the amount adsorbed and percentage removal of Cd (II) was respectively increased.

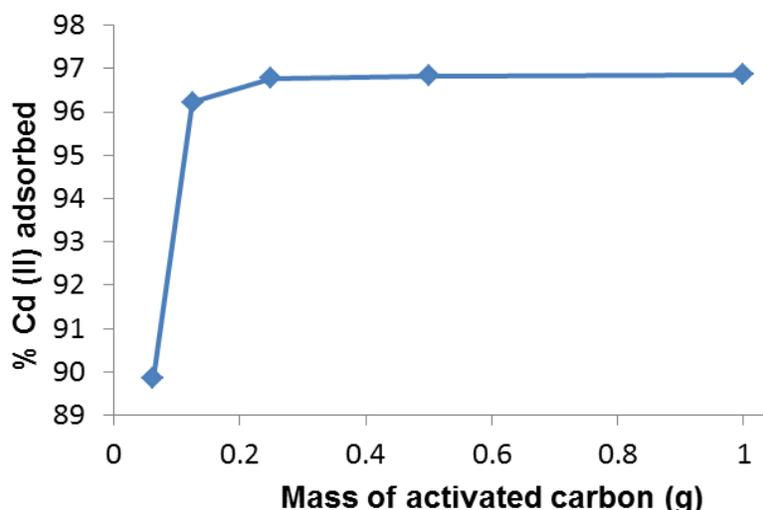


Figure 1 Adsorption efficiencies of Cd (II) onto AC

Experimental conditions: Concentration of Cd (II) = 100 mg L^{-1} ; volume of Cd (II) solution = 50 mL, contact time = 60 min; stirring speed = 160 rpm, temperature = $20 \text{ }^\circ\text{C}$

The adsorbent dosage affects the adsorption capacity directly, as there is increase in dosage more active sites becomes available for adsorbate. Fig. 1 also showed that after 0.5 g (which was the value of the AC used for the rest of the experiment), the adsorption of Cd (II) onto the AC has already attain equilibration.

Effect of contact time

Experimental conditions: Concentration of Cd (II) = 100 mg L^{-1} ; volume of Cd (II) solution = 50 mL, mass of adsorbent = 0.5 g; stirring speed = 160 rpm, temperature = $20 \text{ }^\circ\text{C}$.

It's very normal observation among all adsorption studies that as the contact time increase, there is enhancement in the adsorption of adsorbate in both cases in percentage as well as amount adsorbed. This is probably

due to a larger surface area of the AC being available at the beginning for the adsorption of Cd. As the surface adsorption sites become exhausted, the uptake rate is controlled by the rate at which the adsorbate is transported from the exterior to the interior sites of the adsorbent particles. The Cd (II) concentration was 100 mg L^{-1} while, other remaining conditions pH = 8, temperature = $20 \text{ }^\circ\text{C}$, stirring speed 160 rpm etc. were constant. Effect of contact time was done at various time intervals from 30 min – 180 min.

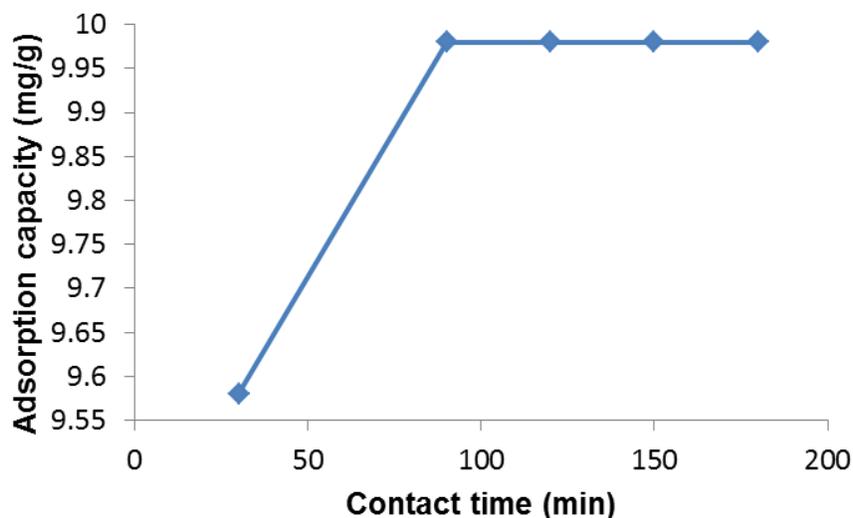


Figure 2 Effect of contact time on Cd (II) adsorption onto AC

The increase in percentage adsorption from 95.82 % to 99.82 % (Fig. 2) was observed up to 120 min. After that, there was no significant change observed. So, for further study the 120 min was fixed as contact time.

To evaluate the kinetics of the adsorption process, the pseudo first-order and pseudo second-order models were tested to interpret the experimental data [11].

Pseudo first-order kinetics

The pseudo first-order was studied with Lagergren equation. k_1 and q_e were calculated using the slope and intercept of $\log(q_e - q_t)$ versus t (Figure 3).

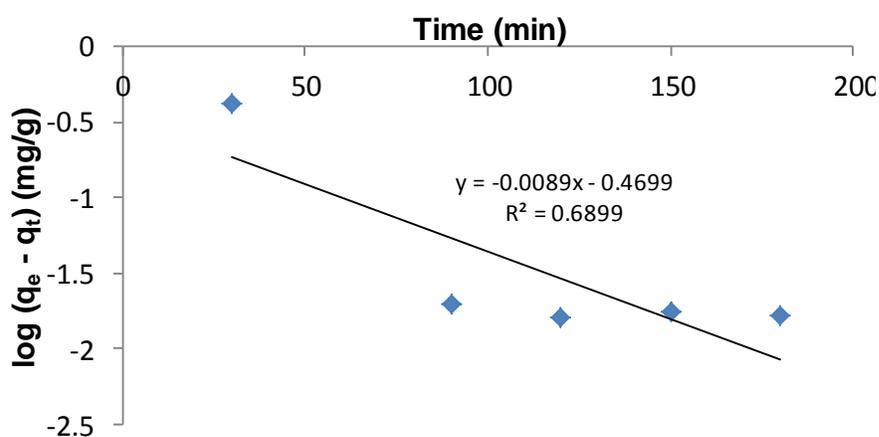


Figure 3 Pseudo first-order rate equation plot for Cd (II) adsorption onto AC

Experimental observations in Fig. 3 suggest that application of Equation 3 is inappropriate as experimental observations are non-linear when plotted. And also, the correlation coefficient which was found to be 0.6899 is very low. This suggests that the adsorption of Cd (II) onto AC did not follow pseudo first-order kinetics.

Pseudo second-order kinetics

Pseudo second-order adsorption parameters q_e and k_2 in Equation 3 were determined by plotting $\frac{t}{q_t}$ versus t . From Fig. 4, we can see that the graph is linear. The correlation coefficient was found to be 0.9999, which is much higher than the correlation coefficient derived from pseudo first-order models fits.

This suggests that Cd adsorption followed the pseudo second-order kinetics and Cd (II) were adsorbed onto the AC surface via chemical interaction. Similar trends have been reported for the adsorption of Cd ions from aqueous solutions by other adsorbents [8, 12]. Table 1 thus provides the evaluated parameters of the kinetics models.

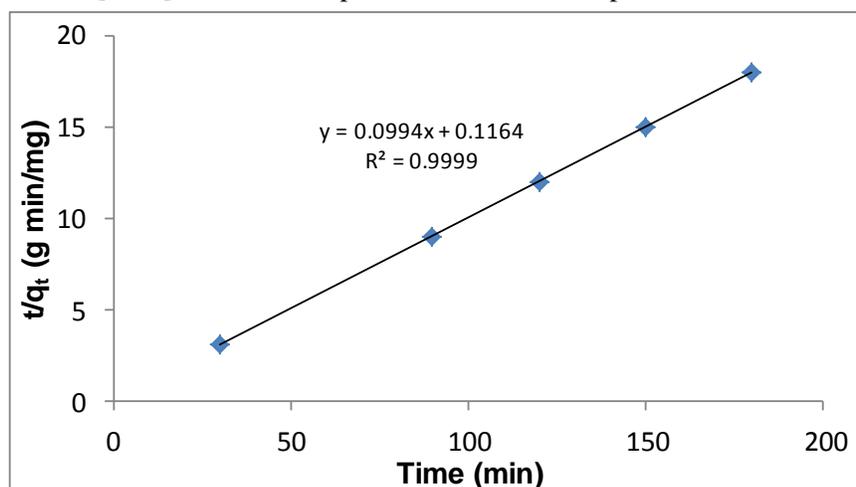


Figure 4 Pseudo second-order rate equation plot for Cd (II) adsorption onto AC

Table 1 Kinetic model parameters

Models	
Pseudo first-order	
k_1 (min ⁻¹)	0.0205
q_e (mg g ⁻¹)	0.3389
R^2	0.6899
Pseudo second-order	
q_e (mg g ⁻¹)	10.06
h (mg g ⁻¹ min ⁻¹)	8.59
k_2 (g mg ⁻¹ min ⁻¹)	0.849
R^2	0.9999

Effect of stirring speed

The stirring speed effect on the adsorption amount and percentage removal of Cd (II) has been investigated. To study this parameter, the stirring speed was varied from 160 - 200 rpm. For this experiment, the period of agitation was 1 h with remaining optimum conditions kept constant. In the present study, it was observed that, the interaction between adsorbate and adsorbent was effective at high speed 170 rpm and more up to 200 rpm.

It is very clear from the **Figure 5** that, there was increase in adsorption with respect to speed and above 170 rpm no any significant change was observed. So the rpm was fixed at 170 for further study.

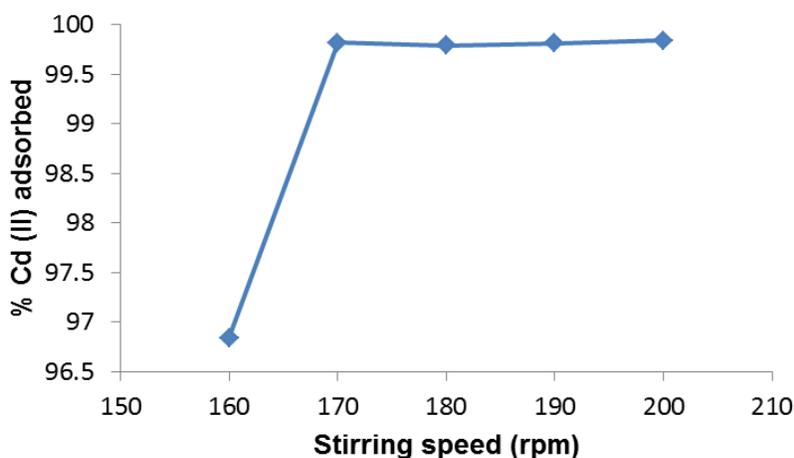


Figure 5 Effect of stirring speed on Cd (II) adsorption onto AC

Experimental conditions: Concentration of Cd (II) = 100 mg L⁻¹; volume of Cd (II) solution = 50 mL, mass of adsorbent = 0.5 g; contact time = 60 min; temperature = 20 °C

Langmuir and Freundlich adsorption isotherms

Adsorption equilibrium isotherms are basic requirements for designing any adsorption system. The adsorption isotherm indicates how the adsorbate distributes between the liquid phase and the solid phase when the adsorption process reaches an equilibrium state. Isotherm data obtained with a range of initial Cd concentration showed an increase in the amount of Cd adsorbed when the initial metal concentration was raised from 5 to 100 mg L⁻¹. Adsorption isotherms express the mathematical relationship between the quantity of adsorbate and equilibrium concentration of adsorbate remaining in the solution at a constant temperature.

The Langmuir equation is as given in Equation 4. A plot of $\frac{C_e}{q_e}$ versus C_e (Fig. 6a) indicated a straight line of slope $\frac{1}{q_m}$ and an intercept of $\frac{1}{k_L q_m}$. The Langmuir constants (q_m and k_L) were calculated from the plot (Fig. 6a) and are presented in Table 2. The correlation coefficient was found to be 0.6993, which agree with the fact that the adsorption of Cd (II) did not follow the Langmuir isotherm. The maximum adsorption capacity of adsorption of Cd (II) by Langmuir isotherm was 5.0364 mg g⁻¹.

The Freundlich equation used is as given in Equation 5. The plot of the $\log q_e$ versus $\log C_e$ (Fig. 6b) gives a linear trace with a slope of $\frac{1}{n}$ and intercept of $\log k_F$. The k_F is the measure of adsorption capacity and n is the adsorption intensity which is given in Table 2. The Freundlich adsorption capacity by this plot is 5.52 x 10⁶ mg/g (L/mg)^{1/n} and regression factor was > 0.95 (0.9685). From the results it was clearly observed that the Freundlich

models was well suited for adsorption of Cd (II) on the AC, on this basis it could be concluded that, Cd (II) ion form monolayer on surface of the AC and the adsorption was chemisorption.

The experimental results obtained on the effect of temperature showed that the percentage adsorption removal of Cd (II) onto AC increases with increase in the solution temperature (Fig. 7a). This indicated that the adsorption of Cd (II) onto the AC is endothermic. The endothermic nature of the adsorption process is in support of the result by

Okasha et al. [7]. A graph of $\log K_c$ versus $\frac{1}{T}$ (K^{-1}) is presented in Fig. 7b and the calculated thermodynamic parameters presented in Table 3.

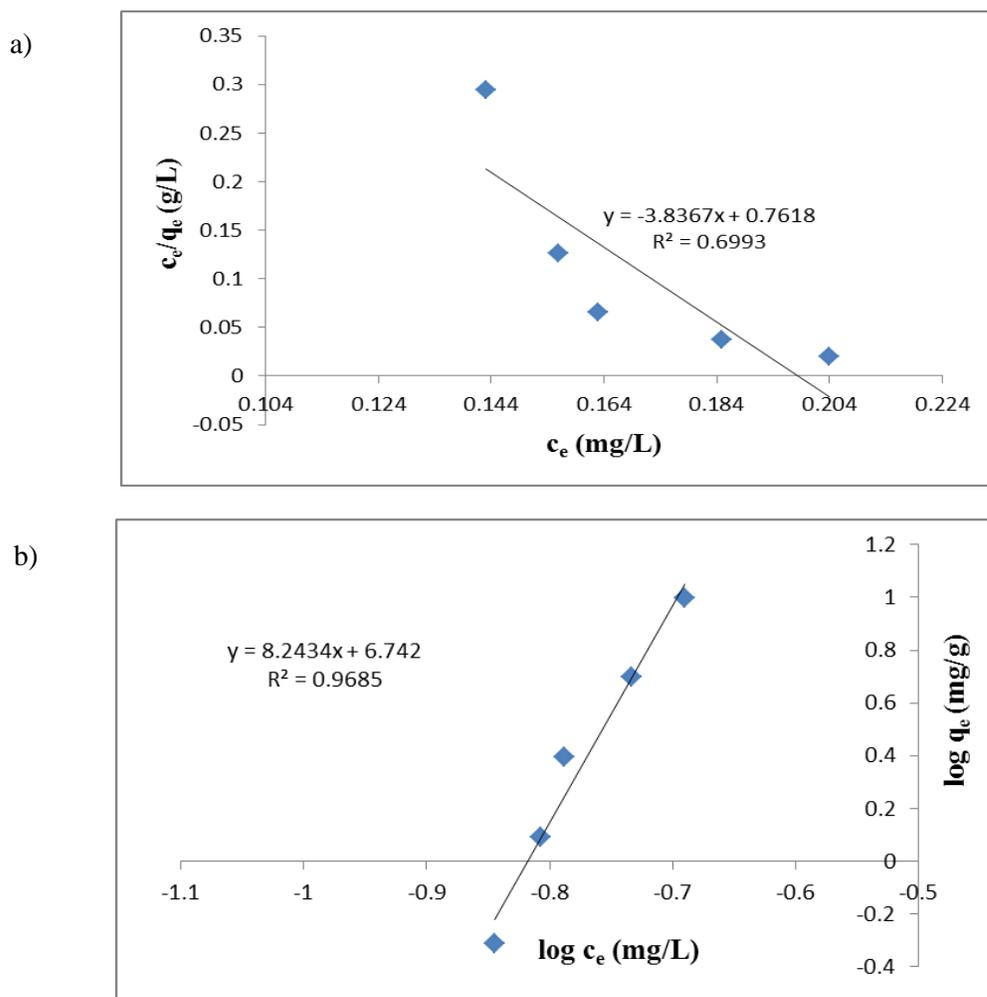


Figure 6 Langmuir (a) and Freundlich (b) isotherms for adsorption of Cd (II) onto AC

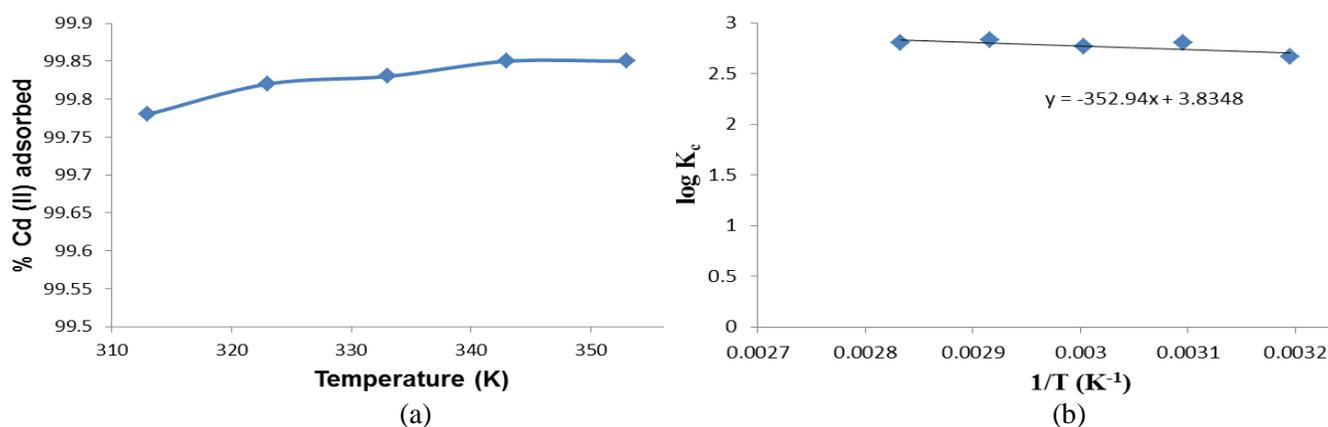
Experimental conditions: Concentration of Cd (II) = 100 mg L⁻¹; volume of Cd (II) solution = 50 mL, mass of adsorbents = 0.5 g; contact time = 60 min; stirring speed = 160 rpm

The positive values of ΔS° correspond to an increase in degree of freedom of the adsorbed Cd (II) and suggest the increase in concentration of adsorbate in solid–solution interface indicating an increase in Cd (II) onto the solid phase.

It is evident from Table 3 that ΔG° values were found to be more negative as the temperatures increases, this indicated that the adsorption efficiency of Cd (II) onto the AC increases with increase in temperature.

Table 2 Isotherms constants

Equilibrium models	
Langmuir	
k_L (L/mg)	5.0364
q_m (mg/g)	0.2606
R^2	0.6993
Freundlich	
k_F (mg/g (L/mg) ^{1/n})	5.52 x 10 ⁶
n (g/L)	0.1213
R^2	0.9685

Effect of temperature**Figure 7** Effect of temperature on the adsorption of Cd (II) onto AC (a) and $\log K_c$ versus $\frac{1}{T}$ (K⁻¹) (b)**Table 3** Thermodynamic parameters

T °C	ΔG° (KJmol ⁻¹)	ΔS° (JK ⁻¹ mol ⁻¹)	ΔH° (KJmol ⁻¹)	K_c
40	-15.95			459.83
50	-17.34			635.94
60	-17.62	73.43	6.76	580.40
70	-18.58			674.68
80	-18.96			640.03

The AC was subjected to scanning electron microscope (SEM) analysis before and after the adsorption process and is presented in Fig. 8. Fig 8 shows that the AC surface morphology was not changed after adsorption. This indicates that the AC are not destroyed and their structure is unaffected during Cd adsorption and could be further reused after desorption and activation.

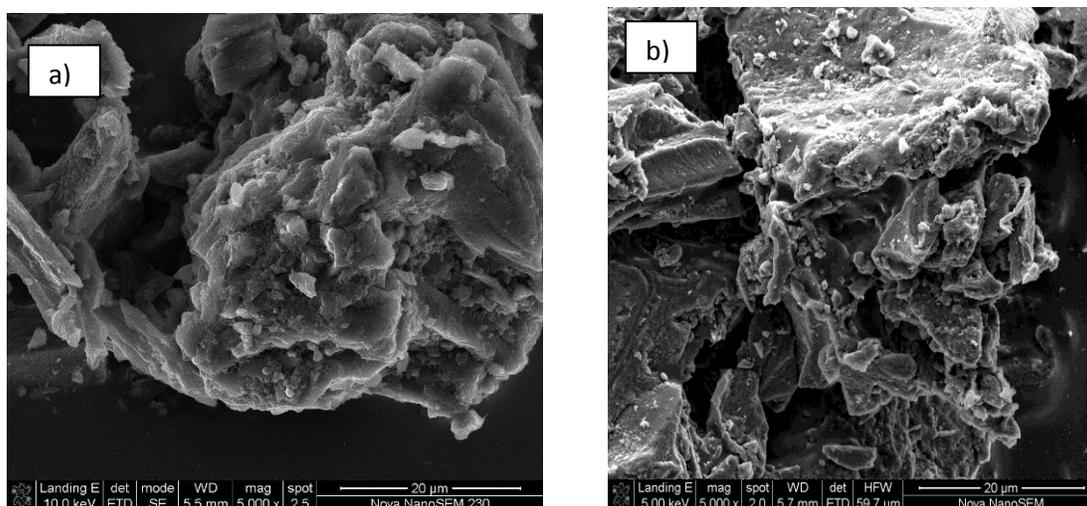


Figure 8 SEM of AC before (a) and after (b) Cd (II) adsorption

Conclusion

Cd is highly toxic for all mammals and aquatic animals, its levels have constantly been increasing in the environment and hence a need to reduce its concentration to the barest minimum in wastewaters. This present study shows that the percentage adsorption of Cd from Cd – contaminated simulated seawater onto AC increases with increasing adsorbent dose, contact time, stirring speed, initial Cd (II) concentration and solution temperature. The Cd adsorption is endothermic, ΔS° was $73.43 \text{ JK}^{-1}\text{mol}^{-1}$ and ΔH° was 6.63 KJmol^{-1} . The pseudo second-order kinetic model accurately described the adsorption kinetics. The Freundlich isotherm showed a better fit than the Langmuir isotherm, thus, indicating the applicability of monolayer and multilayer coverage of Cd on the AC and the adsorption mechanism was found to be chemisorption. AC can therefore be used as an effective adsorbent for removing Cd from Cd – contaminated seawaters such as the shipyard process wastewaters before its discharge into the marine environment.

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