

Isotherm, kinetics, and thermodynamics of arsenic(III) adsorption onto activated carbon

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ORIGINAL RESEARCH ARTICLE

ABSTRACT

Activated carbon was used as adsorbent for the removal of As(III) ions in the present study. The experiment was carried out as a function of the initial As(III) concentration, adsorbent dose, contact time, solution pH, and temperature. The optimal percentage removal of As(III) ions achieved by the activated carbon was found to be approximately 50.0% when 25 mL of 100 mg/L As(III) solution was contacted with 2.5668 g of activated carbon for 120 min at 120 rpm. The kinetic study showed that the experimental data fitted well with the pseudo-second order kinetic model, while the equilibrium study showed that the adsorption of As(III) onto activated carbon described well by the Langmuir isotherm. The adsorption of As(III) onto activated carbon was exothermic with ΔS° and ΔH° approximately equals -83.04 J/K/mol and -23.29 kJ/mol, respectively.

KEYWORDS

activated carbon; arsenic; isotherm; kinetics; thermodynamics

1. INTRODUCTION

Arsenic is a natural component of the earth crust and is found in air, water, soil etc. High concentration of arsenic can lead to poisoning and their impact to the environment and human health can be very disastrous. The oxidation states in which arsenic occurs are (III) and (V) and its compounds are mainly used in the processing of glass, wood preservatives, textiles, ammunition, paper, pigments, agricultural insecticides, poisons and also for the treatment of cancer (Bissen and Frimmel, 2003; Yao et al., 2014). The presence of elemental arsenic and arsenic compounds in groundwater is either because of natural origin or due to human activity. Arsenic occurs naturally in small concentration in soil or minerals and due to human activity like mining, copper and zinc

producing industries; the released arsenic spreads and pollutes the soil, ground and surface water. Arsenic is a non-biodegradable substance therefore it cannot be destroyed when released and will accumulate with time (Dhar et al., 1997). Consequently, the plants that can easily absorb arsenic present in water are directly affected, in particular the presence of highly toxic inorganic arsenic compounds in water alter the genetics of fishes and sea wildlife, the birds that eat fishes can die due to arsenic poisoning and humans are exposed to high levels of arsenic through contaminated water and food (Dhar et al., 1997). Arsenic is very toxic (Nicomel et al., 2016), exposure to even low level of arsenic can cause various acute health effect to humans such as diarrhoea, vomiting and abdominal pain. High exposure to inorganic arsenic can cause long term health effects such as skin lesions, infertility, heart disruptions, brain damage and skin cancer

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(Karim, 2000). Organs that are usually affected by arsenic are the liver, kidney, gastrointestinal tract, circulatory system, other sensitive tissues and the heart (Fatoki et al., 2013). The crisis in Bangladesh and West Bengal highlights the health problems associated with arsenic poisoning. Skin problems such as keratosis, pigmentation, de-pigmentation and skin cancer are widespread. Patients who have been exposed to arsenic for a longer period of time developed internal organ problems such as cancer and many more were reportedly dead (Fatoki et al., 2013). At this stage, arsenic is considered as a serious toxin to the environment and the contamination of arsenic in water represents a big problem as it affects the wildlife and health of many people around the world.

There have been various methods used for heavy metal removal from water and wastewater. These methods include precipitation, adsorption, ion exchange, filtration, electrodeposition, reverse osmosis, etc. (Sekar et al., 2004). However, adsorption remains the preeminent method compared to the others because it is inexpensive, easy to use, and it is very efficient for the removal of organic and inorganic compounds (Yadla et al., 2012). The adsorption of arsenic from aqueous solutions by Fe(III)-Si binary oxide has been investigated by Zeng (2004). The author explored arsenate and arsenite adsorption on iron(III) oxide/silica adsorbent with Fe/Si molar ratio of 3, and reported that the adsorption of arsenite was faster than that of arsenate. The equilibrium adsorption capacity for As(III) was reported to be higher than that for As(V). The calculated thermodynamic parameters reflected the spontaneous nature of As(V) and As(III) adsorption on the binary oxide adsorbent. The opposite values of ΔH° indicated that the adsorption of As(V) was exothermic, whereas that of As(III) was endothermic. Payne and Abdel-Fattah (2005) also studied the adsorption of arsenate and arsenite by iron-treated activated carbon and zeolites. The authors discovered that the iron-treated activated carbon and chabazite showed promise as efficient low-cost adsorbents for arsenate and arsenite removal. Adsorption was significantly affected by pH with adsorption generally highest for arsenate and arsenite in the pH interval 7.0–11.0 for iron-treated activated carbon and zeolites. Increasing temperature and ionic strength improved adsorption performance for Fe modified activated carbon and zeolites. Furthermore, Van Vinh et al. (2015) investigated As(III) removal from aqueous solution by raw and zinc loaded pine cone biochar. They reported that the adsorption of As(III) was well represented by the pseudo-second order kinetic model

and that the adsorption process was spontaneous and exothermic.

The aim of this present study is to investigate the removal of As(III) from aqueous solution by adsorption onto activated carbon. The adsorption isotherms, kinetics and thermodynamics were studied. Equilibrium adsorption isotherms were fitted using the Langmuir and Freundlich models, while the adsorption kinetic data were described using the pseudo-first order and pseudo-second order models. This research supports worldwide research efforts (World Health Organisation) to obtain drinking water with arsenic levels below 10 $\mu\text{g/L}$.

2. MATERIALS AND METHODS

2.1. Materials

All chemicals used for the experiments are analytical grade. Stock solution of As(III) (1000 mg/L) and activated carbon (100-400 mesh) were purchased from Sigma Aldrich, USA, while sodium hydroxide (NaOH) and hydrochloric acid (HCl) were supplied by Merck. Deionized water was used for all analytical preparations. The concentrations of As(III) before and after adsorption was determined with inductively coupled plasma-optical emission spectroscopy (ICP-OES; Spectro Arcos).

2.2. Adsorption Experiment

Adsorption experiments were conducted by varying the initial As(III) concentration, adsorbent dose, contact time, solution pH, and temperature. The effect of initial As(III) concentration was performed by preparing 10 to 100 mg/L As(III) from the stock solution. About 25 mL of each solution were poured in Erlenmeyer flasks and mixed for 60 min with the adsorbent (2.5668 g) at 20 °C and pH 8. The effect of the adsorption dose was performed at 20 °C in Erlenmeyer flasks, stirred on an orbital shaker (Orbita Shake Labotec) for 60 min. Different masses of the adsorbent (0.0134 to 2.5668 g) were thoroughly mixed in 25 mL As(III) solution. The effect of contact time was performed at 20 °C in Erlenmeyer flasks containing 2.5668 g of the adsorbent and 25 mL of As(III) aqueous solution. The flasks were stirred at contact time of 10 min to 2 h. The effect of pH of As(III) aqueous solution was maintained at a desired value (pH 2 to 10) by adding 0.1 M NaOH and/or 0.1 M HCl. The aqueous solutions containing 2.5668 g of the adsorbent were shaken for

60 min. The effect of temperature was conducted at different As(III) solution temperatures ranging from 18 to 82 °C in Erlenmeyer flasks containing 2.5668 g of the adsorbents and 25 mL of the As(III) solution. After each of the experiments, the reaction mixtures were filtered and the filtrate analysed by Spectro Arcos ICP-OES.

2.3. Theory

2.3.1. Amount of As(III) adsorbed

The amount of As(III) adsorbed (mg arsenic per g activated carbon) was determined according to Equation 1.

$$q = \frac{(C_o - C_{aq})xV}{m} \quad (1)$$

where C_o and C_{eq} are As(III) concentration (mg/L) at time 0 and t, respectively, V is the volume of the solution (mL), m is the mass of the activated carbon and q is the amount of As(III) uptake by the adsorbent in mg/g.

2.3.2. Adsorption isotherms

One of the most commonly used adsorption model, the Langmuir isotherm can be expressed as,

$$\frac{1}{q} = \frac{1}{q_m K_L} \frac{1}{C_{eq}} + \frac{1}{q_m} \quad (2)$$

where K_L is the Langmuir equilibrium constant (L/mg) that is related to the heat of adsorption and q_m is the maximum monolayer sorption capacity (mg/g).

The Freundlich isotherm is expressed by Equation 3.

$$\log q = \log K_f + \frac{1}{n} \log C \quad (3)$$

where q is the quantity of the solute adsorbed per unit weight of the adsorbent (mg/g), C is the equilibrium concentration of the adsorbing compound (mg/L), and K_f represents the adsorption capacity (mg/g (L/mg)^{1/n}), and n represents the degree of dependence of adsorption on equilibrium concentration.

2.3.3. Thermodynamic study

The free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) changes during adsorption were evaluated by Equations 4, 5 and 6.

$$K_c = \frac{C_{Ae}}{C_e} \quad (4)$$

$$\Delta G^\circ = -RT \ln K_c \quad (5)$$

$$\log K_c = \frac{\Delta S^\circ}{2.303R} - \frac{\Delta H^\circ}{2.303RT} \quad (6)$$

where K_c is the equilibrium constant, C_e is the equilibrium concentration in solution (mg/L), C_{Ae} is the solid-phase concentration at equilibrium (mg/L), R is the gas constant (8.314 J/mol/K) and T is the temperature (K).

2.3.4. Adsorption kinetic models

The pseudo-first order kinetic model is given by Equation 7.

$$\log(q_e - q_t) = \log q_e - \frac{k_{ad}}{2.303} t \quad (7)$$

where q_t and q_e are the adsorption capacity at time t (mg/g) and at equilibrium, respectively, and k_{ad} (min⁻¹) is the pseudo-first order rate constant of the adsorption. A plot of $\log(q_e - q_t)$ versus t should give a straight line if the pseudo-first order kinetic describes the adsorption process.

The linearized-integral form of the pseudo-second order reaction model is represented by Equation 8.

$$\frac{t}{q_t} = \frac{1}{h} + \frac{1}{q_e} t \quad (8)$$

where $h = kq_e^2$ (mg/g/min) and k is the rate constant for pseudo-second order adsorption (g/mg/min). The plot of t/q_t versus t should give a straight line if pseudo-second order kinetic is applicable and q_e , k and h can be determined from the slope and intercept of the plot (Ayanda et al., 2013).

3. RESULTS AND DISCUSSION

3.1. Scanning electron micrograph

Figure 1 illustrates the surface morphology of activated carbon used in the present study. The scanning electron micrograph (SEM) showed that the external surface of the activated carbon exhibited irregular cavities and pores.

3.2. Effect of initial As(III) concentration

The effect of the initial As(III) concentration on the removal efficiency was presented in Figure 2. The

As(III) removal efficiency decreased with increase in initial As(III) concentration. This could be explained with the fact that at higher As(III) concentration, the available sites of adsorption becomes fewer and hence the percentage removal of As(III) decreases. The data obtained on the effect of the initial As(III) concentration was used for the equilibrium studies.

The Langmuir and Freundlich plots presented in Figures 3 and 4, respectively, showed that the R² value of the Langmuir isotherm (0.9901) was higher than the Freundlich isotherm (0.8867). Hence, As(III) adsorption onto activated carbon follows the Langmuir isotherm, this is supported by the work reported by Budinova et al. (2006). Table 1 presents the evaluated parameters of the Langmuir and Freundlich isotherms. The maximum adsorption capacity of As(III) by Langmuir isotherm was 2.1860 mg/g.

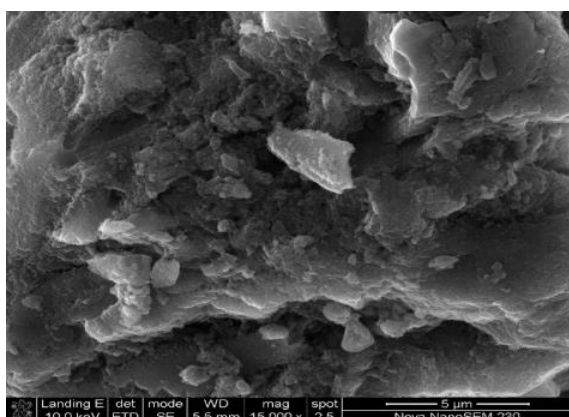


Figure 1. Scanning electron micrograph of activated carbon (mag. 15000x).

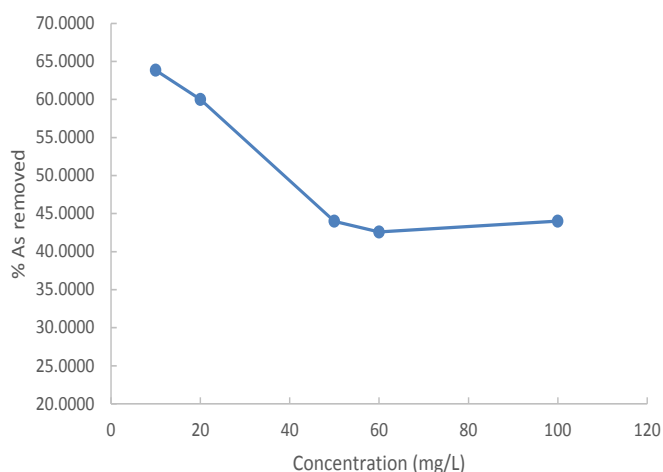


Figure 2. Effect of initial As(III) ions concentration on the adsorption of As(III) ions onto activated carbon.

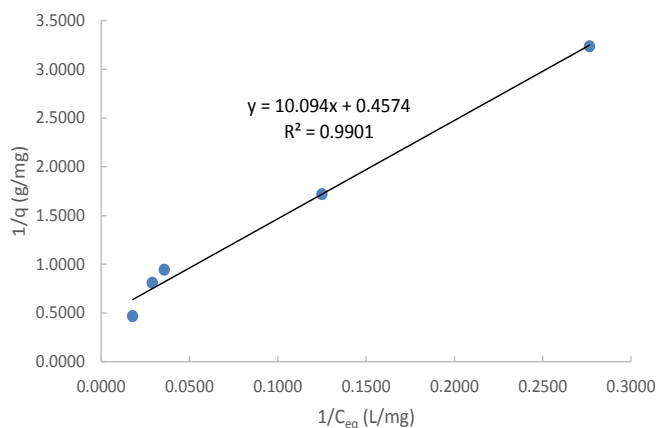


Figure 3. Langmuir isotherm for the adsorption of As(III) ions onto activated carbon.

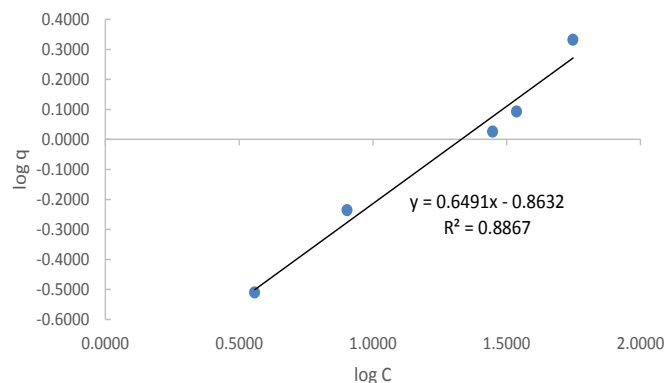


Figure 4. Freundlich isotherm for the adsorption of As(III) ions onto activated carbon.

Table 1. Isotherm model parameters.

Langmuir isotherm		Freundlich isotherm	
K_L (L/mg)	0.0453	K_F (mg/g(L/mg) ^{1/n})	0.1370
q_m (mg/g)	2.1860	n	1.5406
R^2	0.9901	R^2	0.8867

3.3. Effect of the adsorbent dose

The results (Figure 5) obtained showed that as the amount of activated carbon was increased from 0.0134 to 2.5668 g, the amount adsorbed and percentage removal of As(III) was respectively increased. The adsorbent dose affects the adsorption capacity directly; as the dosage increases, more active sites become available for As(III) ions.

3.4. Effect of contact time

It was observed in Figure 6 that as the contact time increases, there was enhancement in the adsorption of As(III) according to both percentage removal as well as amount adsorbed values. This was due to a larger surface area of the activated carbon being made available with time for the adsorption of As(III). The optimal percentage removal of As(III) achieved by the activated carbon was found to be approximately 50.0% when 25 mL of 100 mg/L As(III) solution was contacted with 2.5668 g of activated carbon for 120 min at 120 rpm.

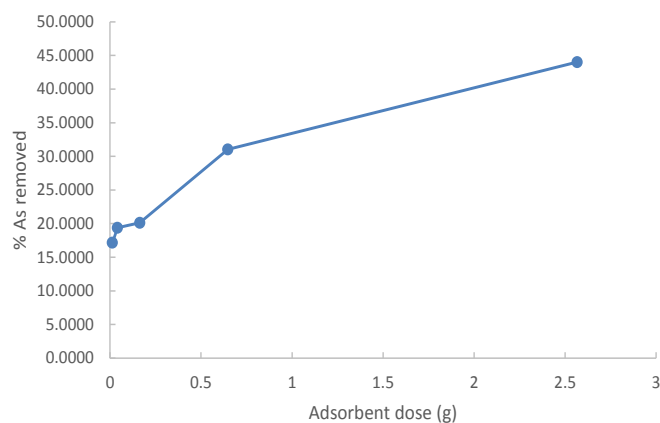


Figure 5. Effect of adsorption dose for the adsorption of As(III) ions onto activated carbon.

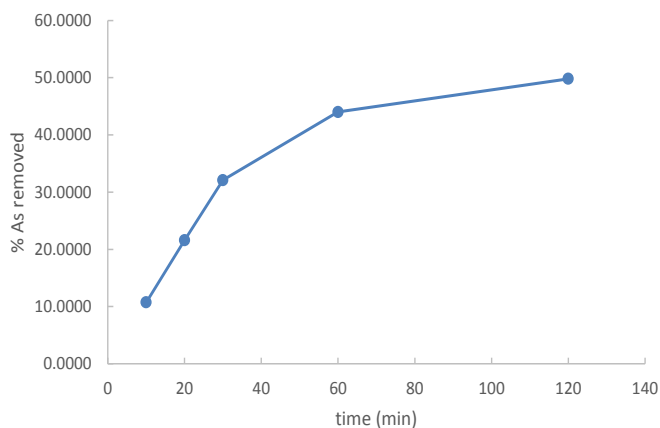


Figure 6. Effect of contact time for the adsorption on As (III) ions onto activated carbon.

To evaluate the kinetics of the adsorption process, the pseudo-first order and pseudo-second order models were tested to interpret the experimental data. Experimental interpretations in Figure 7 suggested that the application of Equation 7 is inappropriate, as experimental observations are non-linear when plotted. And also, the correlation coefficient was found

to be low (0.8417).

On the other hand, the plot according to pseudo-second order model (Figure 8) was linear. The correlation coefficient was found to be 0.9620, which was much higher than the correlation coefficient derived from pseudo first-order models fit. This suggests that As(III) adsorption onto activated carbon followed the pseudo-second order kinetics and As(III) were adsorbed onto the activated carbon surface via chemical interaction. This observation was supported by Yao et al. (2014) and Van Vinh et al. (2015). Table 2 presents the evaluated parameters of the kinetics models.

Table 2. Kinetic parameters.

Pseudo-first order		Pseudo-second order	
		k (g/mg/min)	0.0064
k_{ad} (min ⁻¹)	0.0048	q_e (mg/g)	3.4578
q_e (mg/g)	4.2266	h (mg/g/min)	0.0763
R ²	0.8417	R ²	0.9620

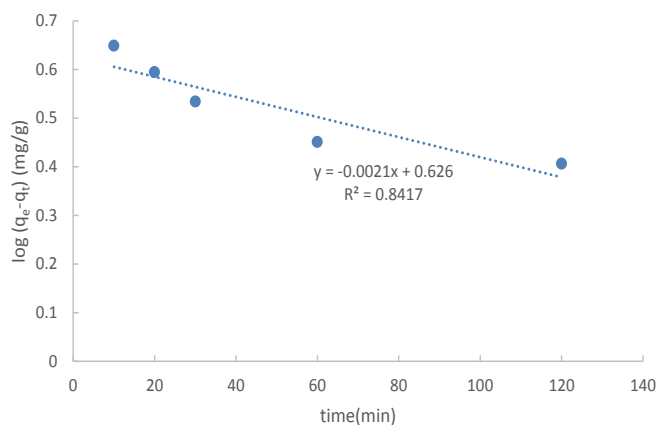


Figure 7. Pseudo-first order reactions of the adsorption of As(III) ions onto activated carbon.

3.5. Effect of solution pH

The pH affects both the activated carbon and As(III) chemistry in solution. The effect of pH on the adsorption of As(III) onto the activated carbon was examined for pH values ranging from 2 to 10. Figure 9 demonstrated that the percentage of As(III) adsorbed steadily increased as the pH of the solution increased from 2 to 10.

The increase in the percentage removal of As(III) from pH 2 to 10 might be due to the decrease in the concentration of H⁺ ions (as the solution becomes

less acidic) which initially compete with As(III) ions for binding onto the surface of the activated carbon.

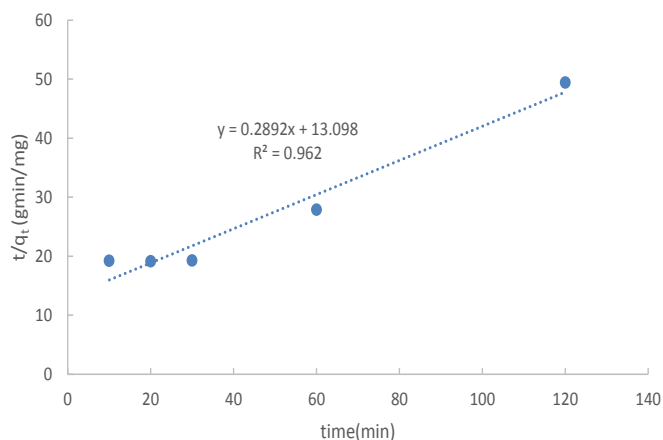


Figure 8. Pseudo-second order reactions of the adsorption of As(III) ions onto activated carbon.

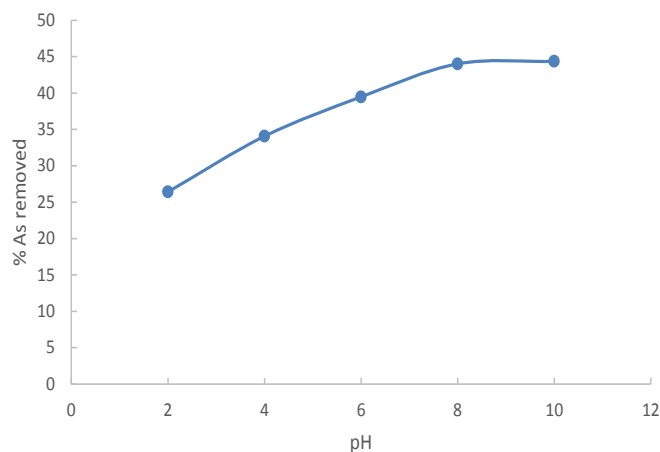


Figure 9. Effect of pH on the adsorption of As(III) ions onto activated carbon.

3.6. Effect of temperature

The experimental results obtained on the effect of temperature showed that the percentage adsorption removal of As(III) onto activated carbon decreases with increase in the solution temperature (Figure 10). This indicated that the adsorption is exothermic.

A graph of $\log K_c$ versus $1/T$ is presented in Figure 11 and the calculated thermodynamic parameters presented in Table 3.

The adsorption of As(III) onto activated carbon was exothermic with the calculated $\Delta S^\circ = -83.035 \text{ J/K/mol}$, and $\Delta H^\circ = -23.288 \text{ kJ/mol}$. Van Vinh et al. (2015) also reported the exothermic nature of the adsorption of As(III) onto raw and zinc loaded pine cone biochar.

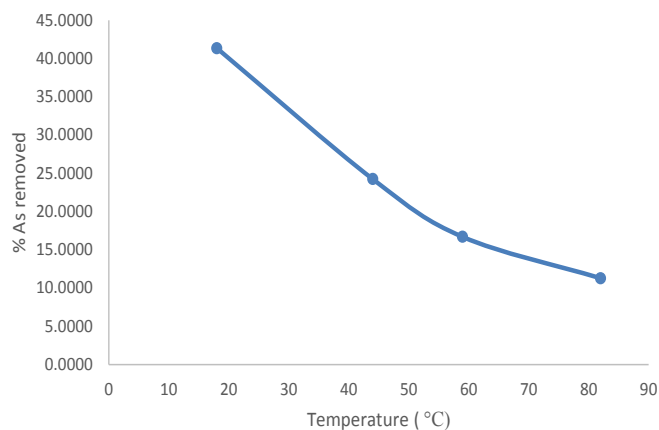


Figure 10. Effect of temperature for the adsorption of As(III) onto activated carbon.

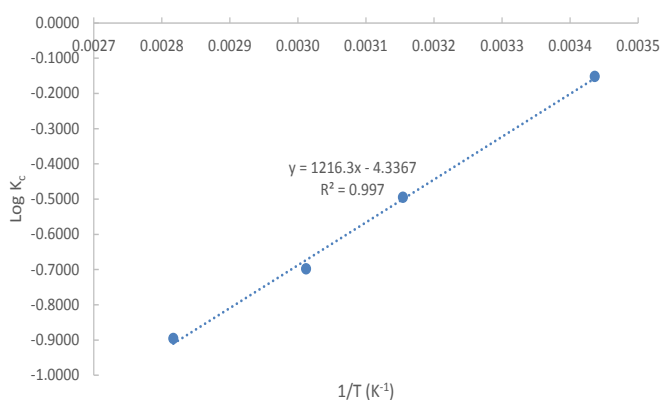


Figure 11. $\log K_c$ versus $1/T$ for the adsorption of As(III) ions onto activated carbon.

Table 3. Thermodynamic parameters.

T (K)	ΔG° (kJ/mol)	ΔS° (J/K/mol)	ΔH° (kJ/mol)	K_c
291	0.8460	-83.035	-23.288	0.7049
317	3.0038			0.3199
332	4.4388			0.2003
355	6.0867			0.1272

4. CONCLUSIONS

Arsenic has become a major challenge around the world due to its harmful effect on animals, human and the environment. Hence there is a greater need to remove arsenic from water and wastewater. The results of the present study indicated that activated carbon effectively removed As(III) from aqueous solutions. The pseudo-second order kinetic model accurately described the

adsorption kinetics. The Langmuir isotherm showed a better fit than the Freundlich isotherm, thus, indicating the applicability of monolayer coverage of As(III) on activated carbon, and the adsorption mechanism was found to be chemisorption. In addition, adsorption of As(III) onto activated carbon was found to be exothermic. Activated carbon may therefore be used as an effective adsorbent for removing As(III) from water and wastewater.

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