

Research Article

Adsorption Studies for Arsenic Removal Using Activated *Moringa oleifera*

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A new low cost adsorbent, activated *Moringa oleifera* has been developed for aqueous arsenic removal. Batch experiments were revealed that As removal was up to 71.3% using activated *Moringa oleifera*. Kinetics studies revealed that Langmuir isotherm was followed with a better correlation than the Freundlich isotherm. The thermodynamic parameters such as ΔH , ΔS , and ΔG were computed from the experimental data. These values show that the adsorption is endothermic and spontaneous in nature. Thus, this recently developed cost-effective novel biosorbent, activated *Moringa oleifera* can be used as household level to mitigate the arsenic problem.

1. Introduction

Heightened awareness of arsenic toxicity and regulatory changes has prompted considerable research efforts toward developing methods for arsenic removal from drinking water [1].

Naturally occurring arsenic contaminates groundwater in many countries including Argentina, Australia, Chile, China, Hungary, India, Mexico, Peru, Taiwan, Thailand, and the United States [2]. Several techniques effectively lower arsenic concentrations in aqueous solutions: coagulation/precipitation, reverse osmosis, ion exchange, and adsorption. Coagulation and softening with metal ions such as aluminum and ferric salts require use of large-scale facilities for implementing water treatment. Adsorbent materials studied for arsenic removal include activated alumina, fly ash, pyrite fines, manganese greensand [3], amino-functionalized meso porous silicas [4], aluminum loaded Shirasu-zeolite [5], clinoptilolite, and other zeolites [6–8]. However, there is still a strong challenge in developing economical and commonly available biosorbents for As removal. Therefore, we focused on the characterization and biosorption efficiency of the cheapest and easily available indigenous biomass taken from the leaves of *Moringa oleifera*. The aim of this research work

is therefore to prepare activated carbon from *Moringa oleifera* and to carry out the thermodynamic and equilibrium studies of arsenic on the activated *Moringa oleifera* leaves carbon sample.

2. Materials and Methods

Fresh and healthy leaves of *Moringa oleifera* were chosen. Prior to analysis, the samples were air dried (away from sunlight). The preparation of activated carbon from *Moringa oleifera* consisted of carbonization of the plant material. Dried raw leaves were cut into small pieces and the carbonization was conducted in a muffle furnace at 400°C. The heating period was 2 hours. After carbonization, the carbon was ground using domestic mixie. The activated carbon obtained was kept in a desiccator and was characterized for the physical parameters (Table 1).

All chemicals were of analytical grade (>99%) and were purchased from Sigma-Aldrich. The As(V) stock solution (1000 mg/L) was prepared by dissolving Na_3AsO_4 (>99%) in de-ionized water in deionized water. Arsenic working solutions were freshly prepared by diluting arsenic stock solutions (1000 mg/L) with deionized water. The concentrations

TABLE 1: Physical parameters of activated *Moringa oleifera*.

Number	Physical parameter	Value
1	pH	8.5
2	Conductivity	0.18
3	Moisture (%)	7.05
4	Ash (%)	10.6
5	Bulk density (Kg/L)	0.92
6	Specific gravity	0.86
7	Porosity (%)	36
8	Surface area (m ² /g)	1.5146
9	Particle size (microns)	>53
10	Color	Black

of arsenic species were always given as elemental arsenic concentration in this study.

2.1. Batch Experiments. To evaluate optimum working conditions, batch mode experiments were performed in conical flasks placed on an orbital shaker with 100 mL of As(V) solution having initial concentration 20 mg/L. To study the effect of adsorbent dose in the range (0.2–1.2 g/100 mL) at room temperature (303 K), pH was adjusted to 7.0, and contents were agitated for 140 min at a speed of 120 rpm. Afterwards, suspensions were filtered to remove adsorbent and filtrates were subjected to analysis on ICP-OES to find out the remaining amount of sorbate in aqueous phase with arsenic standards, drawing regression line to interpolate samples concentration. In the next experiment, most favorable adsorbent dose was added according to the findings of previous trial, while pH was changed from 3.0 to 12.0 with speed of agitation 120 rpm, time of contact 140 min, and temperature 303 K. Likewise, in studying the effect of contact time, adsorbent dose and pH were selected optimally in accordance with the findings of previous trials, while time of contact was changed in the range 20–180 min at 303 K, shaking the contents at 120 rpm.

2.2. Adsorption Isotherms. Isotherm studies were performed in four 250 mL Erlenmeyer flasks. Each flask was filled with 100 mL of As(V) solutions of different initial concentrations (5–20 mg/L) and pH was adjusted to 7.0. To each flask, 1.2 g of adsorbent was added, and solutions were agitated at a speed of 120 rpm for 140 min.

The biosorption data have been subjected to Langmuir, Freundlich, Temkin, Dubinin Radushkevich (D-R), and Flory-Huggins (F-H) isotherm models.

A basic assumption of the Langmuir theory is that sorption takes place at specific homogeneous sites within the sorbent. This model can be written in linear form:

$$\frac{C_e}{q_e} = \left(\frac{1}{q_m} \right) C_e + \frac{1}{(K_a q_m)}, \quad (1)$$

where q_m is the monolayer biosorption saturation capacity (mg/g) and K_a represents the enthalpy of biosorption (L/mg), independent of temperature.

On the other hand, the Freundlich equation is represented by the following:

$$\log q_e = \log K_f + \frac{1}{n} \log C_e, \quad (2)$$

where C_e is the equilibrium concentration (mg/L), q_e is the amount of As adsorbed (mg/g), and K_f and n are Freundlich constants.

The Temkin isotherm, the simple form of an adsorption isotherm model, has been developed considering the chemisorption of an adsorbate onto the adsorbent and is represented as

$$q_e = a + b \log C_e, \quad (3)$$

where q_e and C_e have the same meaning as noted previously and the other parameters are called the Temkin constants. The plot of q_e versus $\log C_e$ will generate a straight line. The Temkin constants a and b can be calculated from the intercept and slope of the linear plot.

The equilibrium data were also analyzed using the D-R isotherm model to determine the nature of biosorption processes as being physical or chemical. The linear presentation of the D-R isotherm equation is expressed by

$$\ln q_e = \ln q_m - \beta \varepsilon^2, \quad (4)$$

where

$$\varepsilon = RT \ln \left(1 + \frac{1}{C_e} \right), \quad (5)$$

where q_e is the amount of As ions adsorbed on per unit weight of biosorbent material (mg/L), q_m is the maximum biosorption capacity (mg/g), β is the activity coefficient (mol²/J²) related to biosorption mean free energy (KJ/mol), and ε is the Polanyi potential, where R (J/mol/K) is the gas constant and T (K) is the absolute temperature. The constants β and q_m were obtained from slope and intercept of the plot of $\ln q_e$ against ε^2 .

On the other hand, the Flory-Huggins (F-H) isotherm equation is represented by the following:

$$\log \left(\frac{\theta}{C} \right) = \log K_{FH} + n_{FH} \log (1 - \theta). \quad (6)$$

In this respect, θ is the degree of surface coverage, where K_{FH} and n_{FH} are the indication of its equilibrium constant and model exponent (Table 2).

3. Results and Discussion

3.1. Effect of Adsorbent Dosage. The adsorbent doses were varied from 0.2 g to 1.2 g. It was observed that the removal of arsenic increased with the increase in dosage, attaining a maximum at 1.2 g of adsorbent dosage (Figure 1). Obviously, higher dose of adsorbent results in higher surface area providing greater number of binding sites for the metal ion.

TABLE 2: Equilibrium constants of various isotherm models for the adsorption of arsenic on activated *Moringa oleifera*.

Isotherm	Isotherm constants	Temperature		
		303 K	313 K	323 K
Langmuir	K_a (L/mg)	0.3542	0.4134	0.4901
	q_{max} (mg/g)	6.2313	6.7672	7.3752
	r^2	0.9958	0.9955	0.9945
	SD	0.0257	0.0261	0.0278
Freundlich	K_f (mg/g) (mg/L) ^{-1/n}	34.4215	29.8751	26.0321
	n	1.6572	1.8756	2.1718
	r^2	0.9935	0.9916	0.9862
	SD	0.0070	0.0082	0.0104
Temkin	a (L/mg)	22.7653	21.7821	20.7317
	b (mg/g)	14.2619	13.1447	11.8766
	r^2	0.9976	0.9965	0.9935
	SD	0.1002	0.1287	0.1839
D-R	β (mol ² /J ²)	0.0294	0.0204	0.0116
	q_m (mol/g)	7.4578	8.0825	9.0467
	r^2	0.9736	0.9638	0.9478
	SD	0.0326	0.0387	0.0471
F-H	n_{FH}	0.6034	0.5332	0.4364
	K_{FH}	59.0391	55.1087	49.6569
	r^2	0.9935	0.9916	0.9881
	SD	0.0070	0.0082	0.0099

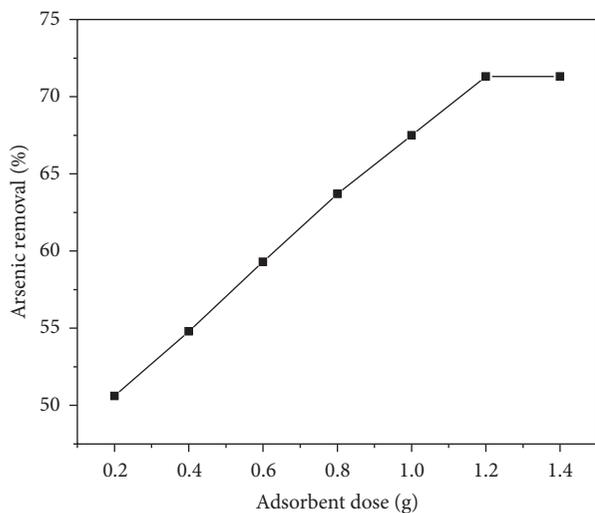


FIGURE 1: Effect of adsorbent dose on biosorption of arsenic.

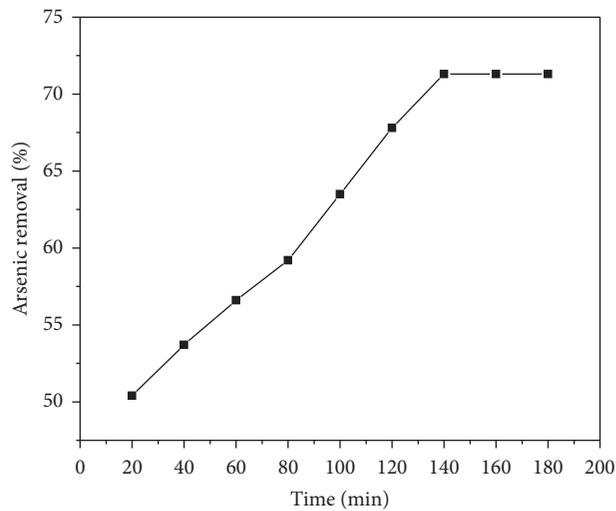


FIGURE 2: Effect of time variation on biosorption of arsenic.

It is observed that, after dosage of 1.2 gm, there was no significant change in percentage of removal of As(V). It may be due to overlapping active sites at higher dosage. So, there was not any appreciable increase in the effective surface area resulting due to the conglomeration of exchanger particles. So, 1.2 g/100 mL was fixed as optimum dose and was used for further study.

3.2. *Effect of Contact Time.* Percentage of arsenic removal was recorded at contact time of 20 min to 180 min. The results are shown in Figure 2. Initially the rate of uptake of arsenic is very fast and gradually increases attaining a steady value after reaching the equilibrium at about 140 min. Hence, 140 min contact time was fixed for further study.

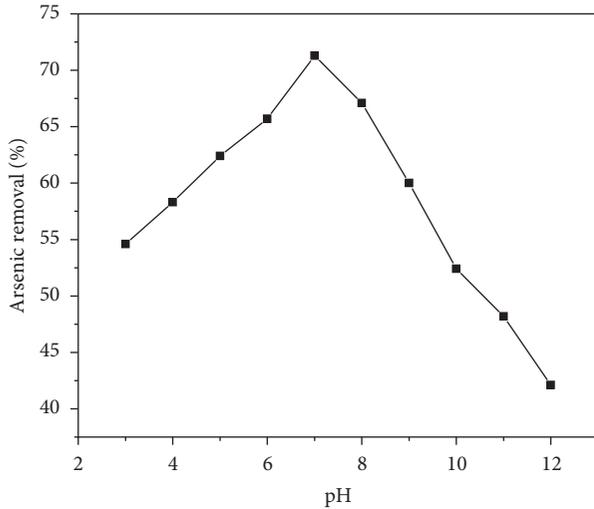


FIGURE 3: Effect of pH on biosorption of arsenic.

3.3. Effect of pH. The effect of pH on removal of arsenic is shown in Figure 3. The study was done in the pH range of 3 to 12. It was found that the adsorption of arsenic ion gradually increases as the initial pH of the solution is raised from 3 to 7. The maximum removal of arsenic was found to be 71.3%, at pH 7. Hence, pH of the arsenic solution was maintained at 7 for further study. This agrees with the other results obtained on iron oxide coated on cement (IOCC) [9], carbon based adsorbents [10], and zero valent iron [11]. At pH more than 7, the removal process is very low. This is due to high OH^- ion concentration, which reverses the process of removal, and hence the process of conversion of adsorbent into its OH^- form plays an important role leaving behind arsenic in the aqueous solution. This is due to the effect of precipitation of Arsenic.

3.4. Adsorption Isotherms. Adsorption of As(V) by *Moringa oleifera* was modeled using the Freundlich, Langmuir, Temkin, D-R, and F-H isotherm with the quality of the fit assessed using the correlation coefficient. Langmuir isotherm parameter fits (Figure 4(a)) for As(V) adsorption on *Moringa oleifera* yielded isotherms that were in good agreement with observed behavior ($r^2 = 0.9958$). The arsenic adsorption capacity on *Moringa oleifera* at room temperature (303 K) was 6.23 mg/g. The essential characteristics of the Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor R_L that is given by the following equation:

$$R_L = \frac{1}{1 + k_a C_0}, \quad (7)$$

where C_0 (mg/L) is initial concentration of adsorbate and k_a (L/mg) is Langmuir constant. Figure 4(b) shows the variation of separation factor (R_L) with initial arsenic concentration. The R_L values were in the range of 0-1 at 303 K, indicating that the sorption of As(V) onto *Moringa oleifera* is favorable. The Freundlich isotherm constants K_F and n are determined

TABLE 3: Thermodynamic parameters of arsenic sorption on activated *Moringa oleifera*.

	Temperature (K)	Value
ΔG° (KJ/mol)	303	-5.5611
	313	-5.7544
	323	-5.9686
ΔH° (KJ/mol)		608.4237
ΔS° (KJ/mol/K)		20.3507

from the intercept and slope of a plot of $\log q_e$ versus $\log C_e$ (Figure 4(c)). In this study, n values are greater than unity indicating chemisorption [12]. Isotherms with $n > 1$ are classified as L-type isotherms reflecting a high affinity between adsorbate and adsorbent and are indicative of chemisorption [13]. The Freundlich constant, K_F , which is related to the adsorption capacity, increased with temperature, indicating that the adsorption process is endothermic. Linear plots for Temkin adsorption isotherm (Figure 4(d)), which consider chemisorption of an adsorbate onto the adsorbent [14], fit well with correlation coefficients (0.9976). This further supports the findings that the adsorption of Arsenic onto *Moringa oleifera* is a chemisorption process.

The other isotherm models, namely, D-R (Figure 4(e)) and Flory-Huggins isotherm (Figure 4(f)), are also carried out, where the dates are partially correlated with correlation coefficients.

Hence the order of isotherm equations obeyed by the present data is Temkin > Langmuir > F-H > Freundlich > D-R isotherm.

3.5. Thermodynamic Studies. An increase in temperature resulted in an increased rate of Arsenic adsorption onto *Moringa oleifera* indicating that the process is endothermic.

The thermodynamic parameters were calculated using the following equations:

$$\Delta G^\circ = -RT \ln K, \quad (8)$$

$$\ln K = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT}.$$

Based on some literature, equilibrium constant can be derived from the point $q_e = 0$ of plot between $(\ln q_e/c_e)$ and q_e at different temperatures [15, 16]. The plot of $\ln K$ versus $1/T$ was found to be linear (Figure 5), and ΔH° and ΔS° values were calculated from the slope and intercept of the plot by linear regression method and are listed in Table 3.

The change in the free energy (ΔG°) is calculated to be -5.5611 KJ/mol at 303 K. The negative value of ΔG° means that the sorption of arsenic on the adsorbent is spontaneous, perhaps due to columbic attraction.

The values of ΔH° and ΔS° are 608.4237 KJ/mol and 20.3507 KJ/mol/K. The positive value of ΔH° confirms that the sorption process is endothermic in nature. The positive values of ΔS° reflect increases the randomness in the system.

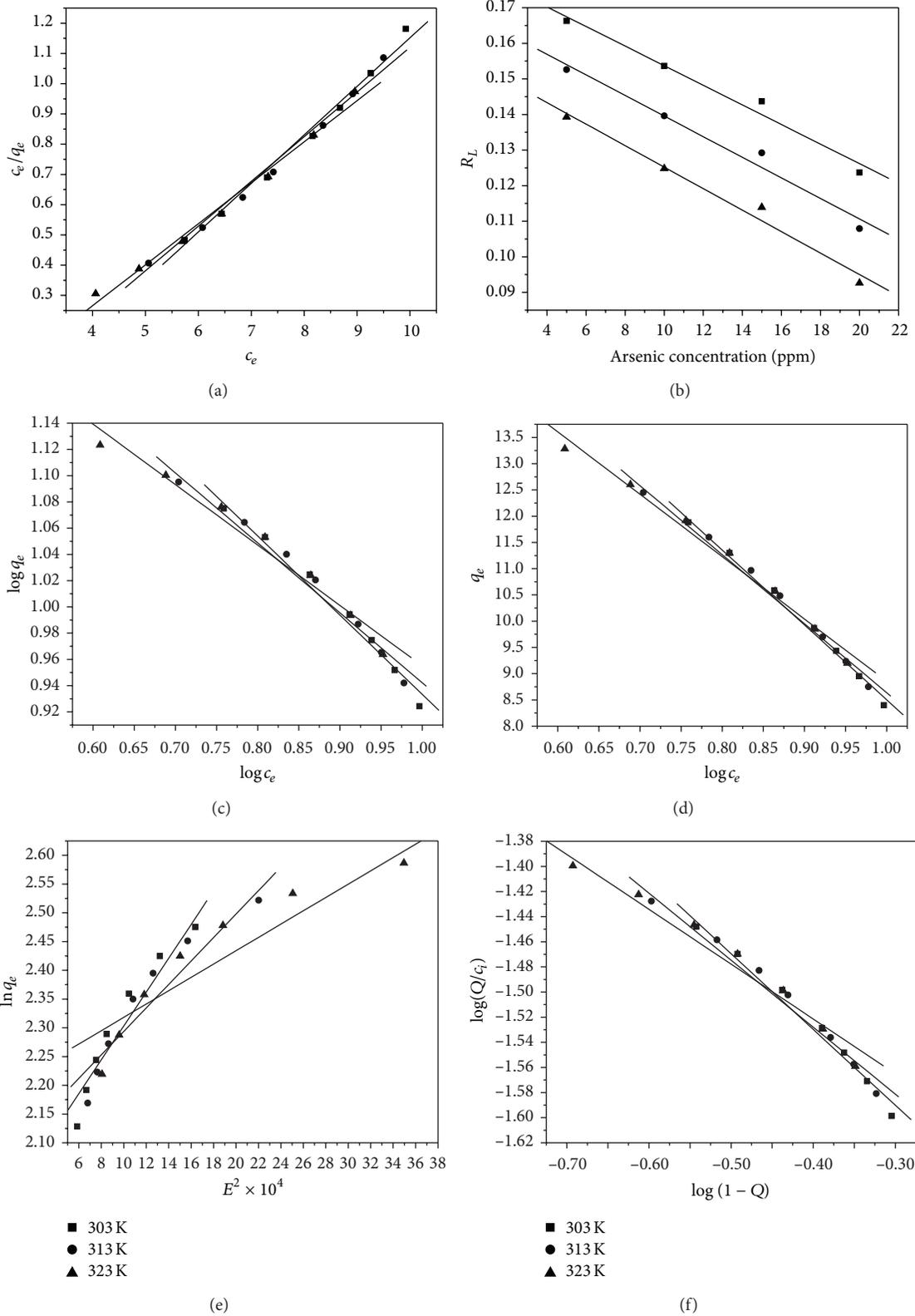


FIGURE 4: (a) Plot of the Langmuir isotherm for arsenic biosorption onto *Moringa oleifera*. (b) Separation factor R_L values versus initial arsenic concentration for various temperatures derived by Langmuir constants. (c) Plot of the Freundlich isotherm for arsenic biosorption onto *Moringa oleifera*. (d) Plot of the Temkin isotherm for arsenic biosorption onto *Moringa oleifera*. (e) Plot of the D-R isotherm for arsenic biosorption onto *Moringa oleifera*. (f) Plot of the F-H isotherm for arsenic biosorption onto *Moringa oleifera*.

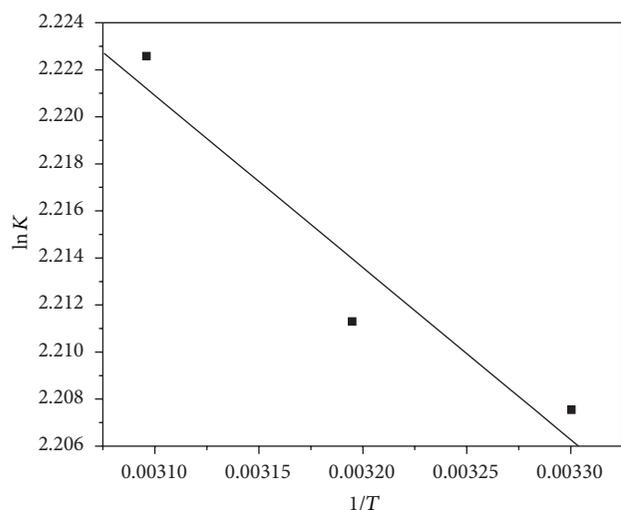


FIGURE 5: $\ln K$ versus $1/T$.

4. Conclusion

This study focused on the biosorption of As(V) onto biosorbent material (*Moringa oleifera*) from aqueous solution.

Moringa oleifera sorption on arsenic was studied in batch mode and found to be strongly dependent on pH value of solution, adsorbent dosage, and temperature. The adsorbent had a high removal capacity towards As(V). Maximal adsorption capacities were 6.23 mg/g at pH 7.0. The adsorption mechanism was found to be chemisorption and the rate-limiting step was mainly surface adsorption. The Langmuir isotherm showed a better fit than the Freundlich isotherm, thus indicating that the applicability of monolayer coverage of arsenic on increasing the temperature increased the arsenic adsorption rate. The equilibrium data were also well described by the Temkin equation further supporting arsenic adsorption on *Moringa oleifera* as a chemisorption process. The negative ΔG° values showed that the biosorption of As(V) onto activated *Moringa oleifera* was feasible and spontaneous. The positive ΔH° values depicted endothermic nature of the adsorption. The positive ΔS° values revealed the increased randomness at the solid-solution interface.

Based on all results, it can be concluded that *Moringa oleifera* is an effective and alternative biomass for removing As(V) from aqueous solution due to high bio-sorption capacity, easy availability, and being environmentally friendly.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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