



# Biosorption of As(III) from aqueous solution by *Acacia auriculiformis* leaves

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## KEYWORDS

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 FTIR.

**Abstract.** The biosorption capability of *Acacia* (*Acacia auriculiformis* A.Cunn. ex Benth.) leaf powder in batch and a small scale column was investigated. The adsorption properties were analyzed with different experimental variables, such as solution pH, amount of biosorbent, initial As(III) concentration and temperature. The maximum adsorption was observed at pH 6.0, while the equilibrium was attained in 5 h. Langmuir and Freundlich equilibrium adsorption isotherm models were utilized for fitting the experimental data. The maximum adsorption capacity of *A. auriculiformis* leaf powder was calculated to be 41.410  $\mu\text{g g}^{-1}$ . The kinetic data were well fitted using a pseudo-first-order model with a correlation coefficient greater than 0.989. The surface morphology of the biosorbent was analyzed using Scanning Electron Microscopy (SEM). Fourier transform infrared spectroscopy (FTIR) was employed to characterize the surface functional groups of *A. auriculiformis* leaf powder. The activation energy ( $E_a$ ) and heat of biosorption ( $\Delta H$ ) were calculated to be 27.549 and 43.380  $\text{kJ mol}^{-1}$ , respectively. The thermodynamic parameters, such as Gibbs free energy ( $\Delta G$ ), enthalpy ( $\Delta H$ ), and entropy ( $\Delta S$ ), revealed the spontaneous nature of the biosorption followed by a physical activated process. Small Scale Column Tests (SSCT) were also conducted to discover the breakthrough characteristics of the column packed with biosorbent.

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## 1. Introduction

Arsenic (As) is the twentieth most abundant element in the earth's crust. It is considered an ultra-trace nutrient and its deficiency can result in inhibited growth, but, it becomes a potential toxin to plants, animals, and human beings when intake exceeds the necessary level [1]. Many arsenic compounds are

naturally present in the environment and in different biological systems [2]. Since its isolation in 1250 A.D., this element has had a controversial impact on human history, but, recently, arsenic contamination in water, specifically in ground water, has emerged as a major problem of catastrophic proportions [3]. Geological and anthropogenic emissions are responsible for arsenic contamination where the geological mechanism is the salient cause of arsenic pollution [4]. Inorganic arsenicals are also proven beyond doubt to be carcinogens [5].

Arsenic exists in four oxidation states, +5 (arsenate), +3 (arsenite), 0 (arsenic), and -3 (arsine). Since arsenic occurs in the earth's crust to a significant extent, contamination of groundwater with this poisonous

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substance cannot be avoided. The current regulations regarding standards of drinking have become more stringent and require that the arsenic content be reduced to a few parts per billion ( $10 \mu\text{g L}^{-1}$ , WHO, US-EPA). However, many countries have kept the earlier WHO guideline of  $50 \mu\text{g L}^{-1}$  as their standard, including Argentina, Bangladesh and China. The scale of the arsenic problem is most serious in the alluvial and deltaic aquifer of Bangladesh and West Bengal (India), where millions of people drink water with high levels of arsenic [6]. Up to 57 million people are daily exposed to arsenic levels in drinking water that exceed  $10 \mu\text{g L}^{-1}$ ; in some cases, as high as  $2,500 \mu\text{g L}^{-1}$  [7]. UNICEF reported in 2006 that 1.6 million (32%) of the 5 million tube wells so far tested were found to contain arsenic above  $50 \mu\text{g L}^{-1}$ . Even long-term drinking of less-contaminated water can cause skin, lung, bladder, and kidney cancer, and other diseases such as pigmentation changes, skin thickening (hyperkeratosis), neurological disorders, muscular weakness, loss of appetite, and nausea. Acute intoxication can stimulate vomiting, esophageal and abdominal pain, and “rice water” diarrhea [8].

Numerous treatment methods (e.g., solvent extraction, chemical precipitation as synthetic coagulants, ferric-hydrite precipitation, iron co-precipitation, ion exchange and reverse osmosis) have so far been reported capable of the remediation of arsenic content from drinking water. However, treatment cost, the operational complexity of the technology, required skills, and disposal of the arsenic bearing treatment residual are factors that need consideration before selecting an appropriate treatment method [3]. In such context, biosorption by inexpensive biomaterials could offer an excellent alternative for the mitigation of metal ions from water, being highly cost-effective, eco-friendly, and simpler.

Plant-based products, particularly those containing cellulose, show potential metal biosorption capability [9]. Carbon composites are also reported as promising candidates for arsenic removal, with the conjugation of metal oxide leading to an increased surface area [10]. Various types of biosorbent, like chicken fat, coconut fiber, charcoal, Atlantic cold fish scales, chitosan-coated, modified sugarcane bagasse, pine leaves, rice polish, and rice husk etc. were reported to lessen arsenic in drinking water [11–14].

Most biosorbents previously reported have shown promise in arsenic adsorption from an aqueous solution. In our previous papers, we reported arsenic removal by Jute Stick Powder (JSP), Jute Leaf Powder (JLP), Sugarcane Powder (SP), Fish Eyes Powder (FAP), Dheki Vegetable Powder (DVP), Fern Plant Powder (FPP), Water Hyacinth Root Powder (WHRP), neem leaf powder, tea leaf powder, mushrooms, lemon peel and lemon segments [15,16].

In this study, we investigate the arsenic removal efficiency of *Acacia auriculiformis* leaves, locally known as “Akashmoni”, a common fast growing species in the tropics, belonging to the family Fabaceae. Being native to Australia, Papua New Guinea and Indonesia, the species has become prominent in timber production and the reforestation of degraded sites across many regions in the tropics, particularly in South Asia and Bangladesh. Batch and Small Scale Column Tests (SSCT) were performed to evaluate the sorption characteristics. Sorption kinetics and thermodynamic behavior were explained using different fitting models. We believe that this technique, using leaves of a commonly found species, could offer an alternative means of arsenic mitigation in various countries suffering from catastrophic arsenic pollution in drinking water.

## 2. Material and methods

### 2.1. Preparation of biosorbent

Fresh *A. auriculiformis* leaves were collected from the Forestry Department of Shahjalal University, Sylhet, Bangladesh ( $24.8917^\circ\text{N}$ ;  $91.8833^\circ\text{E}$ ). Later, the leaves were washed with distilled water, followed by subsequent drying and oven drying (Miken Instruments, India) at  $80^\circ\text{C}$  for 6 h to remove the moisture located inside the leaf pores. The dried leaves were boiled in hot distilled water for 1 h to remove coloring components and ensure clear water. The samples were then dried and finely crushed manually, followed by washing with 0.001 M HCl to remove any residual precipitate salt inside the pores [10]. Later, the materials were repeatedly washed with Doubly Distilled Water (DDW) to remove all traces of acids and dried at  $40^\circ\text{C}$  for 24 h to volatilize any organic impurities. Finally, the leaf powder was sieved in particle sizes ranging from 150–200  $\mu\text{m}$ . This processed material was stored in the desiccator for further experiment.

### 2.2. Chemicals, equipment and apparatus

All chemicals and reagents were of analytical grade, purchased from BDH (England), Merck (Germany) and Kanto Chemical Co. (Japan), and used without any further purification. The glassware used in the experiment was thoroughly washed with chromic acid followed by caustic soda, soda ash, tap water, distilled water (in that order) and dried in an oven prior to use. DDW was thoroughly used for this study. Batch experiments were carried out using an orbital shaker (Stuart orbital shaker, England). The solution pH was adjusted by 0.5 M HCl or 0.1 M NaOH using a pH meter (pHs -25, REX, CHINA). The total arsenic concentration was determined using UV-Visible spectrometric methods [17]. A homemade U-like arsine generator, consisting of a three neck round bottom flask, especially prepared by quick fit apparatus, was used for

this experiment. The arsine generated in the flask was allowed to pass through glass wool impregnated with lead acetate  $(\text{CH}_3\text{COO})_2\text{Pb}$  to absorb any hydrogen sulfide ( $\text{H}_2\text{S}$ ), which may have evolved during sampling. The arsine gas bubbles into the silver diethyldithiocarbamate (SDDC) (BDH, England) solution containing hexamethylenetetramine in  $\text{CHCl}_3$ , which turn slowly reddish, and the absorbance was taken by a UV-visible spectrophotometer (UV-1650 PC, Shimadzu, Japan) at 535 nm against a reagent blank following the same procedure. This technique can precisely measure the arsenic concentration in the range of 5–235  $\mu\text{g L}^{-1}$ . To maintain the accuracy of the total arsenic concentration, a standard addition technique was employed [18]. Infra-red spectra (Shimadzu prestige-21 FTIR Spectrophotometer, Japan) were recorded for unloaded Acacia Leaf Powder (ALP) and arsenic loaded ALP. Surface morphology and microstructures were observed by scanning electron microscope (SEM; FEI Company Quanta400).

### 2.3. Stock solutions and standards

A standard As(III) stock solution was prepared by dissolving 1.320 g arsenic trioxide ( $\text{As}_2\text{O}_3$ ) in 10 mL of DDW, containing 4 g NaOH, followed by a gentle heating at  $50^\circ\text{C}$ . The desired amount of DDW was added to make the total volume up to 1000 mL. This solution is likely to be stable under ambient conditions. Different concentrations, ranging from 100–500  $\mu\text{g L}^{-1}$ , were prepared by proper dilution with DDW.

### 2.4. Biosorption experiments

The batch experiments were performed in a conical flask placed on an orbital shaker containing 100 mL of As(III) solution, having the biosorbent dosage ranging from 3.0–30  $\text{g L}^{-1}$  at room temperature. The solution pH was pre-adjusted at 6.0 before shaking at the speed of 250 rpm for 5 h. After reaching equilibrium, the biosorbent was separated by filtration through a 0.8  $\mu\text{m}$  cellulose acetate membrane (Whatman), then, the equilibrium concentration of As(III) ions in the filtrate was determined using a standard SDDC method. The amount of As(III) adsorbed was calculated from the difference between the initial and equilibrium concentration. The concentrations were measured three times in each experimental run. A Small Scale Column Test (SSCT) was conducted with a down flow system containing a sandwiched bed supported by normal sand, which was washed with 1.0 M  $\text{HNO}_3$  for 24 h before execution.

### 2.5. Adsorption isotherms and kinetics

Isotherms studies were performed in five 250 mL Erlenmeyer flasks filled with 100 mL of As(III) solution of different initial concentrations (100, 200, 300, 400 and 500  $\mu\text{g L}^{-1}$ ), and the pH was adjusted at 6.0. Each flask containing 15.0  $\text{g L}^{-1}$  of adsorbent was agitated

at a speed of 250 rpm for 5 h. Subsequently, the solutions were filtered and analyzed to calculate the amount of arsenic adsorbed into the biosorbent. According to Eq. (1), Langmuir (Eq. (2)), and Freundlich (Eq. (3)) isotherms were plotted and the corresponding parameters were evaluated. Separation factors ( $R_L$ ) for different initial concentrations were also calculated employing Eq. (4).

$$q_e = \frac{V(C_o - C_e)}{1000W}, \quad (1)$$

$$\frac{1}{q_e} = \frac{1}{QbC_e} + \frac{1}{Q}, \quad (2)$$

$$\log q_e = \log k_f + \frac{1}{n} \log C_e, \quad (3)$$

$$R_L = \frac{1}{1 + bC_0}. \quad (4)$$

In the same way, kinetic studies were undertaken using 15.0  $\text{g L}^{-1}$  of biosorbent at pH 6.0. The agitation speed was maintained at 250 rpm and different temperatures were also controlled. The samples at different time intervals (20–100 min) were pipetted out and analyzed. Then, pseudo-first-order (Eq. (5)) and pseudo-second-order (Eq. (6)) models were fitted with the experimental data. The relevant parameters were also calculated.

$$\ln(q_e - q_t) = \ln q_e - k_1 t, \quad (5)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t. \quad (6)$$

The key thermodynamic parameters, like activation energy, Gibbs free energy, entropy and heat of adsorption, were evaluated by Eqs. (7), (8) and (9), respectively, as follows:

$$\ln k = \ln k_0 - \frac{E_a}{R_g T}, \quad (7)$$

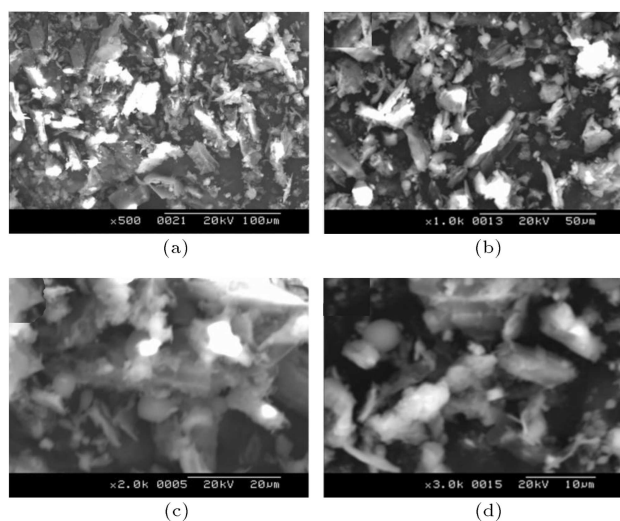
$$\Delta G = -R_g T \ln K_e, \quad (8)$$

$$\ln K_e = \frac{\Delta S}{R_g} - \frac{\Delta H}{R_g T}. \quad (9)$$

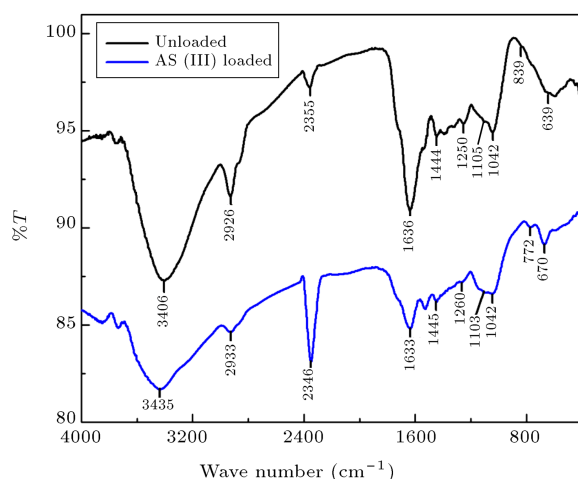
## 3. Results and discussion

### 3.1. Characterization of biosorbent surface by SEM and FTIR

Figure 1 shows the Scanning Electron Microscopic (SEM) images of *A. Auriculiformis* Leaf Powders (ALP) under different magnifications, indicating particle sizes ranging from 5–10  $\mu\text{m}$ . The surface texture suggested a fibrous and porous structure. In order to determine the main functional groups of



**Figure 1.** SEM images of *A. auriculiformis* leaves at different magnifications: (a) 500 $\times$ , (b) 1000 $\times$ , (c) 2000 $\times$  and (d) 3000 $\times$ .



**Figure 2.** FTIR spectra of *A. auriculiformis* leaves unloaded and loaded with As(III) ions.

virgin Acacia Leaf Powder (ALP) for interaction with the As(III) sorption mechanism, a Fourier transform infrared (FTIR) analysis in the solid phase with a KBr disk was performed. Comparative IR spectra of unloaded and As(III) loaded ALP are shown in Figure 2. The broad and strong band ranging from 3000 to 3600  $\text{cm}^{-1}$  stands for the overlapping of -OH and -NH<sub>2</sub> stretching vibration. This observation is also accorded with the existence of peaks at 1045 and 1103  $\text{cm}^{-1}$  for C-O and C-N stretching vibrations [19]. The peak observed near 2926  $\text{cm}^{-1}$  could be assigned to the C-H group. Bands around 1633  $\text{cm}^{-1}$  are indicative of the carboxylic group (C=O). The IR spectra indicated that the carbons possess different surface structures, e.g., aliphatic, aromatic and cyclic, as one can observe bands at 1444  $\text{cm}^{-1}$  and at around 1260 to 1042  $\text{cm}^{-1}$ . It is also evident that all functional

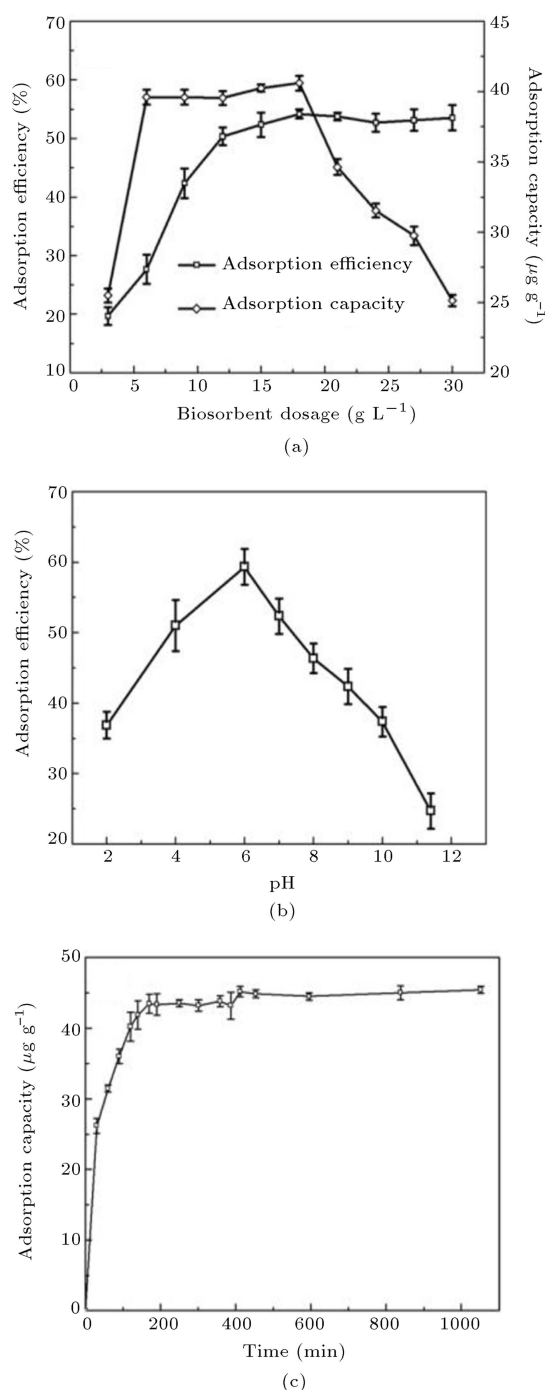
groups originally present on the ALP are intact, even after loaded with As(III). It could also be mentioned that a marginal shift of some peak positions after As(III) loading was observed, which might be related to the chelation of As(III), with some functionalities present in the biosorbent material [20].

### 3.2. Effect of adsorbent dose

The effect of ALP dosage for As(III) uptake was investigated with the variation of biosorbent dose from 3 to 30  $\text{g L}^{-1}$ , as shown in Figure 3(a). The initial concentration and pH of the solution were 500  $\mu\text{g L}^{-1}$  and 7.0, respectively. From Figure 3(a), it was observed that there was an initial quick increase in adsorption efficiency, followed by a final stability with a further increase in biosorbent dose. The adsorption efficiency rose from 19.98% at a dose of 3  $\text{g L}^{-1}$  to 54.02% at 24  $\text{g L}^{-1}$ . The sharp rise in removal efficiency could be related to the greater availability of the exchangeable sites or surface area at higher biosorbent dosage [21]. Generally, the adsorption rate is highly dependent on the amount of bare surface available for effective adsorption. In the early stage of adsorption, the whole surface was uncovered and the adsorption rate was sharply inclined from the initial value of 24.85 to 39.92  $\mu\text{g g}^{-1}$  when the sorbent dosage increased from 3 to 6  $\text{g L}^{-1}$ . Meanwhile, the adsorption rate started to reach equilibrium up to the dosage level of 18  $\text{g L}^{-1}$ . A decrease in sorption capacity above the threshold amount of biosorbent value ( $\sim 15 \text{ g L}^{-1}$ ) was also observed. This observation is mainly affected by the interference of binding sites and insufficiency of metal ions in the solution, with respect to available binding sites between the biosorbent and biosorption medium [22]. The sorbent dosage of 15.0  $\text{g L}^{-1}$  was considered an optimized level of adsorbent and was followed throughout the study.

### 3.3. Effect of pH

Figure 3(b) depicts the effect of pH on adsorption of As(III) into the ALP. The role of hydrogen ion concentration was examined at different pH, ranging from 2.0–11.4. Different pHs were adjusted for the standard solution of 500  $\mu\text{g L}^{-1}$ , for a contact time of 5 h, with a dose of 15.0  $\text{g L}^{-1}$  of biosorbent. FTIR analysis of ALP figured out the presence of various functional groups, such as -COOH, -NH<sub>2</sub> and -OH. These possible active sites of the biosorbent surface played an important role in the sorption process, and the surface groups of biosorbent would become positively charged upon addition of H<sup>+</sup> ions. Also, the protons may bind with As(III) ions, which might govern the mobility or fixedness of arsenic [23]. Under slightly acidic conditions, arsenic can form oxyanions, which might be electrostatically attracted by the protonated active bindings sites (-COOH<sub>2</sub><sup>+</sup>, -NH<sub>3</sub><sup>+</sup> and -



**Figure 3.** (a) Effect of amount of biosorbent. (b) Solution pH. (c) Variation of As(III) sorption on *A. auriculiformis* leaves (initial As(III) concentration: 500 μg L<sup>-1</sup>; agitation speed: 250 rpm; temperature: 25 ± 1°C).

OH<sub>2</sub><sup>+</sup>) of the biosorbent, and effective adsorption may take place [24]. The maximum sorption of around 59.21% took place at pH 6.0, which was selected as the optimum pH condition for further experiments. On the other hand, at relatively higher pH, the surface of the adsorbent would become negatively charged by larger size of OH<sup>-</sup> ions, resulting in an increased diffusion

hindrance for As(III) ions, and leading to decreased adsorption [14].

### 3.4. Equilibrium study

Equilibrium studies were carried out for 1000 mL of 500 μg L<sup>-1</sup> arsenic solution, with a biosorbent dosage of 15.0 g L<sup>-1</sup>, under an agitation speed of 250 rpm. At different time intervals, 20 mL of solution was pipetted for analysis and the amount of arsenic adsorbed per gram of sorbent was plotted against time (Figure 3(c)). It was found that ALP appeared to reach equilibrium in 5 h. The highest concentration was investigated to determine equilibrium time, as a solution concentration of less than 500 μg L<sup>-1</sup> would be expected to attain equilibrium after the same amount of time. Only the adsorption quantity of arsenic might vary for other concentrations [25]. The sorption process was found to be rapid during the initial period of contact time, then, slowed down and equilibrium was established.

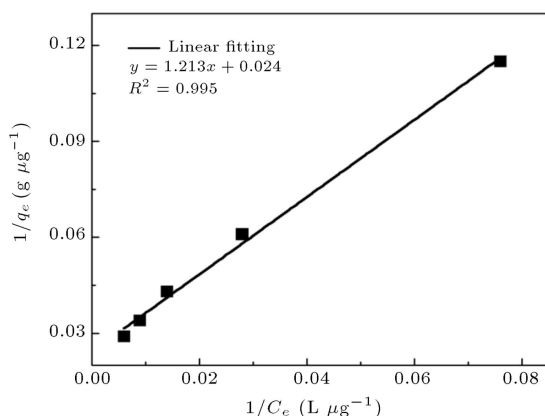
### 3.5. Adsorption isotherms

The equilibrium adsorption isotherms provide the inner understanding and mechanisms of certain adsorption systems. Langmuir and Freundlich isotherm models were used to elucidate the adsorption behavior of As(III) on ALP. Firstly, the Langmuir model was employed to establish the relationship between the amount of As(III) ions adsorbed ( $q_e$ ) on biosorbent and its equilibrium concentration ( $C_e$ ) in the aqueous solution, based on Eq. (2). Figure 4(a) represents the linearized fitting of biosorption data, and the evaluated parameters are listed in Table 1. The correlation coefficient ( $R^2$ ) of the value 0.995 implies the homogeneous distribution of As(III) ions on *A. auriculiformis* leaves. The maximum adsorption capacity ( $Q$ ) and Langmuir constant ( $b$ ) were calculated to be 41.410 μg g<sup>-1</sup> and 0.020 L μg<sup>-1</sup>, respectively, at room temperature. The separation factor,  $R_L$ , resembles the shape of the process.  $R_L > 1$  means unfavorable,  $R_L = 0$  signifies linear,  $R_L = 0 - 1$  entails favorable and  $R_L < 1$  implies irreversible [24]. In this study, the  $R_L$  values were in the range of 0.091-0.334, which indicates a favorable process and the Langmuir isotherm was portrayed correctly.

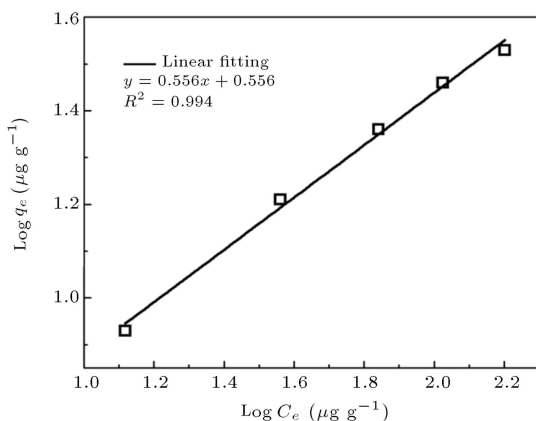
The equilibrium data were also analyzed with the Freundlich model using the linear logarithmic form of Eq. (3). Figure 4(b) shows the linear fitting of the Freundlich model of experimental data, and the parameters were calculated and enlisted in Table 1. The relative adsorption capacity,  $k_f$  (2.139 μg g<sup>-1</sup>) and the empirical constant,  $n$  (1.797), were calculated from the slope and intercept. The value of  $n$  ranging from 1-2 implies a moderate adsorption phenomenon. Both these isotherm models fitted well, according to the correlation coefficient values listed in Table 1. This observation proves the homogeneous and heterogeneous

**Table 1.** Langmuir, Freundlich coefficients and separation factors for biosorption of As(III) at different initial concentration by *A. auriculiformis* leaves.

Initial concentration ( $\mu\text{g L}^{-1}$ )	Separation factor, $R_L$	Langmuir constants		Freundlich constants	
		$Q$ ( $\mu\text{g g}^{-1}$ )	$b$ ( $\text{L } \mu\text{g}^{-1}$ )	$k_f$ ( $\text{L g}^{-1}$ )	$n$
100	0.334	41.410	0.020	2.139	1.797
200	0.201				
300	0.143				
400	0.112				
500	0.091				



(a)



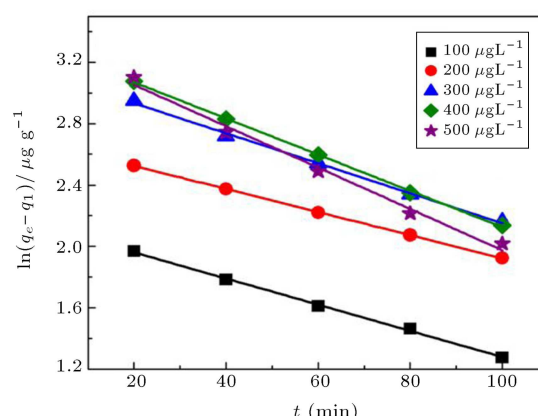
(b)

**Figure 4.** (a) Langmuir and (b) Freundlich isotherm of As(III) biosorption on *A. auriculiformis* leaves (initial pH: 6.0; biosorbent content: 15.0 g L<sup>-1</sup>; agitation speed: 250 rpm; temperature: 25 ± 1°C).

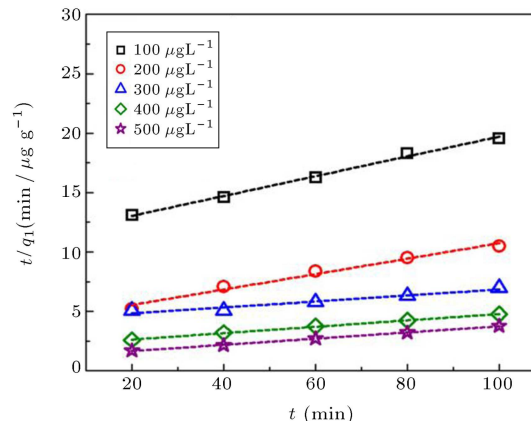
distribution of trivalent arsenic on the surface of *A. auriculiformis* leaves [12].

### 3.6. Kinetic study

In order to examine the mechanisms of adsorption processes, such as mass transfer and chemical reactions, pseudo-first-order (Lagergren) and second-order kinetic models were employed to test the experimental data. The plots of both Eqs. (5) and (6) exhibited straight



(a)



(b)

**Figure 5.** (a) Pseudo-first-order (b) pseudo-second-order kinetic model fitting for As(III) biosorption of different initial concentrations (initial pH: 6.0; biosorbent amount: 15.0 g L<sup>-1</sup>; agitation speed: 250 rpm).

lines with very promising correlations, presented in Figure 5. The slopes and intercepts were used to calculate the adsorption rate constant and theoretical adsorption capacity, which are presented in Table 2. However, the data was further linked when examined with the first-order kinetic model as depicted by high correlation values and the closeness of the theoretical adsorption capacities with experimental ones. The rate constants and theoretical adsorption capacities were

**Table 2.** Kinetic parameters obtained from pseudo-first-order and pseudo-second-order model for As(III) biosorption onto *A. auriculiformis* leaves.

Initial conc. $C_o$ , ( $\mu\text{g L}^{-1}$ )	Pseudo-first-order			Experimental, $q_e$ ( $\mu\text{g g}^{-1}$ )	Pseudo-second-order		
	$k_1 \times 10^3$ ( $\text{min}^{-1}$ )	Theoretical, $q_e$ ( $\mu\text{g g}^{-1}$ )	$R^2$		$k_2 \times 10^4$ ( $\text{g } \mu\text{g}^{-1} \text{min}^{-1}$ )	Theoretical, $q_e$ ( $\mu\text{g g}^{-1}$ )	$R^2$
100	8.535	8.429	0.999	8.684	6.108	11.996	0.999
200	7.552	14.536	0.999	16.369	9.932	15.406	0.998
300	9.783	22.846	0.998	23.053	1.461	39.766	0.946
400	11.802	27.275	0.999	29.422	3.482	15.406	0.982
500	13.485	27.732	0.989	34.106	5.902	38.454	0.996

**Table 3.** Thermodynamic parameters of the As(III) biosorption on *A. auriculiformis* leaves.

Arrhenius parameters			Thermodynamic parameters		
$E_a$ ( $\text{kJ mol}^{-1}$ )	$\Delta H$ ( $\text{kJ mol}^{-1}$ )	$\Delta S$	$\Delta G$		
			296.5 K	301 K	306 K
27.549	43.380	149.691	-983.023	-1718.29	-2405.95

found to be dependent on the initial concentration of As(III) ions. The first order and second order adsorption rate constants were calculated to be  $13.485 \times 10^{-3} \text{ min}^{-1}$  and  $5.902 \times 10^{-4} \text{ g } \mu\text{g}^{-1} \text{ min}^{-1}$  for the initial arsenic concentration of  $500 \mu\text{g L}^{-1}$ . Thus, it could be conferred that As(III) adsorption on *A. auriculiformis* leaves is kinetically controlled by the pseudo-first-order model.

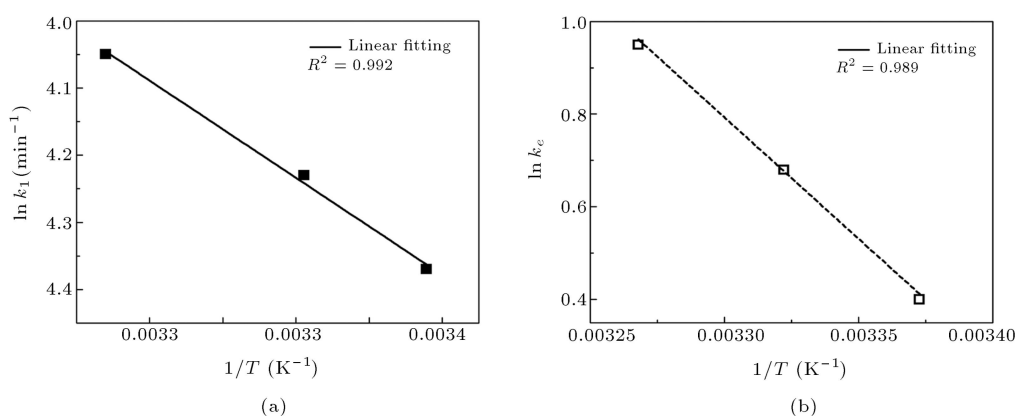
### 3.7. Thermodynamic study

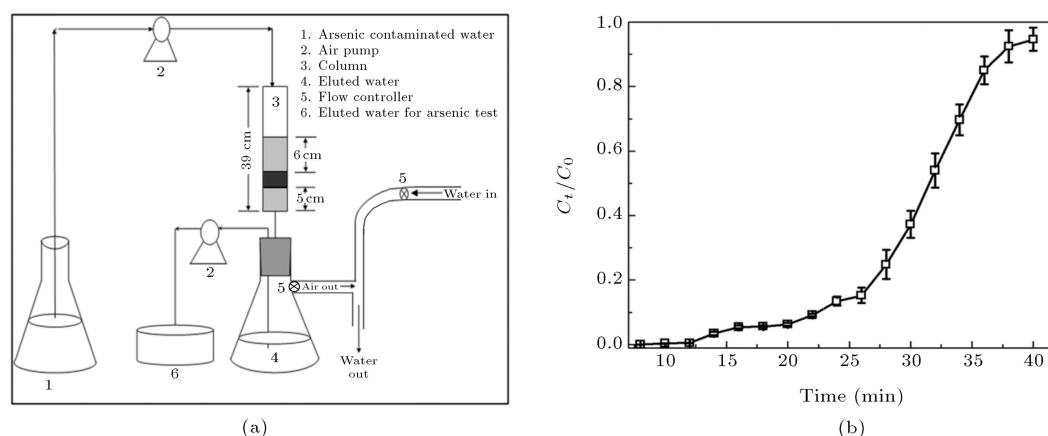
The activation energy ( $E_a$ ) was obtained from the slope of the plot between  $\ln k_1$  versus  $1/T$  (Figure 6(a)). The relatively lower activation energy of  $27.549 \text{ kJ mol}^{-1}$  is attributed to the involvement of the activated physical process for adsorption. The thermodynamic parameters of  $\Delta H$ ,  $\Delta S$  were also calculated from linear regression, according to Eq. (9). The van't Hoff plot is shown in Figure 6(b) and the obtained parameters are

listed in Table 3. The  $\Delta H$  was observed to be  $43.380 \text{ kJ mol}^{-1}$ , which implies the endothermic nature of As(III) adsorption on *A. auriculiformis* leaves. The Gibbs free energy change ( $\Delta G$ ) was calculated according to Eq. (8), which indicates the spontaneous nature of the sorption process [26]. In addition, the positive value of  $\Delta S$  suggests an increase in randomness at the solid/liquid interface during biosorption of As(III) ions on ALP.

### 3.8. Small Scale Column Tests (SSCT)

To investigate the removal efficiency of arsenite by ALP, Small Scale Column Tests (SSCT) were executed, which consist of a glass column with 3.6 cm inner diameter loaded with 10 g of biosorbent and sand as a supporting layer. To eliminate the supporting material contribution for As(III) removal, a blank test was performed. The assembly used for the purpose of SSCT

**Figure 6.** (a) Arrhenius and (b) van't Hoff plot of As(III) biosorption at different temperatures (initial concentration:  $500 \mu\text{g L}^{-1}$ ; initial pH: 6.0; biosorbent amount:  $15.0 \text{ g L}^{-1}$ ).



**Figure 7.** Schematic illustration of Small Scale Column Test (SSCT) assembly and (b) experimental breakthrough curve for As(III) removal on *A. auriculiformis* leaves bed.

is shown in Figure 7(a). An arsenic solution possessing a concentration of  $500 \mu\text{g L}^{-1}$  was passed through a down flow column at a flow rate of  $20 \text{ mL min}^{-1}$ . The pH of the influent water was 6.0. The effluents were analyzed for As(III) concentration at different time intervals [11]. The breakthrough curve for As(III) from the column loaded with *A. auriculiformis* leaves is shown in Figure 7(b). The plot indicates that an arsenic concentration below the WHO standard ( $10 \mu\text{g L}^{-1}$ ) was found in the effluent up to 14 min of continuous flow, whereas the curve broke down after 22 min of continuous flow, according to the Bangladesh standard ( $50 \mu\text{g L}^{-1}$ ). Thus, the SSCT shows the mini scale applicability of the *A. auriculiformis* leaves packed column for removing As(III) from an aqueous solution.

### 3.9. Comparison with other biosorbents

The comparative As(III) uptake capacity of *A. auriculiformis* leaves with other biosorbents are illustrated in Table 4. It was observed that the As(III) remediation efficiency by ALP is moderate in nature, under experimental conditions, compared to other literature values. It is also worthwhile mentioning that

the absolute value of arsenite uptake from aqueous solution is somewhat lower than that of arsenate [27]. The reported methods in Table 4 adopted some sophisticated processes, such as subculture and incubation under sterile conditions and high temperature pyrolysis ( $550^\circ\text{C}$ ) under a helium atmosphere, which need expert handling for proper utilization [32,33]. On the other hand, our proposed method is cheap and user friendly, and is easily available in a laboratory as one of the cheapest methods. Therefore, it could be concluded that this study shows the implications of using a low cost biosorbent to mitigate arsenic from aqueous solutions.

## 4. Conclusions

*A. auriculiformis* leaf powder was investigated for As(III) mitigation from aqueous solution containing arsenic concentrations of 100 to  $500 \mu\text{g L}^{-1}$ . The adsorption characteristics were thoroughly studied by Langmuir and Freundlich isotherms. The biosorption was observed to be a combination of homogeneous and heterogeneous processes. Adsorption kinetics

**Table 4.** Comparison of adsorption capacity ( $Q$ ,  $\mu\text{g g}^{-1}$ ) of various biosorbents to uptake As(III) from aqueous solution.

Sl No.	Biosorbents	Uptake capacity ( $\mu\text{g g}^{-1}$ )	pH	Reference
1	Human hair	10.00	7.0	[28]
2	Atlantic Cod fish scale	26.67	4.0	[29]
3	Coconut charcoal	38.00	5.0	[30]
5	Rice waste	41.00	6.8	[31]
6	Saccharomyces cerevisiae	54.132	5.0	[32]
7	Pyrolysed sewage sludge	71.00	3.0-3.5	[33]
8	Rice polish	138.88	7.0	[29]
9	<i>A. auriculiformis</i> leaves	41.410	6.0	Present study



were better described by a pseudo-first-order kinetic model, compared to a pseudo-second-order model. The endothermic and spontaneous nature of adsorption was confirmed by thermodynamic study. A Small Scale Column Test (SSCT) also reveals the feasibility of using this biosorbent under real conditions. This paper demonstrates use of an easily accessible biosorbent, which is economical, and effective, and could be an alternative to more costly adsorbents without any adverse effects on the human body.

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## References

- Mandal, B.K. and Suzuki, K.T. "Arsenic round the world: A review", *Talanta*, **58**(1), pp. 201-235 (2002).
- Ng, J.C. "Environmental contamination of arsenic and its toxicological impact on humans", *Environ. Chem.*, **2**(3), pp. 146-160 (2005).
- Choong, T.S.Y., Chuah, T.G., Robiah, Y., Gregory Koay, F.L. and Azni, I. "Arsenic toxicity, health hazards and removal techniques from water: An overview", *Desalination*, **217**(1-3), pp. 139-166 (2007).
- Bissen, M. and Frimmel, F.H. "Arsenic ? a review. Part I: Occurrence, toxicity, speciation, mobility", *Acta Hydrochim. Hydrobiol.*, **31**(1), pp. 9-18 (2003).
- Bissen, M. and Frimmel, F.H. "Arsenic ? A review. Part II: Oxidation of arsenic and its removal in water treatment", *Acta Hydrochim. Hydrobiol.*, **31**(2), pp. 97-107 (2003).
- Chowdhury, U.K., Biswas, B.K., Chowdhury, T.R., Samanta, G., Mandal, B.K., Basu, G.C. et al. "Groundwater arsenic contamination in Bangladesh and west Bengal, India", *Environ. Health Perspect.*, **108**(5), pp. 393-397 (2000).
- Rahman, M.S., Molla, A.H., Saha, N. and Rahman, A. "Study on heavy metals levels and its risk assessment in some edible fishes from Bangshi River, Savar, Dhaka, Bangladesh", *Food Chem.*, **134**(4), pp. 1847-1854 (2012).
- Ng, J.C., Wang, J. and Shraim, A. "A global health problem caused by arsenic from natural sources", *Chemosphere*, **52**(9), pp. 1353-1359 (2003).
- Hamdaoui, O. and Chiha, M. "Removal of methylene blue from aqueous solutions by wheat bran", *Acta Chim. Slov.*, **54**(2), pp. 407-418 (2007).
- Zhang, Q.L., Lin, Y.C., Chen, X. and Gao, N.Y. "A method for preparing ferric activated carbon composites adsorbents to remove arsenic from drinking water", *J. Hazard. Mater.*, **148**(3), pp. 671-678 (2007).
- Rahaman, M.S., Basu, A. and Islam, M.R. "The removal of As(III) and As(V) from aqueous solutions by waste materials", *Bioresour. Technol.*, **99**(8), pp. 2815-2823 (2008).
- Boddu, V.M., Abburi, K., Talbott, J.L., Smith, E.D. and Haasch, R. "Removal of arsenic (III) and arsenic (V) from aqueous medium using chitosan-coated biosorbent", *Water Res.*, **42**(3), pp. 633-642 (2008).
- Karnitz, Jr. O., Gurgel, L.V.A., de Melo, J.C.P., Botaro, V.R., Melo, T.M.S., de Freitas Gil, R.P. et al. "Adsorption of heavy metal ion from aqueous single metal solution by chemically modified sugarcane bagasse", *Bioresour. Technol.*, **98**(6), pp. 1291-1297 (2007).
- Islam, M.A., Khan, M.M.R. and Mozumder, M.S.I. "Adsorption equilibrium and adsorption kinetics: A unified approach", *Chem. Eng. Technol.*, **27**(10), pp. 1095-1098 (2004).
- Al-Mamun, M., Yousuf, M.A. and Subhan, M.A. "Efficiency of some bio-adsorbents for mitigation of arsenic from drinking water", *J. Bangladesh Chem. Soc.*, **22**(1), pp. 72-76 (2009).
- Islam, M.J., Hossain, M.R., Yousuf, A. and Subhan, M.A. "Removal of arsenic from drinking water using bio-adsorbent", *Proc. Pakistan Acad. Sci.*, **44**(3), pp. 157-164 (2007).
- Kundu, S. and Gupta, A.K. "Analysis and modeling of fixed bed column operations on As(V) removal by adsorption onto iron oxide-coated cement (IOCC)", *J. Colloid Interface Sci.*, **290**(1), pp. 52-60 (2005).
- Christian, G.D., *Analytical Chemistry*, J. Wiley & Sons, 4 th Edn., p. 439, New york, USA (1986).
- Gundogdu, A., Ozdes, D., Duran, C., Bulut, V.N., Soylak, M. and Senturk, H.B. "Biosorption of Pb(II) ions from aqueous solution by pine bark (*Pinus brutia* Ten.)", *Chem. Eng. J.*, **153**(1-3), pp. 62-69 (2009).
- Baig, J.A., Kazi, T.G., Shah, A.Q., Kandhro, G.A., Afridi, H.I., Khan, S. et al. "Biosorption studies on powder of stem of *Acacia nilotica*: Removal of arsenic from surface water", *J. Hazard. Mater.*, **178**(1-3), pp. 941-948 (2010).
- Pandey, P.K., Choubey, S., Verma, Y., Pandey, M. and Chandrashekhar, K. "Biosorptive removal of arsenic from drinking water", *Bioresour. Technol.*, **100**(2), pp. 634-637 (2009).
- Fan, T., Liu, Y., Feng, B., Zeng, G., Yang, C., Zhou, M. et al. "Biosorption of cadmium(II), zinc(II) and lead(II) by *Penicillium simplicissimum*: Isotherms, kinetics and thermodynamics", *J. Hazard. Mater.*, **160**(2-3), pp. 655-661 (2008).
- Mohan, D. and Pittman, Jr. C.U. "Arsenic removal from water/wastewater using adsorbents-A critical review", *J. Hazard. Mater.*, **142**(1-2), pp. 1-53 (2007).

24. Shafique, U., Ijaz, A., Salman, M., Zaman, Wu., Jamil, N., Rehman, R. et al. "Removal of arsenic from water using pine leaves", *J. Taiwan Inst. Chem. Eng.*, **43**(2), pp. 256-263 (2012).
25. Eugenia, R., Pilar, Rg., Roberto, H., Manuel, E. and Sastre, de Vicente. "Adsorption of methylene blue on chemically modified algal biomass: Equilibrium, dynamic, and surface data", *J. Chem. Eng. Data*, **55**(12), p. 5707 (2010).
26. Urbano, B.F., Rivas, B.L., Martinez, F. and Alexandratos, S.D. "Equilibrium and kinetic study of arsenic sorption by water-insoluble nanocomposite resin of poly[N-(4-vinylbenzyl)-N-methyl-D-glucamine]-montmorillonite", *Chem. Eng. J.*, **193-194**, pp. 21-30 (2012).
27. Leist, M., Casey, R.J. and Caridi, D. "The management of arsenic wastes: Problems and prospects", *J. Hazard. Mater.*, **76**(1), pp. 125-138 (2000).
28. Wasiuddin, N.M., Tango, M. and Islam, M.R. "A novel method for arsenic removal at low concentrations", *Energy Sources*, **24**(11), pp. 1031-1041 (2002).
29. Ranjan, D., Talat, M. and Hasan, S.H. "Biosorption of arsenic from aqueous solution using agricultural residue 'rice polish' ", *J. Hazard. Mater.*, **166**(2-3), pp. 1050-1059 (2009).
30. Wu, Y., Wen, Y., Zhou, J., Cao, J., Jin, Y. and Wu, Y. "Comparative and competitive adsorption of Cr(VI), As(III), and Ni(II) onto coconut charcoal", *Environ. Sci. Pollut. Res.*, **7**, pp. 1-10 (2012).
31. Hasan, S.H., Ranjan, D. and Talat, M. "Rice Polish for the removal of arsenic from aqueous solution: Optimization of process variables", *Ind. Eng. Chem. Res.*, **48**, pp. 4194-4201 (2009).
32. Wu, Y., Wen, Y., Zhou, J., Dai, Q. and Wu, Y. "The characteristics of waste *Saccharomyces cerevisiae* biosorption of arsenic(III)", *Environ. Sci. Pollut. Res.*, **19**(8), pp. 3371-3379 (2012).
33. Tavares, D., Lopes, C., Coelho, J., Sánchez, M., Garcia, A., Duarte, A. et al. "Removal of arsenic from aqueous solutions by sorption onto sewage sludge-based sorbent", *Water, Air & Soil Pollution*, **223**(5), pp. 11-21 (2012).

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