

## Biosorptive Removal of Arsenate by *Ficus benghalensis* Stem Powder from Aqueous Medium

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### ABSTRACT

The adsorption characteristics of As(V) on stem powder of *Ficus benghalensis*, a low-cost natural biosorbent, were studied through batch mode of experimental investigation, resulting into reasonably remarkable As(V) removal efficiency over a wide range of pH (3.0–11.0). The kinetics studies evidenced that the removal of As(V) by above-mentioned biosorbent which is favored by pseudo-first-order kinetics. The equilibrium data of the adsorption were modeled using Langmuir, Freundlich, Temkin, and DR isotherm. The adsorption isotherm was well described by Freundlich isotherm model, with maximum correlation coefficient ( $R^2 = 0.999$ ), adsorption intensity ( $n = 1.920$ ), and adsorption capacity ( $K_F = 1.303$ ). Thermodynamic parameters such as the positive value of  $\Delta H^\circ$ ,  $\Delta S^\circ$ , and negative results of  $\Delta G^\circ$  indicated that adsorption process is endothermic, increased randomness, and spontaneous in nature, respectively. The presence of interfering ions such as anion  $F^-$ ,  $Cl^-$ ,  $NO_3^-$ , and  $SO_4^{2-}$  significantly reduces the As(V) removal efficiency of the biosorbent while cations such as Fe(III), Cu(II), Ni(II), Zn(II), Pb(II),  $Ca^{2+}$ , and  $K^+$  increases the adsorption efficiency. On the other hand, desorption studies revealed that As(V) can be easily desorbed by (0.1–0.01 M) HCl and  $HNO_3$  and such biosorbent can be reused.

**Key words:** Arsenic, Biosorbent, Adsorption isotherm, Stem powder of *Ficus benghalensis*, Desorption.

### 1. INTRODUCTION

The presence of toxic metals in aqueous system is hazardous to living organism including human being due to bio-accumulation through the food chain which is perpetual in nature. Among all toxic metals, arsenic is supposed to be very toxic due to their adverse effect on human health. Arsenic is widely distributed in the environment from natural as well as anthropogenic sources [1,2]. In water, arsenic exists in both the organic and inorganic form. Inorganic arsenic in aqueous medium occurs in number of forms such as As(0) metalloid arsenic, As(III) arsenite ( $AsO_3^{3-}$ ), and As(V) arsenate but only two oxidation states As(III) arsenite and As(V) arsenate are predominate. It is also reported that arsenite is more toxic than arsenate and other organic arsenical compound. Arsenate is highly prevalent in oxidizing environment (surface water) while arsenite is abundantly present in groundwater (anaerobic conditions) [3,4]. Actual oxidation states of arsenic depend on the aerobic or anaerobic environment of the water system and it may differ from place to place. Consumption of arsenic contaminated water may cause liver, skin, gastrointestinal, and nerve tissue injuries. Thus, finding out a methodology for decontamination of both the state of arsenic from water is a great challenge of world scientific communities.

To remove the arsenite from aqueous medium is usually a difficult task in compare to arsenate because the predominant arsenite species is neutral while at the same pH range (4–10), arsenate species is negatively charged [5]. Sometimes pre-oxidation steps are followed to oxidize arsenite to arsenate to remove arsenite. There are number of methodologies which were used to remove arsenic from aqueous system. The selection of treatment methodologies will depend on the arsenic concentration level in the water and other physicochemical properties of water as well as economic conditions. Arsenic cannot be

destroyed; it only can be transformed from one form to another form [6]. Inorganic form of arsenic, that is, arsenite and arsenate is generally present in natural water whereas organic form mainly occurs in saline water and biological system [7]. An extensive research has been done for removing excess arsenic from water which includes coagulation, followed by lime softening, precipitation, membrane separation, ion exchange, adsorption, etc. However, the aforementioned technique being safe for handling, effective to filtrate and separate the arsenic contaminated sludge but it is not cost-effective.

To overcome such problems, huge amount of work has been done on arsenic removal through adsorption process due to being cost-effective and simple to operate. So far, several adsorbents either from natural or synthetic sources have been used to remove arsenic from aqueous medium. These include biomaterial such as Pod of green Peas [8] *Portulaca oleracea* for As(III) [9], orange waste both for As(III) and As(V) [10], Cupressus female Cone to remove As(III) [11], Garcinia cambogia for As(III) [12], Cellulose loaded iron oxyhydroxide [13], modified and unmodified coconut fiber for As(III) [14], Banana peel [15] to remove As(III), chemically modified sawdust of spruce [16], orange peel waste [17], and hydrated ferric oxide treated

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sugarcane bagasse [18]. As it is convenient to remove the adsorbent from the aqueous system after treatment, adsorption methodology is generally considered as promising method. The cost-effectiveness and removal efficiency of the adsorbent of both the states of arsenic are a great challenge in the context of present day scenario.

Keeping this in mind, the current study was focused on the characterization and biosorption studies of easily and economically available native biosorbent stem powder of *Ficus benghalensis* (FBH), family Moraceae, commonly known as the Indian banyan, a tree which is native to the Indian subcontinent. The plant of this family having significant medicinal value includes anti-inflammatory, antitumor, anti-diabetic, and antipyretic [19]. The phyto-chemical constituents of FBH are rutin, friedelin, lupeol, and bergapten conforming the presence of functional group OH, C=C, acetone, and ethereal -O-CH<sub>3</sub>, respectively, which is further conformed by Fourier-transform infrared (FTIR) spectra. Hence, the present study was planned to explore an additional properties to decontaminate arsenic from aqueous medium.

## 2. MATERIALS AND METHODS

### 2.1. Preparation of Biosorbent

The stem powder of FBH which is cheap and easily available was collected in the form of waste materials from saw mill (near B.I.T More, Ranchi Jharkhand, India). It was washed with distilled water several times to remove color, dust, and other adhering impurities. After washing, it was dried in an oven at 80°C overnight and sieved out a particular grain size (2.80-1.40 mm). The obtained dried biomass was stored in airtight plastic bottle for future use without any chemical treatment.

### 2.2. Preparation of Synthetic Test Solution

As(V) stock solution (1000 ppm) was prepared by dissolving 4.1644 g of sodium arsenate (Na<sub>2</sub>HAsO<sub>4</sub>·7H<sub>2</sub>O, Sigma-Aldrich) in 1000 mL of ultra-pure water (UPW, Millipore, 18 Ω). Working stock solutions were prepared by diluting the stock solution at the time of requirements by proper dilution.

### 2.3. Batch Experiment Study of As(V) Removal

Biosorbent prepared from stem powder of (FBH) was studied to evaluate the potential to remove As(V) from the arsenic test solution of different concentrations. The experiment was done through batch procedure. 100 ml of As(V) test solution (from 0.1 to 0.5 mgL<sup>-1</sup>) concentration was taken into different Erlenmeyer flask and varying amount (1.0–5.0 g) of biosorbent (FBH) was added, the temperature (10–50°C) and different pH range (3.0–11.0) were maintained using NaOH or HCl. The Flask was shaken for 40 min using horizontal rotary shaker (speed 150 rpm.), until to attain equilibrium. Just after this, the biomass (FBH) was removed by filtration (using Whatman filter paper having pore size 0.45 μm). The resulting solution was analyzed using (Inductively coupled plasma optical emission spectroscopy [ICP-OES]) for As(V).

The removal percentage of arsenic (*R*%) and the amount of arsenic adsorbed per unit weight of adsorbent (mg/g) at time (*t*<sub>*i*</sub>) and at equilibrium (*q*<sub>*e*</sub>) were calculated from the following equation:

$$R\% = \frac{(C_0 - C_e)}{C_0} \times 100 \quad (1)$$

$$q_t = \frac{(C_0 - C_t)}{m} \quad (2)$$

$$q_e = \frac{(C_0 - C_e)}{m} \times V \quad (3)$$

where *C*<sub>0</sub>, *C*<sub>*e*</sub>, and *C*<sub>*t*</sub> (mgL<sup>-1</sup>) are the arsenic concentrations in solution before adsorption, at equilibrium and at time “*t*,” respectively. *V* is volume of solution in liter and *m* is the mass of adsorbent (g) used [20-22]. Each experiment was conducted twice and the results were reported using the mean value.

## 2.4. Characterization and Instrumentation

### 2.4.1. Elemental analysis

The elemental analysis of stem powder of FBH was undertaken with an Elemental Analyzer (Make-M/s Elementar, Germany; Model-Vario EL III). The estimation of five elements, that is, carbon, hydrogen, nitrogen, sulfur, and oxygen was taken.

### 2.4.2. FTIR spectroscopy

The FTIR spectra of stem powder of FBH before use and after use in biosorption studies of As(V) (Figure 1), respectively, were recorded in solid state, by KBr pellet method using a FTIR spectrophotometer (Model IR-PreStige 21, Shimadzu Corporation, Japan) between 4000 and 500 cm<sup>-1</sup>.

### 2.4.3. Scanning electron microscopy (SEM) coupled with EDS

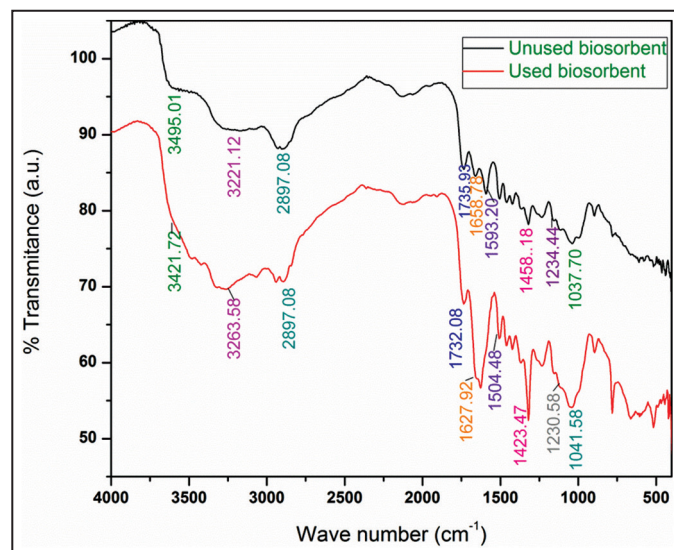
Surface morphology and element distribution of stem powder of FBH, before and after use (Figure 2), was analyzed by SEM in powdered form (Model: JSM-6390LV, Jeol, Japan).

## 3. RESULTS AND DISCUSSION

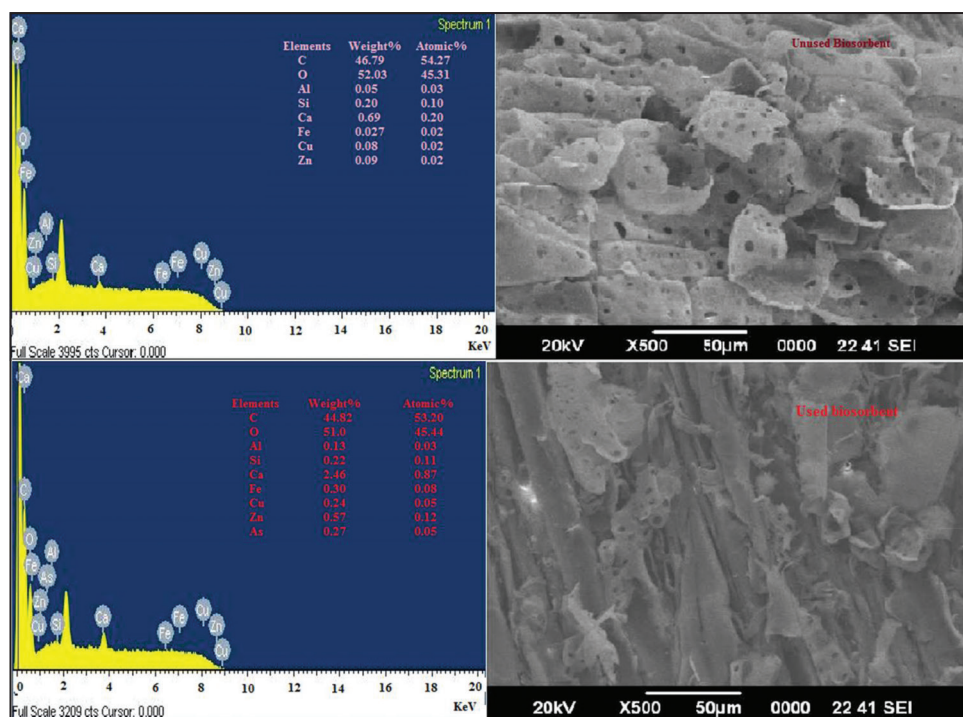
### 3.1. Characterization of Biosorbent

#### 3.1.1. FTIR spectroscopy

FTIR spectrometer was performed (wave number 4000–500 cm<sup>-1</sup>) to analyze the FBH sample before and after biosorption studies. The absorption peak at 3495.01 cm<sup>-1</sup> due to presence of both free -OH and hydrogen bounded groups. The shoulder peak observed at 2897.08 indicated the presence of C-H stretch of alkane. The peak found at 1735.93 cm<sup>-1</sup> revealed the presence of carbonyl stretch of unionized carboxylate. The adsorption peak at 1658.78 cm<sup>-1</sup> shows presence of C=O stretch. The peak at 1593.20 cm<sup>-1</sup> indicates the presence of secondary amino group whereas the absorbance peak at 1458.18 and 1234.44 cm<sup>-1</sup> may be to symmetric bending of CH<sub>3</sub> and -SO<sub>3</sub> stretching, respectively [23]. The presence of such functional groups may get a positive charge when protonated and may electrostatically interacts with negatively charged metal ions [24]. The interaction of



**Figure 1:** Fourier-transform infrared (spectra of unused and used biosorbent stem powder of *Ficus benghalensis*).



**Figure 2:** Scanning electron micrograph (SEM) and corresponding EDS of unused and used biosorbent (stem powder of *Ficus benghalensis* [FBH]) showing the surface morphology of As(V) adsorbed FBH.

As(V) ions with such function groups confirmed by the EDS analysis of biosorbent after biosorption studies by showing the changes of absorption peak values of respective functional groups.

### 3.1.2. Scanning electron micrograph and EDS

The microscopic image of stem powder of FBH before and after biosorption studies obtained from SEM clearly depicted the surface morphology and internal architecture of biosorbent Figure 2. From these micrographic images, it is clear that biosorbent (FBH) has considerable number of pores where there is maximum possibility for metal ions to be adsorbed and trapped. The surface modification of biosorbent after used corresponds to the chemical and physical interaction of As(V) ions with biosorbent surface. The corresponding EDS spectrum is also placed on side by side of SEM image which further confirmed the sorption of As(V) by showing extra peak of arsenic other than prime elements.

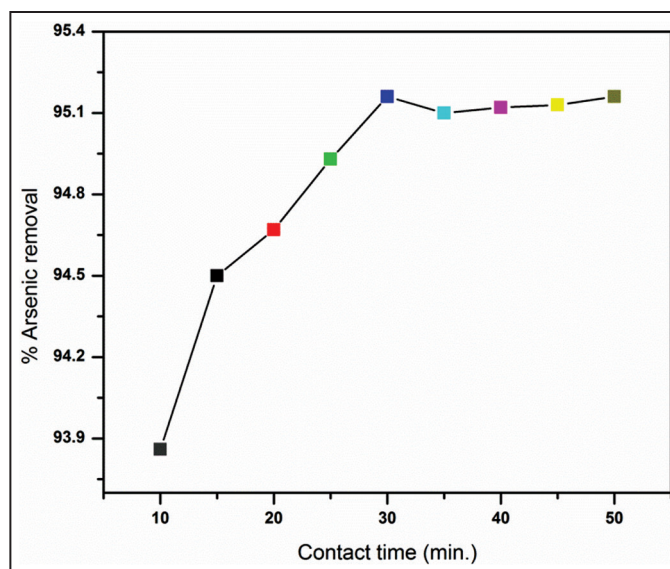
## 3.2. Sorption Studies

### 3.2.1. Effect of contact time

The effect of contact time on As(V) removal from aqueous medium was studied at initial As(V) concentration  $0.1 \text{ mgL}^{-1}$ , biosorbent dose 3.5 g for 100 mL sample water, temperature  $40^\circ\text{C}$ , pH = 6.3, and agitation rate 120 rpm. The results are represented in Figure 3 which stipulated that the adsorption As(V) initially increases with increasing the contact time. A maximum adsorption of As(V) was achieved at 30 min, after which not any significant change of As(V) removal efficiency was observed. This might be attributed to the fact that initially all the adsorption site of the biosorbent is available for As(V) and solute concentration gradient also high. Once the saturation of adsorption site was achieved, the uptake efficiency of As(V) remained almost constant with increase of contact time which can be due to the presence of less number of adsorption site and as well as decrease of As(V) concentration gradient.

#### 3.2.1.1. Sorption kinetics models

To interpret the experimental data, kinetic experiments were carried out and data were fitted into the pseudo-1<sup>st</sup>-order, pseudo-2<sup>nd</sup>-order,



**Figure 3:** Effect of contact time on As(V) removal by stem powder of *Ficus benghalensis*, biosorbent dose 3.5 g for 100 mL test sample; pH of solution 6.0; As(V) concentration  $0.1 \text{ mgL}^{-1}$ ; temperature  $40^\circ\text{C}$ .

and intra-particle diffusion model. The mathematical representations of these models are given in equation 1–3.

#### 3.2.1.2. Pseudo-first-order kinetics

The pseudo-first-order kinetics model developed for irreversible sorption onto solid/liquid phase. Lagergren pseudo-first-order rate equation is expressed as [25,26].

$$\text{Log}(q_e - q_t) = \text{Log} q_e - K_1 t \quad 4$$

Where  $q_t$  and  $q_e$  are the amount of As(V) adsorbed ( $\text{mg.g}^{-1}$ ) at time “ $t$ ” and at equilibrium, respectively,  $K_1$  ( $\text{min}^{-1}$ ) is the rate constant for

pseudo-first-order kinetics. Linear plot of  $\log(q_e - q_t)$  vs “t” (Figure 4) is presentation of pseudo-first-order kinetics with good correlation coefficient ( $R^2 = 0.982$ ) and estimated equilibrium adsorption capacity ( $q_e$ ) value is  $6.74 \times 10^{-4} \text{ mg.g}^{-1}$  and is approximately similar with experimental value  $2.27 \times 10^{-3} \text{ mg.g}^{-1}$  (Table 1). Therefore, the adsorption of As(V) onto stem powder of FBH is best described by pseudo-first-order kinetics and implies that adsorption process is controlled by mass transfer process.

3.2.1.3. Pseudo-second-order kinetics

The pseudo-second-order kinetics is based on the assumption that chemisorption is one of the factors which control the adsorption kinetics [20,27]. The equation is represented as follows:

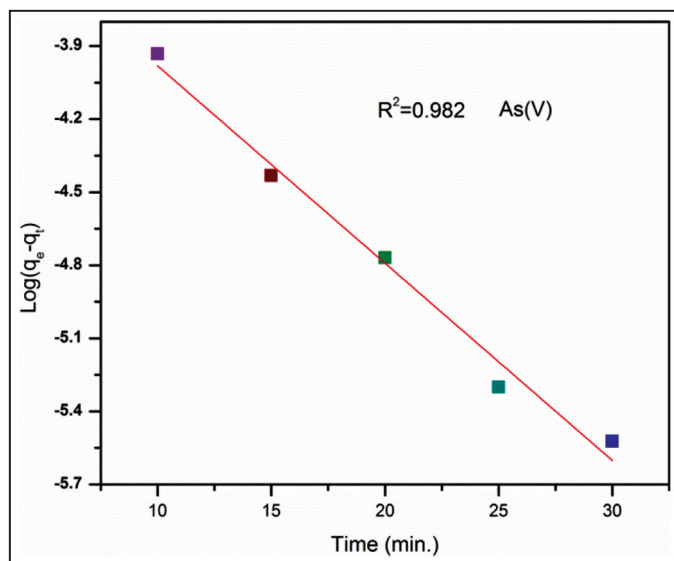
$$t/q_t = 1/K_s(q_e)^2 + t/q_e \tag{5}$$

where  $K_s$  ( $\text{g.mg}^{-1} \text{ min}^{-1}$ ) is rate constant for pseudo-second-order kinetics  $q_t$  and  $q_e$  are the amount ( $\text{mg.g}^{-1}$ ) of As(V) adsorbed at time “t” and equilibrium, respectively.

**Table 1:** Kinetic parameters for the adsorption of As(V) onto stem powder of FBH at optimized conditions of physical parameters such as As(V) ion concentration  $0.1 \text{ mgL}^{-1}$ ; temperature  $40^\circ\text{C}$ ; contact time 30 min; adsorbent dose  $3.0 \text{ g}$  for 100 mL water sample; and pH of solution 6.0.

Kinetics	Parameters	Unit	As(V)
Pseudo-first-order	$q_{e, \text{exp}}$	$\text{mg.g}^{-1}$	$2.27 \times 10^{-3}$
	$K_f$	$\text{min}^{-1}$	0.186
	$q_{e, \text{cal}}$	$\text{mg.g}^{-1}$	$6.74 \times 10^{-4}$
	$R^2$		0.982
Pseudo-second-order	$K_s$	$\text{mg.g}^{-1} \text{ min}^{-1}$	0.121
	$q_{e, \text{cal}}$	$\text{mg.g}^{-1}$	2.229
	$R^2$		0.968
Intra-particle diffusion model	$K_i$	$\text{mg.g}^{-1} \text{ min}^{-1/2}$	0.032
	$I$	$\text{mg.g}^{-1}$	2.534
	$R^2$		0.672

FBH: *Ficus benghalensis*



**Figure 4:** Linear model of pseudo-first-order reaction kinetics.

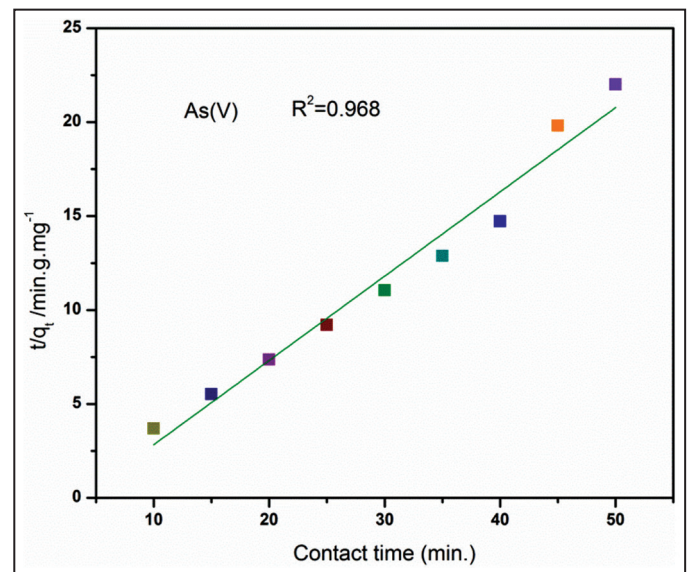
The pseudo-second-order rate constant ( $K_s$ ), calculated from the intercept of the plot of  $t/q_t$  vs “t” and  $q_e$  from slope of the plot (Figure 5). The obtained values are reported in Table 1. A comparison of experimental ( $q_{e, \text{exp}}$ ) and calculated ( $q_{e, \text{cal}}$ ) adsorption capacities values obtained from equation 1 and 2 observed that pseudo-first-order kinetics best described the adsorption kinetics than pseudo-second-order.

3.2.1.4. Intra-particle diffusion model

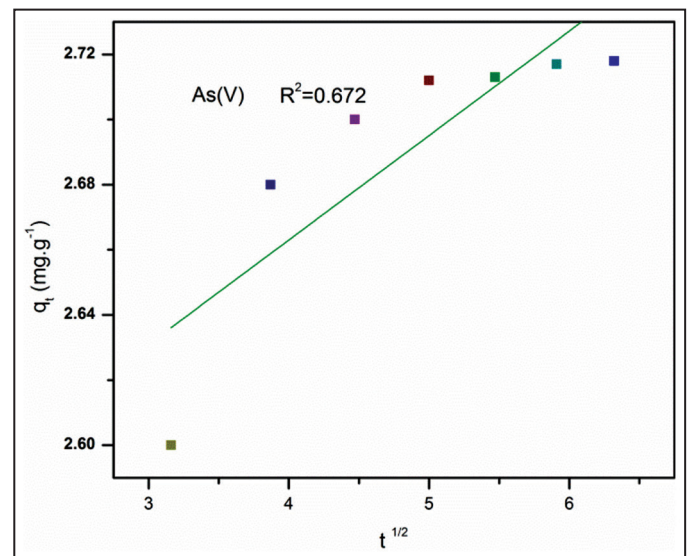
The intra-particle diffusion model based on the theory proposed by Weber and Morris [28] expressed as:

$$q_t = K_i t^{1/2} + I \tag{6}$$

where,  $q_t$  is the amount of As(V) adsorbed ( $\text{mg.g}^{-1}$ ) at any time “t” (min), I is intercept and  $K_i$  ( $\text{min}^{-1/2}$ ) is the rate constant of intra-particle diffusion model. The value of I and  $K_i$  is estimated from the intercept and slope of the plot  $q_t$  vs  $t^{1/2}$ , respectively. If intra-particle diffusion is a rate-controlling step, then plot must be linear and passing through the origin [28]. As shown in (Figure 6); however, the plot is linear



**Figure 5:** Linear model of pseudo-second-order reaction kinetics.



**Figure 6:** Linear model of intra-molecular diffusion reaction kinetics.

but not passing through the origin. This specified that the process of adsorption of As(V) onto the biosorbent surfaces of stem powder of FBH is a complex process and intra-particle diffusion was not only the rate controlling step. The estimated value of intercept (I) gives the information regarding the thickness of boundary layer, that is, resistance to the external mass transfer [29]. All the estimated values are reported in Table 1.

### 3.2.2. Variation with pH

The pH of the aqueous medium is one of the deciding factors which control the adsorption process at the water-adsorbent interfaces. In the present work, the biosorption of As(V) on stem powder of FBH was tested in the pH range (3.0–11.0) (Figure 7) at optimized conditions of experimental setup. It was found that percentage removal of As(V) initially increases with increase in pH of the medium. The maximum percentage (94.2%) of As(V) removal was observed at pH 6.3. Sodium arsenate ( $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$ ) exists as monovalent ( $\text{H}_2\text{AsO}_4^-$ ) and divalent ( $\text{HAsO}_4^{2-}$ ) anionic state at pH range (6.0–8.0), for example, slightly acidic and alkaline medium [30]. These anionic species could be adsorbed on protonated active site of the biosorbent [31].

### 3.2.3. Effect of biosorbent dose

To investigate, the optimum value of biosorbent dose on the percentage removal of As(V) was studied at optimized conditions of experimental setup. The maximum percentage As(V) removal was found 91.6% at the biosorbent (stem powder of FBH) dose 3.5 g for 100 ml of test sample. Further increase in biosorbent did not show any quantitative effect on the percentage removal of As(V). The percentage removal of As(V) was enhanced with increasing biosorbent dose, which is obvious since number of active sites increases with increase in the dose of biosorbent.

### 3.2.4. Variation with initial metal ion concentration

The effect of initial As(V) concentration on the removal process was studied within the concentration range of 0.1–0.5 ( $\text{mg}\cdot\text{L}^{-1}$ ). The other optimized experimental conditions were as follows: (i) Volume of test sample 100 ml, (ii) contact time 40 min, (iii) pH = 6.3, biosorbent dose 3.5 g, and (iv) temperature 40°C. The result showed that As(V) removal percentage was high (up to 94%) at the lower concentration (0.1  $\text{mg}\cdot\text{L}^{-1}$ ). Further increase in the concentration of As(V) shows

negative trends of removal percentage (Figure 8). This could be due to saturation of active site of the adsorbent as a result of increasing the concentration of As(V) in test sample water. For further investigation, 0.1  $\text{mg}\cdot\text{L}^{-1}$  was chosen as an optimum concentration of As(V).

#### 3.2.4.1. Langmuir isotherm

The Langmuir isotherm assumes a monolayer adsorption onto a surface having a restricted amount of adsorption sites. In this isotherm, the consistent schemes of adsorption with no transmigration of the solute taking place along the surface of the adsorbent. The straight line equation of the Langmuir isotherm can be written as:

$$1/q_e = 1/K_L q_m \cdot C_e + 1/q_m \quad 7$$

where  $q_m$  ( $\text{mg}\cdot\text{g}^{-1}$ ) and  $K_L$  ( $\text{L}\cdot\text{mg}^{-1}$ ) are rate of adsorption and the Langmuir constant concerned with adsorption capacity and rate of adsorption, respectively,  $C_e$  ( $\text{mg}\cdot\text{L}^{-1}$ ) concentration of metal ion at equilibrium and  $q_e$  ( $\text{mg}\cdot\text{g}^{-1}$ ) is the amount of metal ion adsorbed onto biosorbent.  $K_L$  and  $q_m$  were determined from slope and intercept of plot  $1/q_e$  vs  $1/C_e$ , respectively (Figure 9), and respective values are reported in Table 2.

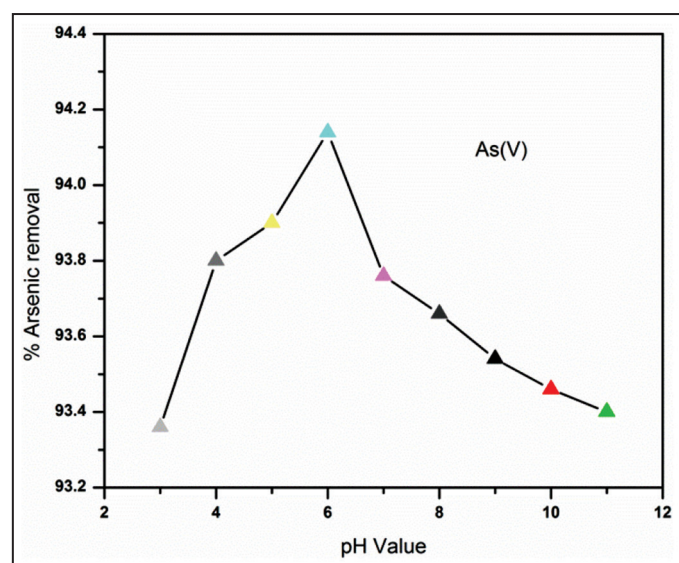
The most important characteristics of Langmuir adsorption isotherm can be expressed in term of separation factor ( $R_L$ ) a dimensionless constant, which can be determined by the using the following equation:

$$R_L = 1/1+K_L C_o \quad 8$$

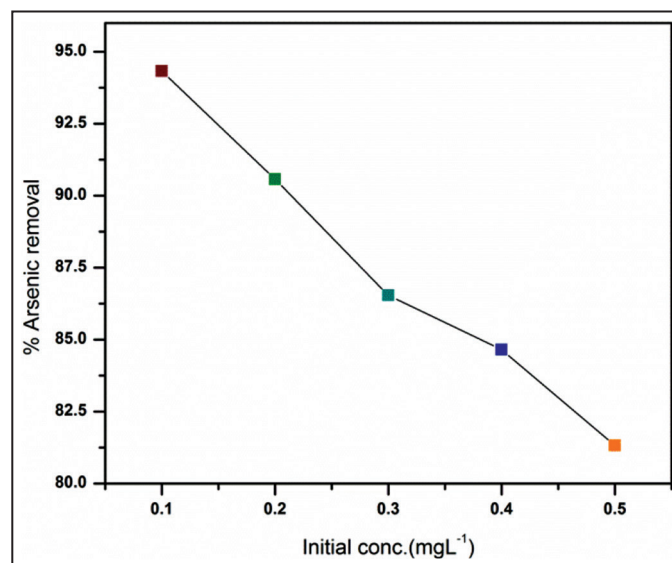
where  $K_L$  is the Langmuir adsorption constant and  $C_o$  is the initial concentration of As(V). The magnitude of  $R_L$  gives an idea regarding the nature of adsorption isotherm, if  $R_L > 1.0$  unfavorable,  $0 < R_L < 1.0$  favorable,  $R_L = 0$  for irreversible, and  $R_L = 1.0$  linear [32]. The  $R_L$  values from concentration range (0.1 to 0.5) at 40°C are reported in Table 3 and found that values lies between 0.999 and 0.997 confirmed that adsorption process is favorable.

#### 3.2.4.2. Freundlich isotherm

The Freundlich isotherm is the most commonly assumed to describe the adsorption on the surface having heterogeneous surface energy distribution. The linear forms of Freundlich isotherm can be represented as [33]:



**Figure 7:** Effect of pH on As(V) removal by stem powder of Ficus benghalensis initial As(V) concentration 0.1  $\text{mg}\cdot\text{L}^{-1}$ , adsorbent dose 3.5 g for 100 mL test sample; contact time 30 min; pH 6.0; concentration 0.1  $\text{mg}\cdot\text{L}^{-1}$ ; temperature 40°C.



**Figure 8:** Effect of initial As(V) concentration on arsenic removal capacity of stem powder of Ficus benghalensis; pH of solution 6.0; contact time 30 min; temperature 40°C; biosorbent dose 3.5 g for 100 mL test sample.

**Table 2:** Adsorption isotherm error data concerned to the biosorption of As(V) onto stem powder of FBH using six commonly used functions showing applicability of Freundlich adsorption isotherm.

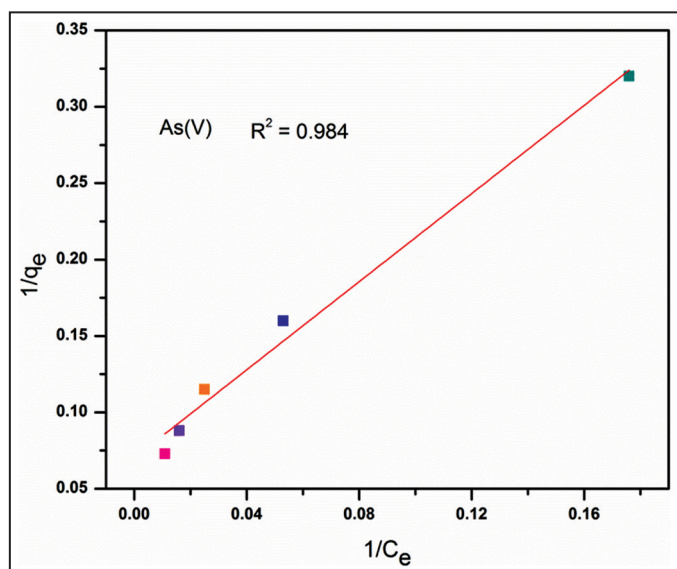
Error functions	R <sup>2</sup>	ARED	SSE	SAE	MPSED	HYBRID
As(V)						
Langmuir	0.984	8.80434	5.06851	4.1240	12.66570	14.67368
Freundlich	0.999	0.02400	0.25518	0.9290	5.84287	3.37338
Temkin	0.945	12.25214	2.78470	3.3300	35.36889	20.42024
D-R	0.734	9.95732	3.99870	4.3700	28.74432	16.59554

SSE: Sum of square of errors, MPSED: Marquardt's percent error deviation, HYBRID: Hybrid error function deviation, SAE: Sum of absolute errors, R<sup>2</sup>: Relative standard deviation, FBH: *Ficus benghalensis*

**Table 3:** Various constant values of Langmuir, Freundlich, Temkin, and D-R adsorption isotherm for the adsorption of As(V) onto stem powder of FBH at optimized conditions of physical parameters such as As(V) ion concentration 0.1 mgL<sup>-1</sup>; temperature 40°C; contact time 30 min; adsorbent dose 3.5 g for 100 mL water sample; and pH of solution 6.0.

Isotherm models	Parameters	Unit	As(V)
Langmuir isotherm model	K <sub>L</sub>	l mg <sup>-1</sup>	48.6×10 <sup>-3</sup>
	R <sub>L</sub>	(separation factor)	0.97–0.99
	q <sub>m</sub>	mg g <sup>-1</sup>	14.28
	R <sup>2</sup>		0.984
Freundlich isotherm model	K <sub>F</sub>		1.303
	n		1.920
	R <sup>2</sup>		0.999
Temkin isotherm model	A		0.344
	B <sub>1</sub>	mg g <sup>-1</sup>	3.260
	R <sup>2</sup>		0.945
D-R isotherm model	X <sub>m</sub>	g g <sup>-1</sup>	9.954
	R <sup>2</sup>		0.734
	E	kJmol <sup>-1</sup>	0.281

FBH: *Ficus benghalensis*



**Figure 9:** Langmuir isotherm model for As(V) adsorption on stem powder of *Ficus benghalensis*.

$$\text{Log } q_e = \text{Log } K_F + 1/n \text{ Log } C_e \tag{9}$$

where K<sub>F</sub> (mg.g<sup>-1</sup>) is Freundlich constants indicates the adsorption capacity and n related to adsorption intensity by which the adsorption process takes place. The value of n and K<sub>F</sub> was found out from slope and intercept of the plot Log q<sub>e</sub> against Log C<sub>e</sub> (Figure 10), respectively, and the respective values reported in Table 2. The reported values of n (1.920) much higher than unity, indicating that the biosorption process of As(V) is favorable.

3.2.4.3. Temkin isotherm

Temkin isotherm model takes into account of adsorbate-adsorbent interaction and based on assumptions that fall in the sorption heat is linear rather than logarithmic, which is applicable in Freundlich equation. The straight line form of Temkin equation is presented as [34]:

$$q_e = B \ln A + B \ln C_e \tag{10}$$

where

$$B = RT/b$$

where R is the universal gas constant (8.314 J mol<sup>-1</sup> K<sup>-1</sup>), T is absolute temperature (K), and b is the constant concerned to adsorption heat (J mg<sup>-1</sup>). A and B determined from the intercept and slope of the plot q<sub>e</sub> vs lnC<sub>e</sub> (Figure 11), respectively, and all the constant values are enlisted in Table 2.

3.2.4.4. D-R isotherm

D-R isotherm was used to estimate the porosity, apparent free energy, and the characteristics of adsorption isotherm [35]. The straight line equation of D-R isotherm expressed as:

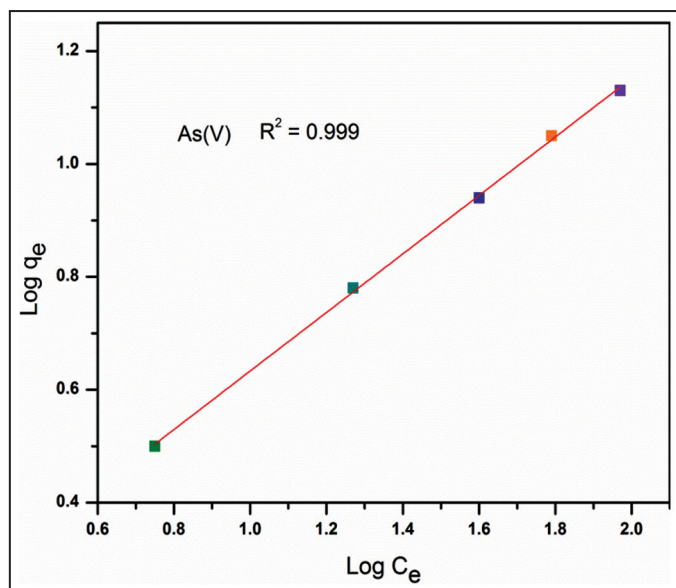
$$\ln q_e = \ln X_m - \beta \epsilon^2 \tag{11}$$

$$\epsilon = RT \ln(1 + 1/C_e) \tag{12}$$

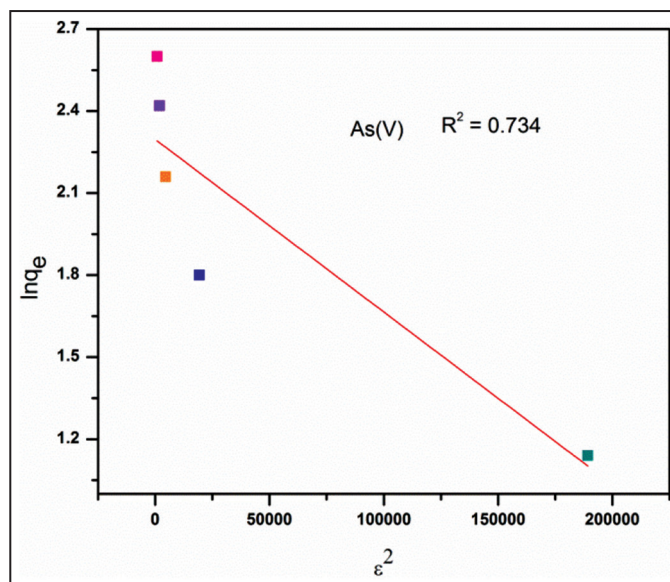
where R (8.314 × 10<sup>-3</sup> kJmol<sup>-1</sup>K<sup>-1</sup>) is universal gas constant, T is absolute temperature (K), β is D-R adsorption constant concerned with the mean free energy of adsorption (mol<sup>2</sup>k<sup>-1</sup>J<sup>-2</sup>), ε is the Polanyi potential, and X<sub>m</sub> (mg.g<sup>-1</sup>) is the theoretical saturation capacity C<sub>e</sub> is equilibrium concentration of As(V) in solution. The D-R isotherm drawn by plot lnq<sub>e</sub> versus ε<sup>2</sup> (Figure 12) and the magnitudes of X<sub>m</sub> and β were estimated from intercept and slope of the plot, respectively. The mean free energy (E), defined as free energy change when one mole of ions transferred from infinite to the surface of the biosorbent, is calculated by the using following equation:

$$E = 1/(2\beta)^{1/2} \tag{13}$$

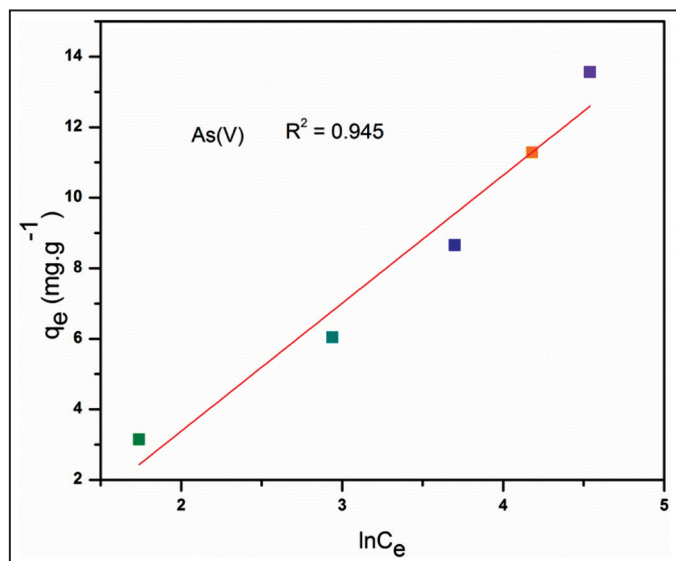
The estimated value of E is helpful to determine the type of adsorption. If the value of E lies in the range of 8<sup>-16</sup> kJmol<sup>-1</sup>, the adsorption process is considered as ion exchange [36] and if it is less than or equal to 8 kJmol<sup>-1</sup>, then process of adsorption is physical due to weak Van



**Figure 10:** Freundlich isotherm model for As(V) adsorption on stem powder of *Ficus benghalensis*.



**Figure 12:** D-R isotherm model for As(V) adsorption on stem powder of *Ficus benghalensis*.



**Figure 11:** Temkin isotherm model for As(V) adsorption on stem powder of *Ficus benghalensis*.

der Waal forces. In the present study, the estimated  $E$  value is  $2.81 \text{ kJ mol}^{-1}$  confirmed that process of adsorption is physical in nature.

### 3.2.5. Estimation of Error Using Alternative Statistical Tools

To optimize the regression analysis data using six different error functions were done, they are, the average relative errors deviation, the sum of square of errors, the Marquardt's percent error deviation, the hybrid error function deviation (HYBRID), the sum of absolute errors, and relative standard deviation ( $R^2$ ). The obtained results of all six different error functions are reported in Table 4. Thermodynamic parameters for the adsorption of As(V) onto stem powder of FBH at optimized conditions As(V) ion concentration  $0.1 \text{ mgL}^{-1}$ , temperature  $40^\circ\text{C}$ ; contact time 30 min; adsorbent dose 3.5 g for 100 mL water sample; and pH of solution 6.0.

### 3.2.6. Variation with Temperature

The effect of temperature ( $10\text{--}50^\circ\text{C}$ ) on sorption of As(V) onto natural biosorbent (stem powder of FBH) was studied under optimized

conditions of pH, biosorbent dose, contact time, and initial metal ion concentration. It has been observed that percentage arsenic removal increases with the increase in temperature and achieved maximum (89.5%) removal at  $35^\circ\text{C}$  temperature than after a steady state achieved (Figure 13). It may attribute due to enlargement of pore size and activation of sorbent surface with increase in temperature [37], may cause decrease the biosorption efficiency. Again increase in temperature, the mobility of metal ions increases and swelling effect of biosorbent reduced [37]. Thus,  $40^\circ\text{C}$  temperature was chosen as an optimum value for further investigation.

### 3.2.7. Sorption Thermodynamics

To find out the feasibility of adsorption process using the stem powder of FBH, a natural biomaterial, different thermodynamic parameters were evaluated by investigating the effect of temperature on sorption process. Three fundamental thermodynamic parameters, namely, enthalpy change ( $\Delta H^\circ$ ), free energy change ( $\Delta G^\circ$ ), and entropy change ( $\Delta S^\circ$ ) of sorption can be evaluated using the following equation [37]:

$$\Delta G^\circ = -RT \ln K_C \quad 14$$

where  $R$  is the universal gas constant ( $8.314 \text{ Jmol}^{-1}\text{K}^{-1}$ ),  $T$  is the absolute temperature (K), and  $K_D$  is distribution coefficient.

$$K_C = q_e/C_e \quad 15$$

Further, the relationship between  $K_D$  versus enthalpy change ( $\Delta H^\circ$ ) and entropy change ( $\Delta S^\circ$ ) can be represented as follows:

$$\ln K_C = \Delta S^\circ/R - \Delta H^\circ/RT \quad 16$$

The estimated values of  $\Delta H^\circ$ ,  $\Delta G^\circ$ , and  $\Delta S^\circ$ , reported in Table 5, were determined from plot  $\ln K_C$  versus  $1/T$  (Figure 14). The negative values of  $\Delta G^\circ$  at all temperature revealed the nature of sorption process as spontaneous whereas biosorptive process as feasible comparatively at a higher temperature. The positive values of  $\Delta H^\circ$  ( $1.40 \text{ kJmol}^{-1}$ ) showed nature of sorption as endothermic. Further, the positive value of  $\Delta S^\circ$  ( $22.44 \text{ Jmol}^{-1}\text{K}^{-1}$ ) reflected increasing randomness at adsorbent-solution interface at the time of fixation of the adsorbate on the active site of adsorbent.

Sticking probability ( $S^*$ ) is the function of adsorbate/adsorbent system and often depends on temperature. It is the measure of potential of

**Table 4:** Thermodynamic parameters for the adsorption of As(V) onto stem powder of FBH at optimized conditions As(V) ion concentration 0.1 mgL<sup>-1</sup>, temperature 40°C; contact time 30 min; adsorbent dose 3.5 g for 100 mL water sample and pH of solution 6.0.

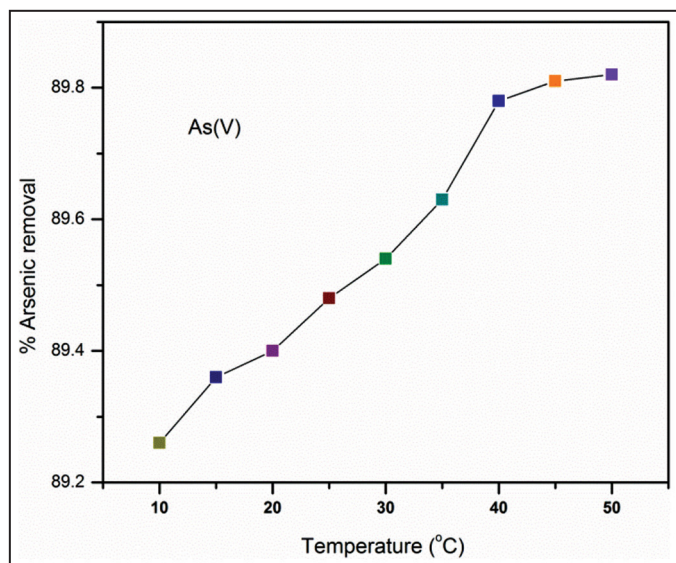
Thermodynamic parameters	E equation	P plot	Values
$\Delta G^\circ = -RT \ln K_c$	$\Delta G^\circ$ (kJ mol <sup>-1</sup> ) temperature range	283 K 293 K 303 K 313 K 323 K	-5.96 -5.19 -5.39 -5.62 -5.85
$\ln K_c = \Delta S^\circ / R - \Delta H^\circ / RT$	$\Delta H^\circ$ (kJ mol <sup>-1</sup> ) $\Delta S^\circ$ (J mol <sup>-1</sup> K <sup>-1</sup> )	lnKc Vs 1/T	-1.40 22.44
$\text{Log}(1-\theta) = \text{Log} S^* + E_a / 2.303RT$	S* Ea (kJ mol <sup>-1</sup> )	Log (1-θ) Vs 1/T	0.0637 0.540

FBH: *Ficus benghalensis*

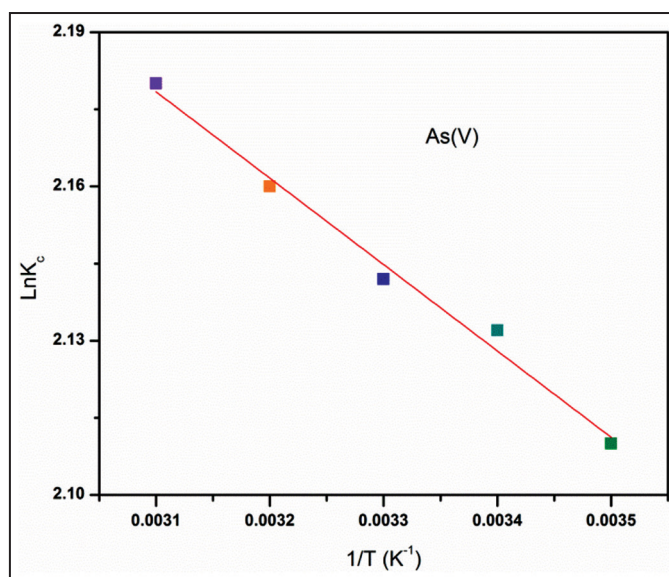
**Table 5:** Inferences of common ions on bioremediation of As(V) onto stem powder of FBH.

Anions	% Removal As(V)	Anions	% Removal As(V)
As(V)	88%	Cl <sup>-</sup>	88.4
Pb(II)	87.53	F <sup>-</sup>	77.54
Ni(II)	82.26	SO <sub>4</sub> <sup>2-</sup>	85.34
Cu(II)	88.96	NO <sub>3</sub> <sup>-</sup>	84.34
Fe(III)	89.43		
Cr(VI)	88.63		
K <sup>+</sup>	88.6		
Zn <sup>2+</sup>	89.36		
Ca <sup>2+</sup>	89.76		

FBH: *Ficus benghalensis*



**Figure 13:** Effect of temperature on As(V) removal potential of stem powder of *Ficus benghalensis*; concentration; contact time 30 min; adsorbent dose 3.5 g for 100 mL test sample; pH of solution 6.0; concentration 0.1mgL<sup>-1</sup>.



**Figure 14:** Plot of Ln Kc against 1/T for As(V) adsorption onto stem powder of *Ficus benghalensis*.

adsorbate remain on the surface of absorbent [38]. The equation is written as:

$$S^* = (1-\theta)\exp(-E_a/RT) \tag{17}$$

Rearranging equation (13) and taking log both side

$$\text{Log}(1-\theta) = \text{Log} S^* + E_a / 2.303RT \tag{18}$$

where θ is surface coverage area and E<sub>a</sub> is activation energy

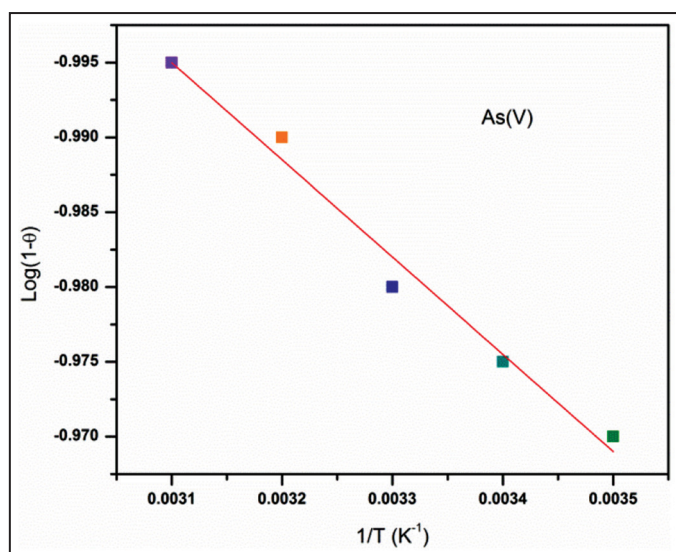
$$\theta = (1 - C_e / C_0) \tag{19}$$

The value of S\* and E<sub>a</sub> was calculated from intercept and slope of the plot Log (1-θ) versus 1/T (Figure 15), respectively. The positive values of activation energy (E<sub>a</sub>) further revealed that the adsorption process was endothermic. Furthermore, sticking probability (S\*) of biosorbent surface observed for As(V) was 0.0637 which is more than zero again referred that sorption process is physisorption.

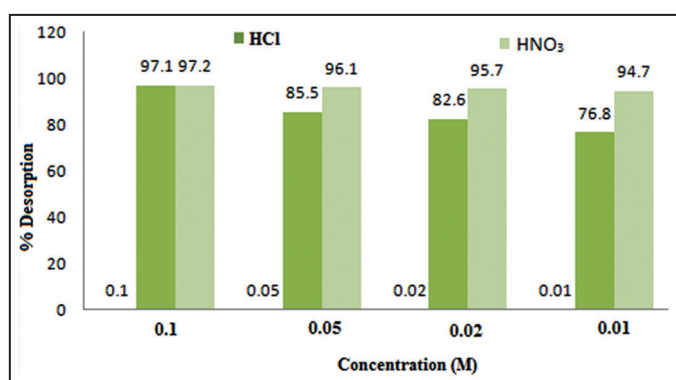
### 3.3. Common Ions Effects

Drinking water may contain a number of common ions which may interfere with As(V) for active site of sorption. The removal As(V)





**Figure 15:** Plot of  $\text{Log}(1-\theta)$  against  $1/T$  for the adsorption of As(V) onto stem powder of *Ficus benghalensis*.



**Figure 16:** Desorption of As(V) from exhausted stem powder of *Ficus benghalensis* using nitric and hydrochloric acid.

from contaminated water in the presence of common ions may affect the removal efficiency due to formation of complex or competition for common absorption site. Cations Fe(III), Cu(II), Zn(II), Cr(VI), Ca(II), and  $K^+$  increase the biosorption efficiency of As(V) due to effective electrostatic interaction between opposite charges or formation of complex, while Pb(II) and Ni(II) reduce arsenic absorption capacity of adsorbent. On the other hand, anions such as  $NO_3^-$ ,  $F^-$ ,  $Cl^-$ , and  $SO_4^{2-}$  reduce As(V) removal efficiency of stem powder of FBH, it may be explained on the basis of common ions repulsion and ionic sizes. The outcomes are in the same way with other investigations [33,39].

#### 3.4. Desorption

The desorption studies of As(V) from the loaded stem powder of FBH were conducted through batch mode of experiment. A known amount of stem powder of FBH (3.0 g), 100 mL of varying concentration ranges (0.01–0.1 M) of eluting agent (HCl and  $HNO_3$ ) separately was taken in a 250 ml conical flask and put in a horizontal shaker for 40 min at 30°C temperature. The biosorbent was separated from solution by Whatman filter paper. Then, the strength of As(V) ( $mgL^{-1}$ ) was determined in ICP-OES. From Figure 16, highest desorption 97.2% was observed by nitric acid (0.1 M).

#### 4. CONCLUSIONS

The stem powder of FBH has been found to be a potential biosorbent for As(V) removal from aqueous system under optimum conditions

of contact time 30 min. temperature 40°C, As(V) concentration 0.1  $mgL^{-1}$ , pH 6.0, and biosorbent dose 3.5 g for 100 mL test sample having removal efficiency >95%. The different kinetics study performed with the experimental data were best correlated with pseudo-first-order kinetics than that of pseudo-second-order kinetics (0.081, 0.042, and 0.982 value of  $K_f$ ,  $q_{e,cal}$ , and  $R^2$ , respectively). The experimental data also were evaluated by Langmuir, Freundlich, Temkin, and D-R isotherm model; the results indicated that it is best fitted with Freundlich isotherm which is confirmed by optimization of regression analysis by six different error function having maximum  $R^2$  value and minimum error functions values. Negative value of standard Gibbs free energy ( $\Delta G^\circ$ ) indicates the adsorption is spontaneous. The adsorption efficiency ( $R_L$ ) values were found between 0 and 1, which confirms that biosorption of As(V) is favorable in nature. Based on all results, it can be concluded that stem powder of FBH is an efficient biomass and alternative material for As(V) removal from water due to easy handling, indigenous, economical, having high adsorption capacity, and eco-friendly.

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