

AQUEOUS REMOVAL OF ARSENIC (III) USING ACID TREATED DEVDARU (POLYALTHIA LONGIFOLIA) LEAF POWDER

Moonmoon Choudhary* and Krishna G. Bhattacharyya

Department of Chemistry, Gauhati University, Guwahati 781014, Assam, India

*For correspondence. (moonschem@gmail.com)

Abstract: The present study investigates the use of acid treated devdaru leaf powder (*Polyalthia Longifolia*) for adsorptive removal of arsenite from arsenite spiked distilled water. Adsorptions were studied at temperature 303K by batch processes. Rapid equilibrium was reached within 90 mins. The pseudo-second-order kinetic model was found to best correlate to the experimental data. Adsorption equilibrium data were well described by Langmuir, Freundlich and Temkin models. The Langmuir adsorption capacity was found to be 1.51 mg/g. This work can be used to remove As(III) from drinking water by using low cost adsorbent.

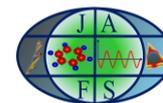
Keywords: As(III) removal; devdaru leaf powder; drinking water; isotherm; kinetics

1. Introduction:

Arsenic the 20th most abundant element in the earth's crust, is one of the most toxic pollutants introduced into the environment by natural weathering reactions, biological activity, geochemical reactions, volcanic emissions and other anthropogenic activities like industrial waste discharges, agricultural use of arsenic pesticides, discharges from coal fired thermal power plants, herbicides, fertilizers, petroleum refining and ceramic industries, etc[1,2,3]. The toxicity of arsenic greatly depends on its form (organic or inorganic) and oxidation number. Organic arsenic is less toxic than inorganic since organic arsenic species are readily eliminated by the body. The inorganic arsenic in natural water exists as trivalent arsenite and pentavalent arsenate forms, of which As(III) regardless of pH, being more soluble and mobile is more toxic than As(V)[4,5,6]. Arsenite (as H_3AsO_3^0 and H_2AsO_3^-) predominantly occurs in moderately reducing anaerobic environments such as groundwater while arsenate (as H_2AsO_4^- and HAsO_4^{2-}) in oxygen rich aerobic environments[7].

Arsenic generally increases the risk of skin, lung, bladder and kidney cancer as well as pigmentation changes, skin thickening (hyperkeratosis) neurological disorders, muscular weakness, loss of appetite, and nausea[8,9]. The toxicity of arsenic and its compounds is well established and is a well known carcinogen and hence groundwater pollution due to arsenic is a global problem in concern of health[3,10,11]. Arsenic pollution has been reported recently in the USA, China, Chile, Bangladesh, Taiwan, Mexico, Argentina, Poland, Canada, Hungary, New Zealand, Japan and India. The largest population at risk among the 21 countries with known groundwater arsenic contamination is in Bangladesh, followed by West Bengal in India[12]. Due to the adverse health effect of arsenic, the maximum allowed concentration of arsenic, according to WHO, in drinking water is 10 $\mu\text{g}/\text{L}$ [13].

Methods of arsenic removal from water include solvent extraction, chemical precipitation, ferrihydrite precipitation, iron coprecipitation, ion exchange, and reverse osmosis. These methods require highly operational, expensive, produce large amount of toxic sludge and involve complicated procedure[14,15,16]. Comparatively adsorption process has been found superior and effective for water decontamination process because of cheap and clean, simplicity of design, flexibility, ease of operation, insensitive to toxic pollutants and no formation of toxic substances[17]. Most of the adsorbents used for the removal of arsenic, however, entail several problems in terms of efficiency and cost. In this context, biosorption by inexpensive biomaterials promises to be an excellent alternative and hence provide more cost-effective, ecofriendly, and relatively simpler means for the removal of arsenic from water in developing countries like India[18]. Various biosorbents including agricultural waste and microorganisms have been reported for efficiently accumulating arsenic from water[19,20]. Adsorption on biomass, adsorption on inorganic adsorbents and various bioadsorbents like Blue Pine (*Pinus wallichiana*) and Walnut (*Juglans regia*), coconut coir pith, biomass (powdered) taken from stem of a thorny *Acacia nilotica*, polyethylenimine modified *Zea mays*, biochars derived from rice husk, organic solid



wastes and sewage sludge etc[21,22,23,24,25,26]. Over the years, adsorption has emerged as the most promising technique for removal of arsenic from water due to its easy handling, minimal sludge production and its regeneration capability.

In the present work, acid treated devdaru (*Polyalthia longifolia*) leaf powder (ADLP) was used to remove As(III) from aqueous solution under different experimental conditions. The sorption capacity of ADLP was compared with other biosorbents already used for aqueous removal of arsenite.

2. Materials and methods:

Biosorbent preparation.

Mature leaves of the Devdaru plants were collected from Botanical garden, Gauhati University. The collected leaves were thoroughly washed with clean water 4-5 times to remove dust and other impurities. The leaves were first sun dried and then dried in an oven at around 343K for several hours till they became crisp. These were then crushed in a grinder to obtain leaf powder, followed by several washings till the washings are colourless. This ensures that the powder is free of plant pigments and soluble substances which may interfere with the measurements later. The washed leaf powder was again dried in an oven for several hours up to 343K till water is removed completely. The acid treatments of the bioadsorbents were carried out by constantly stirring 5.0 g of bioadsorbent in 50 ml 1.0 N HCl for 60 min. The resulting mixture is then filtered washed repeatedly until the filtrate is free from Cl⁻ ions. The acid treated mixture was dried in an oven at 343K. Lumps were ground in a mortar and the powder was sieved through a 75 µm and then by 63 µm sieve to obtain particles of uniform size, which were preserved in clean plastic containers. ADLP of size between 75-63 µm were used for carrying out adsorptions.

Preparation of As (III) solution.

A stock of 1000 ppm sodium arsenite solution was prepared by dissolving the required amount of NaAsO₂ in double distilled water. Solutions of desired concentrations were prepared from the stock solution in its natural pH. Sodium arsenite AR (Loba Chemie, Mumbai) was used without further purification and obtained as sealed from the chemical store.

Adsorption experiments.

The adsorption experiments were carried out in 100 ml Erlenmeyer flasks by mixing a fixed amount of bioadsorbents with 50 ml of aqueous As (III) solution. The mixture was agitated in a thermostatic water bath (NSW, Mumbai, India) for a pre-determined time interval. The mixture was centrifuged for 15 min (Eltec centrifuge, TC4100 ~ 8000 rpm) and As (III) remaining unadsorbed in the supernatant liquid was determined with the help of an atomic absorption spectrophotometer (Varian SpectrAA 220). Before the actual experiments, sets of blank experiments were done to find if there was any adsorption on the walls of the container. The batch adsorption experiments were done under different conditions (Table 1).

Table 1: Various experimental conditions for adsorption of As (III) on acid-treated Devdaru leaf powder (ADLP)

pH	: 6.0 – 8.5
Interaction time (min)	: 5, 10, 20, 30, 45, 60, 90, 120, 150, 180, 240, 300, 360
Amount of bioadsorbent (g L ⁻¹)	: 1.0, 2.0, 3.0, 4.0, 5.0
As (III) (mg L ⁻¹)	: 1.0, 1.5, 2.0, 2.5, 3.0, 4.0, 5.0.
Temperature (K)	: 303

Adsorption kinetics.

Sorption kinetics depends on the physical and/or chemical characteristics of the biosorbent material, which helps us to predict the most probable sorption mechanism by applying different sorption kinetic models. In the present study, pseudo-first-order, pseudo-second-order, Intraparticle diffusion and liquid film diffusion model were applied to the data.

Pseudo-first-order model : Pseudo-first-order model given by the equation[27],

$$\log (q_e - q_t) = \log q_e - k_1 t / 2.303 \quad (i)$$

which shows how the amount, q_t , adsorbed per unit mass at time t is related to the amount, q_e , adsorbed per unit mass at equilibrium, k_1 being the first order rate coefficient. A plot of $\log (q_e - q_t)$ against time (min) gives slope is calculated by k_1 .

Pseudo-second-order model : Pseudo-second-order kinetics as per the well known rate equation[28],

$$t/q_t = 1 / (k_2 q_e^2) + (1/q_e) t \quad (ii)$$

The equation constants k_2 and q_e can be determined by plotting t/q_t against t .

Internal diffusion sorption model : Assuming constant diffusion through adsorbent pores, the relation between amount adsorbed and the reaction time can be expressed as follows[28],

$$q_t = k_i t^{0.5} \quad (iii)$$

where, k_i ($\text{mg g}^{-1} \text{min}^{-1/2}$) is the intra particle diffusion rate constant. The plot of q_t (mg g^{-1}) verses the square root of time($t^{1/2}$) would give a straight line passing through the origin if the sorption process obeyed the intraparticle diffusion model. The slope of straight line gives k_i , the intraparticle diffusion rate constant.

Liquid film diffusion model : There is also a possibility of diffusion of adsorbate molecules slowly across the liquid film over the adsorbent before interacting with the surface active sites is represented by the liquid film diffusion model given by the equation[29,30],

$$\log (1 - F) = - k_{fd} t / 2.303 \quad (iv)$$

where, F the fractional attainment of equilibrium = q_t/q_e , k_{fd} the film diffusion rate coefficient. The plots of $-\log (1 - F)$ versus t were drawn to validate the model.

Adsorption isotherms.

In the search for a novel adsorbent and to access an ideal adsorption system, it is necessary to establish the most appropriate mathematical description of the adsorption equilibrium over the entire range of experimental conditions. Adsorption isotherms are considered the most appropriate technique in this regard, but the validity of the conclusions made from the isotherm depends on the adequacy of a model to describe a particular situation[31,32]. Adsorption isotherms generally describe how different adsorbates interact with the adsorbent. In this study, Langmuir, Freundlich and Temkin isotherms are used to analyze the adsorption experimental data and to calculate the isotherms parameters as listed in Table 4.

Langmuir isotherm : The Langmuir sorption isotherm describes that the uptake occurs on a homogeneous surface by monolayer sorption without interaction between sorbed molecules and that the surface sites have the same energy. The linear form of the Langmuir isotherms may be represented as[33]:

$$C_e/q_e = 1/(bq_m) + (1/q_m) C_e \quad (v)$$

where, b (L/mg) is the Langmuir constant related to the energy of adsorption, q_m is the quantity of adsorbate required to form a single monolayer on unit mass of adsorbent (mg/g) and q_e is the amount adsorbed on unit mass of the adsorbent (mg/g) when the equilibrium concentration is C_e (mg/L). A plot between C_e/q_e and C_e , gives a slope and intercept of $1/q_m$ and $1/(bq_m)$ respectively.

In this model, the dimensionless constant separation factor for equilibrium parameter (R_L) can be defined as[34]:

$$R_L = 1 / (1 + bC_0) \quad (vi)$$

where C_0 (mg/L) is the initial concentration of arsenic.

Freundlich isotherm : The Freundlich isotherms model, which assumes a heterogeneous surface and a multilayer adsorption with an energetic nonuniform distribution, can be expressed as[35]:

$$\log q_e = 1/n \log C_e + \log K_f \quad (vii)$$

where, K_f ($\text{mg}^{1-1/n} \text{L}^{1/n} \text{g}^{-1}$) and n are Freundlich coefficients related to adsorption capacity and adsorption intensity, respectively. The values of K_f and n can be calculated from the intercept and slope of the plot $\log q_e$ versus $\log C_e$.

Temkin isotherm : The Temkin isotherm was developed by taking into consideration the Heat of adsorption and the adsorbate-adsorbent interaction on adsorption isotherm, who suggested that because of these interactions, the energy of adsorption of all the molecules decrease linearly with coverage. The Temkin isotherm has been used in the form as [36,37],

$$q_e = RT / b \ln k_T + RT / b \ln C_e \quad (\text{viii})$$

where $RT / b = B$, k_T (L mg^{-1}) being the equilibrium binding constant corresponding to maximum binding energy and b (J mol^{-1}) and B the Temkin coefficients. The dimensionless constant, B is thought to be related to heat of adsorption of the process. The adsorption data can be analysed according to Eq. (viii). The linear plots of q_e versus $\ln C_e$ able to determine the constant k_T and b .

3. Results and discussions:

Kinetics study

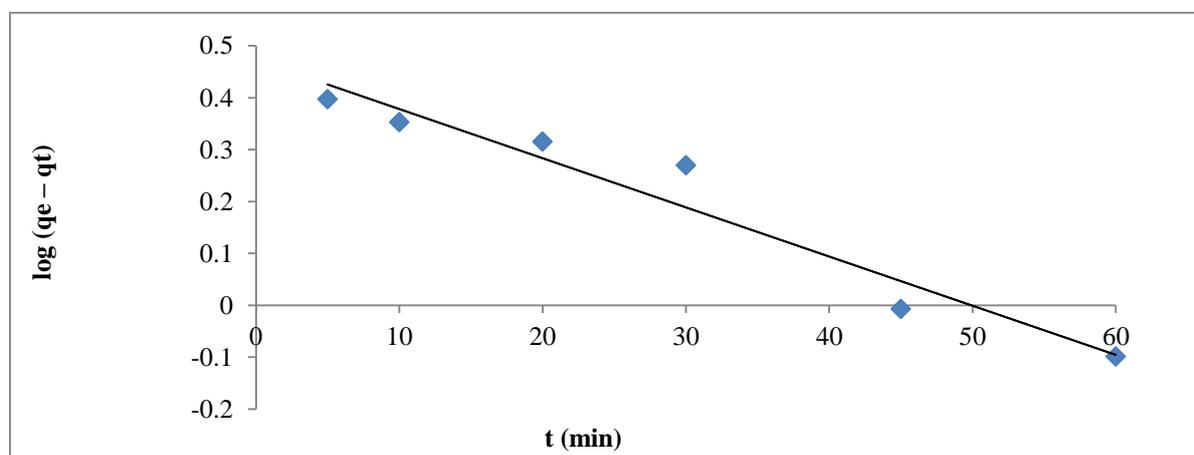


Figure 1: Application of pseudo first order kinetic model for As(III) adsorption by ADLP (bioadsorbent 1 g L⁻¹, initial As (III) concentration 5.0 mg L⁻¹; pH 7.46; temperature 303 K)

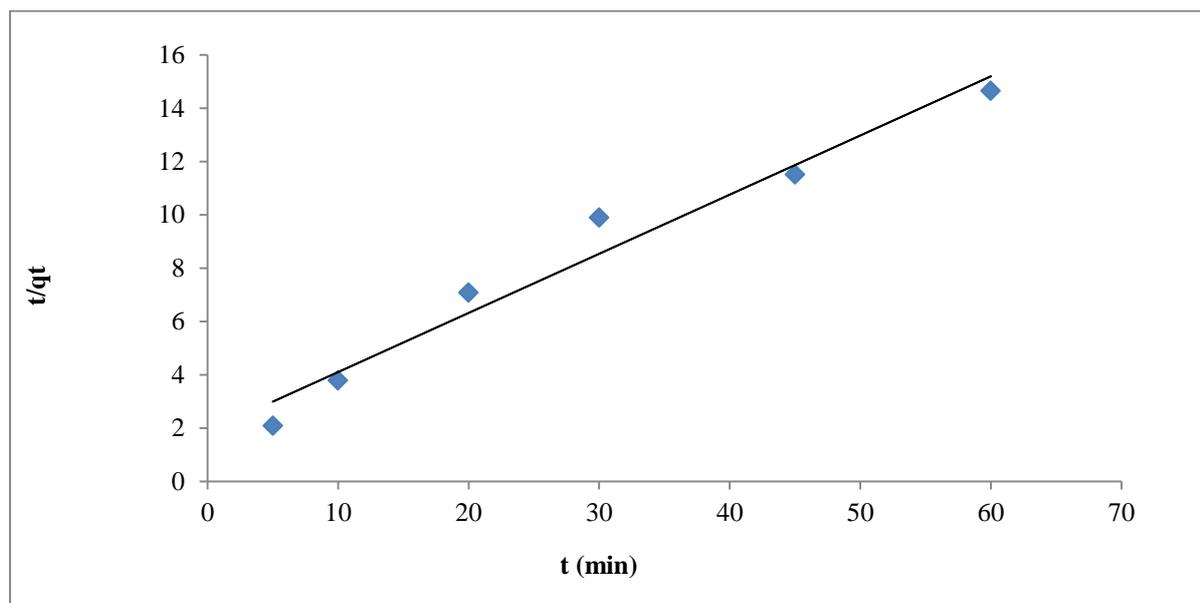


Figure 2: Application of pseudo second order kinetic model for As(III) adsorption by ADLP (bioadsorbent 1 g L⁻¹, initial As (III) concentration 5.0 mg L⁻¹; pH 7.46; temperature 303 K)

Table 2: Lagergren first order and second order rate coefficients for adsorption of As (III) on Acid-treated Devdaru leaf powder (ADLP) (bioadsorbent 1 g L⁻¹, initial As (III) concentration 5.0 mg L⁻¹; pH 7.46; temperature 303 K, k₁ in min⁻¹ and k₂ in g mg⁻¹min⁻¹)

Temp (K)		Rate coefficient	ADLP
303	First order	k ₁ x 10 ⁻²	2.2
		r	- 0.97
	Second order	k ₂ x 10 ⁻²	2.6
		r	+ 0.98

Table 3: Experimental and computed q_e from Lagergren and second order plots for adsorption of As (III) on Acid-treated Devdaru leaf powder (ADLP) (bioadsorbent 1 g L⁻¹, initial As (III) concentration 5.0 mg L⁻¹; pH 7.46; temperature 303 K)

Experimental	q _e (mg g ⁻¹)		Deviation (%)	
	Lagergren plots	Second order plots	Lagergren plots	
			Lagergren plots	Second order plots
4.98	2.97	4.50	39.21	+7.80

Adsorption of As (III) on ADLP yield linear log (q_e - q_t) vs. t plots (Figure 1, with r = -0.97, Table 2) suggesting the adsorption process might follow first order kinetics. The first order mechanism, however, becomes invalid since q_e obtained from the plots does not match the experimental values and showed large deviation (+39.2 %, Table 3).

On application of pseudo second order, linear plots (Figure 2) are obtained for t/q_t vs. t (r ~ + 0.98) and the second order rate coefficient is 2.60 x 10⁻² g mg⁻¹ min⁻¹ (Table 2). The close agreement between the experimental q_e values and those obtained from the plots (deviation +7.80 %, Table 3) strongly support a pseudo second order mechanism for As (III) take-up by the adsorbent.

In batch process due to constant shaking it is not likely that the As (III) molecules could enter into the pores of the adsorbent due to Intraparticle diffusion. Although the plot of q_t (mg g⁻¹) versus t^{1/2} is linear (r = +0.96), they do not fulfill the necessary condition of zero intercepts and therefore, the intra-particle diffusion rate (k_i = 0.32 mg g⁻¹ min⁻¹) has no real significance in the adsorption process.

On applying liquid film diffusion model, despite the plots being linear (r = +0.97) and k_{fd} = 2.2 x 10⁻² min⁻¹, the plots again did not meet the condition of zero intercept (+0.50).

Hence, it is safe to say that the As (III) interaction with acid-treated Devdaru leaf powder can be best represented by a pseudo second order process. Ranjan et al. (2009) and Lin et al. (2012) also reported pseudo second order to be most preferable kinetic process for adsorption of As (III) on agricultural residue ‘rice polish’ and Long-root *Eichhornia crassipes* respectively.

Isotherm study

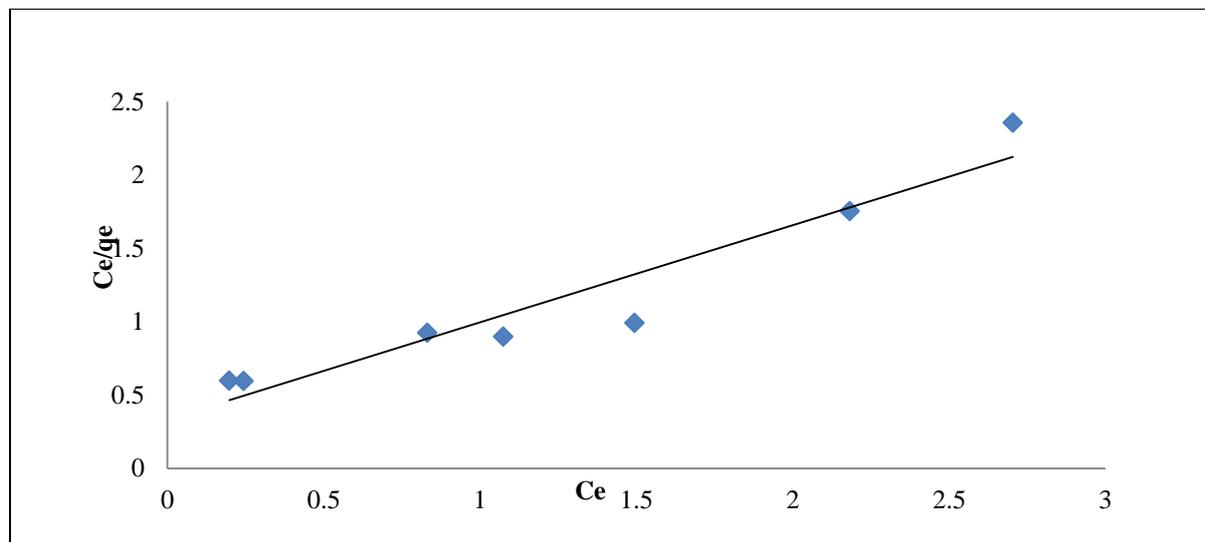


Figure 3: Langmuir adsorption isotherm of ADLP (As (III) 1.0 – 5.0 mg L⁻¹, Dose 1 g L⁻¹, temperature 303 K)

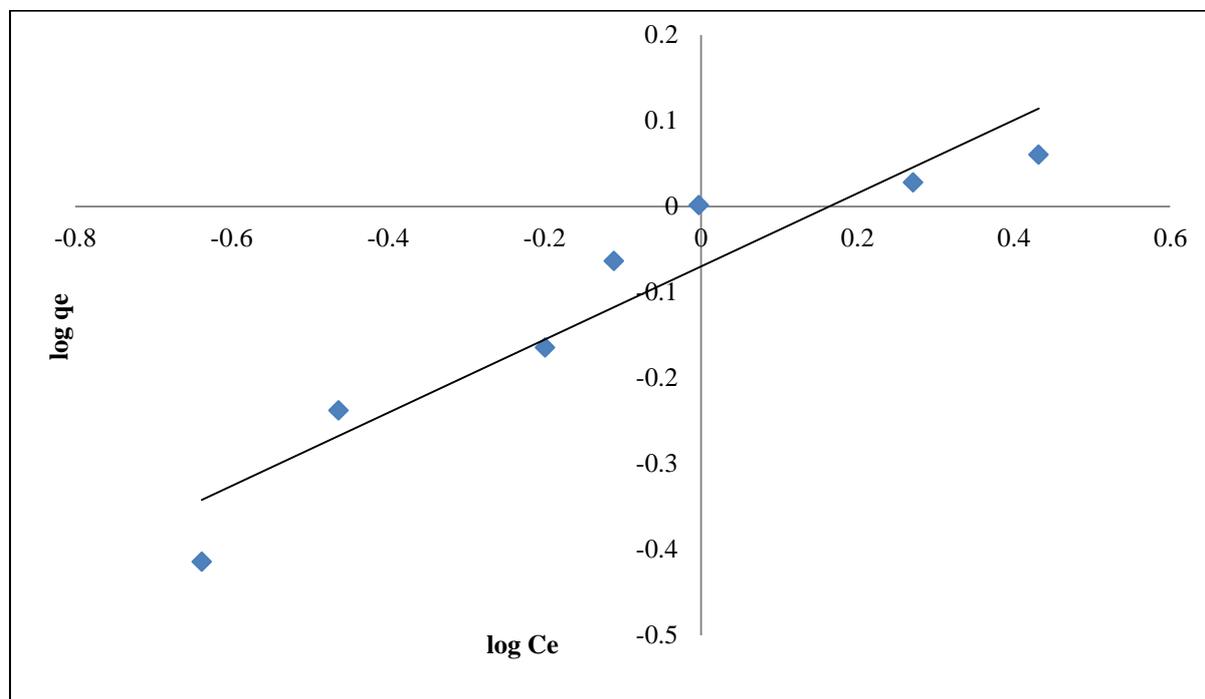


Figure 4: Freundlich adsorption isotherm of ADLP (As (III) 1.0 – 5.0 mg L⁻¹, Dose 1 g L⁻¹, temperature 303 K)

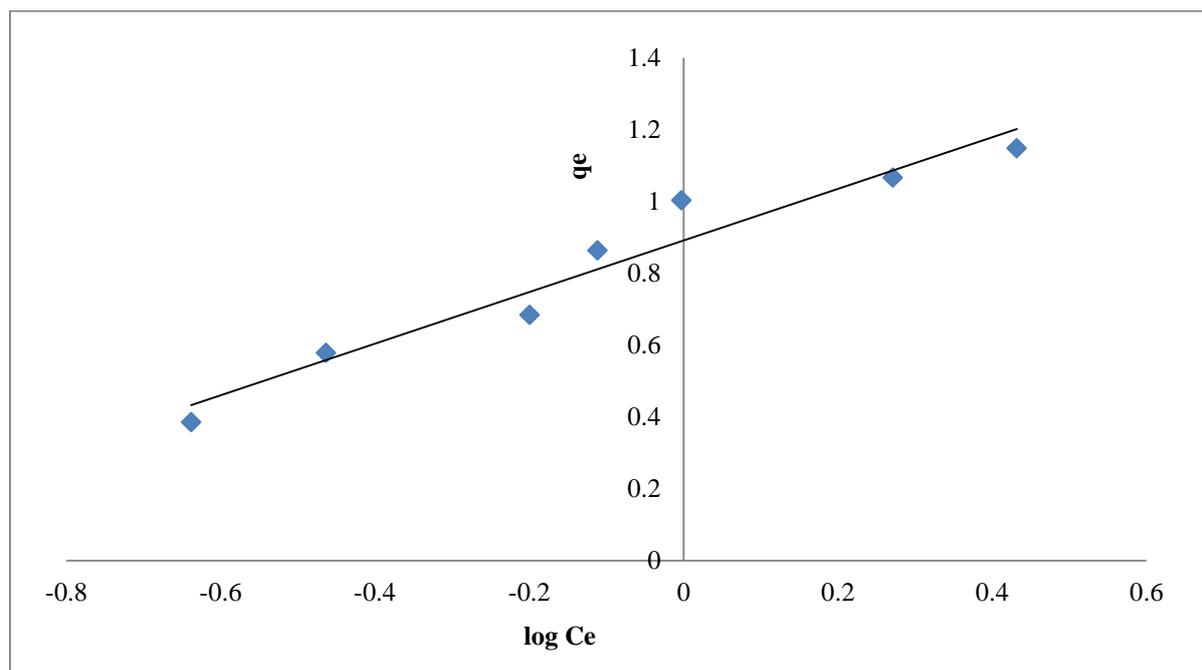


Figure 5: Temkin adsorption isotherm of ADLP (As (III) 1.0 – 5.0 mg L⁻¹, Dose 1 g L⁻¹, temperature 303 K)

Table 4: Freundlich, Langmuir and Temkin isotherm parameters for adsorption of As (III) from aqueous solution (pH) on Devdaru leaf powder (DLP) and acid-treated Devdaru leaf powder (ADLP) at 303 K. [As (III) 1.0 – 5.0 mg L⁻¹, Dose 1 g L⁻¹] K_f in mg^{1-1/n} L^{1/n} g⁻¹, q_m and b are in mg g⁻¹ and L mg⁻¹, k_T in L mg⁻¹.

Parameters	ADLP
Freundlich isotherm	
k _f	0.86
1/n	0.43
R	+ 0.95
Langmuir isotherm	
q _m	1.51
b	1.99
R	+ 0.96
Temkin isotherm	
k _T	6.39
B	0.31
R	+ 0.97

From Langmuir, it was found that, the maximum adsorption capacity (q_m) is 1.51 mg g⁻¹ (Table 4) and the value of R_L lies in the range of 0.091- 0.335 indicating that the adsorption process is favorable (0 < R_L < 1). The Langmuir equilibrium coefficient, b is sufficiently high to suggest a favourable formation of As (III) – biosorbent complex.

At 303 K, the Freundlich isotherm plots were linear (Table 4) with (1/n) < 1 indicating favorable adsorption.

However, when the monolayer adsorption capacities of some other adsorbents for As (III) are compared (Table 5), it is observed that ADLP have reasonably high adsorption capacity for the As (III) molecule.

Temkin isotherm plots were also linear ($r = + 0.99$) indicating that both adsorbate-adsorbate and adsorbate-adsorbent interactions are likely to play role in uptake of As (III) by the biosorbent. The Temkin coefficients are presented in Table 4.

The Langmuir ($R^2=0.916$) and Temkin ($R^2=0.945$) model gives a better fit than the Freundlich model ($R^2 = 0.899$).

Table 5: Langmuir adsorption capacities (q_m) for As (III) adsorption

Adsorbent	q_m (mg g ⁻¹)	Experimental Temp (K)	References
Cellulose-g-GMA-b-TEPA	5.71	303	38
Rice polish	0.139	293	39
Rice polish	0.09709	303	39
long-root Eichhornia crassipes	1.1377-1.9197	293-333	40
fish scale	0.02475	303	19
Magnetic wheat straw	3.90	303	34
Acidithiobacillus ferrooxidans BY-3	0.293	303	41
Acid treated devdaru leaf powder	1.51	303	Present study

4. Conclusions:

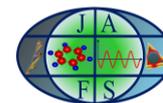
Hence, we can say that, the adsorptive removal of As (III) using a plant based material like ADLP establish a sufficiently good biosorption. In conclusion, devdaru leaf powder being locally available abundantly could be used as an interesting adsorbent with high potential for environmental applications.

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