As(III) and As(V) remediation in an aqueous medium using a cellulosic biosorbent: kinetics, equilibrium, and thermodynamics study

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Received: 9 April 2020 / Accepted: 24 August 2020 / Published online: 9 September 2020
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Abstract

Arsenic is an element of concern, as it is widely distributed in the environment and poses a great threat to the health of humans and other living beings. The present study investigates the uptake of arsenite (As(III)) and arsenate (As(V)) ions from aqueous solution using low-cost *Polyalthia longifolia* leaf powder (PLP). The low-cost adsorbent was characterized by FTIR and SEM–EDX measurements. Adsorption experiments were carried out, with contact time, pH, adsorbent amount, the concentration of As(III) and As(V) and co-existing anions (PO_4^{3-} and BO_3^{3-}) as the variables. Maximum adsorption of As(III) and As(V) was found at pH 7.5 and 3.0, respectively. The presence of PO_4^{3-} and BO_3^{3-} was found to be sufficient for the uptake of As(III) and As(V), respectively. Adsorption of both As(III) and As(V) on PLP was found to follow the pseudo-second-order kinetic model. Freundlich, Langmuir, and Temkin models of adsorption were tested for adsorption of As(III) and As(V) on PLP, and the results indicated that adsorption data closely followed the Langmuir model. The maximum adsorption capacity for As(III) and As(V) was 1.76 mg g^{-1} and 1.87 mg g^{-1} , respectively, under the experimental conditions. Thermodynamic analysis showed that the process of adsorption of both As(III) and As(V) on PLP was spontaneous and exothermic with decreasing degrees of freedom. The results indicated that PLP-As(III) and PLP-As(V) interaction equilibria were efficient and therefore could be explored for practical applications.

Keywords Adsorption · *Polyalthia longifolia* · As(III) · As(V)

1 Introduction

Creating one of the largest pollution problems in the world's history, arsenic (As) is recognized as a Class A human carcinogen by the US Environmental Protection Agency [1, 2]. The present-day scenario is that many developed and developing countries have reported arsenic contamination, with southern and southeastern Asia being the most heavily affected. The river valleys of the Ganga-Meghna-Brahmaputra river system in India and Bangladesh, the Indus River in Pakistan, the Red River in Vietnam, the Irrawaddy River in Myanmar, the Yellow River in China, and the Mekong River in Laos and Cambodia have been reported to have elevated concentrations of As [3].

Arsenic pollution is induced in the environment by both natural and anthropogenic sources, including weathering reactions, volcanic eruptions, biological activity, use of arsenical pesticides and fertilizers, industrial waste discharge, mining, discharge from coal-fired thermal power plants, petroleum refining, and ceramic industries [4, 5].

Arsenic is found in both organic and inorganic form in nature, but inorganic As compounds are known to be 100 times more poisonous than organic As compounds [6]. The oxidation states of inorganic arsenic (i-As) in natural water depends on the environmental conditions. In surface water, under an aerobic and oxidized environment, As(V) is stable as monovalent (H_2AsO_4^-) and divalent (HAsO_4^{2-}) oxy-anions. However, groundwater under anaerobic and

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reduced conditions is dominated by As(III) in the form of the uncharged H_3AsO_3 [4]. The toxicity of As is largely dependent on its chemical form. As(III) is more soluble, toxic, and mobile than As(V). This is due to a lack of electrostatic attraction in As(III), whereas As(V) is adsorbed more strongly on the particle surface to form thermodynamically stable surface complexes with a variety of oxides [5].

It is the inorganic arsenic (i-As) which is primarily responsible for cancer in different organs, arsenicosis, skin lesions, and cardiovascular diseases [7]. As(III) has a higher affinity for proteins than As(V). Research has shown that As cannot be excreted from the human body, where it binds with sulfhydryl groups in proteins and accumulates in tissues with high keratin content (skin, hair, and nails) [8, 9]. It has been reported that i-As is also capable of crossing the placental membrane and may affect the unborn baby [10]. Arsenic also appears in human milk at low concentrations [11]. Because of the widespread negative impact of ubiquitous arsenic on human health, the World Health Organization (WHO), US Environmental Protection Agency (EPA), and the European Commission lowered the maximum permissible arsenic content in drinking water from $50 \mu\text{g L}^{-1}$ to $10 \mu\text{g L}^{-1}$ [12, 13].

Arsenic decontamination of water has received serious attention from researchers over the past decade, as it has become necessary to remove arsenic from water in order to protect aquatic and terrestrial life. Methods of arsenic removal include chemical precipitation, oxidation and filtration, ion exchange, reverse osmosis, and adsorption and membrane technology. These methods involve high energy input, complicated procedures, and production of a large amount of toxic sludge. Adsorption is considered superior to other methods for the removal of dissolved arsenic, as it is found to be cost-effective, sludge-free, renewable, and technologically simple. For any method to be universal, it should rely on facile technology for installation by small communities [14]. Most problems arise in terms of the cost and efficiency of the adsorbent. In this regard, biosorption (adsorption using biomaterials) has gained popularity due to its cost-effectiveness, eco-friendly nature, and abundant availability, especially in a developing country like India. A wide range of raw biomaterials and their modified forms have recently been employed as adsorbents for the removal of metal/non-metal ions, dyes, or other contaminants present in water [15–21]. For example, agricultural waste, waste biomass, and other biological resources have been investigated for this purpose. These include *Moringa oleifera* (Lamarck) seed powder [22], fish scale, chicken fat and coconut fiber [23], rice polish [24], green algae (*Ulothrix cylindricum*) biomass

[25], *Momordica charantia* biomass [26], lichen (*Xanthoria parietina*) biomass [27], green algae (*Maugeotia genulflexa*) [28], long-root *Eichhornia crassipes* [29], the stem of *Acacia nilotica* [30], the biomass of marine macrophytes [31], pine leaves [32], palm bark biomass [33], *Hydrilla verticillata* [34], pulp/sludge of flowers such as *Hibiscus rosa-sinensis*, *Rosa rosa*, *Tagetes erecta*, and *Canna indica* [35], polyethylenimine-modified *Zea mays* [36], *Leucaena Leucocephala* seed powder [37], *Arthrobacter* spp. biomass [38], multi-amino-functionalized cellulose [39], *Saccharum officinarum* (sugarcane) bagasse [40], and neem (*Azadirachta indica*) bark [41].

Plant leaves are rich in cellulose, and several studies have revealed that cellulose can adsorb metal ions [42]. However, very few studies have reported the use of plant leaves for the uptake of As(III) and As(V) from aqueous solution. The present study investigates the use of the *Polyalthia longifolia* leaf powder (PLP) as a bioadsorbent for the removal of aqueous arsenic anions. *Polyalthia longifolia* trees are abundantly available in tropical and subtropical regions. Many significant medicinal properties (including anti-cancer properties) of *Polyalthia longifolia* have been reported [43–48]. Because of its excellent availability, low toxicity, and low cost, PLP has been explored for the elimination of aqueous arsenic. Natural water may, however, contain a host of anions along with As(III) and As(V). Among these anions, the influence of phosphate and borate ions could be interesting, as both are trivalent anions similar to As(III), and therefore the influence of these anions on arsenic adsorption is also investigated. It is known that arsenic is a chemical analogue of phosphorus, sharing the same outer shell configuration of s^2p^3 , so they exhibit similar chemical properties and are likely to compete with each other for sorption. The metalloid arsenic also exhibits many similarities to its diagonal neighbor boron. Therefore, the influence, if any, of phosphate and borate on the adsorption of As(III) and As(V) is also investigated in this work.

Thus, the main objective of the present study was to investigate the biomaterial obtained from leaves of *Polyalthia longifolia* as a suitable alternative arsenic adsorbent in aqueous solution. Fourier transform infrared spectroscopy (FTIR) and scanning electron microscopy/energy-dispersive X-ray spectroscopy (SEM–EDX) measurements were utilized for characterization of the functional groups and surface morphology of the adsorbent, and also to explain the interactions of PLP with As(III) and As(V). Optimum experimental conditions were determined with respect to pH, interaction time, adsorbent loading, temperature of interaction, and presence of other anions. The experimental data were subjected to different adsorption and kinetics models.

2 Materials and methods

2.1 Preparation of biosorbent

Mature leaves of *Polyalthia longifolia* were collected from Gauhati University (Assam, India) campus. The leaves were thoroughly washed to remove dust and other impurities, and were then sun-dried followed by drying in an air-oven at a temperature ≤ 343 K for several hours until they became crisp. The leaves were then converted to powder form by crushing them in a grinder followed by washing several times until the washes were colorless. This ensured that the powder was free of plant pigments and soluble substances which might interfere with the adsorption measurements. The washed leaf powder was further dried in the air-oven for several hours at 343 K until the water was completely removed. Lumps were ground in a mortar, and the powder retained between 75 μm and 63 μm sieves was preserved as the biosorbent containing particles of almost uniform size. The biosorbent *Polyalthia longifolia* leaf powder (PLP) was kept in clean plastic containers and stored in a desiccator.

2.2 Characterization of the biosorbent

Arsenic-loaded and unloaded PLP were characterized with FTIR spectra using a KBr pellet technique (IRAffinity-1 Fourier Transform Infrared Spectrophotometer, Shimadzu, range 4000–400 cm^{-1}).

Raw PLP and As(III)- and As(V)-loaded PLP were dried in an oven at a temperature less than 343 K. Degassing preceded by gold-coating of the samples was used to prepare the samples for surface morphology study using a scanning electron microscope (SEM) coupled with EDX (ZEISS Sigma 300; resolution 1 nm at a working distance of less than 6 mm, accelerating voltage 0.2–30 kV) at the Department of Chemistry, Gauhati University, Guwahati, India.

The electrostatic interactions between biosorbent particle surfaces and arsenic anions result in developing an electrical potential in the solid–liquid interface, expressed in terms of zeta potential. The charge distribution at the liquid–solid interface is controlled by the pH of the solution. The surface charge characteristics of PLP at different

pH values (pH = 1–10) were determined from the zeta potential measurements using a Zetasizer Nano ZS90 (Malvern Instruments) at IASST, Guwahati.

2.3 Preparation of As(III) solution

Stock solutions of arsenite (As^{3+}) and arsenate (As^{5+}) of concentration 1000 mg L^{-1} were prepared by dissolving 1.7340 g of NaAsO_2 (Merck, Mumbai) and 4.1634 g of $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$ (Merck, Mumbai) in 1.0 L of double-distilled water. Solutions of desired concentrations were prepared from these stock solutions in their natural pH by appropriate dilution with double-distilled water. The chemicals were used without further purification and were obtained as sealed from the chemical supplier.

2.4 Adsorption experiments

The adsorption experiments were carried out in 50 mL Erlenmeyer flasks. The amount of PLP taken in a flask was 20 mg, with 20 mL of aqueous arsenic(III) or (V) solution, i.e. an adsorbent loading of 1 g L^{-1} (except when PLP amount was varied). The mixture was agitated in a thermostatic water bath shaker for a pre-determined time interval. After the adsorption experiment, the mixture was filtered, and As(III) or As(V) remaining unadsorbed in the filtrate was determined with the help of an atomic absorption spectrophotometer (Agilent Technologies 200 Series AA, Model 240) using a hydride generation technique. All experiments were done in triplicate and the concurrent value was retained. Before the actual experiments, sets of blank experiments were carried out to determine whether there was any adsorption on the walls of the container. These experiments showed no measurable outcome. The batch adsorption experiments were conducted under different conditions as mentioned in Table 1. The amount of arsenic adsorbed per unit mass of the adsorbent and the percentage of adsorption were calculated using Eqs. 1 and 2, respectively, as given below:

$$q_t (\text{mg g}^{-1}) = (C_o - C_t)/m \quad (1)$$

$$\% \text{ of adsorption} = [(C_o - C_t)/C_o] \times 100, \quad (2)$$

Table 1 Experimental conditions for different sets of batch experiments

pH	2.0, 3.0, 4.0, 5.0, 6.0, 6.5, 7.0, 7.5, 8.0, 8.5, 9.0, 10.0
Interaction time (min)	5, 10, 20, 30, 45, 60, 90, 120, 150, 180, 210, 240, 270, 300, 330, 360
Adsorbent amount (g L^{-1})	1.0, 2.0, 3.0, 4.0, 5.0
As (III) or As(V) (mg L^{-1})	0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 4.0, 5.0
Temperature (K)	303, 313, 323
Adsorbent particle size (μm)	63–75

where C_o and C_t are the concentration of arsenic at the beginning and at time ' t ' respectively. The amount of biosorbent used is given by ' m '.

2.5 Co-existing anions PO_4^{3-} and BO_3^{3-} in As(III)/As(V) adsorption

Stock solutions of phosphate and borate were prepared by dissolving 1.8340 g of K_2HPO_4 and 2.4566 g of $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ in 1000 mL double-distilled water. From the stock solutions, phosphate and borate solutions of desired concentrations, viz., 0.5, 2.5, 5.0 mg L^{-1} were obtained. Arsenic solution (As^{3+} and As^{5+}) of strength 1.0 mg L^{-1} was also prepared. To analyze the effects of interfering ions equal volumes of arsenic (As^{3+} or As^{5+}) and interfering ion solution (PO_4^{3-} or BO_3^{3-}) were mixed with PLP (1 g L^{-1}) at a temperature of 303 K and pH unadjusted. After completion of the reaction, the mixture was filtered, and arsenic in the filtrate was estimated.

2.6 Adsorption kinetics

Kinetic study is important in terms of reaction pathways and mechanisms of sorption interaction. Kinetics is also useful for industrial purposes in designing fixed-bed columns. The kinetic rate coefficients are related to the mass transfer coefficient and fluid phase concentration in a fixed-bed column. Adsorption is a multi-step process, and the rate of the adsorption process is determined by the slowest step. The adsorption rate processes were tested with the following well-known kinetic models to understand the possible mechanism.

The pseudo-first-order or Lagergren model is one of the most commonly used models [49] and is given by the equation:

$$\log (q_e - q_t) = \log q_e - k_1 t / 2.303, \quad (3)$$

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 is the first-order rate coefficient. The values of k_1 and q_e were obtained from plots of $\log (q_e - q_t)$ vs. t . The test of validity can again be administered by comparing the experimental ' q_e ' value with that obtained from the pseudo-first-order plots.

The pseudo-second-order model [49] is based on the well-known rate equation:

$$t/q_t = 1/(k_2 q_e^2) + (1/q_e)t, \quad (4)$$

where q_t and q_e (mg/g) are the amount of solute adsorbed per unit mass of PLP at time t (min) and at equilibrium, respectively, and k_2 is the second-order rate coefficient ($\text{g mg}^{-1} \text{min}^{-1}$). k_2 and q_e values are obtained from the

slope and the intercept of the plots of t/q_t vs. t . The test of validity can again be administered by comparing the experimental ' q_e ' value with that obtained from the second-order plots. The second-order rate expression was used to describe interactions involving valence forces via sharing or exchange of electrons between the adsorbent and adsorbate as covalent forces, and ion exchange.

The intra-particle diffusion model [50] is given by the equation:

$$q_t = k_i \cdot t^{0.5}, \quad (5)$$

where k_i ($\text{mg g}^{-1} \text{min}^{-0.5}$) is the intra-particle diffusion rate coefficient. When this relation is valid, k_i values under different conditions are calculated from the slopes of the straight-line portion of the plot. One significant feature of these plots is that they have zero intercept.

2.7 Adsorption isotherm

Adsorption isotherms give a quantitative distribution of metal ions between the liquid phase (solution) and the adsorbent phase (solid) under equilibrium conditions. In the present study, Langmuir, Freundlich, and Temkin isotherms were applied to the experimental data to interpret the experimental results. The Freundlich isotherm assumes the formation of several layers of adsorbate on the heterogeneous surface of the adsorbent with the non-equivalent surface sites [39]. The isotherm equation is:

$$\log q_e = (1/n) \log C_e + \log K_f, \quad (6)$$

where C_e is the equilibrium concentration of As(III) or As(V) (mg L^{-1}), q_e is the amount of the As(III) or As(V) adsorbed per unit mass (mg g^{-1}), and 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. It is generally accepted that the reciprocal Freundlich intensity ($1/n$) is < 1.0 for favorable adsorption.

The Langmuir isotherm model is limited to the formation of a single layer of adsorbate on the adsorbent surface, with all the surface sites being considered as equivalent and no adsorbate-adsorbate interactions on the adsorbent surface [39]. The Langmuir isotherm equation is:

$$C_e/q_e = (1/bq_m) + (1/q_m)C_e, \quad (7)$$

where q_m (mg g^{-1}) and b (L mg^{-1}) are Langmuir coefficients related to the monolayer adsorption capacity and adsorption equilibrium constant, respectively. In the Langmuir model, a dimensionless constant R_L known as the separation factor for equilibrium parameter [39] is introduced as:

$$R_L = 1/(1 + bC_o), \quad (8)$$

where C_o is the initial concentration of As(III) or As(V) (in mg L^{-1}) and b (L mg^{-1}) is the Langmuir equilibrium constant. The value of R_L indicates the type of isotherm, i.e. irreversible ($R_L = 0$), favorable ($0 < R_L < 1$), linear ($R_L = 1$), or unfavorable ($R_L > 1$).

The Temkin isotherm is developed by taking into consideration the effects of adsorbate–adsorbate interactions. This isotherm assumes that (a) the heat of adsorption of all the adsorbate molecules/ions on the surface decreases linearly with coverage due to adsorbate–adsorbate interactions, and (b) adsorption is characterized by a uniform distribution of binding energies, up to some maximum binding energy [39]. The linear form of the Temkin isotherm is:

$$q_e = 2.303B \log k_T + 2.303B \log C_e, \quad (9)$$

with k_T (L mg^{-1}) being the Temkin isotherm constant and b_T (J mol^{-1}) the Temkin coefficient related to the heat of adsorption, B a dimensionless constant such that $B = R_T/b_T$, R the gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$), and T the absolute temperature (K) of adsorption.

2.8 Thermodynamics of adsorption

Adsorption is a surface phenomenon involving adsorbate–adsorbent interactions resulting in the binding of adsorbate molecules/ions to the adsorbent surface. Determining the strength of binding of a species to a solid surface is essential. This can be done by measuring the heat evolved or absorbed during the adsorption of a solute from the liquid phase to a solid surface. The thermodynamic parameters of entropy (S), enthalpy (H), and Gibbs energy (G) for the adsorption process are studied in this work. The changes in standard Gibbs energy (ΔG°) [50] was calculated from the equation:

$$\Delta G^\circ = -2.303RT \log K, \quad (10)$$

where R is the universal gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$), T the temperature (K), and K (q_e/C_e) the equilibrium constant for adsorbate–adsorbent interaction. The standard enthalpy (ΔH°) and standard entropy (ΔS°) parameters were obtained from the classic van 't Hoff equation [40]:

$$\log (q_e/C_e) = \Delta S^\circ / (2.303R) - \Delta H^\circ / (2.303RT), \quad (11)$$

where the ratio q_e (mg g^{-1})/ C_e (mg L^{-1}) is known as the adsorption affinity.

3 Results and discussion

3.1 Characterization of PLP

FTIR measurements of the raw PLP and PLP after adsorption of As(III) and As(V) helped to identify the functional groups that are likely involved in binding of arsenic anions to the biosorbent surface (Fig. 1). The FTIR results are summarized in Table 2. The absorption bands at 3415 cm^{-1} , 3471 cm^{-1} , and 3545 cm^{-1} correspond to the presence of hydroxyl ($-\text{OH}$) and amine ($-\text{NH}$) groups. However, the band is broader after adsorption of As(V), which may be due to the involvement of $-\text{NH}$ groups [29]. Stretching vibrations at 2970 cm^{-1} , 2931 cm^{-1} , 2858 cm^{-1} , 1462 cm^{-1} , and 1373 cm^{-1} are due to $-\text{CH}_3$ asymmetric stretching, $-\text{CH}_2-$ asymmetric stretching, $-\text{CH}_2-$ symmetric stretching, $-\text{CH}_3$ asymmetric bending, and $-\text{CH}_3$ symmetric bending vibrations, respectively. The $\text{C}=\text{O}$ stretching vibration at 1728 cm^{-1} shifted to 1712 cm^{-1} for As(III) and 1735 cm^{-1} for As(V) sorption [51]. The peak representing $\text{C}-\text{O}$ stretching of alcohol and carboxylic acid at 1051 cm^{-1} shifted to 1029 cm^{-1} and 1028 cm^{-1} for As(III) and As(V) treated biomass, respectively [52]. The sharp peak at 1562 cm^{-1} indicated $\text{N}-\text{H}$ bending vibrations in primary and secondary amines and amides [53]. A band at 1622 cm^{-1} represents the aromatic ring structure such as in the lignin aromatic group [40]. The FTIR peaks shifted from 1249 cm^{-1} to 1259 cm^{-1} and 1251 cm^{-1} for As(III)- and As(V)-loaded PLP, respectively, thus suggesting a $\text{C}-\text{N}$ stretching vibration [54]. These results can be interpreted as due to the involvement of hydroxyl ($-\text{OH}$), amine ($-\text{NH}$), and

Fig. 1 FTIR spectra of PLP (a), As(III)-loaded PLP (b) and As(V)-loaded PLP (c)

Table 2 Summary of IR bands found in the leaves of the *Polyalthia longifolia* spectrum before and after contact with As(III) or As(V) solution

IR band frequency (cm ⁻¹)			Functional group assignment	References
Raw PLP	As(III)-loaded PLP	As(V)-loaded PLP		
3545	–	–	O–H and N–H stretching	29
3471	3471	–		
3415	3415	3415		
2970	2968	2962	–CH ₃ asymmetric stretching	51
2931	2929	2926	–CH ₂ – asymmetric stretching	51
2858	2858	2858	–CH ₂ – symmetric stretching	51
1728	1712	1735	C=O stretching	51
1622	1633	1651	Aromatic ring structure	40
1562	1560	1562	N–H bending	53
1462	1462	1460	–CH ₃ asymmetric bending	51
1373	1375	1375	–CH ₃ symmetric bending	51
1249	1259	1251	C–N stretching	54
1051	1029	1028	C–O stretching	52

carboxyl (–COOH) groups in binding As(III) and As(V) anions to the surface of PLP particles.

The SEM micrographs were taken at a resolution of ×20,000 and operated at 5 kV accelerating voltage. The micrograph of unloaded PLP reveals a rough surface with irregular cavities and highly broken edges on the surface. After adsorption of As(III) and As(V), the cavities and broken edges may have been filled with As(III) and As(V) ions, resulting in a comparatively smoother surface with decreased porosity as shown in Fig. 2a, c, e. The probability of arsenic anions, trapped and adsorbed into the pores of PLP, could be observed when the EDX spectra were analyzed. Native PLP consists mainly of C, N, and O, with some traces of Ca. After adsorption, these and other peaks were reduced or enhanced, with a new peak of arsenic in the spectra becoming visible (Fig. 2b, d, f).

A graphical representation of the surface charge of PLP at different pH values at 303 K is given in Fig. 3. The value of zeta potential decreased with increasing pH from 1 to 10. The point of zero charge (pzc; pH value corresponding to zero zeta potential) was found to be 2.3. The surfaces of PLP particles were negatively charged at pH > pzc. Earlier it was shown that the pzc of the bioadsorbent *Eichhornia crassipes* was 1.9 [29], which is slightly lower than that in the case of PLP determined in this work.

3.2 Adsorption experiments

3.2.1 Effects of pH

The pH is an important factor that greatly influences the adsorption process. In the present work, the pH was varied from 2.0 to 10.0 for the adsorbate–adsorbent mixture, with 1.0 g L⁻¹ as the adsorbent loading and 2.0 mg L⁻¹ as the concentration of As(III) or As(V) solution. The solutions were shaken for 120 min (arsenite solution) and 60 min (arsenate solution) at a temperature of 303 K (contact time explained in the next section). Arsenite remained as a neutral species (H₃AsO₃) in the pH range of 2–7. The pK_a values of H₃AsO₃ (pK₁ = 9.2, pK₂ = 12.3 and pK₃ = 13.4) and zeta potential measurements with respect to pH suggested that under acidic conditions, the surface –OH and –NH groups are protonated [29]. Thus there is no electrostatic attraction between the positively charged surface and neutral As(III) species. At pH of around 7.5, H₃AsO₃ starts dissociating to arsenite ions (H₂AsO₃¹⁻ and HAsO₃²⁻). At around neutral pH, strong interactions are observed between partially neutral and partially negatively charged arsenite species and the positively charged adsorbent surface. Thus, PLP–As(III) interactions resulted in maximum adsorption of 63.3% at pH 7.5 (Fig. 4). As pH was further increased, the repulsion between the anionic species and negatively charged surface resulted in a decrease in adsorption of the anions.

Arsenate exists as a monovalent ion, H₂AsO₄¹⁻, in the pH range of 2–6.1. Arsenate (H₂AsO₄¹⁻) pK_a values are pK₁ = 2.2, pK₂ = 7.1 and pK₃ = 11.5, which are lower than those of the arsenite divalent ion (as HAsO₄²⁻ in the pH range of 6.1–11.5) [29, 35]. At pH > pzc (2.3) and pH > pK₁, the surface of the PLP particles acquires negative charge. Under acidic conditions, however, the surface is highly protonated. There is a strong electrostatic attraction between positively charged surface sites (–OH and –NH groups) and negatively charged arsenic anions [20], showing maximum As(V) removal of 67.6% at pH 3.0 (Fig. 4). As the pH of the solution increases, the substrate ends may acquire negative charge by adsorbing OH⁻ ions or by ionization of weak acidic functional groups or both, so there involve strong repulsive forces between the negative surface and HAsO₄²⁻.

A similar observation was reported earlier by Ranjan et al., where adsorption reached a maximum at pH 7.0 for As(III) and pH 4.0 for As(V) when rice polish was used as the adsorbent [24]. Another study by Lin et al. reported maximum adsorption (> 50%) for As(III) at pH 7.5 and (> 60%) for As(V) at pH 3.0 [29].

Fig. 2 SEM micrographs (at magnification $\times 20,000$) of raw PLP (a), As(III)-loaded PLP (c), and As(V)-loaded PLP (e); EDX analysis of raw PLP (b), As(III)-loaded PLP (d), and As(V)-loaded PLP (f)

Fig. 2 (continued)

Fig. 3 Zeta potential of PLP suspensions against pH at 303 K

Fig. 4 Effects of pH on adsorption of As(III) and As(V) by PLP. Concentration of As^{3+} or As^{5+} solution 2.0 mg L^{-1} ; adsorbent amount 1 g L^{-1} and temperature 303 K

3.2.2 Effects of contact time and adsorption kinetics

The effects of contact time and adsorption kinetics were studied with PLP loading of 1.0 g L^{-1} and As(III) or As(V) concentration of 2.0 mg L^{-1} at 303 K, without adjusting the pH. The Erlenmeyer flasks were removed from the thermostatic water bath shaker at adsorption time intervals of 5 to 360 min to measure the extent of adsorption. Adsorption of As(III) and As(V) on PLP was found to attain equilibrium within 120 and 60 min, respectively (Fig. 5). The process appeared to be a two-step process, firstly consisting of a fast adsorption step at the

beginning, indicating rapid filling of the sites from the large number of available bare binding sites, followed by a slower step, with no significant increase in arsenic uptake. At equilibrium, some of the binding sites were saturated by adsorption of arsenic anions. The remaining unsaturated sites could no longer be approached by arsenic anions in solution due to (i) repulsive forces generated among the adsorbed arsenic anions and (ii) repulsion of arsenic anions in the solid phase (PLP) and those in the solution [55].

Fig. 5 Effects of time on adsorption of As(III) and As(V) by PLP. Concentration of As^{3+} or As^{5+} solution 5.0 mg L^{-1} ; adsorbent amount 1 g L^{-1} and temperature 303 K

The pseudo-first-order kinetics plots as per Eq. (3) are shown in Fig. 6a. The pseudo-first-order rate constant k_1 and the equilibrium solid-phase concentration q_e , obtained respectively from the slopes and the intercepts of the plots of $\log(q_e - q_t)$ vs. t , are listed in Table 3. The good linearity of the plots is indicated by the correlation coefficient (R^2) values of 0.95 for As^{3+} and 0.90 for As^{5+} , but the differences between the values of q_e obtained from the plots and the experimentally measured $q_e(\text{exp})$ are very large, and the pseudo-first-order model has to be discarded for arsenic adsorption on PLP. The large deviation (63.96% for As^{3+} and 65.96% for As^{5+}) between $q_e(\text{exp})$ and $q_e(\text{plot})$ could have been because $q_e(\text{plot})$ was obtained from the intercept at $t=0$ when As uptake was much lower than that at equilibrium [56].

Pseudo-second-order kinetics plots for As(III) and As(V) adsorption on PLP are presented in Fig. 6b, and the corresponding q_e , k_2 , R^2 values are reported in Table 3. The plots of t/q_t versus t are highly linear ($R^2=0.99$) and show good agreement between $q_e(\text{plot})$ and $q_e(\text{exp})$, with only small deviations. The values of the pseudo-second-order rate coefficient, k_2 , computed from the plots were 6.79×10^{-2} and $10.18 \times 10^{-2} \text{ g mg}^{-1} \text{ min}^{-1}$ for As(III) and As(V), respectively. These values compare well with the second-order kinetics coefficient of $6.55 \times 10^{-2} \text{ g mg}^{-1} \text{ min}^{-1}$ measured for As(III) adsorption on acidified laterite by Glocheux et al. for particles of size $< 75 \mu\text{m}$ at 303 K [57]. However, the few works on the removal of As(III) by cellulose-based adsorbents have reported lower k_2 values of $0.061 \times 10^{-2} \text{ g mg}^{-1} \text{ min}^{-1}$ (rice polish) [24] and $0.069 \times 10^{-2} \text{ g mg}^{-1} \text{ min}^{-1}$ (*Acacia nilotica* leaf powder) [58] in comparison with those found in the present work. Much smaller k_2 values of $0.011 \times 10^{-2} \text{ g mg}^{-1} \text{ min}^{-1}$ and $0.921 \times 10^{-2} \text{ g mg}^{-1} \text{ min}^{-1}$ were obtained for As(V)

Fig. 6 Fitting of experimental data based on pseudo-first-order (a), pseudo-second-order (b) and intra-particle diffusion kinetic (c) models. Concentration of As^{3+} or As^{5+} solution 5.0 mg L^{-1} ; adsorbent amount 1 g L^{-1} and temperature 303 K

adsorption by multi-amino-functionalized cellulose [39] and by *Arthrobacter* sp. biomass [38], respectively.

The values of k_i were determined from the slopes of the respective plots, as indicated in Fig. 6c (Table 3). Although the plots were linear, the straight line did not pass through the origin. This non-zero intercept of the intra-particle diffusion model reflects the boundary layer thickness, which is attributed to film diffusion; the larger the intercept, the greater the contribution of the boundary layer (film) diffusion in the rate-controlling step. Thus, it is possible that arsenite and arsenate ions diffuse through a large boundary layer and prefer surface sorption [59, 60].

Table 3 Kinetic parameters obtained from adsorption of As(III) and As(V) onto PLP

Kinetics	Parameters	PLP-As(III)	PLP-As(V)
Pseudo-first order	$k_1 \times 10^2 \text{ min}^{-1}$	3.04	5.00
	R^2	0.95	0.90
	$q_e \text{ (exp) mg g}^{-1}$	2.83	3.09
	$q_e \text{ (plot) mg g}^{-1}$	1.02	1.05
	% deviation	63.96	65.96
Pseudo-second order	$k_2 \times 10^2 \text{ g mg}^{-1} \text{ min}^{-1}$	6.79	10.18
	R^2	0.99	0.99
	$q_e \text{ (exp) mg g}^{-1}$	2.83	3.09
	$q_e \text{ (plot) mg g}^{-1}$	2.91	3.20
	% deviation	-2.82	-3.56
Intra-particle diffusion	$k_i \times 10^2 \text{ mg g}^{-1} \text{ min}^{-0.5}$	9.26	14.14
	R^2	0.95	0.93
	Intercept (mg g^{-1})	1.86	2.02

3.2.3 Effects of adsorbent loading and As(III), As(V) concentration

Adsorption of As(III) and As(V) was studied by varying the PLP amount from 1.0 to 5.0 g L⁻¹, with a fixed concentration of arsenite or arsenate solution of 2.0 mg L⁻¹, and without adjusting the pH. The interactions were carried out until equilibrium was attained at 303 K. Adsorption of arsenic anions was enhanced with the increase in the biosorbent amount due to an increase in the number of binding sites available on the surface of the adsorbent for the uptake of arsenic anions [61]. Maximum removal was 79.9% for As³⁺ and 80.5% for As⁵⁺, and these values were achieved with 4.0 g L⁻¹ PLP (Fig. 7a). No significant increase in adsorption was observed when the PLP amount was further increased. This may be because equilibrium conditions were reached between the liquid-phase and the solid-phase arsenite or arsenate ions. On the other hand, the adsorption capacity (q_e) of the adsorbent was reduced from 1.11 to 0.316 mg g⁻¹ (As³⁺) and from 1.18 to 0.318 mg g⁻¹ (As⁵⁺). This is because, although the adsorbent amount increases, the number of arsenic anions adsorbed by a unit mass of adsorbent decreases.

In a separate experiment, As(III) at an initial concentration varying from 0.5 to 5.0 mg L⁻¹ was mixed with a constant PLP amount (1.0, 2.0, and 3.0 g L⁻¹ constant for each set of the experiments) at a temperature of 303 K and pH as prepared. The adsorption of As(III) decreased from 72.00 to 41.72% (PLP amount, 1.0 g L⁻¹), 78.8 to 45.72% (PLP amount, 2.0 g L⁻¹), and 86.4 to 58.96% (PLP amount, 3.0 g L⁻¹) (Fig. 7b). Free adsorption sites were sufficiently available at low arsenite concentrations. At a relatively higher concentration of As(III), there are too many arsenite ions competing for each binding site on the

Fig. 7 Adsorption of arsenic when: adsorbent amount is varied from 1 to 5 g L⁻¹ at constant As(III) or As(V) concentration of 2 mg L⁻¹ (a); As(III) concentration is in the range of 0.5–5.0 mg L⁻¹ at adsorbent amounts of 1, 2 and 3 g L⁻¹ (b); and As(V) concentration is in the range of 0.5–5.0 mg L⁻¹ at adsorbent amounts of 1, 2 and 3 g L⁻¹ (c)

biosorbent surface, and this results in decreased adsorption. The active sites available for adsorption are gradually saturated with As(III) ions per unit mass of PLP. Thus, the q_e value increases almost linearly for each set of As(III) concentration at a constant amount of PLP. For each set of As(III) concentration, the parameter q_e decreases with an increase in PLP amount.

Another set of experiments with varying As(V) concentration (0.5–5.0 mg L⁻¹) and PLP amount constant (1.0, 2.0, and 3.0 g L⁻¹ for each set) at a temperature of 303 K gave similar results (Fig. 7c). The removal of As(V) decreased from 72.4 to 44.84% (PLP amount, 1.0 g L⁻¹), 79.2 to 47.24% (PLP amount, 2.0 g L⁻¹), and 92.8 to 60.6% (PLP amount, 1.0 g L⁻¹), while q_e plots were in reverse order.

3.2.4 Effects of co-existing anions

The effects of phosphate on As(III) and As(V) removal were studied in the presence of three PO₄³⁻ concentrations (0.5, 2.5, and 5.0 mg L⁻¹) at a constant concentration of arsenic anions with adsorbent amount of 1 g L⁻¹ at 303 K. The percentage removal of As(III) and As(V) was 67.2 and 68.4%, respectively, at an initial As concentration of 1.0 mg L⁻¹ in the absence of phosphate ions. When phosphate ions were present, the As(III) and As(V) removal capacity decreased sharply, from 67.2 to 36.6% and from 68.4 to 24.6%, respectively (Fig. 8a). The pH of the solutions was found to be in the range of 5.5–7.5. Under neutral conditions, the competition between HPO₄²⁻ and H₃AsO₃ or HAsO₄²⁻ for the adsorption sites of the adsorbent may result in reduced sorption of the arsenic species [24, 29]. The removal rate of As(III) and As(V) decreased to approximately 45% and 64%, respectively, in the presence of phosphate, as compared with that of the control (absence of phosphate). The greater influence of phosphate on the adsorption of arsenate may be attributed to the fact that phosphoric acid and arsenic acid are triprotic acids with similar structure and

properties. A further increase in PO₄³⁻ concentration showed no significant decrease in As(III) or As(V) adsorption on PLP. It is likely that the PLP surface became saturated with the increasing number of phosphate ions, blocking many of the binding sites, and the competition for the adsorption sites between As(III) and As(V) ions on the one hand and phosphate ions on the other reaching some kind of a dynamic equilibrium. Similar results were obtained by Lin et al. [4] and Ansone et al. [29] for adsorption of arsenic on plant-based biomaterials.

Similarly, the effects of the presence of borate ions on As(III) and As(V) removal was studied by varying the BO₃³⁻ concentration from 0.5 to 5.0 mg L⁻¹. It was found that As(III) adsorption decreased dramatically from 67.2 to 30.2% in the presence of borate ions. A further increase in borate concentration decreased arsenite sorption only gradually (Fig. 8b). The effects of borate ions on As(III) adsorption on PLP can be explained in a way identical to the effects of the presence of phosphate ions on the adsorption of As(III) and As(V). This might be because under neutral conditions, arsenite and borate exist as H₃AsO₃ and H₃BO₃, respectively, both having a trigonal planar structure. The two anionic species share common sorption sites, and there is likely to be stiff competition between arsenite and borate for the available adsorption sites on the surface of PLP particles, resulting in the inhibition of As(III) adsorption in the presence of borate ions. Similar trends were reported earlier by Su and Puls [62]. The absence of such structural similarity between arsenate and borate species could be the reason that the PLP particles demonstrated very little or no change with respect to As(V) adsorption even in the presence of BO₃³⁻ ions (Fig. 8b). These results further confirm that the process of removal of As(III) and As(V) anions by PLP occurs through surface adsorption, which is not affected by the presence of other anionic species if they do not have structural similarity with arsenite or arsenate ions.

Fig. 8 Effect of co-existing anions phosphate (PO₄³⁻) (a) and borate (BO₃³⁻) (b). Concentration of As(III) and As(V) 1 mg L⁻¹; adsorbent amount of 1 g L⁻¹ at 303 K

3.3 Adsorption isotherms

The adsorption isotherm experiments were conducted by preparing a set of solutions (concentration range, 0.5–5.0 mg L⁻¹) in which the amount of adsorbent was varied at 1, 2, and 3 g L⁻¹ at 303 K. The adsorption capacity and other parameters obtained from the adsorption isotherm models by varying the amount of PLP are given in Table 4. The experimental data are in good agreement with the Freundlich isotherm, as the plots show good linearity (correlation coefficient, $R^2 = 0.96$ As(III) and 0.98 As(V)) (Fig. 9a,b). The uptake of arsenic species on PLP is found to be favorable, as $1/n = 0.55$ and 0.52 is less than unity for As(III) and As(V), respectively. The Freundlich adsorption capacity is found to be the same (1.28 mg^{1-1/n} L^{1/n} g⁻¹) for both As(III) and As(V) adsorption.

Application of the Langmuir model showed that the adsorption of As(III) and As(V) by PLP was the best-fit isotherm model, with high correlation coefficient values of 0.99 and 0.98 for As(III) and As(V), respectively (Fig. 9c, d). The Langmuir separation factor (R_L) was found to be 0.27 (As³⁺) and 0.28 (As⁵⁺), again indicating that the uptake of arsenic is favored on the PLP surface ($0 < R_L < 1$). Langmuir monolayer capacity of 1.76 mg g⁻¹ (As³⁺) and 1.87 mg g⁻¹ (As⁵⁺) was obtained from the linear Langmuir isotherm plots. The results of the Freundlich and Langmuir models together suggest that arsenic anions were adsorbed on the heterogeneous surface of PLP in a monolayer by very strong adsorbate–adsorbent interactions [63]. A comparison of the Langmuir monolayer adsorption capacity of PLP with that of a few other biomaterials (Table 5) shows that PLP has a sufficiently large capacity to take up arsenic in both trivalent and pentavalent form from aqueous solution [22–24, 26, 29, 31–33, 40, 41, 54, 63, 64].

These observations are further supported by linear Temkin plots (Fig. 9e, f) revealing strong As(III)-PLP and

As(V)-PLP interactions with negligible adsorbate–adsorbent interactions during the process. The Temkin coefficient, k_T , is large, with a value of 16.28 and 22.60 L mg⁻¹ for arsenite and arsenate, respectively, showing that chemical interactions had precedence in the whole process of adsorption.

3.4 Thermodynamics of the adsorption process

To study the thermodynamics of adsorption, 1 g L⁻¹ PLP was added to a set of solutions of As(III) or As(V) (concentration range, 0.5–5.0 mg L⁻¹). Different sets of such solutions were shaken at temperatures of 303, 313 and 323 K. The average values of the thermodynamic parameters were determined mathematically from Eqs. (10) and (11), which are summarized in Table 6. The adsorption process is exothermic, which is supported by the negative values of enthalpy of reaction. This may be attributed to the weakening of adsorptive forces between arsenic anions and the adsorbent surface as the temperature rises, resulting in increased anion mobility. The adsorption capacity values decrease with an increase of temperature from 303 to 323 K. The average values of standard enthalpy of reaction, ΔH°_{av} , were obtained in the range of 5.71–20.46 kJ mol⁻¹ and 3.44–10.19 kJ mol⁻¹ for adsorption of As(III) and As(V), respectively. This corresponds to physical adsorption [25]. Therefore, adsorption of As(III) and As(V) occurs through physisorption, where arsenic species are held by weak van der Waals forces [58, 65].

The negative values of standard entropy change of reaction, ΔS°_{av} , indicate that arsenic adsorption on PLP is accompanied by a decrease in entropy (for both As³⁺ and As⁵⁺ adsorption), which may be due to immobilization or association of arsenic anions on the adsorbent surface. Baig et al. [30] and Yu et al. [39] reported similar trends in the values of ΔG° , ΔH° , and ΔS° [39, 58].

Table 4 Freundlich, Langmuir, and Temkin isotherm parameters for As(III) and As(V) adsorption on PLP

Isotherm	Parameters	As(III) adsorption				As(V) adsorption			
		Adsorbent amount (g L ⁻¹)			Mean	Adsorbent amount (g L ⁻¹)			Mean
		1	2	3		1	2	3	
Langmuir	R^2	0.99	0.99	0.99	0.99	0.98	0.99	0.98	0.98
	q_m (mg g ⁻¹)	2.65	1.39	1.24	1.76	3.05	1.44	1.12	1.87
	b (L mg ⁻¹)	1.06	1.65	1.67	1.46	0.85	1.44	2.77	1.69
	R_L	0.34	0.22	0.25	0.27	0.38	0.28	0.18	0.28
Freundlich	R^2	0.97	0.94	0.98	0.96	0.99	0.97	0.98	0.98
	K_f (mg g ⁻¹)	1.34	1.25	1.24	1.28	1.29	1.28	1.27	1.28
	N	1.77	1.78	1.89	1.81	1.69	1.88	2.18	1.92
Temkin	R^2	0.98	0.99	0.98	0.98	0.96	0.98	0.96	0.96
	b_T (kJ mol ⁻¹)	4.48	8.42	9.96	7.62	4.10	8.38	12.00	8.16
	k_T (L mg ⁻¹)	11.58	17.28	19.99	16.28	10.22	16.15	41.43	22.60

Fig. 9 Isotherm models for As(III) adsorption: Freundlich (a), Langmuir model (c) and Temkin model (e); for As(V) adsorption: Freundlich (b), Langmuir model (d) and Temkin model (f). Concentration of As^{3+} or As^{5+} solution 0.5–5.0 mg L^{-1} ; adsorbent amounts of 1, 2 and 3 g L^{-1} and temperature 303 K

Negative values of standard free-energy change, ΔG° , suggest that the adsorption processes were spontaneous. The ΔG° values shifted to lower negative values with an increase in temperature, indicating the instability of the adsorption process at higher temperature. It was also observed that ΔG° values shifted to high positive values at higher concentrations of As(III) and As(V) solutions, indicating that the spontaneity of the adsorption process was disturbed. It may be thus concluded that the uptake of As(III) and As(V) by PLP remained thermodynamically favorable only at room temperature and at lower arsenic concentrations. It has been shown that at high temperatures, unstable complexes are formed between arsenite or arsenate species and the adsorbent surface without

any kind of electrostatic attraction [39]. The anions might have escaped from the adsorbent surface to the bulk of the solution at higher temperatures, or alternatively, the pores on the PLP surface might have opened up at a higher temperature, releasing As(III) or As(V) anions back to the solution [66].

4 Conclusion

This work shows that a cellulosic biosorbent, PLP, can be successfully utilized for removal of both trivalent and pentavalent arsenic from water at concentrations in which the problem of arsenic contamination is found in different

Table 5 Langmuir monolayer capacity of biosorbents

Adsorbents	q_m (mg g ⁻¹)		Temperature (K)	References
	As(III)	As(V)		
Shelled <i>Moringa oleifera</i> Lamarck seeds	1.59	2.16	–	22
Cod fish scales	0.025	0.027	303	23
Agricultural residue ‘rice polish’	0.139	0.147	293	24
	0.097	0.101	303	
	0.064	0.068	313	
<i>Momordica charantia</i> biomass	0.88	–	301	26
Long-root <i>Eichhornia crassipes</i>	1.17	1.78	303	29
<i>Ceramium ciliatum</i> (red algae)	–	0.88–1.24	–	31
<i>Gracilaria bursa-pastoris</i> (red algae)	–	0.86–0.96	–	31
<i>Ulva rigida</i> (green algae)	–	0.24–0.76	–	31
<i>Caulerpa racemosa</i> (green algae)	–	0.38–0.45	–	31
<i>Dictyopteris polypodioides</i>	–	0.92–1.00	–	31
<i>Cystoseira compressa</i> (brown algae)	–	0.0–0.72	–	31
<i>Zostera marina</i> (seagrass)	–	0.59–0.87	–	31
Pine leaves	–	3.27	298	32
Palm bark	1.030	–	298	33
<i>Saccharum officinarum</i> (sugarcane) bagasse	1.203	2.375	298	40
<i>Azadirachta indica</i> (neem) bark	0.167	–	303	41
Stem of <i>Tecomella undulata</i>	0.108	0.159	298–318	54
<i>Saccharomyces cerevisiae</i>	0.063	–	308	64
Japanese oak wood-derived biochar	3.16	3.89	293	65
<i>Polyalthia longifolia</i> leaf powder (PLP)	1.76	1.87	303	Present study

Table 6 Thermodynamic parameters for adsorption of As(III) and As(V) onto PLP

As(III) conc. (mg L ⁻¹)	ΔH°_{av} (kJ mol ⁻¹)	ΔS°_{av} (J mol ⁻¹ K ⁻¹)	ΔG° (kJ mol ⁻¹)		
			303 K	313 K	323 K
0.5	-12.26	-34.52	-1.90	-1.41	-1.18
1.0	-17.79	-52.87	-1.81	-1.23	-0.71
1.5	-20.46	-62.49	-1.60	-0.85	-0.30
2.0	-16.79	-51.05	-1.18	-0.87	-0.13
2.5	-12.49	-39.24	-0.71	-0.16	0.10
3.0	-9.12	-30.83	-0.08	0.69	0.56
4.0	-5.71	-20.64	0.52	0.76	0.95
5.0	-15.69	-54.73	0.78	1.50	1.91
As(V) conc. (mg L ⁻¹)	ΔH°_{av} (kJ mol ⁻¹)	ΔS°_{av} (J mol ⁻¹ K ⁻¹)	ΔG° (kJ mol ⁻¹)		
			303 K	313 K	323 K
0.5	-9.20	-22.16	-2.43	-2.30	-1.97
1.0	-8.82	-22.54	-1.94	-1.80	-1.47
1.5	-6.75	-17.20	-1.54	-1.38	-1.18
2.0	-4.94	-13.27	-0.96	-0.78	-0.68
2.5	-3.44	-9.62	-0.55	-0.42	-0.35
3.0	-10.19	-33.26	-0.25	0.30	0.43
4.0	-5.59	-18.92	0.19	0.31	0.58
5.0	-9.01	-31.27	0.52	0.74	1.16

parts of the world. The adsorption process is rapid and reaches equilibrium in a comparatively short time interval. Pseudo-second-order kinetics of the adsorption process shows that arsenic may bond to two similar or dissimilar sites on the adsorbent surface. While surface adsorption is likely to be the major mechanism of arsenic uptake, some amount may be held through intraparticle diffusion. The maximum adsorption capacity of *Polyalthia longifolia* leaf powder (PLP) was found to be 1.76 mg g^{-1} (As^{3+}) and 1.87 mg g^{-1} (As^{5+}), which is better than similar biosorbents. Although the adsorption capacity is low when compared to that of commercial adsorbents, the low cost and eco-friendly nature of the biosorbent makes it attractive for tackling the problem of arsenic contamination in developing countries. The process is thermodynamically spontaneous, works at around room temperature, and is simple, without the need for complex technical know-how. That arsenic can be removed in both a single and binary solute systems confirms that surface adsorption is the major mechanism for arsenite or arsenate removal.

Acknowledgements The authors gratefully acknowledge Prof. D.K. Kakati, Head, Department of Chemistry, Gauhati University, Guwahati, for providing SEM-EDX (scanning electron microscope and energy dispersive X-ray analyzer) instrument facilities and other necessary facilities.

Compliance with ethical standards

Conflict of interest The authors declare that they have no competing interests.

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