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Process Parameter Optimization And Isothermal Modeling: Removal Of Arsenic(V) Ion From Contaminated Water Using Palm Bark (PB) Biomass

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ABSTRACT

In present investigation activated carbon derived from palm bark (PB) biomass was used for removal of As(V) ion from contaminated water by biosorption. The effect of various parameters such as pH, temperature, adsorbent dose and contact time were studied in batch experimental setup. Topographical and morphological analysis of the biosorbent was carried out through Scanning electron microscopy (SEM) and Fourier transmission infrared spectroscopy (FTIR). This analysis showed that the surface of biosorbent became porous and uneven after activation. Energy Dispersive X- ray (EDX) analysis of the activated carbon before and after As(V) ion sorption indicated that chemical ion exchange was the preferred mode of As(V) ion binding on biosorbent surface. The biosorption of As(V) ion was found to be highly pH dependent. At the optimum treatment conditions of pH (4), temperature (25^{0}C), contact time (90 min) and adsorbent doses (4 g/l), 85.70% removal of As(V) ion was obtained. Sorption equilibrium was studied using Langmuir and Freundlich isotherms. Freundlich isotherm was found to be best fitted to equilibrium sorption data with higher linear correlation coefficient (R^2 = 0.990).

Keywords: As(V) ion, Sorption, Palm bark biomass, Parameters optimization, Isotherm models, ICP-MS

1. INTRODUCTION

Arsenic contamination in ground water has caused serious health effects to untold hundreds of millions of people across the world [1,2]. Effluent of industries like metal-processing, semi conductor, copper smelting, galvanization unit, electroplating, metal finishing, mining, battery, pigment, dyestuff and paint and acid mine drainage wastewaters contain significant amount of arsenic [3,4]. On exposure to high arsenic concentrations may cause acute and chronic metabolic disorders, such as dermal pigments (Blackfoot disease) and skin, liver and lung cancer [5]. Due to high toxicity of arsenic, US Environmental Protection Agency (USEPA) and World Health Organization (WHO) have recommended that the maximum contaminant level (MCL) for arsenic in drinking water of 10 ppb and the water treatment system must comply with this standard. However, some countries like India, Bangladesh and China have adopted MCL of 50 ppb (0.05 mg/l) as their drinking water standard [6,7].

Researchers in many countries are studying the removal of arsenic from contaminated water using several techniques, namely oxidation/precipitation, electrocoagulation/co-precipitation, lime softening, metal-oxide adsorption, reverse osmosis and nanofiltration, ion-exchange resin, coagulation-microfiltration, etc [8,9,10]. Most of these methods suffer from some drawbacks, such as high capital and operational cost or the disposal of the residual metal sludge, and are not suitable for small-scale industries [11].

Biosorption is one of the latest techniques used for the removal of heavy metals from aqueous solutions. Some of the biosorbents such as *Eichhornia crassipes* [12], wooden ash [13], Psidium guajava leaf [14], Moringa oleifera Lamarck seed powder [9], Orange waste gels [1], Jute leaf powder, sugarcane powder, lily leaf powder, fish ayes powder and water hyacinth root powder [15], have currently been employed for the removal of arsenic from liquid media. In this investigation, palm bark (PB) was chosen as biosorbent due to being of its natural, renewable and thus cost-effective biomass [16]. The objective of the present work is to investigate the potential of palm bark (PB) biomass for the removal of As(V) ion from contaminated water by biosorption. Fourier transmission infrared spectroscopy (FTIR), scanning electronic microscopy (SEM) and Energy Dispersive X- ray (EDX) were used to analyze the characteristic of palm bark (PB) biomass. Optimum biosorption conditions were determined as a function of pH, biomass dosage, contact time, and temperature. The Langmuir and Freundlich models were used to describe equilibrium isotherms.

2. MATERIALS AND METHODS

2.1 Chemicals and stock preparation

All chemicals used in the present experiment were of analytical reagent (AR) grade. For preparation of stock solutions and dilutions, double deionized water (Millipore 17.9 MΩ/cm) was used. Stock solution of 1000 mg/l concentration of As (V) was prepared by using 8.8 mg of sodium arsenate ($Na_2HAsO_4.7H_2O$).

2.2 Biosorbent preparation and characterization

For the present investigation, palm bark (PB) collected from the campus of Indian institute of Technology, Roorkee, India was used for the experiment. The grime content of BP was removed by repeated washing with distilled water and used it as biosorbent. The moisture content of biosorbent was initially air-dried for 4-5 hours and then kept inside the oven for about 24 hrs at 50°C. Subsequently, grounded and sieved biosorbent (around 1.18 mm) was stored in container. Morphology and characterization of PB biomass were determined by using Scanning Electron Microscopy (SEM), Energy Dispersive X- ray (EDX) and Fourier Transform Infrared Spectroscopy (FTIR).

2.3 Method of analysis

Initially a known amount of prepared biosorbent was added in the sample and then agitated at 180 rpm inside the orbital shaker. The batch biosorption procedures were conducted at pH of 4, reaction temperature of 25°C, dosage of 4 g and contact time of 90 minutes, respectively. The final sample was filtered and analyzed through the spectrophotometer (Tashniwal TVS 25A made) by SDDC (Silver diethyldithiocarbamate) method [17] at a wavelength (λ) of 540 nm by occasional crosschecking with ICP-MS.

The percentage removal of arsenic ions was calculated as follows [18]

$$\text{Biosorption (\%)} = \frac{(C_i - C_f)}{C_i} \times 100 \ldots\ldots\ldots\ldots\ldots (1)$$

where C_i and C_f are the initial and final concentrations of arsenic ions present in the biosorption studies.

The amount of arsenic sorbed per unit mass of the biosorbent (mg/g) was evaluated by using following equation [19]

$$\text{Uptake capacity, } q_e = (C_i - C_e)\frac{V}{W} \ldots\ldots\ldots\ldots\ldots (2)$$

where C_i and C_e were initial and equilibrium concentrations of As(V) (mg/l), q_e, V and W were equilibrium uptake of metal ion (mg/g), volume of solution in liters (l) and mass of adsorbent in grams (g) respectively.

3. RESULTS AND DISCUSSION

3.1 Characterization of biosorbent

Fig. 1(a) represent the SEM photographs of As(V) ion unloaded indicating the porous structure and an irregular surface of PB biomass. The presence of voids on the surface of PB biomass revealed that the possibility of As(V) ion accumulation [20]. EDX analysis of As(V) ion unloaded showed the percentage weight of chemical compositions available on the surface of PB biomass was as follows: 30.12% of C, 42.63% of O, 14.49% of K, 1.52% of Si, 0.28 of Ca, 2.06% of Na, 0.7% of Al and 2.25% of Mg. In case of loaded As(V) ion onto PB biomass surface as shown in Fig. 1(b), it was observed that highly accumulation of As(V) ion resulting in loss of surface porosity and roughness. The percentage weight of chemical compositions available on the surface of PB biomass after loading of As(V) ion was as follows: 23.23% of C, 38.74% of O, 14.49% of K, 1.52% of Si, 8.28 of Ca, 7.30% of As, 1.21% of Na, 0.3% of Al and 4.03% of Mg.

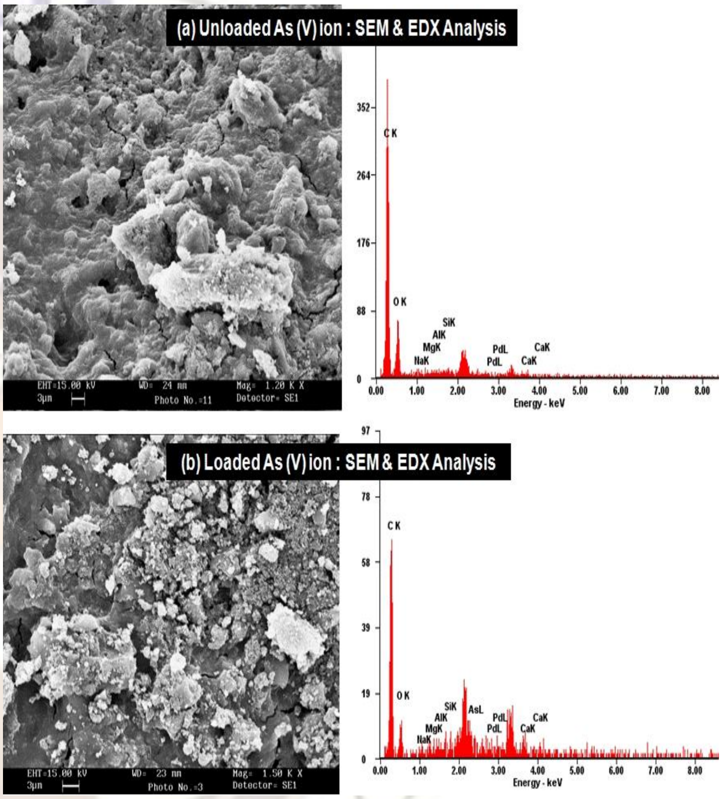


Fig. 1: SEM and EDX analysis of PB biomass (a) unloaded As(V) ion and (b) loaded As(V) ion

Fig. 2 shows that FTIR analysis of unloaded As(V) onto PB biomass surface, the functional groups such as carboxyl, methyl, hydroxyl, carbonyl and methyl were present in sufficient amount on As(V) ion unloaded biomass surface [6, 21]. FTIR vibrations present on the surface of PB biomass before loading of As(V) ion, i.e., 3500 – 3000, 2924.35, 1738.27 – 1431.86, 1428.48 – 1073.63, 898.38 – 776.06 cm^{-1} shifted to weak and diminished reflectance pattern between 3500 – 3000 cm^{-1} and 2000 -1000 cm^{-1} after loading of As(V) ion onto PB biomass surface. It was observed that most of the peaks of functional groups in case of unloaded As(V) ion were disappeared or diminished after loading of As(V) ion on the surface of PB biomass, indicating the involvement of biosorbent surface chemistry in As(V) ion biosorption across liquid phase.

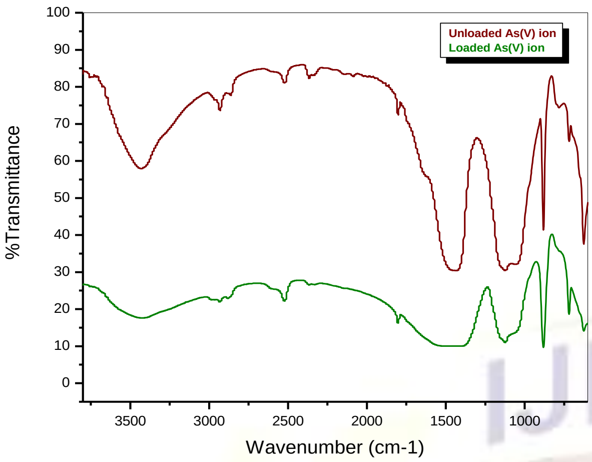


Fig. 2. FTIR spectrum of BP biomass: unloaded As(V) ion and loaded As(V) ion (3500 - 500 cm^{-1})

3.2 Effect of pH and dosage on As(V) ion biosorption

The effect of pH was studied ranges from pH 2 to pH 8 as shown in Fig.3. As the pH value increased above pH 4, biosorption of As(V) ion was observed to be decreased due to electrostatic repulsion between the negatively charged As(V) species, $HAsO_4^{2-}$, and the biosorbent surface [9, 22]. Since the pH of the system of was found optimized at **4, hence in the further studies pH 4 was used.**

Fig. 3 shows that the maximum removal of As(V) ion was observed at 4 g under the given experimental condition. Increase in the biosorbent dosage results in the increase in the number of active sites, which lead to increase in the percentage removal of As(V) ion [23]. However increased in dosage after 4 g results no further removal of As(V) ion since internal saturations of pores occurred. Hence, the optimum dosage of PB biomass for removal of As(V) ion from liquid phase could be taken as 4 g/l PB biomass. For further studies an optimum dosage of biosorbent has been used.

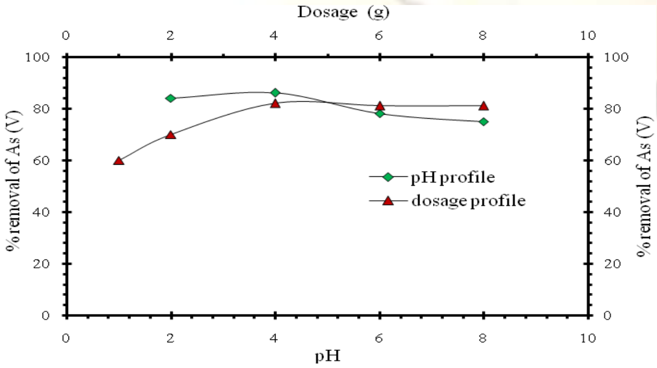


Fig. 3. Effect of pH/dosage on the % removal of As(V) ion onto PB biomass (C$_o$ = 50 mg/l and 180 rpm)

3.3 Effect of temperature and contact time on As (V) biosorption

Fig. 4 shows increased in temperature increased percentage removal of As(V) ion also increased up to 25^{0}C and then decreased due to breaking down of As(V) ion bond on the surface of PB biomass at higher temperature [24]. Further increased in temperature has no significant percentage removal of As(V) ion, thus optimum temperature was considered as 25^{o}C.

The effect of contact time on removal of As(V) ion onto PB biomass surface was investigated as shown in Fig. 4. Rapid removal of As(V) ion was obtained initially and later on rate of removal became slow and then reached optimum state (90 min). Maximum percentage removal of 85.70% As(V) ion was achieved at 90 min. Futher extension of contact time (>90 min) did not significantly effects percentage removal of As(V) ion due to the accumulation arsenic species [4]. Hence, the batch experiment contact time was considered as 90 min on biosorption of As(V) ion from liquid phase.

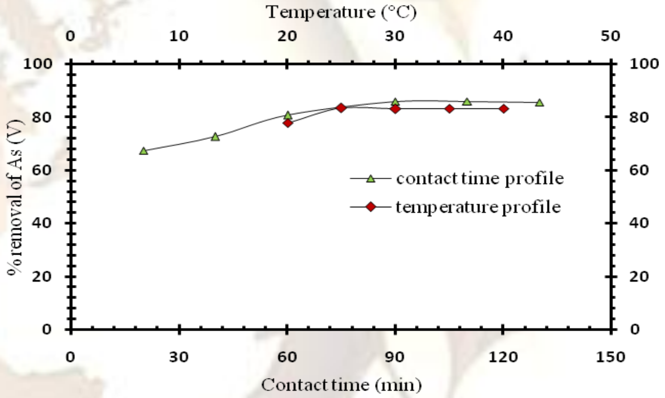


Fig. 4: Effect of temperature/contact time on the % removal of As(V) ion onto PB biomass (C$_0$=50 mg/l, 180 rpm, dosage=4 g and pH=4).

3.4 Equilibrium Studies

To describe the equilibrium state for As(V) ion biosorption experiments, Langmuir isotherm and Freundlich isotherm were tested. Langmuir isotherm model assumes that there are a finite number of binding sites having the same affinity for adsorption of monolayer and there is no interaction between adsorbed molecules [13]. The mathematical form of equation can be expressed as

$$q_e = \frac{K_L \times C_e}{(1 + b \times C_e)} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots (3)$$

where, K_L and b are the maximum uptake capacity (mg/g) and Langmuir constant related to the capacity (l/mg), respectively. C$_e$ is the equilibrium arsenic concentration (mg/l).

Freundlich isotherm model assumes the heterogeneous nature of the biosorbent surface and the multilayer coverage of biosorbent surface by sorbate species [25]. The empirical form of equation can be expressed as

$$q_e = K_f \times C_e^{(1/n)} \quad \text{……………………} (4)$$

where K_f and n are constants for adsorption capacity (l/mg) and adsorption intensity, respectively. The hybrid fractional error function (HYBRID) was used as a criterion in finding the best isotherm model to fit the experimental data [26]. The HYBRID is given by following equation:

$$HYBRID = \frac{100}{n-p}\sum_{i=1}^{n}\left[\frac{(q_{e,\exp} - q_{e,calc})}{q_{e,\exp}}\right]_i \quad \text{..................} (5)$$

The experimental data were fitted with the selected isotherm model. Fig. 5 represent the isotherm plot for sorption of As(V) ion onto the biosorbent. Constant parameters and correlation coefficient values of each model obtained are given in Table 1. From the correlation coefficient (R^2) values of all isotherm equations, Freundlich model provides a better understanding of As(V) ion biosorption with linear correlation coefficients (R^2) near to unity, which revealed that biosorption occurred on heterogeneous surface of solid biomass. However, Langmuir model did not fit well experimental data. The HYBRID value of isotherm models were tested. It was observed that HYBRID value of Freundlich model was smaller as compared to that of Langmuir model. So, it can be concluded that Freundlich model was best suited for the experimental data, represents that sorption occurs multilayer of solid/liquid phase interaction. The maximum uptake capacity of As(V) ion was 2.23 mg/g, it is showed that PB has a potential to be a good biosorbent for removal of As(V) ion from contaminated water due to its high sorption capacity and availability.

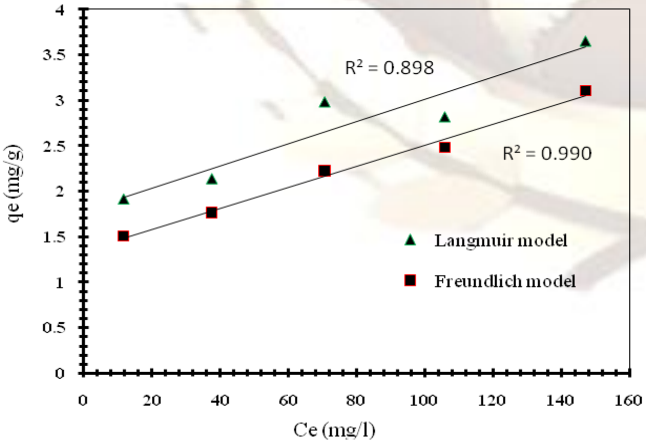
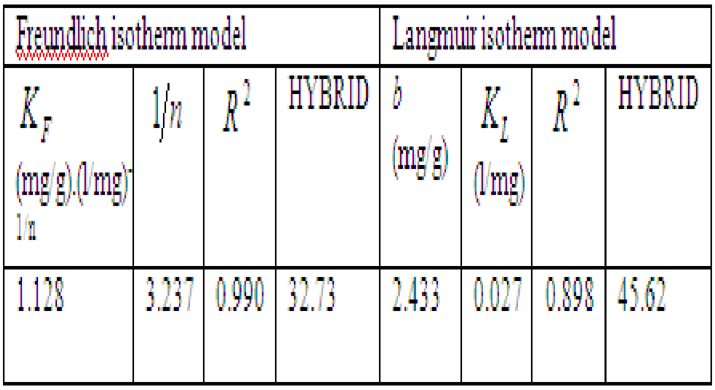


Fig. 5. Langmuir and Freundlich models for As(V) ion removal mediated by biosorption onto PB biomass surface (particle size = 1.18 mm, dosage = 4 g, agitation rate = 180 rpm and pH 4).

Experimental best data points are predicted by Freundlich equation.

Table 1: Parameters of Langmuir and Freundlich models for the biosorption of As(V) ion onto PB biomass at 25°C



Freundlich isotherm model				Langmuir isotherm model			
K_F (mg/g).(l/mg)$^{1/n}$	$1/n$	R^2	HYBRID	b (mg/g)	K_L (l/mg)	R^2	HYBRID
1.128	3.237	0.990	32.73	2.433	0.027	0.898	45.62

4. CONCLUSION

In the present investigation it was evident that PB biomass can be used as an economically feasible biosorbent for the removal of As(V) ion from contaminated water. Characterization of biosorbent surface by SEM and EDX revealed that highly accumulation of As(V) ion resulting in loss of surface porosity and roughness. FTIR analysis evident that most of the peaks of functional groups in case of unloaded As(V) ion were disappeared or diminished after loading of As(V) ion on the surface of PB biomass. The sorption of As(V) ion was found to be highly pH dependent. It was observed that maximum percentage removal of As(V) ion was observed as 85.70% at 2.23 mg/g uptake capacity, pH of 4, dosage of 4 g, contact time of 90 minutes and reaction temperature of 25°C, respectively. The equilibrium sorption data was best represented by Freundlich isotherm model (R^2=0.990).

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