

A POTENTIAL OF BIOSORBENT DERIVED FROM BANANA PEEL FOR REMOVAL OF As (III) FROM CONTAMINATED WATER

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ABSTRACT:

The main aim of this work is to evaluate the potential of application of banana peel (BP) as a biosorbent for removal of As(III) ion from contaminated water. Characterization of biosorbent was analyzed with FTIR, EDX and SEM. Equilibrium isotherms and kinetics were obtained and the effects of solution pH, temperature, dosage and contact time were studied in batch experiments. Maximum percentage removal (82.23%) of As(III) ion was obtained at optimized pH 7, contact time (t_c) of 90 min, dosage (d_c) of 8 g, temperature (t_c) of 35°C and 10 mg/l As(III) ion concentration (C_i), respectively. Equilibrium was well described by Freundlich isotherm model ($R^2 = 0.993$). Moreover, it was also found that sorption kinetics favour pseudo-second order model with high linear regression coefficient ($R^2 = 0.998$).

Keywords : As(III) ion, Biosorption, Banana peel (BP), Isotherm models and Kinetics

1. INTRODUCTION

The presence of toxic arsenic in ground water has caused serious health effects to untold hundreds of millions of people across the world [1]. The main sources of arsenic pollution in environment are industrial sectors like galvanization unit, copper smelting, acid drainage, electroplating industry, paint and pigment industry, metallurgical units and metal finishing plants [2, 3]. On exposure to arsenic concentrations above 100 ppb may cause acute and chronic metabolic disorders, such as dermal pigments (Blackfoot disease) and skin,

liver and lung cancer [4, 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].

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 [7, 8, 9]. 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 [10].

In this investigation, banana peel was chosen as biosorbent due to being of its natural, renewable and thus cost-effective biomass [11]. The objective of the present work is to investigate the biosorption potential of banana peel (BP) biomass in the removal of As(III) ion from contaminated water. 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. Biosorption mechanism of As(III) ion onto banana peel (BP) biomass was also evaluated in terms of kinetic rate of reaction.

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 solutions of 1000 ml concentration of As(III) was prepared from sodium meta arsenite (As₂O₃).

2.2 Biomass preparation

For the present investigation, banana peel (BP) was collected from fruit stall located near Indian institute of Technology Roorkee campus, Uttarakhand, India. The grime content of BP was removed by repeated washing with distilled water and used it as biosorbent. Initially the moisture content of biosorbent was air-dried for 4-5 hours and then kept inside the oven for about 24 hrs at 50°C. Subsequently, the dried BP biomass was grounded and sieved (range 1.18 mm to 425 μm) and stored in container. Morphology and characterization of solid BP biomass were determined by using Scanning Electron

Microscopy (SEM) and Fourier Transform Infrared Spectroscopy (FTIR). Percentage weight of chemical compositions available on the surface of BP biomass was determined through EDX (Energy Dispersive X-ray Spectroscopy) analysis.

2.3 Batch 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 7, reaction temperature of 35°C, dosage of 8 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 diethyl dithiocarbamate) method [12] at a wavelength (λ) of 540 nm by occasional crosschecking with ICP-MS (Perkin Elmer model ELAN-DRC-e).

The percentage removal of As(III) ion was calculated as follows [2]

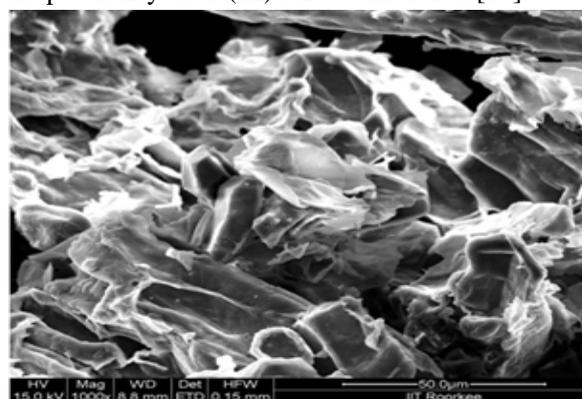
$$\text{Biosorption (\%)} = \frac{(C_i - C_f)}{C_i} \times 100 \dots\dots (1)$$

where, C_i and C_f are the initial and final concentrations of As(III) ion present in the biosorption studies.

3. RESULTS AND DISCUSSIONS

3.1 Characterization of biosorbent

Figure 1 (a) represents the characterization of BP biomass. Scanning Electron Microscopy (SEM) pictorially represents the porous structure and an irregular surface of BP biomass. The presence of voids on the surface of BP biomass revealed that the possibility of As(III) ion accumulation [13].



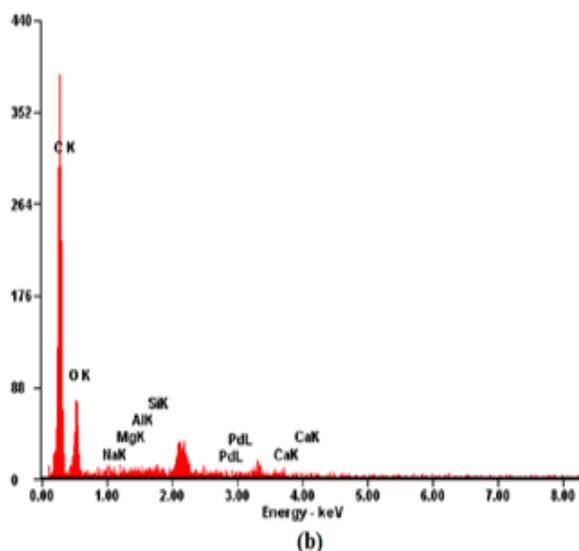


Figure 1: (a) SEM micrograph of BP biomass and (b) EDX analysis of BP biomass

EDX analysis of BP biomass has been represented in the figure (b). It showed the percentage weight of chemical compositions available on the surface of BP biomass were as follows: 49.60% of C, 28.34% of O, 12.02% of K, 1.46% of Si, 2.52% of Ca, 0.56% of Na, 0.67% of Al, and 0.73% of Mg. Hence the existence of proteins and polysaccharides inside the biomass cell cover were observed [6].

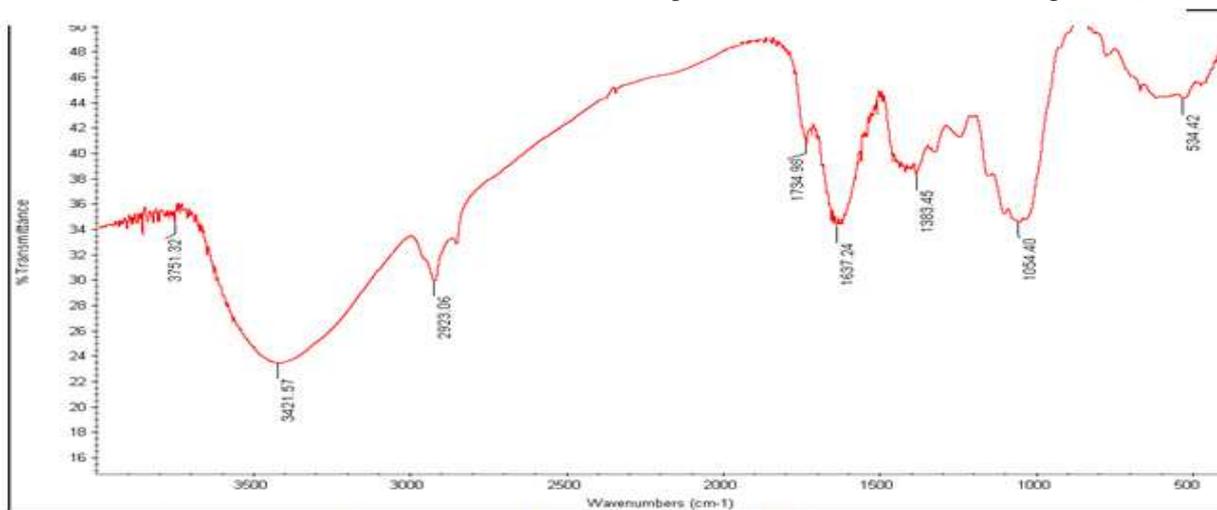


Figure 2: FTIR spectrum of BP biomass (3500 – 500 cm^{-1})

Figure 2 shows Fourier Transform Infrared (FTIR) analysis of BP biomass. The peak at 3421.57 cm^{-1} was attributed to N-H and O-H functional groups.

The C-H stretching vibration occurred at 2923.06 cm^{-1} which represents the aliphatic nature of the adsorbent. The absorption bands at around $1734.98 - 1383.45 \text{ cm}^{-1}$ were characteristics of C=C in aromatics rings. Furthermore, peaks at $1054.40 - 534.42 \text{ cm}^{-1}$ were attributed to Si-O stretching and Si-O bending indicating of the silica presence [14].

3.2 Effect of pH and temperature

From the figure 3, it was observed that percentage removal of As(III) ion increased with pH of the solution and reached to an optimum value of 86% (removal) at pH 7.

As the pH value became lower than 7, electrostatic repulsion between metal ion and H^+ ion increased and low removal of As(III) ion was obtained. At the pH over 7, electrostatic repulsion decreases due to low positive charge density on the sorption sites and the metal adsorption process enhances. From the literature reports, the maximum removal of As(III) ion occurred at neutral conditions (pH of about 6 to 8) [7, 15].

As the temperature increased percentage removal of As(III) ion also increased up to 35°C and then decreased due to breaking down of As(III) ion bond on the surface of BP biomass at higher temperature ($>35^\circ\text{C}$) as shown in figure 3 [16]. It

was evident that sorption of As(III) ion onto the biosorbent was temperature dependent. Further increased in temperature

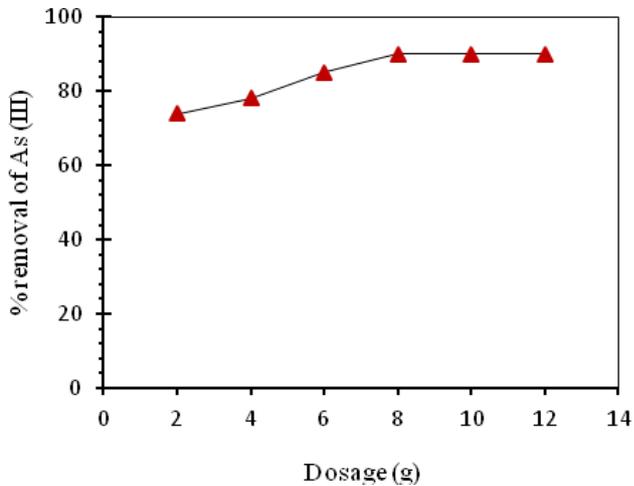


Figure 3: Effect of pH/Temperature (°C) on biosorption of As(III) ion ($C_i = 10 \text{ mg/l}$, $P_c = 1.18 \text{ mm}$, $d_c = 8 \text{ g}$, $\text{rpm} = 180$) has no significant percentage removal of As(III) ion, thus optimum temperature was considered as 35°C.

3.3 Effect of dosage

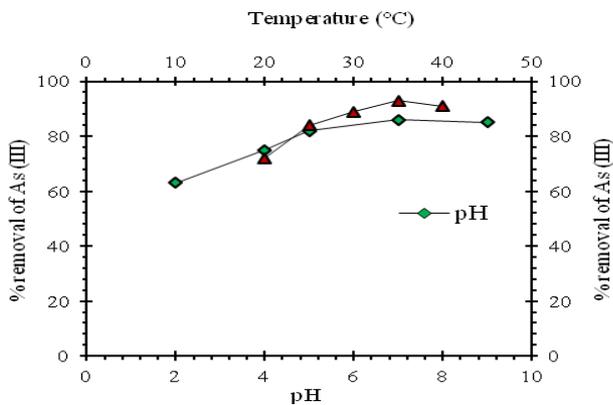


Figure 4: Effect of dosage (g) on biosorption of As(III) ion ($C_i = 10 \text{ mg/l}$, $t_c = 90 \text{ min}$, $\text{pH} = 7$, $\text{rpm} = 180$)

Figure 4 shows that the maximum removal of As(III) ion was observed at 8 g under the given experimental condition. Increase in the biosorbent dose results in the increase in the number of active sites, which lead to increase in the percentage removal of As(III) ion [17]. However no significant increase in the percentage removal was observed with the increase in biosorbent concentration beyond 8 g/l. This may be due to the two stages of As(III) ion biosorption (i.e. fast

formation of monolayer followed by slow plateau stage). Hence, the optimum dose of BP biomass for removal of As(III) ion from liquid phase could be taken as 8 g/l BP biomass. For further studies an optimum dosage of biosorbent has been used.

3.4 Effect of contact time

The effect of contact time on removal of As(III) ion onto BP biomass surface was investigated as shown in figure 5. At the initial stage of experiment the rapid removal of As(III) ion was obtained and later on rate of removal became slow and then reached optimum state (90 min). Further extension of contact time (>90 min) did not significantly effects percentage removal of As(III) ion due to the accumulation arsenic species [18]. Hence, the batch experiment contact time was considered as 90 min on biosorption of As(III) ion from liquid phase.

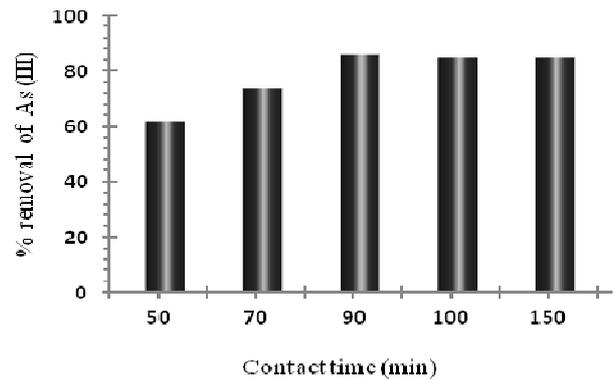


Figure 5: Effect of contact time (min) on biosorption of As(III) ion ($C_i = 10 \text{ mg/l}$, $P_c = 1.18 \text{ mm}$, $\text{pH} = 7$, $d_c = 8 \text{ g}$, $\text{rpm} = 180$)

3.5 Equilibrium studies

To describe the equilibrium state for As(III) ion biosorption experiments, Langmuir isotherm and Freundlich isotherm were tested. Langmuir isotherm assumes that there are a finite number of binding sites having the same affinity for adsorption of mono layer and there is no interaction between adsorbed molecules [19]. The linearization form of equation is expressed as

$$q_e = \frac{K_L \times C_e}{(1 + b \times C_e)} \dots\dots\dots (2)$$

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 assumes that the adsorption energy of a metal binding to a site on an adsorbent depends on whether the adjacent sites are already occupied or not [20]. The empirical form of equation can be expressed as

$$q_e = K_f \times C_e^{(1/n)} \dots\dots\dots (3)$$

where K_f and n are constants for adsorption capacity (l/mg) and adsorption intensity, respectively. Batch experiments of biosorption of As(III) ion onto BP biomass followed Freundlich isotherm model best with high linear regression coefficients (R^2) under optimum conditions as shown in figure 6 and table 1, which revealed that biosorption occurred on heterogeneous surface of solid biomass.

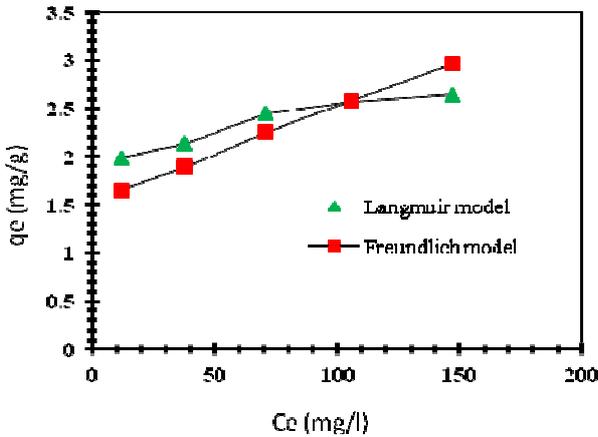


Figure 6: Langmuir and Freundlich models for As(III) ion removal mediated by biosorption onto BP biomass surface (particle size = 1.18 mm, dosage = 8 g, agitation rate = 180 rpm and pH 7). Experimental best data points are predicted by Freundlich equation.

Isotherm model	Temp. (°C)	Model parameters
Langmuir model	35	$K_L = 1.03$, $b = 0.29$, $R^2 = 0.928$
Freundlich model	35	$K_f = 0.78$, $n = 1.35$, $R^2 = 0.993$

Table 1: Parameters of Langmuir and Freundlich models for the biosorption of As(III) ion onto BP biomass

3.6 Kinetic studies

In the present investigation, the kinetic mechanism that controls the biosorption process onto BP biomass was evaluated by using pseudo-first-order and pseudo-second-order models. The Lagergren pseudo first order model [3] can be expressed as

$$\frac{dq}{dt} = K_1(q_e - q) \dots\dots\dots (4)$$

where K_1 is the pseudo first order rate constant (h^{-1}). The graph of pseudo second order model has been represented in figure 7 (a).

The biosorption kinetic data can be described by pseudo second-order equation [21].

$$\frac{dq_t}{dt} = K_2(q_e - q)^2 \dots\dots\dots (5)$$

The initial sorption rate, h (mg/g.h) at $t \rightarrow 0$ is defined as

$$h = K_2 q_e^2 \dots\dots\dots (6)$$

The equilibrium sorption capacity (q_e) and the initial sorption rate (h) along with the pseudo second order constant K_2 (g/mg.h) can be determined from slope and intercept of the plot of t/q_t versus t . The graph of pseudo second order model has been represented in figure 7 (b). From the table 2, it was evident that biosorption of As(III) ion onto BP biomass follows pseudo second order model best with high linear regression coefficients ($R^2 = 0.998$), which revealed that the rate limiting step was chemisorption involving valance forces through sharing or exchange of electrons between As(III) ion [22].

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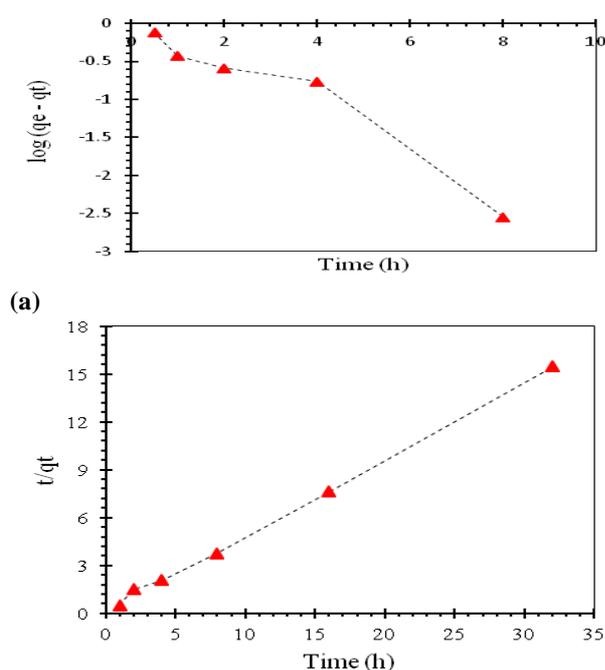


Figure 7: Study of kinetic reaction model (pH = 7, temperature = 35°C, dosage = 8 g and 180 rpm). (a) Pseudo first order model, and (b) Pseudo second order model. Experimental best data points are predicted by pseudo-second order equation.

Metal ion	Experimental q_e (mg/g)	Pseudo first order model			Pseudo second order model		
		Calculated q_e (mg/g)	K_1 (h^{-1})	R^2	Calculated q_e (mg/g)	K_2 (g/mg.h)	R^2
As (III)	0.843	0.985	0.902	0.938	0.683	0.382	0.998

Table 2: Summary of kinetic model parameters for the biosorption of As(III) ion onto BP biomass at 35°C

4. CONCLUSION

In the present investigation it was evident that BP biomass can be used as an economically feasible biosorbent for the removal of As(III) ion from contaminated water. The sorption of As(III) ion was found to be highly pH and temperature dependent. It was observed that maximum percentage removal of As(III) ion was observed as 82.23% at 0.843 mg/g uptake capacity, pH of 7, dosage of 8 g, contact time of 90 minutes and reaction temperature of 35°C, respectively. The equilibrium sorption data was best represented by Freundlich isotherm model ($R^2=0.993$). Moreover, it was found that sorption kinetics favour pseudo

second order model ($R^2=0.998$) compared to pseudo first order model ($R^2=0.938$).

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