

Studies on surface characterisation and isotherm modelling: Biosorption of arsenic(III) onto low cost biosorbent derived from orange peel

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The paper described the removal of As(III) from contaminated water by orange peel (OP) by a low cost biosorbent. The effects of various parameters such as mesh size, pH, temperature, adsorbent dosage and contact time were studied in batch experimental setup. Physiochemical analysis of OP biomass was carried out through scanning electron microscopy (SEM) and fourier transmission infrared spectroscopy (FTIR). It was observed that the pH had a strong effect on biosorption capacity. At the optimum treatment conditions of pH (7), temperature (30°C), contact time (90 min) and adsorbent dosage (4 g), OP biomass was found to be effective for the removal of As(III) with 82.45% sorption efficiency at a concentration of 50 mg/l As(III), and thus uptake capacity was 1.18 mg As(III)/gm of biomass. To establish the most appropriate correlation for the equilibrium curves, isotherm studies were performed for As(III) ion using Freundlich and Langmuir adsorption isotherms. Langmuir isotherm was found to be best fitted to equilibrium sorption data with higher linear correlation coefficient ($R^2 = 0.992$). A low cost OP biosorbent shows a potential and promising simple method for the removal of As(III) ion.

Keywords: As (III) ion, Biosorption, OP biomass, Optimization of parameters, Sorption isotherms

Introduction

Contamination of potable ground water with arsenic and its removal in water treatment have become the focus of increasing attention worldwide. In natural waters, usually inorganic arsenic in the form of As(III) and/or As(V) is found to be prevalent and is more toxic than organic arsenic¹⁻³. Arsenic is one of the contaminants found in the environment which is notoriously toxic to man and other living organisms. It is a matter of worry that although WHO and USEPA lowered the guideline value for arsenic from 50 to 10 ppb, some countries like Bangladesh and China still have 50 ppb arsenic in drinking water⁴. The presence of arsenic in ground water is mostly due to minerals dissolving naturally from rocks and soils. Moreover, biological and mining activities, geochemical reactions, volcanic emissions, use of arsenic additives, pesticides, herbicides and crop desiccants make the problem more serious for animal and human beings⁵⁻⁷.

Arsenic-contaminated water may cause numerous diseases of the skin and internal organs. An inorganic form of arsenic is highly toxic compared to organic arsenic. Inorganic arsenate (AsO_4^{3-}) and arsenite

(AsO_3^{3-}), referred to as As(V) and As(III) are most common in natural waters⁸. Although, As(V) tends to be less toxic compared to that of As(III), it is thermodynamically more stable due to which it predominates under normal conditions and becomes the cause of major contaminant in ground water. Most cited example is that the ground water in inner Mongolia of China is mainly affected by As(V). Hence removal of As(V) is potentially important as As(III) irrespective of toxicity^{9,10}. Many technologies, including co-precipitation with FeCl_3 or alum, adsorption onto coagulated floc, ion-exchange resin, reverse osmosis, and membrane techniques, have been used to remove As from aqueous solution¹¹. In these methods, however, the adsorption techniques are simple, low cost, highly efficient and convenient, and have the potential for regeneration and sludge-free operation. So far, various adsorbents for arsenic removal have been developed that include such materials as metal-loaded coral limestone, hematite and feldspar, activated carbon, activated alumina and hydrous zirconium oxide¹²⁻¹⁴. However, most of these adsorbents entail several problems in terms of efficiency and cost. Limitations in the conventional adsorbents advise for new alternative adsorbent for the removal of arsenic from aqueous solutions. Plant waste is abundant in nature,

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inexpensive as they are of no or very low economic value¹⁵. Therefore, the purpose of this study was to evaluate the feasibility of using orange peel without any pretreatment as an alternative sorbent for removal of As (III) ion from contaminated water. The parameters affecting the biosorption process such as mesh size, pH, dosage, contact time and temperature were studied. Moreover, sorption equilibrium was evaluated for Langmuir and Freundlich isotherms in this work.

Materials and Methods

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 (III) was prepared from sodium meta arsenite (As_2O_3).

Biosorbent Preparation

Orange peel (OP) was obtained from local fruit shop and was washed three times with tap water followed by double wash with deionized water. The biosorbent was allowed to sundry for two days after washing. Dried biosorbent was grounded and sieved (425-925µm) and used as biosorbent.

Characterization of biosorbent

Fourier Transform Infrared Spectroscopy (FTIR) analysis of the biomass sample was done by making 1% pellet of spectrophotometric potassium bromide (KBr) using Shimadzu FTIR instrument, 3400 model. The range of FTIR analysis was 4000 – 400 cm^{-1} . Scanning Electron Microscopy (SEM) of the metal unloaded and loaded biomass sample was done at 20 kV using FEI Quanta 200 FEG micrograph, USA. Percentage of volatile matter, moisture content, ash and fixed carbon were determined through proximate analysis.

Batch sorption studies

Batch biosorption experiments were carried out using a thermostatically orbital shaker at 180 rpm at 30°C in 100 ml conical flasks by adding OP biomass suspended in 100 ml of liquid medium containing 50 mg/l As(III). The effect of initial solution pH, ranging 2 to 8, was determined by agitation 4 g of orange peel at 50 mg/l of As (III) concentration. Agitation contact time was kept for 90 min which was sufficient to reach equilibrium with a constant agitation speed of 180 rpm at 30°C. The desired pH was adjusted with 1N NaOH or 1N HCl

using a pH meter (pH 510 Eutech Instruments, Cyberscan). After the biosorption studies on effect of parameters viz. pH, temperature, mesh size, dosage and contact time, the sample was filtered and the filtrate was analysed for arsenic concentration by Inductively coupled plasma mass spectrometry (ICP-MS). The experiments were conducted in duplicate and the negative controls (without biosorbent) were simultaneously carried out. The amount of arsenic sorbed per unit mass of the biosorbent (mg/g) was evaluated using following equation¹⁵

$$q_t = (C_i - C_e) \frac{V}{W} \quad \dots (1)$$

where C_i and C_e were initial and equilibrium concentrations of As(III) (mg/l), q_t , 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.

Method of Analysis

After biosorption, biosorbents were separated from the solution by passing through a Whatman grade no.1 (11 µm) filter and the filtrate was subjected to residual As (III) concentration determination. The residual concentration of As (III) was analyzed by ICP-MS (Perkin Elmer model ELAN-DRC-e). The percent removal of As (III) ion by orange peel biomass was calculated using the equation¹⁶

$$\text{Removal (\%)} = \frac{(C_i - C_f)}{C_i} \times 100 \quad \dots (2)$$

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

Sorption isotherms

The Langmuir sorption isotherm describes that the uptake occurs on a homogeneous surface by monolayer sorption without interaction between sorbed molecules¹⁷. It has been mathematically described as follows

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

The linearization of above equation results in equation (4)

$$\frac{C_e}{q_e} = \frac{1}{b \times K_L} + \frac{C_e}{K_L} \quad \dots (4)$$

Table 1—Physiochemical characteristics of OP biomass

Characteristics analysis	OP biomass			
Proximate analysis	Moisture (%)	Ash (%)	Volatile (%)	Fixed carbon (%)
	8.9	6.5	53.9	30.2
CHNS analysis	C (%)	H (%)	N (%)	S (%)
	43.41	3.43	2.74	0
Particle size (μm) = 425	Heat intensity (kJ/g) = 17.65			
BET surface area (m^2/g) = 128.69	Bulk density (kg/m^3) = 19.03			

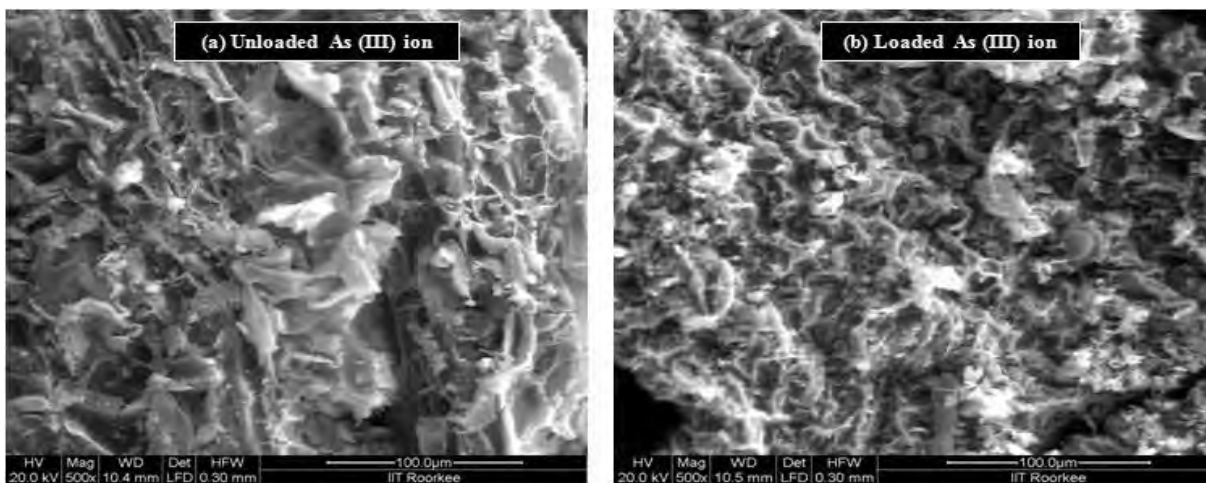


Fig.1—Scanning electron microscopy analysis of OP biomass (a) unloaded As(III) ion and (b) loaded As(III) ion

where K_L is binding constant and b is sorbent capacity

The Freundlich isotherm has been found to be suitable for heterogeneous surfaces and for extremely low concentrations. The Freundlich isotherm is an empirical model relating the adsorption intensity of the sorbent towards adsorbent. The isotherm was adopted to describe reversible adsorption and not restricted to monolayer formation¹⁸. Mathematical expression of Freundlich model can be expressed as

$$q_e = K_f \times C_e^{\frac{1}{n}} \quad \dots (5)$$

where K_f and n are constants for adsorption capacity (l/mg) and adsorption intensity, respectively. Linear form of isotherm can be expressed as

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \quad \dots (6)$$

The hybrid fractional error function (HYBRID) was used as a criterion in finding the best isotherm model to fit the experimental data¹⁹. The HYBRID is given by following equation:

$$HYBRID = \frac{100}{n-p} \sum_{i=1}^n \left[\frac{(q_{e,exp} - q_{e,calc})}{q_{e,exp}} \right]_i \quad \dots (7)$$

Results and Discussion

Physiochemical characteristics of biosorbent

Moisture content of the biosorbent was determined by keeping the sample at 105°C for an hour inside the furnace. Volatile matter was determined by keeping the sample in cylindrical crucible with lid for 7 minutes at temperature of 925°C. Ash content was determined by keeping the sample in flat crucible for one hour at temperature of 800°C. Fixed carbon was determined by deducting the moisture, volatile matter and ash from the original weight of the sample (table1).

SEM and FTIR analysis of biosorbent

Figures 1 (a) and (b) represent the SEM photographs of As(III) ion unloaded and loaded biomass. It shows that the surface texture or topology of unloaded As(III) ion onto the surface of OP biomass has highly mesoporous, rough and heterogeneous in nature

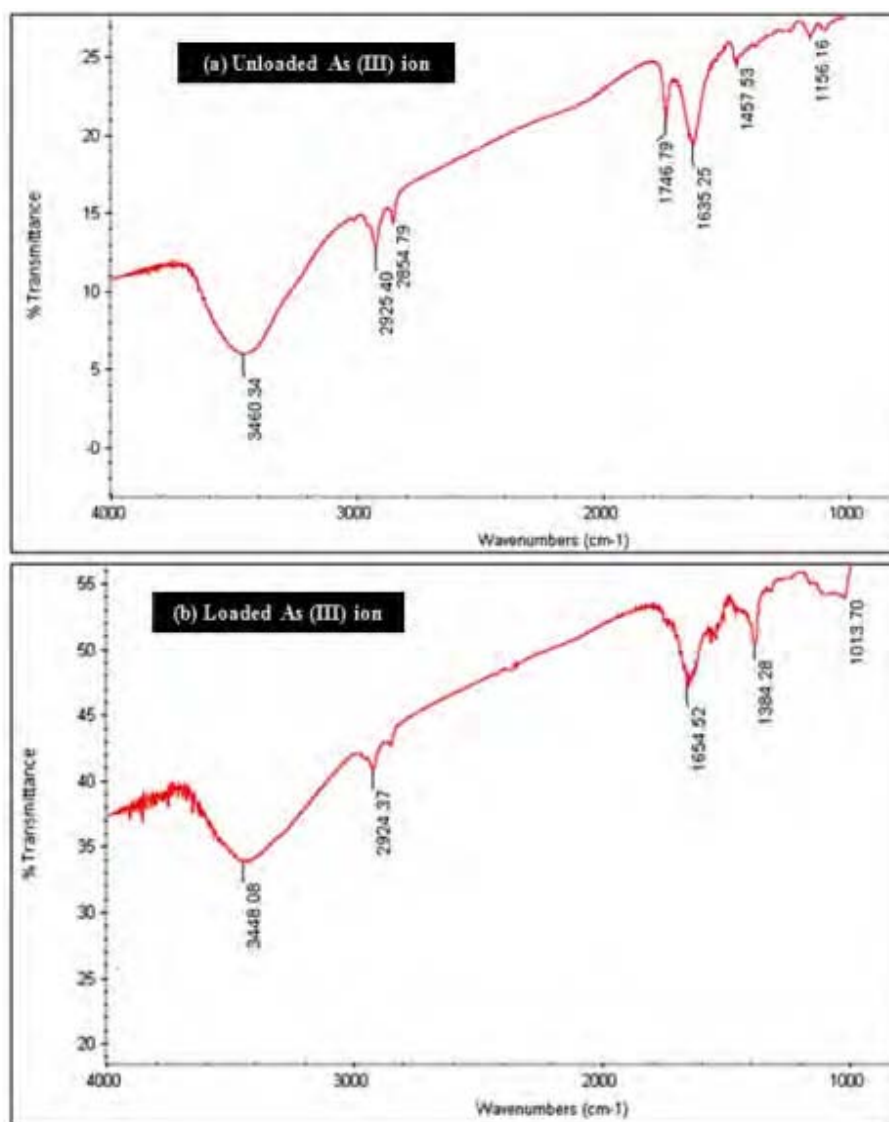


Fig. 2—FTIR spectrum of OP biomass (a) unloaded As(III) ion and (b) loaded As(III) ion

consisting of protrusions. The protrusions seemed to be elongated deeply inside surface of biosorbent with deep void space which in turn lead to heterogeneous and rough surface texture. The roughness of surface indicates the high surface area meant for As(III) ion adherence. In the case of loaded As(III) ion onto OP biomass surface, it was speculated that high accumulation of As(III) ion (As(III) ion impregmentation) resulting in loss of surface porosity and roughness^{20,21}, as can be seen from figures 1 (a) and (b).

FTIR spectroscopic analysis was conducted in the range of 1000–4000 cm^{-1} to find out the types of functional groups present on the surface of OP biomass. Fig. 2 (a)

shows that FTIR analysis of unloaded As(III) onto OP biomass surface. The broad peak 3460.34 cm^{-1} indicating presence of hydroxyl groups of macromolecular association (cellulose, pectin, etc.). The band between 2925.40 - 2854.79 cm^{-1} shows the presence of C-H asymmetric stretching vibration. Carboxylic acid salts typically show a strong, characteristic asymmetric stretching absorption from the CO_2 group in the 1746.79 - 1635.25 cm^{-1} region. The regions around 1456.53 - 1156.16 cm^{-1} were due to the presence of -CN and C-C stretching²²⁻²⁴. Fig. 2 (b) shows the FTIR spectra of As(III) loaded OP biomass. The shifting and broadening of peaks around 3448.08 cm^{-1} indicated the presence of

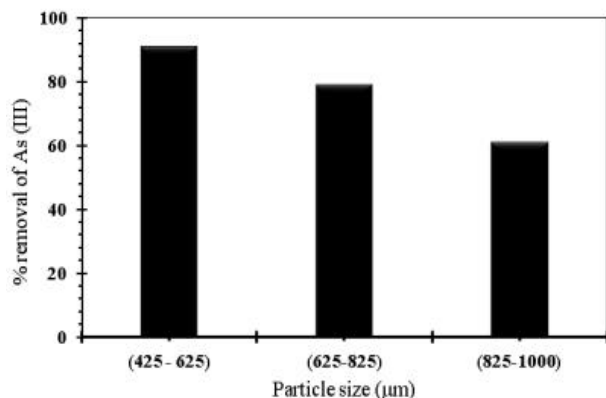


Fig. 3—Effect of mesh size on the % removal of As (III) ion onto OP biomass

-NH and -OH functional bounded groups. The CH_3 asymmetric stretching vibration occurred at 2924.37 cm^{-1} . Furthermore, peaks at around $1654.52 - 1013.70 \text{ cm}^{-1}$ express the enhanced character of carbonyl stretching ($\text{C}=\text{O}$) on the surface of OP biomass. Compared to unloaded biomass almost all the peaks of functional groups having affinity for As(III) ion disappeared or diminished in As(III) loaded biomass, indicating the involvement of biosorbent surface chemistry in As(III) ion adsorption across liquid phase.

Effect of mesh size

The effect of biosorbent's mesh size was studied in the range of $425\mu\text{m}$ to $925\mu\text{m}$ mesh size ($425\text{-}625\mu\text{m}$, $625\text{-}825\mu\text{m}$, $825\text{-}1000\mu\text{m}$) to check the maximum biosorption of As(III) ion. From fig. 3, it is evident that the smallest mesh size ($425\text{-}625\mu\text{m}$) was found best suited for biosorption as particles with smallest size presents a larger surface area. From the literature reports, it was found that mesh size is inversely related with particle size. As the mesh size is larger, the size of particle is accordingly decreased which results in more surface area available for biosorption²⁵.

Effect of pH and dosage on As (III) ion biosorption

The pH of sorption mechanism had a strong influence on the removal of As(III) ion. It was observed that maximum percentage removal of As (III) was achieved at pH 7 as shown in fig. 4. From the literature reports it was found that better removal of As(III) was achieved at pH 7².

The effect of sorbent dosage on the removal of As(III) ion is also represented in fig. 4, which shows that sorption efficiency increased as the dosage of sorbate increased.

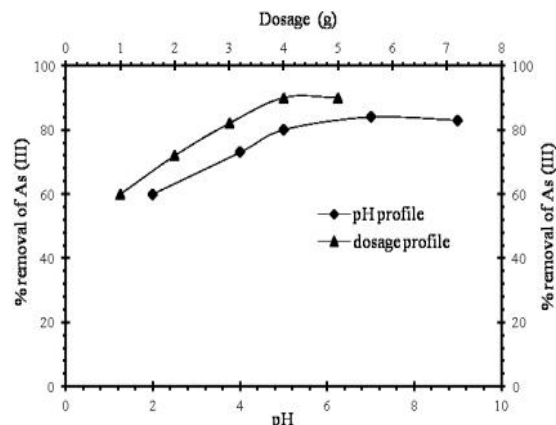


Fig. 3—Effect of mesh size on the % removal of As (III) ion onto OP biomass

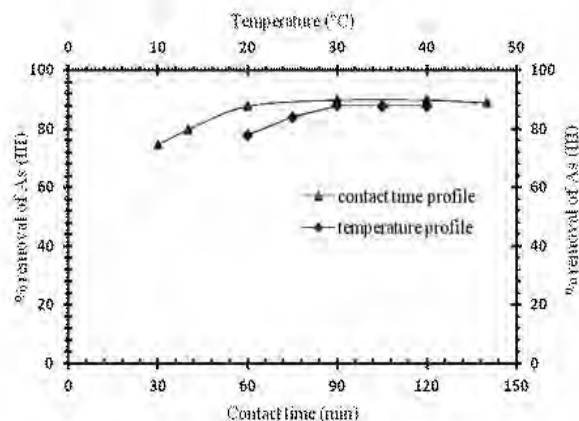


Fig. 5—Effect of contact time/temperature on the % removal of As (III) ion onto OP biomass ($C_0 = 50 \text{ mg/l}$ and 180 rpm)

Because of at higher dosage, more pores and surface were available²⁶. Maximum percentage removal of As(III) ion occurred at dosage of 4 g. Increase in dosage after 4 g resulted in no further removal of As(III) ion since internal saturations of pores occurred.

Effect of contact time and temperature on As (III) biosorption

At initial stage percentage removal of As(III) onto biosorbent surface was rapid and apparent equilibrium achieved after 90 mins as shown in fig. 5. A rapid uptake rate of sorbate at initial stage was due to the availability of a large number of sorption sites at the onset of the process. The sticking probability was also high on the bare surface accounting high sorption rate. Further, the material was exclusively mesoporous and therefore, the diffusion of solute into the pores appears to be easier. Faster solute removal as well as low equilibration time attributes highly favourable sorptive interactions¹⁶.

Table 2—Isotherm parameters for the removal of As (III) by OP biomass ($t=90$ min, $C_0=50$ mg/l, 180 rpm and $T=30^\circ\text{C}$)

Freundlich isotherm model				Langmuir isotherm model			
K_F (mg/g) (l/mg) $^{-1/n}$			HYBRID	b (mg/g)	K_L (l/mg)		HYBRID
1.145	4.268	0.918	57.42	3.432	0.027	0.992	46.33

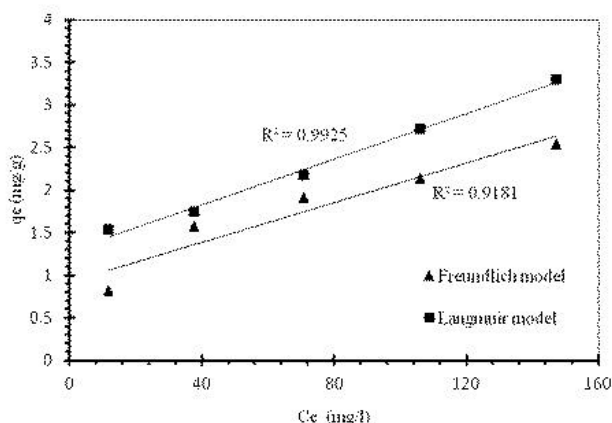


Fig 6—Equilibrium biosorption isotherms for As (III) ion onto OP biomass, $t=90$ min, $C_0=50$ mg/l, 180 rpm, dosage=4 g and $\text{pH}=7$. Experimental best data points are predicted by Langmuir equation

The plot of As(III) sorbed by OP biomass at initial concentration of 50 mg/l by varying the temperature from 10°C to 40°C is shown in fig. 5. With the increase in temperature, removal of As(III) increased upto 30°C and after 30°C , it was decreased due to breaking down of As(III) ion bond on the surface of OP biomass at higher temperature. Temperature of the sorption medium was important for energy dependent mechanisms in biosorption²⁷. For this reason, 30°C was chosen to carry out equilibrium studies.

Sorption isotherms

The experimental data were fitted with the selected isotherm model. Fig. 6 represent the isotherm plot for sorption of As (III) ion onto the biosorbent. Constant parameters, correlation coefficient HYBRID values of each model obtained are given in table 2. The adsorption of As(III) ion is best explained by Langmuir model as the value of correlation regression is near to unity ($R^2 = 0.992$) and the maximum uptake capacity of As (III) ion onto OP biomass is 1.18 mg/g. The R^2 value (given in table 2) alone is insufficient in determining the best isotherm model to represent the experimental data. The HYBRID value of isotherm models is tested. It was observed that HYBRID value of Langmuir model is

smaller as compared to that of Freundlich model. So, it can be concluded that Langmuir model is best suited for the experimental data and represents that sorption occurs monolayer of solid/liquid phase interaction.

Conclusions

Orange peel (OP) biomass has been used in the present work to biosorb As(III) ion across liquid phase in batch test. The FTIR analysis of the OP surface indicated that the unloaded OP surface was enriched with the functional groups like carboxyl, methyl, hydroxyl and carbonyl. Additionally, the SEM study of metal unloaded OP surface showed that the surface of the biosorbent was quite porous, rough and full of protrusions. Maximum percentage removal of As (III) ion was obtained as 82.45% at temperature of 30°C , contact time of 90 min, dosage of 4 g, pH 7 and 180 rpm, respectively. Equilibrium sorption data was found to be well described by Langmuir isotherm. Hence biosorption of As(III) ion onto the surface of OP biomass occurs by monolayer of solid/liquid phase interaction.

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