



## Biosorption of arsenic from aqueous solution using agricultural residue 'rice polish'

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### ABSTRACT

'Rice polish' (an agricultural residue) was utilized successfully for the removal of arsenic from aqueous solution. Various parameters viz. pH, biosorbent dosage, initial metal ion concentration and temperature were studied. Langmuir, Freundlich and Dubinin–Radushkevich (D–R) isotherm models were used and the system followed all three isotherms, showing sorption to be monolayer on the heterogeneous surface of the biosorbent. The maximum sorption capacity calculated using Langmuir model was 138.88  $\mu\text{g/g}$  for As(III) at 20 °C and pH 7.0 and 147.05  $\mu\text{g/g}$  at 20 °C and pH 4.0 for As(V). The mean sorption energy ( $E$ ) calculated from D–R model indicated chemisorption nature of sorption. Study of thermodynamic parameters revealed the exothermic, spontaneous and feasible nature of sorption process in case of both As(III) and As(V). The pseudo-second-order rate equation described better the kinetics of arsenic sorption with good correlation coefficients than pseudo-first-order equation. Mass transfer, intraparticle diffusion, richenber and elovich models were applied to the data and it was found that initially the sorption of arsenic was governed by film diffusion followed by intraparticle diffusion. Rice polish was found to be efficient in removing arsenic from aqueous solution as compared to other biosorbents already used for the removal of arsenic.

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### 1. Introduction

Arsenic poisoning has emerged as a major threat to human society in recent past. Although arsenic has been known as one of the most toxic substance since long but recently its increasing role as a contaminant of water has gained attention of researchers throughout the world because of its continuously increasing concentration in water sources through geothermal dissolution of minerals and ores [1]. The major industrial processes that contribute to anthropogenic arsenic contamination of water resources are mining, smelting of non-ferrous metals and burning of fossil fuel [2,3]. It has been estimated that 70% of the world arsenic production is used in timber treatment as copper chrome arsenate (CCA) and 22% in agricultural chemicals, and the remainder in glass, pharmaceuticals and non-ferrous alloys [3]. The toxicity of arsenic varies greatly according to its oxidation state and form (i.e. organic or inorganic). Inorganic arsenic can occur in the environment in several forms, e.g. As(0) (metalloid arsenic), As(III) (arsenites,  $\text{AsO}_3^{3-}$ ), and As(V) (arsenates,  $\text{AsO}_4^{3-}$ ), but in natural waters and thus in drinking water, it is mostly found as As(III) and As(V) [4]. Organic arsenic species, abundant in seafood, are much

less harmful to health and readily eliminated by the body. Among inorganic species As(III) is 60 times more toxic than As(V), due to its greater cellular uptake [5]. Arsenic poisoning leads to death from multisystem organ failure by allosteric inhibition of sulfhydryl containing essential metabolic enzymes. It also interferes with some biochemical processes involving phosphorous due to the similarity in their chemical properties. Arsenic exposure leads to black foot disease, diffused and spotted melanosis, diffused and spotted keratosis, nonpitting oedema, Bowen's disease and gangrene. It can cross the placental membrane and is known to be teratogenic to animals. It is also known to cause skin, liver and lung cancer [6–9]. The maximum allowed concentration of arsenic, according to WHO and US EPA, in drinking water is 10  $\mu\text{g/L}$  [10]. However, arsenic concentrations, about 100 times more than the permissible limit, are found in many parts of the world. According to a survey conducted by WHO in 2006, the number of people poisoned by arsenic in India and Bangladesh alone is about 70 million, perhaps the largest poisoning in the world's history [1,11,12]. The conventional techniques, utilized for removing arsenic species from aqueous streams such as solvent extraction, chemical precipitation as synthetic coagulants, ferrihydrite precipitation, iron co-precipitation, ion exchange and reverse osmosis, are associated with disadvantages such as incomplete metal removal, high cost of reagent, and energy requirements [6,8,13]. Adsorption has emerged as an alternative to these traditional methods with advantage of being technically easy, and

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**Nomenclature**

$b$	Langmuir constant related to the free sorption energy (L/ $\mu\text{g}$ )
$C_{\text{Ae}}$	equilibrium concentration of solute on the sorbent ( $\mu\text{g/L}$ )
$C_e$	equilibrium concentration of solute in bulk solution ( $\mu\text{g/L}$ )
$C_i$	initial concentration of solute in the solution ( $\mu\text{g/L}$ )
$C_t$	concentration of solute in the solution at any time ( $\mu\text{g/L}$ )
$F$	polar potential
$\Delta G^\circ$	Gibb's free energy change ( $\text{kcal mol}^{-1}$ )
$h$	initial sorption rate of pseudo-second-order sorption ( $\mu\text{g g}^{-1} \text{min}^{-1}$ )
$\Delta H^\circ$	enthalpy change ( $\text{kcal mol}^{-1}$ )
$k$	constant obtained by multiplying $Q^0$ and $b$ (Langmuir's constant)
$K_F$	Freundlich constant indicative of the relative sorption capacity of the sorbent ( $\mu\text{g/g}$ )
$k_s$	equilibrium rate constant of pseudo-first-order sorption ( $\text{min}^{-1}$ )
$k_{\text{id}}$	rate constant of intraparticle pore diffusion ( $\mu\text{g g}^{-1} \text{min}^{-1/2}$ )
$K_c$	equilibrium constant
$k_2'$	equilibrium rate constant of pseudo-second-order sorption ( $\text{g } \mu\text{g}^{-1} \text{min}^{-1}$ )
$m$	mass of the sorbent per unit volume (g/L)
$n$	Freundlich constant indicative of the intensity of sorption
$Q^0$	Langmuir constant related to the monolayer sorption capacity of ( $\mu\text{g/g}$ )
$q_e$	amount of solute adsorbed per unit weight of sorbent at equilibrium ( $\mu\text{g/g}$ )
$q_t$	amount of solute adsorbed per unit weight of sorbent at any time ( $\mu\text{g/g}$ )
$R$	universal gas constant ( $8.314 \text{ J}/(\text{mol K})$ )
$R_L$	equilibrium parameter
$\Delta S^\circ$	entropy change ( $\text{cal mol}^{-1} \text{K}^{-1}$ )
$S_s$	outer specific surface of the sorbent particle per unit volume of particle free slurry ( $\text{cm}^{-1}$ )
$T$	absolute temperature (K)
$t$	time (min)
$t_{1/2}$	time for half of the sorption
$V$	the volume of particle-free slurry solution (L)
$W$	the weight of the sorbent (g)
$X_m$	maximum sorption capacity of the sorbent ( $\text{mol/g}$ )
<i>Greek letters</i>	
$\beta$	constant related to energy ( $\text{mol}^2/\text{kJ}^2$ )
$\beta_t$	mathematical function
$\beta_1$	mass transfer coefficient ( $\text{cm s}^{-1}$ )

has the potential for regeneration and sludge free operation. So far, various adsorbents for arsenic removal have been developed that include such materials as activated carbon, activated alumina, aluminum oxide, silica gel impregnated by ferric hydroxide, activated carbon impregnated with ferric hydroxide and tartaric acid, basic yttrium carbonate, metal-loaded coral limestone, hematite and feldspar, and hydrous zirconium oxide [14]. Most of these adsorbents however entail several problems in terms of efficiency and cost. At this juncture advances in the knowledge of biosorption has gained important credibility during recent years because of its ecofriendly nature, excellent performance, and low cost domestic

**Table 1**

Physicochemical properties of biosorbent rice polish.

Surface area ( $\text{m}^2/\text{g}$ )	452.00
Bulk density ( $\text{g}/\text{cm}^3$ )	0.3010
Particle size ( $\mu\text{m}$ )	<178
Porosity	0.39
Proximate analysis (%)	
Volatile matter	43.12
Moisture	8.3
Fixed carbon	30.14
Ash (oxides of Ca, Mn, Si, Fe, Mg, etc.)	18.44

technique for remediating even heavily metal loaded water [15]. Various biosorbents have been reported for efficiently accumulating arsenic from water [1,13,14,16–21]. However, there still lies a strong challenge in developing biosorbents for arsenic removal with high uptake efficiency, low cost and well-elucidated sorption mechanism. Rice polish, an undesirable agricultural residue, is a by-product of the rice milling industry. The estimated annual rice production of 500 million tonnes in developing countries, approximately 100 million tonnes of rice polish is available annually for utilization in these countries [22]. The compositions of rice polish are cellulose, hemi-cellulose, lignin, silica, extractives, water and mineral ash [23]. The high silica content (ca. 20%) gives it the structural strength as a sorbent without having to undergo a cross-linking process [24]. The present work aims to investigate the possible use of rice polish for the biosorption of arsenic from aqueous solution. The effects of various factors such as pH, biosorbent dosage, initial metal ion concentration and temperature on biosorption were systematically examined. The sorption capacity of rice polish was tested and compared with various other sorbents already used for the removal of arsenic. Further kinetic, thermodynamic and equilibrium studies have also been carried out.

**2. Materials and methods***2.1. Preparation and characterization of biosorbent*

Rice polish was used in experiments with double washing with double-distilled water to remove soluble lighter materials. The untreated rice polish was dried in an oven at  $60^\circ\text{C}$  over a period of 24 h and crushing and sieving to  $<178 \mu\text{m}$ . The surface area of rice polish was determined by a three point  $\text{N}_2$  gas adsorption method using quanta sorb surface area analyzer (model Q5-7, Quanta Chromo Corporation, USA). Density of biosorbent was determined using Densitometer. Particle size distribution analysis was carried out using a particle size analyzer (Model no. 11708, Malvern Instrument, USA). Porosity of the biosorbent was determined by porosimeter (model H: M7V, NGRI, Hyderabad, India). Percentage of volatile matter, ash and moisture were determined as given in Ref. [25]. All the measurements were taken in triplicate and results reported were either the concurrent value or as the average of them. Various physicochemical properties of the biosorbent, i.e. rice polish are given in Table 1.

*2.2. Preparation of standards and reagents*

All the chemicals used in the study were of analytical grade and used without further purification. Deionized double-distilled water was used for the preparation of standards, modifier and wash solution [for sample dispenser of atomic absorption spectrophotometer (AAS)]. Standards for calibration were prepared from As(III) standard reference [Sodium (meta)arsenite solution (arsenic atomic spectroscopy standard concentrate ampule)] purchased from Fluka chemicals. As(III) stock solution (1000 mg/L) for batch experiments was prepared by dissolving 1.320 g  $\text{As}_2\text{O}_3$  (Sigma–Aldrich) in mini-

imum volume (approx. 10 mL) of 5 M NaOH solution. It is neutralized with nitric acid. It is diluted with deionized double-distilled water upto 1000 mL to give 1000 mg/L of arsenic stock solution. As(V) stock solution (1000 mg/L) was prepared by dissolving 4.164 g of sodium arsenate ( $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$ ; Loba Chemicals) in deionized double-distilled water to make a solution volume of 1 L. The stock solutions were preserved with 1% trace metal grade nitric acid. The sodium borohydride ( $\text{NaBH}_4$ ) solution (0.4%) was made up of a mixture of  $\text{NaBH}_4$  and NaOH. The 500-mL  $\text{NaBH}_4$  solution was prepared by dissolving 2.5 g NaOH and 2.0 g  $\text{NaBH}_4$ , in this order, in deionized distilled water and diluting to mark. The  $\text{NaBH}_4$  reagent was always prepared immediately before use. The 5 M hydrochloric acid solution was prepared with 208.33 mL of concentrated HCl diluted to 500 mL. For the reduction of As(V) into As(III) 2 mL of (35–37%) HCl and 2 mL of 20% (w/v) potassium iodide was added to 20 mL of the standard or sample solution and left for about 15 min.

### 2.3. Batch sorption experiments

Batch experiments were carried out in Erlenmeyer flasks by adding rice polish in 50 mL of aqueous arsenic solution [As(III) and As(V)] of desired initial pH, metal ion concentration and temperature. The initial pH of the solution was adjusted by adding 0.1 M HCl and 0.1 M NaOH solution as required. The flasks were gently agitated in an electrically thermostated reciprocating shaker at 200 rpm for a period of 150 min. All the experiments were performed in triplicates at the desired initial conditions and the concurrent value was taken. The content of flask was separated from biosorbent by centrifuging at 15,000 rpm and was analyzed for remaining arsenic concentration in the sample. The amount of arsenic sorbed per unit mass of the biosorbent ( $\mu\text{g/g}$ ) was evaluated by using following equation:

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

where  $C_i$  and  $C_e$  are the arsenic concentrations in mg/L initially and at equilibrium, respectively,  $V$  the volume of the arsenic solutions in mL, and  $W$  is the weight of biosorbent in mg.

To study the effect of initial pH (2–10) on arsenic uptake by rice polish, sorption experiments were performed by using 50 mL of solution with initial arsenic concentration [As(III) and As(V)] of 1000  $\mu\text{g/L}$  and adsorbent dose of 20 g/L at temperature 20 °C. Effect of variation of initial metal ion concentration and contact time was studied with an initial arsenic concentration of 100, 500 and 1000  $\mu\text{g/L}$  and rice polish of 20 g/L; pH was kept at 7 for As(III) and at 4 for As(V) and contact time was varied from 10 to 150 min at 20 °C. The effect of temperature (20, 30 and 40 °C) on arsenic uptake was studied at initial arsenic concentrations of 1000  $\mu\text{g/L}$  and adsorbent dose of 20 g/L at pH 7 for As(III) and 4 for As(V).

### 2.4. Analysis of arsenic in aqueous system

A Shimadzu AA-6300 atomic absorption spectrophotometer was used as detector with hollow cathode lamp light source set at 193.7 nm wavelength, using 12 mA lamp current and 0.7 nm slit width, and with deuterium lamp for background correction. Instrument grade (98%) acetylene, delivered at 4.0 L/min at a pressure of 0.9 kg/cm<sup>2</sup>, was used to generate the flame for the AAS together with compressed air supplied at 17.5 L/min flow rate and 3.5 kg/cm<sup>2</sup> gas pressure. For hydride generation, the basic unit was the Shimadzu HVG-1, a continuous flow hydride generator which is linked to the AAS. High purity (99.99%) argon was used as purge gas at a rate of 70 mL/min and supply pressure of  $3.2 \pm 0.2$  kg/cm<sup>2</sup>. The instrument was calibrated from 5 to 20 ppb. Other range samples were diluted until results within the calibration range were obtained.

## 3. Theory

### 3.1. Sorption isotherms

Different isotherm models have been utilized for describing sorption equilibrium for wastewater treatment. Langmuir, Freundlich and Dubinin–Radushkevich equations are being used for present work. The study of isotherm was carried out by varying initial metal ion concentration from 100 to 1000  $\mu\text{g/L}$  at various temperatures (20–40 °C).

#### 3.1.1. Langmuir sorption isotherm

The Langmuir sorption isotherm describes that the uptake occurs on a homogeneous surface by monolayer sorption without interaction between sorbed molecules [26,27]. The linear form of the Langmuir isotherms may be represented as

$$\frac{C_e}{q_e} = \frac{1}{Q^0 b} + \frac{C_e}{Q^0} \quad (2)$$

The isotherm constants  $Q^0$  and  $b$  were calculated from the slope and intercept of plot between  $C_e/q_e$  and  $C_e$ .

#### 3.1.2. Freundlich sorption isotherm

The Freundlich sorption isotherm which describes the equilibrium on heterogeneous surfaces and the linear form of the isotherm can be represented as [27]

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (3)$$

The isotherm constants  $n$  and  $K_F$  were calculated from the slope and intercept of the plot  $\log q_e$  versus  $\log C_e$ .

#### 3.1.3. Dubinin–Radushkevich (D–R) sorption isotherm

The data were also applied to Dubinin–Radushkevich (D–R) isotherm [28] to evaluate the nature of sorption. This model envisages about the heterogeneity of the surface energies and can be written in the following linear form:

$$\ln q_e = \ln X_m - \beta F^2 \quad (4)$$

$$F = RT \ln \left( 1 + \frac{1}{C_e} \right) \quad (5)$$

where  $q_e$  is the amount of sorbate sorbed by rice polish ( $\mu\text{mol/g}$ ) and  $C_e$  is the concentrations at equilibrium ( $\mu\text{mol/L}$ ).

The constant ( $\beta$ ) and  $X_m$  were obtained from slope and intercept of the plot of  $\ln q_e$  against  $F^2$ . The mean sorption energy,  $E$ , which is defined as the free energy transfer of 1 mol of solute from infinity of the surface of the sorbent, can be calculated using the calculated value of  $\beta$ , from:

$$E = \frac{1}{\sqrt{-2\beta}} \quad (6)$$

If the magnitude of  $E$  is between 8 and 16 kJ mol<sup>-1</sup>, the sorption process is supposed to proceed via chemisorption, while for values of  $E < 8$  kJ mol<sup>-1</sup>, the sorption process is of physical nature [29].

### 3.2. Thermodynamic evaluation of the process

Thermodynamic parameters such as free energy of sorption ( $\Delta G^\circ$ ), the heat of sorption, i.e. enthalpy ( $\Delta H^\circ$ ) and standard entropy ( $\Delta S^\circ$ ) change of sorption can be evaluated from the following equations on a temperature range of 20–40 °C [30,31]:

$$K_c = \frac{C_{Ac}}{C_e} \quad (7)$$

The  $K_c$  values are used in Eqs. (8) and (9) to determine the  $\Delta G^\circ$ ,  $\Delta H^\circ$  and  $\Delta S^\circ$ .

$$\Delta G^\circ = -RT \ln K_c \quad (8)$$

The  $K_c$  may be expressed in terms of the  $\Delta H^\circ$  (kcal mol<sup>-1</sup>) and  $\Delta S^\circ$  (cal mol<sup>-1</sup> K<sup>-1</sup>) as a function of temperature:

$$\ln K_c = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \quad (9)$$

The values of  $\Delta H^\circ$  and  $\Delta S^\circ$  calculated from the slope and intercept of a plot of  $\ln K_c$  vs.  $1/T$  (van't Hoff plot).

### 3.3. Sorption kinetics

Sorption kinetics show large dependence on the physical and/or chemical characteristics of the biosorbent material, which also influenced the sorption mechanism. In order to predict the sorption kinetic models of arsenic, pseudo-first-order, pseudo-second-order kinetic models were applied to the data.

#### 3.3.1. Pseudo-first-order model

Pseudo-first-order equation can be given as [17,32]

$$\log(q_e - q_t) = \log(q_e) - \frac{k_s t}{2.303} \quad (10)$$

where  $k_s$  the equilibrium rate constant is calculated by the slope of  $\log(q_e - q_t)$  against time (min) plots for both arsenic species As(III) and As(V) (Fig. 8).

#### 3.3.2. Pseudo-second-order model

Pseudo-second-order kinetic model is presented as follows [17,33]:

$$\frac{t}{q_t} = \frac{1}{k'_2 q_e^2} + \frac{t}{q_e} \quad (11)$$

$$h = k'_2 q_e^2 \quad (12)$$

The equation constants  $k'_2$  and  $h$  can be determined by plotting  $t/q_t$  against  $t$ .

#### 3.3.3. Mass transfer study

The uptake of pollutant species from the liquid phase to the solid phase is carried out by transfer of mass from former to the latter. For the present study the McKay et al. [34], model is used. The three steps involved in the sorption process according to this model are as follows:

1. Mass transfer of the solid from the aqueous phase onto the solid surface;
2. Adsorption of solute on to the surface sites; and
3. Internal diffusion of solute via either a pore diffusion model or homogeneous solid-phase diffusion model.

During the present investigation, step (2) has been assumed rapid enough with respect to the other steps and therefore it is not rate limiting in any kinetic study. Taking into account these probable steps, the McKay et al. model [34] has been used for the present investigation

$$\ln \left( \frac{C_t}{C_i} - \frac{1}{1+mk} \right) = \ln \left( \frac{mk}{1+mk} \right) - \left( \frac{1+mk}{mk} \right) \beta_1 S_s t \quad (13)$$

The value of  $\beta_1$  were calculated from the slopes of the plots of  $\ln((C_t/C_i) - 1/(1+mk))$  vs.  $t$  (min).

#### 3.3.4. Intraparticle diffusion study

During the batch mode of operation, there was a possibility of transport of sorbate species into the pores of sorbent, which is often the rate controlling step. The rate constants of intraparticle diffusion ( $k_{id}$ ) at different temperatures were determined using the following equation [35]:

$$q_t = k_{id} t^{1/2} + C \quad (14)$$

where  $C$  is the intercept and  $k_{id}$  is the intraparticle diffusion rate constant ( $\mu\text{g/g h}^{0.5}$ ) calculated from the slopes of respective plot  $q_t$  versus  $t^{1/2}$ .

#### 3.3.5. Richenberg model

The Richenberg model [36] was applied to check that sorption proceeds via film diffusion or intraparticle diffusion mechanism and can be written in the following form:

$$X = \left( 1 - \frac{6}{\pi^2} \right) e^{-B_t} \quad (15)$$

where  $X = q_t/q_e$  and  $B_t$  is a mathematical function of  $X$  which can be evaluated from each value of  $X$  as

$$B_t = -0.4977 \ln(1 - X) \quad (16)$$

If the plots of  $B_t$  vs.  $t$  does not pass through the origin then it is concluded that intraparticle diffusion is not the sole rate controlling step.

#### 3.3.6. Elovich equation

The Elovich equation is commonly used to determine the kinetics of chemisorption of gases onto heterogeneous solids and in recent years, this equation has also been used to describe the sorption of pollutants from aqueous solutions [17,28]. The Elovich equation can be written in the following form:

$$\frac{dq_t}{dt} = a \exp(-bq_t) \quad (17)$$

where  $a$  represents the rate of chemisorption at zero coverage (mg/(g min)) and  $b$  is related to the extent of surface coverage and activation energy for chemisorption (g/mg). These constants were calculated from the slope and intercept of the plots of  $q_t$  vs.  $\ln(t)$ .

Application of Eq. (17) is usually tested by converting it to the integrated form, viz.

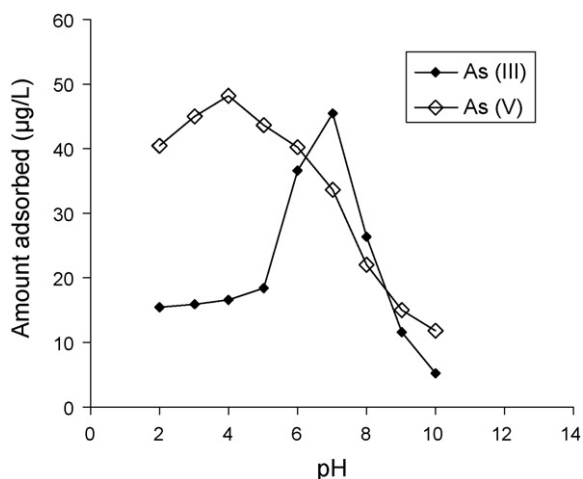
$$q_t = \frac{1}{b} \ln(ab) + \frac{1}{b} \ln \left( t + \frac{1}{ab} \right) \quad (18)$$

and assuming  $q_t = 0$ ,  $t = 0$  as the lower limit of integration. For large values of  $t$ , i.e.  $t \gg 1/ab$ , the plots of  $q_t$  vs.  $\ln(t)$  should be linear.

## 4. Results and discussion

### 4.1. Effect of pH

The effect of pH on As(III) and As(V) sorption by rice polish was studied in the initial pH range between 2 and 10 at the contact time of 1 h and the results are obtained in Fig. 1. As(III) exists in non-ionic ( $\text{H}_3\text{AsO}_3$ ) and anionic ( $\text{H}_2\text{AsO}_3^-$ ) forms in the pH range of 2.0–9.0 and 10–12, respectively. Reports show that As(V) at pH range between 3 and 6, As(V) occurs mainly in the monovalent form of  $\text{H}_2\text{AsO}_4^-$ , however, a small degree of  $\text{H}_3\text{AsO}_4$  also exists at pH near 2. While at higher pH values (>8) a divalent anion  $\text{HASO}_4^{2-}$  dominates; in the intermediate region of pH 6–8, both species co-exist. In case of As(III) almost no change was observed in the amount adsorbed in the pH range of 2.0–5.0 and thereafter the removal increases abruptly and reaches a maximum at pH 7.0 followed by a sharp decrease in the adsorption density. In



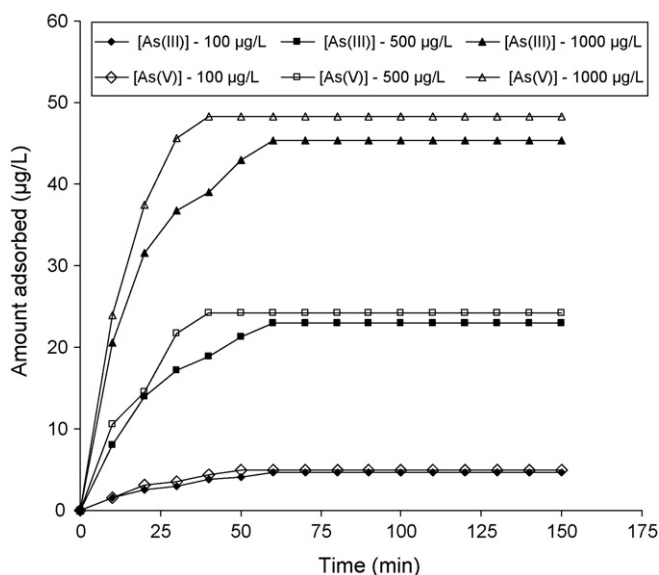
**Fig. 1.** Effect of initial pH on the removal of arsenic at initial metal ion concentration of 1000 µg/L, biosorbent dose 20 g/L and temperature 20 °C.

extreme acidic conditions, the adsorbent surface are highly protonated and such a situation is not favourable for As(III) removal resulting almost no change in the extent of adsorption within the pH range 2.0–5.0. With the increase in pH of the system, the degree of protonation of the surface reduces gradually. The maximum removal of As(III) at pH 7.0 where only neutral species  $H_3AsO_3$  are available, may be attributed to various unspecified reaction products in the adsorption process. In alkaline medium, the negative charged  $H_2AsO_3^-$  species starts dominating and surface also tends to acquire negative charges. This tendency of adsorbate species and adsorbent surface will continue to increase with increase of pH causing a gradual increase in the repulsive forces between the surface and adsorbate species resulting in a decrease of adsorption.

In case of As(V) the uptake first increased from pH 2 to 4, reached a maximum at pH 4 and then after decreased with further increase in the pH upto 10. At pH 2–4 species  $H_3AsO_4$  and  $H_2AsO_4^-$  exists, however the predominating is  $H_2AsO_4^-$ . At low pH (2–4) the surface of biosorbent is highly protonated and as a result a strong attraction exists between oxyanion and positively charged surface of the biosorbent. And the uptake increased in this pH range because of the increase in  $H_2AsO_4^-$  species along with the pH. The further decrease in metal uptake with increase in pH (4–10) may be explained as at higher pH values, the substrate may be negatively charged by adsorbing hydroxyl ions on the surface or by ionisation of very weak acidic functional groups of the adsorbent, or both. A repulsive force may develop between the negatively charged surface and the anions. This results in decreased metal uptake at higher pH values.

#### 4.2. Effect of contact time and initial metal ion concentration

Fig. 2 represents the effect of contact time and initial metal ion concentration on the uptake of arsenic. The time required to attain equilibrium for As(III) and As(V) sorption on rice polish is 60 and 40 min, respectively. It is further noted from the results that in all the systems, the saturation time is independent of concentration of the adsorbate solution. The uptake of arsenic [As(III) and As(V)] was found to increase as the initial metal ion concentration increased. It was because the number of ions adsorbed from solutions of higher concentrations is more than that removed from less concentrated solutions. It was also found that the uptake of adsorbate species is rapid in the initial stages and gradually decreases with the lapse of time till equilibrium in each case. The curves thus obtained are

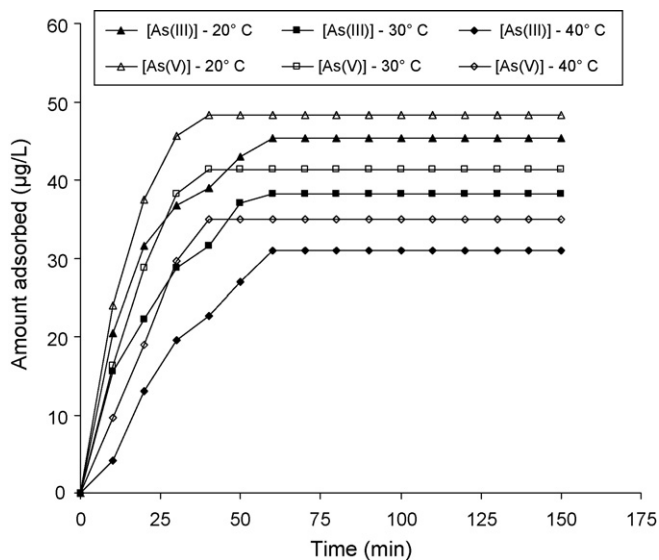


**Fig. 2.** Effect of contact time and initial metal ion concentration on the removal of As(III) [pH 7.0, biosorbent 20 g/L and temperature 20 °C]; As(V) [pH 4.0, biosorbent 20 g/L and temperature 20 °C].

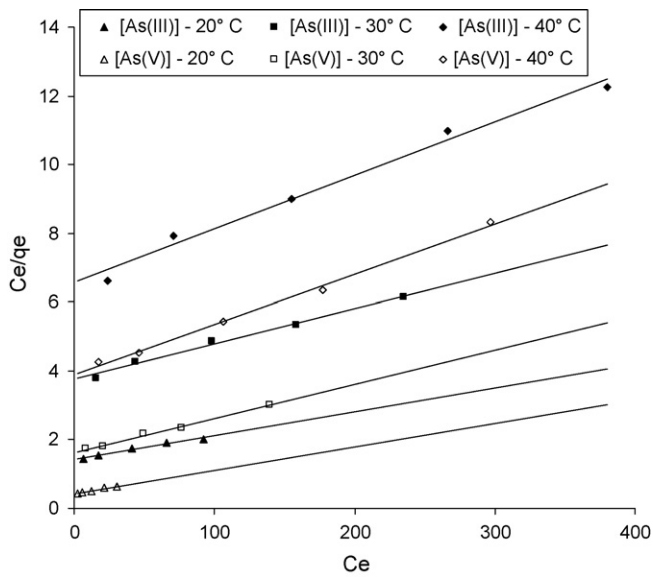
single, smooth and continuous leading to equilibrium and suggest the probability of monolayer coverage of the sorbate on the surface of the sorbent.

#### 4.3. Effect of temperature

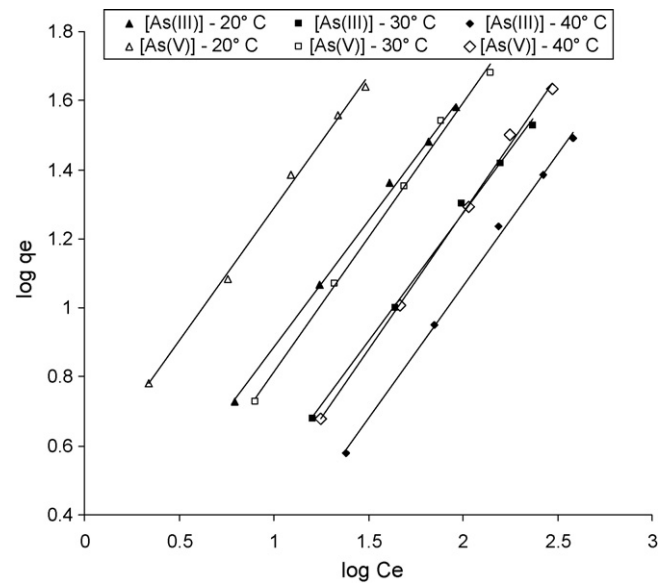
The results of time-rate studies for the uptake of arsenic [As(III) and As(V)] at different temperatures are given in Fig. 3. These curves are smooth, continuous and leading towards saturation. Further, these data show that in the initial stages of adsorption, the uptake of the adsorbate species is comparatively rapid, becomes slow in the later stages and finally attains saturation. The period of saturation [(60 min for As(III) and 40 min for As(V)] remains unaltered with the rise in temperature in each case of adsorption and thus is independent of temperature. The above results also showed that the sorption of both As(III) and As(V) are exothermic in nature.



**Fig. 3.** Effect of temperature on the removal of As(III) [initial metal ion concentration of 1000 µg/L pH 7.0 and biosorbent 20 g/L]; As(V) [initial metal ion concentration of 1000 µg/L pH 4.0 and biosorbent 20 g/L].



**Fig. 4.** Langmuir isotherm plot for arsenic removal [As(III)–pH 7.0, biosorbent dose 20 g/L; As(V)–pH 4.0, biosorbent dose 20 g/L].



**Fig. 5.** Freundlich isotherm plot for arsenic removal [As(III)–pH 7.0, biosorbent dose 20 g/L; As(V)–pH 4.0, biosorbent dose 20 g/L].

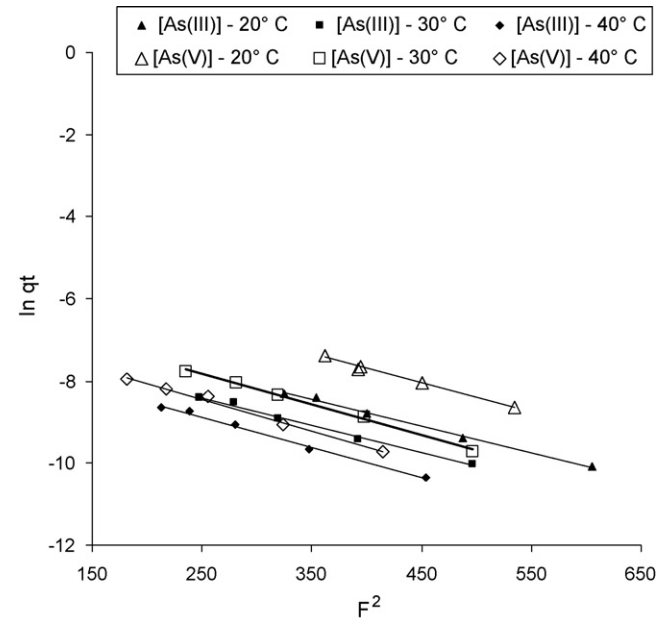
**4.4. Sorption isotherms**

The Langmuir isotherm constants  $Q^0$  and  $b$  were calculated from the slope and intercept of plot between  $C_e/q_e$  and  $C_e$  (Fig. 4) and are presented in Table 2. The isotherm showed good fit to the experimental data with good correlation coefficients (Table 2). The sorption capacity of rice polish was found to be 138.88  $\mu\text{g/g}$  for As(III) at 20°C and pH 7.0 and 147.05  $\mu\text{g/g}$  for As(V) at 20°C and pH 4.0. The values of  $Q^0$  show a decrease with the increase in temperature, which accounts for the exothermic nature of the ongoing process.

Freundlich isotherm constants  $n$  and  $K_F$  were calculated from the slope and intercept of Fig. 5 (Freundlich isotherm for As(III) and As(V)) respectively and presented in Table 2. The sorption capacity ( $K_F$ ) was found to decrease with increase in temperature, which suggests sorption process is exothermic in nature. The values of  $n$  (intensity of sorption) between 1 and 10 (i.e.,  $1/n$  less than 1) represents a favourable sorption. For the present study the value of  $n$  also presented the same trend representing a beneficial sorption.

The plots of  $\ln q_e$  against  $F^2$  (D–R isotherm plot for As(III) and As(V)) gave straight lines (Fig. 6). The values of constants  $\beta$  and  $X_m$  thus obtained are given in Table 2. The estimated values of  $E$  for the present study was found in the range expected for chemisorption (Table 2). Thus the sorption of arsenic species on the surface of the rice polish was chemical in nature.

All the three isotherms showed good fit to the experimental data with good correlation coefficients (Table 2). The applicability of all the three isotherms to the arsenic sorption [As(III) and As(V)]



**Fig. 6.** Dubinin–Radushkevich isotherm plot for arsenic removal [As(III)–pH 7.0, biosorbent dose 20 g/L; As(V)–pH 4.0, biosorbent dose 20 g/L].

**Table 2**  
Parameters of Freundlich, Langmuir and D–R isotherm for biosorption of arsenic on rice polish at various temperatures.

Temperature (°C)	Langmuir constants			Freundlich constants			D–R constants			
	$Q^0$ ( $\mu\text{g/g}$ )	$b$ (L/ $\mu\text{g}$ )	$r^2$	$n$	$K_F$	$r^2$	$\beta$ ( $\text{kJ}^2/\text{mol}^2$ )	$X_m$ ( $\mu\text{mol/g}$ )	$r^2$ (kJ/mol)	$E$
<b>As(III)</b>										
20	138.88	0.0050	0.9958	1.366	1.429	0.9981	–0.0065	0.00214	0.9950	8.771
30	97.09	0.0027	0.9906	1.354	0.625	0.9962	–0.0067	0.00119	0.9939	8.638
40	64.10	0.0024	0.9985	1.307	0.341	0.9980	–0.0074	0.00089	0.9945	8.219
<b>As(V)</b>										
20	147.05	0.0156	0.9976	1.297	3.288	0.9972	–0.0071	0.00795	0.9917	8.392
30	101.01	0.0060	0.9959	1.280	1.082	0.9962	–0.0074	0.00253	0.9958	8.219
40	68.49	0.00374	0.9989	1.263	0.494	0.9982	–0.0077	0.00149	0.9939	8.058

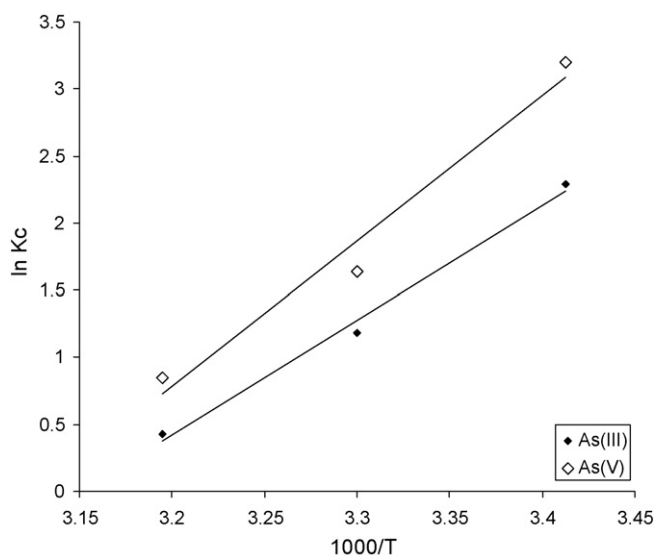


Fig. 7. van't Hoff plot for arsenic removal by rice polish

shows that both monolayer sorption and heterogeneous energetic distribution of active sites on the surface of the sorbent are possible.

#### 4.5. Thermodynamic evaluation of the process

Plot of  $\ln K_c$  vs.  $1/T$  (van't Hoff plot) for both As(III) and As(V) are shown in Fig. 7. The constant values thus calculated are given in Table 3. The negative values of  $\Delta G^\circ$  (for both As(III) and As(V)) (Table 3) indicate the spontaneous nature of the sorption process, i.e. the adsorptive forces are quite strong to overcome the potential barrier and less negative value with increase of temperature shows that an increase in temperature does not favour the sorption process. The negative values of  $\Delta H^\circ$  in both the cases indicate that the sorption process was exothermic in nature. It is further noted that the change in entropy ( $\Delta S^\circ$ ) is negative for both As(III) and As(V). It is expected that association, fixation or immobilization of solute molecules on the surface of the sorbent reduces the degree of freedom owing to sorption and thus the orderliness prevails, which explains the negative entropy change in the present study for both As(III) and As(V).

#### 4.6. Sorption kinetics

For the pseudo-first-order sorption rate constant, the straight-line plots of  $\log(q_e - q_t)$  against time (Fig. 8) were analyzed. Approximately, linear fits were observed for all temperatures. The correlation coefficient and constant  $k_s$  have been calculated and summarized in Table 4. The kinetic constant and correlation coefficients of pseudo-second-order model were also calculated from Fig. 9 and given in Table 4. Good correlation coefficients were

**Table 3**  
Thermodynamic parameters for sorption of arsenic on rice polish at different temperatures.

Temperature (°C)	$-\Delta G^\circ$ (kcal mol <sup>-1</sup> )	$-\Delta H^\circ$ (kcal mol <sup>-1</sup> )	$-\Delta S^\circ$ (cal mol <sup>-1</sup> K <sup>-1</sup> )
<b>As(III)</b>			
20	1.3339		
30	0.6877	16.456	51.7238
40	0.2512		
<b>As(V)</b>			
20	1.9329		
30	0.9044	22.635	70.9634
40	0.4937		

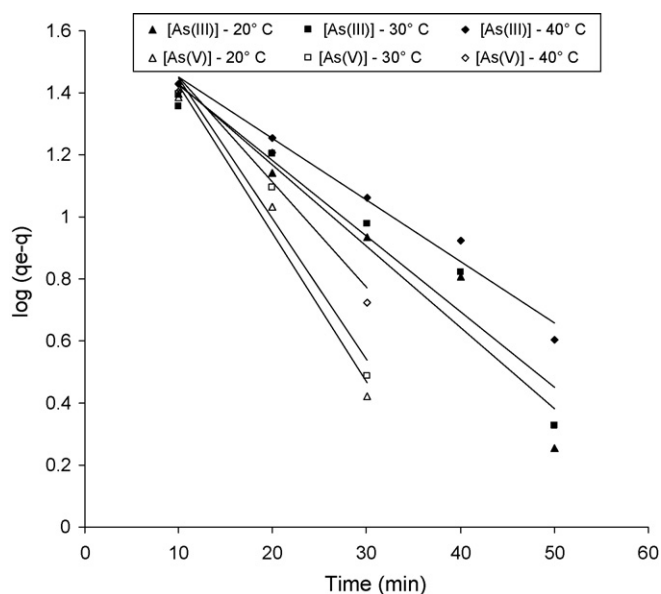


Fig. 8. Pseudo-first-order plot for arsenic removal [As(III)]–pH 7.0, initial metal concentration 1000  $\mu$ g/L, biosorbent dose 20 g/L; As(V)–pH 4.0, initial metal ion concentration 1000  $\mu$ g/L, biosorbent dose 20 g/L.

**Table 4**

Kinetic parameters for the sorption of arsenic onto rice polish obtained under different temperatures.

Temperature (°C)	Pseudo-first-order			Pseudo-second-order			
	$k_s$ ( $\times 10^{-2}$ )	$q_e$ (cal)	$r^2$	$k_2$ ( $\times 10^{-4}$ )	$h$	$q_e$ (cal)	$r^2$
<b>As(III)</b>							
20	6.03	49.317	0.9382	9.27	3.21	58.82	0.9969
30	5.61	46.731	0.9392	6.09	1.97	56.82	0.9908
40	4.55	44.627	0.9794	2.95	0.93	56.18	0.9967
<b>As(V)</b>							
20	11.07	80.891	0.9771	6.88	3.72	73.52	0.9913
30	10.50	80.223	0.9633	4.29	2.16	70.92	0.9967
40	7.81	61.673	0.9440	2.52	1.25	70.42	0.9952

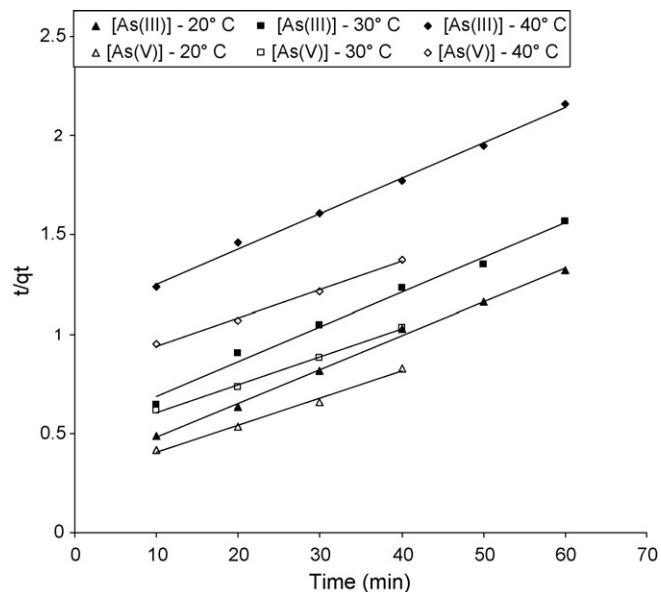
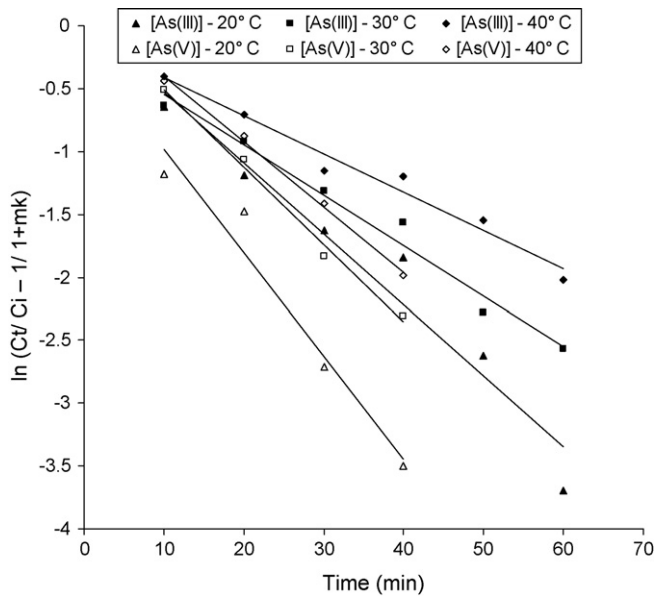


Fig. 9. Pseudo-second-order plot for arsenic removal [As(III)]–pH 7.0, initial metal concentration 1000  $\mu$ g/L, biosorbent dose 20 g/L; As(V)–pH 4.0, initial metal ion concentration 1000  $\mu$ g/L, biosorbent dose 20 g/L.



**Fig. 10.** Mass transfer plot for arsenic removal [As(III)–pH 7.0, initial metal concentration 1000  $\mu\text{g/L}$ , biosorbent dose 20 g/L; As(V)–pH 4.0, initial metal ion concentration 1000  $\mu\text{g/L}$ , biosorbent dose 20 g/L].

observed for pseudo-second-order kinetic model in comparison to pseudo-first-order model indicating that arsenic [As(III) and As(V)] uptake process can be approximated with the pseudo-second-order kinetics model. Thus the pseudo-second-order kinetics was pathway to reach the equilibrium. This means, the adsorption rate would be proportional to the metal ion concentration and the square of the number of free sites of the rice polish, which corresponds to the term  $(q_e - q_t)^2$  in the second-order model.

#### 4.6.1. Mass transfer study

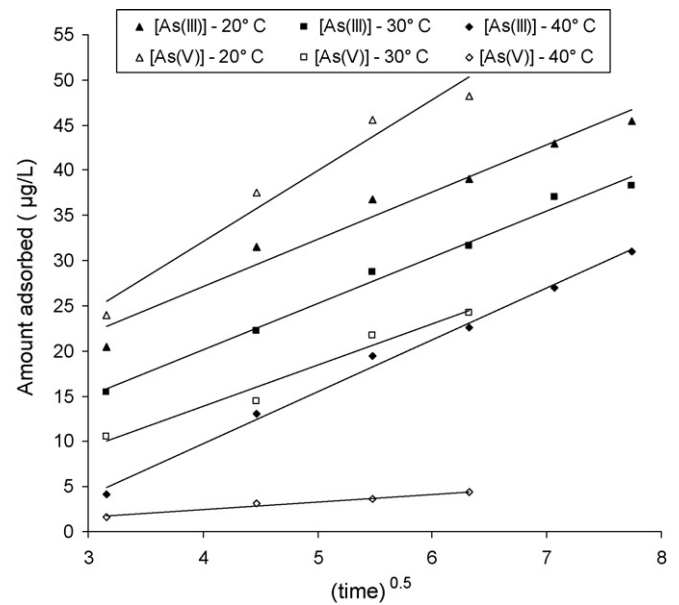
The value of  $\beta_1$  [ $2.54 \times 10^{-5}$ ,  $1.65 \times 10^{-5}$  and  $1.23 \times 10^{-5}$   $\text{cm s}^{-1}$  for As(III) and  $6.15 \times 10^{-5}$ ,  $3.03 \times 10^{-5}$  and  $2.74 \times 10^{-5}$  for As(V)] were calculated from the slopes of the plots (Fig. 10) of  $\ln((C_t/C_i) - 1/(1+mK))$  vs.  $t$  (min) at different temperature 20, 30 and 40  $^\circ\text{C}$ , respectively. These results show that the rate of transfer of mass from bulk solution to the biosorbent surface was rapid enough to use this sorbent for the treatment of wastewater rich in arsenic and it also suggests that mass transfer cannot be rate controlling step.

#### 4.6.2. Intraparticle diffusion study

The values of  $k_{id}$  [ $5.22$ ,  $5.13$  and  $5.73$   $\mu\text{g g}^{-1} \text{min}^{-1/2}$  for As(III) and  $7.85$ ,  $4.55$  and  $0.84$   $\mu\text{g g}^{-1} \text{min}^{-1/2}$  for As(V) at temperatures 20, 30 and 40  $^\circ\text{C}$ , respectively] were calculated from the slopes of respective plot ( $q$  versus  $t^{1/2}$ , Fig. 11). The intercept of the plot reflects the boundary layer effect. The larger the intercept, the greater the contribution of the surface sorption in the rate-controlling step. If the regression of  $q_t$  vs.  $t^{1/2}$  is linear and passes through the origin, the intraparticle diffusion is the sole rate-limiting step. However, the linear plots at each temperature for both As(III) and As(V) did not pass through the origin. This indicates that the intraparticle diffusion was not only the rate controlling step. This indicates the mechanism of metal ion adsorption by rice polish is complex and both, the surface adsorption as well as intraparticle diffusion contribute to the rate determining step.

#### 4.6.3. Richenberg model

Plots of  $B_t$  vs.  $t$  at various temperatures for both the arsenic species [As(III) and As(V)] are shown in Fig. 12 which are straight lines with a correlation coefficient ( $r^2$ ) of 0.967, 0.939 and 0.979

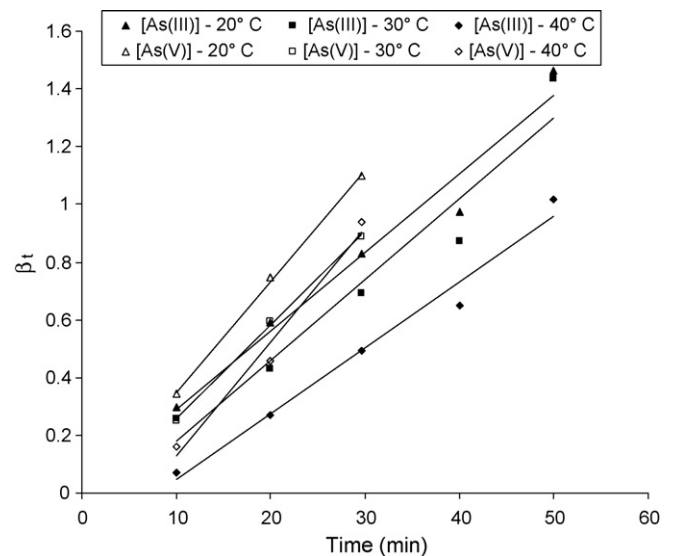


**Fig. 11.** Intraparticle diffusion plot for arsenic removal [As(III)–pH 7.0, initial metal concentration 1000  $\mu\text{g/L}$ , biosorbent dose 20 g/L; As(V)–pH 4.0, initial metal ion concentration 1000  $\mu\text{g/L}$ , biosorbent dose 20 g/L].

for As(III) and 0.998, 0.997 and 0.982 for As(V) at 20, 30 and 40  $^\circ\text{C}$ , respectively. The results also suggest that intraparticle diffusion is not the sole rate controlling step because the plot does not pass through the origin at various temperatures. This is in agreement with the results that obtained by using intraparticle diffusion.

#### 4.6.4. Elovich equation

As can be shown from Fig. 13 (plots of  $q_t$  vs.  $\ln(t)$  for both the arsenic species), good linear relationships were found with a correlation coefficient ( $r^2$ ) of 0.993, 0.984 and 0.992 for As(III) and 0.989, 0.992 and 0.996 for As(V) for the temperatures 20, 30 and 40  $^\circ\text{C}$ , respectively. This suggests that the sorption systems studied belong to the pseudo-second-order kinetic model based on the assumption that the rate determining step may be chemisorption

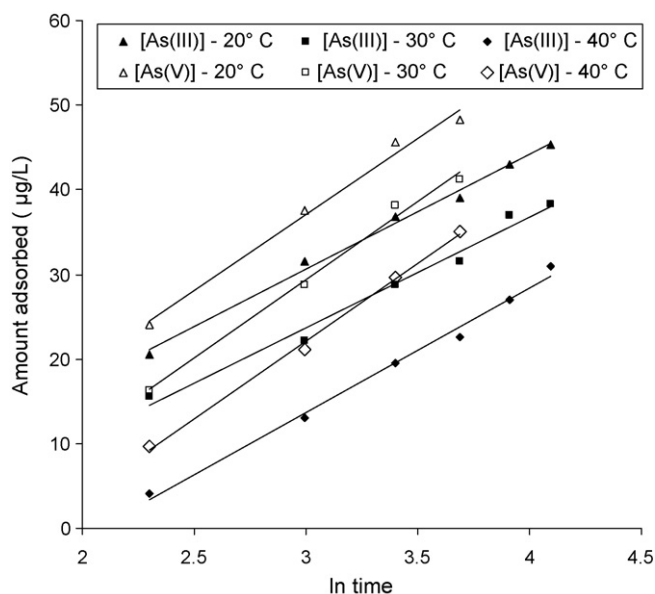


**Fig. 12.** Richenberg plot for arsenic removal [As(III)–pH 7.0, initial metal concentration 1000  $\mu\text{g/L}$ , biosorbent dose 20 g/L; As(V)–pH 4.0, initial metal ion concentration 1000  $\mu\text{g/L}$ , biosorbent dose 20 g/L].



**Table 5**  
Comparison of sorption capacities of the rice polish for the removal of arsenic with those of other adsorbents [12].

S. No.	Adsorbent	Sorption capacities (mg/g)				
		pH	Concentration range	Temperature (°C)	As(III)	As(V)
1.	Rice polish (present study)	7.0 for As(III) and 4.0 for As(V)	100–1000 µg/L	20	0.139	0.147
2.	Iron oxide coated sand IOCS	–	100 µg/L	22 ± 2	0.136	–
3.	Atlantic Cod fish scale	4.0	–	–	0.02667	0.02475
4.	<i>L. nigrescens</i>	2.5	50–600 mg/L	25	–	45.2
5.	Tea fungal biomass	7.20	1.3 mg/L for As(III) and 0.9 mg/L for As(V)	30	1.11	4.95
6.	Fresh biomass	6.0	50–2500 mg/L	30	128.1	–
7.	Iron oxide coated cement IOCC	~7.0	0.5–10.0 mg/L	35	3.98	–
8.	Iron oxide coated cement IOCC	7.0	0.7–3.5 mg/L	35	0.67	–
9.	<i>Penicillium purpurogenum</i>	5.0	10–750 mg/L	20	35.6	–



**Fig. 13.** Elovich plot for arsenic removal [As(III)]—pH 7.0, initial metal concentration 1000 µg/L, biosorbent dose 20 g/L; As(V)—pH 4.0, initial metal ion concentration 1000 µg/L, biosorbent dose 20 g/L.

involving valence forces through sharing or exchange of electrons between sorbent and sorbate.

#### 4.7. Rice polish as a biosorbent for arsenic

From the above studies we can conclude that rice polish is a potential biosorbent for the removal of arsenic from aqueous solution and thus it can be recommended for the successful removal of arsenic in developing countries which are suffering with the arsenic contamination of ground and surface water. The sorption capacity of arsenic in this study was found to be 138.88 µg/g for As(III) at 20 °C and pH 7.0 and 147.05 µg/g for As(V) at 20 °C and pH 4.0. When it was compared (Table 5) with other sorbents already used for the arsenic removal purpose, it was found that rice polish was much better. Rice polish is an agricultural residue being available in millions of tonne quantity without any cost from the rice milling industry. Rice polish was used as such in this study that is without any pretreatment like treatment with acid or alkali or any type of coating. Moreover, the use of biomass of microorganisms (although being a natural source) for the removal of arsenic, has the disadvantages like the cultivation of biomass in such a amount that it can be used for the removal purpose, the requirement of nutrients during cultivation and the risk of contamination of the culture. In addition to this Table 5 also shows that rice polish is well able to remove a sufficient quantity of arsenic (below the required drinking water standard i.e. 10 ppb) from even low initial concentration

solution as compared to other sorbents. Other conditions like pH and temperature are also very easily achievable

## 5. Conclusion

Rice polish has been found to be a potential biosorbent for the removal of both the species of arsenic [As(III) and As(V)] when compared to other sorbents. The sorption of arsenic onto rice polish was found to be highly pH dependent. The sorption of arsenic was found to increase with the increase in initial metal ion concentration and decrease with the increase in the temperature. Equilibrium sorption data showed good fit to all the three isotherms, Langmuir, Freundlich and Dubinin–Radushkevich. Thus the sorption is monolayer on the heterogeneous surface of the biosorbent. The maximum sorption capacity of the sorbent was found to be 138.88 µg/g for As(III) at 20 °C and pH 7.0 and 147.05 µg/g for As(V) at 20 °C and pH 4.0. Sorption energies calculated with the help of D–R isotherm were found to be between 8 and 16 kJ mol<sup>-1</sup> suggesting the chemisorption nature of sorption process. Thermodynamic studies indicated that the process of sorption of both arsenic species was feasible, spontaneous and exothermic in nature. The pseudo-second-order kinetic model was found to best correlate to the experimental data for arsenic sorption from aqueous solutions than the pseudo-first-order model. The rate determining step was found to be controlled by both surface sorption as well as intraparticle diffusion. It was further confirmed by the application of Richenberg model. The application of Elovich suggested that the rate determining step may be chemisorption.

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