



# Characterization and modelling of biosorptive performance of living cells of *Bacillus arsenicus* MTCC 4380 for the removal of As(III) and As(V)



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## ABSTRACT

One of the main environmental concerns of today is the occurrence of arsenic in wastewater. Targeting a solution for this problem, several efforts have been made towards research and application of cost-effective and easily adaptable processes for removing arsenic. The potential of living cells of *Bacillus arsenicus* MTCC 4380 to biosorb both As(III) and As(V) was examined in batch experimentations targeting the treatment of wastewater with high concentrations. Optimum parameters for biosorption process were determined as a function of contact time and temperature. The equilibrium was achieved after about 90 min at 30 °C temperature. Non-linear regression analysis was done for determining the best-fit kinetic model based on three correlation coefficients and three error functions and also to predict the parameters involved in kinetic models. The results showed that both Brouers–Weron–Sototlongo models for both As(III) and As(V) were proficient to provide realistic explanation of biosorption kinetic. Applicability of mechanistic models in the current research showed that the rate controlling step in the biosorption of both As(III) and As(V) was film diffusion rather than intraparticle diffusion. The estimated thermodynamic parameters  $\Delta G^\circ$ ,  $\Delta H^\circ$  and  $\Delta S^\circ$  exposed that biosorption of both As(III) and As(V) was exothermic, spontaneous and feasible under studied conditions. The activation energy ( $E_a$ ) estimated from Arrhenius equation specified the nature of biosorption being ion exchange type. The results acquired are very favorable and encourage the use of living cells in environmental applications.

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## 1. Introduction

In current history arsenic (As) is identified all over the world because of the result of mass poisoning via drinking water ingestion. Long term exposures to even very low concentrations have extremely toxic effects on human health causing damage to the central nervous system, black foot disease, a unique peripheral vascular disease that ends with dry gangrene, lung, kidney, skin, liver and urinary bladder cancer risks [1,2]. Because of its carcinogenic as well as many other adverse health hazards, the maximum contaminant level (MCL) of arsenic in drinking water has been revised to 10 µg/L from 50 µg/L by the World Health Organization (WHO) in 1993 [3] and the European Commission in 2003 [4].

Besides the natural phenomenon of release of arsenic owing to biological activities, weathering of rocks and volcanic activity, var-

ious anthropogenic activities, such as use of arsenical insecticides, pesticides, herbicides, burning of fossil fuels, mine tailing/landfill leaching and smelting are the major sources of water contamination [1]. Copper smelting causes a huge volume of wastewater having large amounts of inorganic compounds, for instance heavy metals like lead, copper, zinc, iron, cadmium and bismuth etc. and highly carcinogenic metalloid like arsenic species (1979 mg/L), poses a serious threat towards man and the flora and fauna of our ecosystem contaminating the natural water tables (ground water and surface water) in the vicinity [5]. Copper smelting wastewater bearing arsenic may contain highly elevated concentrations (approx. 1979 mg/L) of potentially toxic oxyanion, As(III) and As(V) [5]. At the pH range of most natural and wastewater sources, As(III) is more toxic, more mobile and more challenging to be scavenged from water compared to As(V). The toxicity of arsenic is attributed to the substitution of As(V) for phosphate, affinity of As(III) for protein thiol groups and protein-DNA and DNA-DNA cross linking [6].

Due date, conventional methods applied for removing As(III) and As(V) ions from wastewater include precipitation [7],

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**Nomenclature**

$a_E$	Elovich coefficient representing the initial adsorption rate (mg/g min)
$b_E$	Elovich coefficient representing desorption constant (g/mg)
$A$	The frequency factor
$B_{bt}$	A mathematical function of $F$ ( $F = q_t/q_e$ )
$C_0$	Initial concentration of arsenic in the solution (mg/L)
$C_e$	Equilibrium concentration of arsenic in the solution (mg/L)
$C_s$	The concentration of arsenic onto the adsorbent and in the solution (mg/L)
$C_{int}$	The intercept of the intraparticle diffusion plot (mg/g)
$d$	The thickness of the water film adhered to the adsorbent (cm)
$D_1$	Film diffusion constant ( $\text{cm}^2/\text{s}$ )
$D_2$	Pore diffusion constant ( $\text{cm}^2/\text{s}$ )
$D_e$	Diffusivity ( $\text{m}^2/\text{s}$ )
$D_f$	Film diffusion coefficient ( $\text{cm}^2/\text{s}$ )
$D_p$	Pore diffusion coefficient ( $\text{cm}^2/\text{s}$ )
$E_a$	The activation energy of adsorption characterizing the distribution (kJ/mol)
$F$	The adsorption progress ( $F = q_t/q_e$ )
$f_2$	The involvement of pseudo second order model
$f_{eq}$	The Langmuir batch equilibrium factor
$h$	The initial adsorption rate (mg/g min)
$k'_{1,0}$	The fractal-like mixed 1,2 order rate coefficient ( $1/\text{min}$ ) $\alpha$
$k'_{2R}$	The modified second order rate coefficient ( $1/\text{min}$ )
$k''_{2R}$	The Ritchie second order rate coefficient ( $1/\text{min}$ )
$k_{AV}$	The Avrami kinetic rate coefficient ( $1/\text{min}$ )
$k_{a,obs}$	The acquired rate coefficients of adsorption
$k_{d,obs}$	The acquired rate coefficients of desorption
$k_b$	The Bangham model constant (mL/gL)
$k_d$	The adsorption equilibrium constant (L/g)
$k_{DW}$	The Dumwald–Wagner rate constant ( $1/\text{min}$ )
$k_{EXP}$	The exponential rate coefficient (mg/g min)
$k_{int}$	The intraparticle diffusion rate coefficient ( $\text{mg/g min}^{0.5}$ )
$k_M$	The film diffusion rate constant ( $1/\text{min}$ )
$k_{MOE}$	The mixed 1,2 order rate coefficient ( $1/\text{min}$ )
$k_{nBWS,\alpha}$	The reaction constant ( $1/\text{min}$ )
$k_{PF}$	The fractional power model rate constant (mg/g min)
$k_{PFO}$	The pseudo first order rate coefficient ( $1/\text{min}$ )
$k_{PSO}$	The pseudo second order rate coefficient (g/mg min)
$k'_{EXP}$	Division of $k_{EXP}$ by $q_e$ ( $1/\text{min}$ )
$k''_{EXP}$	The fractal-like exponential rate coefficient ( $1/\text{min}$ )
$k'_{PFO}$	The fractal-like pseudo first order kinetic rate coefficient ( $1/\text{min}$ )
$k'_{FPFO}$	The fractal-like pseudo first order kinetic rate coefficient ( $1/\text{min}$ ) $\alpha$
$k'_{FPSO}$	Is the fractal-like pseudo second order kinetic rate coefficient (g/mg min) $\alpha$
$k'_{PSO}$	Multiplication of $q_e$ and $k_{PSO}$ ( $1/\text{min}$ )
$k'_{FPSO}$	Multiplication of $q_e$ and $k'_{FPSO}$ ( $1/\text{min}$ )
$m$	The weight of the adsorbent per liter of solution (g/L)
$m_b$	An integer that describes infinite series solution
$n$	The number of observations in the experimental study

**Greek symbols**

$n_{AV}$	Constant corresponding to the mechanism of adsorption
$n_{BWS}$	A fractional reaction order
$n_R$	Number of surface sites
$p$	The number of parameters to be estimated
$q_e$	The amount of adsorbate adsorbed on the adsorbent surface at equilibrium (mg/g)
$q_m$	The adsorption capacity
$q_t$	The amount of adsorbate adsorbed onto the adsorbent surface at time $t$ (mg/g)
$q_{t,exp}$	The biosorption capacity observed from the batch experiment after time $t$ (mg/g)
$q_{t,model}$	The calculation from the kinetic model corresponding to $C_t$
$r$	Mean radius of adsorbent particle (assumed spherical) (cm)
$r_a$	The rate of adsorption
$r_d$	The rate of desorption
$R$	The universal gas constant (8.314 J/mol K)
$R_e$	% removal
$t$	Contact time (min)
$t_{(1/2)}$	The time necessary for falling the adsorbate concentration to half the initial concentration (sec)
$t^\alpha$	A fractal time
$T$	The absolute temperature (K)
$u_{eq}$	Relative equilibrium uptake
$v$	Adjustment parameter
$V$	The volume of the solution (mL)

**Greek symbols**

$\alpha$	The fractal time exponent
$\alpha_b$	Bangham model constant
$\theta$	The adsorbent surface coverage at at pre-adsorbed stage, ( $\theta = q_t/q_e$ ) dimensionless
$\theta_0$	The adsorbent surface coverage at time $t$ , ( $\theta_0 = q_0/q_e$ ) dimensionless
$\theta_e$	The relative surface coverage at equilibrium
$\tau_{1/2}$	Half-reaction time (min)
$\tau_{nBWS,\alpha}$	The time required for adsorbing half the maximum amount
$\Delta G^\circ$	Gibbs free energy change (kJ/mol)
$\Delta H^\circ$	Enthalpy change (kJ/mol)
$\Delta S^\circ$	Entropy change (J/mol K)

electrochemical treatment [5], electrocoagulation [8] and adsorption [9]. However, these high-technology methods have considerable drawbacks, such as, high capital and operational cost, high reagent or energy necessities, necessities for costly equipment and monitoring systems, production of contaminated sludge or other waste products that require disposal and are not appropriate for small-scale industries and are not eco-friendly [10]. So, there is an immediate requirement for the improvement of unique, effective, eco-friendly and cost-effective approach for the remediation of the environmental contaminants arsenic. Biological water treatment technique for the removal of heavy metals and other inorganic pollutants has been accepted as an alternative treatment method during the last decade.

The use of microorganism for biosorption of arsenic ions from water is an enormously effective process, due to which it is becoming widespread day by day [11–13]. Biosorption plays an important role in the removal of metals and metalloids from aqueous solutions to control water pollution [14]. Low operating cost, reusability of

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