Design and optimization of simultaneous biosorption and bioaccumulation (SBB) system: a potential method for removal of Zn(II) ion from liquid phase

Vishal Mishra[a,b,*], Chandrajit Balomajumder[a], Vijay Kumar Agarwal[a]

[a]*Fluid Particle Research Laboratory, Department of Chemical Engineering, Indian Institute of Technology, Roorkee 247667, India*
[b]*Department of Chemical Engineering, University of Petroleum and Energy Studies, Dehradun, India*
Tel. +91 9415962309; email: vmishra@ddn.upes.ac.in

ABSTRACT

This study has dealt with the design of simultaneous biosorption and bioaccumulation (SBB) batch system for Zn(II) ion removal from liquid phase. *Cedrus deodara* sawdust was used as carrier to immobilize *Zinc sequestering bacteria* "VMSDCM" accession number HQ108109. This methodology was adopted for SBB of metal ion zinc from liquid phase. The surface texture of the biomass was studied through scanning electron microscopy and Fourier transformation infra red spectrum analysis. Physico-chemical analysis of the biomass was performed through proximate carbon, hydrogen, nitrogen and sulphur analysis coupled with measurement of the surface area by Brunauer–Emmett–Teller (BET) method, obtained after the adsorption and desorption of nitrogen gas on the sample. Various isotherm models such as Langmuir (Type I to IV), Freundlich, and Temkin isotherm models have been used in the present work. A modified model was proposed to elucidate the better explanation of the sorption of Zn(II) on the surface of *Zinc sequestering bacterium VMSDCM* accession No. HQ108109.

Keywords: *Cedrus deodara* sawdust; Uptake capacity; Percentage removal; Simultaneous biosorption and bioaccumulation; *Zinc sequestering bacteria VMSDCM* accession number "HQ108109"; Zn(II) ion

1. Introduction

The revolution in industries and development of civilization during few last decades has given thrust in pollution due to discharge of heavy metals in aqueous environment. A series of heavy metal consists of Cu (II), Fe (II, III), Zn(II), Cd (II), Cr (III), etc. Among the series of heavy metals, zinc stands at 74th rank with cumulative score 932.89 [1]. The toxicity of zinc not only impairs the gastrointestinal system but also irreversibly impairs neurological, nephrological, and circulatory system of humans. The level of concentration of zinc in effluent from various industrial units ranges between 0.14 and 70,200 mg l^{-1} [2–5]. Usually, these kinds of effluents are generated from metallurgical plants and need treatment before discharge. The safe and defined limit of zinc in industrial wastewater as demarcated by World Health Organization (WHO) and United States Environmental Protection Agency (USEPA) is below

*Corresponding author.

$5\,mg\,l^{-1}$ (not to exceed). According to the European and national standards, the permissible level of discharge of zinc in wastewater after neutralization is below $10\,mg\,dm^{-3}$. Hence, the removal of zinc ion from wastewater becomes necessary before it is discharged into the main water bodies. Many conventional metal ion removal technologies have been practised earlier viz. hydroxide precipitation, membrane filtration, osmosis, electro coagulation, flocculation, etc. Usually, these technologies at mass scale are not cost effective and their implementation leads to the generation of secondary chemical sludge. Furthermore, these methodologies are not effective below $100\,mg\,l^{-1}$ metal concentration. The biosorption across liquid phase is a very cheap, robust, versatile, and eco-friendly technology of remediation of heavy metal pollution. *Zoogloea ramigera, Rhizopus arrhizus, Pseudomonas veronii* 2E, *Sphaerotilus natans,* etc. [6–8] have been implemented in past to remediate zinc from the liquid phase. Certainly, all these biosorbents are significantly efficient to remove heavy metals from liquid phase. Therefore, the major objective of the present investigation was the designing of an efficient metal ion removal system mediated by immobilized bacterial cells. To the best of our knowledge and until date, none of the research findings has been reported on this system in any expression of heavy metal removal across liquid phase in batch studies. The removal system of metal ion designed in the present investigation was called as simultaneous biosorption and bioaccumulation (SBB) system. In the present work, *Cedrus deodara* sawdust was used as carrier because of its higher porosity, surface area, easy availability, and cost effectiveness.

2. Materials and methods

Stock solution of $20\,mol\,l^{-1}$ was made by dissolving desired amount of $ZnCl_2$ (Zinc chloride, anhydrous, Hi media make, analytical grade (AR)). Rest all the batch experimental solutions were made by subsequently diluting the stock solution up to desired strength. The pH of the stock solution was measured through digital pH meter (Toshniwal make—Ajmer, India). The pH of the stock solution was 6.8 and after dilution, the pH was kept constant by adding suitable volume of 0.2 M HCl and 0.2 M NaOH.

2.1. Isolation, characterization, and design of SBB system

2.1.1. Isolation of microbial strains

Samples of effluents were collected from the industry named Hindustan Zinc Limited (HZL) situated at SIDCUL, Hardwar. Subsequently, all the samples of effluents were diluted and were plated on Luria Bertainy medium [9] containing $100\,mg\,l^{-1}$ of zinc. Various colonies of bacterial cells were observed to grow in the plates. These bacterial isolates were then picked up and purified by streaking several times in LB medium. The purified bacterial strains were then checked for their sensitivity to zinc. The most zinc tolerant microbe was considered as the most competent strain for the removal of zinc. The 16s rRNA sequencing of the most competent strain was performed and the sequences were submitted to NCBI (National Centre for Biotechnology Information) database under the accession No. HQ108109 with the name *zinc sequestering bacterium VMSDCM.*

2.2. Mathematical relations, isotherm models, physical parameters, and bacterial immobilization

2.2.1. Carrier preparation

CDS sawdust particles of various sizes ranging from 0.5 to 2 mm were sieved and the particles were soaked in hot water 333 K for 1 h. These particles were then dried at 353 K. Finally, the dried sawdust particles were steam sterilized at 394 K for 15 min at 15 psi.

2.2.2. Immobilization of microbial cells

In batch studies, 250 ml conical stoppered flasks with predetermined volume of metal ion solution were used. Immobilization of bacterial cell was done by dispensing weighed amount of pre-sterilized sawdust (2,000 mg) on the 48 h old culture of *zinc sequestering bacteria VMSDCM* accession No. HQ108109 growing in 50 ml LB medium. The flasks were incubated at 308 K for another 48 h. Bacterial cell immobilization was confirmed by observing a small amount of bacterial treated sawdust through scanning electron microscopy.

2.2.3. Scanning electron micrograph analysis (SEM)

The SEM of the bacterial sample was done by Perkin Elmer 3600, Germany manufactured automated unit. The samples of immobilized *zinc sequestering bacterium VMSDCM* accession No. HQ108109 were subjected to vacuum condition followed by the application of 15 kV. The SEM study was performed at two stages namely before and after the metal ion adsorption.

2.2.4. Isotherm modeling

Various concentrations of zinc ranging between 4 and $12\,mol\,l^{-1}$ were added to these flasks and incubated

at a temperature of 308 K. Aliquots of the samples were drawn, centrifuged, and the supernatant was analyzed by atomic absorption spectrophotometer (AAS, GBC Avanta make) at 213.9 nm in air acetylene atmosphere for the measurement of residual zinc. The detection limit of the equipment was 0.5 to 1.5 mg/l of zinc in liquid phase and the points to extrapolate the calibration curve were 0.5, 0.7, 1, 1.2, and 1.5 mg/l of zinc in liquid phase.

Eqs. (1) and (2) were used to calculate uptake capacity (q_e, mol g^{-1}) and percentage removal of zinc, respectively.

$$q_e = (C_0 - C_e) \times v/m \tag{1}$$

$$\text{Percentage removal} = (C_0 - C_e)/C_0 \times 100 \tag{2}$$

where C_0, C_e, v, and m represent the initial metal ion concentration (mgl^{-1}), equilibrium metal ion concentration (mgl^{-1}), volume of solution in liters (L), and mass of biosorbent (g), respectively. Eqs. (3)–(8) represent the various isotherm models namely Langmuir (Type I to IV), Freundlich, and Temkin, correspondingly [10–13].

$$q_e = q_{max}(K_L C_e)/1 + K_L C_e \tag{3}$$

$$1/q_e = (1/K_L Q_m)1/C_e + 1/q_m \tag{4}$$

$$q_e = q_m - (1/K_L)q_e/C_e \tag{5}$$

$$q_e/C_e = K_L q_m - K_L q_e \tag{6}$$

$$q_e = K_f C_e^{1/n} \tag{7}$$

$$q_e = B_t \ln(K_t C_e) \tag{8}$$

where q_{max}, K_L, K_f, $1/n$, B_t, and K_t represent the maximum uptake capacity (mol g^{-1}), Langmuir constant (l g^{-1}), Freundlich constant (mg g^{-1}), affinity constant, Temkin model constant, and Temkin constant (l g^{-1}), respectively. The effect of pH, temperature, particle size, adsorbent to adsorbate ratio, and equilibrium time on biosorption of Zn(II) ion was studied between 2–7, 298–313 K, 0.5–2 mm, 0.1–0.6 g l^{-1}, 4–12 mol l^{-1} and 1–3.4 h, respectively.

2.2.5. Proposed isotherm model

The model is based on the assumption that the surface of biomass is heterogeneous and the sorption of metal ion occurs in multilayers. The first layer of ions gets adsorbed on the surface of the biomass and rest all the other layers of metal ions were deposited one over the another by ionic condensation, i.e. heat of condensation is involved. The proposed isotherm model has been represented in Eq. (9).

$$C_e/q_e = [(2 - V_m)/q_m]C_e - [C_{bm}/q_m V_m] + A_a' \tag{9}$$

where V_m is the constant of the various temperature gradients. The value of V_m depends on the various sorption heats related to heat of formation, isosteric heat of adsorption, and heat of condensation. All the heat-related functions are to be correlated as function of initial concentration of metal ion in batch liquid phase. C_{bm} (mol l^{-1}) is saturation concentration of adsorbate in liquid phase, A_a' is the model constant. The graph was extrapolated between C_e/q_e and C_e. The intercept and slope of the curve was used to evaluate the values of various constants present on RHS.

3. Results and discussion

3.1. Study of scanning electron micrograph

The living cells were subjected to a voltage beam of 15 kV. The results of SEM have been shown in Figs. 1 and 2 [14].

The analysis of SEM (Fig. 1) led to the conclusion that the surface of the bacterium *VMSDCM* was quite porous, heterogeneous, and rough. Several protrusions
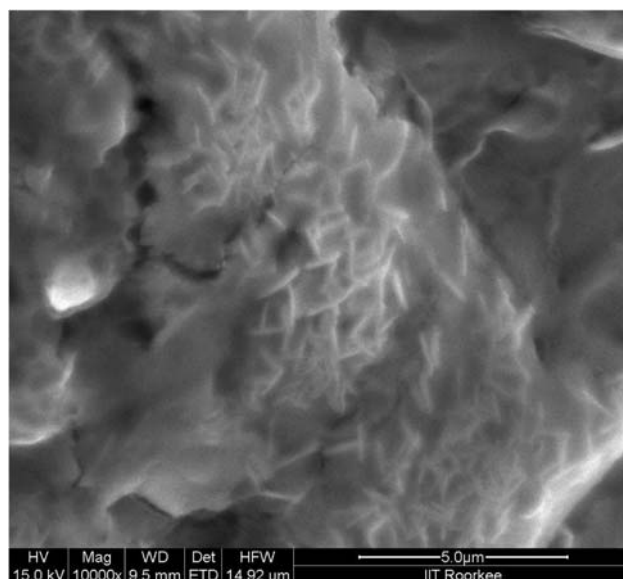

Fig. 1. SEM photograph of *zinc sequestering bacterium VMSDCM* accession No. HQ108109 immobilized on surface of sawdust at metal-unloaded stage.
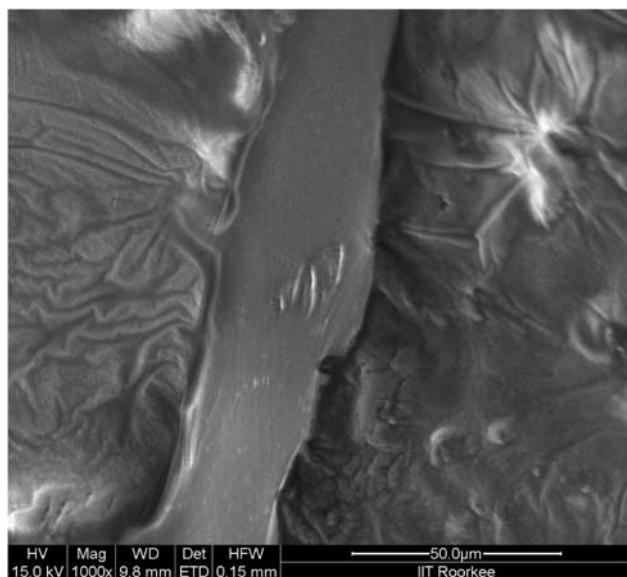
Fig. 2. SEM photograph of *zinc sequestering bacterium VMSDCM* accession No. HQ108109 immobilized on surface of sawdust at metal-loaded stage.

were identified on surface of immobilized bacterium. The rough morphology of bacterium with extensive network of protrusions were an indicator of tremendous effective surface area meant for binding of metal ion on the surface of immobilized bacterium. However, the surface of immobilized (Fig. 2) metal-loaded bacterium was crystalline and smooth in texture without any protrusions. This indicated that the Zn(II) ion was extensively impregnated on bacterium cell surface.

3.4. Physico-chemical analysis of sawdust

Physico-chemical analysis of sawdust has been represented in Table 1. The HHV value estimated in case of sawdust was found similar to other types of

Table 1
Physiochemical analysis of *Cedrus deodara* sawdust

Element	Percentage value by weight
Carbon	48.94
Hydrogen	5.56
Nitrogen	0
Sulfur	0
High heating value (HHV, kJ/g)	18.43
Bulk density (kg/ m^3)	139.2
(Brunaeur–Emmette–Teller) BET surface area (m^2/g)	9.39
Particle size	0.5–2 mm

non-living biomass like pine needles (20.02 kJ g^{-1}), mango pit outer husk (19.02 kJ g^{-1}), walnut shells (19.68 kJ g^{-1}), and mango wood (18.65 kJ g^{-1}) [15]. The absence of nitrogen in the sample indicated the absence of proteins in CDS sawdust. The estimation of surface area of the sample was done by Brunaeur–Emmette–Teller (BET) method. Initially, the sample was dried at 373 K for 24 h to ensure the complete removal of moisture. Before and after the removal of moisture, the weight of the sample was measured by electronic balance; model AW220, Shimazdu Corporation Japan. In the present work, the surface area of the sample was measured by Micrometrics limited model ASAP 200 doped with the software ChemiSoft TPx V1.02. The desorption was carried out with the help of liquid nitrogen. The flow rate of the gas was kept at 10 ml min^{-1} at standard temperature and pressure (STP).

After comparing data tabulated in Table 1 with other sorbent citing literatures, it became evident that the carbon content of sawdust is quite high against rice husk ash (RHA) and bagasse fly ash (BFA) [13]. Ultimate analysis of CDS biomass claimed 48.94% of total carbon. Fixed carbon contents of RHA and BFA obtained through proximate and ultimate analysis were 5.90, 19.20, 7.42, and 16.36%, respectively. Relatively, high carbon content of CDS biomass against BFA and RHA coupled with significant surface area obtained through nitrogen adsorption–desorption BET method indicated all the possible evidences of our biosorbent as a high-quality biosorbent with high organic content and tremendous external surface area meant for metal ion binding.

3.5. Influence of pH on biosorption of Zn(II) ion

The pH of liquid phase in biosorption system significantly affects the metal ion removal [16]. In the present work, the effect of pH on sorption Zn(II) ion was studied in range of 2–8. The results of influence of pH on Zn(II) ion sorption have been shown in Fig. 3. The experimental errors were quantified and have been shown as error bars in Fig. 3.

It became obvious from Fig. 3 that at the pH range < 3, the metal ion removal (39%) was very underprivileged. With the increase in pH from 3 to 6, there was a radical increase in removal of Zn(II) ion. The maximum removal of metal ion was obtained as 98.69% at pH 6. At pH 7 and 8, the metal ion removal was 98.84 and 99.16%, respectively, which was almost constant. Optimum pH for the growth of *zinc sequestering bacteria VMSDCM* was calibrated to be 6.8, therefore maximum adsorption of zinc in SBB system was obtained
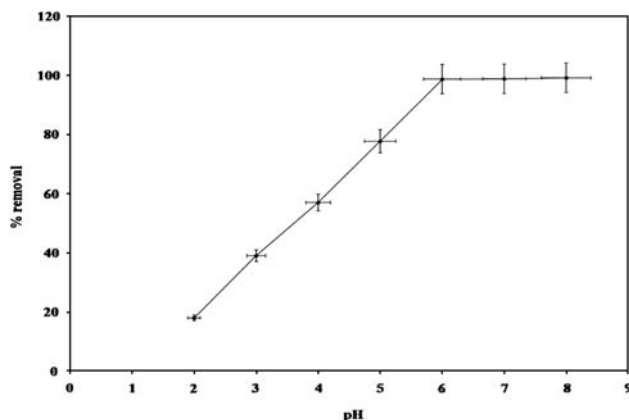
Fig. 3. Influence of pH on Zn(II) ion sorption.

Fig. 4. Influence of temperature on Zn(II) ion sorption at pH 6, particle size 0.5 mm, and temperature range 298–313 K.

at pH 6. At pH more than 6, Zn(II) ion changes its speciation from metal ions to hydroxide complex (Zn(OH)$_2$) [1]. The generation of hydroxide species results in metal hydroxide precipitation rather than the sorption of metal ions on the surface of immobilized bacterium. Furthermore, at low pH <3, the density of hydrogen ion was quite high against the metal ion, which resulted in protonation of the components of the cell walls. The protonation of bacterial cell wall moieties fundamentally decreases the biosorption capacity of the microbial cells [17]. Silva et al. [18] estimated the optimum value of pH equivalent to 7 for *Pseudomonas aeurginosa* AT 18 and obtained the maximum Zn(II) ion removal about 87.7%. Contrary to this, Ozedemir et al. [19] reported the optimum pH as 5 and 4 for maximum removal of Zn(II) ion *Geobacillus thermoleovorans* sub sub sp. *decanicus* and *Geobacillus toebii* sub sp. *stromboliensis*. The reason behind the disparity in optimum pH among bacterial species was the difference in functional groups present on the surface of the cell membrane.

3.6. Influence of temperature on sorption of Zn(II) ion

Temperature dependency of the biosorption system dictates the biosorption as endothermic or exothermic. In the present investigation, the temperature was studied in range of 298 to 313 K and the results of influence of temperature have been shown in Fig. 4. The experimental errors were quantified and have been shown as error bars in Fig. 4.

It became obvious from the Fig. 4 that the percentage removal of Zn(II) across liquid phase got increased. With the rise in the temperature from 298 to 313 K, the metal ion removal increased from 76.34 to 98.69%. The results obtained in the present in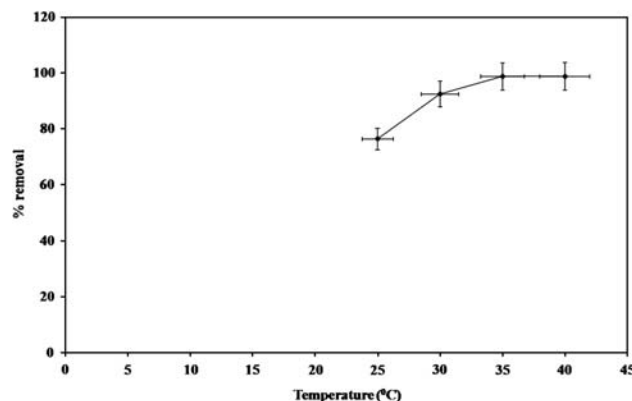vestigation indicated that the metal ion sorption in SBB system was endothermic. Kacar et al. [17] and Ozdemir et al. [19] described in their work about the exothermic behavior of metal ion sorption on the bacterial surface. The authors correlated their research outcomes as an energy independent mediated sorption of metal ions. On the other hand, Fan et al. [20] reported the sorption of Zn(II) ion over *Penicllium simplicissimum* surface as endothermic in nature. Binding of Zn(II) ion on SBB biomass as a linear function of temperature indicated the participation of chemical forces in addition to physical forces of adsorption. Distinctively, the elevation in temperature in the course of sorption of metal ion on the surface of the sorbent increases the number of active sites by rupturing the linkages present in cell wall. Moreover, the rise in temperature increases the stabilty of metal and active complex together with ionization of functional groups present on cell wall surface [21,22]. Maximum removal of zinc was observed at a temperature of 313 K.

3.7. Optimization of adsorbate to biomass ratio

Comparative study of maximum initial concentration of zinc has been shown in Fig. 5. The comparison was made between mobilized microbial cells and immobilized bacterium. The experimental errors were quantified and have been shown as error bars in Figs. 5 and 6.

It became clear from Fig. 5 that with the increase in the initial concentration of Zn(II) ion from 4 to 12 mol l^{-1}, percentage removal of Zn(II) ion was almost constant in SBB process. The removal of Zn(II) was constant (about 100%) up to 10 mol l^{-1} and with the further increase in initial concentration above 10 mol l^{-1} of metal ion, the decrease in the removal of metal ion was from 100 to 98.69%. Furthermore, any further increase in initial metal ion concentration
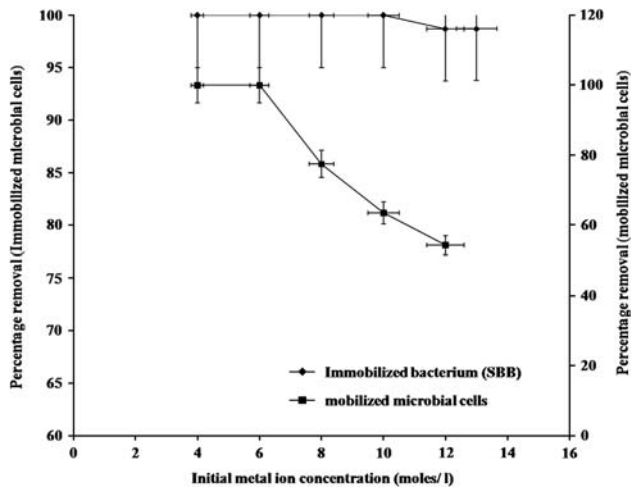
Fig. 5. Influence of initial Zn(II) ion concentration on percentage removal of Zn(II) ion.
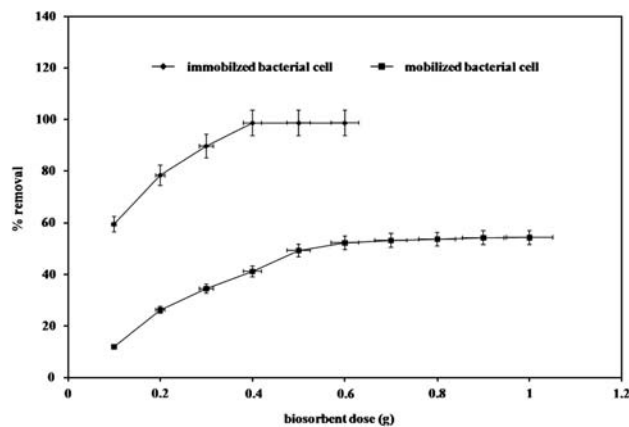

Fig. 6. Influence of biomass dose on percentage removal of Zn(II) ion.

($12 \, mol \, l^{-1}$), almost same percentage removal of Zn(II) ion (98.71%) was obtained. Contrarily, in the case of mobilized bacterial cell, 100% removal was only obtained up to the initial metal ion concentration of $7 \, mol \, l^{-1}$. Further increment of initial metal ion concentration from 8 to $12 \, mol \, l^{-1}$ resulted in the decrease of percentage removal of Zn(II) from 100 to 54.39%. The comparative analysis of the biosorption systems indicated the fact that the SBB system is much more efficient compared to the simple living bacterial biosorption system. The saturation of active sites of both immobilized bacterial cells together with the carrier would have led to the decrease in percentage removal of Zn(II) ion above $10 \, mol \, l^{-1}$. In one of our publications [1], it was reported that minimum inhibitory concentration of Zn(II) ion for mobilized bacterial cells

was $7 \, mol \, l^{-1}$. The attainment of MIC (minimum inhibitory concentration) at $7 \, mol \, l^{-1}$ resulted in decrease in removal of Zn(II) across the liquid phase. The results of influence of SBB immobilized bacterial cell dose and its comparative analysis with simple living biomass have been shown in Fig. 6.

It became evident from Fig. 6 that in both the cases, rise in bacterial dose led to substantial increase in percentage removal of Zn(II) ion. The increase in percentage removal of metal ion was quite high in immobilized bacterium compared to mobilized bacterium. The maximum percentage removal in both the cases, i.e. immobilized bacterium and mobilized bacterial cell was 98.69 and 54.33%, respectively. The maximum removal obtained in immobilized bacterium and mobilized bacterial cell cases was obtained at 0.5 and $1 \, g \, l^{-1}$. The comparative analysis of both systems indicated that the lower dose of immobilized bacterium cell offered in SBB system was much more proficient to remove zinc at all the concentrations present in liquid phase against mobilized bacterium cells.

3.8. Comparative study of equilibrium time

Comparative study of equilibrium time of both immobilized bacterium and mobilized bacterial cell has been shown in Fig. 7. The experimental errors were quantified and have been shown as error bars in Fig. 7.

The comparitive analysis of both the systems, i.e. immobilized bacterium and mobilized bacterial showed that there was substantial difference between attainment of equilibrium times. The equilibrium time obtained for immobilized bacterium and mobilized bacterial system was 3.4 and 10 h, respectively. Initially, the sorption of Zn(II) ion was very rapid and with the passage of time, the removal rate in both sys-
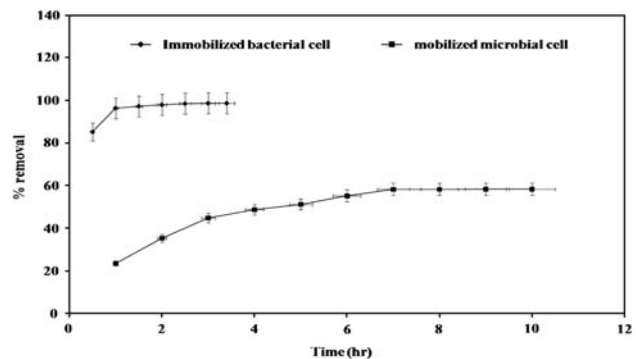

Fig. 7. Determination of equilibrium time for Zn(II) ion sorption on immobilized and mobilized bacterial cells.

tems decreased. The decrease in removal of metal ion at the later stage of the process was due to the lowering of concentration of metal ions [1]. Moreover, the characteristic of the equilibrium time curve showed that the SBB process approaches the equilibrium in short span of time against the biosorption mediated by mobilized bacterial cell.

3.9. Optimization of particle size

The influence of particles of various sizes on the sorption of Zn(II) ion has been shown in Fig. 8. In the present work, the particle size ranging between 0.5 and 2 mm has been studied. The experimental errors
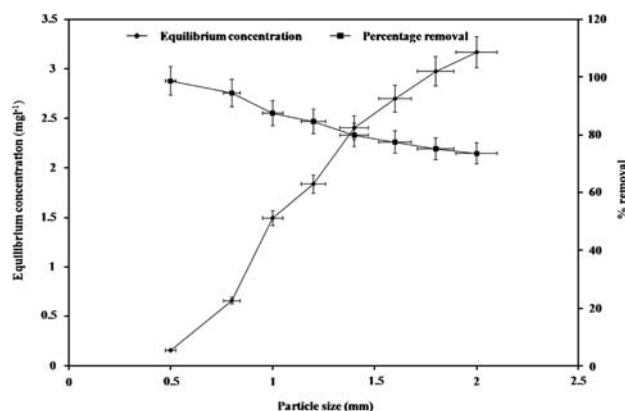

Fig. 8. Influence of particle size on sorption of Zn(II) ion.

were quantified and have been shown as error bars in Fig. 8.

It became obvious from Fig. 8 that the particle size of 0.5 mm diameter yielded the maximum percentage removal of Zn(II) ion across liquid phase. Predominantly, the lower is the particle size of the adsorbent, maximum is the removal of metal ion from liquid phase. The smaller particle size offers tremendous external surface area for metal ion binding. The external surface area in turn increases the number of active sites for metal binding. Dang et al. [23] and Mishra et al. 2010 [1] have clearly reported the fact that the lowest particle size of their biosorbent used in their investigations yielded the maximum percentage removal of metal ion in batch studies.

3.10. Isotherm modeling and design of novel isotherm

Eqs. (3)–(8) represent the convential isotherms namely Langmuir (Type I to IV), Freundlich, and Temkin model. The analysis of models has been shown in Table 2 and the figures have been given in the form of Supplementary data.

The analysis of all the conventional isotherms shown in Supplemenatry data and Table 2 undoubetly have indicated very significant higher values of linear regression coefficient (R^2). However, the conventional model equations did not fit (superimposed) over the derived straight line equations obtained from these

Table 2
Study of Langmuir, Freundlich, and Temkin isotherm

| Isotherm	Equation	χ^2	Sum of square errors (SSE)	Linear R^2 (goodness of fit)	Temperature (K)
Langmuir Type (I)	$y = 0.100x - 0.135$	2.33	4.19	0.992	208
	$y = 0.06x - 0.014$	3.33	7.54	0.998	303
	$y = 0.06x - 0.014$	2.05	3.38	0.998	308
Type (II)	$y = -0.125x + 0.097$	1.11	2.33	0.940	208
	$y = -0.005x + 0.051$	2.64	3.39	0.976	303
	$y = -0.000x + 0.046$	28.11	40.14	0.627	308
Type (III)	$y = 0.771x - 7.835$	5.66	11.39	0.974	208
	$y = 4.328x - 73.34$	13.31	15.68	0.909	303
	$y = 4.328x - 73.34$	14.74	18.91	0.909	308
Type (IV)	$y = 1.262x + 10.33$	9.21	11.36	0.974	298
	$y = 0.210x + 17.33$	15.64	18.18	0.909	303
	$y = 0.017x + 21.40$	22.36	45.11	0.648	308
Freundlich	$y = -0.512x + 3.450$	10.11	16.36	0.984	298
	$y = -0.171x + 3.091$	10.36	13.39	0.971	303
	$y = -0.058x + 3.068$	11.05	16.39	0.909	308
Temkin	$y = -7.976x + 26.73$	1.19	2.22	0.993	298
	$y = -3.440x + 22.00$	13.36	6.11	0.978	303
	$y = -1.286x + 21.55$	14.54	7.88	0.915	308
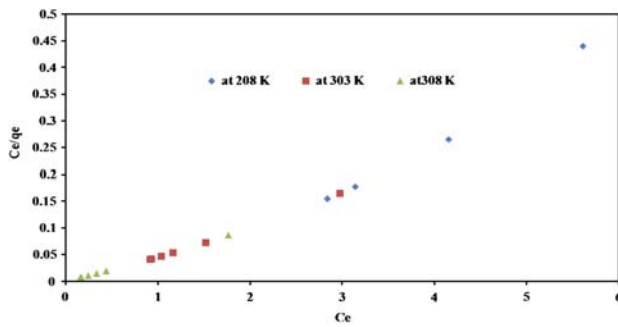
Fig. 9. Proposed isotherm model study at various temperature ranges.

models in the present work either due to the negative slope of the equation or due to the negative intercept. It became evident from the analysis of the data represented in Table 2 and from supplemenatry figure, that none of the equations represented in table resemble with their parental conventional equations, i.e. Eqs. (3)–(8). Moreover, the quantified values of statistical error functions χ^2 and SSE were significantly higher which resulted in unsuitabilty of conventional isotherms.

Therefore, in the present investigation it was concluded that none of the isotherm models was sufficiently able to describe sorption of Zn(II) ion over immobilized bacterium cell. Therefore, in the present investigation, an isotherm model was developed.

The results of the model have been shown in Fig. 9 and Table 3.

The statistical data analysis and goodness of fit of curve were evaluated in terms of linear correlation coefficient (R^2, an inbuilt function of MS word 2003), Chi square (χ^2), and sum of square errors (SSE). The χ^2 and SSE of the isotherm models have been calculated by Eqs. (10) and (11).

$$\chi^2 = \sum [q_e(\text{Exp}) - q_e(\text{Th})]^2 / q_e(\text{Th}) \tag{10}$$

$$\text{SSE} = \sum [q_e(\text{Exp}) - q_e(\text{Th})]^2 \tag{11}$$

Table 3
Study of proposed isotherm model at various temperature ranges

Temperature (K)	R^2	q_e (experimental)	A'_a Model constant	q_e (theoretical)	χ^2	SSE
208	0.99	119.184	119.147	119.517	0.000928	0.11
303	0.99	149.0976	149.098	149.167	3.23×10^{-7}	4.82×10^{-5}
308	0.99	161.484	161.485	161.487	2.83×10^{-8}	4.56×10^{-6}

Table 4
Comparative analysis of equilibrium uptake capacities of various biosorbents with the present investigation

Metal ion	Experimental conditions	Uptake capacity (mg g^{-1})	Biosorbent	Reference
Zn(II)	pH = 5.0, T = 298 K, agitation rate 150 rpm, contact time = 8 h, and particle size 0.5–2 mm	1.028–0.88	Mango bark	[24]
Zn(II)	pH = 5.0, T = 298 K, agitation rate 150 rpm, contact time = 8 h, and particle size 0.5—2 mm	0.45–0.4	Pine apple peel	[24]
Zn(II)	pH = 5.0, T = 298 K, agitation rate 150 rpm, contact time = 8 h, and particle size 0.5–2 mm	1.028–0.88	Eucalyptus bark	[24]
Zn(II)	pH = 5, T = 20 ± 18°C, contact time = 6 h, particle size 0.5–4 mm, and agitation rate 200 rpm	23.5	Eucalyptus leaves powder	[1]
Zn(II)	pH = 4.5, T = 10–400°C, contact time 12 h, and particle size < 325 mesh	31.11	Activated carbon derived from bagasse	[25]
Zn(II)	pH = 5, T = 25°C, and contact time = 2 h	641	Oscillatoria anguistissima	[26]
Zn(II)	pH = 5.0–6.0, T = 25°C, contact time = 30 min, and agitation rate = 120 rpm	12.98 ± 0.96	Botrytis cinera	[27]
Zn(II)	pH = 5, T = 20–25°C, and Fed batch system	0.0577	Powdered waste sludge	[28]
Zn(II)	pH = 6, T = 313 K, contact time = 3.4 h, and particle size of sawdust = 0.5 mm	1,549,089.1	Immobilized bacterium (SBB system)	This study

where q_e (Exp) and q_e (Th) are experimental and theoretical uptake capacities (mg g^{-1}), respectively.

The value of empirical model constant (A'_a) was calculated by using a computer program developed in Developer C++ (supplied as Supplementary material). The values of model constant A'_a at various temptaure levels have been shown in Table 3. It became comprehensible from Table 3 and Fig. 9 that proposed isotherm model has sufficient throughput to interpret the sorption of Zn(II) over immobilized bacterial cell surface successively. The proposed model has high linear correlation coefficient (R^2). The theoretical and experimental uptake capacities (q_e, mol g^{-1}) at various temperature gradients were almost the same resulting in very diminutive value of error functions. Moreover, earlier it was assumed that model constants were derived on the basis of multilayer coverage of ions on immobilized bacterium, thus the suitability of the model indicates that in addition to physical forces of attraction (usually present in case of monolayer coverage by metal ions) chemical forces were involved in the development of one layer over another. The increase in temperature 298 to 308 K increased the uptake capacity (mol g^{-1}) of the immobilized bacterial cells. This means that the temperature increment helped in building of layers of metal ion one over the other, thus making sorption of Zn(II) ion over the immobilized bacterial cells chemisorptive and endothermic in nature. Table 4 represents the comparative analysis of uptake capacities of various biosorbents with the present work.

Though the data represented in Table 4 would have been derived from different environmental condition, yet it provides a very deep relative insight to uptake capacities of various biosorbents against the present work. Certainly, the uptake capacities deciphered in the present investigation are incomparable and significantly high as compared to other sorts of biosorbents.

4. Conclusion

The present investigation has been undertaken to evaluate the biosorption potential of a novel metal ion biosorption system, i.e. simultaneous adsorption and bioaccumulation (SBB) in terms of removal of Zn(II) ion across liquid phase in batch studies. The *zinc sequestering bacterium "VMSDCM"* accession number HQ108109 was immobilized on the surface of *Cedrus deodara* sawdust. The maximum percentage removal and uptake capacity in present investigation were 98.6% and 23.69 mol g^{-1} (1549089.1 mg g^{-1}), respectively. The optimized physical parameters derived for the present investigation were pH 6, temperature

308 K, contact time 3.4 h, particle size 0.5 mm, initial Zn(II) ion concentration 12 mol l^{-1}, and biomass dose 0.5 gl^{-1}. Various conventional isotherm models were implemented but none of them was found suitable to provide sufficient information to interpret the sorption of Zn(II) ion over SBB biomass. Therefore, the proposed isotherm model was developed. The proposed model yielded the highest linear regression coefficient ($R^2 = 0.99$) value with the lowest possible values of error functions, indeed. The suitability of proposed model indicated that the sorption of Zn(II) ion on the surface of SBB biomass was chemisorptive and endothermic in nature.

Supplementary material

The supplementary material for this paper is available online at http://dx.doi.10.1080/19443994.2012.749027.

List of abbreviations

WHO	World Health Organization
USEPA	United States Environmental Protection Agency
SBB	Simultaneous biosorption and bioaccumulation
LB	Luria Bertani
NCBI	National Centre for Biotechnology Information
FTIR	Fourier Transformation Infrared spectrum
SEM	Scanning Electron Micrograph
AAS	Atomic Absorption Spectrophotometer
q_{max}	maximum uptake capacity (mol g^{-1})
K_L	Langmuir constant (l g^{-1})
K_f	Freundlich constant (mg g^{-1})
$1/n$	affinity constant
B_t	Temkin model constant
C_0	initial metal ion concentration (mg l^{-1})
C_e	equilibrium metal ion concentration (mg l^{-1})
v	volume of solution in liters (L)
m	mass of biosorbent in grams

References

[1] V. Mishra, C.B. Majumder, V.K. Agarwal, Zn(II) ion biosorption onto surface of eucalyptus leaf biomass: Isotherm, kinetic, and mechanistic modeling, Clean Soil Air Water, (2010), doi10.1002/clen.201000030.

[2] C.A. Basha, S.J. Selvi, E. Ramasamy, S. Chellammal, Removal of arsenic and sulphate from the copper smelting industrial effluent, Chem. Eng. J. 141 (2008) 89–98.

[3] J.A. Carrera, E. Bringas, M.F.S. Roman, I. Ortiz, Selective membrane alternative to the recovery of zinc from hot dip galvanizing effluents, J. Membr. Sci. 326 (2008) 672–680.

[4] G. Csicsovszki, T. Kekesi, T.I. Torok, Selective recovery of Zn and Fe from spent pickling acid solutions by the combination of anion exchange and membrane electrowinning technique, Hydrometallurgy 77 (2007) 19–28.

[5] M.B. Mansur, S.D.F. Rocha, F.S. Magalhaes, J.D.S. Benedetto, Selective extraction of Zn(II) over Fe (II) from spent hydro-chloric acid pickling effluents by liquid—liquid extraction, J. Hazard. Mater. 150 (2008) 669–678.

[6] Y. Sag, T. Kutsa, Determination of the biosorption heats of heavy metal ions on Zoogloea ramigera and Rhizopus arrhizus, Biochem. Eng. J. 6 (2007) 145–151.

[7] D.L. Vullo, H.M. Ceretti, M.A. Daniel, S.A.M. Ramrez, A. Zalts, Cadmium, zinc and copper biosorption mediated by Pseudomonas vernoii 2E, Bioresour. Technol. 99 (2008) 5574–5581.

[8] A. Lodi, C. Solisio, A. Converti, D.M. Borghi, Cadmium, zinc, copper, silver, chromium (III) removal from wastewaters by Sphaerotilus natans, Bioprocess Eng. 19 (1998) 197–203.

[9] J. Sambrook, E.F. Fritsch, T. Maniatis, Molecular cloning: A laboratory manual, Cold Spring Harbor Press: Cold Spring Harbor, New York, NY, 1989.

[10] R.R Dash, C.B Majumder, A. Kumar, Treatment of metal cya-nide bearing wastewater by simultaneous adsorption and bio-degradation (SBB), J. Hazard. Mater. 152 (2008) 387–396.

[11] A.E. Nemr, Potential of pomegranate husk carbon for Cr (VI) removal from wastewater kinetic and isotherm studies, J. Hazard. Mater. 161 (2009) 132–141.

[12] J. Febrianto, N.A. Kosasih, J. Sunarso, H.Y. Ju, N. Indraswati, S. Ismadji, Equilibrium and kinetic studies in adsorption of heavy metals using biosorbent: A summary of recent studies, J. Hazard. Mater. 162 (2009) 616–645.

[13] V.C. Srivastava, I.D. Mall, I.M. Mishra, Adsorption thermody-namics and isosteric heat of adsorption of toxic metal ions onto bagasse fly ash (BFA) and rice husk ash (RHA), Chem. Eng. J. 132 (2007) 267–278.

[14] A. Ahmad, M. Rafatullah, O. Sulaiman, M.H. Ibrahim, Y.Y. Chii, B.M. Siddque, Removal of Cu (II) and Pb (II) ions from aqueous solutions by adsorption on sawdust of Meranti wood, Desalination 247 (2009) 636–646.

[15] E.M.P. Gonzalez, H.V. Montoya, Characterization of mango pit as raw material in the preparation of activated carbon for wastewater treatment, Biochem. Eng. J. 36 (2007) 230–238.

[16] V.C. Srivastava, M.M. Swamy, I.D. Mall, I.B. Prasad, I.M. Mishra, Adsorptive removal of phenol by bagasse fly ash and activated carbon: Equilibrium, kinetics and thermodynamics, Colloid and Surface A: Physiochemical Engineering Aspects 272 (2006) 89–104.

[17] Y. Kacar, C. Arpa, S. Tan, A. Denizli, O. Genc, M.Y. Arica, Biosorption of Hg (II) and Cd (II) from aqueous solutions: Comparison of biosorptive capacity of alginate and immobi-lized live and heat inactivated Phanerochaete chrysosporium, Process Biochem. 37 (2002) 601–610.

[18] R.M.P. Silva, A.A. Rodriguez, J.M.D.O. Gomez, D.C. Moreno, Biosorption of chromium, copper, manganese, and zinc by Pseudomonas aeruginosa AT 18 isolated from a site contami-nated with petroleum, Bioresour. Technol. 100 (2009) 1533–1536.

[19] S. Ozdemir, E. Kilinc, A. Poli, B. Nicolus, K. Guen, Biosorp-tion of Cd, Cu, Ni, Mn and Zn from aqueous solutions by thermophillic bacteria, Geobacillus toebii sub.sp. decanicus and Geobacillus thermoleovorans sbu.sp. strombolensis: Equilibrium, kinetic and thermodynamic studies, Chem. Eng. J. 152 (2009) 195–206.

[20] T. Fan, Y. Liu, B. Feng, G. Zeng, C. Yang, M. Zhou, Biosorp-tion of cadmium (II), zinc (II) and lead (II) by Penicillium sim-plicissimum: Isotherms, kinetic and thermodynamics, J. Hazard. Mater. 160 (2008) 655–661.

[21] M. Iqbal, R.G.J. Edyvean, Biosorption of lead, copper and zinc ions on loofa sponge immobilized biomass of Phanerochaete chrysosporium, Mineral Eng. 17 (2007) 217–223.

[22] A.M. Marques, X. Roca, M.D. Simon-Pujol, M.C. Fuste, F. Congredo, Uranium accumulation by Pseudomonas sp. EPS—5028, Appl. Microbiol. Biotechnol. 35 (1991) 406–410.

[23] V.B.H. Dang, H.D. Doan, T. Dang–Vu, A. Lohi, Equilibrium and kinetics of biosorption of cadmium (II) and copper (II) ions by wheat straw, Bioresour. Technol. 100 (2009) 211–219.

[24] V. Mishra, C.B. Majumder, V.K. Agarwal, Biosorption of Zn (II) onto the surface: A comparative study of adsorbent parti-cle size and of non-living biomasses removal capacity of three different biomasses, Water Air Soil Pollut. 211 (2010) 489–500.

[25] D. Mohan, K.P. Singh, Single and multicomponent adsorption of cadmium and zinc using activated carbon derived from from- an agriculture waste, Wat. Res. 36 (2002) 2304–2318.

[26] P. Ahuja, R. Gupta, S.K. Saxena, Zn^{2+} biosorption by Oscillato-ria anguistssima, Process Biochem. 34 (1999) 77–85.

[27] S. Tunali, T. Akar, Biosorption properties of Botrytis Cinerea biomass, J. Hazard. Mater. 131 (2006) 137–145.

[28] F. Kargi, S. Cikla, Determination of model parameters for zinc (II) ion powdered waste sludge (PWS) in a fed batch system, J. Environ. Manage. 85 (2007) 883–890.