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Evaluation of new biosorbents prepared from immobilized biomass of *Candida* sp. for the removal of nickel ions

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ABSTRACT

Batch biosorption process for nickel removal was evaluated using three newly developed biosorbents. These three biosorbents were prepared by immobilizing the biomass of *Candida lipolytica*, *Candida tropicalis*, and *Candida utilis* with the help of calcium alginate. Optimum conditions for initial pH, biosorbent dose, contact time, temperature, and initial concentration of nickel ions were determined using batch studies. The equilibrium, kinetic and thermodynamic parameters were determined for batch biosorption process. The maximum biosorption capacity (mg g^{-1}) under optimum experimental conditions and temperature of 45°C was 197.68, 178.06, and 123.43 for immobilized *Candida tropicalis* beads (ICTB), immobilized *Candida utilis* beads, and immobilized *Candida lipolytica* beads, respectively. Hydrochloric acid solution exhibits excellent desorbing efficiency and recovered 98% of adsorbed nickel ions from ICTB. The biosorbent was successfully used for five consecutive biosorption desorption cycles without significant loss in its biosorption capacity. ICTB appeared to be an efficient biosorbent to accumulate and recover nickel ions due to higher biosorption capacity and outstanding regeneration results.

Keywords: Biosorption; *Candida* sp.; Equilibrium; Kinetic; Nickel; Thermodynamics

1. Introduction

Deterioration of freshwater by human activities has the adverse impact on the ecosystems. Pollution caused by agricultural, domestic, and industrial wastes such as sewage, fertilizer, and heavy metals are very harmful for the aquatic species. Heavy metals are being extracted from the Earth and exploited for human products and industry for decades. They have the ability to accumulate in cell tissues, which result in biomagnification. They have potential to be toxic even at low concentrations and are the major inorganic pollutants in the environment because of their mobility and toxicity.

Nickel and its compounds are used in industrial and commercial products. Consequently, the growth of industrial activities has resulted into release of nickel in ecosystems. Nickel is present in industrial effluents of electroplating, silver refineries, and storage battery [1–3]. Its compounds are also used as pigments and catalysts. Nickel at the higher concentration level causes lungs, bones, and nose cancer. The other organs which can be affected by nickel toxicity include blood, cardiovascular, and immune system. Acute dose of nickel causes headache, nausea, dizziness, vomiting, chest pain, dry cough, cyanosis, breath and

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respiration problems, and extreme weakness. Nickel exposure to human in highly polluted environment may result in various pathological effects like lung fibrosis, skin allergies, and iatrogenic poisoning. Nickel interferes with the essential metals metabolism such as calcium, copper, iron, magnesium, manganese, or zinc, which results in toxic effects [4–7].

The conventional methods for the removal of toxic heavy metals include chemical precipitation, flocculation and coagulation, flotation, complexation, solvent extraction, cementation, evaporation, ion-exchange, adsorption, membrane process, and biological process. The drawbacks with the conventional methods are that they are not efficient for removing the heavy metal ions when they are present in low concentrations. Secondly, these methods are costly and may also generate the secondary toxic sludge [8–10].

Expanding knowledge and concern about environment led to search for new techniques for economical treatment of wastewater polluted with heavy metals. The search for new biosorbents focused on biosorption processes depending on metal binding capacities of different biological materials. Research has shown that biosorption is an ideal substitute for the removal of heavy metals from industrial effluents [11,12]. The major issue with most of the previous studies is the use of biosorbents in the powdered form [2,13–24]. This form does not allow the cyclic use of biosorbents. The reason is that the post-separation of biosorbents is difficult and costly when used in the powdered form. Due to these problems, biosorbents are discarded after single use. This results in toxic sludge rich in heavy metals. Its treatment and disposal pose another problem. Secondly, larger size of equipment is required for the biosorption process if the biosorbents have lower biosorption capacity. This results in enhanced operational cost of the biosorption process.

The above issues were the major hurdles in the widespread use of biosorbents for metal ion removal. Thus, there is a need to prepare biosorbents which can be used repeatedly. Therefore, there is a need to investigate whether cyclic use of the biosorbents could be feasible after enhancing their mechanical properties by immobilization. In case of success, biosorption could be used as a cost-effective method for nickel removal. With this background, this study was undertaken with the following objectives: (i) to optimize the process parameters and thereafter use these optimum conditions to study the nickel ions biosorption capacity of three newly developed immobilized biosorbents prepared using *Candida* sp. biomass; (ii) to determine the kinetic, equilibrium, and thermodynamic parameters; and (iii) to evaluate the regeneration and cyclic use of the potential biosorbent.

2. Materials and methods

2.1. Chemicals and microorganisms

The analytical grade chemicals were used in this research work. The culture media was of biological grade. The nickel ions stock solution (2,000 mg L^{-1}) was prepared using nickel sulfate, $NiSO_4$, (BDH, England) and deionized water. All the working solutions of varying concentrations of nickel ions and specific pH were prepared by diluting the stock solution in deionized water.

Three yeast strains of *Candida* sp. namely *Candida tropicalis* (NRRL Y-1552), *Candida utilis* (NRRL Y-900) and *Candida lipolytica* (NRRL Y-1095), were collected from Institute of Industrial Biotechnology, Government College University Lahore (GCU), Pakistan, and used in this study.

2.2. Preparation of biosorbents

Culture of three *Candida* sp. i.e. *Candida lipolytica*, *Candida tropicalis*, and *Candida utilis* was obtained and stored at 4°C in the laboratory. To further grow them, subculturing was carried out on yeast malt (YM) agar in test tubes. These were incubated at 25°C for 24 h. A test tube containing 10 mL YM broth was sterilized for preculturing. Then, a loop full of subcultured yeast was added in it. This was incubated at the same conditions as stated above. Afterwards, 5 mL of preculture was added in a shake flask containing 100 mL of sterilized YM broth. The mixture was incubated again at 25°C for 24 h [25–27]. *Candida* sp. growth occurred during this step, and biomass was separated using centrifugation at 4,500 rpm for 30 min.

A mixture was prepared by adding 40 g L^{-1} of biomass of each of the three *Candida* sp. separately with 2% (w/v) solution of sodium alginate. This mixture was then added dropwise in 0.2 M calcium chloride solution at 4°C. The biomass was entrapped in beads of calcium alginate gel. The mechanical properties of immobilized *Candida lipolytica* beads (ICLB), immobilized *Candida tropicalis* beads (ICTB), and immobilized *Candida utilis* beads (ICUB) were improved by drying them at 70°C in an incubator to a constant weight [26]. The diameter of the beads was ranging from 1.18 to 1.83 mm. Blank calcium alginate beads (without yeast biomass) were also prepared to evaluate its biosorption capacity for the removal of nickel ions.

2.3. Batch biosorption experiments

The batch experiments were performed to find the kinetic, isotherm, and thermodynamic parameters. For the batch experiments, known mass (S, g) of each of the biosorbent (ICLB, ICTB, and ICUB) was separately taken in 250 mL Erlenmeyer flasks. The working volume of nickel bearing solution (V, L) was taken as 50 mL. Nickel solutions of varying concentrations and known pH values were used. Initial pH of nickel solution was adjusted using 0.1 M HCl or 0.1 M NaOH. The Erlenmeyer flasks containing all above constituents were agitated at controlled temperature in an orbital shaker at 150 rpm for specific contact time. The residual concentration, C_f (mg L^{-1}), of nickel ions was determined using the atomic absorption spectrometer (Perkin Elmer-Singapore, AAnalyst 800). The following relationship was used to determine the biosorption uptake capacity, q (mg g^{-1}) [28].

$$q = \frac{V\,(C_i - C_f)}{S} \tag{1}$$

Contact time of 3 h was used for the batch equilibrium experiments. The initial pH value was 6.62 and biosorbent dose was 1 g L^{-1} unless otherwise mentioned. Whereas the initial concentration (mg L^{-1}) of nickel ions was varied from 25 to 460 and temperature (°C) was varied from 25 to 45. Batch kinetic studies were performed for four initial concentrations (mg L^{-1}) of nickel ions i.e. 25, 80, 170, and 300, at a temperature of 25°C; and contact time was varied from 0.25 to 3 h.

Batch studies were also performed using the blank calcium alginate beads. The reason was to evaluate the contribution of calcium alginate in nickel uptake. All the experiments of batch studies were performed in triplicate, and mean values were used for analyses.

2.4. Regeneration of biosorbent

From the batch studies, the biosorbent showing the best performance was used for regeneration studies. Three desorbing agents were used. These were: (i) 0.1 M hydrochloric acid (HCl), (ii) 0.1 M nitric acid (HNO_3), and (iii) 0.1 M sodium hydroxide (NaOH) solutions. The desorption experiments were performed by agitating the biosorbent saturated with nickel ions and desorbing solution in orbital shaker at 150 rpm for contact time of 1 h.

After determining the best desorbing agent, the ability of biosorbent for use in a continuous cyclic process was evaluated. For this, sequential biosorption desorption cycles were continual repeated five times using the best desorbing agent. The same biosorbent was used in the succeeding cycle after regeneration process. The biosorbent was washed with deionized water after each biosorption desorption cycle.

3. Results and discussion

3.1. Effect of pH

The effect of initial pH on the biosorption capacity for nickel ions was studied in a range of 2.41–7.56, at six different levels. Results are exhibited in Fig. 1. For all the three biosorbents i.e. ICLB, ICTB, and ICUB, the optimum value of initial pH of nickel aqueous solution was found to be 6.62. The highest value of equilibrium biosorption capacity of nickel ions was found as 116.18 mg g^{-1} using ICTB. The operational parameters are mentioned in the figure caption. The decrease in the biosorption capacity for higher value of the pH was due to the formation of soluble nickel hydroxylated complexes. Similar results have been reported by other authors. Optimum pH of 6.5 for the biosorption of nickel ions has been reported using silica-gel-immobilized waste biomass of *Phaseolus vulgaris L* [29]. Optimum pH of 6.25 for *Aspergillus niger* in dried powder form and optimum pH of 6.75 for Baker's yeast have been reported used in the inactive from [14,22].

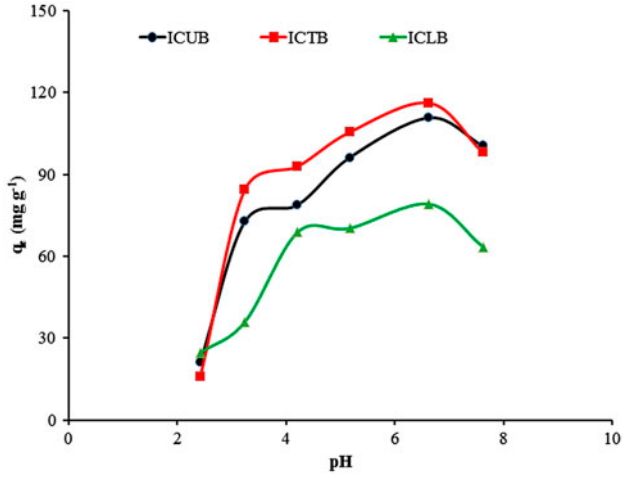

Fig. 1. Effect of pH on biosorption of nickel ions: contact time 3 h; biosorbent dose 1 g L^{-1}; initial concentration 200.46 mg L^{-1}; and temperature 25°C.

3.2. Effect of contact time

The effect of contact time on the biosorption capacity for nickel ions is exhibited in Fig. 2. The highest value of equilibrium biosorption capacity of nickel ions at contact time of 3 h was found as 111.55 mg g^{-1} using ICTB. It can be perceived that the biosorption capacity increased with the increase of contact time. During the first rapid phase of the biosorption process, the empty binding sites of biosorbents were available and hence about 75 to 93% of total uptake capacity was achieved in the first 60 min. Another factor for initial high biosorption rate was a high concentration gradient for nickel ions at the start of the biosorption process. Once the nickel ions are attached on the binding sites, they offered repulsion for the nickel ions present in the liquid phase. Hence, at higher contact time the binding of nickel ions with the biosorbent takes place at a slower rate. The equilibrium time was taken as 3 h for all the three biosorbents.

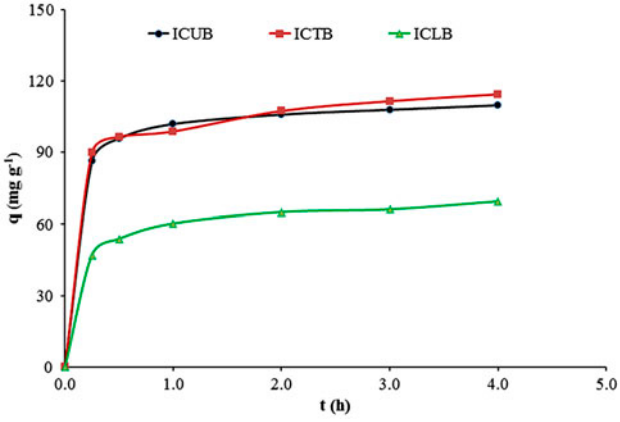

Fig. 2. Effect of contact time on biosorption of nickel ions: pH 6.62; biosorbent dose 1 g L^{-1}; initial concentration 300.78 mg L^{-1}; and temperature 25°C.

3.3. Effect of biosorbent dose

The effect of biosorbent dose was studied in five levels ranging from 0.5 to 4 g L^{-1}. The results for three biosorbents are shown in Fig. 3. The detailed experimental conditions are cited below the caption of Fig. 3. It can be seen that 1 g L^{-1} is the optimum biosorbent dose for all the three biosorbents. For the given experimental conditions, the equilibrium biosorption capacity of ICTB, for nickel ions, increases from 107.21 to 137.45 mg g^{-1} when biosorbent dose is increased from 0.5 to 1.0 g L^{-1}, respectively. For further increase in the ICTB dosage i.e. 2, 3, and 4 g L^{-1}, the biosorption capacity decreases i.e. 98.27, 68.01, and 60.01 mg g^{-1}, respectively. The reason being, as the dose of biosorbent was increased, the amount of nickel ions adsorbed

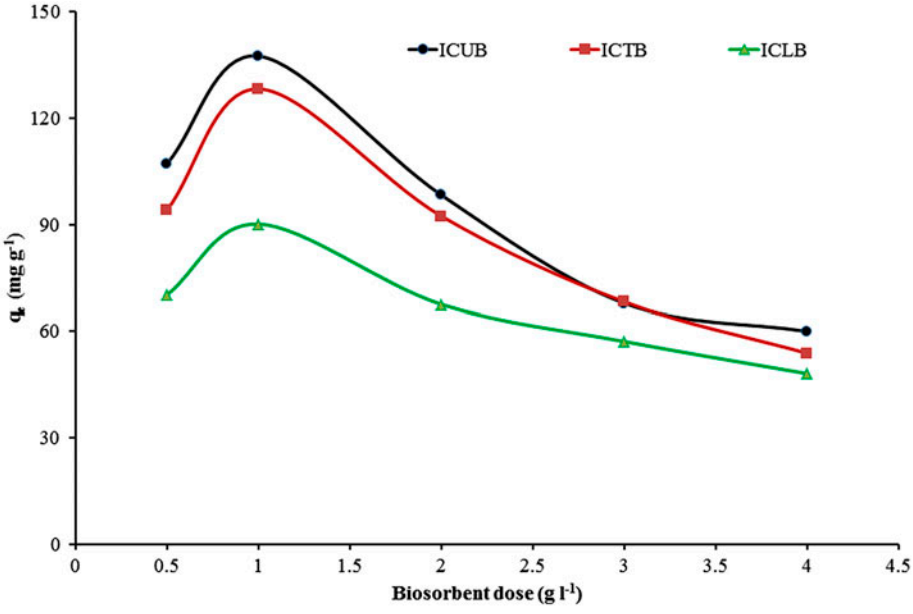

Fig. 3. Effect of biosorbent dose on biosorption of nickel ions: pH 6.62; contact time 3 h; initial concentration 300.18 mg L^{-1}; and temperature 25°C.

per unit mass of biosorbent decreased. Secondly, the decline in the biosorption capacity at the higher doses of biosorbent i.e. 2, 3, and 4 g L^{-1}, is due to the reason that binding sites withstand unsaturated during the biosorption process [30].

3.4. Effect of initial metal ion concentration

The effect of the initial concentration of nickel ions for the three biosorbents is presented in Fig. 4. The experimental conditions are mentioned in the caption of the figure. The biosorption capacity of all three biosorbents increased with the increase of initial concentration of nickel ions in aqueous solution. It can also be seen that the increase remained linear for initial nickel ions concentration of about 140 mg L^{-1} and thereafter became nonlinear. The reason is that with higher initial concentration of nickel ions, the concentration gradient is higher. Hence, more availability of nickel ions for the empty binding sites results in higher biosorption rate. Secondly, the biosorbent has a definite number of binding sites. Therefore, at very high initial concentration of nickel ions, the binding sites become saturated quickly at the start and after that the biosorption process takes place at very slow rate. The highest equilibrium biosorption capacity was exhibited by ICTB for nickel ions, which was 129.98 mg g^{-1} for initial concentration of 460.45 mg L^{-1}, at the given experimental conditions.

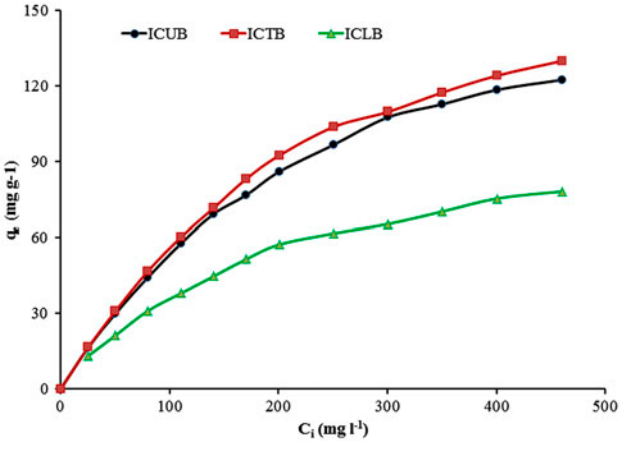

Fig. 4. Effect of initial concentration of nickel ions on its biosorption: pH 6.62; contact time 3 h; biosorbent dose 1 g L^{-1}; and temperature 25°C.

3.5. Biosorption isotherm parameters

Batch biosorption isotherm parameters were determined using the Langmuir isotherm, Freundlich isotherm, Dubinin–Radushkevich (D–R) isotherm, and generalized isotherm models. Nonlinear regression process gives better results for the determination of isotherms parameters [26]. Hence, the isotherm parameters were determined using MATLAB tool "nlinfit" for nonlinear regression.

The Langmuir isotherm model is very often used to compute and compare the efficiency of different biosorbents. This model was originally developed for description of adsorption of gas on the activated carbon [31]. The empirical relationship is based on the assumptions that the biosorption is a monolayer, and biosorbent has the finite number of homogeneous binding sites. The Langmuir isotherm has hyperbolic relation as expressed in Eq. (2) [28].

$$q_e = q_{max} \frac{b_L C_f}{1 + b_L C_f} \tag{2}$$

where q_e is equilibrium biosorption capacity, C_f is equilibrium or residual concentration (mg L^{-1}) of the sorbate, q_{max} is maximum biosorption capacity (mg g^{-1}), and b_L represents the Langmuir constant (L mg^{-1}). Langmuir constant symbolizes the energy and affinity of the biding sites.

The Langmuir isotherm model can be expressed in terms of dimensionless equilibrium parameter "R_L" which is also known as separation factor as given in Eq. (3). Separation factor value helps to determine the nature of the biosorption process to be either unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$), or irreversible ($R_L = 0$) [11].

$$R_L = \frac{1}{1 + b_L C_i} \tag{3}$$

The values of Langmuir constant and maximum biosorption capacity are summarized in Table 1. ICTB showed better performance as compared to other two biosorbents i.e. ICUB and ICLB. The maximum biosorption capacity of ICTB, ICUB, and ICLB was found to be 197.68, 178.06, and 123.43 mg g^{-1}, respectively (at pH value of 6.63 and temperature of 45°C). It is obvious from the experimental results that the biosorption capacity increased with the increase of temperature. The biosorption process may be physical as well as chemical in nature. The higher temperature results in the increase of number of active binding sites due to bond rapture [32]. The value of Langmuir

Table 1
Isotherm parameters for biosorption of nickel ions

Isotherm model parameters	Biosorbent	ICTB			ICUB			ICLB		
	T (℃)	25	35	45	25	35	45	25	35	45
Langmuir	q_m (mg g^{-1})	160.75	169.73	197.68	155.3	168.48	178.06	99.21	106.76	123.43
	b_L (L mg^{-1})	0.0121	0.0208	0.0371	0.0111	0.0225	0.0321	0.009	0.0155	0.0252
	MSE	1.31	3.59	16.3	1.65	7.67	5.89	2.17	1.82	2.76
		0.77	0.62	0.54	0.76	0.64	0.49	0.8	0.71	0.6
		0.46	0.3	0.23	0.45	0.31	0.2	0.51	0.39	0.28
Freundlich isotherm	k_F (mg g^{-1})	10.53	18.89	32.8	9.49	20.1	27.36	5.45	10.35	17.87
	n_F	2.26	2.69	3.13	2.22	2.76	3.05	2.2	2.63	3.07
	MSE	38.7	74.36	141.21	28.33	64.41	104.66	7.55	18.16	39.97
D–R isotherm	q_m (mol g^{-1})	0.0059	0.0058	0.0064	0.0057	0.0057	0.0058	0.0035	0.0036	0.0039
	$B_{D–R}$ (mol^2 J^{-2})	5.71E−09	4.33E−09	3.32E−09	5.85E−09	4.19E−09	3.48E−09	6.07E−09	4.62E−09	3.60E−09
	E (kJ mol^{-1})	9.35	10.74	12.26	9.25	10.92	11.99	9.08	10.4	11.78
	MSE	16.94	36.38	70.69	11.01	78.93	49.99	3.01	8.06	18.72
Generalized isotherm	$q_{max,G}$ (mg g^{-1})	164.14	175.43	211.28	166.21	181.86	189.21	116.39	116.05	132.01
	K_G (mg g^{-1})	0.97	0.94	0.86	0.92	0.87	0.87	0.84	0.87	0.87
	n_G (L mg^{-1})	76.42	40.97	19.27	72.01	31.81	23.01	71.59	45.35	27.91
	MSE	1.22	2.98	10.27	0.97	4.82	2.07	1.24	0.88	0.95

constant ranged from 0.009 to 0.0371 L mg^{-1}. The smaller values of mean squared error (MSE) showed that the Langmuir model fits very well for the equilibrium experimental data. The values of separation factor "R_L" are also given in Table 1. It is apparent from the result that R_L values lie between 0 and 1 which exhibits that the biosorption process is favorable for the removal of nickel ions using ICTB, ICUB, and ICLB.

The biosorption capacity of the blank calcium alginate beads was 30.76 mg g^{-1} for removal of nickel ions. The biosorption capacity of ICTB was found to be much higher as compared to most of the other microbial biosorbents reported in the literature. A graphical presentation of maximum biosorption capacity of various microbial biosorbents is shown in Fig. 5 [2,13,14,17–23,33–35]. In literature, initial concentration of nickel ions has been recorded ranging from 150 to 1,000 mg L^{-1} for the biosorption process using different biosorbents. In the Fig. 5, the values for the present study were taken for 25°C temperature as is the case with most of the referred values. Only dried aerobic activated sludge has the biosorption capacity higher than the ICTB [2]. Dried activated sludge was used in suspension form for the removal of nickel ions, and the equilibrium time was 24 h. This equilibrium time is much longer as compared to the present study i.e. 3 h. Also, initial concentration of nickel ions, which directly affects the maximum biosorption capacity, was higher in case of activated sludge i.e. 500 mg L^{-1}, whereas for this study, it was 460.45 mg L^{-1}.The suspension required centrifugation or filtration process for the post-separation which makes the process costly. Furthermore, no regeneration studies were carried out in order to investigate the reusability of the aerobic activated sludge as a biosorbent in the continuous process. ICTB has an advantage that it can be regenerated and reused, but dried aerobic activated sludge cannot be used in the continuous cyclic process.

The Freundlich isotherm is an empirical model. It assumes that biosorption process takes place in multilayer and it is reversible and nonideal. It also assumes that binding sites are heterogeneous with varying biosorption heat and biosorption affinities. It was originally proposed by Freundlich for animal charcoal adsorption process [36]. It represents that the ratio of metal ions in solid phase (adsorbed on the given mass of biosorbent) to the metal ions in liquid phase (solute) is different for different concentrations of metal ions in the solution. Each of the binding sites has its own bond energy, and the binding sites with higher binding energy are occupied first. The biosorption energy of these biding sites exponentially decreased as they get occupied by the metal ions [37]. The mathematical form of the Freundlich isotherm is represented in Eq. (4) [28]

$$q = k_F C_f^{(1/n_F)} \tag{4}$$

where k_F and n_F are Freundlich constants. The values of Freundlich constants are summarized in Table 1. The results showed that Freundlich isotherm model gives satisfactory fits for the batch equilibrium data. But the Freundlich model does not predict the equilibrium biosorption capacity as good as estimated by Langmuir model. The values of MSE ranged from 7.55 to 104.66 for Freundlich isotherm, while for Langmuir it is from 1.31 to 16.30. The values of n_F ranged from 2.20 to 3.13 mg L^{-1}. It shows that the biosorption process for removal of nickel ions using all three

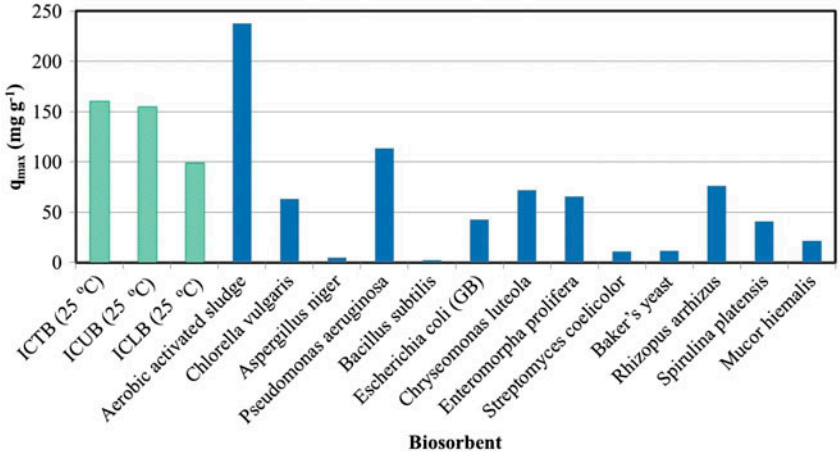

Fig. 5. Comparison of biosorption capacity of nickel ions for various microbial biosorbents.

biosorbents is favorable. Similarly, the value of k_F ranged from 5.45 to 32.80 mg g^{-1}. It shows that the biosorbents have good capacity for the biosorption of nickel ions.

In order to designate the effect of porous structure of a biosorbent, D–R isotherm model assumes heterogeneous sorption sites with distinct sorption potential. Hence, it is more general than Langmuir isotherm. The mathematical expression is given below [38]:

$$q = q_{max} \exp\left(-B_{D-R}\varepsilon^2\right) \quad (5)$$

where q_{max} characterizes the monolayer biosorption capacity (mol g^{-1}), B_{D-R} represents constant (mol^2 kJ^{-2}) which is related to biosorption energy, and ε is the Polanyi potential which is expressed below:

$$\varepsilon = RT \ln\left(1 + \frac{1}{C_f}\right) \quad (6)$$

where R is the gas constant (8.314 J mol^{-1} K^{-1}) and T is absolute temperature (K).

Analysis of the data illustrates that D–R isotherm gives apparently a good description of the biosorption process for the nickel ions. Parameters of D–R isotherm are also presented in Table 1. The values of the biosorption energy, for nickel ions for the three biosorbents ranged between 9.08 and 12.26 kJ mol^{-1}. It shows that biosorption mechanism is ion-exchange in nature as the values of biosorption energy lie within range of 8–16 kJ mol^{-1}. The values of MSE show that the D–R isotherm model has a better potential than the Freundlich model and was poor as compared with the Langmuir isotherm model to predict the equilibrium biosorption capacity of nickel ions.

The generalized isotherm is a combination of Langmuir and Freundlich isotherms models and is given below:

$$q_e = \frac{q_m C_f^{n_G}}{K_G + C_f^{n_G}} \quad (7)$$

where q_m is maximum biosorption capacity (mg g^{-1}), n_G is the cooperative binding constant, and K_G is the saturation constant (mg L^{-1}). The values of generalized isotherm constants i.e. K_G and n_G, along with maximum biosorption capacity were determined. The values of constants are summarized in Table 1. Generalized isotherm model gives a better fit to the equilibrium experimental data for biosorption of nickel ions. The values of MSE were found to be smaller and ranged between 0.88 and 10.27.

After comparing all the isotherm models, it is revealed that Langmuir isotherm model and generalized isotherm model represent the equilibrium biosorption data slightly better as compared with other isotherms.

3.6. Biosorption kinetic parameters

The pseudo-first-order kinetic equation is given in Eq. (8). It is based on the concept of the linear driving force. It has the following form [39]:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \quad (8)$$

Here k_1 represents rate constant for pseudo-first-order biosorption process (g mg^{-1} h^{-1}), q_e is the amount sorbate adsorbed onto biosorbent at equilibrium (mg g^{-1}), q_t is the amount of sorbate adsorbed onto biosorbent at time t (mg g^{-1}), and t is time (h). The integrated form was obtained by taking definite integral at the initial conditions of $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$ and is given in Eq. (9).

$$q_t = q_e(1 - \exp(-k_1 t)) \quad (9)$$

The kinetic parameters for first-order kinetic model were determined using MATLAB tool "nlinfit" for nonlinear regression and are presented in Table 2. The values of sum of squares for error (SSE) for the pseudo-first-order kinetic model are significantly higher ranging from 3.71 to 195.23 for the biosorption process of nickel ions. The first-order kinetic reflects the individual biosorption sites and not the whole biosorption process. It can be concluded that the biosorption of nickel ions using the immobilized biosorbents was not represented well by pseudo-first-order kinetic model. The fluctuation in the values of k_1 is small, and the values of the k_1 increase with the increase in the initial concentration of nickel ions from 25.65 to 300.47 mg L^{-1}.

The pseudo-second-order equation is conceived that biosorption process is second order and follows chemisorption mechanism. It can describe the biosorption process for the whole period of time. It follows the concept of linear driving force. Its mathematical form is given in Eq. (10) below [40]:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad (10)$$

Here k_2 represents the rate constant of pseudo-second-order biosorption (g mg^{-1} h^{-1}), q_e is the amount of

Table 2
Kinetic parameters for biosorption of nickel ions

Kinetic model parameters	Biosorbent	ICTB				ICUB				ICLB			
	C_0 (mg L^{-1})	25.21	80.67	170.48	300.78	25.21	80.67	170.48	300.78	25.21	80.67	170.48	300.78
First-order kinetic	q_e (mg g^{-1})	15.62	46.08	78.00	104.68	15.66	42.11	71.08	104.31	12.49	28.63	47.35	63.41
	k_1 (h^{-1})	2.04	3.68	3.71	7.38	2.32	3.13	4.48	6.62	1.16	2.42	3.88	4.85
	$q_{e,exp}$ (mg g^{-1})	16.32	48.3	81.70	111.55	16.52	43.93	75.50	107.93	12.81	30.34	51.51	66.11
	SSE	1.69	14.82	37.12	122.5	2.19	14.48	58.20	46.06	2.42	8.89	44.98	38.12
Second-order kinetic	q_e (mg g^{-1})	18.38	50.76	85.89	110.15	18.2	47.05	77.22	109.68	15.92	32.97	52.02	68.31
	k_2 (g mg^{-1} h^{-1})	0.129	0.108	0.065	0.145	0.153	0.093	0.094	0.131	0.071	0.091	0.114	0.122
	h_i (mg g^{-1} h^{-1})	43.52	279.01	475.79	1756.95	50.61	205.67	559.89	1577.16	17.9	99.24	307.18	570.67
	SSE	0.09	0.39	2.00	42.53	0.68	0.40	7.04	1.32	1.11	0.97	14.03	3.22
Webber and Morris kinetic	k_{ipd} (g mg^{-1} h^{-1})	6.46	10.65	14.03	16.61	7.23	10.26	15.61	22.78	5.31	9.64	17.12	20.40
	C (h^{-1})	3.39	11.40	21.07	27.37	3.56	20.19	32.28	38.51	3.14	15.65	19.20	24.81
	SSE	4.50	34.90	114.20	8.50	5.60	30.60	45.30	51.10	0.4	10.6	18.10	28.70

sorbate adsorbed onto biosorbent at equilibrium time (mg g^{-1}), q_t is the amount of sorbate adsorbed onto biosorbent at time t (mg g^{-1}), and t is time (h).

$$q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t} \tag{11}$$

The initial sorption rate, h_i, can be determined from the pseudo-second-order rate constant using the mathematical expression as given below:

$$h_i = k_2 {q_e}^2 \tag{12}$$

The kinetic parameters for the pseudo-second-order kinetic model were estimated using the nonlinear regression analysis of experimental data for nickel biosorption. The kinetic parameters for different initial concentrations at a temperature of 25˚C are also presented in Table 2. The results show that the second-order kinetic model gives better characterization of the biosorption process as the value of SSE is lowest ranging from 0.09 to 42.53 for the experimental data sets. Hence, the biosorption process of nickel ions for each of the three biosorbents follows the chemisorption as rate-limiting step. In chemisorption, exchange and sharing of electrons take place between nickel ions and immobilized biosorbents.

The biosorption dynamics can be illustrated by the three successive steps [41]: (1) metal ions can be transported through liquid film of bulk solution to the exterior surface of biosorbent, (2) metal ions may be diffused into the pore of the biosorbent beside the biosorption of small quantity on the external surface, and (3) the biosorption of metal ions may take place on the capillary spaces and interior surface of the pores of biosorbents. Among these three steps, the third step is considered to be rapid and negligible. Hence, the overall rate of biosorption reactions is controlled by either pore diffusion or film diffusion being the slowest step. The controlling step may be divided between the external and intra-particle transport mechanism. The batch biosorption process may take place by the adsorption of metal ions on the surface of the biosorbent and/or diffusion of metal ions inside the interior pores on the biosorbent. The involvement of intra-particle diffusion may be evaluated using the Webber and Morris kinetic model as given below [42]:

$$q_t = k_{ipd} t^{1/2} + C \tag{13}$$

Here q_t is the amount of sorbate i.e. metal ions adsorbed onto biosorbent at time t (mg g^{-1}), k_{ipd} is the rate constant for intra-particle diffusion (g mg^{-1} h^{-1}), and C is intercept. If plot of $t^{1/2}$ vs. q_t is linear, then the biosorption process will involve the intra-particle diffusion. The slope of the line is defined as the intra-particle diffusion rate constant, whereas the intercept of the line describes the boundary layer effects. Further, intra-particle will be the rate-controlling step if the line passes through the origin i.e. value of C is zero. Otherwise, the biosorption process involves more than one mechanism as rate-controlling step of biosorption process.

In order to check the possibility that whether the nickel ions were transported within pores of the biosorbents, the experimental data were analyzed using the intra-particle diffusion plot. Values of the parameter of intra-particle diffusion model for nickel ions biosorption onto the three biosorbents i.e. ICUB, ICTB, and ICLB are given in Table 2. The values of intercept were in a range of 3.14–84.03 showing that the lines for Webber and Morris kinetic model do not pass through the origin. Therefore, pore diffusion is a dominant step in rate controlling instead of the film diffusion for the biosorption of nickel ions using the three biosorbents. For the lager values of C, at higher initial concentration of nickel ions, the surface biosorption has greater contribution in rate-limiting step. Overall model predictions for equilibrium biosorption capacity are satisfactory as the values of SSE are ranging from 0.40 to 114.2.

3.7. Biosorption thermodynamics parameters

The thermodynamic parameters are useful for differentiating the biosorption process as endothermic or exothermic. These are also helpful for checking the spontaneity of the biosorption process. The thermodynamic parameters i.e. entropy change (ΔS), enthalpy change (ΔH), and the Gibbs free energy (ΔG) are helpful in order to determine the nature of biosorption process. Thermodynamic parameters were calculated using the values of equilibrium constants at different temperatures as determined from Langmuir isotherm model. The Gibbs free energy change, for the biosorption reaction, was calculated using the equation given below [43].

$$\Delta G = -RT \ln K_L \tag{14}$$

where "R" represents the universal gas constant (8.314 J mol^{-1} K^{-1}) and "T" is absolute temperature (K). Similarly, the enthalpy change and entropy change can also be related to the equilibrium constant using the Van't Hoff's equation as given below:

Table 3
Thermodynamics parameter for biosorption of nickel ions

Biosorbent	T (K)	K_L (L mol^{-1})	ΔG (kJ mol^{-1})	ΔH (kJ mol^{-1})	ΔS (kJ mol^{-1} K^{-1})
ICTB	25	1,705	−18.405		
	35	2,236	−19.716	21.74	0.135
	45	2,961	−21.098		
ICUB	25	2,812	−19.643		
	35	3,646	−20.966	15.04	0.117
	45	4,114	−21.965		
ICLB	25	1,350	−17.828		
	35	1,878	−19.27	22.80	0.1365
	45	2,406	−20.55		

$$\ln K_L = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \quad (15)$$

where "K_L" is rate constant. Langmuir constant was applied to calculate the values of ΔH and ΔS from slope and intercept of the plot between $\ln K_L$ and $1/T$. The extent of spontaneity is seen to increase with temperature and decrease with concentration.

Van't Hoff's plot for biosorption of nickel ions is shown in Fig. 6. The values of the thermodynamics parameters are summarized in Table 3. The values of Gibbs free energy of biosorption were found to be negative at all temperatures which indicates that the biosorption process for the nickel ions is feasible and spontaneous in nature under all the experimental conditions. The positive value for ΔH confirms the endothermic nature of the biosorption of nickel ions.

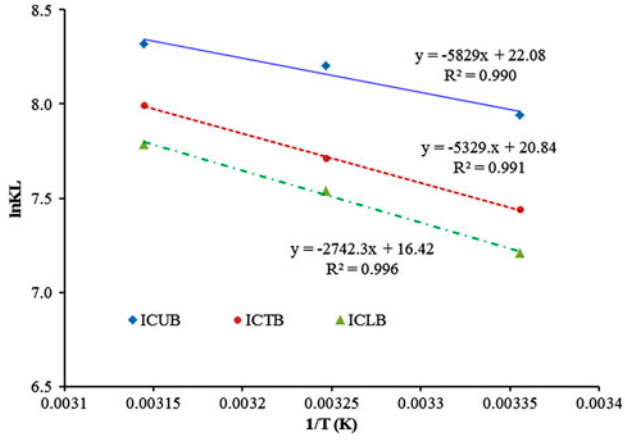

Fig. 6. Van't Hoff's plot of $1/T$ against $\ln K_L$ for biosorption of nickel ions.

The small value of ΔS reveals that the entropy changes during the biosorption process were negligible. Furthermore, the values of ΔS were found positive which reflects randomness increased, at the interface of biosorbent and metal ions during biosorption, due to replacement of ions during the biosorption reaction [44,45].

3.8. Regeneration studies

Nickel ions desorption for the potential biosorbent i.e. ICTB, was eluted using the solutions of hydrochloric acid (HCl), nitric acid (HNO_3), and sodium hydroxide (NaOH) as desorbing agents. 0.1 M solutions were used for the three desorbing agents. HCl gives the best performance for regeneration of ICTB by eluting the nickel ions from the ICTB. The desorption efficiency of 0.1 M HNO_3 and NaOH were found to be 91.75 and 11.93%, respectively. HCl solution (0.1 M) was used for nickel ions in five repeated biosorption and desorption cycles for initial concentration of nickel ions of 301.48 mg L^{-1}. The biosorption efficiency of ICTB for nickel ions did not change considerably, and a minor decrease of about 2.79% was observed as shown in Table 4. Hence, the ICTB could be used in the continuous process for the biosorption of nickel ions.

Table 4
Nickel ions biosorption efficiency for regenerated ICTB

Cycle no.	1	2	3	4	5
q_e (mg g^{-1})	127.9	126.22	125.63	126.85	124.33
Reduction (%)	–	1.31	1.77	0.82	2.79

4. Conclusions

This study showed that ICTB can be used as an efficient biosorbent for the removal of nickel ions from aqueous solution. The optimum conditions for the maximum biosorption capacity of nickel ions from aqueous solution using ICTB, ICUB, and ICLB as biosorbents are pH of 6.62, biosorbent dose of 1 g L^{-1}, and equilibrium time of 3 h. The maximum biosorption capacity was found to be 160.75, 155.30, and 106.76 mg g^{-1} under optimum conditions and at temperature of 25°C for ICTB, ICUB, and ICLB, respectively. The results confirmed that the biosorption capacity increases with the increase of temperature for the biosorption process of nickel ions for all three biosorbents. Equilibrium analysis revealed that the biosorption process is favorable and chemical ion-exchange in nature. The Langmuir and generalized isotherm model provided a better fit to the experimental equilibrium data as compared to the Freundlich and D–R isotherm models.

The biosorption process of nickel ions onto ICTB, ICUB, and ICLB followed the pseudo-second-order kinetics. The thermodynamic analysis showed that biosorption process was spontaneous and endothermic in nature. ICTB can be used as an effective biosorption medium for the removal of nickel ions from the aqueous solution. ICTB has much higher biosorption capacity and affinity for nickel ions as compared to most of the other biosorbent materials reported in the literature. ICTB can be used in a cyclic process for the removal of nickel ions using HCl as a desorbing agent.

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