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Application of response surface methodology for the optimization of Ni^{2+} ions biosorption from aqueous solution using *Sargassum filipendula*

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ABSTRACT

All the experiments were performed in batch mode for biosorption of Ni^{2+} ions from aqueous solution using *Sargassum filipendula*. All the process parameters of Ni^{2+} ions biosorption was optimized by using response surface methodology. The effect of four independent variables temperature (20°C–40°C), pH (3–6), initial Ni^{2+} ions concentration (50–150 mg/L) and biosorbent dosage (1.0–2.5 g/L) on biosorption of Ni^{2+} ions were studied. The biosorbent was characterized by using Fourier transform infrared spectroscopy, field emission electron microscopy, and energy dispersive X-ray spectroscopy. The optimized values of four variables were found as temperature of 41.5°C, initial Ni^{2+} ions concentration of 83.18 mg/L, biosorbent dosage of 1.97 g/L and pH of 5.4 which resulted in 68.45% removal of Ni^{2+} ions. The Redlich–Peterson isotherm model was found to be the best fitted to experimental data of Ni^{2+} ions biosorption with higher value of R^2 and smaller value of Δq%. The best fitted kinetic model was noticed as pseudo-first-order kinetic model ($R^2 > 0.98$) which shows that the rate limiting step was physisorption. Thermodynamic parameters ($\Delta G°$ = –0.097 to –4.060 kJ/mol, $\Delta H°$ = 79.175 J/mol, $\Delta S°$ = 0.270 J/mol K) of Ni^{2+} ions biosorption showed that the process was spontaneous, feasible and endothermic in nature. The biosorption and desorption efficiency were decreased up to 8.5% and 12%, respectively after four successive cycles. Therefore, the present study demonstrated that *S. filipendula* can be used as biosorbent for Ni^{2+} ions biosorption from the synthetic wastewater effectively and economically.

Keywords: Nickel; Biosorption; Kinetics; Isotherms; Thermodynamics; Response surface methodology

1. Introduction

Heavy metals are important for numerous biological activities in living beings but they can toxic at higher concentrations. The presence of toxic metal ions is harmful to the ecosystem and human health due to their toxic, biomagnification and non-degradable in nature. Various industries like mineral processing, copper sulfate manufacture, refining, pulp and paper mills, electroplating, welding, porcelain enameling, battery and accumulator manufacturing are the main sources which discharge metal-laden effluents [1,2]. The permissible limit set by World Health Organization and Environmental Protection Agency for nickel in drinking water is 0.5 mg/L [3]. The trace amount of nickel is beneficial as an activator for some enzyme systems while intake of nickel beyond permissible limit results in various types of diseases. The International Agency for Research on Cancer (IARC) categorized nickel in group 2B (agents which are possibly carcinogenic to humans) and its compounds in group 1 (there is adequate evidence of carcinogenicity in humans) [4,5]. The acute poisoning effects of Ni^{2+} ions at higher concentration are dizziness, headache, tightness of the chest, nausea, vomiting, dry cough, chest pain, rapid respiration, lung fibrosis, cyanosis, shortness of breath and

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extreme weakness [6–11]. The exposure of nickel containing coins and jewelry to skin causes an allergic dermatitis called "Nickel Itch" which is lethal [12].

As compared to conventional techniques like synthetic ion exchange resins or precipitation, biosorption process proves to be an efficient and economical method for the removal of metal containing wastewaters. Biosorption is a property of naturally occurring biomass to bind and concentrate heavy metals from aqueous solution on its cellular structure through physiochemical process [13–15]. The main advantages of biosorption are the use of inexpensive biosorbents, it can remove the heavy metal ions even at very low concentration effectively, low sludge production, non-hazardous and it may permit recovery of the metals from the sorbing biomass [16–19]. Among all the other naturally available biosorbents, marine algae are abundantly existing and available from the ocean at a large scale [20]. It can effectively eliminate very low concentration of metal ions varying from few ppm to several hundred ppm [21]. The main mechanism involved in metals ions removal by the algal biosorbents is the ionic exchange. The acidic polysaccharide content of brown algae cell wall results in more efficient biosorption of metal ions. In brown algae, carboxyl and sulphate are the predominant active groups [21–24]. On the basis of available literature, it has been found that marine brown alga can be used effectively and efficiently used for the removal of heavy metals from wastewater. Thus, for this study *Sargassum filipendula* was chosen as biosorbent for the Ni^{2+} ions biosorption.

The aim of this study is to study the influences of initial Ni^{2+} ions concentration, pH, temperature and *S. filipendula* dosage on Ni^{2+} ions biosorption by *S. filipendula*. The optimization of Ni^{2+} ions biosorption process parameters was done by using response surface methodology (RSM). The biosorption mechanism was also studied in terms of isotherm, kinetics and thermodynamics. The regeneration capacity of the *S. filipendula* was evaluated by desorption study. The present study results in terms of biosorption capacities, isotherms, kinetic and thermodynamic studies were compared with the reported results in the literature available for different brown alga.

2. Material and methods

2.1. Preparation of algae biomass

Dried *S. filipendula* was purchased from Aushadh Agri Science Private Limited, Gujarat (India). It was used for the removal of Ni^{2+} ions from aqueous solution. The deionized distilled water was used to wash *S. filipendula* biomass in order to remove the impurities and ions (Ca^{2+} or Na^{+}) bound on *S. filipendula* surface that alter the biosorption process. It was stored in dessicator after drying it in oven at 80°C for 24 h. The dried *S. filipendula* was then grounded and sieved through 212 μm sieve. The resulted fraction of *S. filipendula* was used as biosorbent for biosorption process.

2.2. Reagent preparation

A stock solution of 1,000 mg/L was prepared by dissolving 4.95 g of $Ni(NO_3)_2$ in a 1,000 mL volumetric flask using deionized water. Further serial dilution of stock solution was carried out to prepare experimental solutions of different concentrations. The pH of solution was monitored by adding 0.1 M HNO_3 and 0.1 M NaOH.

2.3. Batch biosorption

Batch biosorption experiments for Ni^{2+} ions were performed in 250 mL flasks containing 100 mL of Ni^{2+} ions solution at mixing rate of 150 rpm for 85 min, which was sufficient for biosorption equilibrium. The effect of pH on Ni^{2+} ions biosorption capacity of *S. filipendula* was studied in the pH range of 3.0–6.0. The initial pH of each Ni^{2+} ions solution was maintained by adding 0.1 M HNO_3 or 0.1 M NaOH. In the same way, the effect of biomass dosage (1.0–2.5 g/L), initial Ni^{2+} ions concentration (50–150 mg/L), and temperature (20°C–40°C) on the Ni^{2+} ions biosorption were examined. The samples were filtered through Whatman No. 1 filter paper at regular interval. The atomic absorption spectroscopy (AAS) was used to study the filtrates containing remaining metal ion concentration. All experiments were conducted in triplicate and results were examined statistically. The results were given in terms of removal efficiency of metal ion using the following equation:

$$\%\,\text{Removal} = \left(\frac{C_i - C_e}{C_i}\right) \times 100 \tag{1}$$

The metal uptake capacity at equilibrium of a biosorbent was determined by using the given equation:

$$q_t = \left(C_i - C_e\right)\frac{V}{m} \tag{2}$$

where 'm' is mass of biosorbent (g), 'C_i' is initial concentration of Ni^{2+} ions, 'C_e' is equilibrium concentration of Ni^{2+} ions (mg/L) 'q_e' is amount of biosorbate biosorbed at equilibrium (mg/g), and 'V' is volume of solution (L).

2.4. Response surface methodology

The central composite design (CCD) under RSM was used to study the parameters of Ni^{2+} ions biosorption [25–27]. The CCD design was selected in this study as it is flexible, robust and efficient [28,29]. The Design Expert Software (version 10) Stat Ease Inc., USA was used. RSM is a mathematical and statistical tool used to examine the independent and interaction effects of different process parameters and optimizes the process conditions for desired results with least number of experiments [30–33]. RSM involves model formulation to observe which parameters and their interactions effect on the response and optimization of process parameters that affects the performance of the response [34–36]. A second-order polynomial equation was used to fit the experimental data is given below:

$$Y = \beta_0 + \sum_{i=1}^{k}\beta_i x_i + \sum_{i=1}^{k}\beta_{ii} x_i^2 + \sum_{i=1}^{k}\sum_{j>i}^{k}\beta_{ij} x_i x_j \tag{3}$$

where Y is predicted response (dependent), x_i and x_j are variables, β_0 is constant coefficient, β_i, β_{ii} and β_{ij} are interaction coefficients for linear, quadratic, and second-order terms, respectively. In this study, four factors considered were temperature, biosorbent dosage, pH, and initial Ni^{2+} ions concentration. The total 30 runs were attained in order to examine the effect of four variables [37]. This experimental design consists of 8 axial points, 6 center points, and 16 factorial points which can be determined by using the given equation:

$$N = 2^k + 2k + N_0 \tag{4}$$

where k is number of variables, $2k$ are axial points, 2^k are factorial points, and N_0 is number of experiments carried out at the center. All experimental runs were performed in duplicate.

2.5. Characterization of *S. filipendula*

2.5.1. Field emission electron microscopy and energy dispersive X-ray spectroscopy analysis

Field emission electron microscopy (FESEM) and energy dispersive X-ray spectroscopy (EDS) analysis were carried out using FESEM QUANTA 200 FEG (FEI Netherlands). The surface physical morphology of *S. filipendula* was observed under FESEM combined with EDS which provides information about the chemical arrangement of biosorbent before and after biosorption of Ni^{2+} ions.

2.5.2. Fourier transform infrared spectroscopy analysis

The Fourier transform infrared spectroscopy (FTIR) analysis was done to identify the functional groups available on *S. filipendula* surface and their interaction with metal ions. The KBr disc method was used to obtain Infra-red spectra, in which a pellet dried was formed by adding unloaded and Ni^{2+} ions loaded *S. filipendula* to KBr in 1:10 ratio. FTIR spectral analysis was carried out using the Perkin-Elmer model Lambda 35 double beam spectrophotometer.

2.6. Desorption study

The recycling of biosorbent is a most significant step from economical point of view. It is very vital step to regenerate the biosorbent without losing its biosorption capacity. The desirability of biosorption process enhanced by regenerating and recycling process of biosorbent The choice of an appropriate eluent is an important step in desorption process which depends on the type of biosorbent and biosorption mechanism to attain an effective recovery of metal ion from biosorbent. The eluent should be non-damaging to biomass, environment friendly, and cost effective [37,38]. For this study 0.1 M HCl was used as eluent.

The four successive cycles of biosorption-desorption process were carried out by adding 0.5 g of Ni^{2+} ions loaded *S. filipendula* in 100 mL of 0.1 M HCl for each cycle. A single cycle sequence involves biosorption followed by desorption. After mixing of 65 min, the filtered and the desorbed amount of Ni^{2+} ions in the solution was analyzed by using AAS. In order to reuse the *S. filipendula* for next cycle, biomass of *S. filipendula* was washed with 0.1 M HCl solution and distilled water, repeatedly. The desorption efficiency of Ni^{2+} ions was given by the following equation:

$$\text{Desorption efficiency}(\%) = \frac{\text{Amount of desorbed metal ion}}{\text{Amount of biosorbed metal ion}} \times 100 \tag{5}$$

3. Results and discussion

3.1. Characterization of *S. filipendula*

3.1.1. FESEM analysis

Figs. 1a and b show the surface morphology of *S. filipendula* before and after biosorption, respectively. Before biosorption, the surface of *S. filipendula* was found to be rough and porous. After biosorption process, the pores were blocked and surface of *S. filipendula* becomes smooth. It shows that the structure of *S. filipendula* has been modified after biosorption of Ni^{2+} ions.

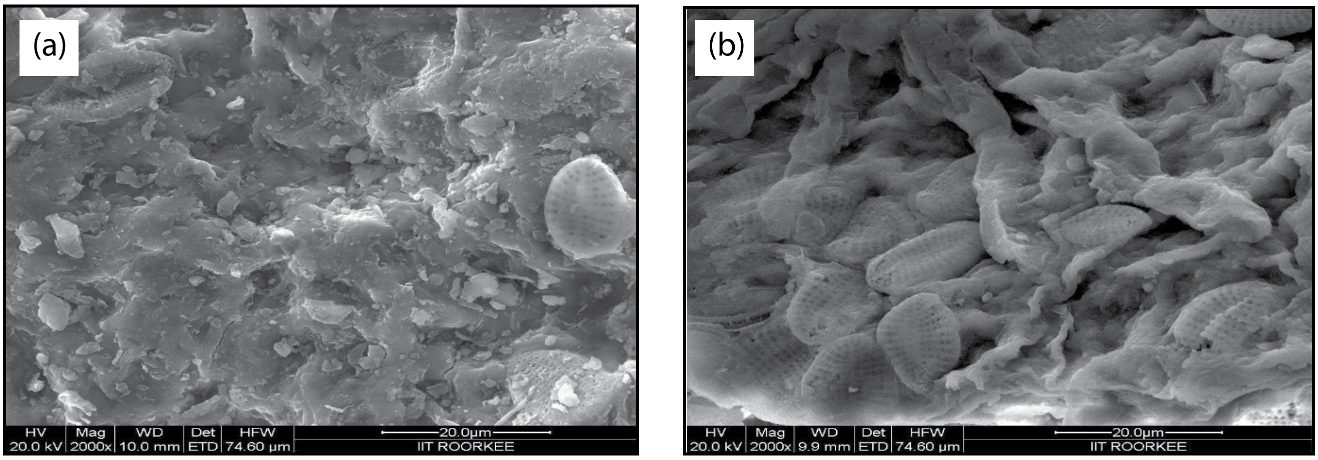

Fig. 1. FESEM images for Ni^{2+} ions biosorption on *S. filipendula* (a) before biosorption and (b) after biosorption.

3.1.2. EDS analysis

EDS spectrum of unloaded and after Ni^{2+} ions loaded *S. filipendula* shows the biosorption of Ni^{2+} ions on *S. filipendula* surface as shown in Figs. 2a and b.

After biosorption, the amount of K^+, Ca^{2+} and other cations decreased in addition to this a new peak of Ni^{2+} ions was observed. This result implied the contribution of ion exchange mechanism for the binding of Ni^{2+} ions to *S. filipendula* surface.

3.1.3. FTIR analysis

The functional groups present in the biosorbents were studied using the FTIR at a wavelength of (400–4,000 cm^{-1}). The capacity of biosorption depends on the functional group reactivity and the surface porosity of the biosorbent. FTIR spectra of fresh biosorbent and Ni(II) adsorbed biosorbent are shown in Fig. 3. From the vibration spectra, it is observed that various functional groups present in the biosorbent plays a vital role in the biosorption of Ni(II) ions [2].

3.2. Experimental analysis of single factor for Ni^{2+} ions removal efficiency

To optimize the biosorption process of Ni^{2+} ions on *S. filipendula*, the effects of four operating parameters namely temperature, pH, initial Ni^{2+} ions concentration, and biosorbent dosage on removal efficiency of Ni^{2+} ions were studied by CCD. The batch runs were conducted according to CCD designed experiments in order to investigate the optimum combination of aforementioned four biosorption process parameters on removal of Ni^{2+} ions.

The matrix of four variables temperature, initial Ni^{2+} ions concentration, pH, and biosorbent dosage were varied at 5 levels ($-\alpha$, –1, 0, +1, $+\alpha$) as shown in Table 1. The lower and higher levels of variables were symbolized as '–' and '+', respectively.

Table 2 shows the result of CCD experiments for analyzing the effect of four independent parameters along with the response as % removal efficiency. The experimental results were determined and approximating functions of percent removal of Ni^{2+} ions were expressed by the following second-order polynomial equation:

$$Y\,(\%) = +57.2 + 12.88A + 8.86B + 3.5C - 3.21D + 3.24AB + 0.49AC - 1.49AD + 0.12BC - 1.36BD - 0.87CD - 6.78A^2 - 10.39B^2 - 7.35C^2 - 8.97D^2 \quad (6)$$

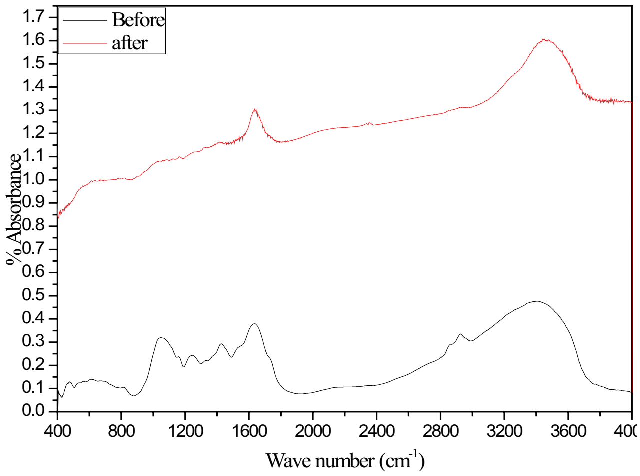

Fig. 3. FTIR analysis of *S. filipendula* (a) before Ni^{2+} ions biosorption and (b) after Ni^{2+} ions biosorption.

Table 1
Range and levels of the independent variables for Ni^{2+} ions biosorption

Independent variables	Range and levels				
	$-\alpha$	–1	0	$+\alpha$	+1
Temperature, °C (*A*)	10	20	30	50	40
pH (*B*)	1.5	3.0	4.5	7.5	6.0
Biosorbent dosage, g/L (*C*)	0.25	1.0	1.75	3.25	2.5
Initial Ni^{2+} ions concentration, mg/L (*D*)	25	50	100	200	150

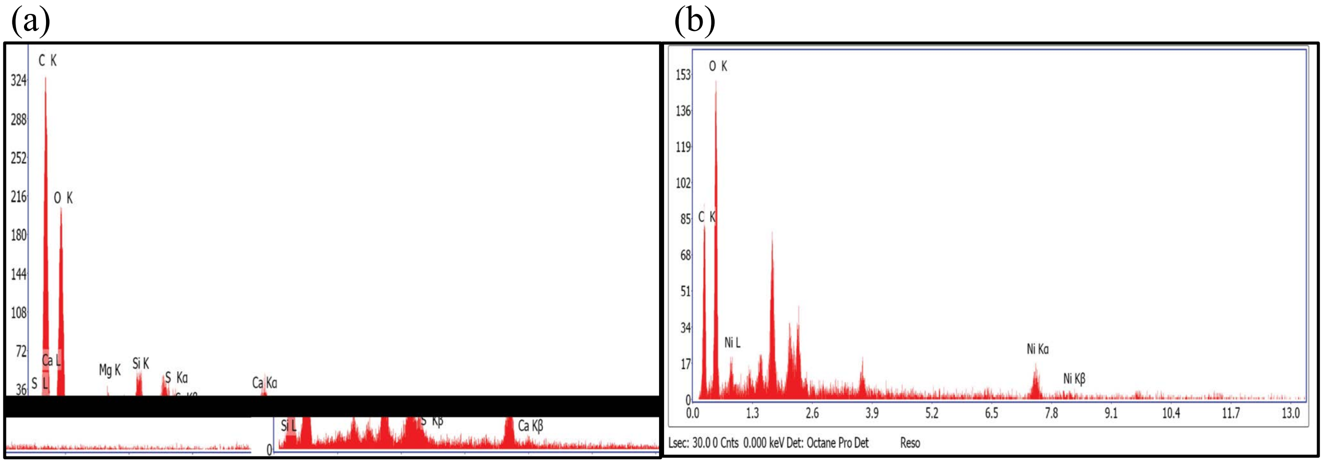

Fig. 2. EDS images for Ni^{2+} ions biosorption on *S. filipendula* (a) before biosorption and (b) after biosorption.

Table 2
Experimental design based on CCD and its response for Ni^{2+} ions biosorption on *Sargassum filipendula*

Run	Temperature (°C)	pH	Biosorbent dosage (g/L)	Initial Ni^{2+} ions concentration (mg/L)	Removal (%)
1	40	3.0	2.5	150	13
2	30	4.5	1.75	200	28.3
3	20	6.0	2.5	50	26
4	30	4.5	1.75	100	58
5	30	4.5	1.75	100	58.7
6	30	4.5	1.75	100	58.5
7	40	6.0	1.0	50	48
8	40	3.0	2.5	50	30
9	30	1.5	1.75	100	6.7
10	30	4.5	1.75	100	57.8
11	50	4.5	1.75	100	71
12	40	3.0	1.0	50	20
13	10	4.5	1.75	100	2.54
14	20	3.0	1.0	50	3
15	30	4.5	0.25	100	22
16	30	4.5	1.5	25	70
17	30	4.5	1.75	100	58
18	20	3.0	2.5	150	3.98
19	30	4.5	1.75	100	58
20	30	4.5	3.25	100	47
21	20	6.0	1.0	50	18
22	40	6.0	2.5	50	52
23	40	6.0	2.5	150	40
24	20	3.0	2.5	50	5
25	30	7.5	1.75	100	38
26	20	6.0	1.0	150	9
27	20	6.0	2.5	150	10
28	20	3.0	1.0	150	1.86
29	40	3.0	1.0	150	11
30	40	6.0	1.0	150	35

where, Y is percent removal of Ni^{2+} ions. A, B, C, and D represents the coded values of temperature, pH, biosorbent dosage and initial Ni^{2+} ions concentration, respectively. The negative sign indicates antagonistic while positive sign indicates synergistic effect of process parameters on removal of Ni^{2+} ions. The statistical significance of the quadratic model was determined by analysis of variance (ANOVA) as given in Table 3. The significant of each coefficient was assessed by p-values and F-values. The significant model term has smallest p-value and largest F-value. In this model the p-value was <0.0001 and F-value was 11.37 implies that the model was significant for removal of Ni^{2+} ions. The value of "Prob > F" less than 0.0500 shows that model terms were significant. In this case A, B, A^2, B^2, C^2, and D^2 were significant model terms. The determination coefficient (R^2 = 0.91) was reasonability good which explained 91% of the total variation in the response. The "Lack of Fit F-value" of 17.69 implies that the Lack of Fit was significant. There was only 0.28% chance that a "Lack of Fit F-value" this large could occur due to noise. The "Adequate precision" ration of this model was 9.78 which was an adequate signal for the model.

Fig. 4a shows that the predicted data values of reduces quadratic model were in well agreement with actual values. Fig. 4b shows a plot of normal probability vs. studentized residuals which indicates whether the residuals follow a normal distribution of points along a straight line.

3.3. Variation of process parameters on Ni^{2+} ions maximum removal efficiency

The optimum levels of different process parameters for Ni^{2+} ions biosorption were predicted from 3D graph as shown in Figs. 5a–d. The 3D response surface plots are graphical representation of regression equation which shows the interaction effect of variables.

3.3.1. Effect of pH

The solution pH is an important factor which governed the extent of metal ions biosorption. The optimal pH value may be different for different metal ions depend on solution chemistry of the species [9]. The pH of solution influences

Table 3
ANOVA for response surface quadratic model of Ni^{2+} ions biosorption

Source	Sum of squares	*df*	Mean square	*F*-value	*p*-value	Remarks
Model	12,288.97	14	877.78	11.37	<0.0001	Significant
A	3,980.44	1	3,980.44	51.58	<0.0001	Significant
B	1,886.12	1	1,886.12	24.44	0.0002	Significant
C	294.84	1	294.84	3.82	0.0709	Not significant
D	176.72	1	176.72	2.29	0.1525	Not significant
AB	167.96	1	167.96	2.18	0.1000	Not significant
AC	3.88	1	3.88	0.050	0.8258	Not significant
AD	35.52	1	35.52	0.46	0.5085	Not significant
BC	0.22	1	0.22	2.863×10^{-3}	0.9581	Not significant
BD	29.81	1	29.81	0.39	0.5442	Not significant
CD	12.04	1	12.04	0.16	0.6988	Not significant
A^2	1,226.49	1	1,226.49	15.89	0.0014	Significant
B^2	2,876.97	1	2,876.97	37.28	<0.0001	Significant
C^2	1,440.34	1	1,440.34	18.66	0.0007	Significant
D^2	1,286.90	1	1,286.90	16.68	0.0011	Significant
Residual	1,080.37	14	77.17	–	–	–
Lack of fit	1,047.47	9	116.39	17.69	0.0028	Significant
Pure error	32.90	5	6.58	–	–	–
Total	13,369.34	28	–	–	–	–

$R^2 = 0.9192$; Adjusted $R^2 = 0.8384$; Predicted $R^2 = 0.80$; Adequate precision = 9.785

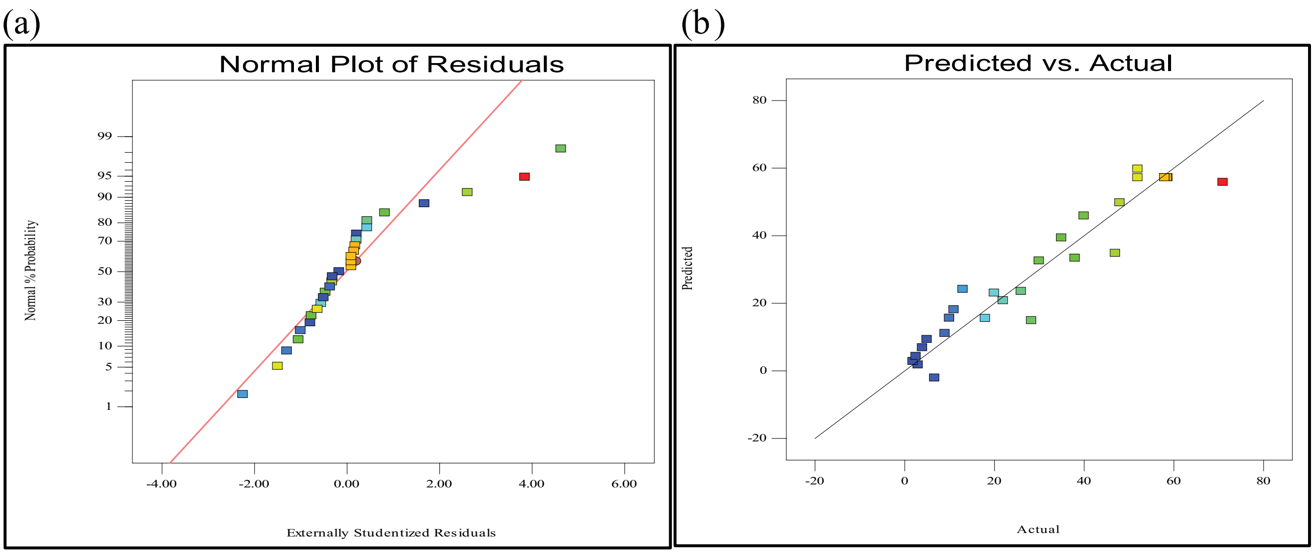

Fig. 4. (a) Normal probability plot and (b) correlation between actual and predicted values.

the species distribution of metal ions in aqueous solution, surface charge of biosorbent, and degree of ionization [42]. The biosorption characteristic of Ni^{2+} ions was studied at different pH values varied from 1.5 to 7.5. For this study the range of pH was selected based on the reported data given in the literature [43]. At acidic pH, the surface of *S. filipendula* becomes positively charged with H^+ ions which cause electrostatic repulsion of Ni^{2+} ions for binding site of *S. filipendula*. While at higher pH, H^+ ions desorbs from binding sites which results in exposure of negatively charged ligands of *S. filipendula* for Ni^{2+} ions biosorption. Hence, the removal percent of Ni^{2+} ions was increased with increase in pH of the solution Fig. 5a. While beyond pH value of 6.0, precipitation of Ni^{2+} ions was occured in form of hydroxides [$Ni(OH_2)$] which results in decrease of removal efficiency [39,40].

3.3.2. Effect of biosorbent dosage

The biosorption process is greatly influenced by biosorbent dosage as it examined the biosorbent potential by the available number of binding sites for metal ions removal. The selected biosorbent dosage range was 0.25–3.25 g/L. Fig. 5a indicates that the removal percent of Ni^{2+} ions was increased with increasing the *S. filipendula* dose. It can be explained as for a particular initial metal ion concentration an increase in biosorbent dosage provides large number of active sites and available surface area [41–43]. Biosorption of Ni^{2+} ions reached equilibrium at 2.0 g/L dose of *S. filipendula*, respectively. Further increase in biomass does not show any significant increase in removal efficiency of Ni^{2+} ions which may be due to the saturation of the *S. filipendula* surface [43]. Similar results were given in the literature [44,45].

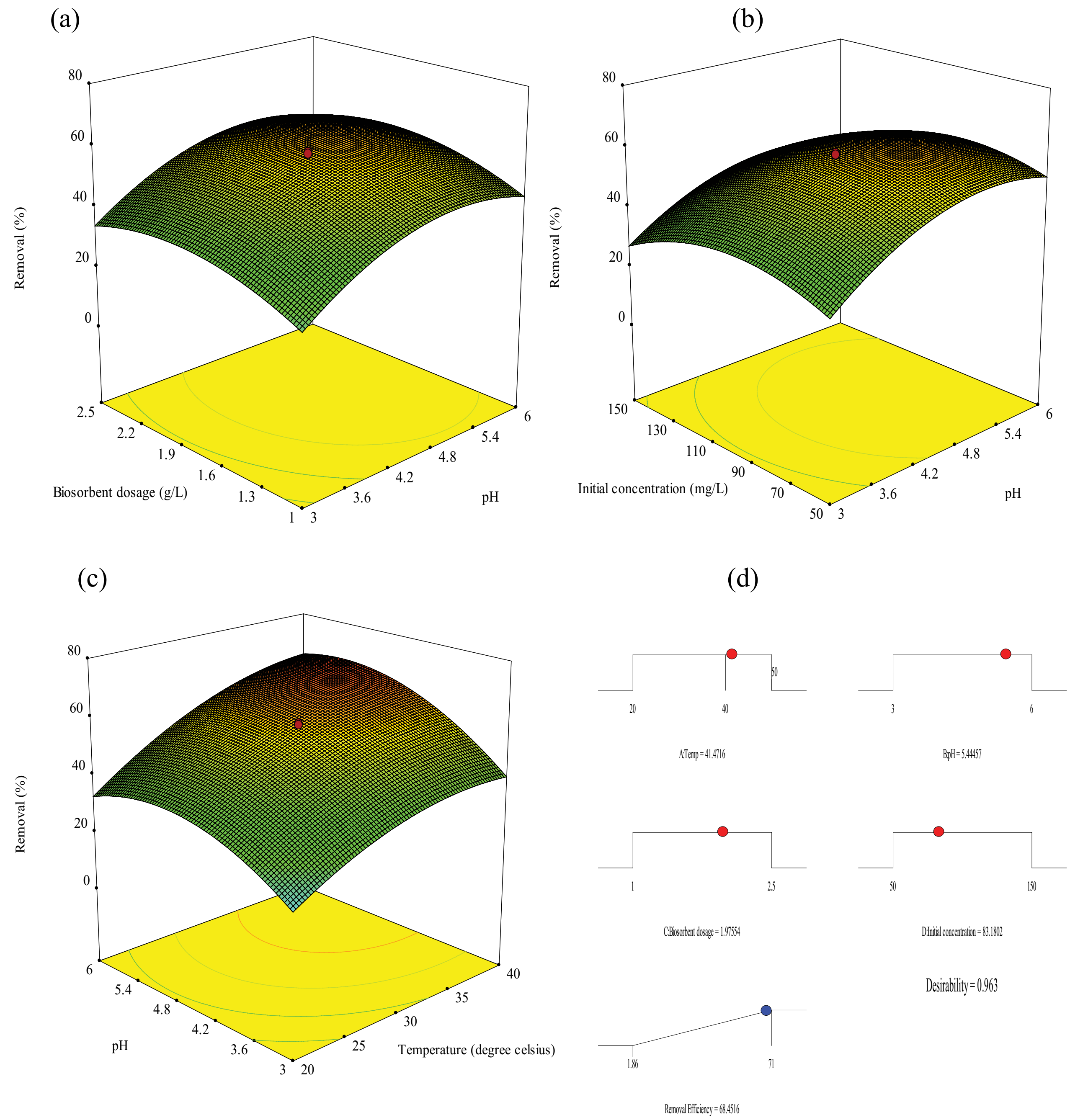

Fig. 5. (a) Interactive effect of biosorbent dosage and pH, (b) Interactive effect of initial Ni^{2+} ions concentration and pH, (c) Interactive effect of temperature and pH and (d) Desirability ramp for numerical optimization of four independent variables and the responses.

3.3.3. Effect of initial Ni^{2+} ion concentration

The removal efficiency of *S. filipendula* as a function of the initial concentration of Ni^{2+} ions was studied for 50–200 mg/L range. Fig. 5b indicates that the removal percent of Ni^{2+} ions was decreased from 70% to 28% with increase in the initial Ni^{2+} ions concentration. It can be explained that biosorbent surface have fixed number of binding sites which are available for metal ions binding at low initial metal ions concentration while saturation of binding sites occurred at high initial metal ions concentration [46]. On the other hand, metal ions uptake capacity was increased with increasing initial metal ions concentration. It may be due to the fact that increase in the initial metal ions concentration provides a larger driving force to overcome mass transfer resistances between the solid and the liquid phase. Similar results were reported in literature [40,47,48].

3.3.4. Effect of temperature

The effect of temperature over the range of 20°C–50°C was examined to determine whether the biosorption process was exothermic or endothermic in nature. Fig. 5c indicates that with rise in temperature from 20°C to 50°C, the removal efficiency of Ni^{2+} ions was increased from 26% to 71%. It showed the endothermic nature of Ni^{2+} ions biosorption process. With rise in temperature the thickness of biosorbent boundary layer decreases due to which external layer resistance decreases. The more surface area for biosorption was available due to widening of micro-pores and the increased accessibility for binding sites [49].

3.3.5. Effect of contact time

Fig. 6 shows that the biosorption of Ni^{2+} ions gradually increased with contact time until equilibrium condition was reached after which there was no change in removal percent. Initially the removal rate of Ni^{2+} ions was very fast for first 10 min. In initial stage, the biosorption of metal ions occurs generally on biosorbent surface instead of pores, whereas ion exchange processes occur between the ions available on the solid and liquid phase. Fast diffusion on outer surface was followed by slow pore diffusion [50]. The equilibrium time for Ni^{2+} ions was found to be 60 min and beyond this time no further significant removal was noted. The fast biosorption rate at the initial stage may be due to the availability of a large number of vacant surface active sites while after a particular time interval the biosorption rate was slow down due to decrease in availability of active sites on *S. filipendula* surface [51,52].

3.4. Optimization using the desirability functions

A point for desirability function was obtained by numerical optimization at which the values of process parameters were fixed within their ranges and maximizing the removal efficiency of Ni^{2+} ions [16]. Fig. 5d shows that the best local maxima value was obtained as temperature of 41.5°C, pH of 5.4, biosorbent dosage of 1.97 g/L and initial Ni^{2+} ions concentration of 83.18 mg/L. In these conditions, Ni^{2+} ions the value of desirability and removal efficiency were found to be 1.0% and 68.45%, respectively. This optimum condition was experimentally verified and results revealed that Ni^{2+} ions removal efficiency was achieved as 70%. The high level of agreement among the repeated experimental results and predicted optimum conditions indicates that RSM can be used as a reliable and effective tool to assess and optimize the effects of different process parameters on Ni^{2+} ions biosorption using *S. filipendula*.

3.5. Validation of predictive model

The model was validated by performing experiments under the obtained optimized bioprocess parameters achieved by software to find out experimental removal percentage of Ni^{2+} ions. The Ni^{2+} ions removal efficiency from the confirmation experiments was found as 69%. It has been observed that the value generated by the software was in conformity with the experimental values. Thus, the RSM approach could be appropriate for the optimization of the Ni^{2+} ions biosorption process from aqueous solution.

3.6. Kinetic study

The six different kinetic models were used to examine the monitoring of biosorption mechanism and rate controlling step (Table 4).

The kinetic study experiments for Ni^{2+} ions biosorption on *S. filipendula* were conducted at temperature of 35°C, pH of 5.5, biosorbent dosage of 2.0 g/L, and initial Ni^{2+} ion concentration of 100 mg/L. The best fitted kinetic model was determined by values of normalized standard deviation ($\Delta q\%$) and coefficient of determination (R^2) which are given in Table 5. The higher R^2 and small $\Delta q\%$ value of pseudo-first-order shows the best fitted kinetic model for Ni^{2+} ions biosorption. It indicates that Ni^{2+} ions biosorption process on *S. filipendula* was more inclined towards physisorption.

3.7. Biosorption isotherm model study

The isotherm study of biosorption provides the relationship between biosorbate and biosorbed amount of biosorbate per unit mass of biosorbent q_e (mg/g) at equilibrium and concentration in liquid phase at equilibrium C_e (mg/L) [53]. It informs about biosorption capacity of biosorbent or

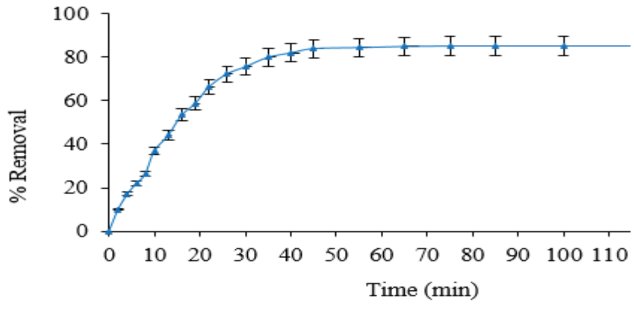

Fig. 6. Effect of contact time on removal efficiency of Ni^{2+} ions at T = 25°C, m = 2 g/L, C_0 = 50 mg/L, pH = 5.0).

Table 4
List of kinetic models with their equation which were fitted to experimental data of Ni^{2+} ion biosorption on *Sargassum filipendula*

S. No.	Kinetic models	Equations
1	Pseudo-first-order	$\ln\left(\frac{q_e - q_t}{q_e}\right) = -k_0 \times t$
2	Pseudo-second-order	$\left(\frac{1}{q_t} - \frac{1}{q_e}\right)q_e^2 = \frac{1}{K_t}$
3	Elovich model	$q_t = \frac{1}{\beta}\ln(\alpha\beta) + \frac{1}{\beta}\ln(t)$
4	Bangham model	$\ln\left(\ln\left[\frac{C_0}{C_0 - q_t m}\right]\right) = \ln\left[\frac{k0m}{V}\right] + \alpha_0 \ln(t)$
5	Intraparticle diffusion model	$q_t = K_{id}t^{0.5} + C$
6	Modified Freundlich model	$\ln q_t = \ln k_3 C_0 + \frac{1}{m_1}\ln(t)$

Table 5
Kinetic model parameters for Ni^{2+} ions biosorption using *Sargassum filipendula*

Kinetic model parameters	Parameters value
$q_{e,\exp}$ (mg/g)	83.230
Pseudo-first-order	
$q_{e,\mathrm{cal}}$ (mg/g)	88.25
k_0 (min^{-1})	0.057
R^2	0.989
Δq%	6.78
Pseudo-second-order	
$q_{e,\mathrm{cal}}$ (mg/g)	108.7
K_2 (g/mg min)	5.47×10^{-4}
R^2	0.963
Δq%	12.13
Elovich	
α	13.81
β	0.042
R^2	0.938
Δq%	20.12
Bangham	
α_0	0.842
k_b	6.97
R^2	0.957
Δq%	15.43
Intraparticle diffusion	
K_{id} (mg min$^{0.5}$/g)	9.58
C	9.612
R^2	0.826
Δq%	32.34
Modified Freundlich	
K_3 (L/g min)	0.173
m_1	2.612
R^2	0.857
Δq%	35.43

amount of biosorbent essential to biosorb a unit mass of biosorbate. The experimental data are fitted to six different isotherm models namely Langmuir, Freundlich, Redlich–Peterson, Radke-Prausnitz, Toth, and Fritz. From these isotherms, Langmuir and Freundlich both are two parameter models, Radke-Prausnitz, Toth, and Redlich–Peterson are three parameter models, and Fritz is a four parameter model (Table 6).

The biosorption isotherms for Ni^{2+} ions was obtained by performing the experiments at pH 5.5, temperature 40°C with varying initial Ni^{2+} ions concentration from 50 to 100 mg/L using a constant biosorbent dosage of 2.0 g/L. The value of each isotherm model with their values of normalized standard deviation Δq% and correlation coefficient (R^2) are shown in Table 7. For Redlich–Peterson model the R^2 value was >0.99 with smallest Δq% value. It indicates that Redlich–Peterson model was found to be the best fitted isotherm model for Ni^{2+} ions biosorption on *S. filipendula*.

Table 6
List of isotherm model fitted to experimental data of Ni^{2+} ions biosorption on *Sargassum filipendula*

S. No.	Isotherm models	Equations
1	Langmuir isotherm	$q_e = \frac{q_0 b C_e}{1 + b C_e}$
2	Freundlich isotherm	$q_e = k_f C_e^{1/n}$
3	Redlich–Peterson isotherm	$q_e = \frac{K_1 C_e}{1 + K_2 C_e^{b_0}}$
4	Toth isotherm	$q_e = \frac{q_e^{\infty} C_e}{(a + C_e)^{1/n_1}}$
5	Fritz isotherm	$q_e = \frac{\alpha_1 C_e^{\beta_1}}{1 + \alpha_2 C_e^{\beta_2}}$
6	Radke-Prausnitz isotherm	$q_e = \frac{q_0 K_0 C_e}{1 + q_0 C_e^{a}}$

Table 7
Different isotherm model parameters for biosorption of Ni^{2+} ions on *Sargassum filipendula*

Isotherm models	Parameters	Parameter values
Langmuir	q_0	34.3
	b	0.343
	R^2	0.81
	$\Delta q\%$	39.27
Freundlich	k_f	23.04
	n	2.28
	R^2	0.994
	$\Delta q\%$	1.039
Radke-Prausnitz	q	26.27
	k_0	6.19×10^{-4}
	a_R	0.187
	R^2	0.994
	$\Delta q\%$	3.352
Redlich–Peterson	K_1	–0.0162
	K_2	26.27
	b_0	0.187
	R^2	0.994
	$\Delta q\%$	0.988
Toth	q_e^{∞}	61.33
	a	5.78
	n_1	40.1
	R^2	0.949
	$\Delta q\%$	39.27
Fritz	α_1	25.93
	α_2	3.56×10^{-13}
	β_1	0.1776
	β_2	6.575
	R^2	0.957
	$\Delta q\%$	3.462

3.8. Thermodynamic study

The negative values of $\Delta G°$ shows the spontaneous nature of Ni^{2+} ions biosorption process and positive values of $\Delta H°$ (+79.175 J/mol) indicates the endothermic nature of Ni^{2+} ions biosorption on *S. filipendula* [66]. The entropy change, $\Delta S°$ (+0.270 J/mol K) indicates the increase in randomness at solid/liquid boundary during Ni^{2+} ions biosorption on *S. filipendula* (Table 8).

3.9. Specific surface area of *S. filipendula* for Ni^{2+} ions biosorption

The specific surface area of 2.43 m^2/g was obtained for Ni^{2+} ions biosorption on *S. filipendula* as the cross sectional area of Ni^{2+} ions is 0.69 m^2 and molecular weight is 58.6 g.

3.10. Desorption study

The recycling and regeneration of biosorbent improves the significance of biosorption process. The regeneration of a biosorbent without losing its biosorption capacity is an important factor. The desorbtion of metal ions from the biosorbent surface depends upon ion-exchange mechanism. The choice of an appropriate eluent is an important stage for desorption process which depends on the kind of biosorbent and biosorption mechanism to attain an effective metal ions recovery from biosorbent surface. The eluent must not be damaging for biomass, cost effective, and ecofriendly [2]. In this work, eluent was chosen to be 0.1 M HCl for the recovery of Ni^{2+} ions from the surface of *S. filipendula*. After four consecutive cycles of biosorption/desorption, the biosorption and desorption efficacy was evaluated. The result showed that biosorption and desorption efficiency was decreased by 8.5% and 12%, respectively (Fig. 7). After four cycles, biosorption/desorption cycle was stopped to prevent biosorbent loss. Therefore, economically it was found that four cycles of biosorption/desorption process were appropriate for the Ni^{2+} ions recovery.

Table 8
Thermodynamic parameters for biosorption of Ni^{2+} ions using *Sargassum filipendula*

T (K)	$\Delta G°$ (kJ/mol)	$\Delta H°$ (J/mol)	$\Delta S°$ (J/mol K)
298	–0.097	79.175	0.270
303	–1.533		
308	–3.188		
313	–4.060		

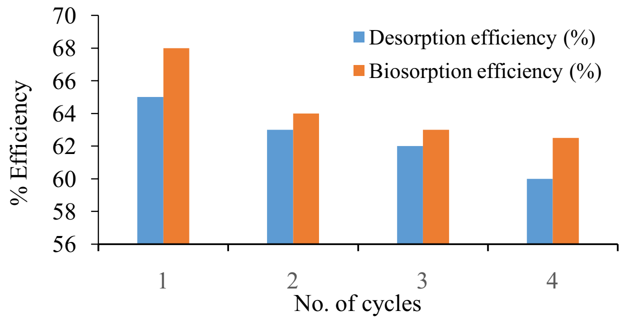

Fig. 7. Efficiency of biosorption-desorption with different number of cycles.

3.11. Comparison of several studies done for Ni^{2+} ions biosorption

For Ni^{2+} ions biosorption, most of the researchers used pseudo-first and pseudo-second-order kinetic models to analyze the kinetic data (Table 9). In most of the studies Langmuir and Freundlich isotherm models have been used to study the equilibrium data of Ni^{2+} ions biosorption (Table 10). Table 11 shows the comparison of biosorption capacity of different biosorbents for Ni^{2+} ions biosorption at various process parameters.

4. Conclusions

The biosorption of Ni^{2+} ions on *S. filipendula* was studied by conducting batch experiments. The optimization of process parameters for Ni^{2+} ions biosorption on *S. filipendula*

Table 9
Comparison of various isotherm models studied for Ni^{2+} ions biosorption using different biosorbents

S. No.	Biosorbent	Biosorption isotherm					
		Langmuir	Freundlich	Redlich–Peterson	Temkin	Radke-Prausnitz	References
1	*Bacillus laterosporus*	q_e = 44.44 mg/g b = 1.44 × 10^{-3} L/mg	k_f = 0.068 n = 1.034	–	–	–	[52]
2	*Yarrowia lipolytica*	q_e = 30.12 mg/g b = 0.020 L/mg	k_f = 1.165 n = 1.61	–	–	–	[53]
3	*Baker's yeast*	q_e = 9.01 mg/g b = 0.212 L/mg	k_f = 3.73 mg^{1-n}/g L^n n = 5.88	K_1 = 4.12 K_2 = 0.813 b = 0.887	–	–	[54]
4	*Mucor hiemalis*	–	k_f = 1.922 n = 0.99	–	–	–	[55]
5	*Sargassum ilicifolium*	q_e = 133.81 mg/g b = 0.325 L/mg	k_f = 0.54 n = 1.51	–	k_T = 3.38 L/mg b_T = 0.49 J/mol	q_m = 110.9 mol/g E = 0.038 kJ/mol	[38]
6	*Laminaria japonica*	q_e = 66.3 mg/g b = 0.212 L/mg	k_f = 0.63 n = 3.78	K_1 = 2.29 K_2 = 10.3 b = 0.89	–	–	[56]
7	*Stenotrophomonas maltophilia*	q_e = 54.3 mg/g b = 0.036 L/mg	k_f = 23.6 L/mg n = 5.83	–	–	–	[57]
8	*Bacillus subtilis*	q_e = 57.8 mg/g b = 0.047 L/mg	k_f = 26 L/mg n = 5.71	–	–	–	[57]
9	*Sargassum* sp.	q_e = 53.58 mg/g b = 0.0276 L/mg	k_f = 0.542 n = 3.613	–	–	–	[21]
10	*Spirogyra neglecta*	q_e = 26.3 mg/g b = 0.042 L/mg	k_f = 74.2 mg^{1-n}/g L^n n = 0.366	–	–	–	[58]
11	*Pithophora oedogonia*	q_e = 11.81mg/g b = 0.039 L/mg	k_f = 1.84 mg^{1-n}/g L^n n = 0.342	–	–	–	[58]
12	*Sargassum filipendula*	q_e = 62.7 mg/g b = 0.0681 L/mg	–	–	–	–	[59]
13	*Arthrospira platensis*	q_e = 43.43 mg/g b = 0.0074 L/mg	k_f = 12.61 n = 1.36	–	–	–	[60]
14	*Sargassum filipendula*	q_e = 34.3 mg/g b = 0.81 L/m	k_f = 23.04 n = 2.28	K_1 = –0.0162 K_2 = 26.27 b = 0.187	–	q_m = 26.27mol/g k_0 = 6.19 × 10^{-4} a_R = 0.187	This study

was done by using RSM. The relationship between independent variables and response (% removal) was achieved by the quadratic model. The range of process parameters was temperature (20°C–50°C), initial concentration of Ni^{2+} ions (50–200 mg/L), pH (1.5–7.5), and biosorbent dosage (0.25–3.25 g/L). The equilibrium has been achieved in 60 min beyond this time no further significant removal was observed. The optimum conditions at which 68.45% removal efficiency of Ni^{2+} ions were obtained as temperature of 41.5°C, pH of 5.4, biosorbent dosage of 1.97 g/L, and initial Ni^{2+} ions concentration of 83.18 mg/L. ANOVA results showed that the linear terms (temperature and pH) and square terms (temperature, pH, biosorbent dosage, and initial Ni^{2+} ions concentration) were significantly affect the Ni^{2+} ions biosorption. Experimental data were fitted to six isotherm models and it was noticed that the Redlich–Peterson was the best fitted isotherm model with higher value of R^2 and small value of Δq%. The biosorption of Ni^{2+} ions follows a pseudo-first-order kinetic model (R^2 > 0.98) indicating that physisorption was the rate limiting step. FESEM result shows that after biosorption process, the surface of alga becomes smooth. It indicates that the pores on surface of *S. filipendula* has been filled after biosorption of Ni^{2+} ions. EDS peaks shows that the contribution of ion exchange mechanism involved for the binding of Ni^{2+} ions to *S. filipendula* surface. FESEM-EDS analysis of *S. filipendula* confirms the presence of Ni^{2+} ions on the surface of *S. filipendula* after biosorption. Thermodynamic parameters ($\Delta G°$ = –0.097 to –4.060 kJ/mol, $\Delta H°$ = 79.175 J/mol, $\Delta S°$ = 0.270 J/mol K) showed that Ni^{2+} ions biosorption process was feasible, spontaneous, and endothermic in nature. After four consecutive cycles of biosorption/desorption, showed that biosorption and desorption

Table 10
Summary of studies done on biosorption of Ni^{2+} ions

S. No.	Biosorbent	pH	T (°C)	Initial Ni^{2+} ions concentration (mg/L)	Biosorbent dosage (g/L)	q_e (mg/g)	References
1	*Bacillus laterosporus*	7.0	30	10–50	4.0	44.44	[61]
2	*Yarrowia lipolytica*	6.0	40	100	2.0	30.12	[53]
3	*Baker's yeast*	6.7	27	400	1.0	9.8	[54]
4	*Mucor hiemalis*	8.0	40	50	0.5	15.83	[55]
5	*Sargassum ilicifolium*	5.0	25	100	6.1	218.91	[24]
6	*Laminaria japonica*	6.0	25	234.7	1	52.81	[56]
7	*Stenotrophomonas maltophilia*	6.0	30	45.6	2.0	54.3	[57]
8	*Bacillus subtilis*	6.0	30	45.6	2.0	57.8	[57]
9	*Sargassum* sp.	5.0	30	0–410	0.1	53.58	[58]
10	*Spirogyra neglecta*	5.0	–	5–200	1	90.19	[58]
11	*Pithophora oedogonia*	5.0	–	5–200	1	71.13	[58]
12	*Sargassum filipendula*	4.5	21	17.6–234.76	3	62.7	[59]
13	*Arthrospira platensis*	5.0	20	29.34–176.0	2	20.77	[60]
14	*Pelvetia canaliculata*	4.0	25	50	0.5	228.89	[30]
15	*Codium vermilara*	6.0	25	100–150	0.5	13.2	[23]
16	*Sargassum filipendula*	5.4	41	83	1.97	34.3	This study

Table 11
Comparison of kinetic models parameters studied for Ni^{2+} ions biosorption

S. No.	Biosorbent	Pseudo-first-order	Pseudo-second-order	References
1	*Yarrowia lipolytica*	k_0 = 0.055 1/min q_e = 2.476 mg/g	K = 0.019 g/mg min q_e = 15.97 mg/g	[53]
2	*Sargassum ilicifolium*	k_0 = 0.057 1/min q_e = 169.61 mg/g	K = 0.013 g/mg min q_e = 136.16 mg/g	[38]
3	*Laminaria japonica*	k_0 = 0.09 1/min q_e = 0.99 mmol/g	K = 0.17 g/mmol min q_e = 1.02 mmol/g	[56]
4	*Baker's yeast*	k_0 = 0.0021 1/min q_e = 57 mg/g	K = 0.0035 g/mg min q_e = 8.1 mg/g	[54]
5	*Mucor hiemalis*	k_0 = 0.0414 1/min q_e = 18.84 mg/g	K = 0.046 g/mmol min q_e = 20.83 mg/g	[55]
6	*Bacillus laterosporus*	k_0 = 0.0792 1/min q_e = 7.033 mg/g	K = 0.0375 g/mg min q_e = 9.66 mg/g	[52]
7	*Sargassum filipendula*	k_0 = 0.054 1/min q_e = 88.25 mg/g	$K = 5.4 \times 10^{-4}$ g/mg min q_e = 108.7 mg/g	This study

efficiency was decreased by 8.5% and 12%, respectively. The results recommended that *S. filipendula* could be used as a potential biosorbent for Ni^{2+} ions biosorption from aqueous solution.

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