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Sequestration of Ni(II) and Zn(II) Ions from Electroplating Wastewater Using Biogenic Manganese Oxides

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Authors' contributions

This work was carried out in collaboration between all authors. All authors read and approved the final manuscript.

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ABSTRACT

A harmonious experimental–gauge approach was used to examine the ability of biogenic manganese oxide, formed in the cultures of a Mn(II) oxidizing bacteria, Mn 21 to sequester Ni(II) and Zn(II) ions. Batch experiments were carried out in order to model and optimize the biosorption process. The influence of four parameters i.e. pH, biosorbent dosage, contact time and temperature on the uptake of Ni(II) and Zn(II) ions was determined using a response surface methodology (RSM). The Mn 21 exhibited the highest 96.8% and 92.1% Ni(II) and Zn(II) removal respectively at an initial pH of 7.0, biosorbent dosage 0.775 g/L, Contact Time 42 hrs and temperature 32℃. The biosorption mechanism was also i nvestigated using Fourier transfer infrared (FT-IR) analysis of untreated, Ni(II) and Zn(II) ions loaded Mn 21 biomass. The biosorbent was characterized by Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray Spectroscopy (EDS). It was found that the newly formed biogenic manganese oxides (BMO) effectively sequestered Ni(II) and Zn(II) ions from electroplating wastewater.

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Keywords: BMO; sequestration; RSM; FTIR; SEM; EDS.

1. INTRODUCTION

Today, our society faced major environmental problem i.e. water pollution which leads to ecological disequilibrium and various health hazards. Industrialization has affected the environment through disposal of waste containing toxic contaminants in the form of heavy metals. Heavy metals are among the main environmental concerns because of their unique characteristics unlike organic pollutants; they are non-biodegradable, hence they are accumulated by living organisms. Heavy metal ions such as cadmium, zinc, lead, copper, nickel, and chromium etc often found in industrial wastewater, having acute toxicity for aquatic and terrestrial life, including humans. As these metals does not degrade biologically, the control of heavy metals pollution has special importance for both organisms that live in water and those that depend on water [1]. Thus, the disposal of industrial effluents containing heavy metals into environment is the major issue, thus for their removal cost-effective technologies are instantly required [2]. The obligation of stringent set of laws enlarged the claim for novel treatment technologies to eradicate metals from wastewater and to accomplish today's toxicity focused concentration limits. The investigation for latest and pioneering treatment technologies has focused the consideration on metal binding capacities of germs such as bacteria, mould and algae, etc [3]. A vast concern has freshly been engaged to the biosorption of heavy metals from solutions by means of different biomaterials as adsorbents. Among a variety of assets in biological wastes, both dead and alive biomass, demonstrate particularly attractive metal-binding capacities [4,5].

Manganese (Mn) oxides are accumulated in the surroundings during microbial oxidation of Mn(II) and these oxides provide a excellent scavengers of different toxic elements such as heavy metal ions [6-8]. Biogenic Mn oxide is enormously reactive with plentiful elements in aquatic and terrestrial environments. Because biogenic Mn(II) oxidation proceeds more quickly than abiogenic (abiotic) Mn(II) oxidation in neutral pH environment [9]. Biogenic Mn oxides (BMOs) are predominant naturally occurring Mn oxides [7]. Also, as a diversity of bacteria and fungi bring into being highly reactive BMOs, these organisms be able to serve as mediators in most element cycles. Heavy metals sorption on BMOs has been widely studied. Earlier studies have confirmed the potential capability of BMOs to sequestrate Ni(II) [10-14] and Zn(II) [15-20] from aqueous solutions.

This paper reports Ni(II) and Zn(II) ions interactions with Mn 21 and the impact of various operating variables on sequestration of these metals with biogenic Mn oxide. The structure of bacteriologically formed Mn oxide was characterized by SEM and EDS. Experiments were conducted with spectroscopic techniques to assess metal binding capacities of Mn 21, and biogenic Mn oxide, and to elucidate sorption mechanisms.

2. MATERIALS AND METHODS

2.1 Selection of Bacterial Species

In the present report, Mn 21 was isolated from the wastewater of Laxmi Precisions Screw Ltd., Rohtak, Haryana, India. Bacterial species were isolated by standard spread plate method using nutrient agar medium and plates were incubated at 30℃ for 48 hr. The heterogeneous bacterial colonies were appeared on plate were further streaked for single purified bacterial colonies. For screening of isolates for manganese oxidation, the isolates were streaked on petriplates containing Mn- oxidation agar media. Plates were incubated at 30℃ & examined every week for the appearance of colonies with dark centers or edges as evidence of deposition of dark (oxidised) Mn. The presence of Mn oxides was confirmed using the colorimetric dye Leucoberbelin blue (LBB). This species was used as model for the synthesis of biogenic manganese oxide (BMO).

2.2 Preparation of Biomass

For the production of BMO, the isolates Mn 21 were inoculated in a 500 ml Erlenmeyer flask containing 300 ml of manganese oxidising medium broth amended with 50 ppm of Mn(II) concentration and incubated for 72 hr in rotary shaker (200 rpm) at 32℃. After incubation, the bacteria were harvested by centrifugation (4000 rpm for 10 min). The pellet was washed with double distilled water and dried in oven at 50℃.

2.3 Characterization of BMOs

SEM was used to observe micro-morphologies of biogenic Mn oxides. First, 1.0 ml of isolated bacterial strain cells grown in Mn oxidising medium for 9 days (with and without adding $MnCl_2$) were centrifuged at 10,000 rpm for 5 min, and the sedimented material was transferred onto a small cover slip which was fixed with double glue for SEM observation [17]. The above samples were examined using a SEM (JSM-6510/LV, JEOL) with 10 or 20 kV accelerating voltage. Detection of Mn on the cell surfaces of isolated bacterial strain was performed by energy-dispersive spectroscopy (EDS) (JSM-6510/LV, JEOL).

2.4 Biosorption Mechanism Study

FTIR spectrum study was carried out to explain biosorption mechanism for identifying the presence of functionalities of the BMOs. The spectra were collected using PerkinElmer spectrum BX FTIR system (Beaconfield Buckinghamshire HP9 1QA) equipped with diffuse reflectance accessory with the range of 400–4000cm^{-1}. The biosorption study for the metal ions was carried out holding temperature 32℃, initial metal ions concentration 50 ppm. The control pure biomass adsorbent was also run parallel in the distilled water at optimum pH. After equilibrium the metal loaded biomass was filtered through Whatman filter paper and washed with double distilled water to remove loosely bind ions or impurities. The metals loaded and pure biomass was dried at 50℃ in a heating oven. The samples were grounded in an agate pestle and mortar with KBr.

2.5 Statistical Optimisation Study

Box-Behnken design model, which is the standard response surface methodology (RSM), was established on the basis Design Expert software (Stat Ease, 8.0.7.1 trial version) for the optimization of biosorption process. The experimental design, four independent variables i.e. pH (5.0-9.0), temperature (27-37℃), contact time (12-72 Hrs) and adsorbent dose (0.05-1.5 g/L) were taken and obtained response biosorption of Ni (II) and Zn (II) ions. The experimental design was applied after selection range of each variable (maximum and minimum) as shown in Table 1. The Box Behnken design contained a total of 29 experiments with 24 experiments organized in a factorial design with 5 experimental trials involving the replication of the central point. Repeated observations at centre point were used to estimate the experimental error employed.

2.6 Statistical Analysis

The quadratic equation model for predicting the optimal point was expressed according to equations (1). RSM makes it possible to represent independent process parameters in quantitative form [21] as:

$$Y = b_0 + \sum b_i X_i \sum b_{ii} X_i^2 + \sum b_{ij} X_i X_j \quad (1)$$

Where, Y is predicted response, b_o is the response function and X_i, X_j, b_i, and b_j are experimental coded variables respectively (Table 1). These coded variables are related to uncoded variables using the following relation eq. (2).

$$Xi = \frac{2(a_i - b_i)}{d_i} \quad (2)$$

Where a_i is the variable value in actual units of the $_i$th observation, b_i is the mean of highest and lowest variable value of a_i and d_i is the difference between the highest and the lowest variable value of a_i and d_i. The variables given Table 1 are based on above relationship in equation (2).

Table 1. The experimental domain factors and levels for Box–Behnken design

Code	Name of factors	Factor range and levels (Coded)		
		−1	0	+1
A	pH	5	7	9
B	Temperature (^oC)	27	32	37
C	Contact time (hrs)	12	42	72
D	Biomass dose (g/L)	0.05	0.775	1.5

3. RESULTS AND DISCUSSION

3.1 Scanning Electron Microscopic (SEM) and EDS Micrograph

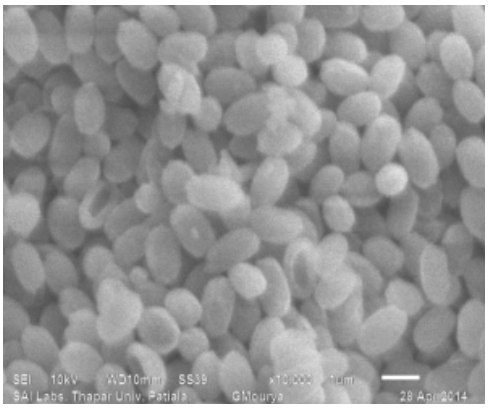
Scanning electron microscopy (SEM) has been used extensively as a tool for biosorbent characterization. SEM micrographs of heavy metals free and metal loaded bacterial biomass of Mn 21 are shown in Fig.1 A-B. It was observed the cell surface morphology considerably changed after metal biosorption. These micrographs were clearly indicated the presence of new shiny bulky particles over the surface of metal loaded bacterial biomass of Mn 21 cells.

These cells looked vague, distorted and seemed to be damaged by the heavy metal ions. The alteration in morphology may also result from the secretion of extra cellular polymeric substance during metal biosorption [22].

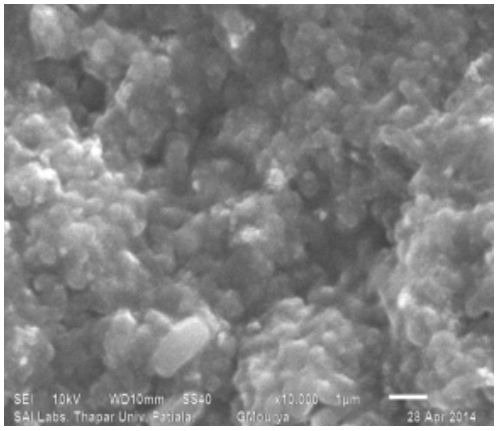
EDS spectra of BMO Mn 21 adsorbents were collected without metals and after Ni(II) and Zn (II)ions uptake (see Fig. 2). EDS analysis of the BMO indicate that a wide range of chemical compounds occur. These includes O, Ca, C, S, Mn, Ni and Z (higher than detection limit of about 0.1 wt %). Results showed that Mn peak was present alone, although observable Ni(II) and Zn(II) peak was obtained while BMO were laden with Ni(II) and Zn(II) confirming the successful Ni(II) and Zn(II) loading on the surface BMO.

3.2 Fourier Transform Infra-red (FTIR) Analysis

Functional groups present on the cell surface can be recognized by Fourier Transform Infrared Spectroscopy (FTIR) as every group has a distinctive energy absorption band [23-25]. Due to complex nature of cell wall composition, it is not possible to decide the precise group responsible for this stretching vibration. FTIR spectral analysis was done before and after metal loaded of Ni (II) and Zn (II) ions in the range of 4000-400 cm^{-1}. Fig. 3 showed FTIR spectroscopic investigation of metal loaded biomass shifted strong asymmetrical stretching bands. The FTIR spectra of inhabitant biomass and shifted broad band after metal loaded biomass with Ni (II) and Zn (II) ions showed a number of adsorption peaks are shown in Table 2 and Fig. 3. These groups are of the bonded amino groups (-NH), hydroxyl groups (OH), carboxylate anions (COO^{-}) and MnOx Stretching. The variation between three peaks ranged from 43, 52.6 and 62.3 cm^{-1} for Ni(II) sorption, and 98.1, 60.9, 13 cm^{-1} for Zn(II) sorption, with corresponding functional groups -NH streatching, C-O stretch and MnOx stretching respectively. There is also noticeable difference in intensity at 1546 cm^{-1} which point out sulphate ions peaks. These findings indicate the participation of the functional groups in biosorption process. FTIR spectral analysis of inactivated dead fungal mycelia of *Aspergillus niger* indicate shifted broad bands at 3307, 1541 and 1319 cm^{-1} when Ni(II) and Zn(II) ions loaded biomass showed similar adsorption at 3380, 1545, and 1377 cm^{-1} for Zn(II) and 3277, 1544, and 1377 cm^{-1} for Ni(II) ions [25].



(A)



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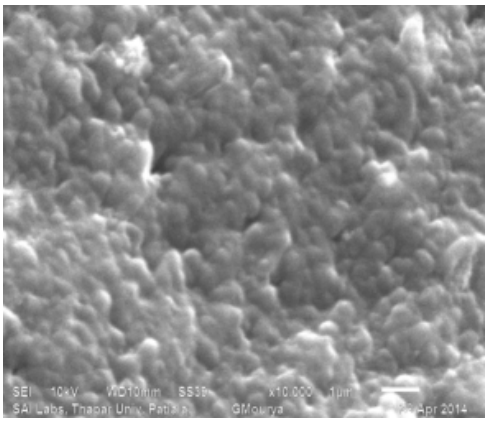


(C)

Fig. 1. SEM micrograph of A) before metal loaded BMOs, B) after Ni (II) loaded, C) after Zn(II) loaded biomass

Table 2. Infra-red (IR) adsorption band and corresponding functional groups before and after absorption of metal loaded

	Bonded-OH, -NH stretching	Aliphatic chain -CH	Asymmetric C=O	Amide II	C-O stretch COOH	C-O-C, C-C, C-O, ring vibrations	Mn-O Stretching
Before metal loaded (C)	3309.8	2363.4	1654.3	1546.8	1388.0	1074.5	669.2
Ni (II)	3385.9(43)	2365.4(2.0)	1653.1(1.2)	1541.3(5.5)	1440.6(52.6)	1073.3(1.2)	606.9(62.3)
Zn (II)	3407.9(98.1)	2363.5(0.1)	1652.3(2.0)	1538.5(8.3)	1448.9(60.9)	1053.5(21)	656.2(13)

Note: Value in parenthesis point out the variation among peaks before and after biosorption. [25-28]

Table 3. Experimental design with definite factors and outcome of the Box–Behnken model

Run	Variables				Responses	
	pH	Temperature (℃)	Contact time (hrs)	Biomass dose (g/L)	Ni Removal (%)	Zn removal (%)
1	7	27	42	0.05	75.3	80.9
2	9	27	42	0.775	75.4	80.1
3	7	37	42	0.05	75.1	81.6
4	5	32	42	0.05	60.7	64.7
5	7	32	42	0.775	96.8	92.1
6	7	32	42	0.775	96.8	92.1
7	7	32	12	1.5	48.5	49.1
8	9	37	42	0.775	68.2	54.9
9	7	27	12	0.775	66.6	63.1
10	7	32	72	0.05	82.1	77.1
11	9	32	12	0.775	46.2	45.3
12	9	32	42	0.05	72.4	73.0
13	7	27	42	1.5	89.6	87.5
14	7	32	42	0.775	96.8	92.1
15	7	32	42	0.775	77.5	84.7
16	5	32	72	0.775	82.5	78.7
17	7	37	12	0.775	47.6	46.5
18	7	37	42	1.5	81.6	83.5
19	5	32	12	0.775	58.5	48.7
20	5	27	42	0.775	68.5	62.0
21	5	32	42	1.5	75.9	74.6
22	7	32	42	0.775	96.8	92.1
23	7	37	72	0.775	67.1	68.7
24	5	37	42	0.775	58.7	66.8
25	7	27	72	0.775	73.9	75.3
26	9	32	72	0.775	72.2	75.3
27	7	32	12	0.05	62.7	68.7
28	9	32	42	1.5	63.9	68.9
29	7	32	72	1.5	75.4	70.8

3.3 Response Surface Methodology (RSM)

The Box-Behnkon design of quadratic model consists of 29 experiments for each response (Tables 3). The second order polynomial equation was practiced to expose the linkage between independent variables and response. The regression equation coefficients were computed data were fitted to a second-order polynomial equation. The analysis of variance (ANOVA) for biosorption of Ni (II) and Zn (II) ions with biogenic manganese oxide was used in order to certify a good model. Table 3 showed the experimental planning and attained results of removal efficiency of metal ions for each run. The ANOVA analysis is vital to justify the significance and adequacy of the model (Table 4). Prob > F less than 0.05 demonstrated that model provisions are significant terms and value > 0.05 expressed the non significant terms. The non significant value of lack of fit (> 0.05) 0.559 and 0.058 for Ni (II) and Zn (II) respectively for biogenic manganese oxide showed that

quadratic model is applicable for present study (Table 4). The r^2 and adjusted r^2 values 0.8673 and 0.7347, 0.9231 and 0.8461 for Ni (II) and Zn (II) correspondingly for biogenic manganese oxide illustrated reasonable agreement with value of r^2, which is closer to 1.0, implied the better suitability of model in the experimental data (Table 4). The quality-of-fit of polynomial model was articulated by the coefficient of determination (r^2) and statistical significance was checked by F-test in the programme. The residual error, pure error and lack-of-fit were calculated from the repetitive measurements [29]. To visualize the relationship between responses and experimental levels for each of the factors, the integral polynomial equation was expressed as 3 D surface plots.

3.3.1 Interactive effect of variables on the biosorption study of metal ions

Response surface methodology practices quantitative data in an experimental design to conclude, and simultaneously resolve multivariate equations, to optimize processes and products [30]. The effect of interacting variables: pH, temperature, contact time and biomass dose on Ni (II) and Zn (II) ions sequestration were interpreted on the basis of quadratic polynomial eqn. (3,–4). The optimistic linear coefficient in the model equation revealed that response increased with increasing the variable level and vice-versa (eqn. 3-4). pH and contact time were the most important factors ($P > 0.0001$) and had a positive effect on removal of Ni (II) and Zn (II) with biogenic manganese oxide [(eqn. (3-4)]. The negative quadratic coefficient for pH was evaluated since it affects the number of cellular surface sites accessible to bind cations, as well as metal speciation [31]. Temperature is also the most vital factor ($P > 0.0001$) had a negative effect on removal of Ni (II) and Zn (II) with biogenic manganese oxide [Eqs. (3) – (4)]. Biomass dose had a positive effect on removal of Ni (II) ions but had a negative effect on Zn (II) ions with biogenic manganese oxide. The expand in metal removal with rising biomass dose might be due to accessibility of more unoccupied binding sites for metal biosorption.

The concluding outcome for biosorption of Ni (II) and Zn (II) ions in terms of coded factors are specified in eqn (3-4).

$$\textbf{\% Ni Removal (BMOs)=}+92.94-0.54*A-4.25*B+10.26*C+0.55*D+0.65*AB+0.50*AC-5.93*AD+3.05*BC-1.95*BD+1.88*CD-14.77*A^2-9.21*B^2-17.25*C^2-7.26*D^2 \quad (3)$$

$$\textbf{\% Zn Removal (BMOs)=}+90.62+0.17*A-3.91*B+10.38*C-0.97*D-7.50*AB+3.216E-015*AC-3.50*AD+2.50*BC-1.17*BD+3.32*CD-14.76*A^2-7.52*B^2-7.97*C^2-3.83*D^2 \quad (4)$$

Where A, B, C and D are the coded terms for pH, temperature, contact time and biomass dose respectively.

Table 4. Analysis of variance (ANOVA) for quadratic model of biogenic manganese oxide for Ni (II) and Zn (II) ions

Responses	Biogenic manganese oxides						
	Source	Sum of squares	df	Mean square	F-value	P- value	Prob>F
Ni Removal	Model	4652.64	14	332.33	4.54	0.0038	Significant
	Residual	1024.56	14	73.18			
	Lack of Fit	726.56	10	72.66	0.98	0.5598	not significant
	Pure Error	297.99	4	74.50			
	Cor Total	5677.20	28				
	r^2	0.8195					
	adjusted r^2	0.6391					
Zn Removal	Model	4855.69	14	346.84	7.56	0.0003	Significant
	Residual	642.68	14	45.91			
	Lack of Fit	598.87	10	59.89	5.47	0.0580	not significant
	Pure Error	43.81	4	10.95			
	Cor Total	5498.37	28				
	r^2	0.8831					
	adjusted r^2	0.7662					

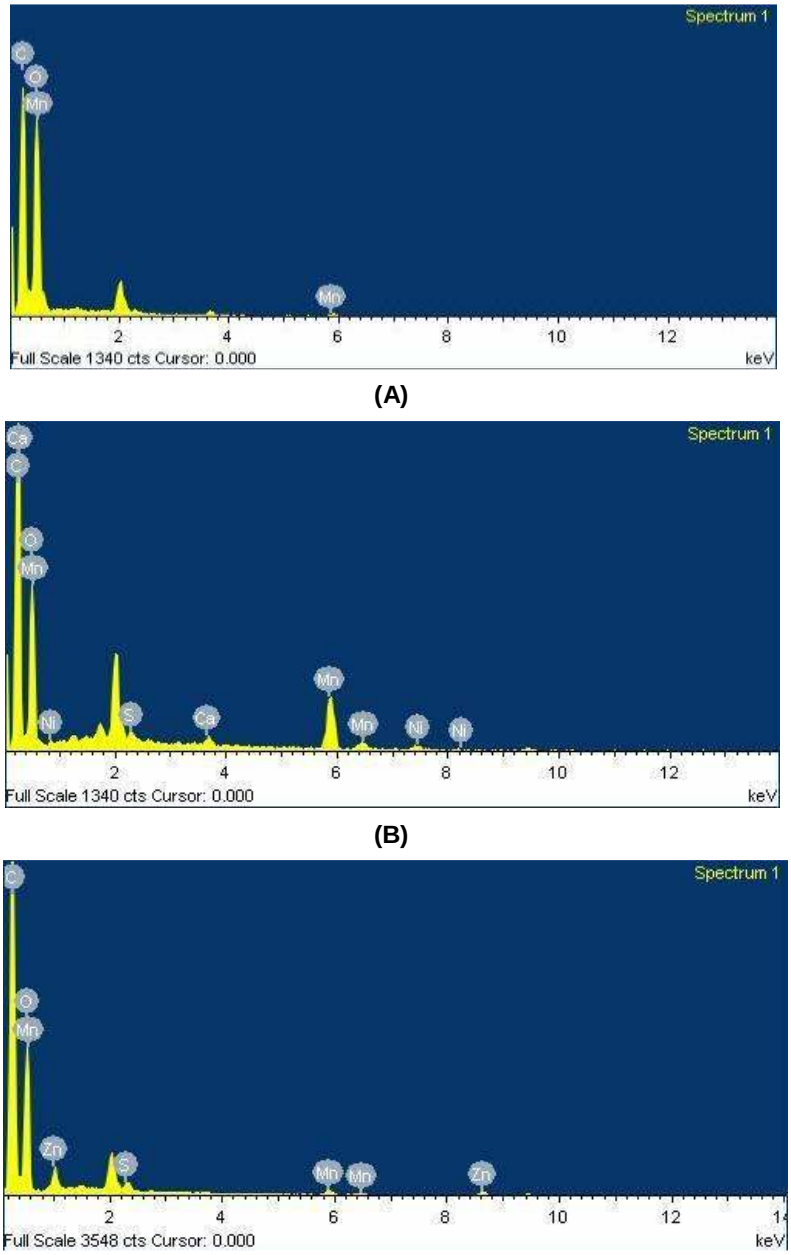
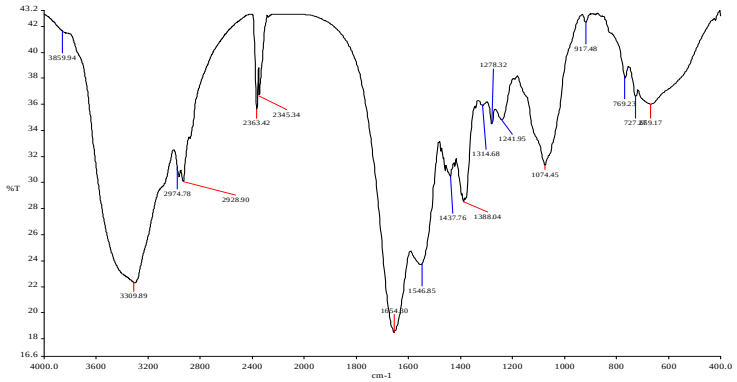


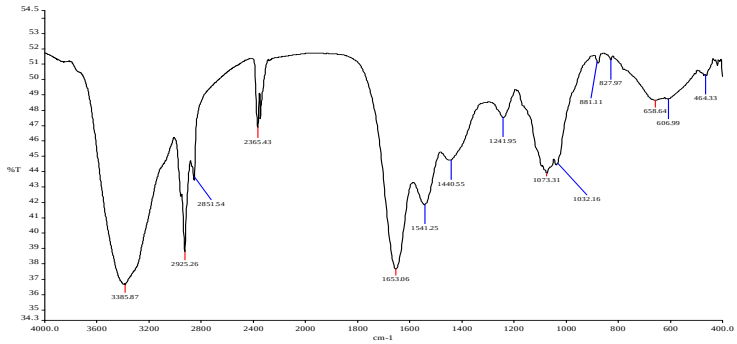
Fig. 2. EDS monograph A) before metal loaded BMOs, B) after Ni (II) ions loaded, C) after Zn(II) ions loaded biomass

Fig. 4 depicts the 3-D surface plots of collective interactive effects of the grouping of independent variables on biosorption of Ni (II) and Zn (II) and with BMOs. These 3-D surface plots were served as a function of two variables by clutching other variables at a fixed level. It can be seen from Fig. 4 (A-B) interactive effect of pH and temperature is highly singnificant and is in great harmony with the results observed. The significant value i.e. Prof > F lesser than 0.05 for both metal ions illustrated that it is the most important variable affecting the biosorption of both heavy metals ions (Table.4). As shown in Fig. 4 (A-D), Ni (II) and Zn (II) removal capability increased with pH from 5.0-7.5 and then decreased when the pH increased from 7.5 to 9.0. The phenomenon may

be firmly related with the diverse interactions among adsorption sites and Ni (II) and Zn (II) species under various pH. It can be observed from Fig. 4 (C-F), Ni (II) and Zn (II) ions adsorption capability increased with increasing contact time from 12 hrs to 52 hrs and after that a slight decrease is observed with further increase in contact time. Biomass dose showed little effect on sequestration of Ni (II) and Zn (II) ions (Fig. 4(G-L)). Also, the interactive effect of temperature and biomass dose on sequestration of the both the metal ions are far less and can be neglected, as publicized in Fig. 4(K-L). Temperature also had modest effect on biosorption of both metal ions Fig. 4 (A-B), (E-F), (K-L). The maximum removal of Ni (II) and Zn (II) ions were found to be 96.8% and 92.1% by BMOs respectively. The most favourable expected end of maximum adsorption capability of various parameters acquired by Design-Expert 8.0.7.1 trial version is listed as: biomass dose 0.775 g/L, contact time 42 hrs, temperature 32ºC and pH 7.0.



(A)



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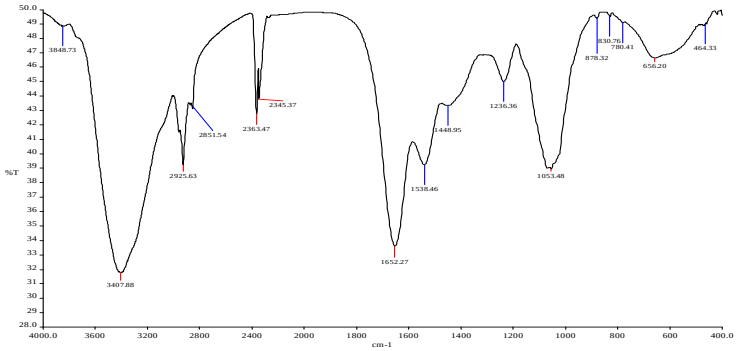
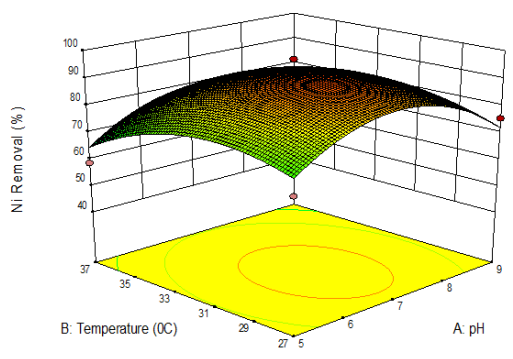
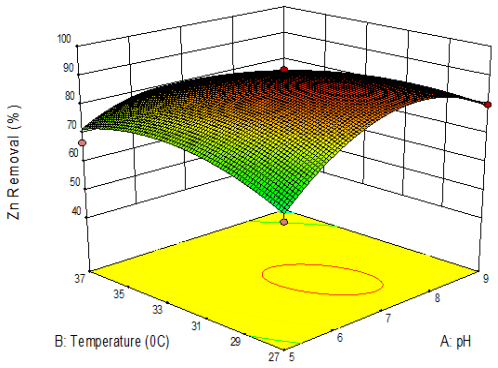


(C)

Fig. 3. Infrared spectra of Mn 21 (a) before metal sorption, (b) after Ni(II) loaded biomass (c) after Zn(II) loaded biomass


Ni Removal (%)
100
90
80
70
60
50
40
37
35
33
31
29
27
B: Temperature (0C)
5
6
7
8
9
A: pH

(A)


Zn Removal (%)
100
90
80
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B: Temperature (0C)
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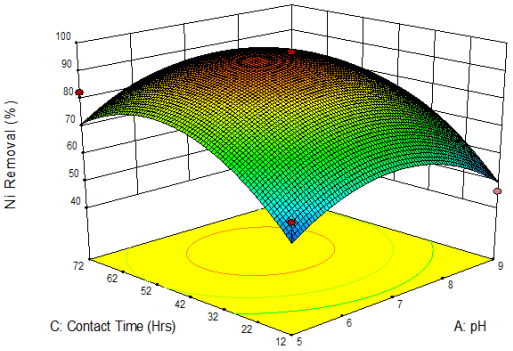
A: pH

(B)


Ni Removal (%)
100
90
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60
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C: Contact Time (Hrs)
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6
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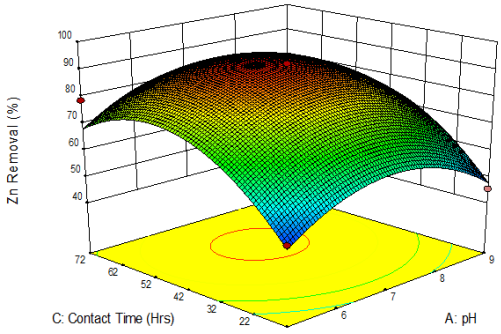
9
A: pH

(C)


Zn Removal (%)
100
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C: Contact Time (Hrs)
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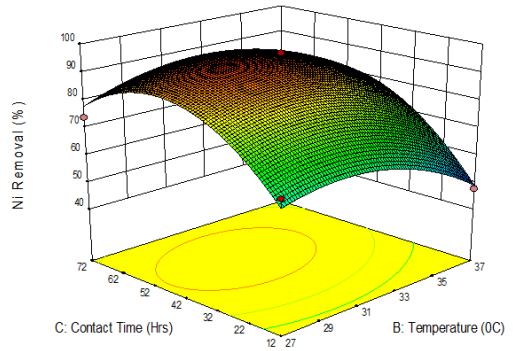
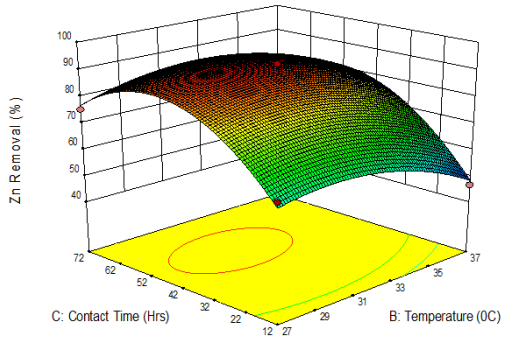
A: pH

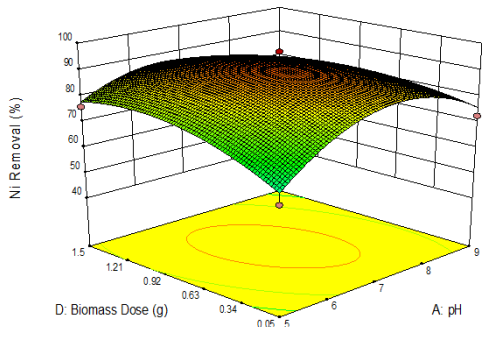
(D)


Ni Removal (%)
100
90
80
70
60
50
40
72
62
52
42
32
22
12
C: Contact Time (Hrs)
27
29
31
33
35
37
B: Temperature (0C)

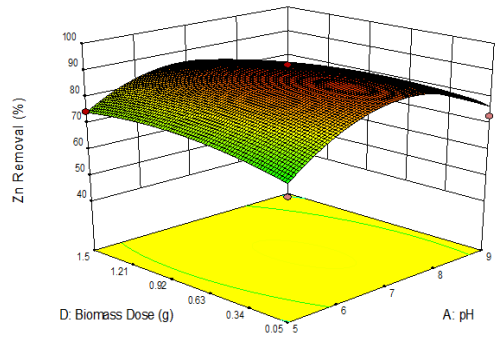
(E)


Zn Removal (%)
100
90
80
70
60
50
40
72
62
52
42
32
22
12
C: Contact Time (Hrs)
27
29
31
33
35
37
B: Temperature (0C)

(F)


Ni Removal (%)
100
90
80
70
60
50
40
1.5
1.21
0.92
0.63
0.34
0.05
D: Biomass Dose (g)
5
6
7
8
9
A: pH

(G)


Zn Removal (%)
100
90
80
70
60
50
40
1.5
1.21
0.92
0.63
0.34
0.05
D: Biomass Dose (g)
5
6
7
8
9
A: pH

(H)

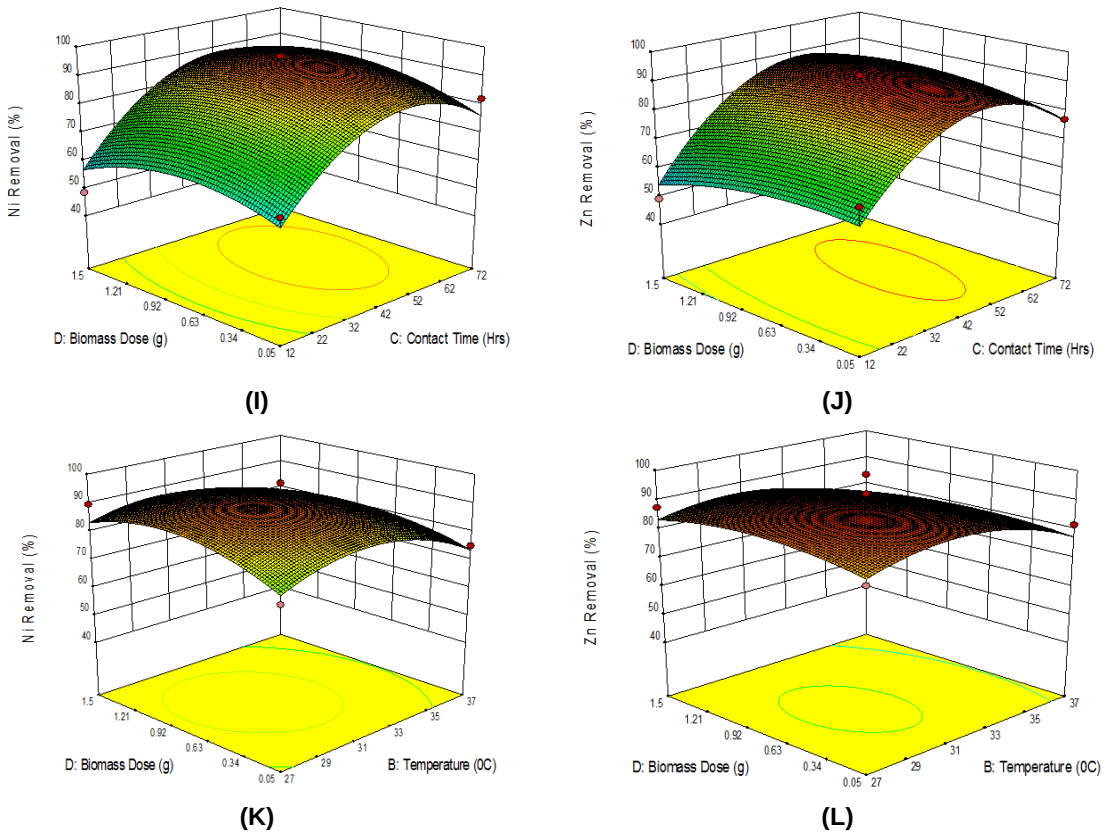


Fig. 4. 3-D surface plots for interactive effect of (A-B) pH and temperature at contact time 42 hrs and biomass dose 0.775 g/L, (C-D) contact time and pH at temperature 32℃ and biomass dose 0.775 g/L, (E-F) contact time and temperature at pH 7.0 and biomass dose 0.775 g/L, (G-H) pH and biomass dose at adsorption temperature 32℃ and contact time 42 hrs (I-J) biomass dose and contact time at pH 7.0 and temperature 32℃, (K-L) biomass dose and temperature at pH 7.0 and contact time 42 hrs for Ni(II) and Zn(II) ions removal

4. CONCLUSION

Biogenic manganese oxides (BMOs) prepared by Mn 21, was found to be an efficient adsorbent for Ni(II) and Zn (II) ions removal. The functional groups identified on bacterial surface by FTIR technique included bonded amino groups (-NH), hydroxyl groups (OH), carboxylate anions (COO^{-}) and MnOx Stretching which could possibly be involved in the sequestration of Ni(II) and Zn (II) ions. From the significant model and mathematical assessment, response surface model has confirmed to be a valuable and precise method to optimize the biosorption process variables for the removal of Ni(II) and Zn (II) ions by manganese oxidizing bacterial strain Mn 21. Independent variables have significant value 0.0001 which indicates the importance of these variables and values of "Prob > F" less than 0.05 indicated that model terms are significant for the biosorption of Ni(II) and Zn (II) ions. The maximum removal of 96.8% and 92.1% Ni (II) and Zn (II) ions respectively by BMOs under optimized conditions of pH 7.0, temperature 32℃, contact time 42 hrs and biomass dose of 0.775 g/L. RSM approach proved to be a very useful and accurate methodology to optimize biosorption process and need to apply at pilot scale for industrial wastewater treatment, As a conclusion, the performance of present method was excellent in removal of Ni(II) and Zn (II) ions with high selectivity.

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

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