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Removal of Zn (II) by using oscillatoria sp. from waste water

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ABSTRACT

Zinc has been used in many industrials and removal of Zn (II) ions from waste waters is significant. Biosorption is one of the economic methods that used for removal of heavy metals. In this project we used oscillatoria (cyanobacteria, microalgae) as per biomass. In this study effect of contact time, initial metal ion concentration, temperature, pH & biomass dosage were studied. Maximum metal uptake was observed at pH 4.5. Maximum metal uptake (q_{max}) was 192.30 mg/g .The biosorption followed both Langmuir and Freundlich isotherm model and the adsorption equilibrium was reached in about 1 h. The kinetic of biosorption followed the second – order rate. The biomass could be regenerated using 0.1 M HNO_3.
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INTRODUCTION

Heavy metal pollution has posed a serious threat to the aquatic environment. At high concentrations, metals are toxic to animals and plants alike, as they could be dispersed in water and consequently in human beings through food chain biomagnifications that could cause serious health hazards.In view of the human health impacts, each metal impartsdifferent effects and symptoms. For instance, in the case of minor zinc exposure,irritability, muscular stiffness, loss of appetite and nausea are common[2]. Zinc is an essential element as enzyme activators in humans, but it is equally toxic atlevels of 100–500 mg/day and it is a known carcinogen[15]. However, these methods were found to be either inefficient or expensive when metal ions exist in low concentrations (<100 mg/L) and may also be associated with the generation of secondary environmental problems from waste disposal[1]. Biosorption is the binding and concentration of heavy metals from aqueous solutions (even very dilute ones) by certain types of inactive, dead, microbial biomass[6]. Some of the advantages of biosorption include competitive performance, heavy metal selectivity, cost-effectiveness, regenerative and no sludge generation. Sources of biomass include seaweeds, microorganisms (bacteria, fungi, yeast, and molds), activated sludge and fermentation waste. Studies using Biosorbents have shown that both living and dead microbial cell are able to uptake metal ions and offer potential inexpensive alternative to conventional absorbents[4,5]. However, living cell is subject to toxic effect of the heavy metals, resulting in cell death. Moreover, living cell often require the addition of nutrients and hence increase the BOD and COD in the effluent. For these reasons, the use of non-living biomaterials or dead cells as metal binding compounds has been gaining advantage because toxic ions do not affect them. In addition, dead require less care and maintenance, and cheaper[7]. Furthermore, dead biomass could be easily regenerated and reused. The capability

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of some living microorganisms to accumulate metallic elements has been observed at first from toxicological point of view[12-14]. Mechanisms responsible for biosorption, although understood to a limited extent, may be one or combination of ion exchange, complexation, coordination, adsorption, electrostatic interaction, chelation and micro precipitation[9,10,17]. Green algae are typically comprised of xylans and mannans; whereas red algaecontain sulphate esters of xylans and galactans in their cell walls[3,15].

MATERIALS AND METHODS

Biomass and culture medium

Oscillatoria was obtaining from agriculture collage from pune, which was isolated and thoroughly pure. The biomass was maintained in modified Bold' basal medium (MBBM) at 25 ^{0}C with 12:12 h of light/ dark cycle using 3000 lx light intensity. After 21 days cultivation period cells were harvested by centrifugation and were washed several times with deionised Water in order to remove culture media and was kept on a filter paper to reduce the water content. The biomass dried at 60 ºC in an oven for 24 h and milled to a gritty consistency. The biomass was sieve for particle size smaller than 1 mm and stored in dark bottle and keeps in a dry cabinet for experiments.

Formula of preparation MBBM to 950 mL of d-H_2O add:10.0 mL of stock solutions 1, 2, 3, 4, 5 and 1.0 mL of stock solutions 7, 8 and 2.0 mL of stock solution 10, 1.0 gm of bacto-peptone and 5.0 gm of sucrose.1) 25.0 gm $NaNO_3$ 2) 2.5 gm $CaCl_2.2H_2O$ 3) 7.5 gm $MgSO_4.7H2O$ 4) 7.5 gm K_2HPO_4 5) 17.5 gm KH_2PO_4 6) 2.5 gm NaCl 7) 50.0 gm disodium EDTA, 31.0 gm KOH 8) 4.98 gm $FeSO4.7H_2O$ 9) 11.42 gm H_3BO_3 10) 8.82 gm $ZnSO_4.7H_2O$, 1.44 gm $MnCl_2.4H_2O$, 0.71 gm MoO_3, 1.57 gm $CuSO_4.5H_2O$, and0.49 gm $CoNO_3.6H_2O$ per liter d-H_2O.MBBM.

Preparation of glass wares and synthetic sample

Cleaning of glassware used in the experiments was done as follows: First, washed with detergent solution, then rinsed with tap water; secondly, rinsed with 10% nitric acid, and then rinsed with tap water; finally rinsed with distilled water. The cleaned glassware was dried prior to use in experiments.A stock solution of

1000 mg/l of Zn (II) was obtained by dissolving zinc chloride (Merck Company) in distilled water. The test solutions of various concentrations range from 10 mg/L to 200 mg/L were prepared from the stock solution. The solution pH was adjust using 0.1 M HNO_3 and 0.1 M NaOH at the beginning of the experiment and not controlled afterwards. The conical flasks (250 mL) were shaken at 200 rpm in a temperature controlled rotatory shaker.

FT-IR spectroscopy

In order to determine the functional groups responsible for Zn biosorption, IR spectroscopy was used that about 0.1 g biomass was mixed with KBr for FT-IR spectra analysis (Shimadzu model 8400).

Analysis of Zinc ions

Zinc as Zn (II) was determined spectrophotometrically by atomic adsorption spectrophotometer (UNICAM, model 929,UK) at 620 nm.

Batch biosorption studies

Batch mode adsorption studies for individual metal compounds were carried out to investigate the effect of different parameters such as adsorbate concentration, adsorbent dose, contact time and pH. Solution containing adsorbate and adsorbent was taken in 250 mL capacity conical flask and agitated at 200 rpm in a shaker at predetermined time intervals. The adsorbate was decanted and separated from the adsorbent using Whatman No.1 filter paper.

Effect of contact time

For the determination of rate of metal biosorption by oscillatoria from 100 ml (at 10, 20, 50, 100 mg/L), the supernatant was analyzed for residual metal at different time intervals. The pH and the adsorbent dosage was kept constant, which varied according to the adsorbent and adsorbate under consideration.

Effect of adsorbent dosage

The effect of adsorbent dosage i.e., the amount of the oscillatoria biomass on the adsorption of metals was studied at different dosages ranging from 0.1 to 3 g with varied metal concentrations of 10, 20 and 50 mg/L. The equilibrium time and the pH were kept constant depending on the metal under consideration.

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Effect of pH

To determine the effect of pH on the adsorption of metal solutions (100 mL) of different concentration ranges (10-50 mg/L) were adjusted to desired pH values and mixed with known weight of adsorbent and agitated at preset equilibrium time. The equilibrium time and adsorbent dosage varied with the metal and adsorbent under consideration.

Desorption studies

After adsorption, the adsorbates – loaded adsorbent were separated from the solution by centrifugation and the supernatant was drained out. The adsorbent was gently washed with water to remove any unadsorbed adsorbate. Regeneration of adsorbate from the adsorbate – laden adsorbent was carried out using the desorbing media – distilled water at pH ranges using dilute solutions of EDTA, HCL and HNO_3 (Stirred at 200 rpm for 120 min at 25 ^{0}C) . Then they were agitated for the equilibrium time of respective adsorbate. The desorbed adsorbate in the solution was separated and analyzed for the residual heavy metals.

RESULTS

Results on the contact time of Zinc (II) at different initial metal ion concentrations by oscillatoria present in the Figure 1. The time required to reach equilibrium for Zinc(II) adsorption by oscillatoria is 60 minutes for all initial metal ion concentrations. The time taken for Zn (II) adsorption by oscillatoria was dependent on initial metal ion concentration and increased with increase in concentration of Zn (II). The amount of metal ions adsorbed increased with increase in initial metal ion concentration that results of that summarized in TABLE 1. Data for the effect of pH and the effect of different initial metal ion concentration is presented in Figure 3 for Zn (II) biosorption by oscillatoria. The results of effect of pH on the removal of metals reveal that irrespective of the oscillatoria metal ions were adsorbed. Zinc removal was optimal at pH4.5 that results of that summarized in TABLE 2. Results on the effect of adsorbent dosage at various initial metal concentrations are presented in this section showed Adsorption of Zn (II) by osillatoria at different initial metal concentrations and various adsorbent dosages are presented in Figure 2. The amount of adsorbent dosage required for the optimum removal of the metal ions increased with increase in the initial metal ion concentration that results of that summarized in TABLE 3. Results on the Zn (II) at different temperature by oscillatoria present in the Figure 4. As shown in that figure, the temperature has no significant effect on the biosorption of Zn (II) over tested 10-40 ºC at pH= 4.5. The temperature independent biosorption of Cr in this study is in accordance with the study of Prerna et al.[8], Wallace et al.[16] and Vitor et al.[11], including biosorption to be a passive energy independent process.

Adsorption isotherms

The isotherm studies were performed in the Zinc solution with the initial concentrations ranging from 10 to 100 mg/L at optimum pH values for Zn (II) (pH=4.5) .After shaking the flask containing the mixture of biomass (200 rpm, 25 ºC) and zinc ions for 120 min, the amount of residual Zinc in the filtrated solution was ana-
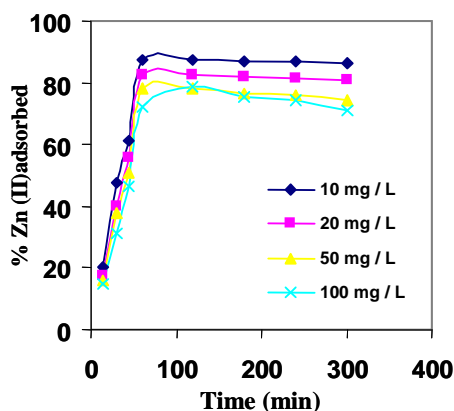
TABLE 1 : Effect of contact time and initial concentration of Zn (II)

contact Time (min)	10 mg/L		20 mg/L		50 mg/L		100 mg/L	
	% Adsorbed	q (mg/g)	% Adsorbed	q (mg/g)	% Adsorbed	q (mg/g)	% Adsorbed	q (mg/g)
15	20.06	2.00	17.22	3.44	15.79	7.89	14.80	14.80
30	47.62	4.76	40.08	8.01	37.67	18.83	31.25	31.25
45	61.11	6.11	55.55	11.11	51.06	25.53	46.21	46.21
60	87.29	8.72	82.26	16.45	78.33	39.16	72.11	72.11
120	87.29	8.72	82.41	16.48	78.13	39.06	78.87	78.87
180	86.79	8.67	81.77	16.35	76.33	38.16	75.19	75.19
240	86.63	8.66	81.30	16.26	76.20	38.10	74.23	74.23
300	86.20	8.62	80.76	16.15	74.09	37.04	71.28	71.28

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TABLE 2 : Effect of PH and initial concentration of Zn (II)

PH	10 mg/L		20 mg/L		50 mg/L	
	% Adsorbed	q (mg/g)	% Adsorbed	q (mg/g)	% Adsorbed	q (mg/g)
2	38.88	3.88	32.66	6.53	28.35	14.17
3	66.29	6.62	65.01	13.00	51.11	25.55
4	80.23	8.02	74.45	14.89	65.92	32.96
4.5	87.29	8.72	82.41	16.48	78.13	39.06
5	83.07	8.30	80.01	16.00	72.20	46.10
5.5	77.21	7.72	70.98	14.19	66.67	33.33
6	68.20	6.82	62.88	12.57	59.93	29.96

Figure 1 : Effect of contact time
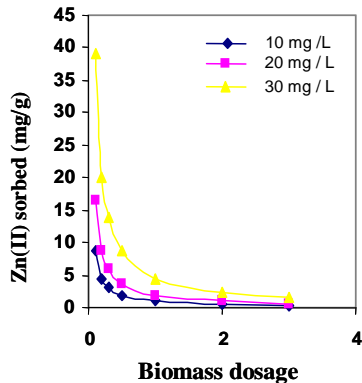
Figure 2 : Effect of biomass dosage

TABLE 3 : Effect of biomass dosage of Zn (II)

Biomass Dosage (g)	10 mg/L		20 mg/L		50 mg/L	
	% Adsorbed	Q (mg/g)	% Adsorbed	Q (mg/g)	% Adsorbed	q (mg/g)
0.1	87.29	8.82	84.41	16.48	78.13	39.06
0.2	89.35	4.46	86.66	8.66	80.37	20.09
0.3	91.20	3.04	88.86	5.92	83.25	13.87
0.5	92.02	1.84	90.01	3.60	86.27	8.62
1	94.46	0.94	92.73	1.85	89.18	4.45
2	95.28	0.47	93.72	0.93	91.00	2.27
3	97.33	0.32	95.12	0.63	93.35	1.55
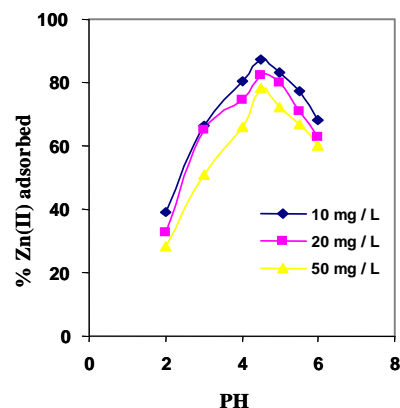
Figure 3 : Effect of pH
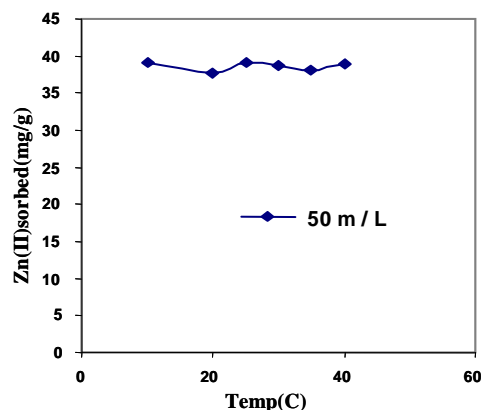
Figure 4 : Effect of temperature

lyzed. The biosorption equilibrium uptake capacity for each sample was calculated according to mass balance on the zinc ions expressed in this equation:

$$q_e = \frac{(C_0 - C_e)}{M} \times V$$

where V is the sample volume (L), C_0 is the initial zinc ion concentration (mg/L), C_e is the equilibrium or final zinc ion concentration (mg/L (, M is the biomass dry weight (g), and q_e is the biomass biosorption equilibrium zinc uptake capacity (mg/g).Langmuir and Freundlich isotherms, the two classical adsorption models, were used to describe the equilibrium between adsorbed zinc ions on the biomass cell (qe,q) and zinc ions in the solution (Ce,q) in this study. Langmuir isotherm model:

$$q_e = \frac{q_{max} C_e b}{1 + C_e b},$$

That after arrange we have;

$$\frac{C_e}{q_e} = \frac{1}{q_{max} \, b} + \frac{C_e}{q_{max}}$$

These values (q_{max} b) can be obtained from the slopes

and the intercepts of the linear plots respectively as shown in Figure 5, where experimental data of Ce/qe as the function of C_e.

The empirical Freundlich equation based on sorption on a heterogeneous surface, on the other hand, is as follows:

$q_e = K_f(C_e)^n$

The equation can be linearized in the following logarithmic form:

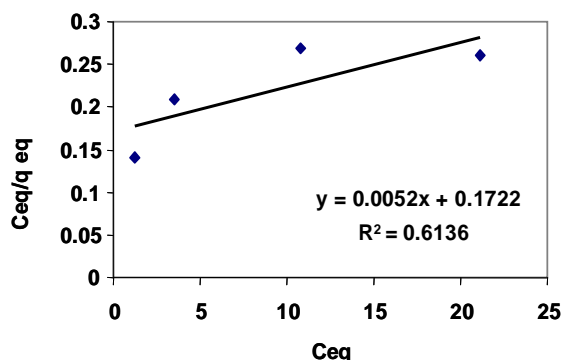$$\ln \ q_e = \ln \ k_f + \frac{1}{n} \ln \ C_e$$
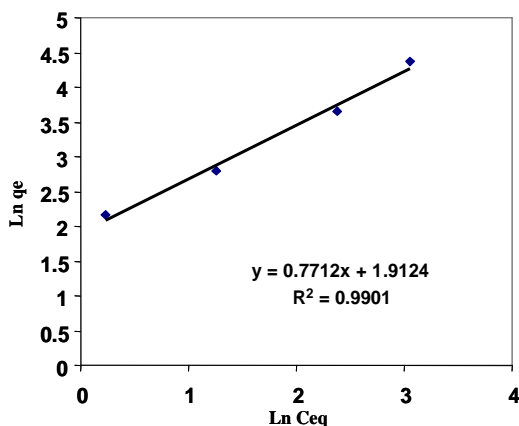
Figure 5 : Langmuir isotherm

Figure 6 : Freundlich isotherm

These values (n & K_f) can be obtained from the slopes and the intercepts of the linear plots respectively as shown in Figure 6, where experimental data of Ln q_e as the function of Ln C_e.

The results of models of isotherm summarized in TABLE 4.

TABLE 4 : Results of isotherm models

Langmuir isotherm			Freundlich isotherm		
$q_{max (mg/g)}$	b(L/mg)	R^2	K_f	n	R^2
192.30	0.030	0.6136	6.77	1.29	0.9901

Kinetic modeling

Figure 7 shows the experimental break through curves for the effects of contact time on a bound rate of Zn (II). It can be observed that the adsorption of zinc ions quickly increased at the beginning of biosorption, but after 15 min, the adsorption slowed down. The result indicated that the maximum adsorbed amount of the zinc ions was achieved within 60-120 min, and then followed by a longer equilibrium period. After this equilibrium period, the amount of adsorbed ions did not significantly change with the adsorption time. Therefore, for the following experiments, the contact time was maintained for 60 min to ensure that equilibrium was fully achieved.

The pseudo-second-order equation is also based on the sorption capacity, which is expressed as:

$$\frac{t}{q_t} = \frac{1}{(K_2 q^2_e)} + \frac{t}{q_e}$$

Where K_2 is the rate constant of pseudo-second-order sorption (g· mg^{-1}·min^{-1}). $K_2 qe^2$ is the initial rate constant (represented by h, mg·g^{-1}·min^{-1}). Plotting t/q_t versus t will give a straight line. The values of qe and K_2 can be determined from the slope and intercept of the plot, respectively. The results showed that the pseudo-second-order model fitted the simulation curve much better than the pseudo-first-order model for Zn (II). The results of pseudo-second-order model showed on the TABLE 5.

TABLE 5 : Results of pseudo-second-order model for 20 mg/L

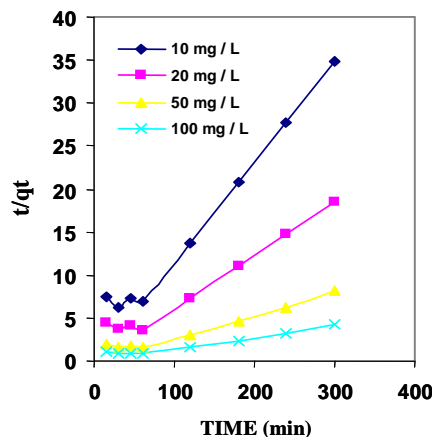| $q_{eq (mg/g)}$	K_2 (g/mg/min)($\times 10^{-3}$)	R^2
18.69	1.58	0.9710

Figure 7 : Pseudo-order kinetic plot

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Equilibrium parameter R_L

The essential characteristics of a Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor or equilibrium parameter R_L, which is defined by

$R_L = 1/1 + bC_o$

Where C_o is the initial adsorbate concentration (mg/L) and b is the Langmuir constant (L/mg). The parameter indicates the shape of the isotherm as follows (TABLE 6):

TABLE 6 : Type of isotherm for various R_L

R_L	$R_L > 1$	$R_L = 1$	$0 < R_L < 1$	$R_L = 0$
Type of isotherm	Un favorable	Linear	Favorable	Irreversible

The R_L values at different initial adsorbate concentrations indicate favorable adsorption for all the adsorbents and adsorbates studied.

Desorption studies

Desorption and regeneration studies of the adsorbates showed that regeneration and recovery of the adsorbates is possible. Chemisorption/ion exchange was the main mechanism by which the adsorbates (metals) were attached to the adsorbents. Physical adsorption played a minimal role in the process .The result of desorption studies of Zn (II) in a batch system showed that HNO_3 (0.1 M) was more efficient in Zn (II) desorption, which remove 95% zinc ions (TABLE 7). Katarzyna et al. (2005) as also reported that HNO_3 (0.1M) was the most efficient desorbent of zinc ions.

TABLE 7 : The desorption efficiency of different desorbent

Desorbent	EDTA (0.1M)	HCL(0.1M)	HNO_3(0.1M)
% Desorption	76	91	94

Infrared spectrum analysis

The FT-IR spectra of biomass before biosorption (Figure 8.) had an adsorption band at a frequency level of 3300 cm^{-1} representing –OH stretching of carboxylic groups. The adsorption band at 2930 cm^{-1} was caused by the stretching of –CH groups. The adsorption peaks at 1660 cm^{-1} could be assigned to vibration of C=O. The adsorption bands at 1515 cm^{-1} and 1040 cm^{-1} were stretching vibrations of C–N and C–O–C of polysaccharides, respectively. The stretching vibra-

tion of –OH, –CH and C–N groups shifted for a certain extent in addition, which indicated that these three groups possibly involved in the biosorption.
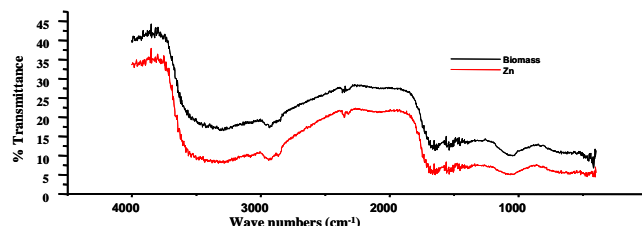

Figure 8 : FTIR spectrum of biomass (before biosorption) and after biosorption

CONCLUSIONS

The batch experiment conducted with the biosorption demonstrated that biomass of Oscillatoria exhibited the potential for Zn (II) removal from aqueous solution. Optimum pH and temperature for biosorption in this study were 1.5 and 25 ºC, respectively. The removal of Zn(II) increase with increase in biosorbent .The biosorption process was followed both Langmuir and Freundlich isotherm model. The pseudo second-order kinetics described the experimental data well. The equilibrium time was between 60-120 min. The R_L values at different initial adsorbate concentrations indicate favorable ($0 < R_L < 1$) adsorption for all the adsorbents and adsorbates studied.HNO_3 (0.1M) had higher efficiency of Zn (II) desorption than EDTA (0.1M) and HCL(0.1M) with 93% efficiency desorption. The stretching vibration of –OH, –CH and C–N groups shifted for a certain extent in addition, which indicated that these three groups possibly involved in the biosorption.

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