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Kinetic and equilibrium study of biosorption of lead from aqueous solutions by cyanobacteria *Fischerellasp*

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ABSTRACT

The main objective of this study was to investigate the characteristics of Pb(II)biosorption bycyanobacteria*Fischerella* sp. The influence of various parameters such as pH, initial metal concentration, initial biomass concentration, contact time and temperature on biosorption was studied in batch experiments. The maximum uptake capacity was found to be 82 mg/g at optimum conditions(pH 6, initial metal concentration 0.2(g/L), initial biomass concentration175(mg/L) at 90 min. Langmuir and Freundlich models were used to describe biosorption isotherm, the experimental data fitted better with the Freundlich model(The correlation coefficient for the Freundlich adsorption isotherm was found to be 0.990). The biosorption followed pseudo second-order-rate kinetics(the correlation coefficient R^2 for the pseudo-second-order model was found to be 0.989). IR analysis indicated that hydroxyl, sulfonic acid and amino groups, are responsible for the biosorption process.

KEYWORDS

Biosorption;
Fischerella sp.*;*
Pb removal;
Heavy metals;
Cyanobacteria.

INTRODUCTION

With rapid industrial development, problems related to pollution are becoming Severe, It adversely affects human life through water resources, agriculture and biological products[1]. Water pollution is one of the most serious problems because inorganic and organic wastes exist in water in the form of soluble and insoluble. Among the inorganic pollutants, heavy metals are the most serious ones because they are non-biodegradable and have the ability to accumulate in living organisms. Lead is considered the most toxic and hazardous reagent (element) to the environment. Lead is currently implemented in industries such as cables, batteries, pigments, paints, steels and alloys, metal, glass, and plastic. Lead has been known for its toxicity for a long time,it poses a great danger for humans, if accumulated in larger amounts. Petrol combustion globally contributes to an estimated 60% of total lead emission[1].

The discharge of these industries environment causes the contamination of the aquatic environment by lea[2]. The removal of heavy metals is considered an important issue with respect to the environment and economical considerations. There are several methods for the removal of heavy metals from aqueous solution including, adsorption on activated carbon, reverse osmosis, ion exchange, chemical pre-

cipitation, and membrane filtration[3].

However, this methods result in the production of harmful by-products. Environmentally friendly processes need to be developed to clean up the environment without creating harmful waste products. The feasibility of economical and technical factors may limit theimplementation of these methods. One of the emerging and attractive technologies to removeheavy metals from aqueous solution is the biosorption process. Various biomasses such as bacteria, yeast, fungi, and algae were investigated as biosorbent for the removal of heavy metals[2].

Cyanobacteria, the photosynthetic prokaryotes are oxygen-evolving organisms that react to stress conditions such as light deprivation[4]. These cells can spontaneously respond to heavy-metals through passive accumulation in cells and through surface binding to various functional groupsCyanobacteria has been shown to have great potential for biosorption of heavy metals[5]. the cell wall of cyanobacteria consists of polysaccharides, proteins, and lipids with charged functional groups such as carboxyl, hydroxyl and amine groups, which are responsible formetal biosorption[6, 7].

Cyanobacteria was chosen as a potential biosorbent to remove Sb(V) from effluents based on its natural abundance and cost-effectiveness. The present study was carried out to evaluate potential cyanobacteria for use in biosorption of Pb, a heavy metal present in effluents from various industries, binding sites involved in the biosorption were also discussed based on the data from attenuated total reflection infrared spectroscopy (ATR-IR).

MATERIALS AND METHODS

Preparation of biomass and metal solutions

In this experimental study, the cyanobacterium *Fischerella* sp. was obtained from the Algal culture collection of research institute of applied science, ACECR, Tehran, Iran. The cyanobacterium was cultured in a 500mL flask containing 150mL of BG-11 medium without being shaked, for 30 days. The incubation temperature was 28°C ± 2 and illumination at 3000 lux with a white continuous light[8]. Stock solution (1000 mg/L) was prepared by dissolving the $Pb(NO_3)_2$ salt (Merck) in deionized water. Working solutions were prepared by diluting the stock solutions to the desired concentrations in deionized water. All chemicals used were of analytical grade.

Biosorption experiments

All biosorption experiments were performed by the batch technique. The experiments wereconducted in 250mL flasks. Biomass was added to Pb(II) solution and then the initial pH was adjusted to required value(2-6) using 0.1M HNO_3 and 0.1 M NaOH.

The effect of contact time, metal ion concentration, adsorbent concentration and temperature were investigated in the batch experiments. The suspension then the mixture was agitated on a magnetic stirrer 100 rpm for 120 min at room temperature. After equilibration, the suspension was filtered through a Whatman paper filter 0.45µm pore-size. The finalPb(II) concentration in the resulting supernatant was determined by flame atomic absorption spectrophotometer (Chem Tech Analytical model CTA2000). Blanks without biosorbent were run simultaneously as control. Amounts of Pb(II) adsorbed by the biomass were calculated using the following equation:

$$q = \frac{V(C_i - Ce)}{M} \quad (1)$$

Where q is the amount of Pb(II) biosorbed by biomass (mg/g); C_i is the initial concentration of Pb(II) (mg/L); C_e is the concentration of Pb(II) (mg/L) at equilibrium; V is the volume of the metal solution(L); and M is the mass of adsorbent (g)[9]. All of the experiments were carried out in thriplets and the experimental results were expressed as mean.

Infrared spectroscopy analysis

Infrared spectra of the original and loaded biomass were performed with a infrared (ATR-IR) spectrometer (BRUKER- VERTEX70). Samples was analyzed in the range of 4000–400 cm^{-1}.

RESULTS AND DISCUSSION

Effect of pH

It has been shown that the affinity of cationic

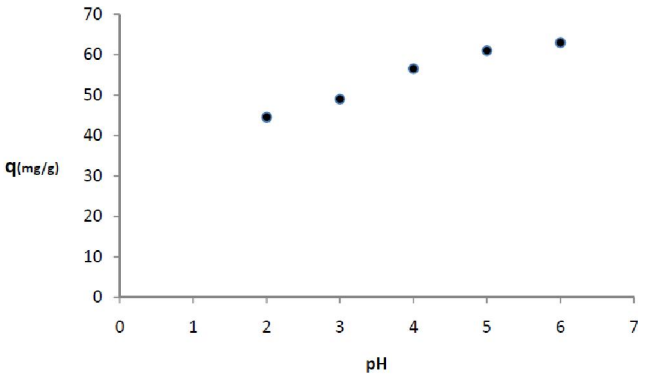

Figure 1 : Effect of pH on Pb(II) biosorption on *Fischerella Sp.* (T=25^{0}C, bacterial dosage=0.5g/L, c_i=75mg/L, contact time=120min)

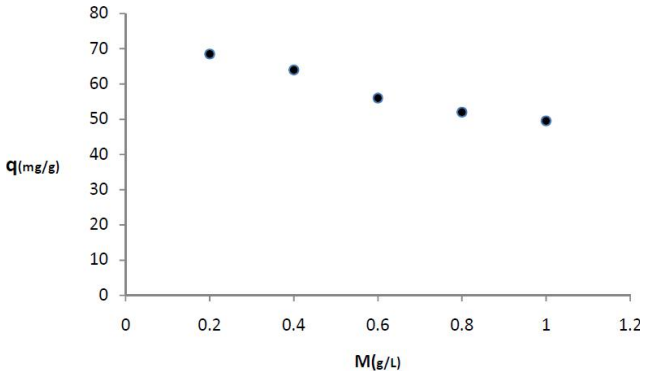

Figure 2 : Effect of bacterial dosage on Pb(II) biosorption on *Fischerella Sp.* (pH=6, T=25^{0}C,c_i=75mg/L, contact time=120min,)

species for the functional groups present on the cellular surface is strongly dependent on the pH of the solution. The effect of pH on the biosorption capacity of Pb(II) bycyanobacteriaas shown in Figure1. It can be seen from Figure1that the biosorpition capacity of Pb(II)by bacteria is very low at low pH values and increases withincreasing pH until reaching an optimum at pH 6.0,This behavior can be explained on the basis of change in the surface charge of the biomass. The maximum negative charge values of both cyanobacteria at the pH of 6.0, which represented the maximum biosorption efficiency of Pb^{2+}. At lower pH, the surface charge of the biomass gets positively charged, so the H^+ ions competes with Pb^{2+} that result in a decrease in q_e value[10]. However, at pH higher than 6.0, the Pb(II) begins to precipitate due to formation of Pb $(OH)_2$. As the pH increases, more ligands, such as carboxyl, phosphate, imidazole, and amino groups, would be exposed and carry negative charges which attract Pb^{2+} and biosorb it onto the cell surface[11].

Effect of biosorbent dosage

Different biomass dosage ranged from 0.2 to 1g/L was applied to study the effect of biomass dose on the biosorption of Pb(II) ions Figure 2. The data revealed that thebiosorption efficiency of Pb(II) ions on *Fischerella Sp.* was significantly affected by the dose of *Fischerella Sp.* in thesolution. It can be seen from Figure 2 that the biosorption of Pb(II) ions was decreased with subsequent increasing in the biosorbent[2]. At a given equilibrium concentration, the lower the biomass concentration the better the efficiency of process[12]. It has been suggested that electrostatic interactions between cells canbe a significant factor in the relationship between biomass concentration and metal sorption. In this connection, at a given metal concentration, the lower the biomass concentration in suspension, the higher will be the metal/ biosorbent ratio and the metal retained by sorbent unit, unless the biomass reaches saturation. High biomass concentrations can exert a shell effect, protecting the active sites from being occupied by metal. The result of this is a lower specific metal uptake, that is, a smaller amount of metal uptake per biomass unit.

Effect of initial Pb(II) concentration

The effect of inlet Pb(II) ion concentration was investigated at the concentration range of 25–225mg/L, at pH 6, and room temperature Figure 3. This fig showed the Pb(II) biosorption capacity(q) increased with increasing of the initial concentration of Pb(II) and then reached a saturation value at 175mg/L of Pb(II) concentration. The initial solute concentration seems to have impact on biosorption, with a higher concentration resulting in a high solute uptake. This is because at lower initial solute concentrations, the ratio of the initial moles of solute to the available surface area is low; subsequently, the fractional sorption becomes independent of the initial concentration. However, at higher concentrations, the sites available for sorption become fewer compared to the moles of solute present and; hence, the removal of solute is strongly dependent upon the initial solute concentration. It is always necessary to identify the maximum saturation potential of a

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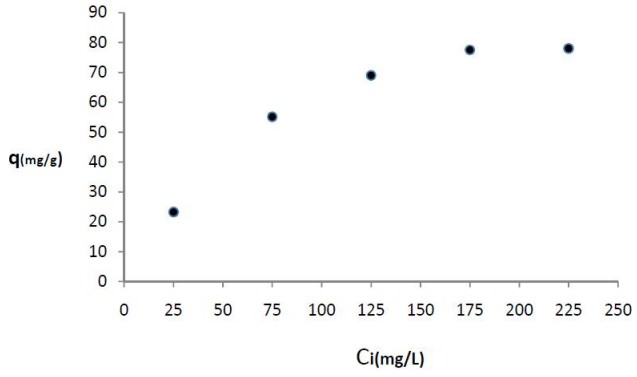

Figure 3 : Effect of initial concenteration of metal on Pb(II) biosorption on *Fischerella Sp.* (pH=6, T=25^{0}C, bacterial dosage=0.2g/L, contact time=120min)

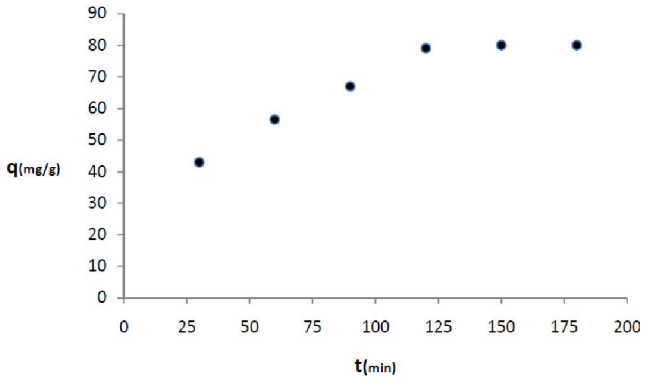

Figure 4 : Effect of contact time on Pb(II) biosorption on *Fischerella Sp.* (pH=6, T=25^{0}C,bacterial dosage=0.2g/ L,C_i=175mg/L)

TABLE 1 : Effect of temperature

T (^{0}C)	q(mg/g)
25	82.5
30	89
40	98

biosorbent, for which experiments should be conducted at the highest possible initial solute concentration[13].

Effect ofcontact time

The optimum time was carried out at optimum pH by conducting batch biosorption experiments with an initial metals ions concentration of 150 mg/L, 0.2g/ L biosorbent dosageroom temperatureat different time periods 30, 60, 90, 120,150,180 min). Figure 4 showed the effect of contact time on the biosorption of Pb(II) ions using the *Fischerella Sp.* These results indicated that the biosorption of metal was rapid in the first 30 min then was gradually increased till the equilibrium attained at 90 min,and the biosorption became almost constant thereafter. Therefore, a contact time 90 min was used as the optimum time for the rest of experiments.

Effect of temperature

TABLE 1 show that the biosorption capacity (*q*) increased with the temperature increasing. Temperature seems to affect biosorption only to a lesser extent within the range from 20 to 40°C. Higher temperatures usually enhance sorption due to the increased surface activity and kinetic energy of the solute. However, physical damage to the biosorbent can be expected at higher temperatures[13].

Kinetic experiments

Kinetics of biosorption is one of the most important characteristics to describe the solute sorption rate which in turn controls the residence time of biomass sorption at the solid–solution interface based on sorption capacity[14]. Three models are used to determine the data to examine the mechanism of adsorption process. and chemical reaction. The pseudo-ûrst-order Lagergren model which considers that the rate of occupation of biosorption sites is proportional to the number of unoccupied sites:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \quad (2)$$

Integrating Eq. (2) between limits, q_t =0 at t= 0 and q_t = q_t at t=t. (2)is obtainedt

$$\log\left[\frac{q_e}{q_e - q_t}\right] = \frac{k_1}{2.303}t \quad (3)$$

Eq. (3) can be rearranged to obtain a linear form:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t \quad (4)$$

Where $q_e$and q_t are the amounts of adsorbed Pb(II) ions on the biosorbent at equilibrium and at time t (mg/g), respectively,and k_1 is the equilibrium rate constant of pseudo-ûrst-order adsorption (1/ min)[15]. The slopes and intercepts of plot of log(q_e - q_t) versus *t* were used to obtain the first-order rate

TABLE 2 : Kinetic models for biosorption of Pb (II)

Pseudo-first-order			pseudo-second order		
$q_{e(mg/g)}$	$k_{1(1/min)}$	R^2	$q_{e\ (mg/g)}$	$k_{2(g/mg\ min)}$	R^2
147	0.034	0.863	106.38	1.9×10^{-4}	0.989

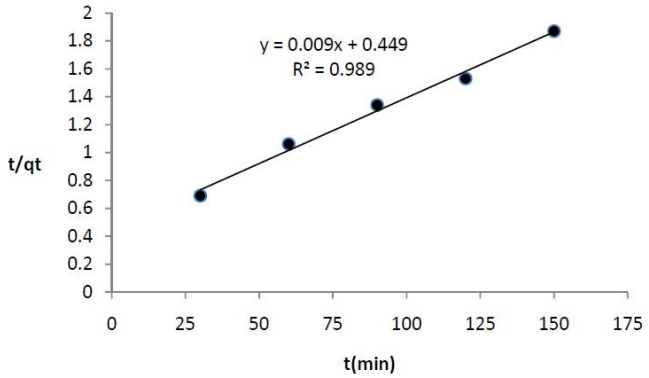

Figure 5 : Plot of the pseudo-second-order equation for the biosorption kinetics of Pb(II) on *Fischerella Sp.* (pH=6, T=25⁰C, bacterial dosage= 0.2g/L, C_i=175mg/L)

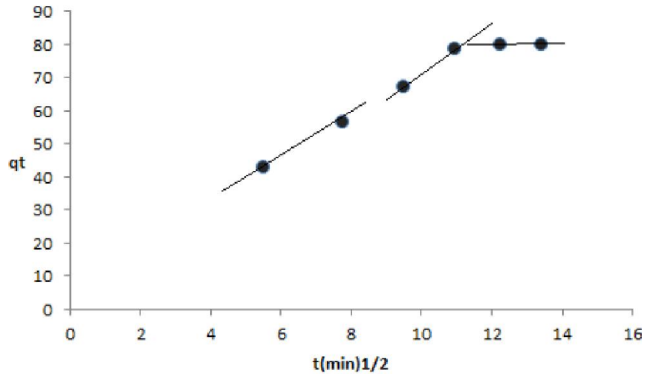

Figure 6 : Plot of the intraparticle diffusion (Weber–Morris model) for the biosorption kinetics of Pb(II) on *Fischerella Sp.* (pH=6, T=25⁰C, bacterial dosage=0.2g/ L, C_i=175 mg/L)

constant k_1 and equilibrium adsorption density q_e. The adsorption kinetics may also be described by pseudo- second-order model. Pseudo second-order model:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \qquad (5)$$

Integrating between boundary conditions, Eq. (5) is obtained:

$$\frac{1}{q_e - q_t} = \frac{1}{q_e} + k_2 t \qquad (6)$$

Eq. (6)can be rearranged to obtain a linear form:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^{\ 2}} + \frac{1}{q_e} t \qquad (7)$$

Where k_2 is the equilibrium rate constant of pseudo-second-order adsorption (g/mgmin)[15]. The slope and intercept of plot t/q_t versus t were used to calculate the second-order rate onstants k_2 and q_e. The straight lines obtained from plot of t/q_tversus t showed good ûtness of experimental data with the first-second kinetic model show in Fig5. As can be seen from TABLE 2, the correlation coefûcient R^2 for the pseudo-ûrst-order and pseudo-second-order model was found to be 0.863 and 0.989 respectively. The amounts of adsorbed Pb(II) on the biosorbent at equilibrium q_{ecal} by first and second order model were147 and 106.3 (mg/g) respectively. Experimental value of q_{ex} was 80(mg/g) at the optimum conditions, therefore pseudo-second -order model have a good agreement with the experimental data.

Other technique used for identifying the mechanism involved in the adsorption process is by fitting the experimental data in an intraparticle diffusion plot. Intraparticle diffusion model used here refers to the theory proposed by Weber and Morris can be used to assess this opinion:

$$q = f\left(\frac{Dt}{r_p^2}\right)^{\frac{1}{2}} = k_i t^{\frac{1}{2}} \qquad (8)$$

Where r_p is particle radius, D is the effective diffusivity of solutes within the particle, q_t(mg/g) is the adsorbed metal ion amount at any time and K_i intraparticle rate constant (mg/g $min^{1/2}$). The slope of plot q versus $t^{1/2}$ obtained k_i was 5.013(mg/g $min^{1/2}$) in optimum conditions. It was observed that the biosorbedPb(II) amounts by*Fischerella Sp.*have a multi-linearity that two steps occur (Fig 6). The first, sharper portion is the external surface adsorption or instantaneous adsorption stage. The second portion is the gradual adsorption stage, where the intraparticle diffusion is rate-controlled, it is final equilibrium stage where the intraparticle diffusion starts to slow down due to extremely low solute concentrations in the solution[16].

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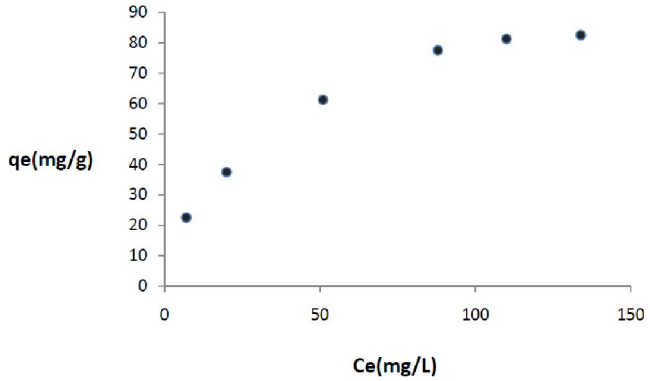


Figure 7 : Isotherm of Pb(II) biosorption on *Fischerella Sp.* (pH=6, T=25^{0}C, bacterial dosage=0.2g/L, contact time =70min)

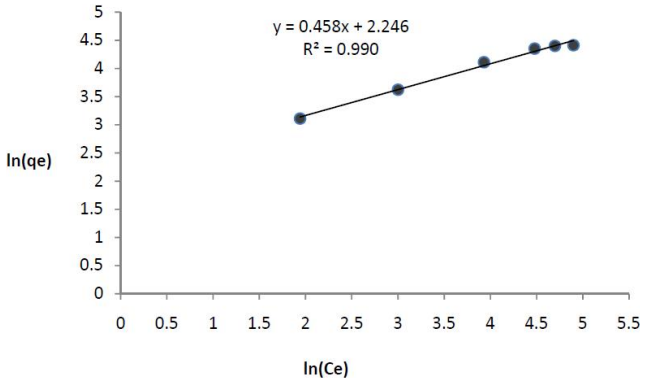
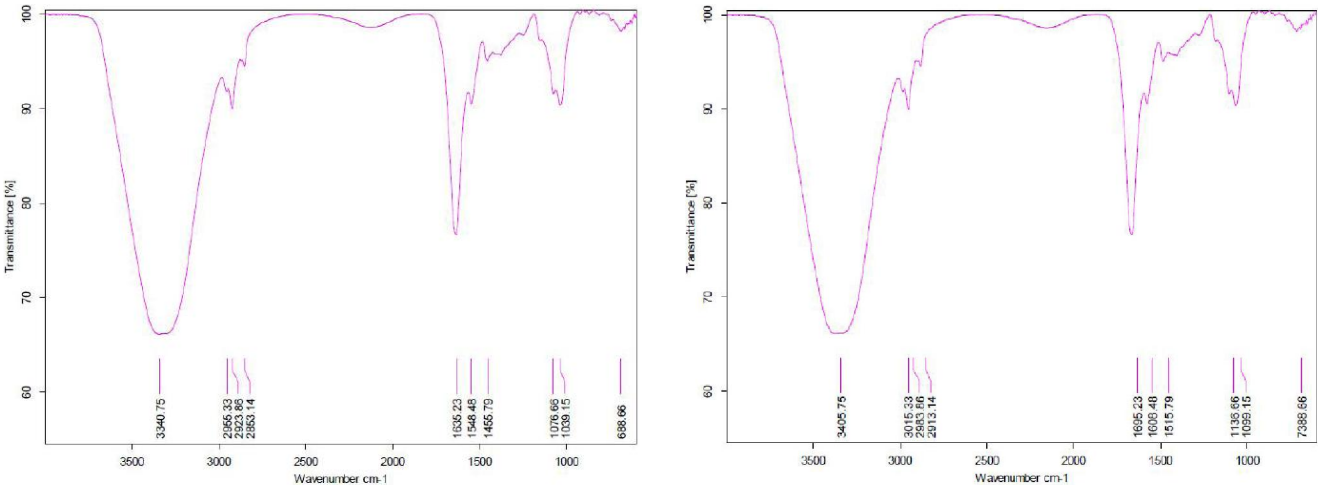


Figure 8 : FreundlichIsotherm of Pb(II) biosorption on *Fischerella Sp.* (pH=6, T=25^{0}C, bacterial dosage=0.2g/L, contact time =70min)

TABLE 3 : Equilibrium models for biosorption of Pb(II)

Freundlich			Langmuir		
k_f	n	R^2	q_{max}(mg/g)	$b_{(mg/g)}$	R^2
9.45	2.18	0.990	102.04	0.033	0.994



a b

Figure 9 : The IR spectra of *Fischerella Sp.* (a) before adsorption (b) afteradsorption

Biosorption isotherm

Isotherms were measured by varying the equilibrium metal ion concentrationsat the optimum conditions for each metal. The biosorption isotherm forPb(II) onto *Fischerella Sp.* biosorbent isshown in Figure 7,It can be seen that q_e increase with increase the C_e in the beginning but then constant. The biosorption isotherm models described the biosorptiondata at equilibrium and showed the correlation between themass of solute adsorbed per unit mass of sorbent at equilibrium[2].

Differentbiosorption models were used for comparison withexperimental data. Langmuir and Freundlich isotherm equations were used to describe the equilibrium state for metal ions adsorption expriments. The Freundlich isotherm is a nonlinear sorption model. This model proposes a monolayer sorption with a heterogeneous energetic distribution of active sites, accompanied by interactions between adsorbed molecules[17]. The general form of this model is:

$$q_e = k_f . c_e^{1/n} \quad (9)$$

WhereK_F (mg/g) and *n* the Freundlich constants. The logarithmic form of Eq. (9) is:

TABLE 4 : The IR spectral characteristics of *Fischerella Sp.* before and after biosorption

Absorption bands (cm^{-1}) functional groups			
Before adsorption	**After**	**Differences**	
688	738	50	N containingbioligands
1076	1136	60	SO_3 group
1635	1695	60	C=O group
2923	2983	60	CH_2,CH_3 groups
3340	3405	65	OH and NH_2groups

TABLE 5 : Comparison of biosorption maximum capacity of Pb(II) on *Fischerella Sp.*and other biosorbents

Biosorbents	Ph	T(^{0}c)	Q_{max}(mg/g)	Reference
Chondracanthus chamissoi(alga)	4	25	283	[17]
Enterobacter sp. J1(alga)	6	25	50	[18]
Cladophora spp. (alga)	5	25	46.51	[19]
tobacco (dustcultural waste)	7	25	39.6	[20]
cork wastes(dustcultural waste)	5	25	13.46	[21]
Bacillus cereus(bacteria)	6	25	22.1	[8]
Bacillus pumilus(bacteria)	6	25	28.06	[8]
Fischerella Sp. (cyanobacteria)	6	25	82	This study

$$\log q_e = \log K_F + 1/n \log C_e \quad (10)$$

Where, intercept log(K_F), and the slope *1/n*. The Langmuir model represents one of the first theoretical treatments of nonlinear sorption and suggests that uptake occurs on a homogeneous surface by monolayer sorption without interaction between adsorbed molecules. In addition, the model assumes uniform energies of adsorption onto the surface and no transmigration of the adsorbate[18]. The general Langmuir equation is commonly presented as:

$$q_e = \frac{q_{max} b c_e}{1 + b c_e} \quad (11)$$

And the equation may be linearized as follow:

$$\frac{c_e}{q_e} = \frac{1}{q_{max} b} + \frac{c_e}{q_{max}} \quad (12)$$

Where $q_e$is the amount of metal ion removed (mg/g),$C_e$is the equilibrium concentration (mg/L), *b* the Langmuir constant related to aûnity,and q_{max} is the maximum metal uptake under the given conditions, the Freundlich and Langmuir constants, along with the regression coeûcients have been calculated from the corresponding plots. *k* and *n*,the Freundlich constants, are related to the sorption capacity and the sorption intensity, respectively[17]. nvalue greater than 1.0 shows that the sorption is favourable physical process[19]. The correlation coefûcient for the Freundlich and Langmuir adsorption isotherm was found to be 0.990 and 0.994 respectively, R^2 values, was same for two model,but q_{max} Langmuir havn·t good agreement with the experimental data(q_{max}82.5). Hence, it was concluded that the data to ût better with Freundlich model show in TABLE 3. Figure 8 show FreundlichIsotherm of Pb(II) biosorption on *Fischerella Sp.*

Infrared(ATR-IR) spectroscopy analysis

In order to understand better the nature of the functional groups responsible for the biosorption, ATR-IR analysis of the biomass *Fischerella Sp.*was carried out. The ATR-IR spectra Compared before and after adsorption of the Pb(II) are shown in Fig 9 (a,b), there were clear band shifts and intensity changed at bands.

The spectrum of raw biomass exhibits a broad absorption bandbetween 3400 and 3200 cm^{-1} stretching vibration, due to bonded –OH and NH_2 indicating represent of hydroxyl and amino groups,alkyl chains(methylene group –CH_2 and methyl group–CH_3) have a band within the range of 2923–2853 cm^{-1},the C=O stretching vibration of the carboxylic groups appears strongly at 1637.04 cm^{-1}. The bands at 1100 cm^{-1} that represent SO_3 stretching, mainly present in sulfonic acids of polysaccharides, such

as fucoidan. Wave numbers 688 cm^{-1} appeared as a peak and this could be attributed to an interaction between lead(II) ions and N containing bioligands.

TABLE 4 show that the functional groups of *Fischerella Sp.*participate in Pb(II) biosorption, and wavenumber of functional groups shifted.

Comparison with other biosorbents

TABLE 5 compares the maximum adsorption capacities obtained in this study with some other results reported in the literature. The value of Pb(II) uptake by *Fischerella Sp.* found in this work is comparable with other biosorbents.

CONCLUSION

Biosorption properties of *Fischerella Sp*were studied as a function of pH, initial Pb(II) concentration,bacterial dosage, contact time and temperature. Maximumbiosorption capacitiywas 82(mg/g) at the optimum conditions. IR analysis indicated that participation of COOH, OH,SO_3, CH_2,CH_3,and NH2 groups in the biosorption process. The batchexperimental results fitted well to Freundlich model model. Thebiosorption followed pseudo second-order-rate kinetics. Biosorption capacity of this sorbent is comparable with other biosorbent

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