The Potential of *Coriandrum Sativum L.* Seeds in the Remediation of Waste Water

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Abstract

The present work aims to investigate the potential of Coriandrum sativum L. seed as a low-cost bio-sorbent for the removal of Zn (II) ions from aqueous medium. It is available as a major waste in food flavoring industries including bakery and confectionery as well as laboratories of traditional medicines. Adsorption of Zn (II) on to Coriandrum sativum L. seed has been investigated after optimizing the experimental parameters, namely, pH, contact time, adsorbent and Zn(II) concentrations and temperature. The characterization was done with Fourier transform infra red spectroscopy for examining the possible interacting sites of the adsorbent. Important isotherm models, namely Langmuir, Freundlich and Dubinin--Radushkevich models have been studied. The spontaneous nature of adsorption is indicated by the observed thermodynamic parameters. The adsorption process was found to follow pseudo-first order kinetic model and also followed the intraparticle diffusion up to 50 minutes of contact time. It was found to retain 98% of the sorption capacity up to 3 cycles of adsorption and elution. Hence, the proposed method offers a very simple, low cost, effective and eco-friendly alternative methodology for waste valorization and extraction of metal ions from wastewater.

Keywords: *green technology, agricultural by-products, isotherm models, adsorption*

1. Introduction

The environment and public health have been put to high risk by the ever increasing pollution of water resources caused by the heavy metals. Heavy metals get introduced into the water resources through discharge from various industries, such as metal plating, tanneries, smelting, alloy industries, storage batteries industries *etc*. As a consequence of the introduction of toxic metal ions into the natural ecosystem, their bioaccumulation in human bodies, and other living beings, takes place through either direct intake or food chains. Hence, their removal from natural resources has become a major concern (Meena *et al.*, 2008). Oyaro *et al.*, (2007) reported that excessive zinc consumption may cause different health problems, such as nausea, anemia, skin irritations, vomiting and stomach cramps.

Among the various water treatment technologies, namely coagulation, filtration, ion exchange, solvent extraction, electrolysis, microbial reduction and activated sludge, foam flotation *etc.*, adsorption is favorable in terms of convenience, ease of operation and simplicity of design (Kumar 2006). Again, Ahmad *et al.*, (2013) used expensive resins and/or polymeric extractant of metals which is gradually giving way to the use of agricultural waste as low cost adsorbents. A promising and effective process in the removal of heavy metal pollutant is offered by biosorption. Kumar (2006) also reported

that the low-cost non-living biomasses, such as potato peels, sawdust, eggshell, seed shells etc., have been investigated as potential biosorbents for heavy metals.

As discussed by Handa *et al.*, (2008), used/spent coriander (*Coriandrum sativum L.*) seeds are a major waste in food flavoring industries including bakery and confectionery as well as laboratories of traditional medicine. The *Coriandrum sativum L.* (coriander) plant is an annual herb that belongs to the botanical family of Apiaceae. Seeds of *Coriandrum sativum L* are rich in polyphenols. Its major component is (+)-linalool (coriandrol). However, the minor chemical constituents are monoterpene hydrocarbons, heterocyclic compounds, Isocoumacin, Phthalides, Phenolic acids and sterols (Bhat et al. 2014). This plant is cheap and grows in abundance in almost all the countries. Its biodegradable nature makes it eco-friendly and promises to open new avenues for green technology.

The present work aims to investigate the potential of *Coriandrum sativum L.* seed as a low-cost bio-sorbent for the removal of zinc (II) ions from aqueous medium. A study of adsorption kinetics and equilibrium isotherms has been carried out so as to get an insight into the adsorption behaviour, thereby making the adsorption mechanism more intelligible for the theoretical evaluation and interpretation of thermodynamic parameters. The adsorption capacity was determined through various kinetic models. The experimental parameters namely amount of adsorbent, concentration of metal ions, temperature and pH have been optimized for efficient removal of the metal ion.

2. Material and Methods

2.1. Instruments and Equipments

The concentration of Zn (II) was determined by Flame atomic absorption spectrometry (Agilent, USA). The pH measurements were carried out with a pH meter (Bellstone, India). A mechanical shaker of 200 rpm (Bellstone, India) was used for the equilibrium studies. The FT-IR analysis (Omnic, USA) was done for characterization. Heating oven (Bellstone, India) was used for drying. A stainless steel grinder was used for reducing the adsorbent to powder. ASTM standard sieves were used for separating particles of the desired size.

2.2. Preparation of Reagents and Adsorbent

All reagents were of analytical grade. The Zn (II) solution was prepared in de-ionised water. The *Coriandrum sativum L.* seeds were procured from the local market, in Jazan. It was extensively washed with de-ionised water and then left overnight in the oven for drying at a constant temperature of 80°C until a constant weight is observed. The dried adsorbent was crushed and then subjected to filtering through sieve for acquiring particle size of 300μm.

2.3. Batch Method for Adsorption Studies

The required amount of an accurately weighed adsorbent was allowed to equilibrate in contact with a suitable volume of the Zn (II) solution of appropriate concentration. The mixture was maintained at a constant pH with the appropriate buffer solution for optimum time with constant shaking. Then the mixture is subjected to filtration to separate out the filtrate, from the adsorbent, for determining the concentration of the filtrate with FAAS.

3. Results and Discussions

3.1. Characterization of the Adsorbent (Coriander Seeds)

3.1.1. FT-IR Analysis: In order to investigate the nature of the interaction between the target metal ion and the adsorbent, a comparative study was done on the FTIR spectra of the loaded and unloaded adsorbent (Figures 1, 2). The relative decrease in the intensities of the broad band at 3710-3902 cm^{-1}, corresponding to ν (NH) and ν (OH), in the spectrum of the metal laden adsorbent is indicative of their possible involvement in the sorption process. Besides the carbonyl stretching band of unionized carboxylates, that was observed at 1748 cm^{-1}, for the unloaded sorbent underwent red shift of $\nu(CO)$ by 102 cm^{-1} in the metal loaded adsorbent, thereby reflecting the participation of CO group in the process of the retention of metal. The band at 2919 cm^{-1}, which may correspond to the combined effect of double bond stretching vibration and NH deformation band, undergoes a shift to 2361 cm^{-1} due to the possible role in metal retention (Kuyucak and Volesky 1989). The appearance of a band at 3390 cm^{-1} in the metal loaded adsorbent represents the shift of ν (NH) after metal retention. Moreover, the disappearance of the band at 1144 cm^{-1} representing the $\nu(C-O)$ and the bending vibration of OH in the spectrum of the metal-loaded adsorbent indicates their role in metal binding.
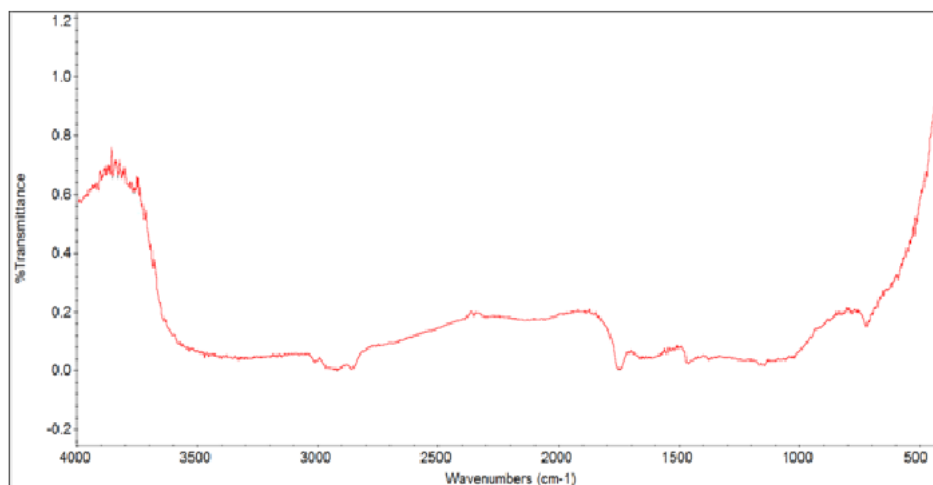

Figure 1. FT-IR Spectrum for Unloaded *Coriandrum Sativum L.* Seed

3.1.2 Hydrogen Capacity and Water Regain Capacity: The movement of the metal ion phase is facilitated by the presence of interstitial and/or trapped aqueous phase in the biomass. The water regain capacity would indicate the hydrophilicity of the biomass (coriander seeds). Water regain capacity may be defined as the amount of water absorbed by 1.0 g of the biomass (Islam *et al.*, 2011). An amount of 2.0 g of dried ground coriander seeds was allowed to soak in doubly distilled water for 48 h, and then filtered by suction. The collected residue of biomass on the filter is then allowed to dry in air and weighed. The air-dried biomass is then dried overnight at 80° C and then the constant weight is noted.
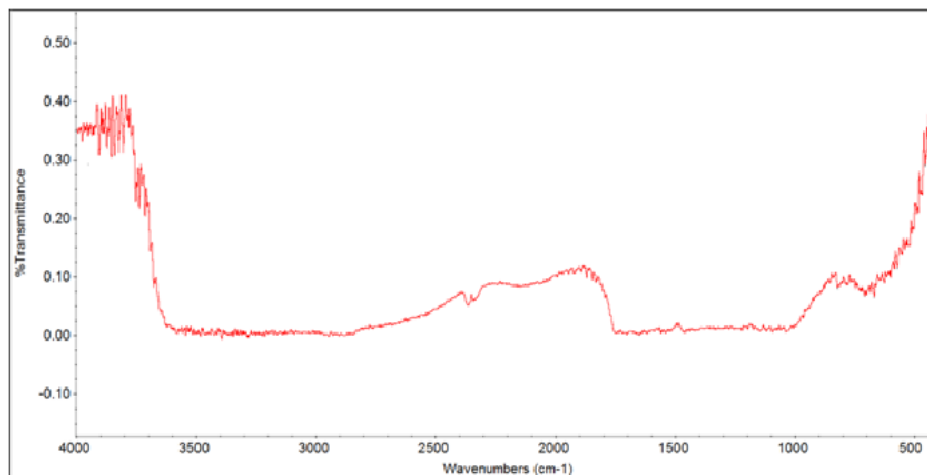
Figure 2. FT-IR Spectrum for Loaded *Coriandrum Sativum L.* Seed

The water regain value was calculated, as discussed by Islam *et al.*, (2011):

$$W = (m_w - m_d)/m_d, \tag{1}$$

Where m_w is the weight of the air-dried polymer after filtration by suction and m_d is the weight of the resin after drying at 100°C overnight. The water regain capacity was found to be 4.9 mmol g^{-1}.

For overall hydrogen ion capacity, an accurately weighed (1.0 g) of dried ground coriander seeds was added to 4.0 M HCl contained in a beaker. After filtering the acid-treated biomass, it was then washed with distilled water until there was no leaching of free acid and subsequently dried at 60°C for 3 h. The acidified biomass was then allowed to reach equilibrium (with constant stirring) with a specific volume of 0.1 M NaOH solution at room temperature. The excess alkali is then titrated against 0.1 M HCl. The overall hydrogen ion capacity was found to be 0.853 mmol /g.

3.1.3 Chemical Stability: Several portions of fixed amount of the dried ground biomass was allowed to soak separately in 2 to 4 M of HCl/HNO$_3$/H$_2$SO$_4$ and 2 to 4 M of NaOH for 30 min (with constant stirring) and then subjected to loading and elution cycle (after washing and drying). It was found that there was no loss in the sorption capacity upto 3 M of mineral acid and 4 M of NaOH. However, about 8% loss in sorption capacity was observed with the samples which were soaked in acids of >3 M and base (NaOH) of >5 M. Hence, it may be concluded that there is no degeneration of the biomass in moderately strong acidic and/or alkaline medium.

3.2. Effect of Contact Time

From the plot of amount of Zn (II) retained versus the equilibration time (Figure 3), it may be noted that a constant adsorption capacity of 8.14 mg g^{-1} was observed after a contact time of 50 min, thereby giving the maximum saturation limit of the adsorbent.

3.3. Effect of pH on Removal of Heavy Metal

Since there is always a competition offered by the hydrogen ions, the consideration of pH of the medium is very important. Hence, the plot of amount of adsorbed Zn (II) versus pH (Figure 4) indicates very low retention at pH 1-3, thereafter a steep rise in the adsorption takes place up to pH 5.0. At pH > 3, the positively charged metal ion dominates over the available H$_3$O$^+$ ions and thus
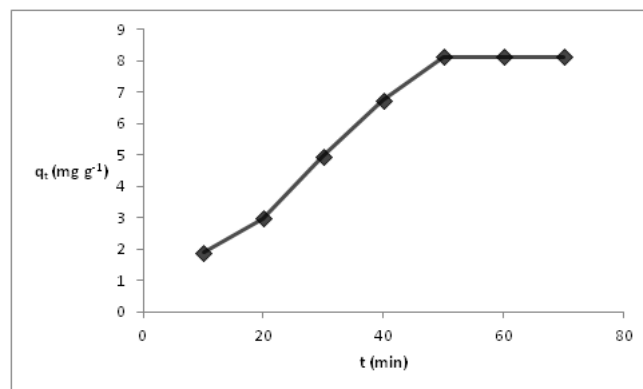
Figure 3. Effect of Time on the Adsorption Capacity of the Adsorbent

more negatively charged metal binding sites are available for binding with metal. Again a decline in the adsorption of metal was observed after pH 5.0, which may be attributed to the deterioration of metal binding sites (Puranik and Paknikar 1997; Gadd 1988).
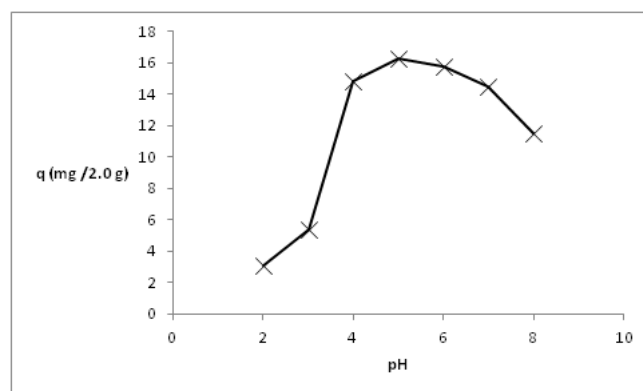

Figure 4. Effect of pH on the Adsorption of Zn (II)

3.4. Effect of Temperature on the Uptake of Metal

The absorption of Zn(II) on to *Coriandrum sativum L.* seed is favored at higher temperature which indicates the involvement of some chemical interactive forces. An increase in the temperature from 20-50°C results in the increase in the adsorption capacity from 0.43 mmol g^{-1} to 0.59 mmolg^{-1} within a contact time of 50 min. Below equilibrium time, a kinetically controlled adsorption is reflected by the fact that with the increase in temperature the adsorption increased. The adsorption trend observed after the equilibrium time suggest the availability of more binding sites at higher temperature that leads to higher adsorption.

3.5. Effect of Initial Concentration and Adsorbent Mass

In the batch equilibration method, the initial concentration of metal ions is an important factor as it offers the driving force for overcoming the mass transfer resistance of metal ions between the aqueous and the solid phase. Therefore, as expected, the amount of retained metal ions increased with increasing initial metal ion concentration. With the increase in the amount of the adsorbent, the uptake of Zn (II) from the solution increased from 5.00 to 8.14 mg g^{-1} (Figure 5), because of the availability of more binding sites.
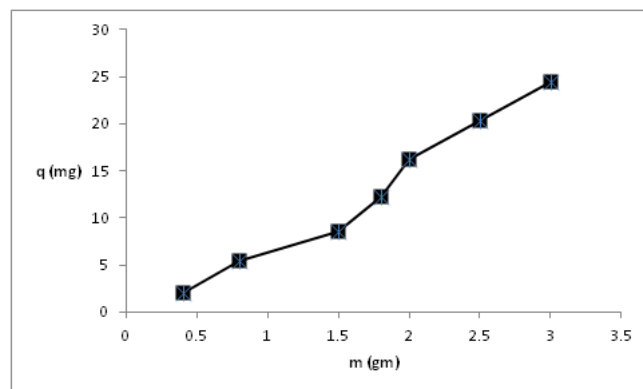
Figure 5. Effect of Amount of Adsorbent on the Adsorption of Zn (II)

3.6. Adsorption Isotherm Studies

Equilibrium isotherms give an insight into some of the important characteristics of the adsorption system. Therefore, three important isotherm models, namely Langmuir, Freundlich and Dubinin-Radushkevich isotherms have been studied at 20-50 °C (Langmuir 1918; Freundlich 1906; Dubinin and Radushkevich 1947).

The Langmuir isotherm may be reproduced as follows:

$$\frac{1}{q_e} = \frac{1}{q_{max}} + \left(\frac{1}{q_{max}K_L}\right)\frac{1}{C_e}, \tag{2}$$

where q_e is the equilibrium Zn(II) concentration on the adsorbent (mol g^{-1}); C_e, the equilibrium Zn(II) concentration in the solution (mol dm^{-3}); q_{max}, the monolayer adsorption capacity of the adsorbent (mol g^{-1}); and K_L, the Langmuir adsorption constant (dm^{-3} mol^{-1}) related to the free energy of adsorption. The separation factor, R_L is calculated using the following equation:

$$R_L = \frac{1}{1+K_L C_o}, \tag{3}$$

While Freundlich isotherm is represented by:

$$\ln q_e = \ln K_F + \frac{1}{n}\ln C_e, \tag{4}$$

Where K_F and n are Freunlich adsorption isotherm constants (dm^3 g^{-1}) and Dubinin-Radushkevich isotherms is represented by:

$$\ln q_e = \ln q_m - \beta\varepsilon^2, \tag{5}$$

where β is a constant related to the mean free energy of adsorption per mole of the adsorbate (mol^2 J^{-2}); q_m, the theoretical saturation capacity, and ε is the Polanyi potential, which is equal to:

$$RT \ln\{1+ (1/C_e)\}, \tag{6}$$

where R (J mol^{-1} K^{-1}) is the gas constant; and T (K), the absolute temperature. The constant β gives an idea about the free energy E (kJ mol^{-1}) of adsorption per molecule of the adsorbate when it is transferred to the surface of the solid from infinity in the solution and can be calculated using the relationship:

$$E = \frac{1}{(2\beta)^{1/2}}, \tag{7}$$

As illustrated in Table 1 and 2, the surface of the adsorbent is composed of both homogeneous as well as heterogeneous adsorption patches since all the isotherm models are befitting. As the experimental data fits well with Langmuir isotherm, it may be inferred that the distribution of the active sites (for binding with the metal) is homogeneous. Moreover, the value of R_L, which is between 0 and 1, indicates the favorable nature of the adsorbents for the sorption of metal ions. The befitting nature may also suggest the involvement of an ion exchange mechanism in the retention of the metal (Yasemin and Zeki 2007). However, since the value of $1/n$ is above one, therefore, the sorption follows both Langmuir and Freundlich isotherm (Haghseresht and Lu 1998). As Freundlich isotherm also fits well with the experimental data, it may be suggested that complexation reaction may also be one of the contributing mechanism for sorption (Yasemin and Zeki 2007). Considering the chemical composition of the adsorbent (coriander), it may be speculated that phthalides, phenolic acids, coriandrol and sterols may be the probable contributing sites for ion exchange and complexation reactions. The magnitude of E (Table 2) reflects the nature of adsorption process as physical (Helfferch 1962).

Table 1. Values of Langmuir Isotherms Constants for the Adsorption of Zn (II) at Various Temperatures

t (°C)	q_{max}(mol g^{-1})	K_L (dm^3 mol^{-1})	r_L^2	R_L
20	4.35 x 10^{-4}	19.64	0.98	0.83
30	5.03 x 10^{-4}	13.74	0.97	0.88
40	5.34 x 10^{-4}	9.49	0.99	0.92
50	5.95 x 10^{-4}	4.48	0.98	0.96

Table 2. Values of Freundlich and Dubinin-Radushkevichisotherm Constants

Freundlich		Dubinin-Radushkevich	
n	0.95	β (mol^2 kJ^{-2})	-0.83
K_F (dm^3 g^{-1})	5.97 x 10^{-3}	E(kJmol^{-1})	0.77
r_F^2	0.99	r_{D-R}^2	0.99

3.7. Kinetics Studies

The appropriate rate expressions, that may represent the adsorption process, may be investigated for supporting the possible reaction mechanisms (Jadhav and Vanjara 2004). Hence, three kinetic models namely, pseudo-first-order equation given as:

$$\frac{1}{q_t} = \frac{1}{q_1} + \frac{k_1}{q_1 t}, \tag{8}$$

where q_1 and q_t are the amounts of the Zn(II) ions adsorbed at equilibrium and at time t (mg g^{-1}) and k_1 is the pseudo-first-order rate constant (min^{-1}) of adsorption, pseudo-second order equation given as:

$$\frac{t}{q_t} = \frac{1}{k_2 q_2^2} + \frac{1}{q_2} t, \tag{9}$$

where q_2 is the maximum adsorption capacity (mg g^{-1}) for the pseudo-second-order adsorption; q_t, the amount of Zn(II) ions adsorbed at equilibrium at time t(mg g^{-1});k_2, the

equilibrium rate constant of pseudo-second-order adsorption (g mg^{-1} min^{-1}) and intraparticle diffusion (Figure 9) represented by:

$$q_t = k_p t^{1/2} + C, \tag{10}$$

where C is the intercept and k$_p$, the intraparticle diffusion rate constant (mg g^{-1} min$^{-1/2}$) have been studied.

From the kinetic parameters obtained (Table 3), it may be inferred that pseudo-first order model (Figure 6) may be one of the routes for the adsorption of Zn(II) as suggested by the value of the correlation coefficients, which is greater than 0.97. Although, the correlation coefficients for the intraparticle diffusion model are lower than that of the pseudo-first-order kinetic model, however the former model suggests that the adsorption of Zn (II) may be partially controlled by intraparticle diffusion, at least up to 50 min of contact time (Figure 7).
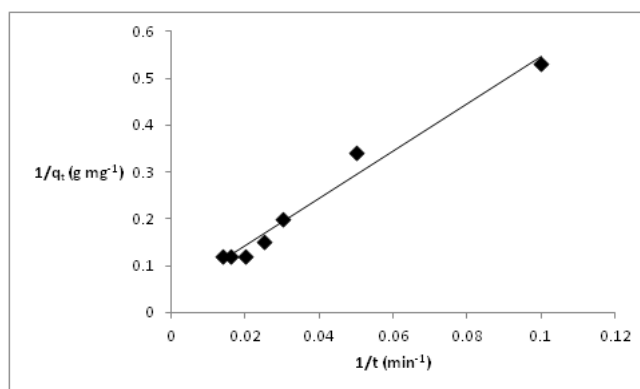

Figure 6. Pseudo-first-order Kinetic Plot for the Adsorption of Zn (II)

The linear portion, corresponding to the bulk diffusion, may be due to intraparticle diffusion process while the plateau may be due to the attained equilibrium. Such dual nature may indicate that the movement of the heavy metal ion, through the particle-solution interface, into the pores of the particle takes place collectively with the adsorption on the available surface of the adsorbent (coriander). Since, the linear portion does not pass through the origin therefore it is not the rate limiting step (Crank 1965). The intercept, which is greater than zero, is proportional to the thickness of the boundary layer effect (Mckay 1980).
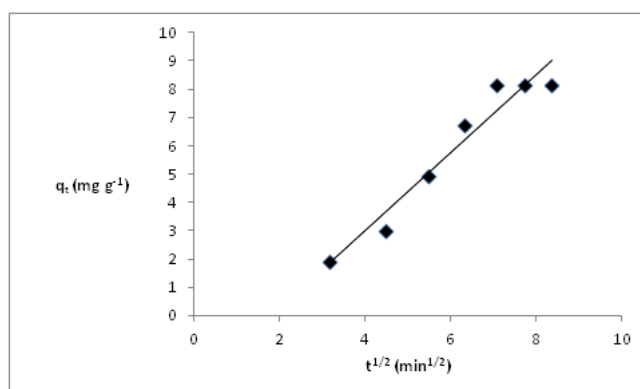

Figure 7. Intraparticle Diffusion Plot for the Adsorption of Zn (II)

Table 3. Kinetic Parameters for the Adsorption of Zn (II)

$k_1 (min^{-1})$	120.42
$q_1 (mg\ g^{-1})$	23.86
r_1^2	0.97
$k_2 (g\ mg^{-1}\ min^{-1})$	3045.04
$q_2 (mg\ g^{-1})$	24.75
r_2^2	0.63
$k_p (mg\ g^{-1}\ min^{-1/2})$	1.38
$C (mg\ g^{-1})$	2.53
r_p^2	0.94

3.8. Thermodynamic Parameters of Adsorption

The correlation between ΔG^0 (free energy), ΔH° (enthalpy), ΔS° (entropy) and K_L (equilibrium constant) is given as:

$$\Delta G^0 = -RT \ln K_L, \tag{11}$$

$$\ln K_L = -\frac{\Delta G^0}{RT} = -\frac{\Delta H^0}{RT} + \frac{\Delta S^0}{R}, \tag{12}$$

The negative value of Gibbs free energies indicates that the adsorption process is spontaneous. The decrease of the negative value of ΔG with the increase in temperature indicates that the spontaneous nature of sorption is inversely proportional to the temperature (Yasemin and Zeki 2007). An endothermic reaction is suggested by the positive value of $\Delta H\circ$, while the positive value of ΔS° indicates that there is an increased randomness at the interface between solid and the solution during the adsorption of Zn(II) onto the adsorbent (Table 4). The increase in randomness may be caused by the displaced water molecules possessing higher translational energy (Yasemin and Zeki 2007).

Table 4. Thermodynamic Parameters Calculated From the Langmuir Isotherm Constant (K_L) for the Adsorption of Zn (II)

t (°C)	ΔG° (kJ mol^{-1})	ΔH° (kJ mol^{-1})	ΔS° (J K^{-1} mol^{-1})
20	-6.69		
30	-6.60	2.63	20.11
40	-5.86		
50	-4.97		

3.9. Regeneration Studies

In order to retrieve the unloaded biomass (for reuse), several mineral acids of varying concentration were tried for eluting the sorbed metal ions. However, 0.1 M HCl was found to give the best result with 100% recovery of the metal ions. The recovered

biomass was then subjected to several cycles of loading and elution and was found to retain 98% of the sorption capacity up to 3 cycles.

4. Conclusion

A cheap and effective biosorbents, for the extraction of metal ions from aqueous solution, is offered by *Coriandrum Sativum L.* seeds. The constituent functional groups offer the feasibility for the adsorption of metal ions through physiochemical route, which may be inferred from the results of the isotherm studies. The kinetic study reflects the influence of both the amount of adsorbent and the concentration of the adsorbate in the process of retention. There is a significant increase in the adsorption capacity with increasing amount of the adsorbent, which may be probably due to availability of more binding sites. The thermodynamic study also traces the favourable energy changes that occur during the process of retention. Therefore, the proposed method offers a very simple, low cost, effective, and ecofriendly alternative methodology for the determination and extraction of metal ions from real water sample.

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