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Removal of cobalt(II) ion from water by adsorption using intact and modified *Ficus carica* leaves as low-cost natural sorbent

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ABSTRACT

A series of experiments were carried out in a batch system to assess the removal of cobalt ion (Co^{2+}) by intact and modified *Ficus carica* leaves (FCLs) from the aqueous solutions in laboratory experiments. Adsorption kinetics and thermodynamic parameters, as well as equilibrium adsorption isotherms, were examined. The effects of pH, initial concentration of metal ions, biosorbent dose, and the treatment of biosorbent on the biosorption process were also studied. Results showed that the optimum uptake (20.2 mg/g with the removal efficiency of 31.02%) was reached at pH 4. It was also found that the FCLs treated with $MgCl_2$ caused an increase in the uptake capacity, 33.9 mg/g (q_{exp}) at pH 6, and removal efficiency was 57.15%. The biosorption data followed the Freundlich ($R^2 = 0.974$), Langmuir ($R^2 = 0.978$), Dubinin–Radushkevich ($R^2 = 0.982$), and Temkin ($R^2 = 0.915$) isotherms. Langmuir, Freundlich, and Dubinin–Radushkevich models exhibited a higher and better fit of the data. The Freundlich constants K_f and n were found to be 0.75 and 1.014, respectively, and the maximum sorption capacity (q_{max}) was 82.64 mg/g. Dubinin–Radushkevich parameters were $K_{D-R} = 0.00142$, $X_m = 0.0067$ mol/g, and E_{D-R} value was 18.782 kJ/mol. The overall biosorption process of Co^{2+} ion was best described by pseudo-second-order kinetic model. The negative ΔG° (−0.124) observed at 20°C revealed that biosorption of Co^{2+} ions onto FCLs was spontaneous at this temperature. Thermodynamic studies also demonstrated positive ΔS° (+0.705), showing increased disorder of the cobalt ion removal process. Ion-exchange mechanism and dominant sorption functional groups determination accomplished using Fourier transform infrared (FTIR) and X-ray fluorescence (XRF) techniques, and hence pseudo-second-order kinetic model. The results from this study showed the raw and modified FCLs are a new biomass for the removal of Co^{2+} from aqueous solutions.

Keywords: Cobalt; Removal; *Ficus carica*; Kinetics; XRF; FTIR

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1. Introduction

Pollution of water and wastewater by heavy metals has globally become a hot issue, causing negative impacts on the environment and threatening human life due to their toxicity, long persistence, and biomagnification in the food chain [1,2]. Of these metals, lead, cadmium, arsenic and mercury are classified as nonessential metals, having no role in biological functions, and are toxic, even in trace amounts. Zinc, manganese, iron and cobalt are among the other group of metals, and in trace amounts, they are essentially needed for metabolism. It has been recognized that cobalt is an essential part of vitamin B_{12}, possessing a regulating role in blood pressure and has been proven to be necessary for appropriate function of thyroid [3]. Despite these beneficial functions, exposure to high levels of cobalt have been associated with adverse health problems such as neurotoxicological disorders and genotoxicity in human beings, as well as cancer in chronic cases [4].

In order to treat heavy metal-polluted water, considering the fact that metals do not destroy or degrade biologically, technologies are needed to remove them. Some alternative techniques such as photocatalytic degradation, and new sorbents like nanotubes, nanoparticles and CNT/magnesium oxide composite, were introduced as novel adsorbents to removal pollutions in last decades [5–11]. Electrolysis, ion exchange, chemical precipitation and reverse osmosis are among the most common treatments used for removing metals from water and wastewater [12,13]; however, most of these methods suffer from drawbacks, such as expensive operation, and the generation of chemical sludge. In addition to these aforementioned complications, there are also the problems related to its disposal, such as inefficient metal removal, and high energy and reagents that it requires [14,15]. According to such limitations and disadvantages, biosorption, which is based on using biological material for removing heavy metals, as a potential alternative technology has been receiving attention in recent decades [16,17]. Interest in the use of biosorption to remove heavy metals pollution has been stimulated duo to attributes including: low operating cost, feasibility of recovering valuable metals, ability of reproducing and reusing biosorbent, and lastly, no generation of sludge [18,19]. There are many studies addressing usage of a wide variety of economically efficient biosorbent like algae, plant, sawdust, fungi, bacteria and agricultural-based material for sequestration and removal of heavy metals [20–23].

In order to improve the sorption capacity of raw biosorbents, modification methods have been developed. Chemical pretreatments are among the recognized methods that could enhance the biosorption of metals, although such modifications might also lead to reduction in the sorption capacity [24,25]. Acidic and alkali modifications are the most widely used chemical pretreatments improving the sorption capacity of biomass through substitution of proton ions for light metal ions from the binding sites; for example, carboxylic and sulfonic (acidic pretreatment), and occupation of binding sites by ions like magnesium and calcium (alkali pretreatment) [26,27].

In the present study, the capability of *Ficus carica* leaves (FCLs) as a biosorbent for the biosorption of cobalt ion (Co^{2+}) were studied on the influence of pH, initial concentration of metal ions, biosorbent dose for raw and treated biosorbent. The adsorption kinetic and equilibrium isotherm models were also investigated. Investigation on the cobalt ion removal using the modified form of FCLs by $MgCl_2$ as a low cost and new biosorbent, as well as the XRF analysis study, revealed that the ion-exchange nature of the biosorption phenomenon could be two dually important and considerable results from this research.

2. Materials and methods

2.1. Chemicals

All the chemical compounds used to prepare the reagent solutions were of analytic grade (Merck, Germany). The stock solution of cobalt (60 mg/L) was prepared by dissolving 295 mg of $Co\ (NO_3)_2{\cdot}6H_2O$ in 1 L of distilled water. The stock solution was diluted to obtain solutions of various known concentrations of cobalt. For pH adjustment, 0.1 M NaOH and 0.1 M HCl solutions were used.

2.2. Preparation and modification of biosorbent

FCLs were collected locally, from the green space of the Research Institute. In the laboratory, these leaves were washed several times with tap water to remove dust and other impurities and were allowed to dry at room temperature. The dried leaves were ground into fine powder using a mechanical grinder. The powder was sieved and the particles that passed through a (250–500 μm) mesh.

These particles were then washed twice by redistilled water and dried at 80˚C for 24 h. Fig leaves may attach to each other after drying and create greater particles so that it is required to sieve again after drying by the same sieve and to grade at former size.

For the modification process, 10 g of desired size of FCLs was soaked in 1 L of 0.1 M HCl and mixed by rotary mixer in 100 rpm at ambient temperature for 1 h. The solution was filtered and washed with distilled water to remove acid contents. The filtered biosorbent was dried at 60˚C for 24 h to completely remove moisture. Dried FCLs were sieved to achieve the same size as described earlier. Similar treatment of FCLs was performed with 0.1 M $MgCl_2$ solution [28].

2.3. Batch biosorption experiments

Batch sorption experiments were carried out by contacting 0.03 g of FCLs with 30 ml of Co^{2+} solution. To study the effect of pH (2.5–8), contact time (15, 30, 60, 120, 180, 360, and 720 min), initial metal concentration (20, 40, 60, 80, 100, and 200 mg/L), biosorbent dose (1, 2, 4, 8, and 16 mg/g), and temperature (20, 35, and 50˚C), different experiments were performed. The flasks were placed on a rotary shaker at 150 rpm for 2 h at 25˚C. The contents of the flasks were then filtered through filter paper (Whatman No. 41, ashless). All the above experiments were done duplicated.

The filtrate was analyzed, using Varian AA240 FS (Australia) atomic absorption spectrophotometer, to determine the content of residual metals. The amount of cobalt biosorbed was calculated by the following equation [19]:

$$Q = V(C_0 - C_e)/m \tag{1}$$

where Q is the uptake (mg/g), C_0 and C_e are the initial and equilibrium concentrations of metal in solution (mg/L); V (L) is the volume of solution, and m is the mass of biosorbent (g).

2.4. Equilibrium isotherm studies

To estimate the biosorption capacity and equilibrium coefficient for cobalt removal, the following models were studied: Langmuir, Freundlich, Temkin, and Dubinin–Radushkevich.

2.4.1. Langmuir isotherm model

Langmuir isotherm model is expressed by the following equation [29–31]:

$$q_e = q_{max} bC_e/1 + C_e \tag{2}$$

where q_e is the amount of biosorbed metal at equilibrium (mg/g), C_e is the equilibrium concentration of metal in solution (mg/L); q_{max} is the maximum biosorption capacity (mg/g), and b is an affinity constant.

The separation factor, R_L, can be calculated, which describes the essential characteristics of the Langmuir isotherm, and is expressed as follows [32]:

$$R_L = \frac{1}{1 + bC_0} \tag{3}$$

where C_0 is the initial concentration (mg/L) of metal ions, and b is the Langmuir constant.

2.4.2. Freundlich isotherm model

Freundlich isotherm model is represented as follows [29]:

$$q_e = K_f(C_e)^{1/n} \tag{4}$$

where K_F and n are the Freundlich coefficients, K_F indicates the biosorption capacity, and n is related to the intensity of biosorption.

2.4.3. Temkin isotherm model

Temkin isotherm model is generally used in the linear form as follows [30,31]:

$$q_e = B \ln A + B \ln C_e \tag{5}$$

where A is the Temkin isotherm constant, corresponding with the maximum binding energy, $B = RT/b_T$, b_T is the Temkin constant related to the heat of sorption (J/mol), R is universal gas constant (8.314 J/mol K) and T is the absolute temperature in Kelvin. The Temkin constants were calculated from the slope and intercept of the regression line of the plot of (q_e) vs. ln C_e.

2.4.4. Dubinin–Radushkevich (D–R) model

Dubinin–Radushkevich (D–R) model was applied to deduce the heterogeneity of the surface energies of adsorption and the characteristic porosity of the adsorbent [30,31]:

$$x = x_m \exp(-K_{D-R}\varepsilon^2) \tag{6}$$

The linearized Dubinin–Radushkevich equation was generated by taking the natural log of both sides is given in Eq. (7):

$$\ln x = \ln x_m - K_{D-R}\varepsilon^2 \tag{7}$$

ε is Polanyi potential and defined as follows:

$$\varepsilon = RT \ln\left(1 + \frac{1}{C_e}\right) \tag{8}$$

x is the amount of cobalt ion sorbed per mass of FCLs, x_m is the Dubinin–Radushkevich constant representing the theoretical monolayer saturation capacity. The plot of $\ln x$ against ε^2 was used to determine the values of K_{D-R} and x_m from the slope and the intercept, respectively.

Finally, mean free energy, or mean adsorption energy value was calculated from the following:

$$E_{D-R} = \frac{1}{\sqrt{2K_{D-R}}} \tag{9}$$

where E_{D-R} is mean free energy (kJ/mol).

2.5. Kinetic studies

Kinetic studies were applied to investigate the controlling mechanism of metal biosorption from a solution. Kinetic models analyzed experimental data including the pseudo-first-order, pseudo-second-order, Elovich and intraparticle diffusion models [2,21,31,33].

2.5.1. Pseudo-first-order kinetic model

Pseudo-first and pseudo-second-order kinetic equations described by Eqs. (10) and (11), respectively [2,14]:

$$dq_t/d_t = k_1(q_e - q_t) \tag{10}$$

$$dq_t/d_t = k_2(q_e - q_t)^2 \tag{11}$$

where q_e and q_t are the metal uptake at equilibrium and time t, respectively (mg/g) and k_1 (1/min) and k_2 (g/mg min) are the rate constants of the pseudo-first-order and pseudo-second-order kinetic equations, respectively

In this model, it is assumed that the speed of the occupation of the binding sites is proportional to the number of not-occupied sites. After integration and applying boundary condition, $(q_e - q_t) = 0$ at $t = 0$, the integrated form of Eq. (10) becomes (Eq. 12):

$$\ln(q_e - q_t) = \ln q_e - k_1 t \tag{12}$$

If the linear figure $\ln(q_e - q_t)$ is drawn on the basis of t, the linear equation and correlation coefficient will be specified.

2.5.2. Pseudo-second-order model

In this model, it is assumed that the speed of the occupation of the binding sites and the speed of sorption has been proportionate to the square root of the number of the not-occupied sites [2,21].

For the boundary conditions $t = 0$ to $t = t$ and $q_t = 0$ to $q_t = q_t$, the integrated form of Eq. (11) becomes (Eq. (13)):

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{13}$$

If a figure of t/q_e is drawn on the basis of t, the linear relation of this model will be obtained.

2.5.3. Intraparticle diffusion model

The intraparticle diffusion model is expressed as follows [31,33]:

$$R = K_{id}(t)^a \tag{14}$$

A linearized form of the equation is followed by:

$$\log R = \log K_{id} + a \log(t) \tag{15}$$

The plot of $\log R$ against $\log t$ will yield a straight line with a slope "a" and an intercept of $\log K_{id}$. R is the percent of Co^{2+} adsorbed, t is the contact time (min), "a" is the gradient of linear plots, and K_{id} is the intraparticle diffusion rate constant (mg/g min$^{-0.5}$).

2.5.4. Elovich model

The Elovich equation has general application to chemisorption kinetics. Elovich equation (Eq. (16)) and the linearized form of equation (Eq. (17)) based on equilibrium adsorption is generally expressed as follows [33–35]:

$$q_t = \frac{1}{\beta}\ln(\alpha\beta) + \frac{1}{\beta}\ln(t) \tag{16}$$

$$\log R = \log K_{id} + a \log(t) \quad (17)$$

where q_t is adsorption capacity, α is the initial adsorption rate (mg/g min), and β is the desorption constant (g/mg) during any experiment.

Thus the constants can be obtained from the slope and intercept of the linear plot of q_t vs. $\ln t$ with a slope of $(1/\beta)$ and an intercept of $(1/\beta) \ln(\alpha\beta)$.

2.6. FTIR and XRF analysis

FTIR analysis was prepared for detecting vibration frequency changes in the biosorption processes. The functional groups involved in metal biosorption were identified with FTIR analysis. FTIR technique was used with a spectrometer instrument within the range 400–4,000 cm^{-1} using a KBr window. KBr pellets were prepared and the proportion of biomass/KBr was 1/100. Cobalt sorption and ion-exchange phenomenon elucidated with XRF technique. To accomplish this experiment, two intact and cobalt-loaded biomasses were examined at the pH of 6, and adsorbents were studied by FTIR and XRF analyses techniques.

3. Results and discussion

3.1. Effect of pH

The initial pH of solution is a significant factor in biosorption mechanism affecting the solution chemistry of the metals, the activity of the functional groups in the biomass, the competition of metallic ions, and the degree of ionization of metals as well as the surface binding sites of the biosorbent [36,37]. The effect of pH on the biosorption of Co^{2+} onto FCLs was investigated in pH range of 2.5–8. The pH 4 was found to be the optimum pH at which the biosorption of Co^{2+} was 20.2 mg/g. At low pH, hydrogen ions predominate in the competition to be adsorbed on the biosorbent surface, owing to their relatively high concentration and consequently, their more availability to binding sites [38,39]. With the increase in pH, the biosorbent surface became deprotonated and negatively charged, which resulted in increased binding of Co^{2+} ions [40,41]. Other studies have also been reported pH 4–7 as the optimum pH for biosorption of Co^{2+} by other biosorbents [42,43].

3.2. Effect of modification

The pretreatment of raw biomass, in order to manipulate affinity of metal toward biomass leading to high sorption capacities, has no effect on the biosorption kinetics, and enhances the stability of the biosorbent material [44]. The FCLs were chemically pretreated with HCl and $MgCl_2$ in order to see the influence of modified biomass on the biosorption capacity of Co^{2+}. The influence of pH on the biosorption capacity of raw and pretreated or modified FCLs is presented in Table 1. As can be seen from this Table, the removal of Co^{2+} ions significantly decreased following HCl pretreatment, whereas $MgCl_2$ modification increased the efficiency of Co^{2+} removal 1.7 times higher than raw FCLs.

If electronegativity of the biomass is higher,then metal biosorption will be greater. However, acidic treatment scan causes a reduction in the electronegativity of biomass surface as a result of proton ions that have remained on the surface of the biosorbent and subsequently decreases the biosorption capacity [4]. Magnesium ions on the surface of $MgCl_2$-modified biomass are easily capable to exchange with metal ions in the solution. Therefore, the enhancement in biosorption of Co^{2+}ions after pretreatment by $MgCl_2$ may result from the introduction of new sites on the biosorbent surface for the binding of metal ions via preparation of biomass in Mg form, which acts like an ion-exchange resin [45,46]. Results of Table 1 revealed that the highest biosorption (q_{exp} = 33.9 mg/g) of Co^{2+} was obtained with FCLs modified by $MgCl_2$ at pH 6. In view of this observation, the further experiments were performed by $MgCl_2$-treated FCLs at pH 6.

3.3. Effect of initial metal concentration

The effect of initial Co^{2+} concentration on the biosorption capacity of modified FCLs has been investigated at six different concentrations of 20, 40, 60, 80, 100, and 200 mg/L (Fig. 1). With the increase in Co^{2+} ion concentration, the uptake increased until the concentration of Co^{2+} reached the value of 80 mg/L, and then decreased thereafter. At low metal ion concentrations, there are numerously accessible sites on the biosorbent, which actively attract metal ions from solution. As the concentration of metal ions increases, the binding sites on the surface of the biosorbent become saturated and, hence, are no longer capable to absorb Co^{2+} ions from solution [47,48].

3.4. Effect of biosorbent dose

The dose of biosorbent is considered as a key variable affecting the efficiency of metal biosorption and controls the equilibrium between sorbate and biosorbent in biosorption procedure [25,39]. The biosorption of Co^{2+} on FCLs, as a function of biosorbent dose, has been studied by varying $MgCl_2$-treated FCLs dose,

Table 1
Effect of pH on the biosorption capacity of raw and modified FCLs

FCLs	Chemicals	pH					
		3	4	5	5.5	6	7
q (mg/g)	Raw	7.35	20.2	15.70	12.80	14.80	17.50
	$MgCl_2$	8.65	25.7	32.40	27.40	33.90	21.40
	HCl	2.75	3.88	4.20	5.85	9.20	11.90

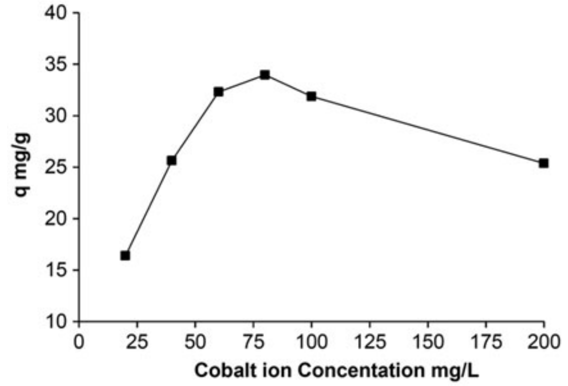

Fig. 1. Effect of initial metal concentration on Co^{2+} biosorption (biosorbent dose = 1 g/L, pH 6, contact time = 2 h).

from 0.1 to 16 g/L, while keeping all other variables constant (Fig. 2). It is clearly evident that the amount of metal uptake (q_e) decreases, and the percent of metal removed increases with each increase in the biosorbent dose. The increase in the percent removal of Co^{2+}, with increase in treated-FCLs dose, could be linked to the increase in active sites on which Co^{2+} ions absorbed [48]. On the other hand, at higher doses of FCLs, slower metal biosorption occurs because of the lower number of Co^{2+} ions compared to availability of exchangeable sites on FCLs, therefore decreasing the value of q_e [1].

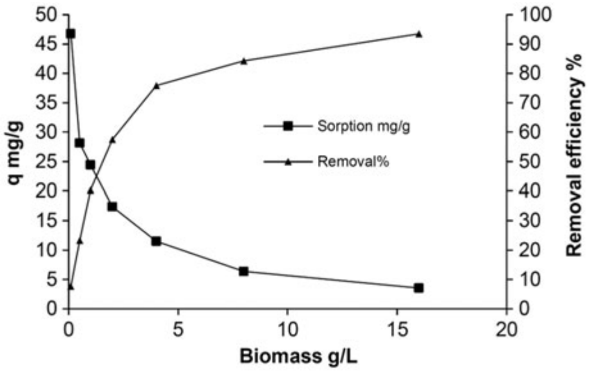

Fig. 2. Effect of biosorbent dose on Co^{2+} biosorption (C_i = 60 mg/L, pH 6, contact time = 2 h).

3.5. Biosorption equilibrium

3.5.1. Freundlich and Langmuir models

Experimental data from the biosorption system were evaluated by isotherm models, which present the equilibrium relationships between the concentrations of biosorbed metal, and metal in solutions at a given temperature [23]. The most common and widely applied kinds of these terms are Langmuir and Freundlich models. Langmuir isotherm is derived from the theory that biosorbed molecules do not interact with each other and that a monolayer sorption occurs on the surface of biosorbent over which a fixed number of approachable sites, with equal affinity in terms of the sorption energy, are homogeneously distribute [49], while Freundlich isotherm lies on the assumption that biosorption takes place on a heterogeneous surface by multilayer sorption and with interaction between the biosorbed molecules [41]. The constants of Langmuir and Freundlich isotherms for Co^{2+} ions sorption onto Mg-treated FCLs are tabulated in Table 2. The Freundlich constants, K_F and n, and correlation coefficient (R^2) were estimated to be 0.75, 1.014, and 0.973, respectively. Maximum monolayer adsorption capacity (q_{max}), affinity constant (b), and correlation coefficient (R^2) for Langmuir model were calculated as 82.64 mg/g, 0.0097 L/mg and 0.977, respectively.

The value of R_L lies between 0 and 1 for favorable sorption, while $R_L > 1$ represents unfavorable sorption; and $R_L = 1$ represents linear sorption, while the sorption process is irreversible if $R_L = 0$. In this study, the value of R_L was between 0 and 1, suggesting a favorable biosorption of Co^{2+} ions.

3.5.2. Temkin model

Heat of adsorption and the adsorbate–adsorbent interactions on adsorption isotherms were studied by Temkin model. The regression analysis results showed

Table 2
Isotherm models for of Co^{2+} biosorption by Mg-treated FCLs

Biosorbent	Freundlich isotherm			Langmuir isotherm			
Ficus carica	K_F (L/mg) 0.75	n 1.014	R^2 0.974	q_{max} (mg/g) 82.64	b (L/mg) 0.0097	R^2 0.977	
Biosorbent	Temkin isotherm			Dubinin–Radushkevich isotherm			
Ficus carica	A_T (L/g) 1.00	b_T (J/mol) 0.0042	R^2	$E_{D–R}$(kJ/mol) 18.872 0.982	$K_{D–R}$(mol^2/kJ^2) 0.00142	x_m (mol/g) 0.0066	R^2 0.982

that the Langmuir, Dubinin–Radushkevich, and Freundlich models could describe the sorption equilibrium data slightly better than Temkin model in the biosorbent dose range studied in terms of R^2. β_T is the Temkin isotherm constant related to heat of sorption (0.0042 J/mol) and A (1.00 L/g) is the equilibrium-binding constant corresponding with the maximum binding energy (Table 2).

3.5.3. Dubinin–Radushkevich model

At the same time, the regression analysis results showed that the Dubinin–Radushkevich isotherm was able to describe the sorption equilibrium data slightly better than Temkin, Freundlich and Langmuir isotherm models in the sorbent dose ranges studied in terms of R^2. The constant $q_{D–R}$ agrees well with experimental data, and the maximum value of 0.0066 mol/g was observed at pH 6. The magnitude of E is useful for estimating the type of sorption reaction. The E values obtained were around 18.872 kJ/mol, which are in the energy range of an ion-exchange reaction [50]. This supports the fact that biosorption of cobalt ion by modified FCLs may be an ion-exchange reaction. The Dubinin–Radushkevich constants and mean free energies are given in Table 2. Although, Freundlich and Temkin models describe the biosorption of Co^{2+} ions ($R^2 > 0.91$), the values of the correlation coefficients obtained for Dubinin–Radushkevich and Langmuir models showed a stronger fit to the experimental data, respectively.

3.6. Biosorption kinetics

3.6.1. Pseudo-first- and pseudo-second-order kinetic models

In order to determine the mechanism of the biosorption process and interpret the experimental data, pseudo-first-order and pseudo-second-order kinetics models were tested at different temperatures. The pseudo-second-order kinetic model fit the equilibrium data for biosorption of Co^{2+}on Mg-treated FCLs quite well accordingly (Figs. 3 and 4). The experimental data and the parameters of both models for all three temperatures studied are listed in Table 3. As shown in Table 3, the calculated values of q_e for the pseudo-first-order model are not close to the experimental values (q_{exp}), while the pseudo-second-order model provides very close approximations to the

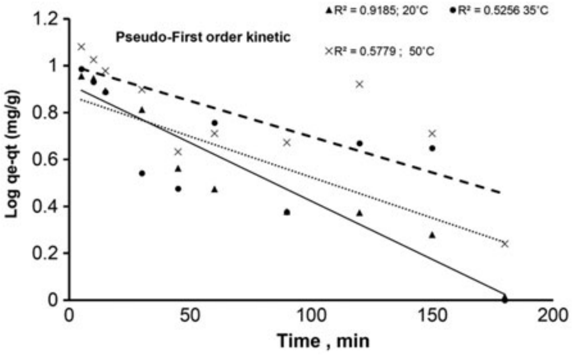

Fig. 3. Pseudo-first-order graph for biosorption of Co^{2+} by Mg-treated FCLs (C_i = 60 mg/L, biosorbent dose = 1 g/L, pH 6).

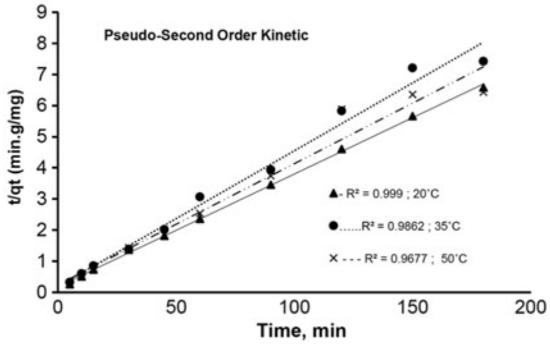

Fig. 4. Pseudo-second-order graph for the biosorption of Co^{2+} by Mg-treated FCLs (C_i = 60 mg/L, biosorbent dose = 1 g/L, pH 6).

Table 3
Kinetic constants for biosorption of Co^{2+} by Mg-treated FCLs

Pseudo-first-order model				Pseudo-second-order model			
T, K (°C)	K_1 (min^{-1})	q_e (mg/g)	R^2	K_2 (g/mg min)	q_e (mg/g)	q_{exp} (mg/g)	R^2
293 (20)	0.005	8.316	0.919	0.184	27.62	27.36	0.999
308 (35)	0.004	7.446	0.526	0.191	22.94	24.25	0.986
323 (50)	0.003	10.055	0.571	0.244	25.71	27.99	0.968

Elovich model				Intraparticle diffusion model			
T, K (°C)	α (mg/gmin)	β (g/mg)	R^2	K_{id} ($mg/gmin^{-0.5}$)	a (mg/g)		R^2
293 (20)	148.703	0.406	0.949	26.044	0.129		0.972
308 (35)	368.660	0.511	0.710	24.660	0.122		0.855
323 (50)	128.317	0.423	0.702	22.055	0.109		0.728

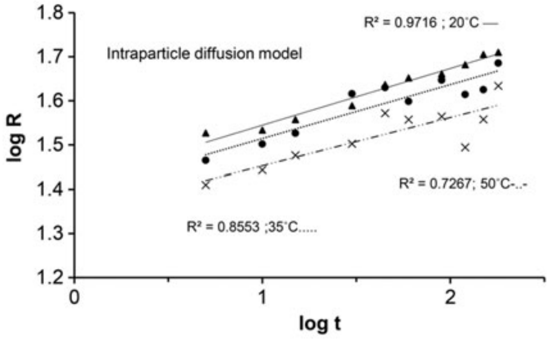

Fig. 5. Intraparticle diffusion kinetics model for the biosorption of cobalt (C_i = 60 mg/L, biosorbent dose = 1 g/L, pH 6, T = 293, 308, 323 K).

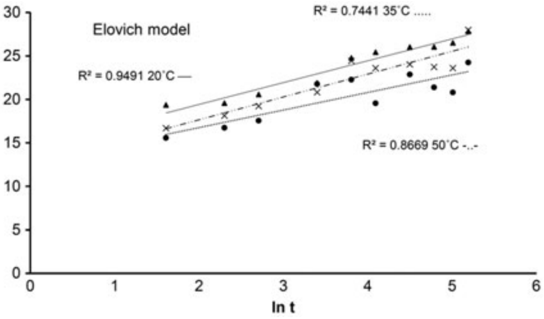

Fig. 6. Elovich kinetics model for biosorption of cobalt (C_i = 60 mg/L, biosorbent dose = 1 g/L, pH 6, T = 293, 308, 323 K).

experimental data. In addition, the correlation coefficients for pseudo-first-order kinetic for all three temperatures were found to be rather low, whereas pseudo-second-order gave a much better correlation of data (all values of R^2 greater than 0.96). The fitness of the pseudo-second-order kinetics model proposed that the biosorption of Co^{2+} onto FCLs was an ion exchange and chemical sorption, involving the sharing of electrons between biosorbent and metal [51]. The obtained results confirm the applicability of pseudo-second-order kinetic as the most fitting kinetic model for the description of Co^{2+} biosorption.

3.6.2. Intraparticle diffusion model

Table 3 presents the values of the parameters calculated from the linearized form of the intraparticle diffusion model isotherm. Comparing the R^2 values of cobalt ion sorption, it can be stated that sorption of cobalt ion can be elucidated using the intraparticle diffusion model. The results also indicated that an intraparticle diffusion mechanism played a significant role during the adsorption process, while the sorption rate was controlled by a film-diffusion step. The plot of log R against log t will yield a straight line with a slope "a" and an intercept of log K_{id} (Fig. 5). Application of this model to analyze data from this test gave a good fit plot with a correlation coefficient of R^2 = 0.972, and a value of "a" which is less than unity (0.129) and the intraparticle diffusion rate constant, K_{id} is 26.044 ($mg/g\ min^{-0.5}$).

3.6.3. Elovich model

The Elovich equation has been shown as a useful model in describing chemisorption on highly heterogeneous adsorbents. The results presented in Table 3 indicated that this kinetic model described the sorption process. Elovich equation constants can be obtained from the slope and intercept of the linear

Table 4
Thermodynamic parameters for biosorption of Co^{2+} by Mg-treated FCLs

ΔH° (kJ mol^{-1})	ΔS° (KJ mol^{-1} K^{-1})	ΔG° (KJ mol^{-1})		
		T = 20℃	T = 35℃	T = 50℃
+0.827	+0.705	–0.124	+0.155	+0.751

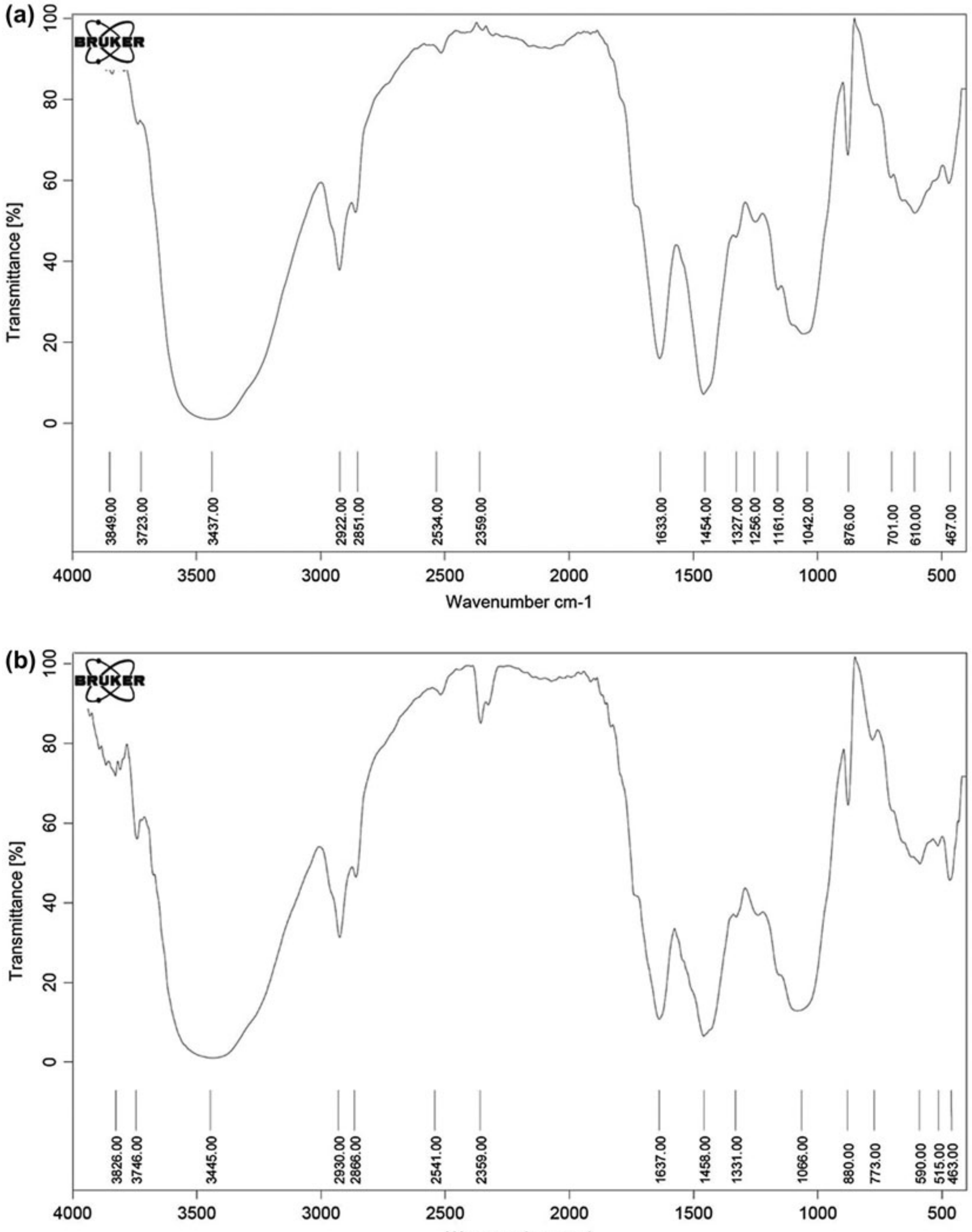

Fig. 7. FTIR analysis of $MgCl_2$-treated FCLs: (a) before and (b) after biosorption cobalt).

Table 5
Composition of modified FCLs before and after cobalt biosorption using XRF analysis

Compound	Before Co sorption (Wt %)	After Co sorption (Wt %)
MgO	4.859	0.974
Al_2O_3	0.362	0.600
SiO_2	46.142	46.405
P_2O5	1.899	1.293
SO_3	3.198	4.056
K_2O	0.438	ND
CaO	42.26	16.017
Fe_2O_3	0.842	ND
Co	ND	30.116

Note: ND: Not Detected.

Table 6
A comparison between cobalt sorption capacity by some biosorbents

Biosorbent	Class	Capacity, q_{max} (mg/g)	Refs.
Chrysanthemum indicum	Plant (Biochar)	45.44	[54]
Chrysanthemum indicum	Plant (Raw)	14.84	[54]
Saccharum bengalensis	Plant	14.7	[55]
Musa acuminata	Banana leaves	65.15	[56]
Jania rubens	Alga	32.6	[57]
Lemon peel	Plant	22	[58]
Peat moss (NaOH treated)	Plant	30.03	[59]
Botryocladia leptopoda	Alga	27.50	[60]
Ulva reticulata	Alga	46.50	[61]
Nizimuddinia zanardini	Alga	33.50	[62]
Cystoseira indica	Alga	34.60	[62]
Ficus carica ($MgCl_2$ treated)	Plant leaves	82.64	Current research

plot of q_t vs. ln t with a slope of $(1/\beta)$ and an intercept of $(1/\beta)$ ln $(\alpha\beta)$ (Fig. 6). The value of α varied as a function of the solution temperature. Thus, on increasing the solution temperature from 20 to 35℃, the value of α increased from 122.562 to 269.363 mg/g min due to the more available surface for cobalt ions. On increasing the solution temperature from 35 to 50℃, the value of α decreased from 269.363 to 55.862 mg/g min. Therefore, the Elovich model experimental data did not give a good correlation for these results at high solution temperature.

The adsorption proceeds according to the pseudo-second-order model, which provides the best correlation with the data for all cases and the experimental $q_{e,exp}$ values agree with the calculated ones. Also, it was found that the correlation coefficients for the Elovich and intraparticle diffusion models are lower than those obtained from pseudo-second-order kinetic model. This result confirmed that the pore diffusion is not the only rate-controlling step.

3.7. Thermodynamic studies

The biosorption thermodynamics developed from the effect of temperature on the biosorption system were studied by varying the temperature in the range 20–50℃ (293–323 K). Thermodynamic parameters such as change in Gibbs free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°), were calculated using the following equations [15,52]:

$$K_0 = C_{\mathrm{Solid}}/C_{\mathrm{liquid}} \tag{18}$$

$$\Delta G = -RT \ln K_0 \tag{19}$$

$$\log K_0 = \Delta S^\circ/(2.303\,R) - \Delta H^\circ/(2.303\,RT) \tag{20}$$

where K_0 is the equilibrium constant, C_{solid} is the solid phase concentration at equilibrium (mg/L), C_{liquid} is the liquid phase concentration at equilibrium (mg/L),

T is the temperature in Kelvin, and R is the gas constant (8.314 J/mol K).

The values of ΔH° and ΔS° were determined from the slope and intercept of Vant Hoff plot. The results of the thermodynamic studies are shown in Table 4. Positive values of ΔG° obtained for Co^{2+} biosorption at temperatures of 35 and 50℃ exhibited that the reaction was not spontaneous at the mentioned temperatures, and requires energy to resume the biosorption process. However, the value of ΔG° at temperature of 20℃ was negative, confirming the feasibility and spontaneous nature of the Co^{2+} biosorption at this temperature. The positive value of ΔH° reflects the endothermic nature of the biosorption process. The positive value of ΔS° is an indication of increase in disorder and randomness at the solid solution interface during the biosorption of Co^{2+} by Mg-treated FCLs.

3.8. FTIR and XRF analyses

Infrared spectra of *Ficus carica* biomass samples, and comparisons of the FTIR spectra before and after biosorption process, were given in Fig. 7. The wave numbers move from 1,042 to 1,066 cm^{-1} suggesting that the solfunic acid group is the dominant functional group taking place in the binding and removal of the cobalt ion [36,53].

Table 5 shows that the XRF analysis was used in order to identify the inherent characteristics of modified FCLs before and after the biosorption process. In other words, biomass composition and cobalt adsorption were proved by this analysis. According to pseudo-second-order kinetic results that show ion exchange sorption mechanism (Table 3), likewise, changing the amount of Mg^{2+} and Ca^{2+} (%) could be attributed to ion exchange or replacement cobalt ion with these ions.

4. Conclusions

In the present study, biosorption of Co^{2+} by raw and modified FCLs was proven to be an effective and low-cost biosorbent. The biosorption capacity of modified FCLs increased from 20.2 to 33.9 mg/g (q_{exp}) through modifying the biosorbent by $MgCl_2$ at the optimum pH of 6. It was also revealed that the Co^{2+} biosorption depended on pH, metal concentration, and biosorbent dose. The temperature of 20℃ could be considered as the optimum temperature for the biosorption process, as the reaction was found to be spontaneous at this temperature. The biosorption reaction also obeyed Dubinin–Radushkevich, Langmuir and Freundlich models. However, the equilibrium data of biosorption could be better described by Dubinin–Radushkevich, and Langmuir isotherms. The maximum biosorption capacity (q_{max}) for Co^{2+} on the Mg-treated FCLs was found to be 82.64 mg/g. The $E_{\text{D–R}}$ value (18.872 kJ/mol) revealed chemisorption nature of cobalt removal according to Dubinin–Radushkevich isotherm. The pseudo-second-order kinetic model provided the closest fit to the experimental data ($R^2 > 0.96$ for all temperatures). XRF analysis results approved cobalt biosorption on the FCLs biosorbent and so ion-exchange phenomenon. Generally, the results identified that Mg-treated FCLs could be used as an economically beneficial biosorbent for the removal of Co^{2+} from aqueous solutions. A comparison of the sorption capacity between some algal and plant tissues to remove the cobalt ion from aqueous solutions, as reported by some researchers, is summarized in Table 6 [54–62].

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