Kinetic and isotherm studies of Cu(II) biosorption onto valonia tannin resin

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ABSTRACT

The biosorption of Cu(II) from aqueous solutions by valonia tannin resin was investigated as a function of particle size, initial pH, contact time and initial metal ion concentration. The aim of this study was to understand the mechanisms that govern copper removal and find a suitable equilibrium isotherm and kinetic model for the copper removal in a batch reactor. The experimental isotherm data were analysed using the Langmuir, Freundlich and Temkin equations. The equilibrium data fit well in the Langmuir isotherm. The experimental data were analysed using four sorption kinetic models – the pseudo-first- and second-order equations, the Elovich and the intraparticle diffusion model equation – to determine the best fit equation for the biosorption of copper ions onto valonia tannin resin. Results show that the pseudo-second-order equation provides the best correlation for the biosorption process, whereas the Elovich equation also fits the experimental data well.

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1. Introduction

Copper is a very common substance that occurs naturally in the environment and spreads through the environment through natural phenomena. The production of copper has lifted over the last decades and due to this copper quantities in the environment have expanded. Copper is present in the wastewater of several industries, such as metal cleaning and plating baths, refineries, paper and pulp, fertilizer, and wood preservatives and it is highly toxic [1]. Most copper compounds will settle and be bound to either water sediment or soil particles. Soluble copper compounds form the largest threat to human health. Usually water-soluble copper compounds occur in the environment after release through application in agriculture. World Health Organization (WHO) recommended a maximum acceptable concentration of Cu^{2+} in drinking water of 1.5 mg/L [2]. Copper does not break down in the environment and because of that it can accumulate in plants and animals when it is found in soils. On copper-rich soils only a limited number of plants has a chance of survival. The excessive intake of copper by man leads to severe mucosal irritation, widespread capillary damage, hepatic and renal damage, central nervous problems followed by depression, gastrointestinal irritation, and possible necrotic changes in the liver and kidney [3].

The main techniques that have been used on copper content reduction from industrial waste are chemical precipitation, ion exchange, membrane filtration, electrolytic methods, reverse osmosis, and solvent extraction. These conventional techniques can reduce metal ions, but they do not appear to be highly effective due to the limitations in the pH range as well as the high material and operational costs. Among these various treatment techniques, activated carbon adsorption is one of the most commonly used due to its high efficiency and easy operation [4,5].

In recent years, considerable attention has been focused on the removal of copper from aqueous solution using adsorbents derived from low-cost materials [6–8].

Tannins, natural biomass containing multiple adjacent hydroxyl groups and exhibiting specific affinity to metal ions, can probably be used as alternative, effective and efficient adsorbents for the recovery of metal ions. During the last years, the interest on biomaterials and specifically in tannins was growing. Tannins are an important class of secondary plant metabolites, water-soluble polyphenolic compounds of molecular weight ranged between 500 and some thousands Daltons. There are three kinds: hydrolyzable, condensed and complex tannins [9]. However, tannins are water-soluble compounds, thus when they are used directly as an adsorbent for recovery of metals from aqueous systems, they have the disadvantage of being leached by water. To overcome this disadvantage, attempts have been made to immobilize tannins onto various water-insoluble matrices [10]. The chemical structures of hydrolyzable tannin are illustrated in Fig. 1.

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Fig. 1. Scheme of chemical structures of valonia tannin.
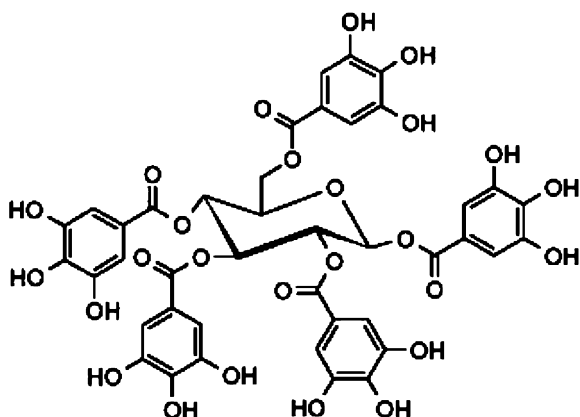
Table 1
BET-specific surface areas for the different tannin resin particle size ranges

Size fractions (μm)	BET surface area (m^2/g)
−100	11.70 ± 0.02
+100	11.64 ± 0.01
+150	11.21 ± 0.01

The study on the removal of heavy metals from wastewater by tannin adsorbents was almost from the application of barks in the similar aspects. Randall [11] observed that adsorption characteristics of barks for heavy metals rested on tannin structures present in the bark adsorbent. Later, researchers synthesized adsorbents from commercial tannins and applied them to remove heavy metals from wastewater, such as uranium [12], americium [13], chromium [14], copper [15], lead [16], thorium [17], gold [18] and palladium [19]. These studies illustrate that it is possible to remove heavy metals from wastewater with tannin adsorbents. The objective of this study is to systematically examine adsorption mechanisms, adsorption isotherms, adsorption kinetics and properties of a tannin gel adsorbent synthesized from valonia tannin for removal of Cu^{2+} from aqueous solutions.

2. Materials and methods

2.1. Preparation of tannin gel particles

8 g of valonia tannin powder, a kind of natural hydrolyzable tannins, was added to 50 mL of 13.3N aqueous NH_3 solution, followed by stirring for 5 min to dissolved it. To resulting solution was added 65 mL of formaldehyde (37 wt%), followed by stirring at room temperature for 5 min for uniform mixing. When this stirring was stopped, a yellow precipitate formed. After the resulting liquid containing the precipitate was stirred for 30 min to complete cross-linking. The product was filtered through filter paper (Toyo Filter Paper No. 2). To the filtered precipitate was added 50 mL distilled water and the product was heated at 70 °C for 3 h. The mixture heated was collected by filtration. To the filtered precipitate was added 0.1N HNO_3 and was stirred for 30 min. The mixture was filtered through filter paper again. The precipitate obtained was allowed to stand at 80 °C to age it, thereby obtaining a tannin adsorbent consisting of an insoluble tannin [20]. The valonia tannin resin (VTR) was prepared by grinding it in a laboratory-type ball-mill. Then, it was sieved to obtain size fractions of −100, +100, +150, +212 and +250 μm using ASTM Standard sieves. The Brunauer–Emmett–Teller (BET) surface area was measured from N_2 adsorption isotherms with a sorptiometer (Micromeriticis FlowSorbII-2300). The specific surface areas of different particle size of the tannin resin are given in Table 1.

2.2. Proton titration experiment

The surface exchange capacity as measured by the proton exchange method was found [21]. The proton titration experiments were carried out to determine the number of valid sites for adsorption present on adsorbent particles. 100 mL 0.1N NaOH solution; with 1.0 g particles were placed in well-sealed glass beaker and the beakers were placed on the thermostatic shaker. The shaking speed was 100 rpm and temperature was 20 °C. After 24 h, the solution in beaker was titrated by 0.1N HCl solution. The surface exchange capacity of the tannin resin was found to be 3.40 mequiv. H^+/g. The titration result suggests that the VTR surface is dominated by H^+ ion exchangeable groups that are largely −OH groups.

2.3. Batch adsorption experiment

A series of batch experiments were conducted to study the adsorption mechanism, adsorption isotherm and adsorption kinetics. Copper stock solution was prepared by dissolving $CuSO_4 \cdot 5H_2O$ (analytical reagent) in deionized water and further diluted to the concentrations required for the experiments. pH adjustment was fulfilled by adding HCl or NaOH into the solutions with known initial copper concentrations (10–150 mg/L).

In the determination of equilibrium biosorption isotherm, 0.1 g VTR and 100 mL of the desired concentration of Cu^{2+} solutions were transferred in 250 mL flask, and shaken on a horizontal bench shaker (Nüve SL 250) for 180 min (the time required for equilibrium to be reached between Cu^{2+} biosorbed and Cu^{2+} in solution) using a bath to control the temperature at 298 ± 2 K. The experiments were performed at 150 rpm.

At the end of the biosorption period, the samples (5 mL) were taken and centrifuged for 15 min at 5000 rpm and then analysed using AAS equipped with an autosampler (Shimadzu AA6701F). The amount of biosorption at equilibrium, Q_e (mg/g), was computed as follows:

$$Q_e = \frac{(C_0 - C_e)V}{W}$$

where C_0 and C_e are the initial and equilibrium solution concentrations (mg/L), respectively; V the volume of the solution (L); and W is the weight of VTR used (g).

Batch kinetic biosorption studies were conducted in a temperature-controlled stirrer using 2000 mL of adsorbate solution and a fixed adsorbent dosage of 2.0 g. The stirring speed of the solution was fixed at 150 rpm for all batch experiments. The samples at different time intervals (5–180 min) were taken and at the end of each agitation period, the mixtures were centrifuged for 5 min. Then, the concentration of Cu^{2+} in the residual solution was analysed by means of atomic absorption spectrophotometry (Shimadzu, Japan). The effects of particle size, pH value, agitation rate, initial concentration and temperature on the adsorption capacity of VTR to Cu^{2+} were also investigated.

3. Results and discussion

3.1. Effect of particle size

A series of experiments have been carried out with a constant initial Cu^{2+} concentration of 100 mg/L and with various particle sizes of the valonia tannin resin. Fig. 2 shows the experimental results obtained from series of experiments performed, using different tannin resin particle size ranges. The result shown in Fig. 2
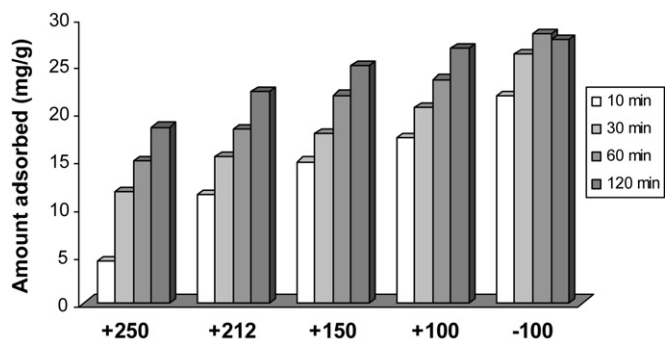
Fig. 2. Effect of particle size on adsorption of copper by valonia tannin. Conditions: 100 mg/L concentration, 1 g/L dose, 298 K temperature and pH 4, stirring speed 150 rpm.

indicates that the saturation capacity of Cu^{2+} adsorption by tannin resin was increased by decreasing the particle size. This behavior can be attributed to the relationship between the effective specific surface area of the adsorbent particles and their sizes. The effective surface area increased as the particle size decreased and as a consequence, the saturation capacity per unit mass of the adsorbent increased. This can be explained by the fact that for small particles a large external surface area is presented to Cu^{2+} in the solution which results in a lower driving force per unit surface area for mass transfer than when larger particles are used. Since C_0 is constant and the mass of tannin resin is constant, the external particle surface area increases as particle size decreases.

3.2. Effect of pH

The uptake of Cu^{2+} was strongly affected by solution pH. At the initial Cu^{2+} concentration of 100 mg/L, copper removal efficiency was 8.06% at a solution pH of 2.0, but it increased sharply when solution pH increases from 2 to 5 (shown in Fig. 3), probably due to acidic dissociation of the phenolic hydroxyl groups of tannin, resulting in stronger complexing ability with metal ions. However, at higher pH values, Cu^{2+} would be precipitated and the phenolic hydroxyl groups of the tannin would more readily be oxidized, making it impractical to apply this approach above pH 8.0 [17].
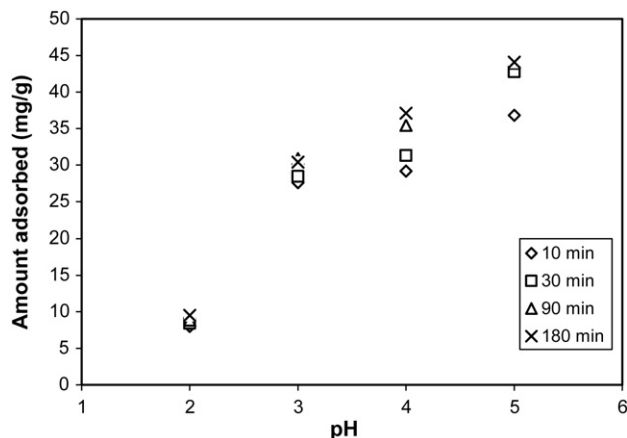

Fig. 3. Effect of pH on adsorption of copper by tannin resin. Conditions: 100 mg/L concentration, −100 μm particle size, 1 g/L dose, stirring speed 150 rpm, 298 K temperature, contact time 180 min.

3.3. Effect of contact time and initial concentration

Adsorption isotherms are usually determined under equilibrium conditions. A series of contact time experiments have been carried out with a various initial concentration. Fig. 4 shows the contact time necessary for Cu^{2+} to reach saturation to be over 180 min. The distribution of Cu^{2+} between the tannin adsorbent and the Cu^{2+} solution, when the system is in a state equilibrium, is important to establish the capacity of the adsorbent for the Cu^{2+}. Tannin resin exhibited equilibrium times of 30 min for Cu^{2+} with Cu^{2+} removals between 96.9% and 29.3%. The initial concentration of Cu^{2+} has little influence of the time of contact necessary to reach equilibrium.

3.4. Equilibrium studies

Fig. 5 shows the equilibrium biosorption of copper (Q_e vs. C_e) using VTR. Equilibrium data, commonly known as sorption isotherms, are basic requirements for the design of sorption systems. These data provide information on the capacity of the biosorbent or the amount required for removing a unit mass of pollutant under the system conditions. Therefore, to optimise the design of sorption system to remove heavy metals from effluents, it is important to establish the most appropriate correlation for the equilibrium curves. Three isotherm equations have been tested in the present study, namely, Langmuir, Freundlich and Temkin. The linear form of these isotherms [22,23] can be expressed by Eqs. (1)–(3), respectively:

$$\frac{C_e}{Q_e} = \frac{1}{K_L} + \frac{a_L}{K_L} C_e \tag{1}$$

$$\log Q_e = \log K_F + \frac{1}{n} \log C_e \tag{2}$$

$$q_e = B \ln A + B \ln C_e \tag{3}$$

where q_e (mg/g) and C_e (mg/L) are the amount of adsorbed Cu^{2+} per unit weight of adsorbent and unadsorbed Cu^{2+} concentration in solution at equilibrium, respectively. The K_L and a_L are the Langmuir isotherm constants and the K_L/a_L gives the theoretical monolayer saturation capacity, Q_0. K_F is the Freundlich constant and $1/n$ the Freundlich exponent. A and B are the Temkin constants. The isotherm constants were determined from linear isotherm graphs for each of the isotherm equations tested. The values of the isotherm constants with the correlation coefficients are given in Table 2 for the copper–VTR system and the isotherms are plotted in Fig. 5 together with the experimental data points. The Langmiur equation represents the better fit of experimental data than the Freundlich and Temkin isotherm equation (Table 2).

In order to quantitatively compare the applicability of each isotherm, a standard deviation (S.D.) is calculated as follows [24]:

$$\text{S.D.} = \sqrt{\frac{\sum \left[(q_{e,\exp} - q_{e,\text{cal}})/q_{e,\exp} \right]^2}{n-1}} \tag{4}$$

where n is the number of data points. Table 2 lists the calculated results for each isotherm equation. Three isotherms were used to fit the experimental data. The comparison of the standard deviation of the isotherms should assist in identifying the best fit equation. Since the S.D. method represents the agreement between the experimental data points and models, the S.D. value provides a numerical value to interpret the goodness of fit of a given mathematical model to the data. Table 2 shows that the least values of S.D. are given by Langmuir isotherm.
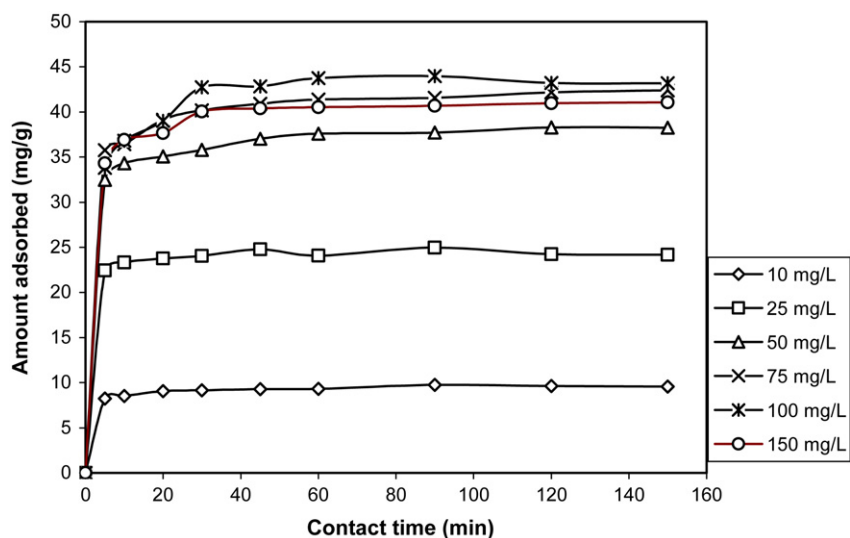
Fig. 4. Effect of contact time on adsorption of copper by valonia tannin resin. Conditions: −100 μm particle size, 1 g/L dose, stirring speed 150 rpm, 298 K temperature and pH 5.

Table 2
Langmuir, Freundlich and Temkin isotherm constants

Langmuir					Freundlich				Temkin			
K_L (L/g)	a_L (L/mg)	Q_0 (mg/g)	r^2	S.D.	K_F (mg/g)/(mg/L)$^{1/n}$	n	r^2	S.D.	B	A (L/g)	r^2	S.D.
44.05	0.995	44.24	0.999	0.052	28.43	9.41	0.80	0.535	5.55	51.76	0.87	0.213

3.5. Kinetic studies

Effects of contact time and initial copper concentration on biosorption of Cu^{2+} by VTR are shown in Fig. 4. The amount of Cu^{2+} biosorbed increased with increase in contact time and reached equilibrium after 60 min. The equilibrium time is independent of initial copper concentration. But in the first 30 min, the initial rate of biosorption was greater for higher initial copper concentration. Because the diffusion of copper ions through the solution to the surface of biosorbent is affected by the copper concentration, the mixing speed is constant. In order to examine the mechanism of biosorption process such as mass transfer and chemical reaction, a suitable kinetic model is needed to analyse the rate data.

The linear pseudo-first-order equation [25] is given as follows:

$$\log(q_{e,1} - q_t) = \log q_{e,1} - \frac{k_1}{2.303}t \tag{5}$$

where q_t and $q_{e,1}$ are the amounts of Cu^{2+} adsorbed at time t and at equilibrium (mmol/g), respectively, and k_1 is the rate constant of pseudo-first-order adsorption process (min^{-1}). Fig. 6 shows a plot of $\log(q_{e,1} - q_t)$ vs. t for biosorption of Cu^{2+} for the pseudo-first-order equation. The values of pseudo-first-order rate constants, k_1, and equilibrium biosorption capacities, $q_{e,1}$, for each initial copper concentration were calculated from slopes and intercepts of straight lines in Fig. 6. The values of pseudo-first-order equation parameters together with correlation coefficients are given in Table 3. The correlation coefficients for the pseudo-first-order equation obtained at all the studied concentrations were low.
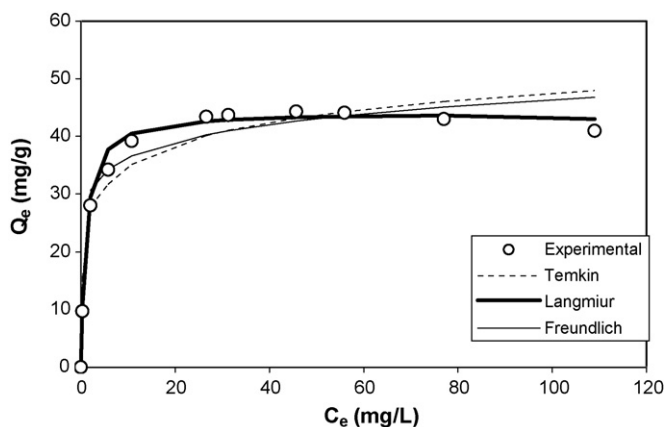

Fig. 5. Equilibrium isotherms of copper on VTR. Conditions: −100 μm particle size, 1 g/L dose, 298 K temperature and pH 5.
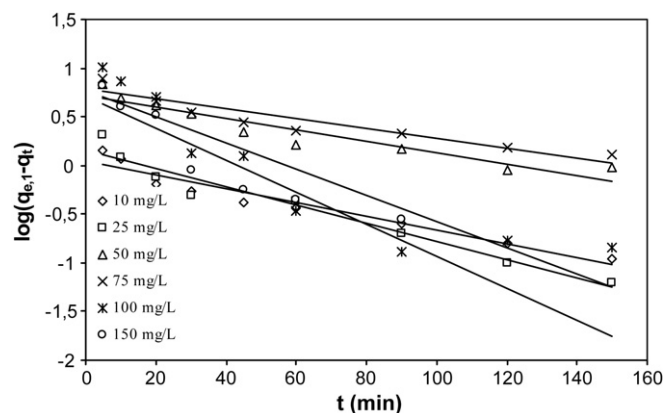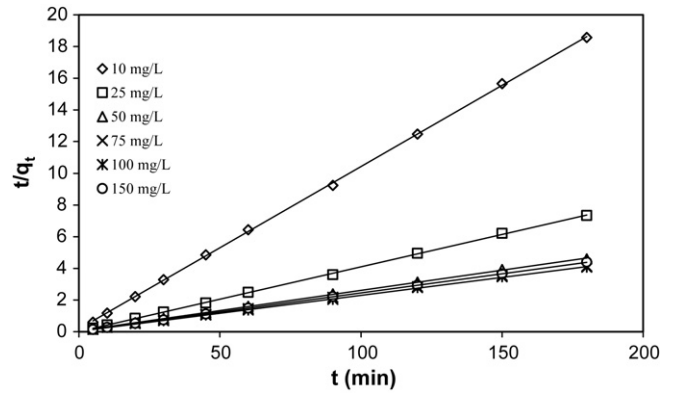

Fig. 6. Plot of the pseudo-first-order equation for the biosorption kinetics of copper on VTR at different initial concentrations.

Table 3
Comparison of the first- and second-order equations, the intraparticle diffusion model and the Elovich equation rate constants, and calculated and experimental q_e values for different initial copper concentrations

C_0 (mg/L)	$q_{e,exp}$ (mg/g)	Pseudo-first-order equation			Pseudo-second-order Equation			Elovich equation			Intraparticle diffusion equation	
		k_1 (min^{-1})	$q_{e,cal}$ (mg/g)	r^2	k_2 (g/mg min)	$q_{e,cal}$ (mg/g)	r^2	α (mg/g min)	β (g/min)	r^2	K_{int} (mg/g min$^{1/2}$)	r^2
10	9.69	0.0163	1.096	0.94	0.0632	9.74	0.999	5.24×10^7	2.434	0.94	0.1987	0.887
25	24.53	0.0216	1.440	0.95	0.1467	24.45	0.999	4.20×10^{18}	1.968	0.68	0.3280	0.757
50	39.21	0.0133	5.151	0.89	0.0112	39.21	0.999	4.87×10^7	0.571	0.97	0.8740	0.966
75	43.69	0.0117	6.117	0.87	0.0092	43.47	0.999	9.55×10^6	0.473	0.96	1.092	0.940
100	44.09	0.0310	5.955	0.82	0.0144	44.24	0.999	2.30×10^5	0.365	0.84	1.815	0.918
150	42.14	0.0380	5.273	0.86	0.0201	41.32	0.999	1.27×10^8	0.555	0.87	1.117	0.887

Fig. 7. Plot of the pseudo-second-order equation for the biosorption kinetics of copper on VTR at different initial concentrations.

Also the theoretical $q_{e,1}$ values found from the pseudo-first-order equation did not give reasonable values. This suggests that this biosorption system is not a first-order reaction.

The linear pseudo-second-order equation [26,27] given by

$$\frac{t}{q_t} = \frac{1}{k_2 q_{e,2}^2} + \frac{1}{q_{e,2}} t \tag{6}$$

where k_2 is the equilibrium rate constant of pseudo-second-order biosorption (g/mg min). Fig. 7 shows typical plots of pseudo-second-order equation for the copper–VTR system as t/q_t vs. t. The straight lines in plot of linear pseudo-second-order equation show good agreement of experimental data with the pseudo-second-order kinetic model for different initial copper concentrations. The values of pseudo-second-order equation parameters together with correlation coefficients are listed in Table 3. The correlation coefficients for the pseudo-second-order equation were 0.999 for all concentrations. The calculated $q_{e,2}$ values also agree very well with the experimental data. This strongly suggests that the biosorption of Cu^{2+} onto VTR is most appropriately represented by a pseudo-second-order rate process.

The adsorption data may also be analyzed using the Elovich equation [28], which has the linear form:

$$q_t = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln t \tag{7}$$

where α is the initial sorption rate constant (mmol/g min), and the parameter β is related to the extent of surface coverage and activation energy for chemisorption (g/mmol). Fig. 8 shows a plot of the Elovich equation for the same data. In this case, a linear relationship
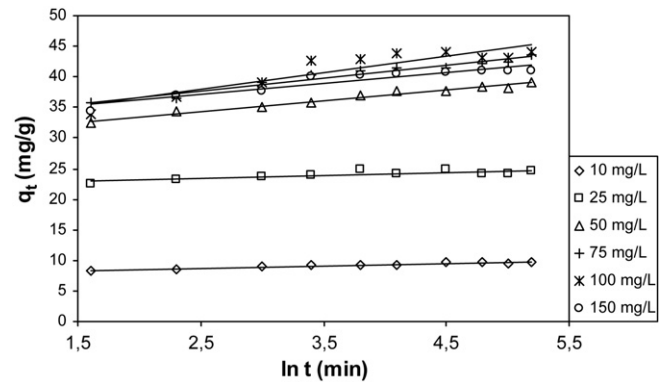
Fig. 8. Plot of the Elovich equation for the biosorption of copper on VTR at different initial concentrations.
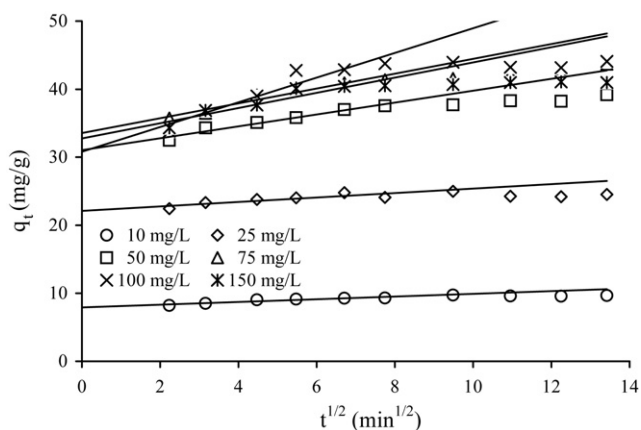
Fig. 9. Plot of the intraparticle diffusion equation for the biosorption of copper on VTR at different initial concentrations.
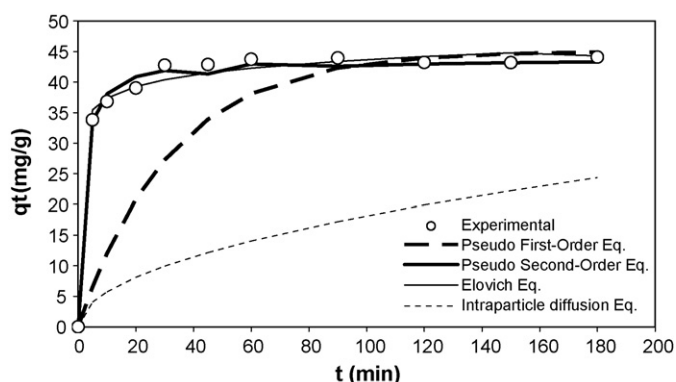

Fig. 10. Comparison between the measured and modelled time profiles for the biosorption of copper on VTR.

was obtained between Cu^{2+} biosorbed, q_t, and $(\ln t)$ over the whole biosorption period, with correlation coefficients between 0.68 and 0.96 for all the lines (Table 3). Also, Table 3 lists the kinetic constants obtained from the Elovich equation. In the case of using the Elovich equation, the correlation coefficients are lower than those of the pseudo-second-order equation. It cannot be used to describe the kinetics of biosorption of Cu^{2+} onto VTR.

Because Eqs. (5) and (7) cannot identify the diffusion mechanisms, the intraparticle diffusion model was also tested [29]. The initial rate of the intraparticle diffusion is the following:

$$q_t = k_{int}t^{1/2} \qquad (8)$$

where k_{int} is the intraparticle diffusion rate constant $(mg/g \, min^{1/2})$. Such plots may present a multilinearity [29], indicating that two or more steps take place. The first, sharper portion is the external surface adsorption or instantaneous adsorption stage. The second portion is the gradual adsorption stage, where intraparticle diffusion is rate-controlled. The third portion is the final equilibrium stage where intraparticle diffusion starts to slow down due to extremely low adsorbate concentrations in the solution.

Fig. 9 shows a plot of the linearized form of the intraparticle diffusion model at all concentrations studied. As shown in Fig. 9, the external surface adsorption (stage 1) is absent. Stage 1 is completed before 5 min, and then the stage of intraparticle diffusion control (stage 2) is attained and continues from 5 min to 60 min. Finally, final equilibrium adsorption (stage 3) starts after 60 min. The copper is slowly transported *via* intraparticle diffusion into the particles and is finally retained in the micropores. In general, the slope of the line in stage 2 is called as intraparticle diffusion rate constant, k_{int}. The rate parameters, k_{int}, together with the correlation coefficients are also listed in Table 3.

A comparison of calculated and measured results for 100 mg/L Cu^{2+} concentration is shown in Fig. 10. As can be seen from Fig. 10, the pseudo-second-order equation provides the best correlation for all of the biosorption process, whereas the Elovich equation also fits the experimental data well. The pseudo-first-order equation and the intraparticle equation do not give good fits to the experimental data for the biosorption of Cu^{2+}.

The Langmuir isotherm and pseudo-second-order kinetic model provide best correlation with the experimental data for the adsorption of copper ions onto VTR for different initial copper concentrations over the whole range studied. Both Langmuir isotherm and pseudo-second-order kinetic model assume that the VTR surface, containing the same reactive –OH groups such as pyrogallol groups binding copper ions, is homogenous and the operating adsorption mechanism is chemisorption involving valency forces through sharing or exchange of electrons between copper and VTR. The homogenous surface of VTR provides multisites to the copper ions. Therefore, the pseudo-second-order equation, which was used in various molecules or ions chemisorption onto homogenous
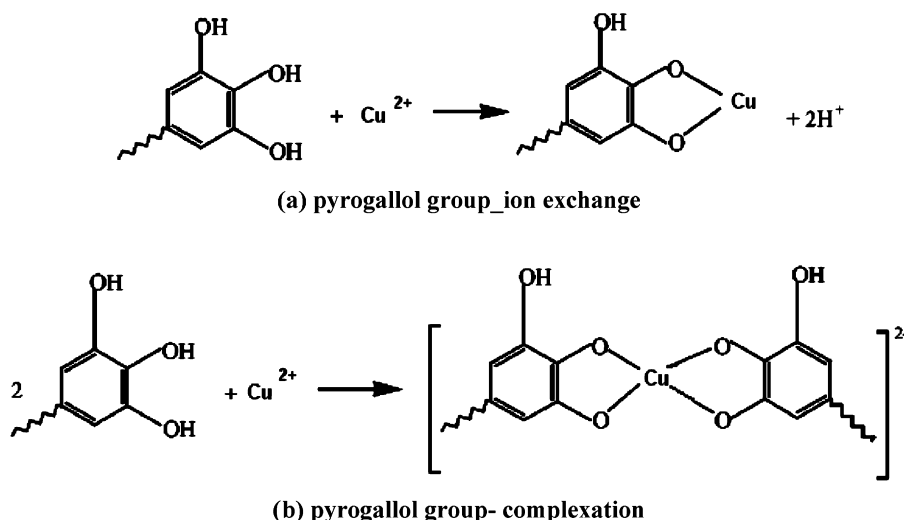

(a) pyrogallol group_ion exchange

(b) pyrogallol group- complexation

Fig. 11. Biosorption mechanisms for the biosorption of Cu^{2+} ion onto VTR.

surface, can be fitted to the adsorption of copper ions very well [30,31].

VTR contains three adjacent hydroxyl groups for binding of metal ions. The mechanism by which metal ions are adsorbed onto different tannin resins has been a matter of considerable debate. Different studies have reached different conclusions. These include ion exchange, surface adsorption, chemisorption, complexation, and adsorption–complexation. It is commonly believed that ion exchange is most prevalent mechanism. Metals react with phenolic groups of the tannin resins to release protons with their anion sites to displace an existing metal. Based on the complex polyhydric phenolic nature of the VTR, a possible mechanism of ion exchange could be considered as Cu^{2+} ion attaching itself to adjacent hydroxyl groups and oxyl groups, which could donate two pairs of electrons to metal ions, forming chelated compounds and releasing two hydrogen ions into solution [32,33].

We believed that the adsorption mechanism may be partly a result of the ion exchange or complexation between the Cu^{2+} ions and phenolic groups on VTR surfaces. Thus, the Cu^{2+} ions/tannin resins reaction may be represented in two ways as shown in Fig. 11 [34]. Adsorption yield at lower pH decreases due to ion exchange equilibrium. H^+ ions release during ion-exchange process. Therefore at lower pH ion exchange equilibrium moves to the left.

4. Conclusion

Equilibrium and kinetic studies were conducted for the biosorption of copper from aqueous solutions onto VTR in the concentration range 10–150 mg/L at pH 5 and 298 K. The equilibrium data have been analysed using Langmuir, Freundlich and Temkin isotherms. The characteristic parameters for each isotherm and related correlation coefficients have been determined. The Langmuir isotherm was demonstrated to provide the best correlation for the biosorption of copper onto VTR. The kinetics of biosorption of copper onto VTR was studied by using pseudo-first- and second-order equations, the intraparticle diffusion model and the Elovich equation. For the copper/VTR system, the pseudo-first-order chemical reaction and the intraparticle diffusion model provides the poorest fit model overall in the rate-controlling step. Also, the calculated $q_{e,1}$ values obtained from the pseudo-first-order equation do not give reasonable values, which are too low compared with experimental q_e values. Although the pseudo-second-order equation can predict the equilibrium capacity of VTR accurately, and related correlation coefficients are 0.999 (Table 3), predicted q_t values deviate from the experimental data points (Fig. 10). The Elovich equation has been successfully used to describe the biosorption of copper ions onto VTR. Although the correlation coefficients for the Elovich equation are lower than those of pseudo-second-order one, the predicted q_t values agree well with the experimental data in the case of the Elovich equation. The adsorption mechanism may be partly a result of the ion exchange or complexation between the Cu^{2+} ions and phenolic groups on VTR surfaces.

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