BIOSORPTION OF COPPER FROM SYNTHETIC WATERS BY USING TOBACCO LEAF: EQUILIBRIUM, KINETIC AND THERMODYNAMIC TESTS

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Abstract. In this study, biosorption of Cu²⁺ ions on to tobacco leaves was investigated. The optimum conditions for biosorption of Cu²⁺ ions onto tobacco leaves were determined: pH – 4.0, temperature – 20 °C, shaking rate – 200 rpm, biosorbent dose – 0.4 g, and initial Cu²⁺ ion concentration – 25 mg/L. The state of equilibrium lasted for 60 minutes. COD, TN and TP analyses were performed to determine the negative impacts of biosorbent on the system. Compliance of equilibrium data of tobacco biosorption of Cu²⁺ ions to Langmuir, Freundlich, Temkin and D–R isotherm models was also investigated. High correlations were achieved in all four isotherm models. Within the scope of kinetic tests, it was observed that biosorption of Cu²⁺ ions with tobacco biosorbent complied with the pseudo second-order kinetic rate constant. FTIR, SEM and EDX analyses were carried out to investigate the surface characteristics and chemical structure of tobacco biosorbent and absorption of Cu²⁺ ions were observed. It was concluded that tobacco leaves are a highly efficient (90.72%) sorbent that can remove Cu²⁺ ions from wastewater.

Keywords: biosorption, heavy metal, tobacco, copper, isotherm, kinetic.

Introduction

Heavy metals are major water pollutants. One of such heavy metals is copper, which can be found as Cu (0), Cu (+) and Cu (2+) in wastewater of various industries, such as metal cleaning and coating, paper, fertilizers etc. Cu (2+) can easily bind to organic and inorganic substances depending on ambient pH levels, which makes it especially dangerous (Hasan et al. 2008). In humans, excessive copper intake may cause serious mucosa irritation, problems of the central nervous system, such as depression, and damage of internal organs, such as liver. The threshold Cu (2+) concentration allowed in drinking water by the World Health Organization is 1.5 mg/L (Kalavathy et al. 2005).

The traditional methods used to remove heavy metals from aqueous ambient are; chemical precipitation, ion exchange, adsorption through active carbon, reverse osmosis, filtration and membrane technologies (Liu et al. 2004). Ambient metals may not be removed fully through these traditional methods. These techniques have also various disadvantages such as high cost equipment and monitoring system requirements, excessive chemical and energy demands, toxic sludge and other waste material creation (Horsfall et al. 2003). Therefore, biotechnological approaches are prominent in recent years as alternative treatment methods (Davis et al. 2003).

Biosorption is a physicochemical process that occurs naturally in certain biomass which allows it to passively concentrate and bind contaminants onto its cellular structure (Churchill et al. 1995). In other words, biosorption is a process that can be explained by adsorption principles and is used to remove heavy metal ions, radioactive elements and dyes through inactive biomass (Özer et al. 2009).

In biosorption, physicochemical principles of metal bindings onto cellular structure are composed of complexion, coordination, chelate formation, ion exchange, adsorption and inorganic micro precipitation processes. In general, ion exchange is the vastly observed mechanism (Volesky 2001). Biosorption process has various advantages such as low operational costs, relative low waste sludge volumes, easy-use of waste materials, seaweeds, natural
substances or raw biosorbents obtained from the other industrial activities (fermentation wastes), recycle of the metals over biosorbent and waste material (Wang, Chen 2006).

In this study, removal of Cu\(^{2+}\) ions from synthetic wastewater by using tobacco leaf through biosorption in an intermittent system was investigated. The effects of ambient pH, initial metal concentration, initial biosorbent concentration, duration of contact, shaking rate and temperature parameters on biosorption were investigated through isotherm, kinetic and thermodynamic assessments. Variations in chemical oxygen demand (COD), total nitrogen (TN) and total phosphorus (TP) values of tobacco-leaf biosorption system were also investigated. Additionally, Fourier Transform Infrared Spectroscopy (FT-IR), Scanning Electron Microscope (SEM) and Energy Dispersive X-Ray (EDX) analyses were also performed over experimental data.

1. Material and methods

1.1. Biosorbent preparation

Tobacco leaves to be used in biosorption tests were supplied from tobacco fields of Pınarbaşı town of Adıyaman Province. The leaves were washed with distilled water until they totally lose their color and dried in an oven at 105°C for 24 hours. Dried leaves were then grinded and made active through keeping inside 1% H\(_2\)SO\(_4\) solution for 24 hours. Activated absorbent washed and filtrated again with distilled water to remove the acid content and dried at 105 °C for 24 hours. The resultant dried tobacco leaves sieved through 0.30 mm sieve and made ready for experiments.

1.2. Preparation of copper solution

Cu\(^{2+}\) solution was prepared by using sufficient (3.929 g) amount of copper sulphate (CuSO\(_4\cdot5\)H\(_2\)O) chemical as to have a solution at 1 L in volume and 1000 mg/L in concentration. Different metal ion concentrations were prepared by making relevant dilutions from the stock solution.

1.3. Experimental setup and method of analysis

Biosorption tests were carried in in 250 mL Erlenmeyer flasks in an intermittent system by using 100 mL copper solution and biosorbent. Wise Shake (SHO–2D) shaking incubator able to operate at constant temperature and shaking rate was used in biosorption tests. The time at which biosorbent added to copper solution is assumed to be t = 0 and analyses were performed at certain intervals. Free Cu\(^{2+}\) ions were read in samples to find out the absorbance at 478 nm wave length and analyzed in a Hach-Lange DR-6000 UV spectrophotometer. During the tests, pH values were read by Thermo Orion – STAR A2145 brand pH meter. The pH levels were adjusted separately with concentrated and diluted H\(_2\)SO\(_4\) and NaOH. Chemical oxygen demand (COD), total nitrogen (TN) and total phosphorus (TP) analyses were performed by using Hach-Lange instant kits. Biosorption capacity (q\(_e\)) and percent removal efficiency (yield) were calculated by using the following equations:

\[
q_e = \frac{V(C_i - C_e)}{X},
\]

\[
(\%) = \left(\frac{(C_i - C_e)}{C_i}\right) \times 100,
\]

where: \(q_e\) (mg/g) is the concentration of the substances bound over adsorbent; \(X\) (g) is the amount of adsorbent used in tests; \(V\) (mL) is the solution volume; \(C_i\) (mg/L) is the initial concentration of the solution; \(C_e\) (mg/L) is the final concentration of the solution.

Compliance of the experimental data with Langmuir, Freundlich, Temkin and D–R isotherm models were investigated. In Langmuir isotherm, adsorption linearly increase with the initial concentration of the adsorbed material (Aksu, Akpınar 2000). Langmuir isotherm equation is provided below (Eq. 3):

\[
q_e = \frac{Q_{\text{max}}K_aC_e}{1 + K_aC_e},
\]

where: \(q_e\) is the amount of adsorbed material over a unit adsorbent (mg/g), \(Q_{\text{max}}\) is Langmuir isotherm constant expressing the maximum amount of material to be adsorbed over the sorbent under operational conditions (mg/g), \(K_a\) is Langmuir constant expressing adsorption energy (L/mg), \(C_e\) is the concentration of material left within the solution following the adsorption (mg/L).

Dimensionless \(R_L\) (dispersion) coefficient is calculated to find out the availability of biosorption (Eq. 4) and a value between 0 and 1 indicates the availability of the adsorption (Başbüyük, Forster 2003):

\[
R_L = \frac{1}{1 + K_aC_e}.
\]

Freundlich isotherm assumes that the amount of adsorbed material increase with the increasing concentration of adsorbed material in solution (Weber 1972). Freundlich isotherm model is expressed by Equation (5):

\[
q_e = K_nC_e^{\frac{1}{n}},
\]

where \(K_n\) and \(n\) are constants depending on temperature, adsorbent and adsorbed material. \(K_n\) is called as adsorption capacity and the term 1/n is called as heterogeneity factor. This isotherm can successfully be used to define heterogeneous systems (Ghoreishi, Haghighi 2003).

According to linearized Freundlich equation (Eq. 6), a graph is drawn with ln Ce versus ln \(q_e\). The term 1/n is
derived from the slope and ln $K_F$ is taken from the interception point on y-axis:

$$\ln q_e = \ln K_F + (1/n) \ln C_e.$$  

(6)

Temkin model was developed by considering adsorption temperature of entire molecules within the layer and linearly decrease because of the area influenced by adsorbent interactions (Kılıç et al. 2011). The equation expressing Temkin isotherm is provided in Eq. (7) (Allen et al. 2004):

$$q_e = \frac{RT}{b} \ln\left(A \cdot C_e\right).$$  

(7)

where: $R$ is gas constant (J/mol K), $T$ is temperature (K), and $A$ is Toth constant (dm$^3$/g). When this equation is linearized and the term $(RT/b)$ in this equation is expressed as $B$, Equation (8) is obtained. $B$ is related to adsorption temperature of Temkin isotherm constant (Allen et al. 2003):

$$q_e = B \ln A + B \ln C_e.$$  

(8)

The constants obtained from Langmuir and Freundlich isotherms do not provide any information about the physical and chemical characteristics of biosorption. However, average adsorption energy ($E$) calculated with D–R isotherm developed by Dubinin and Radushkevich (Dubinin, Radushkevich 1947) provide information about physical and chemical characteristics of the sorption (Ceyhan, Baybaş 2001). D–R isotherm is expressed by Equation (9) provided below (Sarı et al. 2008; Malik et al. 2005):

$$\ln q_e = \ln q_{\text{max}} - \beta e^2.$$  

(9)

The amount adsorbed ($q_e$; mol/g) is related to maximum sorption capacity ($q_{\text{max}}$, mol/g), average adsorption energy ($E$) and relevant activity coefficient ($\beta$; mol$^{-1}$/F) and is a function of Polanyi potential ($e$). The Polanyi potential ($e$) is calculated by using Equation (10) (Sarı et al. 2008):

$$e = RT \ln \left[1 + \frac{1}{C_e}\right].$$  

(10)

Maximum holding capacity $q_{\text{D},\text{R}}$ and $\beta$ can be calculated from the $q_e$–$e^2$ graph of the model drawn by the experimental data. Adsorption energy ($E$; kJ/mol) is calculated by using the Equation (11) (Sarı et al. 2008):

$$E = \frac{1}{\sqrt{2\beta}}.$$  

(11)

1.4. Biosorption kinetics

Kinetic tests were performed at pH levels of 2–3–4–5 for 1–60 minutes to determine the relations of Cu$^{2+}$ ion biosorption onto tobacco sorbent with duration of contact at different pH levels. Compliance of the resultant data with the pseudo first-order and second-order kinetic models was assessed. The kinetic models and expressions used in these tests are provided below:

Pseudo First-Order Kinetic Model: Pseudo first-order rate equation was derived by Lagergren and rate equation is provided below (Ho, Chiang 2001):

$$\log\left(q_e - q_t\right) = \log(q_e) - \frac{k_1}{2.303} \cdot t,$$  

(12)

where: $k_1$ is rate constant (1/min), $q_e$ is adsorption capacity (mg/g), $q_t$ is adsorbed material concentration at time $t$ (mg/g).

When the graph of $\log(q_e - q_t)$ versus $t$ is drawn according to Eq. (12), the slope of the line provides $k_1/2.303$ and y-axis interception point provides $\log(q_e)$. Relevant calculations are then performed to find $k_1$, and $q_e$ values.

Pseudo Second-Order Rate Equation: The pseudo second-order rate equation developed by Ho in 1995 expressed independency of the rate from adsorbent concentration and dependency to adsorption capacity at solid phase and time (Ho, Wang 2004). Pseudo second-order rate equation is provided in Eq. (13) (Ip et al. 2010):

$$\frac{t}{q_t} = \frac{k_1}{q_e^2} + \frac{1}{q_e} \cdot t,$$  

(13)

where: $k_2$ is pseudo second-order rate constant (g/mg-min), $q_t$ is the amount of adsorbed material at equilibrium (mg/g), $q_e$ is the material concentration adsorbed at time $t$ (mg/g). When the graph of $(t/q_t)$ vs $t$ is drawn according to equation, slope of the line provides $1/q_e$ and y-axis interception point provides $1/(k_2q_e^2)$ value.

Inter-Particle Diffusion (Weber-Morris) Model: In case the diffusion mechanism is not explained clearly by the pseudo first and second-order equations, kinetic results are tried to be explained by inter-particle diffusion model (Kılıç et al. 2011). Inter-particle diffusion rate equation is provided in Eq. (14) (Ghasemi et al. 2012):

$$q_t = k_{\text{id}} t^{0.5} + C,$$  

(14)

where: $k_{\text{id}}$ is inter-particle diffusion constant (mg·g$^{-1}$·min$^{-0.5}$), $t$ is time (minute), $C$ is the thickness of boundary layer in adsorption duration (Polat, Aslan 2014). When the graph of $qt$ versus $t^{0.5}$ is drawn, the slope of the line provides $k_{\text{id}}$ adsorption constant.

1.5. Thermodynamic tests

Thermodynamics allows the researchers to gain knowledge about thermal events accompanying chemical reactions, thermal characteristics of reaction materials, especially about entropy and enthalpy, general criteria about volition of reactions and equilibrium (Pahlavanzadeh
et al. 2010). Thermodynamic parameters are provided in Eqs 15–16:

\[
\Delta G^0 = \Delta H^0 - T \Delta S^0,
\]

where: \(\Delta G^0\): Gibbs free energy (kJ/mol), \(\Delta H^0\) is enthalpy exchange (kJ/mol), \(\Delta S^0\) is entropy exchange (kJ/mol K), \(T\) is absolute temperature (Kelvin):

\[
\ln K_c = \frac{\Delta G^0}{R} - \frac{\Delta H^0}{RT}.
\]

Gibbs free energy value of adsorption process carried out at a certain temperature is calculated with \(K_c\) by using the equation \(\Delta G^0 = -RT \ln K_c\) \((R = 8.314 \text{ J/mol K})\). Then the graph of \(\ln K_c\) versus \(1/T\) is drawn and \(\Delta H^0\) and \(\Delta S^0\) can be calculated by using the slope and interception point. \(K_c\) is the ratio of adsorbed \(\text{Cu}^{2+}\) concentration to residual \(\text{Cu}^{2+}\) concentration in solution.

Sorption experiments were performed in triplicate and the average values of samples were presented. Also, blank samples (without \(\text{Cu}^{2+}\)) were used to compare the results through all batch procedures. Data presented are the mean values from the experiments, standard deviation (≤2%) and error bars are indicated in figures.

2. Results and discussion

2.1. Biosorbent characterization

FT-IR analyses

In several previous studies, raw biomass and metal-loaded biomass spectrums of Fourier Transform InfraRed (FT-IR) spectrum analyses were compared to explain biosorption process between biomass and metal ions (Pradhan et al. 2007). FT-IR spectrums of tobacco leaves were taken to investigate the changes in functional groups before and after the biosorption of \(\text{Cu}^{2+}\) ions (Fig. 1).

It was observed that wavelength absorbances and intensities of two spectrums obtained before and after biosorption process were different. Absorbances of \(C = O\) strains of carboxyl groups over 1614.41 cm\(^{-1}\) and 1434.56 cm\(^{-1}\), assumed to play a role especially in binding \(\text{Cu}^{2+}\) ions, were respectively observed as 1614.48 cm\(^{-1}\) and 1429.52 cm\(^{-1}\) after biosorption process. Such a case indicated the existence of broad-band hydroxyl groups (–OH) observed between 3000–3750 cm\(^{-1}\) (Yazıcı 2007). Right at this strain point, the absorbance value of 3356.75 cm\(^{-1}\) before the biosorption changed to 3291.26 cm\(^{-1}\) after the biosorption. The other bands around 2925 and 2893 cm\(^{-1}\) indicate symmetric strain vibrations in alkyl (–CH\(_3\) or –CH\(_2\)) groups (Majumdar et al. 2008). At this point, the absorbance value of 2920.92 cm\(^{-1}\) changed as 2918.08 cm\(^{-1}\).

The increases and decreases (especially the decreases) in FT-IR spectrums after the adsorption process are considered as the indications of participation of these active groups in adsorption process.

SEM (Scanning Electron Microscope) and EDX analyses

SEM (Scanning Electron Microscope) was used to take SEM images of the sorbent before and after the biosorption process and to determine whether or not \(\text{Cu}^{2+}\) ions are adsorbed onto tobacco biosorbent (Fig. 2).

Color coding of the elements within green rectangular in SEM images (Fig. 2) are presented in Figure 3. As it can be seen from Figure 3, \(\text{Cu}^{2+}\) metal was adsorbed onto biosorbent surface with a red color code.

EDX (Energy dispersive X-ray) detector of SEM device was used to make element analyses of tobacco biosorbent before and after the biosorption and different colors...
were coded (Fig. 4). Figures revealed that copper did not exist in EDX analysis before biosorption. However, EDX analyses after biosorption revealed that copper ions were adsorbed.

2.2. Biosorption equilibrium duration

Initial concentration (Co) was selected as 25 mg/L to determine the equilibrium duration of Cu²⁺ biosorption. Other ambient conditions were set as: biosorbent dose (X) = 0.4 g, shaking rate = 200 rpm, pH = 4. Resultant outcomes are presented in Figure 5.

Results revealed a rapid Cu²⁺ ion binding onto biosorbent during the initial 5 minutes (70%). The highest biosorbent capacity was achieved in 60 minutes. Later on, significant changes were not observed. Therefore, equilibrium duration was determined to be 60 minutes.

2.3. Effects of pH on Cu⁺₂ biosorption

Previous biosorption tests revealed that ambient pH had significant impacts on biosorption capacity (Al-Rub et al. 2004; Keskinkan et al. 2004; Gong et al. 2005; Lodeiro et al. 2005). Tests were carried out in this study with pH values in between 2–5 in 0.5 unit increments.

While the yield was 43% at pH of 2, the value increased to 86% at pH of 3. The sorption capacity (qₑ) was 5.58 at pH of 3.5, whereas the value was 5.72 at pH of 5.

COD analyses were carried out to determine the amount of organic pollutants provided to the ambient with the changing pH levels. Increased COD levels were observed when the pH of the ambient is around 2. However, there were not significant changes in COD levels after the pH level of 2.5. Results revealed that tobacco sorbent increased COD level of the ambient (239–363 mg/L).

2.4. Effects of copper concentration on biosorption

There are several studies in literature indicating increasing biosorption capacities with increasing initial metal concentrations (Gülnaz et al. 2005). Similarly, increased biosorption capacities (qₑ) were observed in the present study with increasing initial Cu⁺² concentrations (Fig. 6a). The highest qₑ value (10.66 mg/g) was observed at initial Cu⁺² concentration of 50 mg/L. The highest removal efficiency at Cu⁺² concentrations of 10–15–20 mg/L was observed as 92%. Although the highest qₑ value was achieved at 50 mg/L, the lowest removal efficiency (85%) was also observed at this concentration.

2.5. Effects of biosorbent quantity

Significant effects of biosorbent quantity on biosorption capacity and yield were reported in previous biosorption studies (Al-Qodah 2006; Ju et al. 2008). The tests were carried out in this study with biosorbent quantities of 1–8 g/L.
to determine the effects of biosorbent quantity on Cu²⁺ ion biosorption onto tobacco sorbent (Fig. 6b). The highest yield at 5–6–7 g/L sorbent rates was observed as 93%. Percent removal at 1 g/L biosorbent rate was determined to be 57% and biosorbtion capacity was determined to be 14.36 mg/g.

Effects of changing biosorbent quantities on COD, TN and TP levels were respectively observed as 88 mg/L, 1.66 mg/L and 0.771 mg/L. Results revealed increasing COD, TN and TP values at 8 g/L biosorbent. The data obtained at different initial Cu²⁺ concentrations varied between 208–235 mg/L with varying temperatures. Significant effects of temperature on organic pollutants released to ambient. COD levels were fitted to Langmuir, Freundlich, Temkin and D–R (Dubinin-Radushkevich) models. The coefficients for these models are provided in Table 1. \( Q_{\text{max}} \) indicates the maximum biosorption capacity of tobacco (mg/g). \( K_a \) is Langmuir constant (L/mg) and indicates affinity of adsorbent related to biosorption enthalpy to biosorbent and the strength of the tie between them. \( K_r \) expresses biosorption capacity (L/g), \( n \) expresses intensity of biosorption. High \( K_r \) and \( n \) values indicate higher affinity of biosorbent to biosorption and desired levels of biosorption process.

### 2.8. Isotherm models

The data obtained at different initial Cu²⁺ concentrations were fitted to Langmuir, Freundlich, Temkin and D–R (Dubinin-Radushkevich) models. The coefficients for these models are provided in Table 1. \( Q_{\text{max}} \) indicates the maximum biosorption capacity of tobacco (mg/g). \( K_a \) is Langmuir constant (L/mg) and indicates affinity of adsorbent related to biosorption enthalpy to biosorbent and the strength of the tie between them. \( K_r \) expresses biosorption capacity (L/g), \( n \) expresses intensity of biosorption. High \( K_r \) and \( n \) values indicate higher affinity of biosorbent to biosorption and desired levels of biosorption process.

<table>
<thead>
<tr>
<th>Model</th>
<th>Equation</th>
<th>Sorption Parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>Langmuir</td>
<td>( q_e = \frac{Q_{\text{max}} K_a}{1 + K_a C_e} )</td>
<td>( R^2 ) 0.995, ( K_a ) (L/mg) 0.213, ( Q_{\text{max}} ) (mg/g) 17.182, ( R_L ) 0.158</td>
</tr>
<tr>
<td>Freundlich</td>
<td>( \ln q_e = \ln K_r + \frac{1}{n} \ln C_e )</td>
<td>( R^2 ) 0.979, ( K_r ) (L/g) 3.361, ( n ) 1.700</td>
</tr>
<tr>
<td>Temkin</td>
<td>( q_e = B \ln A + \frac{B}{C_e} )</td>
<td>( R^2 ) 0.991, ( A ) (L/g) 1.994, ( B ) 3.824</td>
</tr>
<tr>
<td>D–R</td>
<td>( q_e = q_{\text{max}} - \beta e^{\frac{E}{R T}} )</td>
<td>( R^2 ) 0.937, ( \beta ) (mol/L) –0.499, ( q_{\text{max}} ) (mg/g) 9.606, ( E ) (kJ/mol) 1.001</td>
</tr>
</tbody>
</table>

As it can be seen from Table 1, correlation coefficients were relatively high in all models. The highest value was observed in Langmuir isotherm with \( R^2 = 0.995 \). Maximum biosorbent capacity of Langmuir isotherm model was 17.182 mg/g, dimensionless \( R_L \) coefficient was calculated as 0.158. This \( R_L \) value indicated that tobacco is...
It was asserted that entire molecules at adsorption layer of Temkin isotherm decreased linearly with adsorption temperature. In this isotherm model, effects of indirect adsorbed/adsorbed interactions on adsorption isotherms are investigated (Temkin, Phyzev 1940). The highest $R^2$ (0.991) value was also observed in Temkin isotherm model and $B$ Temkin isotherm constant related to adsorption temperature was calculated as 3.824.

In D–R model, adsorption energy ($E$) was calculated as 1.001 kJ/mol, $q_{\text{max}}$ as 9.606 mg/g and $\beta$ value as $-0.499 \text{ mol}^{-1/2}$. Of these values, adsorption energies ($E$) between 8–16 kJ/mol indicated that sorption mainly realized through ion exchange mechanism which is a chemical process. $E$ values lower than 8 kJ/mol indicates physical interactions as the binding mechanisms (Sawalha et al. 2006). In the present study, binding mechanisms may be explained by physical interactions ($E = 1.001 \text{ kJ/mol} < 8 \text{ kJ/mol}$).

### 2.9. Kinetic constants

Kinetic tests were carried out at pH levels of 2–3–4–5 and for durations of 1–60 minutes (Fig. 7). Compliance of data with pseudo first-order (Fig. 8) and pseudo second-order (Fig. 9) kinetic models and inter-particle diffusion model (Fig. 10) were assessed. The pseudo first and second order rate constants ($k_1$ and $k_2$), amount of Cu$^{2+}$ adsorbed by a unit biosorbent at equilibrium ($q_d$, teo), initial sorption rate ($h$; mg/g·dk), inter-particle (Weber-Morris model) diffusion rate constant $k_i$ (mg/g·dk$^{0.5}$) are provided in Table 2.

Previous studies indicated relatively low correlations and high errors for the pseudo first and second-order kinetic models (Ho, McKay 1999). As it can be seen from the Table 2, almost identical values of theoretical and experimental $q_d$ values for the pseudo first and second-order kinetic models indicated a well compliance. While the greatest $k_2$ value was observed at pH of 2, the lowest $k_2$ value was obtained from pH of 3. The highest $R^2$ and sorption rate values at pH 4 and 5 were respectively observed as 0.9999–0.9999 and 3.5442–6.4465 mg/g·dk.

### 2.10. Calculation of thermodynamic parameters

The graph of ln$K_c$ versus $1/T$ for different temperatures is presented in Figure 11 and calculated thermodynamic parameters are provided in Table 3.

A negative Gibbs free energy indicates spontaneous biosorption, a positive value indicates nonspontaneous biosorption and a value of zero indicates equilibrium biosorption (Aksu 2002). In Table 3, Gibss energy of Cu$^{2+}$ ions ($\Delta G^\circ$) was negative ($-\text{} \text{)}$. Negative ($\Delta G^\circ$) indicated spontaneous biosorption.
A positive biosorption enthalpy ($\Delta H^o$) value indicates that the system received energy from an external source, in other words the system was endothermic (Ho 2003). Negative $\Delta S^o$ value indicates metal ion affinity to biosorbent at solid-solution interspace or a more regular state of metal ion over biosorbent surface (Padmavathy 2008).

Comparisons of Cu$^{2+}$ biosorption studies carried out with different sorbents are provided in Table 4.

Table 2. Kinetic constant for biosorption of Cu$^{2+}$ ions onto tobacco

<table>
<thead>
<tr>
<th>pH</th>
<th>$q_{d,teo}$ (mg/g)</th>
<th>$k_1$</th>
<th>$q_{d,teo}$ (mg/g)</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>2.68</td>
<td>0.058</td>
<td>0.558</td>
<td>0.911</td>
</tr>
<tr>
<td>3</td>
<td>5.35</td>
<td>0.123</td>
<td>2.979</td>
<td>0.930</td>
</tr>
<tr>
<td>4</td>
<td>5.67</td>
<td>0.059</td>
<td>1.276</td>
<td>0.927</td>
</tr>
<tr>
<td>5</td>
<td>5.72</td>
<td>0.103</td>
<td>1.166</td>
<td>0.990</td>
</tr>
</tbody>
</table>

Table 3. $K_c$, $\Delta G^0$, $\Delta H^o$ and $\Delta S^o$ values of Cu$^{2+}$ ions at different temperatures

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>$K_c$</th>
<th>$\Delta G^0$ (kJ/mol)</th>
<th>$\Delta H^o$ (kJ/mol)</th>
<th>$\Delta S^o$ (kJ/molK)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>11.3153</td>
<td>-5.91011</td>
<td></td>
<td></td>
</tr>
<tr>
<td>25</td>
<td>9.7759</td>
<td>-5.64866</td>
<td></td>
<td></td>
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<tr>
<td>30</td>
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<td>-5.9668</td>
<td></td>
<td></td>
</tr>
<tr>
<td>35</td>
<td>9.9649</td>
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<td>9.1687</td>
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<td>-5.76439</td>
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<td></td>
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<tr>
<td>45</td>
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<td>-5.47402</td>
<td></td>
<td></td>
</tr>
<tr>
<td>50</td>
<td>7.9285</td>
<td>-5.56009</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 4. Comparison of biosorption studies carried out with various biosorbent/adsorbents

<table>
<thead>
<tr>
<th>$q_e$, mg/g</th>
<th>$X$ (g/L) Cu$^{2+}$ (mg/L)</th>
<th>pH</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Waste eggshell</td>
<td>6.48</td>
<td>0.5–5</td>
<td>15–35</td>
</tr>
<tr>
<td>Lobaria pulmonaria (L.)</td>
<td>65.3</td>
<td>1–50</td>
<td>5–100</td>
</tr>
<tr>
<td>Sawdust</td>
<td>3.89</td>
<td>4</td>
<td>10–200</td>
</tr>
<tr>
<td>Eggshell</td>
<td>34.48</td>
<td>4</td>
<td>10–200</td>
</tr>
<tr>
<td>Sugar cane</td>
<td>3.65</td>
<td>4</td>
<td>10–200</td>
</tr>
<tr>
<td>Eichhornia crassipes</td>
<td>27.7</td>
<td>0.3</td>
<td>2–25</td>
</tr>
<tr>
<td>Waste sludge</td>
<td>19.34</td>
<td>0.1–1</td>
<td>25–300</td>
</tr>
<tr>
<td>S. cerevisiae (maya)</td>
<td>8.25</td>
<td>0.1–1</td>
<td>25–300</td>
</tr>
<tr>
<td>Rhizopus oryzae</td>
<td>34.2</td>
<td>0.1</td>
<td>10–300</td>
</tr>
<tr>
<td>Grass</td>
<td>58.34</td>
<td>0.5–2</td>
<td>10–100</td>
</tr>
<tr>
<td>Mangrov shell</td>
<td>6.95</td>
<td>1–3</td>
<td>10–100</td>
</tr>
<tr>
<td>Lentils shell</td>
<td>15.62</td>
<td>0.5–0.8</td>
<td>100–500</td>
</tr>
<tr>
<td>Wheat shell</td>
<td>11.0</td>
<td>0.5–0.8</td>
<td>100–500</td>
</tr>
<tr>
<td>Brass shell</td>
<td>3.60</td>
<td>0.5–0.8</td>
<td>100–500</td>
</tr>
<tr>
<td>Tobacco leaf</td>
<td>14.36</td>
<td>1</td>
<td>25</td>
</tr>
</tbody>
</table>
Conclusions

The present study revealed that tobacco sorbent could reliably be used to remove Cu\(^{2+}\) ions from aqueous solutions. The following conclusions can be drawn from the present study:

1. COD, TN and TP analyses were carried out at different biosorbent quantities and increasing values were observed with increasing biosorbent quantities.
2. A significant change was not observed in biosorbent capacity after a shaking rate of 100 rpm.
3. The amount of COD released to ambient with temperature was also investigated and significant effects of temperature on COD release were not observed.
4. The data on Cu\(^{2+}\) ion biosorption onto tobacco were applied to Langmuir, Freundlich, Temkin and D–R (Dubinin-Radushkevich) isotherm models. The resultant correlations coefficients were relatively high in all models.
5. Kinetic tests revealed that pseudo second-order kinetic model might better define the biosorption system.

It was concluded in this study that tobacco biosorbent had high Cu\(^{2+}\) removal efficiency (90.72%) but it resulted in organic-originated pollution over biosorption system.

References


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