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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 Cu^{2+} ions on to tobacco leaves was investigated. The optimum conditions for biosorption of Cu^{2+} ions onto tobacco leaves were determined: pH – 4.0, temperature – 20 °C, shaking rate – 200 rpm, biosorbent dose – 0.4 g, and initial Cu^{2+} 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 Cu^{2+} 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 Cu^{2+} 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 Cu^{2+} ions were observed. It was concluded that tobacco leaves are a highly efficient (90.72%) sorbent that can remove Cu^{2+} 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 complexation, 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

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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 toplam 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_2SO_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 ($CuSO_4{\cdot}5H_2O$) 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 – STARA2145 brand pH meter. The pH levels were adjusted separately with concentrated and diluted H_2SO_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:

$$q_e = \frac{V\left(C_o - C_e\right)}{X}; \tag{1}$$

$$\left(E\right)\% = \frac{\left(C_o - C_e\right)}{C_o} \cdot 100, \tag{2}$$

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_o (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):

$$q_e = \frac{Q_{\max} K_a C_e}{1 + K_a C_e}, \tag{3}$$

where: q_e is the amount of adsorbed material over a unit adsorbent (mg/g), $Q_{\max}$ 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 (Başıbüyük, Forster 2003):

$$R_L = \frac{1}{1 + K_a C_o}. \tag{4}$$

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):

$$q_e = K_F C_e^{\left(\frac{1}{n}\right)}, \tag{5}$$

where K_F and n are constants depending on temperature, adsorbent and adsorbed material. K_F 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:

$$\ln q_e = \ln K_F + (1/n)\ln C_e. \quad (6)$$

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):

$$q_e = \left(\frac{RT}{b}\right)\ln\left(A{\cdot}C_e\right), \quad (7)$$

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):

$$q_e = B\ln A + B\ln C_e\ . \quad (8)$$

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):

$$\ln q_e = \ln q_{\max} - \beta\varepsilon^2. \quad (9)$$

The amount adsorbed (q_e; mol/g) is related to maximum sorption capacity ($q_{\mathrm{D-R}}$; mol/g), average adsorption energy (E) and relevant activity coefficient (β; mol^2/J^2) and is a function of Polanyi potential (ε). The Polanyi potential (ε) is calculated by using Equation (10) (Sarı *et al.* 2008):

$$\varepsilon = RTln\left(1+\frac{1}{C_e}\right). \quad (10)$$

Maximum holding capacity $q_{\mathrm{D-R}}$ and β can be calculated from the q_e – ε^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):

$$E = \frac{1}{\sqrt{-2\beta}}\,. \quad (11)$$

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):

$$\log\left(q_e - q_t\right) = \log\left(q_e\right) - \frac{k_1}{2.303}\cdot t\ , \quad (12)$$

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):

$$\frac{t}{q_t} = \frac{k_1}{k_2\left(q_e\right)^2} + \frac{1}{q_e}\cdot t\ , \quad (13)$$

where: k_2 is pseudo second-order rate constant (g/mg·min), q_e is the amount of adsorbed material at equilibrium (mg/g), q_t 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 $1/k(q_e)^2$ 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):

$$q_t = k_{id}(t)0.5 + C, \quad (14)$$

where: k_{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_{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:

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 , \qquad (15)$$

where: ΔG^0: Gibbs free energy (kJ/mol), ΔH^0 is enthalpy exchange (kJ/mol), ΔS^0 is entropy exchange (kJ/mol K), T is absolute temperature (Kelvin):

$$\ln K_c = \frac{\Delta G^0}{R} + \frac{\Delta H^0}{RT} . \qquad (16)$$

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 J/mol K). Then the graph of $\ln K_c$ versus $1/T$ is drawn and ΔH^0 and ΔS^0 can be calculated by using the slope and interception point. K_c is the ratio of adsorbed Cu^{2+} concentration to residual Cu^{2+} concentration in solution.

Sorption experiments were performed in triplicate and the average values of samples were presented. Also, blank samples (without 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 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 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 Cu2+ 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, 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

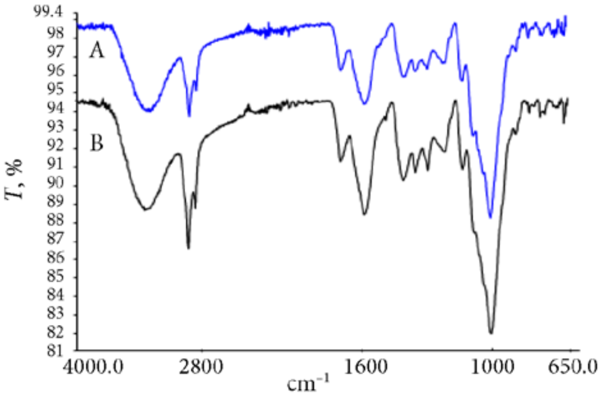

Fig. 1. (a) FT-IR spectrum of tobacco leaf after biosorption and (b) FT-IR spectrum of tobacco leaf before biosorption

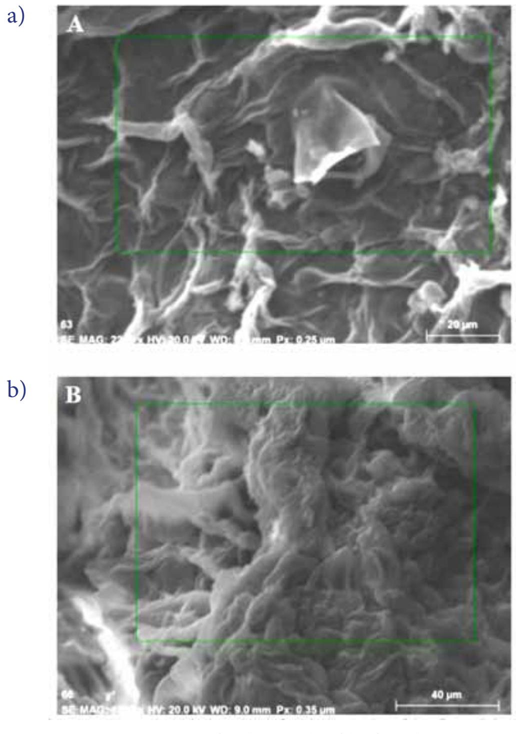

Fig. 2. (a) SEM images of tobacco leaf before biosorption (b) SEM images of tobacco leaf after biosorption

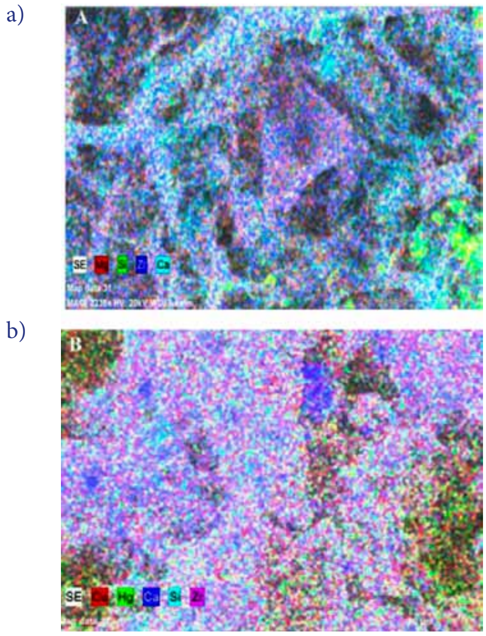

Fig. 3. (a) Element distributions of EDX analysis region before biosorption (b) Element distributions of EDX analysis region after biosorption

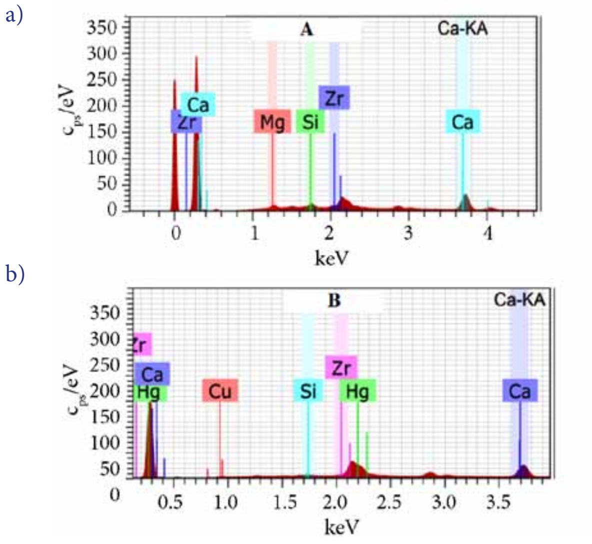

Fig. 4. (a) EDX results of tobacco leaf before biosorption (b) EDX results of tobacco leaf after biosorption

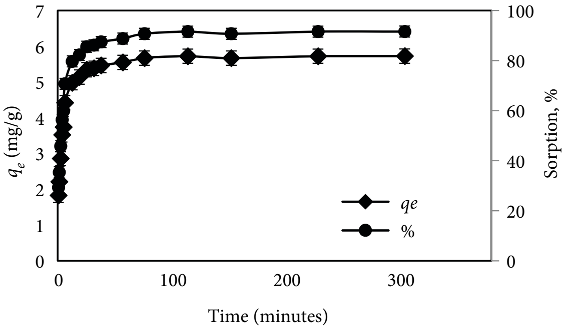

Fig. 5. Variation of biosorption capacity and yield with contact time

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 Cu^{2+} 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 Cu^{2+} 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 (q_e) 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 (q_e) were observed in the present study with increasing initial Cu^{2+} concentrations (Fig. 6a). The highest q_e 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 q_e 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

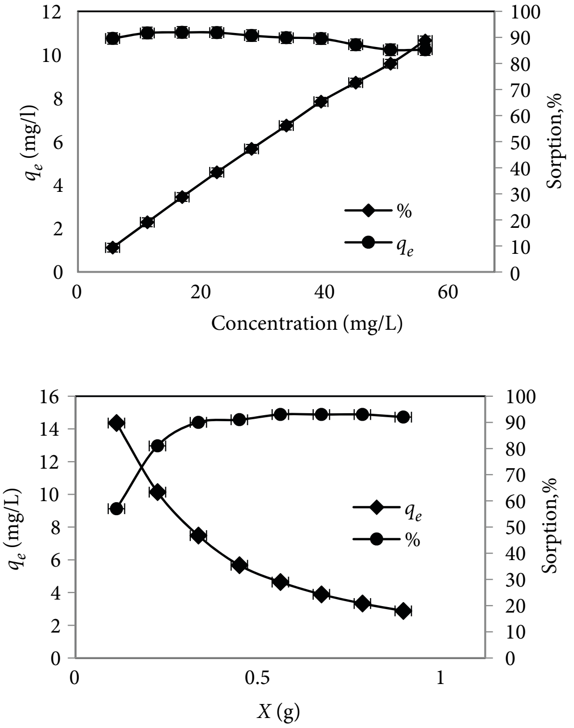

Fig. 6. (a) Effects of initial Cu^{2+} concentrations on biosorption capacity and yield (b) Effects of biosorbent quantity on biosorption capacity and yield

to determine the effects of biosorbent quantity on Cu^{2+} 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 biosorbent capacity was determined to be 14.36 mg/g.

Effects of changing biosorbent quantities on COD, TN and TP levels of the solution were also investigated in this study. COD, TN and TP values at 8 g/L biosorbent quantity were respectively observed as 399 mg/L, 5.37 mg/L and 5.33 mg/L. Same values at 1 g/L biosorbent were respectively determined to be 88 mg/L, 1.66 mg/L and 0.771 mg/L. Results revealed increasing COD, TN and TP levels with increasing biosorbent quantities.

2.6. Effects of shaking rate on biosorption

The yields varied between 90–91% and q_e values varied between 5.60–5.70 mg/g at shaking rates between 100–300 rpm. It was determined that shaking rates over 100 rpm did not have significant impacts on biosorption process (Ho, McKay 1999).

2.7. Effects of temperature on biosorption

Tests were carried out at temperatures in between 20–50 °C to determine the effects of temperature on biosorption. While biosorption capacity was 5.74 mg/g at 20 °C, the value was 5.55 mg/g at 50 °C. Biosorption capacity (q_e) varied between 5.55–5.74 mg/g and yield values varied between 89–91% at temperatures in between 20–50 °C. While some previous studies indicated linear increases in biosorption capacities with increasing temperatures (Polat, Aslan 2014; Martins *et al.* 2004), others indicated decreasing biosorption capacities with increasing temperatures (Aksu 2001; Cruz *et al.* 2004). Some others indicated that temperature did not have any significant effects on biosorption process (Topal *et al.* 2011; Güler, Sarıoğlu 2013). Similarly, significant effects of temperature on biosorption system were not observed in this study.

COD analyses were performed to assess the effects of temperature on organic pollutants released to ambient. Results revealed that temperature did not have any significant impacts of COD release to ambient. COD levels varied between 208–235 mg/L with varying temperatures.

2.8. Isotherm models

The data obtained at different initial Cu^{+2} concentrations were fitted to Langmuir, Freundlich, Temkin and D–R (Dubinin-Radushkevich) models. The coefficients for these models are provided in Table 1. Q_{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_F expresses biosorption capacity (L/g), n expresses intensity of biosorption. High K_F and n values indicate higher affinity of biosorbent to biosorption and desired levels of biosorption process.

Table 1. Sorption parameters and correlation coefficients for different models

Model	Equation	Sorption Parameters	
Langmuir	$1/q_e = (1/Q_{max}K_a)(1/C_e) + (1/Q_{max})$	R^2	0.995
		K_a (L/mg)	0.213
		Q_{max} (mg/g)	17.182
		R_L	0.158
Freundlich	$\ln q_e = \ln K_F + (1/n)\cdot \ln C_e$	R^2	0.979
		K_F (L/g)	3.361
		n	1.700
Temkin	$q_e = B \ln A + B \ln C_e$	R^2	0.991
		A (L/g)	1.994
		B	3.824
D–R	$\ln q_e = \ln q_{max} - \beta\varepsilon^2$	R^2	0.937
		β (mol²/j²)	−0.499
		q_{max} (mg/g)	9.606
		E (kj/mol)	1.001

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

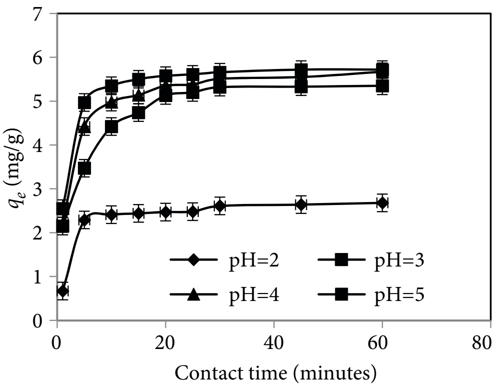

Fig. 7. Variation of biosorption capacity with contact durations at different pH levels

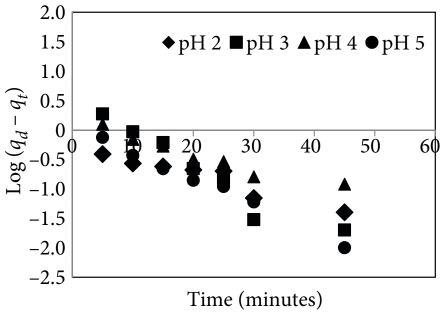

Fig. 8. Graphs of pseudo first – order kinetic models for biosorption of Cu^{2+} ions onto tobacco

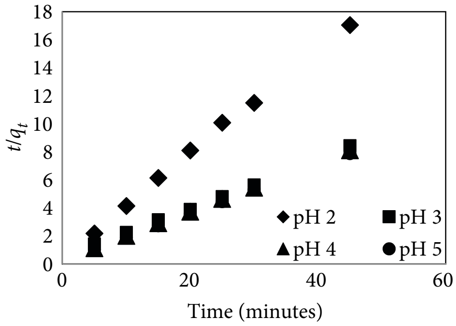

Fig. 9. Graphs of pseudo second-order kinetic models for biosorption of Cu^{2+} ions onto tobacco

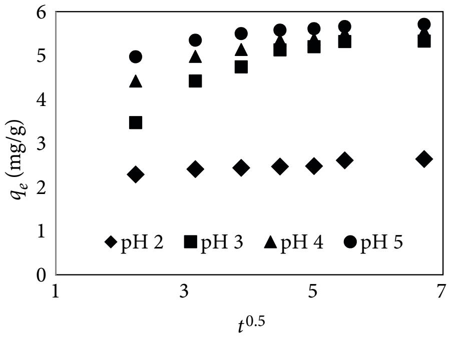

Fig. 10. Graphs of Weber-Morrisi for biosorption of Cu^{2+} ions onto tobacco

an available sorbent for biosorption of Cu^{2+} ions (Doğan, Alkan 2003).

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, $q_{\max}$ as 9.606 mg/g and β value as -0.499 mol^2/j^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 kj/mol < 8 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·dk0.5) 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 (ΔG^0) was negative (–). Negative (–) ΔG^0 indicated spontaneous biosorption.

A positive biosorption entalphy (ΔH^0) value indicates that the system received energy from an external source, in other words the system was endothermic (Ho 2003). Negative ΔS^0 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

pH	$q_{d,den}$	Pseudo-first-order		
		k_1	$q_{d,teo}$ (mg/g)	R^2
2	2.68	0.058	0.558	0.911
3	5.35	0.123	2.979	0.930
4	5.67	0.059	1.276	0.927
5	5.72	0.103	1.166	0.990

pH	Pseudo-second-order			
	k_2	$q_{d,den}$ (mg/g)	h (mg/g·dk)	R^2
2	0.262	2.701	1.879	0.998
3	0.060	5.744	1.718	0.998
4	0.110	5.754	3.544	0.999
5	0.197	5.821	6.447	0.999

Inter-Particle Diffusion (Weber-Morris)			
pH	k_i (mg/g·dk$^{0.5}$)	C	R^2
2	0.077	2.137	0.930
3	0.407	3.004	0.806
4	0.244	4.113	0.850
5	0.155	4.799	0.819

Table 3. K_c, ΔG^0, ΔH^0 and ΔS^0 values of Cu^{2+} ions at different temperatures

Temperature (°C)	K_c	ΔG^0 (kj/mol)	ΔH^0 (kj/mol)	ΔS^0 (kj/molK)
20	11.3153	−5.91011	9.1687	−0.0111
25	9.7759	−5.64866		
30	10.6822	−5.9668		
35	9.9649	−6.14479		
40	9.1626	−5.76439		
45	7.9286	−5.47402		
50	7.9285	−5.56009		

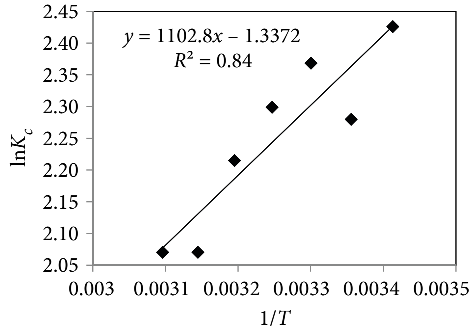

Fig. 11. Van t'Hoff graph of Cu^{2+} biosorption for temperatures in between 20–50 °C

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

	q_e, mg/g	X (g/L)	Cu^{2+} (mg/L)	pH	References
Waste eggshell	6.48	0.5–5	15–35	2–5	Polat, Aslan (2014)
Lobaria pulmonaria (L.)	65.3	1–50	5–100	2–6	Kılıç *et al.* (2014)
Sawdust	3.89	4	10–200	2–6	Putra *et al.* (2014)
Eggshell	34.48	4	10–200	2–6	Putra *et al.* (2014)
Sugar cane	3.65	4	10–200	2–6	Putra *et al.* (2014)
Eichhornia crassipes	27.7	0.3	2–25	2.5–6	Komy *et al.* (2013)
Waste sludge	19.34	0.1–1	25–300	2–7	Güler, Sarıoğlu (2013)
S. cerevisiae (maya)	8.25	0.1–1	25–300	2–7	Güler, Sarıoğlu (2013)
Rhizopus oryzae	34.2	0.1	10–300	3–3,5	Fu *et al.* (2012)
Grass	58.34	0.5–2	10–100	1–8	Hossain *et al.* (2012)
Mangrov shell	6.95	1–3	10–100	2–10	Rozaini *et al.* (2010)
Lentils shell	15.62	0.5–0.8	100–500	2–6	Aydın *et al.* (2008)
Wheat shell	11.0	0.5–0.8	100–500	2–6	Aydın *et al.* (2008)
Brass shell	3.60	0.5–0.8	100–500	2–6	Aydın *et al.* (2008)
Tobacco leaf	14.36	1	25	4	This study

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

Aksu, Z.; Akpınar, D. 2000. Modelling of simultaneous biosorption of phenol and nickel(II) onto dried aerobic activated sludge, *Separation and Purification Technology* 21: 87–99. http://dx.doi.org/10.1016/S1383-5866(00)00194-5

Aksu, Z. 2001. Equilibrium and kinetic modelling of cadmium (II) biosorption by C.vulgaris in a batch systems: effect of temperature, *Seperation and Purification Technology* 21: 285–294. http://dx.doi.org/10.1016/S1383-5866(00)00212-4

Aksu, Z. 2002. Determination of the equilibrium, kinetic and thermodynamic parametres of the biosorption of nickel(II) ions onto Chlorella vulgaris, *Process Biochemistry* 38: 89–99. http://dx.doi.org/10.1016/S0032-9592(02)00051-1

Allen, S. J.; McKay, G.; Porter, J. F. 2004. Adsorption isotherm models for basic dye adsorption by peat in single and binary component systems, *Journal of Colloid and Interface Science* 280: 322–333. http://dx.doi.org/10.1016/j.jcis.2004.08.078

Allen, S. J.; Gan, Q; Matthews, R.; Johnson, P. A. 2003. Comparison of optimised isotherm models for basic dye adsorption by kuzdu', *Bioresour Technology* 88(2): 143–52. http://dx.doi.org/10.1016/S0960-8524(02)00281-x

Al-Rub, F. A. A.; El-Naas, M. H.; Benyahia, F.; Ashour, I. 2004. Biosorption of nickel on blank alginate beads, free and immobilized algal cells, *Process Biochemistry* 39: 1767–1773. http://dx.doi.org/10.1016/j.procbio.2003.08.002

Al-Qodah, Z. 2006. Biosorption of heavy metal ıons from aqueous solution by activated sludge, *Desalination* 196: 164–176. http://dx.doi.org/10.1016/j.desal.2005.12.012

Aydın, H.; Buluta, Y.; Yerlikaya, Ç. 2008. Removal of copper (II) from aqueous solution by adsorption onto low-cost adsorbents, *Journal of Environmental Management* 87: 37–45. http://dx.doi.org/10.1016/j.jenvman.2007.01.005

Başıbüyük, M.; Forster, C. F. 2003. An examination of adsorption characteristics of basic dye on to live activated sludge system, *Process Biochemistry* 38: 1311–1316. http://dx.doi.org/10.1016/S0032-9592(02)00327-8

Ceyhan, Ö.; Baybaş, D. 2001. Adsorption of some textile dyes by Hexadecyltrimethylammonium bentonite, *Turk Journal Chemistry* 25: 193–200.

Churchill, S. A.; Walters, J. V.; Churchill, P. F. 1995. Sorption of heavy metals by prepared bacterial cell surfaces, *Journal of Environmental Engineering* 121(10): 706–711. http://dx.doi.org/10.1061/(ASCE)0733-9372(1995)121:10(706)

Cruz, C. V. C; Da Costa, A. C. A.; Henriques, C. A.; Luna, A. S. 2004. Kinetic modelling and equilibrium studies during cadmium biosorption by dead Sargassum sp. biomass, *Bioresource Technology* 91: 249–257. http://dx.doi.org/10.1016/S0960-8524(03)00194-9

Davis, T. A.; Volesky, B.; Mucci, A. A. 2003. Review of the biochemistry of heavy metal biosorption by brown algae, *Water Research* 37: 4311–4330. http://dx.doi.org/10.1016/S0043-1354(03)00293-8

Doğan, M.; Alkan, M. 2003. Removal of methly violet from aqueous solution by perlite, *Journal of Colloid and Interface Science* 267(1): 32–41. http://dx.doi.org/10.1016/S0021-9797(03)00579-4

Dubinin, M. M.; Radushkevich, L. V. 1947. Equation of the characteristic curve of activated charcoal, *Chemistry Zentralblatt* 1: 875.

Fu, Y. Q.; Li, S.; Zhu, H. Y.; Jiang, R.; Yin, L. F. 2012. Biosorption of copper (II) from aqueous solution by mycelial pellets of Rhizopus oryzae, *African Journal of Biotechnology* 11(6): 1403–1411.

Ghasemi, Z.; Seif, A.; Ahmadi, T. S.; Zargar, B.; Rashidi, F.; Rouzbahani, G. M. 2012. Thermodynamic and kinetic studies for the adsorption of Hg(II) by nano-TiO_2 from aqueous solution, *Advanced Powder Technology* 23(2): 148–156. http://dx.doi.org/10.1016/j.apt.2011.01.004

Ghoreishi, S. M.; Haghighi, R. 2003. Chemical catalytic reaction and biological oxidation for treatment of non-biodegradable textile effluent, *Chemical Engineering Journal* 95: 163–152. http://dx.doi.org/10.1016/S1385-8947(03)00100-1

Gong, R.; Ding, Y. D.; Liu, H.; Chen, Q.; Liu, Z. 2005. Lead biosorption by intact and pretreated spirulina maxima biomass, *Chemosphere* 58: 125–130. http://dx.doi.org/10.1016/j.chemosphere.2004.08.055

Güler, U. A.; Sarioglu, M. C. 2013. Mono and binary component biosorption of Cu(II), Ni(II), and Methylene Blue onto raw and pretreated S. cerevisiae: equilibrium and kinetics, *Desalination and Water Treatment* 52 (25–27): 4871–4888. http://dx.doi.org/10.1080/19443994.2013.810359

Gülnaz, O.; Saygideger, S.; Kusvuran, E. 2005. Study of Cu(II) biosorption by dried activated sludge: effect of physicochemical environment and kinetics study, *Journal of Hazardous Materials* B120: 193–200. http://dx.doi.org/10.1016/j.jhazmat.2005.01.003

Hasan, S.; Ghosh, T. K.; Viswanath, D. S.; Boddu, V. M. 2008. Dispersion of chitosan on perlite for enhancement of copper (II) adsorption capacity, *Journal of Hazardous Materials* 152: 826–837. http://dx.doi.org/10.1016/j.jhazmat.2007.07.078

Ho, Y. S.; McKay, G. 1999. Pseudo-second order model for sorption processes, *Process Biochemistry* 34: 451–465. http://dx.doi.org/10.1016/S0032-9592(98)00112-5

Ho, Y. S.; Chiang, C. C. 2001. Sorption studies of acid dye by mixed sorbents, *Adsorption* 7: 139–147. http://dx.doi.org/10.1023/A:1011652224816

Ho, Y. S. 2003. Removal of copper ions from aqueous solution by tree fern, *Water Research* 37: 2323–2330. http://dx.doi.org/10.1016/S0043-1354(03)00002-2

Ho, Y. S.; Wang, C. C. 2004. Pseudo-ishotherms for the sorption of cadmium ions onto tree fern, *Process Biochemistry* 39: 759–763. http://dx.doi.org/10.1016/S0032-9592(03)00184-5

Horsfall, M. Jnr.; Abıa, A. A.; Spıff, A. I. 2003. Removal of Cu (II) and Zn (II) ions from wastewater by Cassava (Manihot esculenta Cranz) waste biomass, *African Journal of Biotechnology* 2: 360–364. http://dx.doi.org/10.5897/AJB2003.000-1074

Hossain, M. A.; Ngo, H. H.; Guo, W. S.; Setiati, T. 2012. Adsorption and desorption of copper(II) ions onto garden grass, *Bioresource Technology* 121: 386–395. http://dx.doi.org/10.1016/j.biortech.2012.06.119

Ip, A. W. M.; Barford J. P.; McKay, G. 2010. A comparative study on the kinetics and mechanism of removal of reactive Black 5 by adsorption onto activated carbons and bone char, *Chemical Engineering Journal* 157: 434–442. http://dx.doi.org/10.1016/j.cej.2009.12.003

Ju, D. J.; Byun, I. G.; Park, J. J; Lee, C. H.; Ahn, G. H.; Park, T. J. 2008. Biosorption of a reactive dye (Rhodamine-B) from an aqueous solution using dried biomass of activated sludge, *Bioresource Technology* 99: 7971–7975. http://dx.doi.org/10.1016/j.biortech.2008.03.061

Kalavathy, M. H.; Karthikeyan, T.; Rajgopal, S.; Miranda, L. R. 2005. Kinetic and isotherm studies of Cu(II) adsorption onto H3PO4-activated rubber wood sawdust, *Journal of Colloid and Interface Science* 292: 354–362. http://dx.doi.org/10.1016/j.jcis.2005.05.087

Keskinkan, O.; Göksu, M. Z. L.; Başıbüyük, M.; Forster, C. F. 2004. Heavy metal adsorption properties of submerged aquatic plant (Ceratophyllum demersum), *Bioresource Technology* 92: 197–200. http://dx.doi.org/10.1016/j.biortech.2003.07.011

Kılıç, M.; Apaydın-Varol, E.; Pütün, A. E. 2011. Adsorptive removal of phenol from aqueous solutions on activated carbon prepared from tobacco residues: equilibrium, kinetics and thermodynamics, *Journal of Hazardous Materials* 189: 397–403. http://dx.doi.org/10.1016/j.jhazmat.2011.02.051

Kılıç, Z.; Atakol, O.; Aras, S.; Duman, D. C.; Çelikkol, P.; Emregül, E. 2014. Evaluation of different isotherm models, kinetic, thermodynamic, and copper biosorption efficiency of Lobaria pulmonaria (L.) Hoffm., *Journal of the Air & Waste Management Association* 64(1): 115–123. http://dx.doi.org/10.1080/10962247.2013.831383

Komy, Z. R.; Abdelraheem, W. H.; Ismail, N. M. 2013. Biosorption of Cu^{2+} by Eichhornia crassipes: physicochemical characterization, biosorption modeling and mechanism, *Journal of King Saud University – Science* 25: 47–56.

Liu, H.; Chen, B.; Lana, Y.; Chenga, Y. 2004. Biosorption of Zn(II) and Cu(II) by the indigenous Thiobacillus thiooxidans, *Chemistry Engineering Journal* 97: 195–201. http://dx.doi.org/10.1016/S1385-8947(03)00210-9

Lodeiro, P.; Cordero, B.; Barriada, J. L.; Herrero, R.; Sastre de Vicente, M. E. 2005. Biosorption of cadmium by biomass of brown marine macroalgae, *Bioresource Technology* 96: 1796–1803. http://dx.doi.org/10.1016/j.biortech.2005.01.002

Majumdar, S. S.; Das, S. K.; Saha, T.; Panda, G. C; Bandyopadhyoy, T.; Guha, A. K. 2008. Adsorption behavior of copper ions on Mucor rouxii biomass through microscopic and FTIR analysis, *Colloids and Surfaces B: Biointerfaces* 63: 138–145. http://dx.doi.org/10.1016/j.colsurfb.2007.11.022

Malik, U. R.; Hasany, S. M.; Subhani, M. S. 2005. Sorptive potential of sunflower stem for Cr(III) ions from aqueous solutions and its kinetic and thermodynamic profile, *Talanta* 66: 166–173. http://dx.doi.org/10.1016/j.talanta.2004.11.013

Martins, R. J. E.; Pardo, R.; Boaventura, R. A. R. 2004. Cadmium (II) and zinc (II) adsorption by the aquatic moss Fontinalis antipyretica: effect of temperature, pH and water hardness, *Water Research* 38: 693–699. http://dx.doi.org/10.1016/j.watres.2003.10.013

Özer, A.; Gürbüz, G.; Çalımlı, A.; Körbahtii B. K. 2009. Biosorption of copper(II) ions on Enteromorpha prolifera: Application of response surface methodology (RSM), *Chemical Engineering Journal* 146: 377–387. http://dx.doi.org/10.1016/j.cej.2008.06.041

Padmavathy, V. 2008. Biosorption of nickel(II) ions by baker's yeast: Kinetic, thermodynamic and desorption studies, *Bioresource Technology* 99: 3100–3109. http://dx.doi.org/10.1016/j.biortech.2007.05.070

Pahlavanzadeh, H.; Keshtkar, A. R.; Safdari, J.; Abadi, Z. 2010. Biosorption of nickel(II) from aqueous solution by brown algae: equilibrium, dynamic and thermodynamic studies, *Journal of Hazardous Materials* 175: 304–310. http://dx.doi.org/10.1016/j.jhazmat.2009.10.004

Polat, A.; Aslan, S. 2014. Kinetic and isotherm study of cupper adsorption from aqueous solution using waste eggshell, *Journal of Environmental Engineering and Landscape Management* 22(2): 132–140. http://dx.doi.org/10.3846/16486897.2013.865631

Pradhan, S.; Singh, S.; Rai, L. C. 2007. Characterization of various functional groups present in the capsule of Microcystis and study of their role in biosorption of Fe, Ni and Cr, *Bioresource Technology* 98: 595–601. http://dx.doi.org/10.1016/j.biortech.2006.02.041

Putra, W. P.; Kamari, A.; Yusoff, S. N. M.; Ishak, C. F.; Mohamed, A.; Hashim, N.; Isa, I. M. 2014. Biosorption of Cu(II), Pb(II) and Zn(II) ions from aqueous solutions using selected waste materials: adsorption and characterisation studies, *Journal of Encapsulation and Adsorption Sciences* 4: 25–35. http://dx.doi.org/10.4236/jeas.2014.41004

Rozaini, C. A.; Jain, K.; Oo, C. W.; Tan, K. W.; Tan, L. S.; Azraa, A.; Tong, K. S. 2010. Optimization of nickel and copper ions removal by modified mangrove barks, *International Journal of Chemical Engineering and Applications* 1(1): 84–89. http://dx.doi.org/10.7763/IJCEA.2010.V1.14

Sarı, A.; Mendil, D.; Tuzen, M.; Soylak, M. 2008. Biosorption of Cd(II) and Cr(III) from aqueous solution by moss (Hylocomium splendens) biomass: equilibrium, kinetic and thermodynamic studies, *Chemical Engineering Journal* 144: 1–9. http://dx.doi.org/10.1016/j.cej.2007.12.020

Sawalha, M. F.; Videa, J. R. P.; Gonz´alez, J. R.; Gardea-Torresdey, J.L. 2006. Biosorption of Cd(II), Cr(III), and Cr(VI) by Saltbush (Atriplex canescens) biomass: thermodynamic and isotherm studies, *Journal Colloid Interface Science* 300: 100–104. http://dx.doi.org/10.1016/j.jcis.2006.03.029

Temkin, M. J.; Phyzev, V. 1940. Recent modifications to Langmuir isotherms, *ActaPhysiochim USSR* 12: 217–222.

Topal, M.; Arslan Topal, E. I.; Aslan, S. 2011. Removal of Cu(II) from aqueous solutions by using lemon peel, *Erciyes University of the Journal Institute of Science and Technology* 27(3): 265–270.

Volesky, B. 2001. Detoxification of metal-bearing effluents biosorption for the next century, *Hydrometallurgy* 59: 203–216. http://dx.doi.org/10.1016/S0304-386X(00)00160-2

Wang, J.; Chen, C. 2006. Biosorption of heavy metals by Saccharomyces cerevisiae: a review, *Biotechnology Advances* 24: 427–451. http://dx.doi.org/10.1016/j.biotechadv.2006.03.001

Weber, J. R. 1972. *Physicochemical processes for water quality control.* USA: Willey Interscience.

Yazıcı, H. 2007. *The investigation of the biosorption of Cr and Cu^{2+} ions from aqueous solutions by marrubium globosum ssp. globosum plant*: M. Sc. Thesis. Isparta: Süleyman Demirel University Graduate School of Applied and Natural Sciences Department of Environmental Engineering. 140 p.

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