

USE OF CAROTENOID EXTRACTED TOMATO RESIDUE FOR REMOVAL OF Cu (II) IONS FROM AQUEOUS SOLUTION

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Received: July, 02, 2018

Accepted: April, 03, 2019

Abstract: The purpose of this paper is to tested carotenoid extracted tomato residue as a cheap biosorbent for its ability to remove Cu (II) ions from aqueous solution. Batch experiments were carried out to evaluate the effects of *pH*, agitation speed, biosorbent dosage, initial metal concentration and contact time. The maximum removal efficiency of 89.7 ± 0.14 % was reached at *pH* 6.0 by using of adsorbent dosage $4 \text{ g} \cdot \text{L}^{-1}$, initial metal concentration $40 \text{ mg} \cdot \text{L}^{-1}$, temperature $25 \text{ }^{\circ}\text{C}$, agitation speed 200 rpm and contact time 60 min. Pseudo-first order and pseudo-second order models were applied to describe the obtained kinetic data. The pseudo-second order model provided the best fit for experimental data with coefficient of determination $R^2 = 0.999$. Freundlich and Langmuir isotherm models were used to describe metal adsorption. Equilibrium data agreed well with Langmuir isotherm with $R^2 = 0.970$.

Keywords: *biosorption, copper, water, processed waste, kinetics, isotherms*

INTRODUCTION

Environmental pollution with contaminated industrial wastewaters has become one of the major ecological problems nowadays. The raw and waste waters that consist of heavy metals ought to be treated, because it will harm the ecosystems and public health. Heavy metals are non-degradable and causing various diseases and disorders [1]. Copper (II) has been considered as one of the toxic metals due to its poisonousness to human body and it's abundant and naturally-occurring in the environment. The accumulation of Cu (II) in the human body causes different diseases and toxic effects [2 – 4]. Copper may be found as a contaminant of food, water and drinks since it is a widely used material. There are many actual and potential sources of copper pollution [5]. Therefore, it is necessary to treat the copper contaminated water in order to reduce the environmental and human health risks.

The existing methods used for metal removal from the water could be classified as physical, chemical and biological. Adsorption is one of the successful methods of physicochemical treatment process to remove heavy metals from aqueous solution [6]. In the last decades, there has been a tendency to use natural adsorbents, especially waste materials, because of its low price, large availability, high efficiency, biodegradability and safety. Most of the adsorption studies reported in the literature focused on using plant waste materials [7]. Biosorption may be defined as a process of removing the pollutants from the aqueous solution by biological materials. The mechanisms involved in the process of biosorption include chemical sorption, complex formation, surface adsorption, inner porous adsorption, ion exchange, etc. It has been found that in the cellular and tissue materials exist a large number of functional groups which have ability to bind metal ions [8]. Biosorption of Cu (II) has been described in a wide range of biomass, like microorganisms [9], agricultural wastes and by-products [10 – 19]. Rapid progress by the food industry contributed to abundant solid wastes which in turn have caused a significant disposal problem [20]. For example, tomato processing industry generates a large amount of tomato residues. These waste materials, rich in biologically active substances, are usually used for extraction of tomato carotenoids. However, after the extraction process significant amount of waste residues still remain, thereby creating environmental problems.

Yargıç *et al.* [4] reported for the first time application of tomato industry waste, derived from the tomato paste industry, on removing of Cu (II) ions from aqueous solution. To the best of our knowledge, absorbent prepared from tomato residue after carotenoid extraction of industrial tomato processing waste had not been used for the removal of Cu (II) ions from aqueous solution. Therefore, this study examined the performance of carotenoid extracted tomato residue (CETR), as a cheap biosorbent, for its ability to remove Cu (II) ions from aqueous solution. The effects of pH, adsorbent dosage, agitation speed, contact time and initial metal concentration of copper removal efficiency were determined. The Cu (II) ions biosorption kinetic and equilibrium modeling were carried out.

MATERIALS AND METHODS

Materials

Industrial dried tomato processing waste pomace was obtained from a local industry (Parvomay, Bulgaria) in summer 2017. Immediately after receiving it was ground in laboratory mill (Bosh MKM 6003, Germany) and sieved through a 1.0 mm sieve. The resultant raw material was subjected to organic solvent extraction of carotenoids as follow. Sample was placed in a 250 mL conical glass flask, wrapped with aluminum foil, and stirred in acetone on magnetic stirrer (VELP Scientifica, Italy) and solid to liquid ratio 1:35 ($w \cdot v^{-1}$) in temperature controlled water bath for 90 min at 50 °C. After performed extraction the reaction mixture was vacuum filtered through MN640 de filter paper and the residue obtained was washed twice with distilled water (1:10 w/v) for 10 min at 25 °C under continuously stirring. After filtering through MN640 de filter paper the residue was oven-dried at 60 °C for 2 h. The moisture content of the prepared biosorbent (CETR) was determined by gravimetric method at 105 °C and it was found to be 9.10 ± 0.20 %. Finally, biosorbent was stored in plastic bags for further use.

FT-IR spectroscopy was used for identification of functional groups presented in the raw material and biosorbent. The FT-IR spectra of the samples were collected on Nicolet Avatar 330 FT-IR (Termo Science, USA) spectrophotometer in KBr pellets. The spectra were recorded over a wavenumber range of 4000 – 400 cm^{-1} at 132 scans with a spectral resolution of 4 cm^{-1} .

All reagents used in the experiments were of analytical grade. Stock solution ($1000 \text{ mg} \cdot \text{L}^{-1}$) of Cu (II) was prepared by dissolving of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (Merk) in distilled water. This solution was diluted with distilled water to obtain desired concentrations of working solutions for the batch experiments study. The pH value of the samples was adjusted by adding 0.1 M NaOH or HCl solutions.

Biosorption batch experiments

Biosorption experiments were carried out in 250 mL Erlenmeyer glass flasks with 100 mL volume of Cu (II) solution. Batch experiments were conducted to investigate the effect pH (3.0, 4.0, 5.0 and 6.0), initial Cu (II) concentration (10, 20, 40, 80 and $100 \text{ mg} \cdot \text{L}^{-1}$), agitation speed (100, 150, 200, 250 and 300 rpm), biosorbent dosage (1.0, 2.0, 3.0, 4.0 and $5.0 \text{ g} \cdot \text{L}^{-1}$) and contact time (5 - 90 min). All experiments were carried out at ambient temperature 25.0 ± 0.5 °C.

Analytical methods

For determination of Cu(II) concentration in the solutions before and after biosorption, samples were vacuum filtered (MN640 de filter paper) and filtrate was analyzed spectrophotometrically at 600 nm by the method with cuprizone reagent [21, 22], following the procedure described by [23].

The metal uptake q ($\text{mg} \cdot \text{g}^{-1}$) was determined by employing the mass balance. If C_0 and C_e are the initial and final metal concentration ($\text{mg} \cdot \text{L}^{-1}$), respectively; V (L) is the initial volume of Cu (II) solution and m (g) is the mass of biosorbent material, the equilibrium metal uptake q_e ($\text{mg} \cdot \text{g}^{-1}$) can be calculated as (1):

$$q_e = \frac{(C_0 - C_e) \cdot V}{m} \quad (1)$$

The performance of biosorption was evaluated in terms of its removal efficiency as RE (%), estimated by the following equation (2):

$$RE = \frac{(C_0 - C_t)}{C_0} \cdot 100 \quad (2)$$

where C_t is the Cu (II) concentration at time t .

Kinetic study

Kinetic study was carried out to determine the equilibrium time of Cu (II) biosorption. Batch kinetic experiments were carried out at pH 6.0 and 25.0 ± 0.5 °C. For this purpose, 0.4 g of biosorbent were contacted with 100 mL of copper (II) aqueous solution with initial metal concentration $40 \text{ mg} \cdot \text{L}^{-1}$ in 250 mL Erlenmeyer glass flasks on a magnetic stirrer at 200 rpm. At different time intervals ranging from 5 to 90 min the concentrations of copper (II) in the treated solutions were determined as described in analytical methods. Two different kinetic models were used to model experimental data. The pseudo-first-order Lagergren model is expressed as (3):

$$\frac{dq}{dt} = K_{1,ads} (q_e - q) \quad (3)$$

where: q_e ($\text{mg} \cdot \text{g}^{-1}$) and q are amounts of adsorbed metal ions on the biosorbent at the equilibrium and any time t , respectively; and $K_{1,ads}$ is the Lagergren rate constant of the first-order biosorption (min^{-1}). The model is based on the assumption that the rate is proportional to the number of free site [24, 25].

Integrating Eq. (3) between the limits, $t = 0$ to $t = t$ and $q = 0$ to $q = q$ yields the linearized version of this model (4):

$$\log(q_e - q) = \log q_e - \frac{K_{1,ads} \cdot t}{2.303} \quad (4)$$

Linear plots of $\log(q_e - q)$ versus t were plotted to evaluate this kinetic model and to determine rate constant and q_e from the slope and intercept, respectively.

The pseudo-second-order model is based on the assumption that biosorption follows a second-order mechanism, whereby the rate of sorption is proportional to the square of the number of unoccupied sites [24, 25] (5):

$$\frac{dq}{dt} = K_{2,ads} (q_e - q)^2 \quad (5)$$

where: $K_{2,ads}$ is the rate constant of second-order biosorption ($\text{g} \cdot \text{mg}^{-1} \cdot \text{min}^{-1}$). Integrating Eq. (5) from $t = 0$ to $t = t$ and $q = 0$ to $q = q$ and linearization yields (6):

$$\frac{t}{q} = \frac{1}{K_{2,ads} \cdot q_e^2} + \frac{t}{q_e} \quad (6)$$

The parameters q_e and $K_{2,ads}$ are calculated from the slope and the intercept of the plot t/q versus t . It is not necessary to independently determine q_e to apply this model.

Isotherm study

Equilibrium sorption experiments were performed as follow. Biosorbent (0.4 g) were exposed to 100 mL copper (II) solution with an initial concentrations from 10.0 to 100.0 $\text{mg}\cdot\text{L}^{-1}$ at constant pH 6.0, agitation time 200 rpm and ambient temperature 25.0 ± 0.5 °C for 24 h in order to reach equilibrium. Sorption isotherm is plotted of the sorbate uptake (q_e) versus the equilibrium concentration of the residual sorbate remaining in the solution (C_e).

Isotherm study is important to establish the most appropriate correlations for the equilibrium data of the system for optimizing the adsorption process. The Freundlich and the Langmuir isotherms were used to correlate the equilibrium data for Cu (II) removal [4].

The Freundlich isotherm which has been widely used in correlating equilibrium data can be expressed by the following linearized logarithmic form (7):

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (7)$$

where: q_e ($\text{mg}\cdot\text{g}^{-1}$) is the amount of Cu (II) removed per unit mass of the adsorbent, C_e ($\text{mg}\cdot\text{L}^{-1}$) is the residual Cu (II) concentration of the aqueous solution, K_F and n are Freundlich constants and measures of adsorption capacity and adsorption intensity, respectively. A higher n value (lower value of $1/n$) implies stronger sorbent-pollutant interaction whereas $1/n$ equal to 1 indicates linear adsorption leading to identical adsorption energies for all sites [24].

The Langmuir isotherm is based on three assumptions: namely adsorption is limited to monolayer coverage, all surface sites are alike and only can accommodate one adsorbed atom and the ability of a molecule to be adsorbed on a given site is independent of its neighboring sites occupancy [24].

This isotherm can be described by the following linearized form (8):

$$\frac{1}{q_e} = \left(\frac{1}{K_L q_{\max}} \right) \frac{1}{C_e} + \frac{1}{q_{\max}} \quad (8)$$

where: q_e ($\text{mg}\cdot\text{g}^{-1}$) is the equilibrium amount of Cu (II) adsorbed, C_e ($\text{mg}\cdot\text{L}^{-1}$) is the equilibrium concentration of Cu (II) in the solution, q_{\max} ($\text{mg}\cdot\text{g}^{-1}$) and K_L ($\text{L}\cdot\text{mg}^{-1}$) are Langmuir constants representing the maximum monolayer adsorption capacity for the solid phase loading and the energy constant related to the heat of adsorption, respectively.

For the Langmuir isotherm analysis, the separation factor (R_L) value is of special importance (9):

$$R_L = \frac{1}{1 + K_L C_0} \quad (9)$$

where: C_0 ($\text{mg}\cdot\text{L}^{-1}$) is the initial Cu (II) concentration in the solution.

Four possibilities for the separation factor values which determine the isotherm type: $R_L = 0$ (irreversible isotherm), $R_L = 1$ (linear isotherm), $R_L > 1$ (unfavorable isotherm) and $R_L < 1$ (favorable isotherm) have been reported [26].

Statistical analysis

All experiments were run in triplicate. The data were analyzed and presented as mean values. Statistical techniques, incl. ANOVA and Duncan's Multiple Range Test, were applied to determine the significant differences at 95 % confidence ($P < 0.05$) level.

RESULTS AND DISCUSSION

FT-IR characterization of raw material and biosorbent

The FTIR spectra of raw material (*a*) and biosorbent (*b*) contained bands (Figure 1) typical for cell-wall polysaccharides. The broad bands at 3400 cm^{-1} were assigned with stretching vibrations of intramolecular and intermolecular H-bridge between the OH groups. Yargiç *et al.* [4], who investigated copper (II) biosorption from aqueous solution by chemically-treated tomato waste explained that these bands revealed a presence of alcohol, phenol or carboxylic acids. Bands at 2926 and 2854 cm^{-1} were due to asymmetric and symmetric stretching of aliphatic methyl and methylene groups. Our observation in this spectral region was the same with [4] and [27] whose experiment were connected with tomato cell walls. Chylińska *et al.* [27] reported the CH stretching region from 2700 cm^{-1} to 3060 cm^{-1} with characteristic for carbohydrate, intense bands assigned to pectin, hemicellulose and cellulose were observed at 2952 , 2930 , 2897 cm^{-1} , respectively. In our spectra the carbonyl ester (C=O) stretching vibration occurred at 1745 cm^{-1} . According to [27] band of $\nu(\text{C}=\text{O})$ vibration at 1742 cm^{-1} could be assigned to both hemicellulose and pectin presented in cell wells of tomato, as this ester band allows us to distinguish between hemicellulose and cellulose.

However, in our spectrum of biosorbent the frequency of this band lower to 1737 cm^{-1} which can be explained possible changes in methyl ester groups or COOH groups after extraction process. The band at 1635 cm^{-1} could be also assigned with adsorption of water in tomato wastes (Figure 1a). The other new band at 1516 cm^{-1} was also appeared after treatment of tomato waste as bio absorbent. Moreover, characteristic bands for protein content in samples were observed as amide bands, amide I at 1656 cm^{-1} (C=O stretching), amide II at 1541 cm^{-1} (N—H bending) and amide III at 1240 cm^{-1} (C—N stretching) [28]. Additionally, the 1630 cm^{-1} was also assigned to the C=C stretch in the coniferaldehyde unit of lignin [29]. Bands at 1241 cm^{-1} were assigned to CH=CH stretching and also bands between 1100 and 1000 cm^{-1} were detected to C—O stretching vibrations of lignin [4].

The OH in-plane bend coupled with the methine deformation (1455 cm^{-1}) [29]. In addition, we found the bands typical for cellulose 1160 cm^{-1} , 1316 cm^{-1} , 1370 cm^{-1} and 1424 cm^{-1} , and xylan 1734 cm^{-1} , 1460 cm^{-1} and 1240 cm^{-1} in both raw tomato waste material (a) and biosorbent, as previously reported [30].

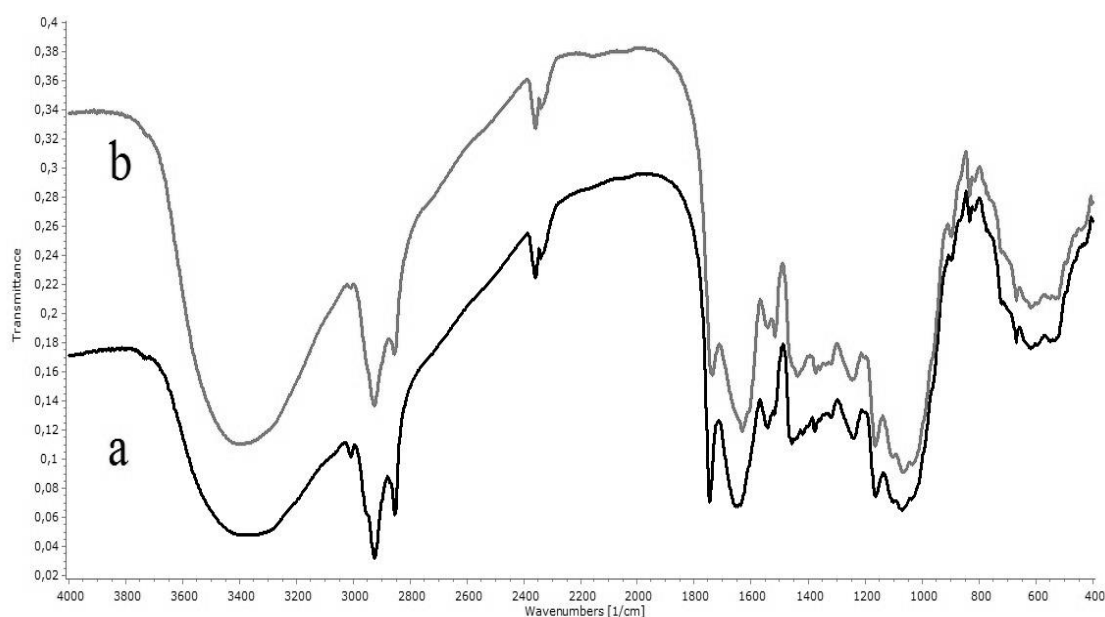


Figure 1. FT-IR spectra of raw material (a) and biosorbent (b)

The band at 1340 cm^{-1} peak was associated with methine deformation coupled with methylene wag [29]. According to [31] the region between 1200 and 900 cm^{-1} showed intense bands attributed to $\nu(\text{C-O-C})$ that is typical for various carbohydrates and organic acids, abundantly distributed groups in tomatoes. Our bands coincided with reported regions for tomato FT-IR spectra that contained bands at $1100 - 400\text{ cm}^{-1}$ (C-C and C-C-H stretching), and $1170 - 1115\text{ cm}^{-1}$ (C-O-C stretching of glycoside bonds) [31]. The bands from 1220 to 1011 cm^{-1} corresponded to vibrations of $-\text{C-O-C}$ glycoside ring bond, C-O stretching in COOH and O-H bending. Bands at 1378 and 971 cm^{-1} also indicated the presence of cellulose in the sample [27]. The region between $892 - 895\text{ cm}^{-1}$ was typical for C-anomeric groups stretch, C1-H-deformation; ring stretches. The bands at 897 and 834 cm^{-1} showed the presence of β -glucopyranose and some xylopyranoses, respectively [32] that are building blocks of cellulose and hemicelluloses, respectively.

Effect of pH

The hydrogen ion concentration (pH) of aqueous solutions is an important parameter since it affects the surface charge of the sorbent and the degree of speciation and ionization of the sorbate during adsorption [1]. It is important, from a practical point of view, to determine the optimal pH at which the investigated system could reach its maximum removal efficiency [33]. To investigate the effect of pH on biosorption, the experiments were conducted at Cu (II) concentration of $40\text{ mg}\cdot\text{L}^{-1}$, biosorbent dosage $1.0\text{ g}\cdot\text{L}^{-1}$ for 1 h contact time under constant temperature of $25\text{ }^{\circ}\text{C}$ and agitation speed of 100 rpm. The pH effect on the efficiency of the Cu (II) removal from the aqueous solution by the biosorbent studied is illustrated in Figure 2. Removal efficiency increased when solution pH increased. Similar results were reported for chemically-treated tomato waste, but in this research authors reported maximum removal efficiency at pH 8.0 [4]. However, we found that the maximum removal efficiency ($70.7 \pm 0.52\%$) was reached at pH 6.0. Experiments were restricted to pH 6.0 as at higher pH > 6.5 the

Cu (II) ions precipitates out in form of insoluble $\text{Cu}(\text{OH})_2$ and the removal may not only be due to adsorption [34 – 37].

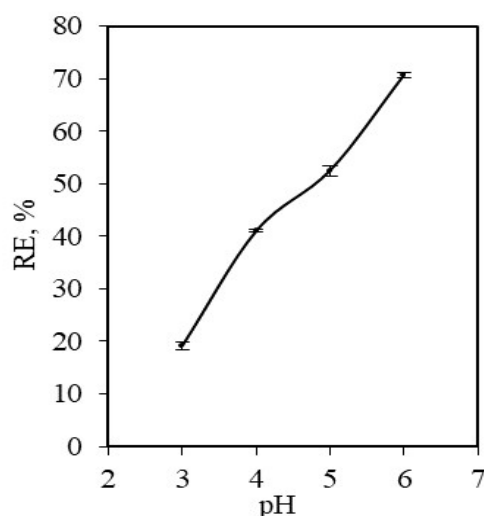


Figure 2. Effect of pH on the removal efficiency of Cu (II) from aqueous solution by CETR (initial metal concentration $40 \text{ mg}\cdot\text{L}^{-1}$, biosorbent dosage $1 \text{ g}\cdot\text{L}^{-1}$, 25°C , 1 h, agitation speed 100 rpm)

Effect of agitation speed

The effect of agitation speed on removal efficiency of Cu (II) ions was studied by varying the speed from 100 to 300 rpm. The results obtained are presented in Figure 3. The removal efficiency increased with increase agitation speed and the maximal efficiency was at 200 rpm, then the efficiency sharply decreased. The increase of agitation speed improves the diffusion of metal ions towards the surface of the adsorbent. However, speed higher than 200 rpm, lowered the metal removal, not allowing enough time to metal ions to adsorb [38].

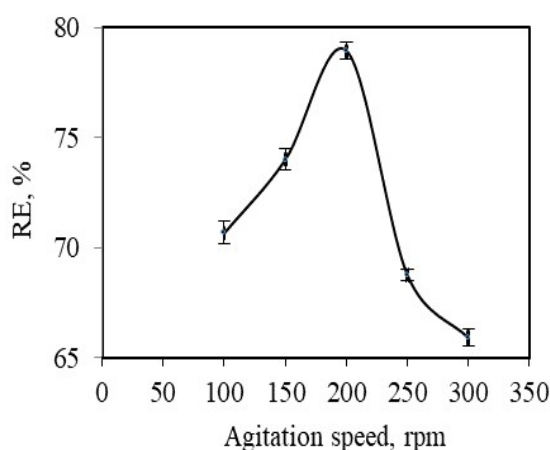


Figure 3. Effect of agitation speed on the removal efficiency of Cu (II) from aqueous solution by CETR (initial metal concentration $40 \text{ mg}\cdot\text{L}^{-1}$, pH 6.0, biosorbent dosage $1 \text{ g}\cdot\text{L}^{-1}$, 25°C , 1 h)

Effect of adsorbent dosage

The biosorbent dosage is other major factor that affects biosorption efficiency. To investigate the effect of the biosorbent dosage on biosorption, the experiments were conducted at a constant Cu (II) concentration of $40 \text{ mg}\cdot\text{L}^{-1}$, and samples with different biosorbent dosages ranging from 1.0 to $5.0 \text{ g}\cdot\text{L}^{-1}$ were used under constant temperature of 25°C , pH 6.0, contact time of 1 h and agitation speed of 200 rpm. The data are presented in Figure 4. The Cu (II) removal efficiency was found to increase from $78.9 \pm 0.38 \%$ to $86.5 \pm 0.50 \%$ with the increase in the biosorbent dosage from 1.0 to $4.0 \text{ g}\cdot\text{L}^{-1}$, which can be explained by an increase in the contact surface available for adsorption and the presence of a larger number of groups binding the Cu (II) ions.

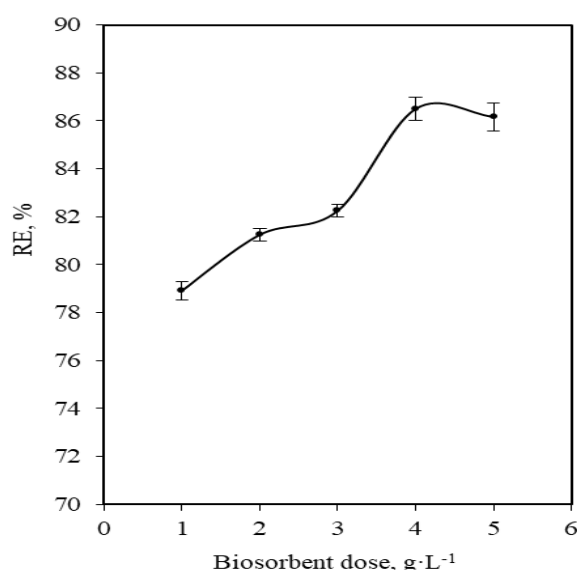


Figure 4. Effect of biosorbent dosage on the removal efficiency of Cu (II) from aqueous solutions by CETR (initial metal concentration $40 \text{ mg}\cdot\text{L}^{-1}$, pH 6.0, 25°C , 1 h, agitation speed 200 rpm)

The application of higher biosorbent dosages above $4.0 \text{ g}\cdot\text{L}^{-1}$ did not lead to significant increase ($P < 0.05$) in metal removal efficiency due to possible aggregation of the biomass particles and disturbance of the mass transfer of the metal ions from the liquid to solid phase of the system. Yargıç *et al.* [4] also found that a dose of $4 \text{ g}\cdot\text{L}^{-1}$ of chemically-treated tomato waste could be sufficient for the optimum removal of Cu (II) ions from aqueous solution.

Effect of initial metal concentration

The initial metal concentration is essential for the biosorption duration and the rate of metal removal from aqueous solutions. Results on the influence of the initial Cu (II) concentration in the solution on metal removal efficiency are presented in Figure 5. The highest level of removal efficiency ($86.4 \pm 0.38 \%$) was established at an initial metal concentration of $40 \text{ mg}\cdot\text{L}^{-1}$. The removal efficiency of Cu (II) ions from aqueous solutions by the biosorbent used was found to decrease with the increase in the initial

metal concentration over 40 mg·L, probably due to the restriction or saturation of the biosorbent active groups. As regards the metal uptake, results indicated that Cu (II) biosorption capacity of CETR increased as the initial metal ion concentration increased. Increasing the initial concentration is an important driving force to overcome all mass transfer resistance of metal ion between the aqueous and solid phases, thus increased the uptake [37]. Similar results have been reported for biosorption of Cu (II) ions from aqueous solutions by chemically-treated tomato waste [4].

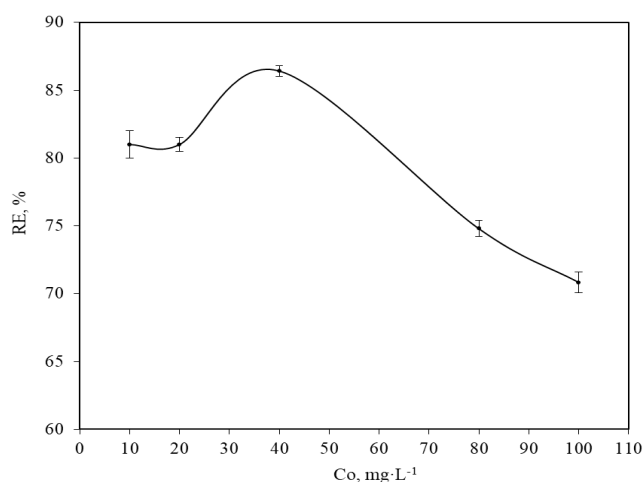


Figure 5. Effect of initial metal concentration (C_0 , $\text{mg}\cdot\text{L}^{-1}$) on the removal efficiency of Cu (II) from aqueous solutions by CETR (biosorbent dosage $4\text{ g}\cdot\text{L}^{-1}$, pH 6.0, $25\text{ }^\circ\text{C}$, 24 h, agitation speed 200 rpm)

Adsorption kinetics data

The contact time of the biosorbent and sorbate also has a significant impact on the biosorption efficiency. To investigate the effect of contact time on biosorption, the experiments were carried out at Cu (II) concentration of $40\text{ mg}\cdot\text{L}^{-1}$, biosorbent dosage $4.0\text{ g}\cdot\text{L}^{-1}$, pH 6.0, under constant temperature of $25\text{ }^\circ\text{C}$ and agitation speed of 200 rpm. The biosorption kinetic of Cu (II) ions on CETR indicated that the biosorption process could be divided into two main stages: the initial rapid stage where biosorption was fast, and a second slow stage which refers to gradual biosorption before Cu (II) uptake reached equilibrium. A similar phenomenon was observed by others as well [39, 40]. The time taken to reach equilibrium was 60 min and the maximum removal efficiency was 89.7 %. The kinetic data were fitted onto two kinetic models of pseudo-first and pseudo-second order with the obtained parameters listed in Table 1. A linearized plot for the pseudo first-order Lagergren and pseudo second-order models are shown in Figures 6 and 7.

Table. 1 Kinetic parameters for the biosorption of Cu (II) ions onto CETR

Initial Cu(II) ions concentration (C_0), [$\text{mg}\cdot\text{L}^{-1}$]	Experimental metal uptake (q_e^{exp}), [$\text{mg}\cdot\text{g}^{-1}$]	Pseudo-first order model			Pseudo-second order model		
		q_e^{cal} , [$\text{mg}\cdot\text{g}^{-1}$]	$K_{1\text{ads}}$, [min^{-1}]	R^2	q_e^{cal} , [$\text{mg}\cdot\text{g}^{-1}$]	$K_{2\text{ads}}$, [$\text{g}\cdot\text{mg}^{-1}\cdot\text{min}^{-1}$]	R^2
40	8.97	2.171	0.045	0.850	9.17	0.071	0.999

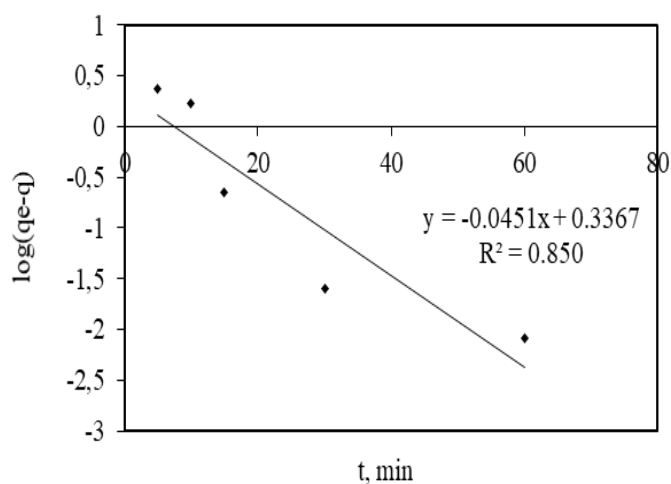


Figure 6. Linearized pseudo first-order model for the biosorption of Cu (II) ions onto powder of CETR (initial metal concentration $40 \text{ mg}\cdot\text{L}^{-1}$, biosorbent dosage $4 \text{ g}\cdot\text{L}^{-1}$, pH 6.0, 25°C , agitation speed 200 rpm)

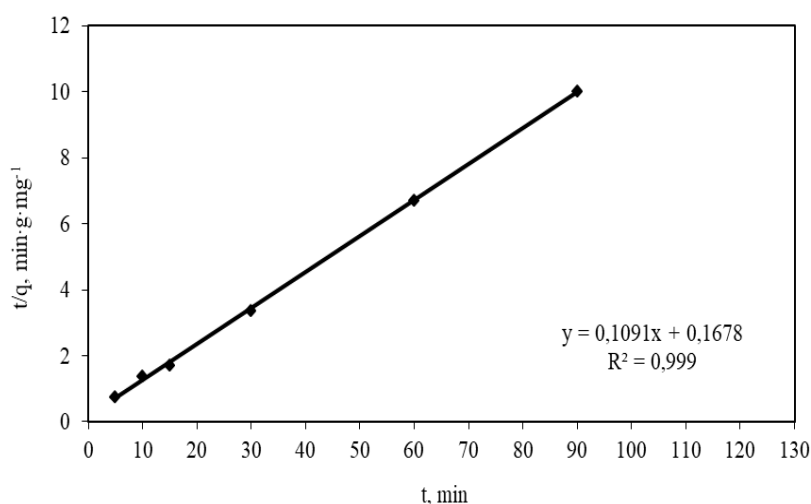


Figure 7. Linearized pseudo second-order model for the biosorption of Cu (II) ions onto powder of CETR (initial metal concentration $40 \text{ mg}\cdot\text{L}^{-1}$, biosorbent dosage $4 \text{ g}\cdot\text{L}^{-1}$, pH 6.0, 25°C , agitation speed 200 rpm)

When the fitting results were compared, the pseudo-second model seems to give better representation of the experimental data. Moreover, the calculated values of the equilibrium metal uptake (q_e^{cal} , $\text{mg}\cdot\text{g}^{-1}$) from the pseudo-second model agree quite well with the experimentally obtained values (q_e^{exp} , $\text{mg}\cdot\text{g}^{-1}$).

Equilibrium isotherms data

The study of equilibrium adsorption isotherms is of fundamental importance in the design of adsorption systems since it provides the basic physicochemical data for evaluation of the sorption process suitability for removal of different pollutants, incl. heavy metals, from aqueous solutions. Adsorption equilibrium is usually described by an isothermal equation whose parameters express the surface properties and the affinity

of the adsorbent at a given temperature and pH of the solution. Therefore, an adequate mathematical description of the experimentally obtained equilibrium isotherm is essential for the efficient design of the system. In this work, two of the most frequently used models were tested [41].

The results of the application of the Langmuir and Freundlich linearized models to the experimental data on the biosorption of Cu (II) ions from aqueous solutions by the investigated biosorbent under equilibrium conditions are presented in Figures 8 and 9. Model parameters were determined using a linear regression toolbox in Microsoft Excel software. They are summarized in Table 2.

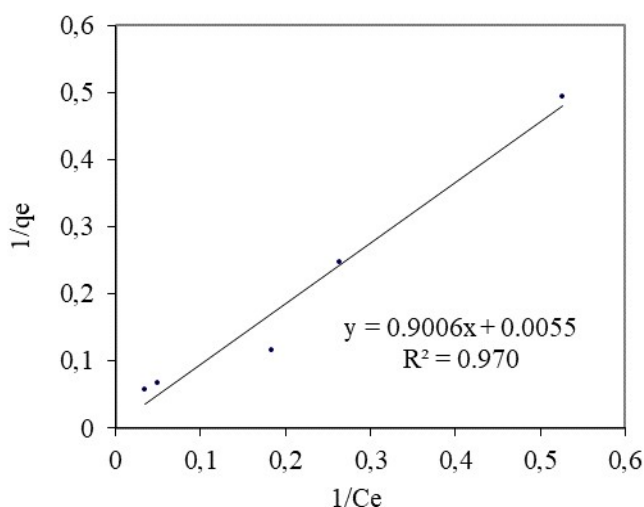


Figure 8. Linearized Langmuir isotherm for biosorption of Cu (II) ions onto powder of CETR (biosorbent dosage $4 \text{ g} \cdot \text{L}^{-1}$, pH 6.0, 25°C , 24 h, agitation speed 200 rpm)

Table 2. Isotherm parameters of Langmuir and Freundlich models for biosorption of Cu (II) ions onto powder of CETR

Langmuir isotherm model			Freundlich isotherm model		
q_{\max} [$\text{mg} \cdot \text{g}^{-1}$]	K_L [$\text{L} \cdot \text{mg}^{-1}$]	R^2	$1/n$	K_F [$\text{mg} \cdot \text{g}^{-1}$]	R^2
181.82	0.0061	0.970	0.7621	1.548	0.923

The regression parameters and coefficients of determination (R^2) presented in table 2 indicate that the Langmuir and Freundlich models fitted very well the experimental data with the calculated coefficients of determination (R^2) of 0.970 and 0.923, respectively.

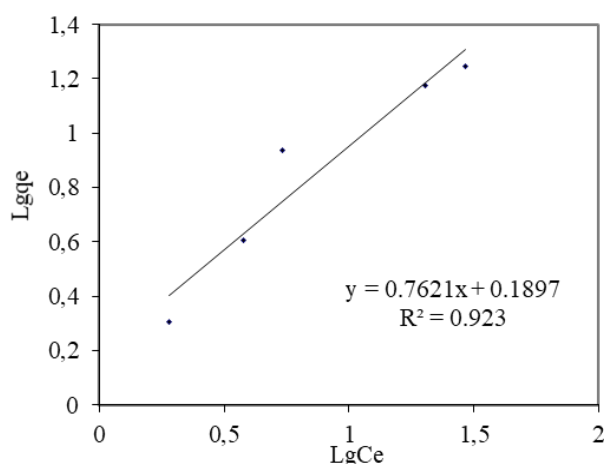


Figure 9. Linearized Freundlich isotherm for biosorption of Cu (II) ions onto powder of CETR (biosorbent dosage $4 \text{ g}\cdot\text{L}^{-1}$, pH 6.0, 25°C , 24 h, agitation speed 200 rpm)

Similar results were reported for Cu (II) biosorption by chemically-treated tomato waste [4]. The R^2 value for the Langmuir model was slightly higher than that for the Freundlich model, and the Langmuir adsorption capacity (q_{max}) was larger than that obtained by application of the Freundlich model (K_F). The Langmuir R_L values were found to range between 0 and 1, which confirmed that the biosorbent prepared from the CETR was favorable for biosorption of Cu (II) ions under the conditions applied in this study. The metal adsorption capacity is one of the main factors influencing the acceptability of biosorbents. In comparison with chemically-treated industrial tomato waste biosorbent (TWB), which has been reported the first time for Cu (II) biosorption by Yargiç *et al.* [4], the CETR showed higher adsorption capacity ($181.82 \text{ mg}\cdot\text{g}^{-1}$) than that reported for TWB ($34.48 \text{ mg}\cdot\text{g}^{-1}$).

In regards to waste discharging problem, further research has to be carried out for regeneration of CETR retained Cu (II) and for determination of the reused cycles of the biosorbent.

CONCLUSION

The present research showed that powder of CETR was a potential biosorbent for removal of Cu (II) ions from aqueous solutions. The batch study parameters, such as the solution pH, agitation speed, biosorbent dosage, contact time and initial Cu (II) concentration, were found to be important for the biosorption process. Finally, the experimental results of the present study indicated that maximum removal efficiency of Cu (II) ions of $89.7 \pm 0.14 \%$ was obtained at pH 6.0, agitation speed 200 rpm, adsorbent dosage $4 \text{ g}\cdot\text{L}^{-1}$, initial metal concentration $40 \text{ mg}\cdot\text{L}^{-1}$, temperature 25°C and contact time 60 min. The pseudo-second order kinetic model was found to fit well the experimental data with $R^2 = 0.999$, and the adsorption isotherm followed the Langmuir model ($R^2 = 0.970$). However, more detailed studies are needed to clarify the Cu (II) biosorption mechanism by powder of CETR.

ACKNOWLEDGMENTS

The authors wish to thank to the University of Food Technologies-Plovdiv and the Bulgarian canning plant “Bulcons-Parvomay JSC” for the experimental support.

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