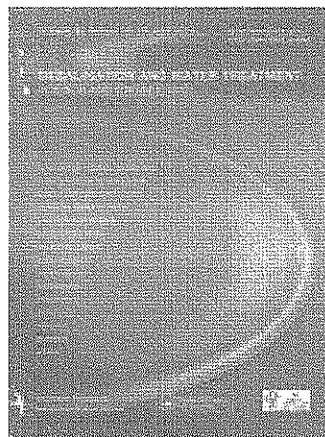


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## Desalination and Water Treatment

Publication details, including instructions for authors and subscription information:

<http://www.tandfonline.com/loi/tdwt20>

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Published online: 31 May 2013.

**To cite this article:** Huseyin Serencam, Duygu Ozdes, Celal Duran & Hasan Basri Senturk (2014) Assessment of kinetics, thermodynamics, and equilibrium parameters of Cu(II) adsorption onto Rosa canina seeds, *Desalination and Water Treatment*, 52:16-18, 3226-3236, DOI: [10.1080/19443994.2013.797377](https://doi.org/10.1080/19443994.2013.797377)

**To link to this article:** <http://dx.doi.org/10.1080/19443994.2013.797377>

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## Assessment of kinetics, thermodynamics, and equilibrium parameters of Cu(II) adsorption onto *Rosa canina* seeds

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Received 2 January 2012; Accepted 10 April 2013

### ABSTRACT

*Rosa canina* seeds (RCS) is considered as a low-cost and promising adsorbent in removal of metal ions; hence, in the present study, we aimed to test the adsorptive removal of Cu(II) ions from aqueous solutions by utilizing RCS in a batch process. After characterization of RCS by using several techniques, the effects of various experimental parameters such as initial pH of aqueous solution, contact time, initial Cu(II) concentration, RCS concentration, temperature, and electrolyte concentration were studied upon the adsorption process. The desorption conditions of Cu(II) ions from the loaded RCS were also evaluated. Maximum Cu(II) adsorption was found to occur at pH 6.0 and the equilibrium was established after 60 min of contact time. The adsorption isotherms were described by means of Langmuir, Freundlich, Temkin, and Dubinin Radushkevich models. The adsorption kinetics were analyzed using pseudo-first-order, pseudo-second-order, Elovich and intraparticle diffusion models and the adsorption data were well described by the pseudo-second-order model. Thermodynamic parameters such as the Gibbs free energy ( $\Delta G$ ), enthalpy ( $\Delta H$ ), and entropy ( $\Delta S$ ) changes were also evaluated and it has been found that the adsorption process was feasible, spontaneous, and endothermic in the temperature range of 278–313 K.

**Keywords:** Adsorption; Removal; *Rosa canina* seeds; Kinetics; Thermodynamics; Equilibrium

### 1. Introduction

Copper can be released into the environment from a variety of industrial applications such as plating, metal finishing, automotive, brass manufacture, electroplating, petroleum refining, tannery, and paint manufacturing [1]. Although the intake of Cu(II) by the humans within the tolerable limits is essential, the excessive intake of it may cause a serious of health problems such as liver and kidney damage, anemia,

immunotoxicity, gastrointestinal, and central nervous system irritation [2]. Also several symptoms have been reported, usually occurring after drinking beverages containing excess Cu(II) ions [3]. According to the World Health Organization drinking water guidelines, the maximum allowable limit for Cu(II) is  $1.5 \text{ mg L}^{-1}$  [4].

Some of the techniques including pH neutralization which is followed by precipitation using various methods, such as lime and peroxide addition, solvent extraction, ion exchange, membrane processes, and

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reverse osmosis have been developed for the removal of heavy metals from waters and industrial wastewaters [5]. However, some of these methods have significant drawbacks such as low efficiency and selectivity, high operating cost, difficult handling, and production of chemical or biological sludge during the process. Although precipitation through neutralization is one of the cost-effective and simple techniques, in order to maintain the pH values at a desired level, excessive amount of alkaline is needed. In addition, this method produces a large amount of metal hydroxide sludge, which is difficult for disposal [6]. Besides them, the adsorption is widely preferred technique for pollutants' removal with selection of a proper sorbent [7–12] due to its simplicity, cheapness, and effectiveness in removing of pollutants from aqueous solutions with very low concentrations [13]. A large variety of adsorbents such as activated carbon fiber [14], immobilized magnetite nanoparticles [15], peat moss [16], activated alumina [17], and magnetic iron oxide [18] have been tested and used for their heavy metal adsorption capability. However, most of them, especially activated carbon, are too expensive and the recovery of the adsorbent particles from the treated water is difficult.

The agricultural by-products are recognized as the most abundant, low-cost and effective adsorbents. Therefore, in this study, *Rosa canina* (commonly known as Dog Rose or Rose Hip) seeds (RCS) were evaluated as a potential adsorbent for Cu(II) removal from aqueous solution. For that purpose after being evaluated the various experimental parameters affecting the adsorption process, in order to clarify the mechanism of the Cu(II) adsorption, the suitability of different kinetic models and isotherm models were investigated. Thermodynamic parameters were also evaluated to decide the spontaneity and thermodynamic feasibility of the adsorption process of Cu(II) onto RCS.

## 2. Materials and methods

### 2.1. Preparation and characterization of RCS

The RCS was used as an adsorbent without any previous physical or chemical pretreatment for the adsorption of Cu(II) ions. It was supplied from Gumussu Herbal Juice Factory in Turkey. This factory processes 100 tons RCS annually and 23 tons of RCS remains as an industrial waste product. The RCS was washed with deionized water several times to remove surface impurities, and then dried in an oven (Nüve FN 400) at 40°C for four days. The dried RCS samples

were ground and sieved to obtain a particle size of <150 µm, and stored in desiccators to be used for all adsorption experiments.

The fourier transform infrared (FTIR) spectra of the RCS and Cu(II) loaded RCS were obtained to determine the ionizable surface functional groups (i.e. carboxyl and hydroxyl) which were able to interact with Cu(II) ions by using Perkin Elmer 1600 FTIR spectrophotometer in the range of 4,000–400 cm<sup>-1</sup>. Scanning electron microscope (SEM) analyses were applied on the RCS and also Cu(II)-loaded RCS by SEM EVO LS15 model apparatus in order to disclose the surface texture and morphology of the adsorbent. The surface acidic functional groups containing oxygen were determined according to Boehm titration [19] and other characterization parameters such as pH value of the RCS, pH of zero charge (pH<sub>pzc</sub>), and moisture content were determined using standard methods [20].

### 2.2. Adsorption experiments

A batch process was performed for the adsorption of Cu(II) ions onto RCS. For preparing different concentrations of the working solutions, 5,000 mg L<sup>-1</sup> of Cu(II) stock solution was prepared by dissolving Cu(NO<sub>3</sub>)<sub>2</sub> in deionized water. A digital pH meter (Hanna pH-211) with a glass electrode was used for the adjustment of the initial pH value of the working solutions to 6.0 by the addition of either dilute HNO<sub>3</sub> or NaOH solutions. For adsorption tests, 10 mL of Cu(II) solution in the concentration range of 60–600 mg L<sup>-1</sup> was added into a polyethylene centrifuge tube. Then 50 mg of RCS (5.0 g L<sup>-1</sup> suspension) was transferred into the solution, and then the mixture was agitated on a mechanical shaker (Edmund Bühler GmbH) at 400 rpm. After reaching the equilibrium (60 min), the suspension was centrifuged at 3,000 rpm for 10 min, and the concentration of the dilute phase was analyzed for the Cu(II) concentration using a flame atomic absorption spectrometer, FAAS (ATI/ Unicam AA-929). The amount of the Cu(II) adsorbed by the RCS was calculated as the following equation:

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

where  $C_0$  (mg L<sup>-1</sup>) is the initial concentration of Cu(II) solution,  $C_e$  (mg L<sup>-1</sup>) is the equilibrium concentration of Cu(II) in aqueous solution,  $V$  (L) is the volume of solution,  $m_s$  (g) is the mass of the RCS, and  $q_e$  (mg g<sup>-1</sup>) is the calculated Cu(II) adsorption amount onto 1.0 g of RCS.

### 3. Results and discussion

#### 3.1. Characterization of RCS

The FTIR spectra of RCS and Cu(II)-loaded RCS are depicted in Fig. 1(a) and (b), respectively. The broadbands observed at 3,418, 2,923, 1,735, 1,622 and 1,522, 1,445 and 1,378, and 1,049  $\text{cm}^{-1}$  are due to stretching vibrations of O–H, C–H (aromatic and aliphatic), C=O, C=C (aromatic), C–H (deformation vibration) and C–O groups, respectively [21]. Although the band intensities decreased in the FTIR spectrum of Cu(II)-loaded RCS, there is no change in the functional groups on its surface.

The SEM micrographs of RCS and Cu(II)-loaded RCS are shown in Fig. 2(a) and (b), respectively. The RCS has heterogeneous pores on its surface where there is a good possibility for Cu(II) trapped and adsorbed. The structure of RCS changed upon Cu(II) adsorption and exhibited a tendency to form agglomerates.

Other characterization parameters such as surface acidic functional groups, self pH value of the RCS, pH of zero charge ( $\text{pH}_{\text{PZC}}$ ), and moisture content are listed in Table 1.

#### 3.2. Effect of initial pH

Because the surface charge of the RCS depends on the pH of the aqueous solutions, the effects of initial

pH on the adsorption of Cu(II) ions onto RCS were evaluated by changing the initial pH over a range of 2.0–7.0. The experiments were conducted with initial Cu(II) concentration of  $100 \text{ mg L}^{-1}$  and RCS concentration of  $5.0 \text{ g L}^{-1}$ . The  $\text{pH}_{\text{PZC}}$  of any adsorbent is a very important characteristic that determines the pH at which the surface has net electrical neutrality [22]. The effects of initial pH can be explained by considering the surface charge of RCS at different pH values. The surface of RCS is negatively charged when pH value is higher than  $\text{pH}_{\text{PZC}}$ , whereas when pH value is lower than  $\text{pH}_{\text{PZC}}$ , the surface charge of RCS becomes positive. Because of the  $\text{pH}_{\text{PZC}}$  value of RCS was found to be 4.01, the Cu(II) ions can bind easily to the surface of RCS, at a pH value of higher than 4.01 (Fig. 3). The maximum adsorption amount was obtained at initial pH 6.0. Therefore, all further adsorption experiments were carried out at initial pH 6.0.

#### 3.3. Effect of contact time and adsorption kinetics

The effect of contact time on the adsorption of Cu(II) ions onto RCS was evaluated in the time range of 5–480 min by using initial Cu(II) concentration of  $100 \text{ mg L}^{-1}$  and RCS suspension of  $5.0 \text{ g L}^{-1}$ . At the initial adsorption phase, since the active adsorption sites were more available and metal ions could interact easily with these sites, the Cu(II) ions uptake was very fast for

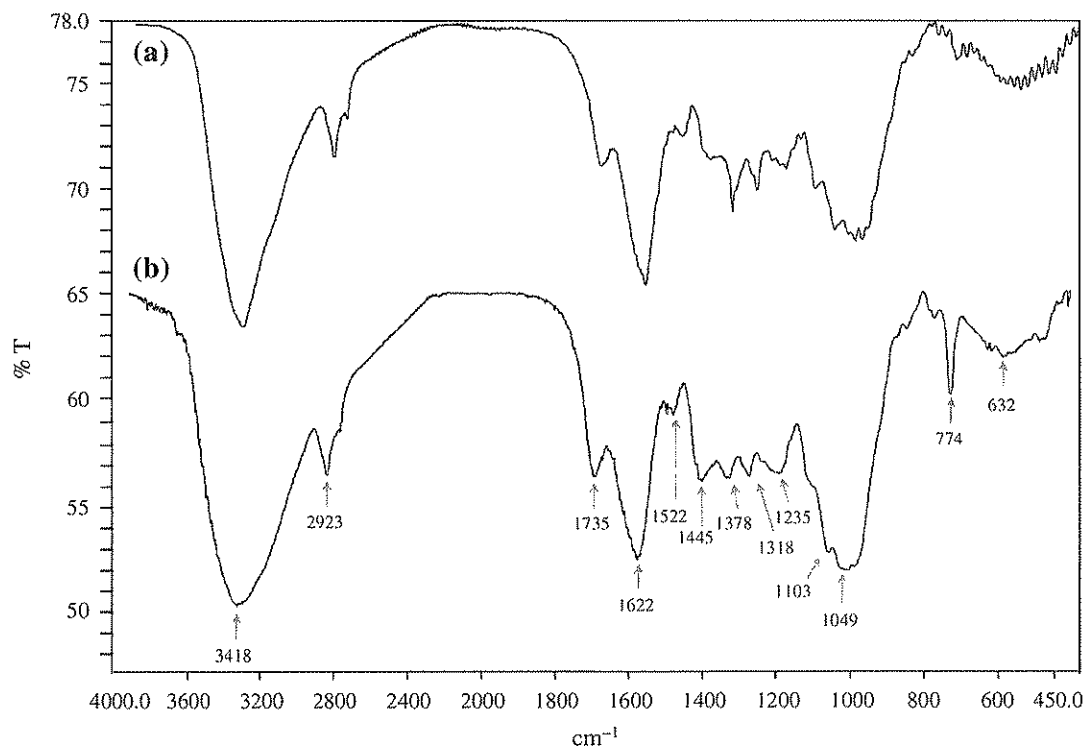


Fig. 1. FTIR spectra of (a) RCS and (b) Cu(II)-loaded RCS.

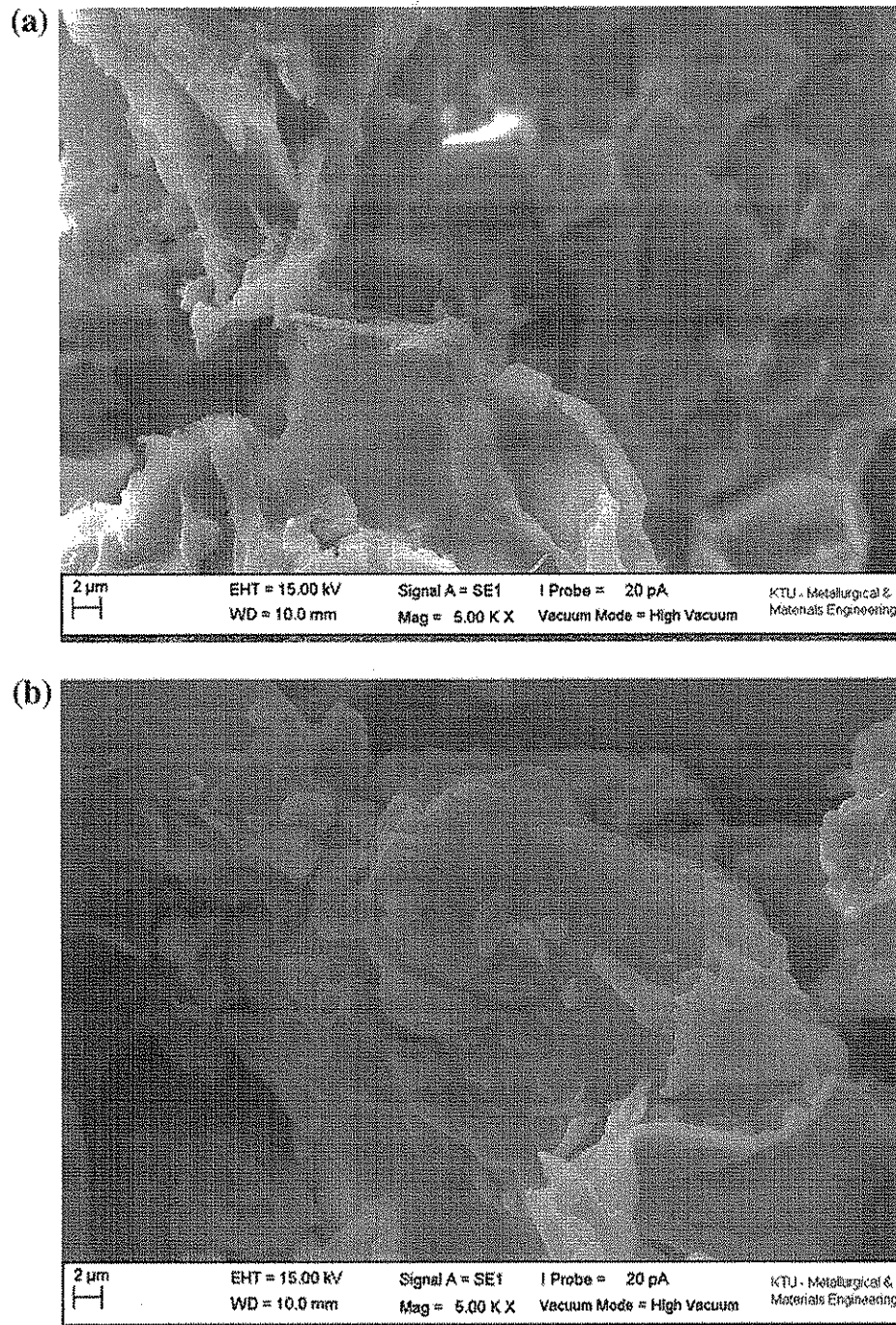


Fig. 2. SEM of (a) RCS and (b) Cu(II)-loaded RCS.

the first 10 min of contact time. Then, the uptake continued at a slower rate and eventually the equilibrium was reached through the saturation of the adsorption sites in 60 min. Hence, further adsorption experiments were carried out for a contact time of 60 min (Fig. 4(a)).

In order to estimate the mechanism of the adsorption process, the pseudo-first-order, pseudo-

second-order, Elovich, and intraparticle diffusion models were applied to the experimental data.

The pseudo-first-order equation can be written as follows [23]:

$$\frac{d_q}{dt} = k_1(q_e - q_t) \quad (2)$$

Table 1  
Characteristics of RCS

|   |       |
|---|-------|
| pH  | 4.40  |
| pH <sub>pzc</sub>                                 | 4.01  |
| Moisture content (%)                              | 12.08 |
| Surface functional groups (mmol g <sup>-1</sup> ) |       |
| Carboxylic  | 1.73  |
| Phenolic  | 0.69  |
| Lactonic  | 3.79  |
| Total acidic value                                | 6.21  |

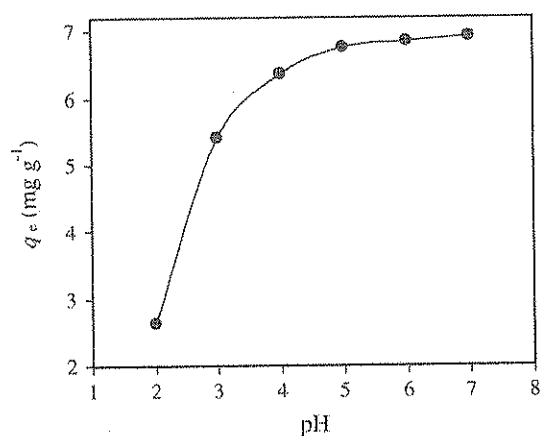


Fig. 3. Effect of initial pH on Cu(II) adsorption onto RCS (initial Cu(II) concentration: 100 mg L<sup>-1</sup>; adsorbent concentration: 5.0 g L<sup>-1</sup>).

After integration and applying boundary conditions  $q_t=0$  at  $t=0$  and  $q_t=q_e$  at  $t=t$  the integrated form of Eq. (2) becomes:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (3)$$

The pseudo-second-order model is in the following form [24]:

$$\frac{dq}{dt} = k_2(q_e - q_t)^2 \quad (4)$$

After definite integration by applying the conditions  $q_t=0$  at  $t=0$  and  $q_t=q_t$  at  $t=t$  the Eq. (4) becomes the following:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (5)$$

The Elovich equation is given as follows [25]:

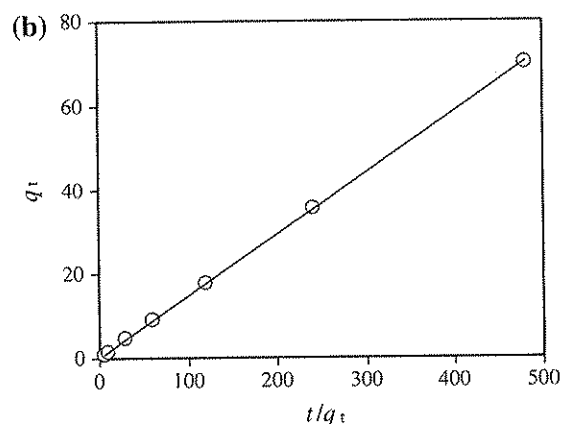
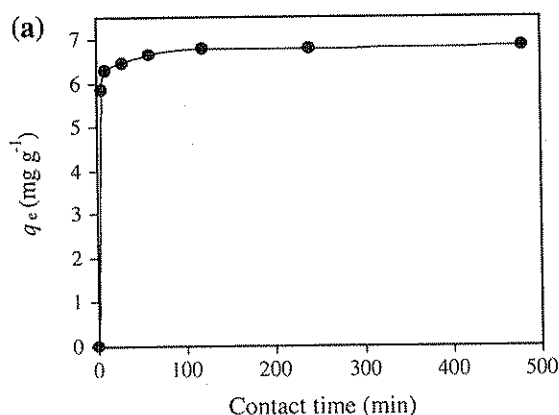


Fig. 4. (a) Effect of contact time on Cu(II) uptake by RCS (initial Cu(II) concentration: 100 mg L<sup>-1</sup>; adsorbent concentration: 5.0 g L<sup>-1</sup>; initial pH: 6.0) and (b) Pseudo-second-order kinetic model.

$$q_t = (1/\beta) \ln(\alpha\beta) + (1/\beta) \ln t \quad (6)$$

where  $q_e$  (mg g<sup>-1</sup>) and  $q_t$  (mg g<sup>-1</sup>) are the amounts of the metal ions adsorbed on the adsorbate at equilibrium and at any time  $t$ , respectively;  $k_1$  (min<sup>-1</sup>) is the rate constant of the first-order adsorption,  $k_2$  (g mg<sup>-1</sup> min<sup>-1</sup>) is the rate constant of the second-order equation,  $\alpha$  (mg g<sup>-1</sup> min<sup>-1</sup>) is the initial sorption rate, and  $\beta$  (g mg<sup>-1</sup>) is related to the extent of surface coverage and activation energy for chemisorption.

The pseudo-first-order model constants,  $k_1$  and  $q_e$  were calculated from the slope and intercept of the linear plot of  $\ln(q_e - q_t)$  vs.  $t$ , respectively. The calculated  $q_e$  ( $q_{e \text{ cal}}$ ) value by applying the model was not in a good agreement with the experimental value of  $q_e$  ( $q_{e \text{ exp}}$ ). The Elovich model constants,  $\alpha$  and  $\beta$  values were also obtained from the intercept and slope of the plot of  $q_t$  vs.  $\ln(t)$ , respectively. The obtained lower values of the correlation coefficients suggested that the pseudo-first-order and Elovich models are not suitable for describing the adsorption of Cu(II) ions

onto RCS (Table 2). The pseudo-second-order kinetic model constants,  $k_2$  and  $q_e$  values were determined from the intercept and slope of the plot of  $t/q_t$  vs.  $t$  (Fig. 4(b)), respectively, and presented in Table 2 along with the corresponding correlation coefficient. By comparison the  $q_e$  value calculated as described above with the experimental value, it can be seen that they are very close to each other. Also the correlation coefficient value obtained from the pseudo-second-order kinetic model was relatively high. Hence, it would be fairly free of speculation that the pseudo-second-order adsorption mechanism is predominant for the adsorption of Cu(II) ions onto RCS.

The intraparticle diffusion model equation is expressed as [26]:

$$q_t = k_{id}t^{1/2} + c \quad (7)$$

where  $q_t$  ( $\text{mg g}^{-1}$ ) is the amount of sorption at time  $t$  (min) and  $k_{id}$  ( $\text{mg g}^{-1} \text{min}^{-1/2}$ ) is the rate constant of intraparticle diffusion model. Most of the adsorption process occurs in three stages, which are film diffusion, intraparticle or pore diffusion, and sorption onto interior sites, hence the plot of  $q_t$  vs.  $t^{1/2}$  may present multilinearity. Most of the times, the sorption of an adsorbate onto interior sites of an adsorbent takes place rapidly hence the sorption process is envisioned to be controlled by film diffusion or pore diffusion; depending on the rate of these stages. As a result of the evaluation of the intraparticle mass transfer curve of Cu(II) adsorption, two distinct phases were noticed. The diffusion of Cu(II) ions into the external surface of RCS is the first phase, and the intraparticle diffusion of Cu(II) ions into the pores of RCS is the second phase. The intraparticle rate constants for the first phase ( $k_{id,1}$ ) and second phase ( $k_{id,2}$ ) and  $c$  parameters were obtained from the plot of  $q_t$  vs.  $t^{1/2}$  and the results were given in Table 2. The  $k_{id,2}$  value is smaller than  $k_{id,1}$ , then it can be said that the intraparticle diffusion occurs slower than the film diffusion and therefore the intraparticle diffusion

is the rate limiting step for Cu(II) adsorption process. However, the line corresponding to the intraparticle diffusion phase does not pass the origin so the Cu(II) adsorption onto RCS can be considered as a complex process, both intraparticle diffusion and surface sorption contributes to the rate-limiting step [27].

### 3.4. Effect of initial Cu(II) concentration and adsorption isotherms

The effects of initial Cu(II) concentration on the adsorption process were evaluated by varying the initial Cu(II) concentration in the range of 60–600  $\text{mg L}^{-1}$  at initial pH 6.0. Multiple factors may play role on the metal uptake efficiency by the changes in the initial metal ion concentration. These factors are the combination of availability of specific surface functional groups and the ability of these groups to bind metal ions [28]. As increasing the initial Cu(II) concentration from 60 to 600  $\text{mg L}^{-1}$ , the equilibrium concentration increased from 3.7 to 26.8  $\text{mg L}^{-1}$ , whereas the adsorption percentage decreased from 30.8 to 22.3% (Fig. 5 (a)). The increase in the metal ion concentration causes an increase in the driving force of the metal ions towards to the active adsorption sites. As a result of this, the adsorbed amount of Cu(II) ions per unit mass of the adsorbent increased. However, when higher Cu(II) concentrations are used, the saturation of the available adsorption sites on the adsorbent surface prevents further metal ion binding and as a result, the adsorption percentages decreased [29].

Langmuir, Freundlich, Temkin, and Dubinin Radushkevich (D-R) isotherm models were used to estimate the possible mechanisms of Cu(II) adsorption onto RCS.

The Langmuir isotherm model has the following form [30]:

$$q_e = \frac{bq_{\max}C_e}{1 + bC_e} \quad (8)$$

Table 2  
Parameters of pseudo-first-order, pseudo-second-order, Elovich, and intraparticle diffusion models

| $q_{e \text{ exp}} (\text{mg g}^{-1})$          | Pseudo-first-order kinetic model |  |       | Pseudo-second-order kinetic model        |  |   |       |
|---|----------------------------------|--|-------|--|--|---|-------|
|   | $k_1 (\text{min}^{-1})$          | $q_{e \text{ cal}} (\text{mg g}^{-1})$ | $R^2$ | $k_2 (\text{g mg}^{-1} \text{min}^{-1})$ | $q_{e \text{ cal}} (\text{mg g}^{-1})$ | $R^2$                                       |       |
| 6.84  | -0.015                           | 1.00                                   | 0.617 | 0.100                                    | 6.85                                   | 0.999                                       |       |
| Intraparticle diffusion model                   |                                  |  |       | Elovich model                            |  |   |       |
| $k_{id,1} (\text{mg g}^{-1} \text{min}^{-1/2})$ | $R^2$                            | $k_{id,2}$                             | $R^2$ | $C$                                      | $\beta (\text{g mg}^{-1})$             | $\alpha (\text{mg g}^{-1} \text{min}^{-1})$ | $R^2$ |
| 0.124   | 0.833                            | 0.006                                  | 0.830 | 6.14                                     | 0.199                                  | $3.2 \times 10^{12}$                        | 0.883 |



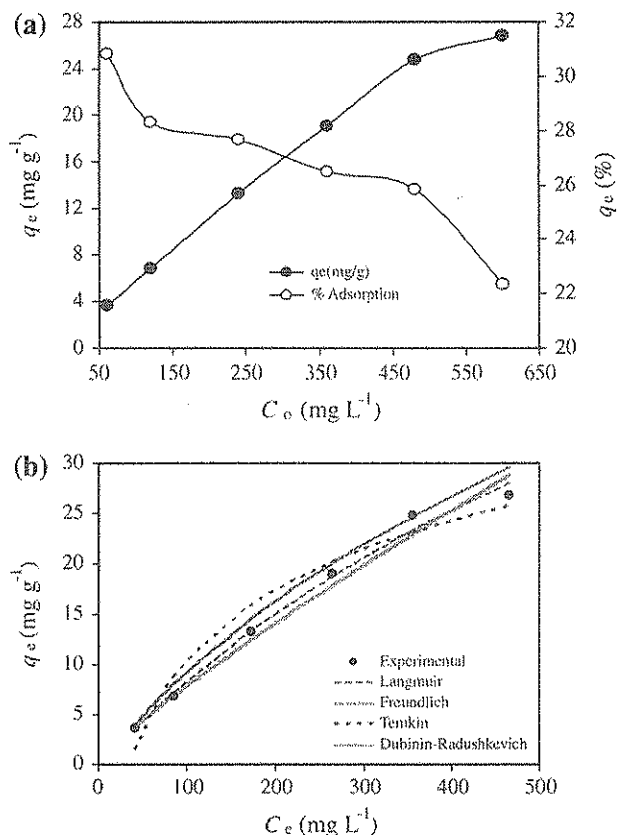


Fig. 5. (a) Effect of initial Cu(II) concentration on Cu(II) adsorption onto RCS (initial pH:6.0; adsorbent concentration: 5.0 g L<sup>-1</sup>; contact time: 60 min) and (b) Comparison of equilibrium isotherms between the experimental and theoretical data for Cu(II) uptake.

The Langmuir model in linear form:

$$\frac{C_e}{q_e} = \frac{C_e}{q_{\max}} + \frac{1}{bq_{\max}} \quad (9)$$

where  $q_e$  (mg g<sup>-1</sup>) is the amount of the metal ions adsorbed per unit mass of adsorbent,  $C_e$  (mg L<sup>-1</sup>) is the equilibrium metal ion concentration in aqueous solution,  $q_{\max}$  (mg g<sup>-1</sup>), and  $b$  (L mg<sup>-1</sup>) are the Langmuir constants related to the adsorption capacity and free energy or net enthalpy of adsorption, respectively. The linear plot of  $C_e/q_e$  vs.  $C_e$  shows that sorption obeys the Langmuir model, and the constants  $q_{\max}$  and  $b$  are evaluated from slope and intercept of the linear plot, respectively. According to the Langmuir isotherm model, the maximum monolayer adsorption capacity of RCS for Cu(II) was found to be 81.97 mg g<sup>-1</sup>. The  $q_{\max}$  values of other adsorbents for the adsorption of Cu(II) ions by activated carbon from hazelnut husks [31], activated carbon from rice hulls [32], rubber (*Hevea brasiliensis*) leaf powder [33], and

dehydrated wheat bran [34] were 6.64, 3.90, 8.92, and 51.5 mg g<sup>-1</sup>, respectively.

The Freundlich isotherm model has the following form [35]:

$$q_e = K_f C_e^{1/n} \quad (10)$$

The Freundlich model in linear form:

$$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e \quad (11)$$

where  $K_f$  is a constant related to sorption capacity (mg g<sup>-1</sup>) and  $1/n$  is an empirical parameter related to the sorption intensity. The value of  $n$  varies with the heterogeneity of the sorbent and gives an idea for the favorability of the sorption process. The value of  $n$  should be less than 10 and higher than unity for favorable sorption conditions. The Freundlich constants  $K_f$  and  $1/n$  can be determined from the intercept and slope of linear plot of  $\ln q_e$  vs.  $\ln C_e$ , respectively. According to the Freundlich isotherm model,  $n$  value is found to be 1.17 which implies that the adsorption process is favorable under the studied experimental conditions.

The Temkin isotherm model which considers that the heat of the adsorption of all the molecules would decrease linearly with coverage due to adsorbate/adsorbate interactions, is given as [36]:

$$q_e = RT/b(\ln A.C_e) \quad (12)$$

$$B = RT/b \quad (13)$$

The Temkin model in linear form is:

$$q_e = B(\ln A) + B(\ln C_e) \quad (14)$$

where  $B$  (J mol<sup>-1</sup>) is the Temkin constant related to heat of adsorption,  $A$  (L g<sup>-1</sup>) is the equilibrium binding constant corresponding to the maximum binding energy,  $R$  (8.314 J mol<sup>-1</sup> K<sup>-1</sup>) is the universal gas constant, and  $T$  (Kelvin) is the absolute solution temperature. The Temkin constants  $A$  and  $B$  can be determined from the intercept and slope of the linear plot of  $q_e$  vs.  $\ln C_e$ , respectively.

The D-R isotherm model is used to estimate the adsorption type; physical or chemical and given as follows [37]:

$$q_e = q_m \exp(-\beta e^2) \quad (15)$$

where  $q_e$  (mol g<sup>-1</sup>) is the amount of metal adsorbed onto per unit mass of adsorbent,  $q_m$  (mol g<sup>-1</sup>) is the



monolayer adsorption capacity,  $\beta$  ( $\text{mol}^2 \text{kJ}^{-2}$ ) is the activity coefficient related to the mean sorption energy, and  $\varepsilon$  is the Polanyi potential and can be calculated as following equation:

$$\varepsilon = RT \ln(1 + 1/C_e) \quad (16)$$

The linear form of D-R isotherm model is expressed as:

$$\ln q_e = \ln q_m - \beta \varepsilon^2 \quad (17)$$

where  $C_e$  ( $\text{mol L}^{-1}$ ) is the equilibrium metal ion concentration in aqueous solution. The mean adsorption energy,  $E$  ( $\text{kJ mol}^{-1}$ ), can be calculated using the following equation:

$$E = 1/(-2\beta)^{1/2} \quad (18)$$

The D-R model constants,  $q_m$  and  $\beta$ , can be determined from the intercept and slope of the linear plot of  $\ln q_e$  vs.  $\varepsilon^2$ , respectively. The mean sorption energy ( $E$ ), obtained from D-R isotherm model, gives information about the mechanisms of the adsorption process. If  $E$  value lies between 8 and 16  $\text{kJ mol}^{-1}$  the adsorption process takes place chemically, while  $E < 8 \text{ kJ mol}^{-1}$ , the adsorption process proceeds physically [38]. The value of  $E$  was found to be as 6.59  $\text{kJ mol}^{-1}$ , may suggest that the mechanisms for the adsorption of Cu(II) ions onto RCS is physical in nature.

The equilibrium data obtained from the adsorption of Cu(II) ions onto RCS were fitted the Langmuir, Freundlich, Temkin, and D-R isotherm models (Fig. 5(b)). All of the isotherm constants and correlation coefficients were calculated from the linear equations of the models and provided in Table 3. By comparing the correlation coefficient values obtained from the models, it can be concluded that the experimental data were fitted well to Freundlich and D-R isotherm models. The suitability of the Freundlich isotherm model reflects the heterogeneous distribution of the active adsorption sites on the surface of the RCS.

### 3.5. Effect of temperature and thermodynamics of adsorption

To test the impact of temperature on the adsorption amount, the adsorption experiments were conducted in the temperature range of 278–313 K with initial Cu(II) concentration of 100  $\text{mg L}^{-1}$  and RCS suspension of 5.0  $\text{g L}^{-1}$ . The adsorption of Cu(II) ions onto RCS was endothermic, since the adsorption capacity of Cu(II) ions increased from 5.0  $\text{mg g}^{-1}$

Table 3

Langmuir, Freundlich, Temkin, and D-R isotherm parameters for the adsorption of Cu(II) adsorption onto RCS

|   |                       |
|---|-----------------------|
| Langmuir isotherm model                   |                       |
| $q_{\text{max}}$ ( $\text{mg g}^{-1}$ )   | 81.97                 |
| $b$ ( $\text{L mg}^{-1}$ )                | $1.12 \times 10^{-3}$ |
| $R^2$                                     | 0.907                 |
| Freundlich isotherm model                 |                       |
| $K_f$ ( $\text{mg g}^{-1}$ )              | 0.156                 |
| $n$                                       | 1.17                  |
| $R^2$                                     | 0.994                 |
| Temkin isotherm model                     |                       |
| $A$ ( $\text{L g}^{-1}$ )                 | 0.028                 |
| $B$                                       | 10.06                 |
| $b$ ( $\text{J mol}^{-1}$ )               | 246.28                |
| $R^2$                                     | 0.954                 |
| D-R isotherm model                        |                       |
| $q_m$ ( $\text{mg g}^{-1}$ )              | 152.46                |
| $\beta$ ( $\text{kJ}^2 \text{mol}^{-2}$ ) | 0.011                 |
| $E$ ( $\text{kJ mol}^{-1}$ )              | 6.59                  |
| $R^2$                                     | 0.996                 |

(25.0% removal) to 6.7  $\text{mg g}^{-1}$  (33.4% removal) after increasing the temperature from 278 to 313 K. There may be two reasons which may explain these observations: either the increase in the number of active surface sites on RCS or increase in the mobility of Cu(II) cations [39,40].

The thermodynamic parameters including Gibbs free energy ( $\Delta G$ ), enthalpy ( $\Delta H$ ), and entropy changes ( $\Delta S$ ) can be calculated using the following equations [41];

$$\Delta G = -RT \ln K_d \quad (19)$$

where  $R$  is the universal gas constant ( $8.314 \text{ J mol}^{-1} \text{K}^{-1}$ ),  $T$  is the temperature (K), and  $K_d$  is the distribution coefficient. The  $K_d$  value was calculated using following equation:

$$K_d = q_e/C_e \quad (20)$$

where  $q_e$  ( $\text{mg L}^{-1}$ ) and  $C_e$  ( $\text{mg L}^{-1}$ ) are the equilibrium concentration of Cu(II) ions adsorbed onto RCS and remained in the solution, respectively. The enthalpy ( $\Delta H$ ), and entropy changes ( $\Delta S$ ) of adsorption were estimated from the following equation:

$$\Delta G = \Delta H - T\Delta S \quad (21)$$

This equation can be written as:

Table 4  
Thermodynamic parameters of Cu(II) adsorption onto RCS at different temperatures

| Thermodynamics parameters |                                     |  |   |
|---------------------------|-------------------------------------|--|---|
| T (K)                     | $-\Delta G$ (kJ mol <sup>-1</sup> ) | $\Delta S$ (J mol <sup>-1</sup> K <sup>-1</sup> ) <sup>a</sup> | $\Delta H$ (kJ mol <sup>-1</sup> ) <sup>a</sup> |
| 278                       | 1.80                                | 20.70  | 8.20  |
| 288                       | 1.85                                |  |   |
| 298                       | 1.87                                |  |   |
| 308                       | 2.14                                |  |   |
| 313                       | 2.54                                |  |   |

<sup>a</sup>Measured between 278–313 K.

$$\ln K_d = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad (22)$$

The  $\Delta H$  and  $\Delta S$  values were calculated from the slope and intercept of the plot between  $\ln K_d$  vs.  $1/T$ , respectively. The  $\Delta G$  values were obtained by using Eq. (19) in the temperature range of 278–313 K. The negative values of  $\Delta G$ , suggested the feasibility of the present adsorption process and spontaneous nature of the adsorption of Cu(II) ions onto RCS (Table 4). The positive value of  $\Delta H$  indicated that the endothermic nature of adsorption which was also supported by the increase in amount of metal uptake with the rise in temperature. The positive  $\Delta S$  value suggested an increase in the randomness at the solid/solution interface during the adsorption of Cu(II) ions onto RCS.

### 3.6. Effect of RCS concentration

In order to investigate the effects of RCS concentration on the removal of Cu(II) ions, a series of experiments were performed by varying RCS concentrations in the range of 1–30 g L<sup>-1</sup>. The experiments were conducted for 60 min of contact time by using initial Cu(II) concentration of 125 mg L<sup>-1</sup> at pH 6.0. The influences of RCS concentration on the removal of Cu(II) are shown in Fig. 6. The results showed that the percentage amount of adsorption increased with increasing the RCS concentration because of the increase in the active sites on the RCS surface and thus making easier penetration of the Cu(II) ions into the sorption sites. On the other hand, the adsorbed Cu(II) ions per unit mass of the RCS ( $q_e$ ) decreased with increasing the RCS concentration because of the aggregation of the adsorbent particles [42].

### 3.7. Effect of ionic strength

In this study, KCl, CaCl<sub>2</sub>, NaNO<sub>3</sub>, and Na<sub>2</sub>HPO<sub>4</sub> were selected as model salts to evaluate the effects of

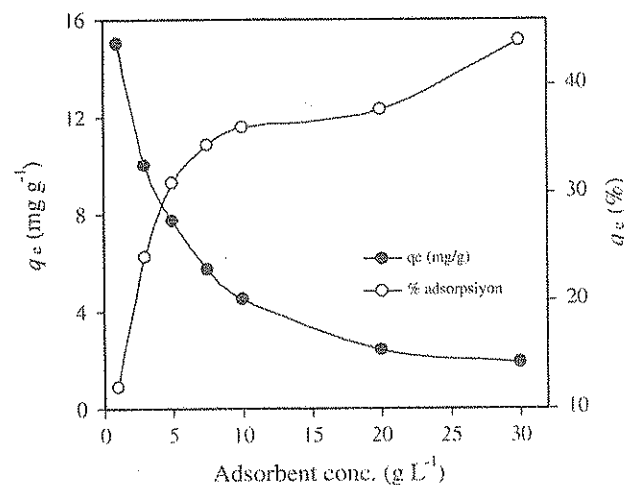


Fig. 6. Effect of adsorbent concentration on Cu(II) uptake by RCS (initial Cu(II) concentration: 125 mg L<sup>-1</sup>; initial pH: 6.0; contact time: 60 min).

ionic strength on Cu(II) adsorption onto RCS. For that purpose, different concentrations of salts solutions (in the range of 0.01–0.5 M) were treated with initial Cu(II) concentration of 100 mg L<sup>-1</sup> at pH 6.0. The RCS suspensions were 5.0 g L<sup>-1</sup>, and the equilibrium time was 60 min (Fig. 7). A decrease was observed in the adsorption amount of Cu(II) with increasing the concentration of the electrolytes as a result of the competition between Cu(II) ions and cations of the salts for the active adsorption sites of RCS.

### 3.8. Desorption of Cu(II) ions

Desorption of Cu(II) ions from the loaded RCS was also studied in a batch system and various concentrations of NaOH (in the range of 0.1–3.0 M) were tried as desorbing agent to desorb the Cu(II) ions.

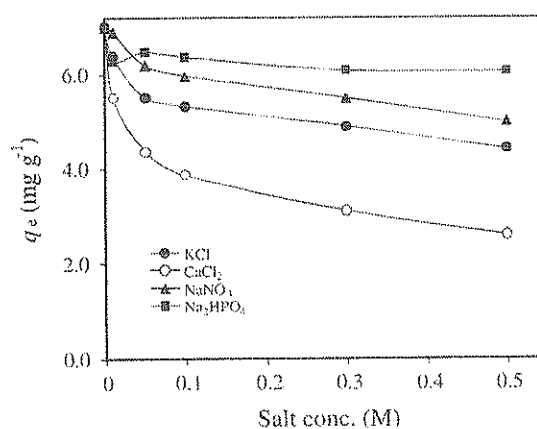


Fig. 7. Effect of ionic strength on Cu(II) uptake by RCS (initial Cu(II) concentration: 100 mg L<sup>-1</sup>; adsorbent concentration: 5.0 g L<sup>-1</sup>; initial pH: 6.0; contact time: 60 min).

For desorption experiments,  $5.0 \text{ g L}^{-1}$  of RCS suspension was equilibrated with  $100 \text{ mg L}^{-1}$  of Cu(II) solution. After reaching the equilibrium, the RCS was separated by centrifugation, then the equilibrium concentration of Cu(II) in the filtrate was determined by FAAS. The Cu(II)-loaded RCS was washed with deionized water and then dried in air for one day. The loaded adsorbent was treated with NaOH by agitating at 400 rpm for 60 min. The desorption efficiency reached from 36.0 to 46.2% when the concentration of NaOH increased from 0.1 to 3.0 M. However, a complete desorption of Cu(II) ions could not be achieved, which might be due to Cu(II) ions becoming trapped in the intrapores and, therefore, difficult to release [43].

#### 4. Conclusions

The utilization of RCS, which is an agricultural byproduct, in adsorptive removal of Cu(II) ions from aqueous solutions has been examined. The study is important with respect to recycle of an unused resource which presents serious disposal problems. The RCS was used without any previous activation treatment; this also decreases the adsorption costs. The Cu(II) removal efficiency of the RCS was tested in the light of equilibrium, kinetics, and thermodynamics parameters. The kinetics of Cu(II) adsorption onto RCS followed by the pseudo-second-order model. The equilibrium data were best fitted to the Freundlich and D-R isotherm models. The monolayer adsorption capacity of RCS was found to be  $81.97 \text{ mg g}^{-1}$  by using Langmuir model equations. The thermodynamic parameters indicated that the adsorption of Cu(II) onto RCS was feasible, spontaneous, and endothermic in nature. In the light of these results, it can be concluded that the natural RCS can be used as an effective, low-cost and easily available adsorbent in removal of Cu(II) ions from aqueous solutions by using the present adsorption process.

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