The sorption of copper on almond shell: optimization and kinetics
S. Aber, D. Salari and B. Ayoubi Feiz

ABSTRACT

Batch sorption studies using almond shell as an sorbent for the removal of Cu (II) from aqueous solutions, showed that copper removal decreased from 74.9% to 45.6% with increasing its concentration from 10 to 70 ppm. The removal increased with increasing sorbent dose and pH, respectively. Copper removal was obtained equal to 63.7%, 69.6% and 58.6% at 26 °C, 40 °C and 55 °C. The sorption of Cu (II) on almond shell was also optimized by Taguchi method. The optimized conditions were the sorbent mass of 4 g, the ion initial concentration of 10 ppm, pH 7, the temperature of 40 °C and contact time equal to 60 min. The pH and initial Cu (II) concentration with respectively 32.75% and 31.20% contribution had more influence on the removal of Cu (II). The kinetic data fit pseudo-second-order model with correlation coefficients greater than 0.99 and rate constants in the range of 0.26–7.87 g mg⁻¹ min⁻¹.

Key words | almond shell, Cu (II), kinetics, sorption, Taguchi

INTRODUCTION

Water pollution by heavy metals through the discharge of industrial wastewaters is a worldwide environmental problem. Since heavy metals are not biodegradable, their presence in surface water leads to bioaccumulation in living organisms and causes health problems in animal and human (Argun & Dursun 2008). Maximum permissible concentrations of copper in drinking water reported by World Health Organization (WHO) and Environmental Protection Agency (EPA) are 1–2 and 1.3 ppm, respectively. The permissible level of copper in industrial wastewater to be discharged to the surface water is 3 ppm (Chakravarty et al. 2008). Hence the treatment of copper-containing-wastewaters before discharge into surface waters is necessary.

In comparison with the different wastewater treatment methods, sorption phenomenon has advantages because of simple design without generating sludge. Activated carbon has been recognized as a highly effective adsorbent for the removal of heavy metal ions but it has not been used by small and medium scale industries for the treatment of their metal-containing-effluents, because of high manufacturing cost of activated carbon (Han et al. 2008). For this reason, the use of low-cost materials as sorbent for metal ion removal from wastewaters has been highlighted. A low-cost sorbent is defined as the one which is abundant in nature, or is a by-product or waste material from another industry. Some of these materials such as soya cake (Daneshvar et al. 2002), pomegranate peel (El Ashtoukhy et al. 2008), newspaper pulp (Chakravarty et al. 2008), fly ash (Sharma et al. 2007) and Areca (as a kind of food waste) (Zheng et al. 2008) are used as low cost sorbents. Since almond is an important crop in North West of Iran (East Azarbaijan province), almond shell as an agricultural by-product and readily available material without previous activation was used for the removal of Cu (II) in this study.

The aim of this paper is to assess the ability of almond shell in the sorption of Cu (II) from aqueous solution and to investigate the influence of the initial Cu (II) concentration (C₀), the dose of sorbent (m), the initial pH of solution and temperature (T) on the sorption process. This process was also optimized by Taguchi method. Finally the kinetics of the sorption was studied.
MATERIALS AND METHODS

Preparation of copper solution

Copper solution was prepared by dissolving Cu(NO₃)₂·3H₂O obtained from Fluka company in distilled water to make 1000 ppm Cu²⁺ stock solution. The solution was diluted to the required concentrations of 10 ppm to 70 ppm. The intrinsic pH of the solution was measured equal to 5.6 ± 0.04 by pH meter (Philips PW9422, England). The initial pH of the solution was adjusted between 2 and 10 either by hydrochloric acid or sodium hydroxide solutions.

Preparation of the sorbent

Almond shell as an agricultural by-product was obtained from Maraghe in East Azarbaijan. The almond shell was washed with distilled water, dried in an oven for 10 h at 373 K, ground with a grinder and sieved in sieves with sizes 16 mesh/inch (1 mm) and 24 mesh/inch (0.707 mm). Particles between these two sieves were used in the experiments without any further treatment.

Almond shell characterization

The surface area of almond shell was determined by N₂ gas adsorption method at 77 K using Brunauer-Emmett-Teller (BET) Measurement Micromeritics (Shimadzu, Gemini 2375, Japan). Mean pore diameter of almond shell was also calculated using BET analysis. The pH of the Zero Point of Charge (ZPC) of the almond shell was determined in 40 ml of 0.1 M NaNO₃ solutions at 26 °C with 0.5 g of almond shell. The pH of these solutions remained constant after 24 h shaking the solutions and plotted against initial pH values. The pHZPC value of the sorbent was calculated from this plot, as the pH at which ΔpH is equal to zero. The surface chemical characterization was performed by Fourier Transform Infrared (FTIR) Spectrometer (Bruker, Tensor 27, Germany) and expressed as transmittance in the 400-4000 cm⁻¹ range.

Batch experiments

The sorption experiments were carried out by shaking 0.5–4 g (± 0.0004 g) of the almond shell samples with 50 ml of the copper solutions with the concentration range of 10–70 ppm (± 0.2 ppm) at 26, 40 and 55 °C (± 0.2 °C) and initial pH values of 2–10 (± 0.04). The number of replicates for each experiment was three. The suspensions were agitated at 200 ± 3 rpm using a shaker incubator (Fanavaran, ISH55LD, Iran) for a known period of time ranging between 5 and 60 min. After prescribed contact times, the solutions were filtered by Blue Ribbon filter paper (Schleicher & Schuell, Germany) and digested by the addition of concentrated H₂SO₄ and HNO₃ acids and heating until appearance of dense white SO₃ fumes (Clesceri et al. 1989). The copper ion concentration in the solutions was then analyzed by a photometer (Palintest 7100; program number: PHOT. 10, England) based on colorimetric method using tablet reagents. The removal percent of copper was calculated using the following equation:

\[
R\%_0 = \frac{C_0 - C_t}{C_0} \times 100
\]  

where \( C_0 \) (ppm) is the initial concentration of Cu (II) and \( C_t \) (ppm) is the concentration of Cu (II) at time \( t \). The amount of Cu (II) sorbed per unit mass of almond shell at time \( t \), \( q_t \) (mg g⁻¹), was evaluated using the following expression:

\[
q_t = \frac{(C_0 - C_t)V}{m}
\]

where \( m \) (g) is the mass of almond shell and \( V \) (L) is the volume of solution.

Taguchi method

Taguchi method allows to find the optimized condition with minimum number of experiments thus saves time and resources. In this study Taguchi method has been used to determine the optimum conditions required to obtain the maximum removal percent of copper ions using almond shell. Also, Taguchi method has been used to determine the effectiveness of each parameter. The experimental design proposed by Taguchi involves using orthogonal arrays to organize the parameters affecting the process and the levels at which they should be varied (Bhardwaj et al. 2008).

Five parameters each at 4 levels including initial copper concentration (10, 30, 50 and 70 ppm), almond shell dose (0.5, 1, 2 and 4 g), initial pH (2, 4, 5.6 and 7), temperature (26, 40, 50 and 55 °C) and contact time (15, 30, 45 and 60 min) were considered in accordance with L16 Taguchi orthogonal array (Bhardwaj et al. 2008).

The experimental observations are transformed into signal-to-noise (S/N) ratios by following equation which...
calculates S/N ratio using “the larger the better” algorithm:

\[
S/N = -10 \log \left( \frac{1}{n} \sum_{i=1}^{n} \frac{1}{y_i^2} \right)
\]

(3)

where \(y_i\) presents the observed data (copper removal percent in our work) and \(n\) is the number of observations (Bhardwaj et al. 2008). Also the effectiveness of each factor \((p)\) was calculated, as percentage, by Taguchi method. A bigger value of \(p\) for a parameter means that it has more effectiveness on the experimental results (Hesampour et al. 2008).

**Sorption kinetics**

In order to investigate the mechanism of sorption, various kinetic models have been suggested. These include pseudo-first-order, pseudo-second-order and intraparticle diffusion models (Demirbas et al. 2008).

**Pseudo-first-order model.** This model is generally expressed as follows:

\[
\ln(q_e - q_t) = \ln q_e - k_1 t
\]

(4)

where \(q_e\) and \(q_t\) respectively are the amounts of copper ions sorbed at equilibrium and time \(t\) (mg g\(^{-1}\)) and \(k_1\) (min\(^{-1}\)) is the rate constant of pseudo-first-order sorption (El Ashtoukhy et al. 2008). A straight line of \(\ln(q_e - q_t)\) versus \(t\) indicates the fitting of the pseudo-first-order kinetic model to experimental data.

**Pseudo-second-order model.** If the rate of sorption follows second-order mechanism, the pseudo-second-order model is used which is expressed as:

\[
\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}
\]

(5)

where \(k_2\) (mg g\(^{-1}\) min\(^{-1}\)) is the rate constant of pseudo-second-order sorption (El Ashtoukhy et al. 2008). A linear plot of \(t/q_t\) against \(t\) shows the agreement of pseudo-second-order kinetic model with experimental data.

**Intraparticle diffusion model.** The sorption data can also be analyzed using intraparticle diffusion mechanism, which is described as:

\[
q_t = k_i t^{0.5}
\]

(6)

where \(k_i\) (mg g\(^{-1}\) min\(^{-1/2}\)) is the intraparticle diffusion rate constant (Wan Ngah & Hanafiah 2008). If the plot of \(q_t\) obtained from experimental results versus \(t^{0.5}\) gives a straight line, the sorption process is controlled by intraparticle diffusion.

**RESULTS AND DISCUSSION**

**Physical and chemical characteristics of almond shell**

The BET surface area of the almond shell determined equal to 0.95 m\(^2\) g\(^{-1}\). It is considerable that the value of surface area of the almond shell is higher than the shell of lentil, wheat and rice which have been reported as 0.19 m\(^2\) g\(^{-1}\), 0.67 m\(^2\) g\(^{-1}\) and 0.85 m\(^2\) g\(^{-1}\) (Aydin et al. 2008), respectively. The pores of adsorbents are classified in accordance with the classification adopted by the International Union of Pure and Applied Chemistry (IUPAC) to micropores (diameter \(d\) < 2 nm), mesopores (2 nm < \(d\) < 50 nm), and macropores (\(d\) > 50 nm) (Allen 1968). The average pore diameter of the almond shell in this study determined equal to 4.6 nm using BET method, suggesting that the porosity of the almond shell mainly consists of mesopores. The chemical characterization of the sorbent surface was performed by FTIR analysis. The most important functional groups on the almond shell surface were: O-H (3423.44 cm\(^{-1}\); stretch vibration), aromatic and aliphatic C-H (2926.03 cm\(^{-1}\); stretch vibration), C = O (1740.84 and 1629.69 cm\(^{-1}\); stretch vibration), aromatic C = C (1508.91 cm\(^{-1}\); stretch vibration), C-H (1463.64 and 1324.11 cm\(^{-1}\); deformation vibration) and C-O (1247.84 cm\(^{-1}\); stretch vibration). The presence of hemicelloses, cellulose and lignin as the main constituents of almond shell are probably responsible for the appearance of these bonds. The composition of almond shell is as follows: hemicelloses 28.9%, cellulose 50.7% and lignin 20.4% (Estevinho et al. 2006).

**The effect of initial copper ion concentration**

The results in Figure 1a indicate that the rate of Cu (II) removal is dependent on the contact time. It is extremely rapid in the first 5 min, and then the rate of sorption decreases. According to Figure 1a, the variation in Cu (II) removal percent is negligible after shaking for about 1 h so, in each experiment the maximum shaking time was set to 60 min. As can be seen in the figure, the removal percent decreases from 74.9% to 45.6% when the initial Cu (II) concentration increases from 10 to 70 ppm at 26 C, pH 5.6 and the almond shell mass of 1 g after 1 h. This is because of the saturation of the sorbent at higher Cu (II) concentrations. Amarasinghe & Williams (2007), has been obtained similar results for the removal of Cu and Pb from wastewater by Tea waste. The amount of copper sorbed per unit mass of almond shell, increases from 0.37 to 1.59 mg g\(^{-1}\) by increasing the copper concentration from 10 to 70 ppm after 1 h contact time.
The effect of sorbent dosage

The effect of sorbent dosage was studied on Cu (II) removal, keeping experimental conditions constant at 26 C, pH 5.6 and initial Cu (II) concentration of 30 ppm. As it is shown in Figure 1b, in the first 5 min the uptake rate is very fast. The removal percent of Cu (II) ions increases from 53.1% to 84.8% by increasing the sorbent dosage from 0.5 to 4 g after 1 h.

An increase in Cu (II) removal percent with increase in sorbent dosage can be attributed to greater surface area while the number of Cu (II) ions is constant. However, the amount of sorbed ions per unit mass of the sorbent decreases from 1.57 to 0.31 mg g⁻¹ as the sorbent dosage increases at mentioned conditions. The decrease in the amount of sorption per unit mass of sorbent with increase in sorbent dose is due to the adsorption sites remaining unsaturated during the adsorption process (Eren & Acar 2006).

The effect of initial pH

The pH of aqueous solutions is an important controlling factor in the sorption process thus the effect of pH has been studied by varying it in the range of 2–10 at 26 C, at almond shell mass equal to 1 g and initial copper concentration of 30 ppm. As shown in Figure 1c, the uptake of Cu (II) in the first 10 min for pH 2 is equal to 24%. The rate of sorption is rapid in the first 5 min for all pH values. Cu (II) removal percent increases from 24% to 73.3% after 1 h with increasing pH from 2 to 7.

The pH\text{ZPC} of the almond shell was obtained equal to 5.9 and so at pH values lower than 5.9, the almond shell surface will be covered with H⁺ ions and copper ions can not compete with them for adsorption sites. Also, H⁺ ions on the surface of the almond shell repel Cu²⁺ ions existing in the solution. These factors decrease the removal percent of Cu (II) at pH values lower than 5.9. Increasing in the removal percent of Cu (II) at pH values more than 5.9 may be due to the presence of negative charges on the surface of almond shell which can attract positive Cu (II) ions (Argun & Dursun 2008). Initial increase in the removal percent at pH 10 may be due to the copper hydroxide precipitation. In the experiments which were done at initial pH values ranging from 2 to 7, the pH of the solutions during the sorption process was approximately constant. But when the initial pH of the solution was 10, it decreased to nearly 7 during the sorption process and this dissolves some of the precipitated copper hydroxides and lowers the Cu (II) removal percent after 10 min. A behavior similar to this has also been observed in the removal of copper from aqueous solutions using sawdust by Larous et al. (2005).

![Figure 1](https://iwaponline.com/wst/article-pdf/63/7/1389/445693/1389.pdf)
The effect of temperature

As can be seen in Figure 1d, like other factors discussed above, the sorption rate is very fast in first 5 min of sorption process. Cu (II) removal percent is 56.1%, 61.2% and 52.7%, respectively for temperatures 26, 40 and 55°C at pH 5.6, the initial Cu (II) concentration of 30 ppm and sorbent dosage equal to 1 g after 15 min contact time. The removal percent increases slowly between 15–30 min and reaches to about 65.7%, 69.6% and 58.6%, respectively after 60 min contact time.

The results indicate that the copper uptake by almond shell increases while the temperature increases until 40°C. The increase of the temperature can change the pore sizes and make them wider and can encourage the efficient contacts between surface activated sites of solid and adsorbate (Larous et al. 2005). The removal percent of Cu (II) decreased at 55°C. The decrease in Cu (II) removal percent at higher temperatures (above 40°C) may be attributed to desorption and bond rupture (Duygu Ozsoy et al. 2008). It is also obvious from this phenomenon that physisorption of Cu (II) ions onto almond shell prevails over chemisorption. A behavior similar to this has also been observed by Larous et al. (2005) for the removal of copper from aqueous solutions using sawdust.

Process optimization by Taguchi method

Table 1 lists the average S/N ratios for the removal of Cu (II) by almond shell. In this study greater amounts of S/N ratio implies better Cu (II) removal. The number of replicates for each experiment was three. The optimum conditions for the sorption of Cu (II) on almond shell were C₀ = 10 ppm (first level), m = 4 g (fourth level), pH = 7 (fourth level), T = 40°C (second level) and t = 60 minutes (fourth level). Experimental results which were done at optimum conditions showed a Cu (II) removal efficiency of 100%.

According to the table, P values of initial Cu (II) concentration and pH are almost the same, respectively 31.20% and 32.78% and are higher than the others. So, they are the most important factors in the process nevertheless, all of the investigated parameters have acceptable contribution on the removal of copper ions using almond shell.

Sorption kinetics

$k_1$, $k_2$ and $k_i$ are the sorption rate constants obtained from the slopes of corresponding linear plots of pseudo-first-order, pseudo-second-order and intraparticle diffusion kinetic models. Table 2 shows the rate constants and the correlation coefficients ($R^2$) obtained from fitting the models to the experimental data for the sorption of Cu (II) onto almond shell at different initial Cu (II) concentrations, almond shell masses, initial pH values and temperatures. Experimental results show that pseudo-second-order model provides the best description of the data with correlation coefficients of 0.999. Also the values of pseudo-second-order rate constant, $k_2$, which are between 0.26 and 7.87 g mg⁻¹ min⁻¹ are greater than the values of rate constants of pseudo-first-order and intraparticle diffusion models which are in the range of 0.04–0.07 min⁻¹ and 0.03–0.18 mg g⁻¹ min⁻¹/², respectively.

CONCLUSIONS

Almond shell as a cheap and abundant material is a good natural sorbent for copper ions. Taguchi method can be used

Table 1 S/N ratio to determine the optimized conditions for the removal of Cu (II) by almond shell and to evaluate the effectiveness of each parameter

<table>
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<th>Parameters</th>
<th>Level I</th>
<th>Level II</th>
<th>Level III</th>
<th>Level IV</th>
<th>P (%)</th>
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<td>35.69</td>
<td>35.55</td>
<td>32.92</td>
<td>29.26</td>
<td>31.20</td>
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<td>32.45</td>
<td>33.18</td>
<td>36.98</td>
<td>23.41</td>
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<td>Initial pH</td>
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<td>34.41</td>
<td>35.13</td>
<td>35.14</td>
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<tr>
<td>Temperature (°C)</td>
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<td>35.29</td>
<td>33.89</td>
<td>31.03</td>
<td>10.82</td>
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<tr>
<td>Contact time (min)</td>
<td>32.85</td>
<td>32.97</td>
<td>33.19</td>
<td>34.42</td>
<td>1.78</td>
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to optimize the conditions of the sorption of Cu (II) ions on almond shell. Nearly 100% removal of Cu (II) ions from solution can be observed at optimized conditions. Initial Cu (II) concentration and the initial pH of solution are the most effective factors on the sorption of Cu (II) by almond shell. Pseudo-second-order is a suitable kinetic model to describe the sorption of Cu (II) on the almond shell.

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**REFERENCES**


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<td>(R^2)</td>
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\(a\) min\(^{-1}\), \(b\) g g\(^{-1}\) min\(^{-1}\), \(c\) mg g\(^{-1}\) min\(^{-1/2}\)


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