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Removal of copper ions from aqueous solutions by hazelnut shell

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Abstract

There is a great potential of woody hazelnut shell to use in some applications. Sorption studies are one of these. For this reason in this paper, batch adsorption of Cu^{2+} ions onto hazelnut shells was studied. The capacity of the adsorption for the removal of copper ions from aqueous solution was investigated under different conditions such as solution contact time (1–360 min), particle size (0–75, 75–150 and 150–200 μm), temperature of solution (25–60°) and solution pH (3–7). Moreover, zeta potential of particles at different initial pHs (2–10) was measured. The equilibrium data were processed according to Langmuir and Freundlich's models and higher adsorption capacity values towards Cu^{2+} ions were shown. The adsorption kinetics was investigated and the best fit was achieved by a second-order equation.
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1. Introduction

Most metals in the fourth period of periodic table are carcinogenic. It can be assumed that the carcinogenicity is related to the electronic structure of transition and inner transitional metals [1]. Since copper is an essential metal in a number of enzymes for all forms of life, problems arise when it is deficient or in excess. Excess copper accumulates in the liver and the most toxic form of copper is thought to be Cu^{2+}. Its toxicity is highly pH dependent and it has been reported to be more toxic to fish at lower pH values [2]. In some respect the intake of essential elements is more critical than for toxic elements. However, epidemiological evidence, such as a high incidence of cancer among coppersmiths, suggests a primary carcinogenic role for copper [1]. The cocarcinogenic character of copper is accepted. There is a long history of human exposure to abnormally elevated levels of toxic metals in food and drink, due to practices such as cooking in copper-lined or copperglazed pots and the supply of water through copper pipes [3]. Moreover,

some industrial plants discharges their heavy metal wastes in the river or lake, so removal of the toxic metals from aqueous effluent and food is extremely important.

One of the major methods for the removal of pollutants from aqueous effluent is adsorption by using porous solid adsorbents. Adsorption has demonstrated its efficiency and economic feasibility as a wastewater treatment process compared to the other purification and separation methods, and has gained importance in industrial applications [4,5], such as removal of heavy metals cations from aqueous solution by choosing some adsorbents under optimum operation conditions. The removal of heavy metal ions from industrial wastewaters using different adsorbents is currently of great interest [6]. Studies so far have focused on adsorbents such as alumina, magnetite, pyrolusite, rutile, zirconia, hydrous manganese oxide, silica, geothite, heamatite, amorphous ferric oxide, bentonite, activated carbon, sphalerite, anatase, red mud, mica, illite, clay [7], sepiolite [8], kaolinite [9] and perlite [10]. We have already studied the adsorption properties of sepiolite, perlite and kaolinite in our previous works.

In recent years, agricultural by-products have been widely studied for metal removal from water. These include peat [11], wood [12], pine bark [13], banana pith [14], rice bran, soybean and cottonseed hulls [15], peanut shells [16], hazelnut shell [17],

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rice husk [18], sawdust [19], wool [20], orange peel and compost [21] and leaves [22]. Most of this work has shown that natural products can be good sorbents for heavy metals. Indeed, it could be argued that many of these natural sorbents remove metals more by ion exchange than by adsorption. Nevertheless, many previous workers tend to base their analyses on sorption theories. These include: the acidic properties of carboxylic and phenolic functional groups present in humic substances [23,24].

Therefore, biomass or biosolids have been already used as an adsorbent. Every type of combustible organic substances except fossil fuels is described as biomass. Municipal solid wastes, biosolids, industrial wastes, agricultural and forest wastes and aquatics are some of the well-known classes of biomass [25]. For this reason, hazelnut shell is a biomass and especially important in Turkey, because Turkey is the biggest hazelnut producer country in the world [26]. North coasts of Turkey are so suitable to grow hazelnut that approximately 80% of the total hazelnut production in the world is supplied from this region [27]. Therefore, there is a great potential of woody hazelnut shell to use in some industrial applications in that region. Consequently, some investigations with hazelnut shell have been conducted below. Usta et al. [28] investigated the possibility of the production of a methyl ester biodiesel from hazelnut waste/sunflower oil mixture using methanol, sulphuric acid and sodium hydroxide in a two-stage process. Haykiri-Acma [26] investigated the effects of particle size on the non-isothermal slow pyrolysis of hazelnut shell from ambient to 1173 K with a linear heating rate of 20 K/min under dynamic nitrogen atmosphere. Demirbaş et al. [29] investigated Ni(II) removal from simulated solution using hazelnut shell activated carbon. They found that metal adsorption improved with an increasing temperature. With an initial metal concentration of 15 mg/L, the optimum Ni(II) removal took place at pH 3.0 with metal adsorption capacity of 10.11 mg/g. In another study, hazelnut shell was also employed for Cr(VI) adsorption from simulated solution with an initial Cr(VI) concentration of 1000 mg/L [30]. About 170 mg/g of Cr(VI) capacity occurred at pH 1.0. The results indicate that the adsorption capacity of individual adsorbent depends on the initial metal concentration. Bayrak et al. [31] described the batch adsorption characteristics of Cr(VI) on hazelnut shell ash (HSA) and activated bentonite. Dogan et al. [32] investigated the effects of low and high dose irradiation on hazelnut tissue at the molecular level and secondly to employ mid-FTIR in food irradiation research. Ferrero [33] studied the dye adsorption behavior of ground hazelnut shells was compared with that of wood sawdust; a low cost adsorbent already experimented for dye removal. Bulut and Tez [34] investigated the adsorption behavior of Ni(II), Cd(II) and Pb(II) from aqueous solutions by shells of hazelnut and almond and found the selectivity order of the adsorbents was Pb(II) > Cd(II) > Ni(II).

The investigation reported here deals with equilibrium studies of hazelnut shell, which is a very cheap, combustible and readily available material for the removal of Cu^{2+} from aqueous solutions. The effects of contact time, particle size, temperature of solution and pH on the removal of Cu^{2+} moreover, zeta potential of particles at different initial pHs was evaluated. The thermodynamic parameters and the kinetics of the adsorption of Cu^{2+} were also calculated and discussed.

2. Materials and methods

2.1. Materials

Hazelnut shell was obtained from species of *Corylus avellana L.* (the variety is Tombul) from Giresun in Turkey and its estimated reserves are approximately 3×10^5 t/year [35]. After obtained, fresh hazelnut shells were washed several times with distilled water to remove surface impurities and then dried at 373 K for 24 h. Then samples were crushed by grinder and then sieved and separated into three particle size fractions of $(-75\,\mu m)$, $(75–150\,\mu m)$ and $(150–200\,\mu m)$. Some physical and chemical properties and surface functional groups of hazelnut shell were given by Bulut and Tez [34]. The surface functional groups containing oxygen were determined according to Boehm titration [36,37] and found $0.318\,mmol\,g^{-1}$ carboxylic, $0.075\,mmol\,g^{-1}$ lactonic and $0.793\,mmol\,g^{-1}$ phenolic groups. Surface area (BET), contents of C and H (%) of hazelnut shell were given as $4.31\,m^2\,g^{-1}$, 42.67 and 4.74, respectively [34]. All chemicals were obtained from Merck and Aldrich, and were of analytical grade.

2.2. Zeta potential measurements

The zeta potential of hazelnut shell suspensions was measured using a Zeta Meter 3.0+ (Zeta Meter Inc.) equipped with a microprocessor unit. The unit automatically calculates the electrophoretic mobility of the particles and converts it to the zeta potential using the Smoluchowski equation. The zeta potential measurements were carried out as a function of the equilibrium pH. The suspension pH was adjusted by addition of HCl and NaOH. A sample of 0.2 g the hazelnut shell in 50 mL distilled water containing desired pH values was added to an orbital shaker incubator and rinsed for 24 h at $25 \pm 1\,^\circ C$. The samples were allowed to stand for 1 min to let larger particles settle. An aliquot taken from the supernatant was used to measure the zeta potential. The applied voltage during the measurements was generally varied in the range of 50–150 mV [38].

2.3. Adsorption experiment

Aqueous solutions of copper were prepared from copper nitrate. Ultrapure water was used throughout the study. The adsorption experiments were carried out by mechanically shaking 0.2 g of the hazelnut shell samples with 50 mL of aqueous solution containing the metal ions in a concentration range of 1.575×10^{-5} to $1.45 \times 10^{-3}\,mol\,L^{-1}$ for the required pH, temperature and particle size in 100 mL covered polyethylene containers. The equilibration time was found to be 3 h but for practical reasons the adsorption experiments were run for 24 h. Polyethylene flasks were shaken (150 rpm) at constant temperature using a GFL model incubator orbital shaker with temperature control in the range of 4–60 °C. The solution pH was controlled by addition of HCl and NaOH by using an Orion

920 A pH meter with a combined pH electrode. The pH meter was standardized with NBS buffers before every measurement. The concentration of copper ions was determined by using a Unicam 929 Atomic Absorption Spectrometer with air–acetylene flame. Quantification of the metals was based upon calibration curves of standard solutions of copper ion. These calibration curves were determined several times during the period of analysis. All the adsorption studies were repeated three times; hence, the reported value of metal ion adsorbed is the average of three measurements. Blanks containing no Cu^{2+} were used for each series of experiments. The adsorption capacity of the hazelnut shell was evaluated using the following expression:

$$q_e = (C_0 - C_e)\frac{V}{W} \tag{1}$$

where q_e is the amount of metal ion adsorbed onto the unit mass of the hazelnut shell (mol g^{-1}), C_0 and C_e the concentration of the metal ion in the initial solution and in the aqueous phase after treatment for a certain period of time (mol L^{-1}), V the volume of the aqueous phase (L) and W is the amount of hazelnut shell used (g).

3. Results and discussion

3.1. Zeta potential

Adsorption is a process of considerable complexity and an interesting challenge in understanding the solution and interfacial behavior of suspensions. Therefore, it is necessary to investigate the electrokinetic properties of adsorbent suspensions. The study of zeta potential can also lead to a better knowledge of the double layer region, especially for ionic solids [38]. The hazelnut shell carries the surface functional groups containing oxygen such as carboxylic, lactonic and phenolic. These compounds are the active ion exchange compounds. In acidic and basic solutions, these groups can be protonated or deprotonated. The electrophoretic mobility of solid suspensions may be measured as a function of pH. By this technique, it may also be observed that the colloid passes through a net zero point of charge at which its mobility is zero. The point at with charge reversal is observed electrophoretically is called as the isoelectric point (iep). The pH$_{iep}$ also indicates that at this point, there is no charge at the surface, that is, the total positive charges are equal to the total negative charges. Fig. 1 illustrates the effect of pH on the zeta potential of hazelnut shell sample. As shown in this figure, the sample has no isoelectric point and exhibits negative zeta potential value at all studied pH values. Consequently, it may be said that the hazelnut shell surface has a negative charge at studied pH values.

3.2. Mechanism of adsorption

Hazelnut shell contains polar functional groups such as aldehydes, ketones, acids and phenolics. These groups can be involved in chemical bonding and are responsible for the cation-exchange capacity of the shell. Thus, the shell/copper reaction may be represented in two ways (Scheme 1).
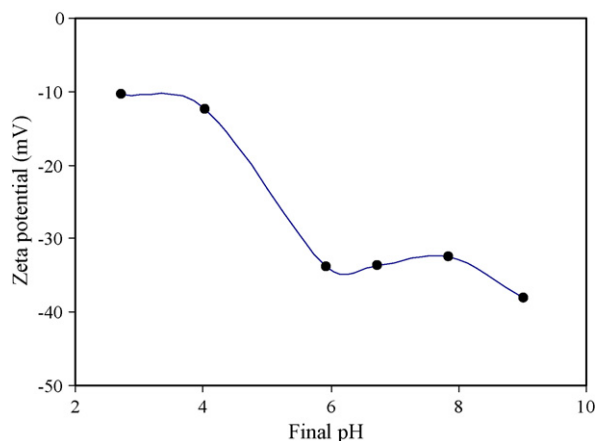

Fig. 1. The variation of zeta potential with equilibrium pH of hazelnut shell suspensions at 25 °C and −75 μm particle size.

According to this scheme, possible mechanisms of ion exchange can be considered as a divalent heavy metal ion (M^{2+}) attaches itself to two adjacent hydroxyl groups and two-oxyl groups which could donate two pairs of electrons to metal ions, forming four coordination number compounds and releasing two hydrogen ions into solution [39].

3.3. Adsorption capacity as a function of incubation time of hazelnut shell

The adsorption of Cu^{2+} ions on hazelnut shell was carried out in aqueous solutions at pH 3 and 25 °C. The initial concentration of Cu^{2+} ions was 40 ppm (6.3×10^{-4} mol L^{-1}) and the solid concentration was 4 g L^{-1}. Measuring the concentration of Cu^{2+} in solution at different incubation times generated in a time course of the adsorption. The result is shown in Fig. 2. According to Fig. 2, the time required to reach a stationary concentration is about 3 h.

3.4. Effect of particle size

Sorption isotherms of copper ions at various particle sizes of hazelnut shell are shown in Fig. 3. The amount of copper ion sorbed increased under the condition that the particle size of the sorbent decreased. Langmuir parameters Q_m and K for each of the three isotherms have been calculated and are listed in Table 1. It is clear that Q_m, the monolayer coverage for each par-
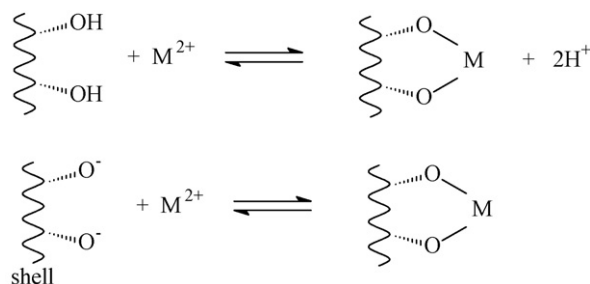
Scheme 1. Possible mechanisms of ion exchange.

Table 1
Thermodynamic parameters and isotherm constants for Cu^{2+} adsorption onto hazelnut shell

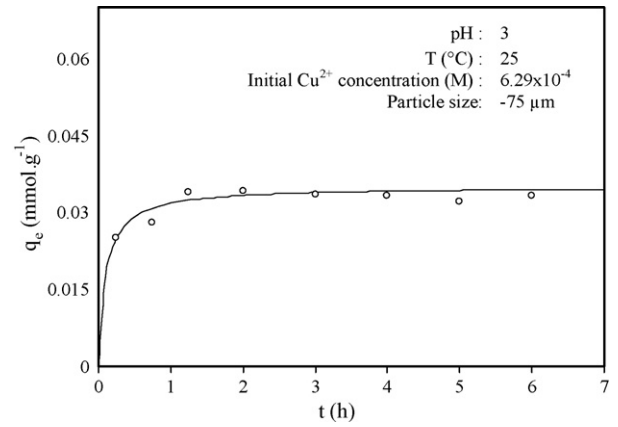| Temperature (°C)	Initial pH	Particle size (μm)	Surface area of particle (m^2 g^{-1})	Thermodynamic parameters			Langmuir isotherm			Freundlich isotherm		
				$\Delta G°$ (kJ mol^{-1})	$\Delta S°$ (J mol^{-1} K^{-1})	$\Delta H°$ (kJ mol^{-1})	Q_m (×10^5 mol g^{-1})	K (×10^{-5} L mol^{-1})	R^2	n	K_F (×10^3)	R^2
25	3.0	<75	0.62	−26.87	44.31	13.58	6.578	0.512	0.987	1.58	5.46	0.952
35	3.0	<75	0.71	−27.24			7.534	0.415	0.996	1.30	20.85	0.888
45	3.0	<75	0.73	−27.60			7.759	0.341	0.999	1.41	12.40	0.815
60	3.0	<75	0.80	−28.45			8.487	0.289	0.999	1.23	31.42	0.759
25	5.0	<75	0.66	–	–	–	6.998	0.363	0.980	2.32	1.28	0.978
25	7.0	<75	0.98	–	–	–	10.400	0.080	0.994	2.27	2.76	0.961
25	3.0	75–150	0.55	–	–	–	5.812	0.827	0.981	1.47	6.40	0.959
25	3.0	150–200	0.53	–	–	–	5.623	0.629	0.995	1.91	2.07	0.971

Fig. 2. Adsorption capacity as a function of incubation time of hazelnut shell.

ticle size, increased from 5.62×10^{-5} to 6.57×10^{-5} mol g^{-1} with decreasing particle size from 150–200 to 0–75 μm. This may be attributed to the larger external surface available with smaller particles at a constant total mass of hazelnut shell in the system. The plateau on each isotherm corresponds to monolayer coverage of the surface by the metal ions and this value is the ultimate sorptive capacity at high concentrations can be used to estimate the specific surface area, S, of hazelnut shell using the following equation [40] and the results are shown in Table 1:

$$S = \frac{q_m N_A A}{M_A} \tag{2}$$

where S is the specific surface area of hazelnut shell (m^2 g^{-1}), Q_m the monolayer sorption capacity, gram metal per gram of hazelnut shell, N_A the Avogadro number (6.02×10^{23}), A the cross-sectional area of metal ion (m^2) and M is the molecular weight of metal. For Cu^{2+} ion, the molecular weight is 63.5 and the cross-sectional areas of Cu^{2+} have been determined to be 1.58 Å^2 (Cu^{2+} radius is 0.71 Å) in a close packed monolayer [40]. Therefore, the specific surface areas can be calculated for Cu^{2+} (Table 1). As seen in this table, the maximum specific surface area of hazelnut shell is 0.62 m^2 g^{-1} for −75 μm particle size.
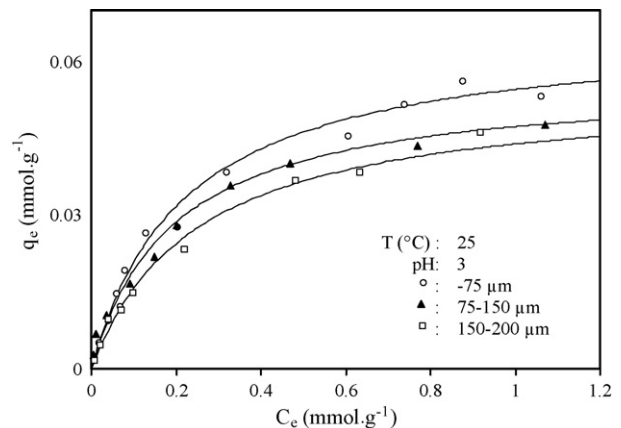

Fig. 3. The effect of particle size on adsorption capacity of hazelnut shell.
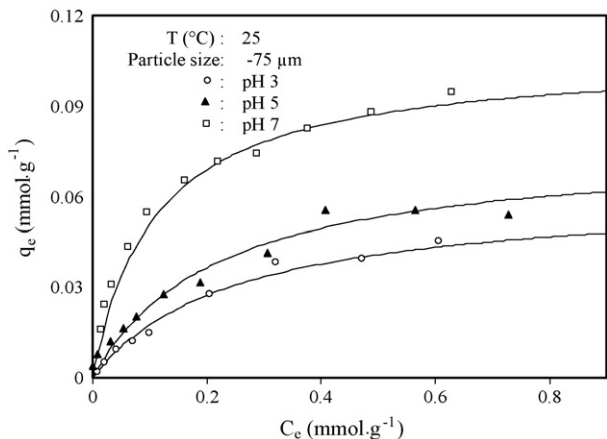
Fig. 4. The effect of suspension pH on adsorption capacity of hazelnut shell.

3.5. Effect of pH

In fact the suspension of hazelnut shell in distilled water was already acidic (∼pH 4.55 for this study) owing the presence of carboxylic and phenolic groups and shell surface has negative charge (see Fig. 1). Therefore, it can be considered that the adsorption of heavy metal ions onto hazelnut shell is quite favorable in natural situation. The influence of pH on the sorption capacity of hazelnut shell for copper is shown in Fig. 4 as seen this figure, the sorption capacities increased with increasing pH values. But as the pH approaches 7 it can be observed that the saturation capacity is beginning to maximum increase probably due to competition with hydrogen ions at low pH. This suggests that as more copper ions are adsorbed onto the hazelnut shell, more hydrogen ions are released from the shell in to the solution (see Section 3.3), consequently decreasing the pH of the reaction mixture. According to Dissanayake and Weerasooriya [41], pH was found to have a marked effect on copper ions adsorption. Below pH 7, the adsorption of copper ions by hazelnut shell was low. When the adsorption of copper ions was carried out at the initial pHs 3.0, 5.0 and 7.0, the final pHs were about 2.9, 4.2 and 6.3. Adsorption density at lower initial pH was much lower. It is, therefore, concluded that the adsorption of copper competes with hydrogen ions. Similar experimental details have been reported by Ho et al. [42,43].

3.6. Effect of temperature and thermodynamic parameters

Sorption isotherms of copper ions at various temperatures (298–333 K) of solution are shown in Fig. 5. The degree of adsorption increases with increased temperature, indicating that the adsorption is endothermic. The free energy of adsorption (ΔG°) can be related with the equilibrium constant K (L mol^{-1}) corresponding to the reciprocal of the Langmuir constant, K, the values of enthalpy change (ΔH°) and entropy change (ΔS°), for the adsorption process were calculated, using the following equations [25–29]:

$$\Delta G^\circ = -RT \ln K \qquad (3)$$

$$\ln K = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \qquad (4)$$

Thus, a plot of $\ln K$ versus $1/T$ should be a straight line. ΔH° and ΔS° values were obtained from the slope and intercept of this plot, respectively [44]. Table 1 presents the values of thermodynamic parameters. Positive values of ΔH° suggest the endothermic nature of the adsorption and the negative values of ΔG° indicate the spontaneous nature of the adsorption process. However, the value of ΔG° decreased with an increase in temperature, indicating that the spontaneous nature of adsorption is inversely proportional to the temperature. The positive values of ΔS° show the increased randomness at the solid/solution interface during the adsorption process. The adsorbed water molecules, which are displaced by the adsorbate species, gain more translational energy than the energy lost by the adsorbate ions, thus allowing the prevalence of randomness in the system. The enhancement of adsorption at higher temperatures may be attributed to the enlargement of pore size and/or activation of the adsorbent surface [45].

3.7. Adsorption isotherms

The adsorption data obtained for equilibrium conditions have been analyzed by using the linear forms of the Freundlich and Langmuir isotherms. Langmuir and Freundlich models are the simplest and most commonly used isotherms to represent the adsorption of components from a liquid phase onto a solid phase [46]. The Langmuir model assumes monolayer adsorption while the Freundlich model is empirical in nature. The data are analyzed to obtain Freundlich and Langmuir parameters. The linear plot for Langmuir isotherm has been obtained using following equation:

$$\frac{C_e}{q_e} = \frac{1}{q_m K} + \frac{C_e}{q_m} \qquad (5)$$

where C_e is the equilibrium concentration of adsorbate in solution (mol L^{-1}), q_e the equilibrium loading of adsorbate on adsorbent (mol g^{-1}), q_m the ultimate adsorption capacity (mol g^{-1}) and K is the relative energy of adsorption (L mol^{-1}). The Langmuir model can be linearized to obtain the parameters
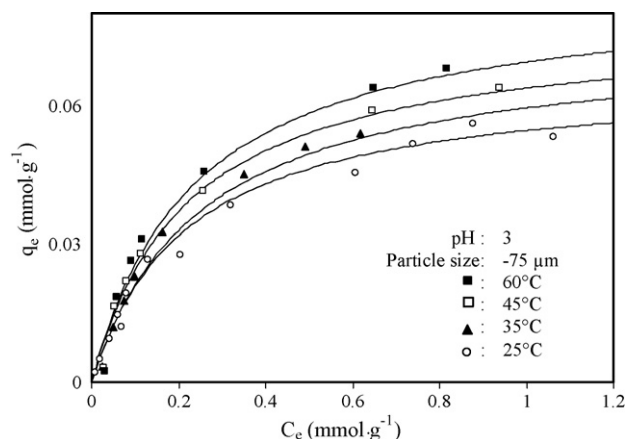

Fig. 5. The effect of temperature on adsorption capacity of hazelnut shell.

Table 2
Kinetic values calculated for Cu^{2+} adsorption onto hazelnut shell

First-order kinetic equation	
k_1 ($\times 10^3$ min^{-1})	7.9
q_e (calculated) ($\times 10^6$ mol g^{-1})	5.60
R^2	0.81
$t_{1/2}$ (min)	87.74
Second-order kinetic equation	
k_2 ($\times 10^{-2}$ g mol^{-1} min^{-1})	62.46
q_e (calculated) ($\times 10^5$ mol g^{-1})	3.35
R^2	0.99
$t_{1/2}$ (min)	47.79
Intraparticle diffusion equation	
k_{int} ($\times 10^6$ mol g^{-1} min$^{-1/2}$)	0.72
R^2	0.83

Experimental conditions: 25 °C, pH 3.0, amount of initial Cu^{2+}: 6.29×10^{-4} M.

q_m and K from experimental data on equilibrium concentrations and adsorbent loading.

The Freundlich model at logarithmic form is expressed as

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \qquad (6)$$

where k and $1/n$ are Freundlich isotherm constants.

Sorption equations were obtained by experimental data with Eqs. (5) and (6). The isotherm constants were calculated from the least square method and presented in Table 1. The Langmuir equation represents the sorption process well, the R^2 value is higher for Langmuir isotherm than the Freundlich isotherm. This may be due to homogenous distribution of active sites on shell surface [47–49].

3.8. Adsorption kinetics

In order to examine the controlling mechanism of sorption process, several kinetic models were used to test the experimental data. From a system design viewpoint, a lumped analysis of sorption rates is thus sufficient for practical operation [50,51].

3.8.1. Pseudo first-order equation

The pseudo first-order equation is generally expressed as follows [50–52]:

$$\ln (q_e - q_t) = \ln q_e - k_1 t \qquad (7)$$

where q_e and q_t are the amounts of copper ions adsorbed at equilibrium and time t (mol g^{-1}), respectively and k_1 is the rate constant of pseudo first-order adsorption (min^{-1}).

The half-adsorption time of the copper ions, $t_{1/2}$, is the time required for the oxide samples to take up half as much copper ions as it would at equilibrium. This time is often used as a measure of the rate of adsorption and given by

$$t_{1/2} = \frac{\ln 2}{k_1} \qquad (8)$$

The values k_1 and $t_{1/2}$ are given in Table 2.

Table 3
Some agricultural waste and oxide minerals utilized for removal of Cu^{2+} ions by adsorption

Samples	Optimum pH	Adsorbed amount (mmol g^{-1})	Reference
Pecan shell	3.6	1.496	[53]
Coirpith	4–5	0.161	[54]
Peanut hulls	NA	0.160	[55]
Hazelnut shell	5–7	0.104	In this study
Orange peel	6–8	0.095	[56]
Banana peel	6–8	0.075	[56]
Cocoa shell	2.0	0.045	[57]
Kaolinite	NA	0.170	[58]
Vermiculite	6.0	0.135	[59]
Natural zeolite	5.5–6.5	0.393	[60]
Perlite	NA	0.016	[61]

NA: not available.

3.8.2. Pseudo second-order equation

If the rate of adsorption is a second-order mechanism, the pseudo second-order equation is expressed as [50–52]:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \qquad (9)$$

where q_e is the amount of copper ions adsorbed at equilibrium (mol g^{-1}) and k_2 is the equilibrium rate constant of pseudo second-order sorption (g mol^{-1} min^{-1}).

The half-adsorption time of the copper ions, $t_{1/2}$, is

$$t_{1/2} = \frac{1}{k_2 q_e} \qquad (10)$$

The values k_2, q_e and $t_{1/2}$ are given in Table 2.

3.8.3. Intraparticle diffusion equation

The fractional approach to equilibrium changes according to a function of $(Dt/r^2)^{1/2}$, where r is the particle radius and D is the diffusivity of solute within the particle. The initial rate of the intraparticle diffusion is in the following equation [50]:

$$q_t = k_{int} t^{1/2} + C \qquad (11)$$

where k_{int} is the intraparticle diffusion rate constant (mg g^{-1} min$^{-1/2}$) and given in Table 2.

3.9. Comparison of hazelnut shell with other agricultural adsorbents

A comparison between the adsorption capacities of hazelnut shell and other adsorbents is presented in Table 3. From Table 3, it can be concluded that the pecan shell adsorbed copper ion more than other adsorbents. Also, hazelnut shell is quite favorable for the adsorption of copper ions from aqueous solution. In this case, we can say that hazelnut shell can be used for the removal of copper from wastewaters.

4. Conclusion

The adsorption of copper ions with hazelnut shell was systematically investigated under various conditions:

- Surface of hazelnut shell exhibits negative zeta potential value at all studied pH values. One clear conclusion is that hazelnut shell has no isoelectrical point in the studied pH ranges.
- The sorption capacities increased with increasing pH and decreasing particle size values.
- The adsorption process becomes more favorable with increasing temperature. The Langmuir isotherm model appears to fit the isotherm data better than the Freundlich isotherm model.
- The data obtained from adsorption isotherms at different temperatures were used to calculate thermodynamic quantities such as Gibbs energies (-26.87, -27.24, -27.60 and $-28.45\,kJ\,mol^{-1}$ for 25, 35, 45 and 60 °C), enthalpy ($+13.58\,kJ\,mol^{-1}$) and entropy of adsorption ($44.31\,J\,(mol^{-1}\,K^{-1})$).
- The correlation coefficients for the second-order kinetic model are greater than 0.99 indicating the applicability of this kinetic equation and the second-order nature of the adsorption process of copper ions on hazelnut shell.
- As a result of hazelnut shell can be used as an adsorbent for batch adsorption of Cu^{2+} ions from aqueous solution under different conditions.

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