Desalination and Water Treatment
www.deswater.com
doi: 10.1080/19443994.2013.866053

53 (2015) 2692–2700
March

Taylor & Francis
Taylor & Francis Group

Biosorption of zinc ions onto *Corylus avellana* L.

Özkan Demirbaş[a,*], Adem Karadağ[b]

[a]*Department of Chemistry, Faculty of Science and Literature, University of Balikesir, Balikesir 10145, Turkey*
Tel. +90 266 6121000, +90 342 3601200; Fax: +90 266 6121215; email: ozkan@balikesir.edu.tr
[b]*Naci Topcuoglu Vocational School of Higher Education, University of Gaziantep, Gaziantep 27180, Turkey*

Received 19 January 2013; Accepted 12 November 2013

ABSTRACT

Hazelnut is one of the most important agricultural products of Turkey. 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. There is a great potential of woody hazelnut shell (obtained from species of *Corylus avellana* L.) to use in some applications in that region. Sorption studies are one of these. For this reason in this paper, batch adsorption of Zn^{2+} ions onto ground and sieved hazelnut shells was studied in comparable with sawdust of various species of wood and in order to explore the potential use of this material as low cost adsorbent for heavy metal removal in industrial effluents. The capacity of the adsorption for the removal of zinc ions from aqueous solution was investigated under different conditions such as solution contact time (1–360 min), particle size (–75, 75–150 and 150–200 μm), temperature of solution (25 °C–60 °C) 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 isotherm models and higher adsorption capacity values towards Zn^{2+} ions were shown. The adsorption kinetics was investigated and the best fit was achieved by a pseudo-second-order equation.

Keywords: Adsorption; Kinetics; Hazelnut shell; Zeta potential; Zinc ion

1. Introduction

Heavy metal pollution by industrial activities and technological development is posing significant threats to the environment and public health because of its toxicity, nonbiodegradability, and bioaccumulation. Even though zinc is an essential requirement for a healthy body, excess zinc can be harmful. Zinc is introduced into the water from metal mining, melting, plating, pesticides, oil-based paint pigments, alloy processing, and sewage sludge. The free zinc ion in solution is highly toxic to plants, invertebrates, and even vertebrate fish [1]. Micromolar amounts of the free ion kill some organisms. A recent example showed six micromolar killing 93% of all *Daphnia* in water [2].

Various methods have been suggested and applied for the removal of toxic metals from aqueous solutions, such as chemical precipitation, evaporation, ion exchange, adsorption, cementation, electrolysis, and reverse osmosis. 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

*Corresponding author.

a wastewater treatment process compared to the other purification and separation methods, and has gained importance in industrial applications [3,4], 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. 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, and clay [5]; sepiolite [6]; kaolinite [7]; and perlite [8]. 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 [9], wood [10], pine bark [11], banana pith [12], rice bran, soybean, and cottonseed hulls [13], peanut shells [14], hazelnut shell [15], rice husk [16], sawdust [17], wool [18], orange peel and compost [19], and leaves [20]. 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.

Hazelnut shell is a biomass and especially important in Turkey, because Turkey is the biggest hazelnut producer country in the world [21]. 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 [22]. Therefore, there is a great potential of woody hazelnut shell to use in some industrial applications in that region.

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 Zn(II) from aqueous solutions. The effects of contact time, particle size, temperature of solution, and pH on the removal of Zn(II) and, moreover, zeta potential of particles at different initial pHs were evaluated. The thermodynamic parameters and the kinetics of the adsorption of Zn(II) 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 ton/year [23]. 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 (0–75 μm), (75–150 μm), and (150–200 μm). Some physical and chemical properties and surface functional groups of hazelnut shell were given by Bulut and Tez [24]. The surface functional groups containing oxygen were determined according to Boehm titration [25,26] and found 0.318 mmol/g carboxylic, 0.075 mmol/g lactonic, and 0.793 mmol/g phenolic groups. Surface area (BET), contents of *C*, and *H* (%) of hazelnut shell were given as 4.31 m^2/g, 42.67, and 4.74 respectively [24]. The sample of hazelnut shell particles was also subjected to morphological and microstructural analysis using a SCM 5,000 Benchtop scanning electron microscope (SEM) (Neoscope). Fig. 1 gives morphological features of the hazelnut shell sample. The original hazelnut shell sample has a leafy structure rather than regular particles and there are large gaps and cavities in its framework; consequently, it does not have a mechanically firm structure and its density should be low. Thermal properties of hazelnut were obtained from thermogravimetric analysis (TGA), including moisture, volatile matter, fixed carbon, and ash content. Fig. 2 shows the TGA of hazelnut shell. Generally, three different regions can be distinguished from a particular TG curve, in spite of materials tested.

In Fig. 2, different stages of decomposition curves were clearly shown by the red vertical lines. The first stage (temperature below 200°C) corresponds to the drying period where light volatiles, mainly water, were liberated throughout the procedure. Devolatilization is the major step in all thermochemical conversion process involving biomass. This step is represented by the second stage of decomposition, occurring at

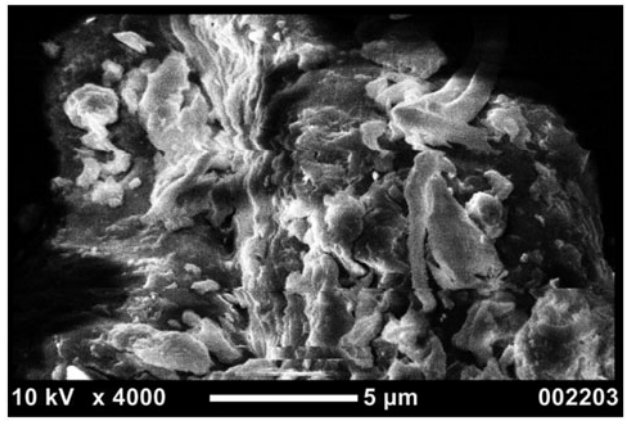

Fig. 1. SEM image of hazelnut shell.

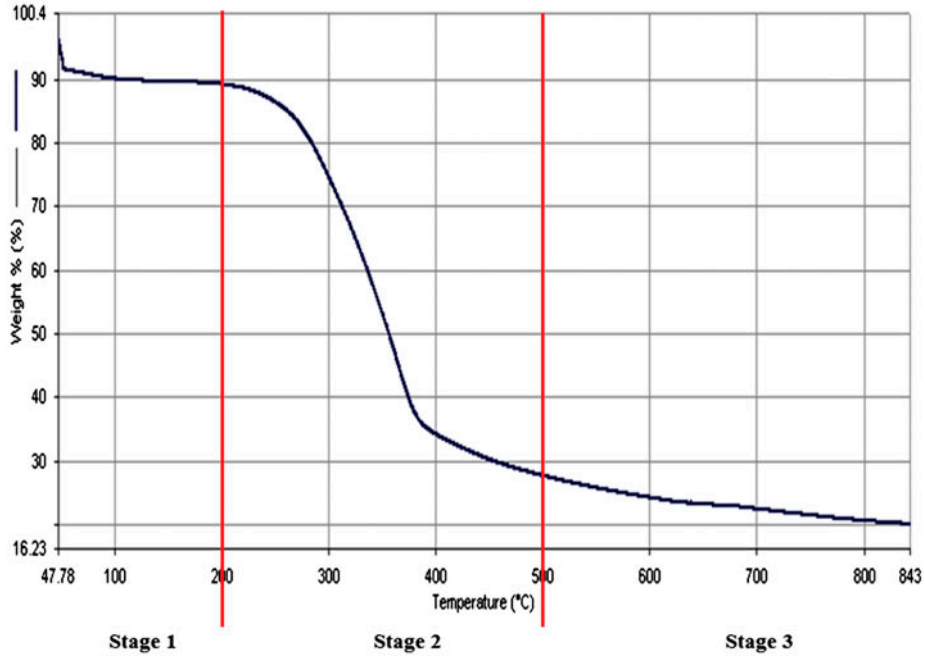

Fig. 2. TG analaysis of hazelnut shell.

temperature between 200 and 500°C, where remarkable slope of the TG curves is observed, corresponding to significant drop in weight of samples due to liberation of volatile hydrocarbon from rapid thermal decomposition of hemicelluloses, cellulose, and some part of lignin. At this stage, weight of the hazelnut shell material is reduced to above 50%. For stage 3, weight loss is not as momentous as in stage 2, primarily due to the steady decomposition of the remaining heavy components mainly from lignin.

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 ± 10°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 [27].

2.3. Adsorption experiment

Aqueous solutions of zinc were prepared from zinc 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}–1.45×10^{-3} mol/L for the required pH, temperature, and particle size in 100 mL covered polyethylene containers. The equilibration time was found to be 2 h but for practical reasons the adsorption experiments were run for 24 h. Polyethylene flasks were shaken (150 rpm) at a constant temperature using a GFL model incubator orbital shaker with temperature control in the range of 40°C–60°C. The solution pH was controlled by addition of HCl and NaOH by using an Orion 920A pH meter with a combined pH electrode. The pH meter was standardized with NBS buffers before every measurement. The concentration of zinc 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 zinc 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 Zn^{2+} were used for each series of experiments. The

adsorption capacity of the hazelnut shell was evaluated using the following expression:

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

where q_e is the amount of metal ion adsorbed onto the unit mass of the hazelnut shell (mol/g); C_0 and C_e respectively are 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); V is 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

The study of zeta potential can also lead to a better knowledge of the double-layer region, especially for ionic solids [27]. 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 zeta potentials of solid suspensions may be measured as a function of pH. 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. 3 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.

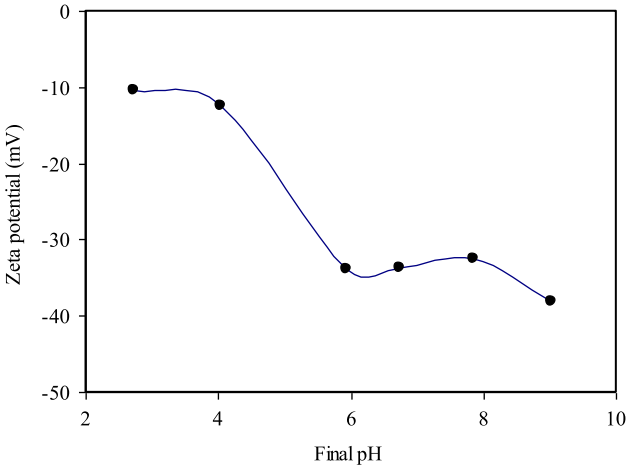

Fig. 3. The variation of zeta potential with equilibrium pH of hazelnut shell suspensions at 25°C, –75 μm particle size.

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/zinc reaction may be represented in two ways as shown in the Fig. 4.

According to this figure, possible mechanism of ion exchange is that is a divalent heavy metal ion (Zn^{+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 [28].

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

The adsorption of Zn^{2+} ions on hazelnut shell was carried out in aqueous solutions at pH 3 and 25°C. The initial concentration of Zn^{2+} ions was 40 ppm (6.1×10^{-4} mol L^{-1}) and the solid concentration was 4 g L^{-1}. Measuring the concentration of Zn^{2+} in solution at different incubation times generated in a time course of the adsorption. The result is shown in Fig. 5. According to Fig. 5, the time required to reach a stationary concentration is about 2 h.

3.4. Effect of particle size

Sorption isotherms of zinc ions at various particle sizes of hazelnut shell are shown in Fig. 6. The amount of zinc 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 particle size, increased from 2.36×10^{-5} to 3.48×10^{-5} mol/g with decreasing particle size from150–200 to 0–75 μm. This may be attributed to the

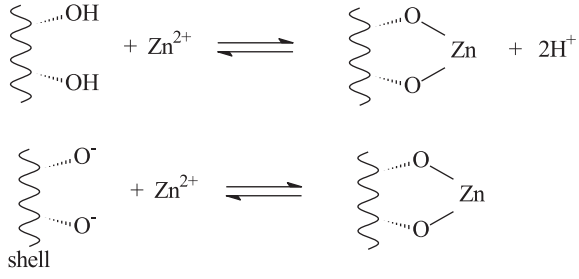

Fig. 4. Possible mechanisms of ion exchange.

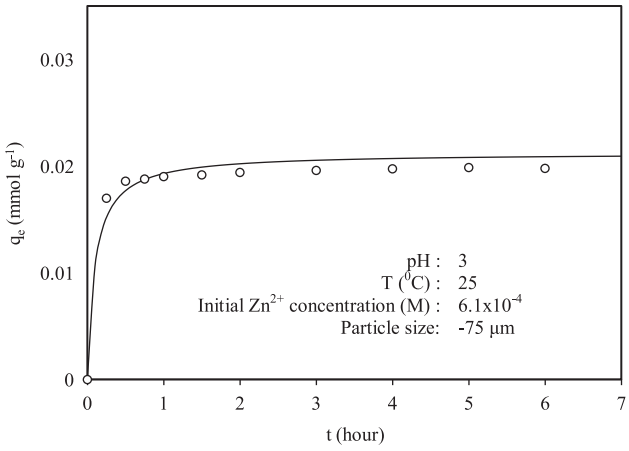

Fig. 5. Adsorption capacity as a function of incubation time of hazelnut shell.

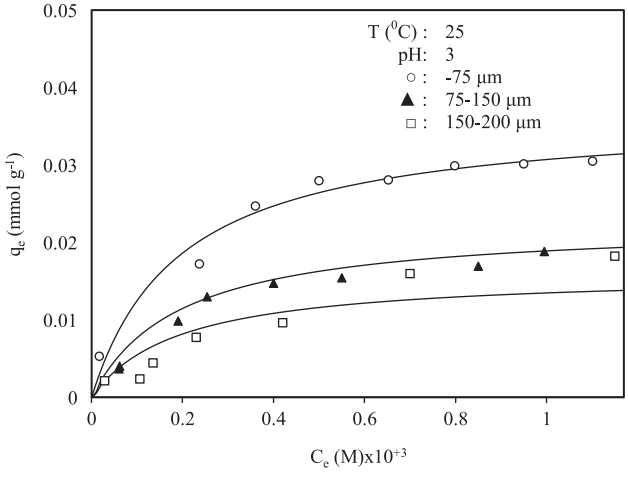

Fig. 6. The effect of particle size on adsorption capacity of hazelnut shell.

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 that can be used to estimate the specific surface area, *S*, of hazelnut shell using the following equation [29] and the results are shown in Table 1.

$$S = \frac{Q_m N_A A}{M_A} \quad (2)$$

where *S* is the specific surface area, m^2/g hazelnut shell; Q_m is the monolayer sorption capacity, gram metal per gram hazelnut shell; N_A is Avogadro number, 6.02×10^{23}; A is the cross-sectional area of metal ion, m^2; and M is the molecular weight of metal. For Zn^{2+} ion, the molecular weight is 65.38 and the cross-sectional areas of Zn^{2+} have been determined to be 1.72 $Å^2$ (Zn^{2+} radius is 0.74 Å) in a closely packed monolayer. Therefore, the specific surface areas can be calculated for Zn^{2+} (Table 1). As seen in this table, the maximum specific surface area of hazelnut shell is 1.47 m^2/g for –75 μm particle size.

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. 3). 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 zinc is shown in Fig. 7. As seen this figure, the sorption capacities

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

				Thermodynamic Parameters			Langmuir isotherm			Freundlich isotherm		
Temp. (℃)	Initial pH	Particle size (μm)	Surface area of particle (m^2/g)	ΔG^0 kj/mol	ΔS^0 kj/mol	ΔH^0 kj/mol	$Q_m \times 10^5$ (mol g^{-1})	$K \times 10^{-5}$ (L mol^{-1})	R^2	n	$K_F \times 10^3$	R^2
25	3.0	−75	0.36	−29.03	27.68	31.51	3.48	1.227	0.980	1.77	3.49	0.889
35	3.0	−75	0.74	−28.71			7.18	0.741	0.990	1.82	3.45	0.986
45	3.0	−75	0.83	−28.85			7.99	0.550	0.996	1.23	13.40	0.911
60	3.0	−75	0.86	−29.51			8.34	0.313	0.996	2.12	1.20	0.986
25	5.0	−75	0.72	–	–	–	6.93	0.368	0.980	2.32	2.16	0.945
25	7.0	−75	1.47	–	–	–	12.20	0.100	0.985	1.52	1.52	0.959
25	3.0	75–150	0.26	–	–	–	2.54	0.495	0.930	1.65	1.61	0.916
25	3.0	150–200	0.24	–	–	–	2.36	0.504	0.980	1.77	3.49	0.889

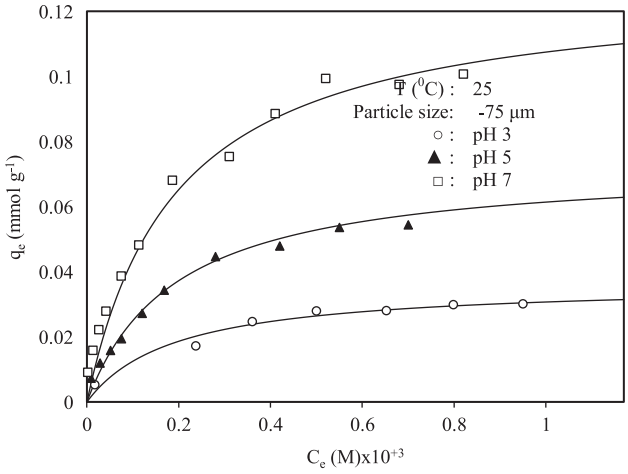

Fig. 7. The effect of suspension pH on adsorption capacity of hazelnut shell.

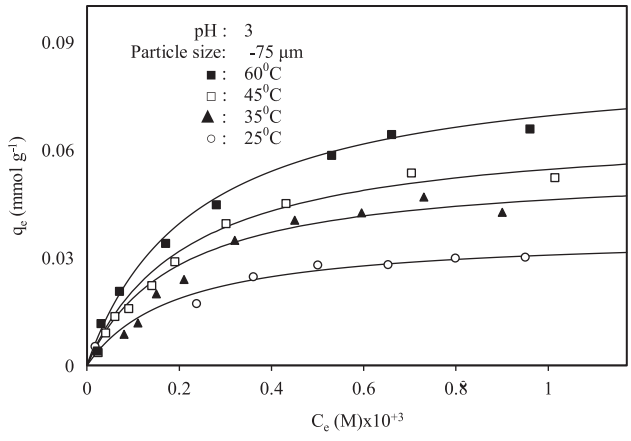

Fig. 8. The effect of temperature on adsorption capacity of hazelnut shell.

increased with increasing pH values. But, as the pH approaches 7, it can be observed that the saturation capacity is beginning to increase to its maximum probably due to competition with hydrogen ions at low pH. This suggests that as more zinc ions are adsorbed onto the hazelnut shell, more hydrogen ions are released from the shell into the solution (see Section 3.3), consequently decreasing the pH of the reaction mixture. Below pH 7, the adsorption of zinc ions by hazelnut shell was low. When the adsorption of zinc ions were carried out at the initial pHs 3.0, 5.0, and 7.0, and the final pHs were about 3.1, 4.0, and 6.0. Adsorption density at lower initial pH was much lower. It is, therefore, concluded that the adsorption of zinc competes with hydrogen ions. Similar experimental details have been reported by Ho et al. [30,31].

3.6. Effect of temperature and thermodynamic parameters

Sorption isotherms of zinc ions at various temperatures (298–333 K) of solution are shown in Fig. 8. The degree of adsorption increases with increasing temperature, indicating that the adsorption is endothermic. The free energy of adsorption (ΔG^0) can be related with the equilibrium constant K (L/mol) corresponding to the reciprocal of the Langmuir constant, K, and the values of enthalpy change (ΔH^0) and entropy change (ΔS^0) for the adsorption process were calculated, using the following equations [21,22]:

$$\Delta G^0 = -RT \ln K \quad (3)$$

$$\ln K = \Delta S^0/R - \Delta H^0/RT \quad (4)$$

Thus, a plot of $\ln K$ vs $1/T$ should be a straight line. ΔH^0 and ΔS^0 values were obtained from the slope and intercept of this plot, respectively [32]. Table 1 presents the values of thermodynamic parameters. Positive values of ΔH^0 suggest the endothermic nature of the adsorption and the negative values of ΔG^0 indicate the spontaneous nature of the adsorption process. However, the value of ΔG^0 decreased with an increase in temperature, indicating that the spontaneous nature of adsorption is inversely proportional to the temperature. The positive values of ΔS^0 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 [33].

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 [34]. 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:

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

First-order kinetic equation				Second-order kinetic equation				Intraparticle diffusion equation	
$k_1 \times 10^3$ (min^{-1})	q_e (calculated) mol $g^{-1} \times 10^6$	R^2	$t_{1/2}$ (min)	$k_2 \times 10^{-2}$ g (mol min)$^{-1}$	q_e (calculated) mol $g^{-1} \times 10^5$	R^2	$t_{1/2}$ (min)	$k_{int} \times 10^6$ mol (g $min^{1/2})^{-1}$	R^2
0.019	4.24	0.86	36.48	10.06	1.99	0.99	49.95	0.20	0.72

Note: Experimental conditions: 250°C, pH 3.0, amount of initial Zn^{2+}: 6.1×10^{-4}M.

$$\frac{C_e}{q_e} = \frac{1}{q_m K} + \frac{C_e}{q_m} \tag{5}$$

where C_e is the equilibrium concentration of adsorbate in solution (mol/L), q_e is the equilibrium loading of adsorbate on adsorbent (mol/g), q_m is the ultimate adsorption capacity (mol/g), and K is the relative energy of adsorption (L/mol). The Langmuir model can be linearized to obtain the parameters q_m and K from experimental data on equilibrium concentrations and adsorbent loading.

The Freundlich model at logarithmic form is expressed as:

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \tag{6}$$

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 are presented in Table 1. The Langmuir equation represents the sorption process well; the R^2 value is higher for Langmuir isotherm than for the Freundlich isotherm. This may be due to homogenous distribution of active sites on shell surface [35–37].

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 [38,39].

3.8.1. Pseudo-first-order equation

The pseudo-first-order equation is generally expressed as follows [38–40]:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \tag{7}$$

where q_e and q_t are the amounts of copper ions adsorbed at equilibrium and time t (mol/g), 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:

$$t_{1/2} = \frac{\ln 2}{k_1} \tag{8}$$

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

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 [38–40]:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \tag{9}$$

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

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

$$t_{1/2} = \frac{1}{k_2 q_e} \tag{10}$$

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 the diffusivity of solute within

Table 3
Some agricultural waste and oxide minerals utilized for removal of zinc ions by adsorption

Samples	Optimum pH	Adsorbed amount (mmol g^{-1})	Ref.
Syzygium cumini L.	6	0.56	[41]
Botrytis cinerea	5–6	0.19	[42]
Red mud	5–7	0.19	[43]
Hazelnut shell	5–7	0.14	in this study
P. digitatum	5.5	0.14	[44]
Peat	5–7	0.14	[45]
Coir	5.5	0.13	[46]
Barley straw	5.5	0.08	[46]
Na-Montmorillonite	5	0.05	[47]

the particle. The initial rate of the intraparticle diffusion is [38]:

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

where k_{int} is the intraparticle diffusion rate constant (mg (g $min^{1/2})^{-1}$ 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 *Syzygium cumini* L. adsorbed zinc ion more than other adsorbents. Also, hazelnut shell is quite favorable for the adsorption of zinc ions from aqueous solution. In this case, we can say that hazelnut shell can be used for the removal of copper from wastewaters.

4. Conclusions

Hazelnut shell shows a good efficiency in removing from aqueous solution toxic ions such as zinc. This capacity is found to be similar to that of other comparable raw cellulosic materials and biomass.

- 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 free energy, enthalpy, and entropy of adsorption and they were calculated as –29.03 kj/mol, 27.68 j/molK, and 31.51 kj/mol, respectively.
- 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 zinc ions on hazelnut shell.

Acknowledgments

The authors thank the support from Balikesir University Research Foundation (Project No: BAP(2008/26) and the Balikesir University Research Center of Applied Science (BURCAS) for the zeta potential measurements and SEM images is gratefully acknowledged.

References

[1] R. Eisler, Zinc Hazard to Fish, Wildlife, and Invertebrates: A Synoptic Review. Contaminant Hazard Reviews, US Department of the Interior, Fish and Wildlife Service, Laurel, Maryland, 1993.
[2] T.A.M. Brita, K.A.C. De Schamphelaere, C.R. Janssen, Mechanisms of chronic waterborne Zn toxicity in Daphnia magna, Aquat. Toxicol. 77(4) (2006) 393–401.
[3] G. McKay, Use of Adsorbents for the Removal of Pollutants from Wastewater, CRC Press, Tokyo, 1996.
[4] B.S. Girgis, M.F. Ihsak, Activated carbon from cotton stalks by impregnation with phosphoric acid, Mater. Lett. 39 (1999) 107–114.
[5] S.E. Bailey, T.J. Olin, R.M. Bricka, D.D. Adrian, A review of potentially low-cost sorbents for heavy metals, Water Res. 33 (1999) 2469–2479.
[6] M. Alkan, Ö. Demirbaş, S. Çelikçapa, M. Doğan, Sorption of acid red 57 from aqueous solution onto sepiolite, J. Hazard. Mater. B116 (2004) 135–145.

[7] N. Tekin, Ö. Demirbaş, M. Alkan, Adsorption of cationic polyacrylamide onto kaolinite, Micropor. Mesopor. Mat. 85(3) (2005) 340–350.
[8] Ö. Demirbaş, M. Alkan, M. Dogan, The removal of victoria blue from aqueous solution by adsorption on a low-cost material, Adsorption 8 (2002) 341–349.
[9] Y.S. Ho, G. McKay, The kinetics of sorption of divalent metal ions onto sphagnum moss peat, Water Res. 34 (2000) 735–742.
[10] V.J.P. Poots, G. McKay, J.J. Healy, Removal of basic dye from effluent using wood as an adsorbent, J. Water Pollut. Con. F. 50 (1978) 926–935.
[11] S. Al-Asheh, Z. Duvnjak, Sorption of cadmium and other heavy metals by pine bark, J. Hazard. Mater. 56 (1997) 35–51.
[12] K.S. Low, C.K. Lee, A.C. Leo, Removal of metals from electroplating wastes using banana pith, Bioresour. Technol. 51 (1995) 227–231.
[13] W.E. Marshall, M.M. Johns, Agricultural by-products as metal adsorbents: Sorption properties and resistance to mechanical abrasion, J. Chem. Technol. Biotechnol. 66 (1996) 192–198.
[14] W. Wafwoyo, C.W. Seo, W.E. Marshall, Utilization of peanut shells as adsorbents for selected metals, J. Chem. Technol. Biotechnol. 74 (1999) 1117–1121.
[15] G. Cimino, A. Passerini, G. Toscano, Removal of toxic cations and Cr(VI) from aqueous solution by hazelnut shell, Water Res. 34 (2000) 2955–2962.
[16] S.P. Mishra, D. Tiwari, R.S. Dubey, The uptake behaviour of rice (Jaya) husk in the removal of Zn(II) ions: A radiotracer study, Appl. Radiat. Isotopes 48 (1997) 877–882.
[17] B. Yu, Y. Zhang, A. Shukla, S.S. Shukla, K.L. Dorris, The removal of heavy metals from aqueous solutions by sawdust adsorption:Removal of lead and comparison of its adsorption with copper, J. Hazard. Mater. 84 (2001) 83–94.
[18] D. Balkose, H. Baltacioglu, Adsorption of heavy metal cations from aqueous solutions by wool fibers, J. Chem. Technol. Biotechnol. 54 (1992) 393–397.
[19] M.S. Azab, P.J. Peterson, The removal of cadmium from water by the use of biological sorbents, Water Sci. Technol. 21 (1989) 1705–1706.
[20] F.R. Zaggout, Removal of copper from water by decaying Tamrix gallica leaves, Asian J. Chem. 13 (2001) 639–650.
[21] H.H. Acma, The role of particle size in the non-isothermal pyrolysis of hazelnut shell, J. Anal. Appl. Pyrolysis 75 (2006) 211–216.
[22] A. Topuz, M. Topakci, M. Canakci, I. Akinci, F. Ozdemir, Physical and nutritional properties of four orange varieties, J. Food Eng. 66 (2005) 519.
[23] Y. Bulut, Z. Baysal, Removal of Pb (II) from wastewater using wheat bran, J. Environ. Manage. 78 (2006) 107–113.
[24] Y. Bulut, Z. Tez, Adsorption studies on ground shells of hazelnut and almond, J. Hazard. Mater. 149(1) (2007) 35–41.
[25] H.P. Boehm, Surface oxides on carbon and their analysis: A critical assessment, Carbon 40 (2002) 145–149.
[26] T.J. Bandosz, I.I. Salame, Surface chemistry of activated carbons: Combining the results of temperature-programmed, J. Colloid Interf. Sci. 240 (2001) 252–258.
[27] M. Alkan, Ö. Demirbaş, M. Doğan, Electrokinetic properties of sepiolite suspensions in different electrolyte media, J. Colloid Interf. Sci. 281 (2005) 240–248.
[28] K.L. Dorris, B. Yu, Y. Zhang, A. Shukla, S.S. Shukla, The removal of heavy metal from aqueous solutions by sawdust adsorption-removal of copper, J. Hazard. Mater. B80 (2000) 33–42.
[29] Y.S. Ho, C.T. Huang, H.W. Huang, Equilibrium sorption isotherm for metal ions on tree fern, Process Biochem. 37 (2002) 1421–1430.
[30] Y.S. Ho, D.A.J. Wase, C.F. Forster, The adsorption of divalent copper ions from aqueous solution by *sphagnum* moss peat, Trans. Inst. Chem. Eng. Part B Process Saf. Environ. Prot. 17 (1994) 185–194.
[31] Y.S. Ho, D.A.J. Wase, C.F. Forster, Batch nickel removal from aqueous solution by *Sphagnum* moss peat, Water Res. 29 (1995) 1327–1332.
[32] Y. Bulut, A. Aydın, A kinetics and thermodynamics study of methylene blue adsorption on wheat shells, Desalination 194 (2006) 259–267.
[33] I. Gaballah, G. Kilbertus, Recovery of heavy metal ions through decontamination of synthetic solutions and industrial effluents using modified barks, J. Geochem. Explor. 62 (1998) 241–286.
[34] G. McKay, H.S. Blair, J.K. Gardner, Adsorption of dyes on chitin. I. Equilibrium studies, J. Appl. Polym. Sci. 27 (1982) 3043.
[35] M. Alkan, S. Çelikçapa, Ö. Demirbaş, M. Doğan, Removal of reactive blue 221 and acid blue 62 anionic dyes from aqueous solutions by sepiolite, Dyes Pigm. 65 (2005) 251–259.
[36] M. Alkan, M. Karadaş, M. Doğan, Ö. Demirbaş, Zeta potentials of perlite samples in various electrolyte and surfactant media, Colloid Surf. A 259 (2005) 155–166.
[37] M. Dogan, M. Alkan, Removal of methyl violet from aqueous solutions by perlite, J. Colloid Interf. Sci. 267 (2003) 32–41.
[38] M. Doğan, M. Alkan, Adsorption kinetics of methyl violet onto perlite, Chemosphere 50 (2003) 517–528.
[39] M. Özacar, İ.A. Şengil, A kinetic study of metal complex dye sorption onto pine sawdust, Process Biochem. 40 (2005) 565–572.
[40] Y.S. Ho, G. McKay, Pseudo-second order model for sorption processes, Process Biochem. 34 (1999) 451–465.
[41] P. King, N. Rakesh, S.B. Lahari, Y.P. Kumar, V.S.R.K. Prasad, Biosorption of zinc onto *Syzygium cumini* L: Equilibrium and kinetic studies, Chem. Eng. J. 144 (2008) 181–187.
[42] S. Tunali, T. Akar, Zn(II) biosorption properties of *Botrytis cinerea* biomass, J. Hazard. Mater. 131B (2006) 137–145.
[43] D. Mohan, K.P. Singh, Single- and multi-component adsorption of cadmium and zinc using activated carbon derived from bagasse an agricultural waste, Water Res. 36 (2002) 2304–2318.
[44] M. Galun, E. Galun, B.Z. Siegel, P. Keller, H. Lehr, S.M. Siegel, Removal of metal ions from aqueous solutions by *Penicillium* biomass: Kinetic and uptake parameters, Water Air Soil Pollut. 33 (1987) 359–371.
[45] A. Agrawal, K.K. Sahu, B.D. Pandey, Removal of zinc from aqueous solutions using sea nodule residue, Colloid Surf. A. 237 (2004) 133–140.
[46] C. Kathrine, H.C.B. Hansen, Sorption of zinc and lead on coir, Bioresour. Technol. 98(1) (2007) 89–97.
[47] O. Abollino, M. Aceto, M. Malandrino, C. Sarzanini, E. Mentasti, Adsorption of heavy metals on Na-montmorillonite. Effect of pH and organic substances, Water Res. 37 (2003) 1619–1627.