Desalination and Water Treatment
www.deswater.com

1944-3994 / 1944-3986
doi: 10.5004/dwt.2010.1228

20 (2010) 123–132
August

Utilization of shells of hazelnut modified with Reactive Orange 122 as adsorbent for the removal of Cu(II)

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Received 9 June 2009; Acepted in revised form 4 January 2010

ABSTRACT

The influence of reactive dye modification on the efficiency of adsorption capacities of hazelnut shells was investigated. To that end, natural adsorbents such as shells of unmodified hazelnut (RH), and modified hazelnut (MH) were used. The removal of Cu(II) by these adsorbents from aqueous solution was investigated by using several parameters such as modification, contact time, temperature and pH. The adsorption process attained equilibrium within 60 min. The extent of Cu(II) removal increased with increasing the contact time, temperature and pH and also with modification by Reactive Orange 122 as the adsorbent. Optimum pH value for Cu(II) adsorption was determined between 4–5. The experimental data were analysed by the Langmuir and Freundlich models of adsorption. It was found that the Langmuir equation fited better than the Freundlich equation. The maximum adsorption capacities for Cu(II) onto RH and MH at 298, 308 and 318 K were found to be 3.95, 4.65, and 4.74, 7.00, 8.12 and 8.61 mg/g, respectively. In addition, the adsorption data obtained at different temperatures of Cu(II) by adsorbents were applied to the pseudo first-order, pseudo second-order and Weber–Morris equations, and the rate constants of the first-order adsorption (k_1), the rate constants of the second-order adsorption (k_2) and intraparticle diffusion rate constants (k_3) at these temperatures were calculated, respectively. The rates of adsorption were found to conform the pseudo second-order kinetics with good correlation ($R^2 \geq 0.991$). The data obtained from the adsorption isotherms at different temperatures were used to calculate some thermodynamic quantities such as free energy of adsorption (ΔG^o), enthalpy (ΔH^o) and entropy (ΔS^o). It is expected that ΔG^o is negative, indicating that the nature of the adsorption process for Cu(II) is spontaneous. The positive value of ΔH^o indicates that the adsorption of Cu(II) onto adsorbents is an endothermic process. The positive value of ΔSo reflects the affinity of the adsorbent for Cu(II). As a result, the hazelnut shells (both modified and unmodified), inexpensive and easily available material, can be an alternative for more costly adsorbents used for Cu((II) removal from wastewater.

Keywords: Adsorption; Adsorbents; Hazelnut shell; Kinetics; Thermodynamics; Modification; Isotherm

1. Introduction

Removal of toxic metal ions and recovery of valuable metal ions from mine wastewaters, soils and waters are important in regard to economic and environmental problems [1]. Their presence in streams and lakes is responsible for several health problems with animals, plants and human beings. Numerous metals such as Sb,

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Cr, Cd, Cu, Pb, Hg, etc. have toxic effects on human beings and environment [2]. Since copper is a widely used material, there are many actual or potential sources of copper pollution. Copper may be found as a contaminant in food, expecially shellfish, liver, mushrooms, nuts and chocolate. Briefly, any processing or container involving copper material may contaminate the products such as food, water or drink. Copper is essential to human life and health, but like all heavy metals, it is potentially toxic as well. For example, continued inhalation of copper-containing spray is linked with an increase in lung cancer among exposed workers [3].

Precipitation, ion exchange, extraction, biosorption, filtration, electrochemical treatment and adsorption are conventional methods for the removal of heavy metals from aqueous solutions. All these methods have significant disadvantages such as incomplete ion removal, high-energy requirements and production of toxic sludge or other waste products that require further disposal. Therefore, these methods do not meet the needs of developing countries [4]. Among the above mentioned methods, adsorption is considered to be relatively superior to other techniques because of its low cost, simplicity of design, availabity and ability to treat dyes in a more concentrated form [5]. Activated carbon is the most widely used adsorbent since it has excellent adsorption efficiency for heavy metals, but its use is usually limited due to its high cost [6]. It has been applied with varying success rates in metal removal [7]. The reactive dye loaded cheap cellulosic and lignosellulosic materials were quite efficient for heavy metals removal from their aqueous solutions. The use of fibrous lignocellulosic materials for heavy metals has been explored recently by a number of researchers [4]. To find an effective and ideal adsorbent, researchers have exploited many low-cost and biodegradable subtitutes obtainable from natural resources for the removal of different metals from aqueous solutions at different operational conditions.

At present, there is a growing interest in using low-cost and commercially available materials for the adsorption of heavy metals. A wide variety of materials such as rice husk [8], modified cellulosic materials [9], fly ash [10], modified bark [11], sawdust [12], pine bark [13], animal bones [14], holly oak [15], modified sawdust of walnut [16] and modified barks [17] are being used as low-cost alternatives to expensive adsorbents.

The aim of this work is to investigate the effect of several parameters such as contact time, temperature and pH, on the adsorption efficiency of Cu(II) from aqueous solutions by unmodified (RH) and modified (MH) hazelnut shells which is a very cheap and readily available material in most countries. Furthermore, the thermodynamic parameters for the adsorption of Cu(II) were computed and discussed. The kinetics and the factors controlling the adsorption process were also studied.

2. Materials and methods

2.1. Materials

The hazelnut shells supplied from the Black Sea Region of Turkey were used as adsorbent biomaterials. The collected material (the last hard layer of hazelnut) was then washed several times with distilled water to remove all dirt particles. The washing process was continued till the wash water contained no colour. The washed material was then dried in a hot oven at 100°C for 24 h. The dried material was then ground using a steel mill. The adsorbent was sieved through a 2-mm sieve. This material was subjected to cleaning by boiling it in 1 g/L soap solution for 15 min followed by thoroug washing with water. The purified biomaterial was also loaded with Reactive Orange 122. Characteristics of the RH and MH were determined, and the results are summarized in Table 1.

2.2. Chemicals

A monochlorotriazine type reactive dye, Reactive Orange 122 (λ_{max} 490 nm, solubility in water 75 g/L, molecular weight 875.5 g/mol, degree of purity 80–85%) supplied by Aldrich was used as a commercially available powder for modification of materials (Fig. 1) [18]. The other chemicals used, such as $CuSO_4.5H_2O$, $NaHCO_3$, Na_2SO_4, Na_2CO_3, HCl, NaOH, were also of analytical reagent grade, supplied by Merck. A stock solution of Cu(II) 1000 mg/L was prepared, which was diluted to

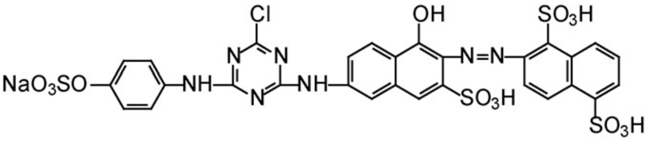

Fig. 1. Chemical structure of Reactive Orange 122.

Table 1
Physical and chemical properties of the unmodified hazelnut shells used in the experiments

Chemical characteristics	
Moisture content, %	5.49
Water soluble components, %	7.41
Insoluble components, %	86.68
Ash, %	2.10
Total loss of ignition, %	81.10
C content, %	42.67
H content, %	4.74
pH	4.99
Physical characteristics	
Surface area (BET), m^2/g	4.31

Bulk density, g/mL, 0.46. Results of Boehm titration (mmol/g) of adsorbent: carboxylic – 0.182, lactonic – 0.060, phenolic – 0.978, basic – 0.000, acidic – 1.220.

required initial concentrations. Demineralised water was used for all experiments.

2.3. Apparatus

Absorbance values were measured with a Unicam Model 929 atomic absorption spectrometer (AAS). A pH-meter (Jenway 3010) and shaker (Nuve ST 400) were used for pH adjustment and shaking, respectively. The surface area was determined by a single-point N_2 gas adsorption method by using a model micromeritics Flow Sorb II. 2300. Elemental analysis (C and H content) was carried out with an EA 1108 Fisons instrument.

2.4. Methods

2.4.1. Modification of hazelnut shells

1.0 g of the dye powder was dissolved in 100 mL of warm water in order to prepare a 1% stock solution of the dye. For dye loading of hazelnut shells, the procedure for dyeing of cotton textiles with reactive dyes was used [19]. Then 100 g of hazelnut shells was added to 4 L of the diluted solution (material to liquor ratio 1:40) containing 50 mL of the stock solution of dye at 40°C, and the temperature was slowly raised to 85°C. After about 10 min, 65 g/L sodium sulphate was added in two lots in 10 min for improving the dye exhaustion onto the material. After another 20 min, 15 g/L sodium carbonate was added to the same bath and the treatment continued at 85°C for further 30 min. At the end, the material was filtered and washed thoroughly with hot water. This was followed by treating the dye loaded material with 1 g/L soap solution at boil for 20 min and by thoroughly washing it with water to remove completely the unfixed dye and the by-product of the reaction, the hydrolysed dye. The coloured material was then dried in an oven at 50°C overnight and used as adsorbent.

2.4.2. Estimation of dye loading on the materials

The estimation of the amount of dye loaded onto the hazelnut shells was carried out by using a Shimadzu UV spectrophotometer, model 160. Each dyestuff gives the colour absorption value at a particular $\lambda_{\max}$ specific to it. A calibration curve is plotted by using pure dye dissolved in water in which a known quantity of dye concentration (mg/L) is linearly related to its absorbance (%) value at the particular $\lambda_{\max}$. The absorbance of the initial dye liquor used for dye loading was measured at $\lambda_{\max}$ of 490 nm, (A). After completion of the dyeing process, the material was carefully removed from the bath without spilling any drop of the spent liquor. Water after washing, the soap liquor as well as final washings were carefully collected together, added to the exhausted dye bath and its absorbance was measured (B). This absorbance is equal to the amount of dye not loaded on the adsorbent. Therefore, (A–B) is related to the dye loaded onto the material. By making use of the calibration curve, the amount of dye in mg/g of material was established. Thus, the dye loading observed for hazelnut shells was 4.56 mg/g.

2.4.3. Batch adsorption experiments

Batch studies were conducted with the Cu (II) solutions prepared in the laboratory. The effect of contact time on the amount of Cu(II) adsorbed was investigated at 100 mg/L initial concentration of Cu(II), at different temperatures (298, 308 and 318 K) and optimum pH (pH: 5.0). A weighed sample of RH and MH (1.0 g) was mixed with a 50 mL metal solution. For the other adsorption experiments, 50 mL of Cu(II) solution of known initial concentration (75, 100, 125, 150,175, 200 and 225 mg/L) was shaken with a certain amount of the adsorbent at a desired pH and temperature at 150 rpm for 60 min. The pH of the solution was adjusted with 0.5 N HCl or 0.1 N NaOH by using a pH-meter with a combined pH electrode. The pH-meter was standardized with NBS buffers before each measurement. A constant bath was used to keep the temperature constant. At the end of the adsorption period, the solution was centrifuged for 10 min at 3000 rpm. After centrifugation, the Cu(II) concentration in the supernatant solution was analyzed using an atomic absorption spectrophotometer. The samples were pipetted from the medium reaction by the aid of a very thin point micropipette, which prevented the transition to the solution of the RH and MH samples. The amount of Cu(II) adsorbed was calculated by using the equation

$$q_e = (C_i - C_e)V / M \tag{1}$$

where q_e is the amount adsorbed per gram of adsorbent, C_i and C_e are the concentrations of Cu(II) (mg/L) at initial and equilibrium, respectively. V is the volume of metal solution (L) and m is adsorbent dosage (g). All experiments were repeated three times, and the average values are presented in this communication (standard deviation = 0.011).

2.4.4. C, H analysis

A sample of adsorbents was placed in an oven at 1273 K under oxygen in order to obtain a quick and complete combustion. H_2O and CO_2 were released and conducted in a copper oven at 923 K, then passed through a 2-m column with helium vector gas, and analyzed by a catharameter detector. The results of analysis are shown in Table 1.

2.4.5. Functional group dosage

Knowing the chemical structure of the used adsorbent is important to understand the adsorption processes. The adsorption capacity of the adsorbent is strongly influenced by the chemical structure of its surface [20]. The oxygenated surface groups were determined according to the method by Bohem. First, 1.0 g of the adsorbent was placed in 50 mL of each of the following 0.05 N solutions: sodium hydroxide, sodium carbonate, sodium bicarbonate and hydrochloric acid. Vials were sealed and shaken for 24 h, and then 5 mL of each filtrate was pipetted; the excess of the base or acid was titrated with HCl or NaOH, as required. The numbers of acidic sites of various types were calculated on the assumption that NaOH neutralizes carboxylic, phenolic, and lactonic; Na_2CO_3 neutralizes carboxylic and lactonic groups; and $NaHCO_3$ neutralizes only carboxylic groups [21]. The number of surface basic sites was calculated from the amount of hydrochloric acid reacted with the adsorbents; the results of Bohem titration (numbers of acidic and basic groups) are summarized in Table 1.

3. Results and discussion

3.1. Other chemical-physical characteristics

Characteristics of the adsorbents such as bulk density, moisture content, ash content, solubility in water, total loss of ignition were investigated. The ash content was determined by burning it in a furnace at 1173 K [20]. The results are summarized in Table 1.

3.2. Contact time

Adsorption of Cu(II) at a fixed concentration on RH and MH was studied as a function of contact time in order to determine the equilibration time for maximum adsorption. The contact time experiments were carried out at 298, 308 and 318 K. The dependence of adsorption of Cu(II) with time is presented in Fig. 2. The adsorption increased with increasing contact time, and the equilibrium was attained after shaking for 60 min. Therefore, in each experiment, the shaking time was set to 60 min.

3.3. Effect of pH

The pH of the aqueous solution is an important controlling parameter in the adsorption process [22]. In order to study the influence of pH on the adsorption capacity of RH and MH, experiments were performed by using various initial solution pH values varying from 1.0 to 5.0, with other parameters being kept constant. Fig. 3 depicts the effect of pH on adsorption of metal ions on both modified and unmodified hazelnut shells. The removal of Cu(II) increased with increasing pH. The peak adsorption of Cu(II) was attained at pH 5.0. One of the reasons for the metal ions adsorption behaviour of the bio-adsorbent (RH, MH) is that the adsorbent surface contains a large number of active sites. The metal uptake depends on these active sites as well as on the nature of the metal ions in the solution. The affinities of the surface sites of RH and MH depend on the nature of ions. This may be further explained in relation to a competition effect between the H_3O^+ and Cu(II) ions. At low pH values, the concentration of metal ions, hence the former ions occupy the binding sites on the RH and MH, leaving metal ions free in the solution. When the pH increases, the concentration H_3O^+ ions decreases, and the sites on the adsorbent surface mainly turn into the dissociated forms and can exchange H_3O^+ ions with metallic ions in the solution [2]. As pH of the system increased, the number of negatively charged adsorbent sites increased, and the number of positively charged surface sites decreased, which did favour the adsorption of positively charged Cu(II) ions.

3.4. Effect of modification

In order to increase the adsorption capacity of hazelnut shells, they were modified with Reactive Orange 122. Fig. 4 depicts the effect of modification on adsorption of metal ions by hazelnut shells at different temperatures

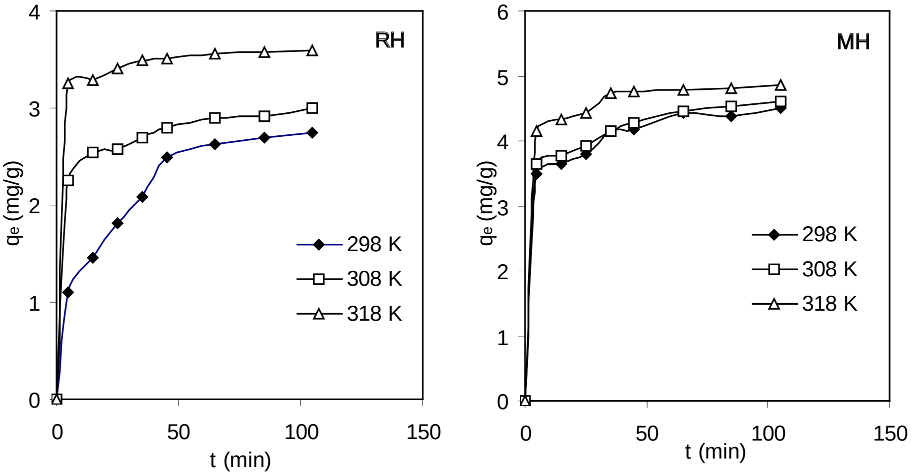

Fig. 2. Effect of contact time on adsorption of Cu(II) at different temperatures (C_i 100 mg/L, adsorbent 1.0 g, agitation speed 150 rpm, pH 5.0).

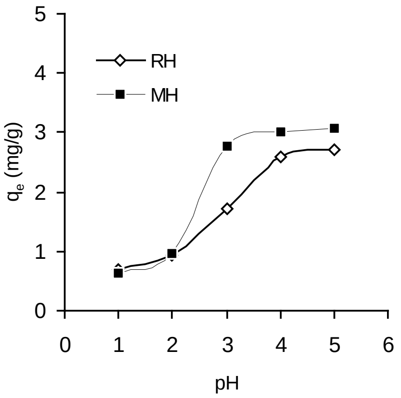

Fig. 3. The effect of pH on the adsorption of Cu(II) (C_i 100 mg/L, t 60 min, adsorbent 1.0 g, agitation speed 150 rpm).

(298, 308, 318 K). Fig. 4 shows the adsorption efficiency of modified adsorbent for Cu(II) as a function of temperature. As seen in Fig. 4, the removal efficiency of Cu(II) from aqueous solution by hazelnut shells increased with modification.

During the modification process the dyestuff molecules bind to the acidic grup of the adsorbent surface with non-covalent interactions. Then, we think that when the modified materials are reacted with the metal solution, a complex is formed between the dyestuff molecules and metal ions. Therefore, the metal can be removed from the solution with the modified adsorbent more efficiently than with the raw one.

3.5. Adsorption kinetics

Adsorption is a physical-chemical process that involves the mass transfer of the solute (adsorbate) from the fluid phase to the adsorbent surface [23]. A study of kinetics of adsorption is desirable as it provides information about the mechanism of adsorption, which is important for efficiency of the process [24]. In order to investigate the mechanism of adsorption, characteristic constants of adsorption rates were determined, using a pseudo first-order equation of Lagergren based on solid capacity, and pseudo second-order equation based on the solid phase adsorption and an intraparticle diffusion model. Temperature, pH and stirring speed were constant for all experiments. The first-order rate expression of Lagergren based on solid capacity is generally expressed as follows [7]:

$$\log\left(q_e - q_t\right) = \log q_e - k_1 t / 2.303 \tag{2}$$

where q_e is the amount adsorbed (mg/g) at equilibrium, q_t is the amount adsorbed (mg/g) at time t and k_1 the adsorption rate constant (1/min). The straight line of the plot of log ($q_e - q_t$) vs. time (Fig. 5) suggests the applicability of the Lagergren equation for the present system [21]. The values of k_1 were determined from the slope of the plots and are given in Table 2.

Recently, Ho and Mc Kay [25] have reported that most of the sorption systems follow a second-order kinetic model which can be expressed as:

$$t / q_t = 1 / k_2 q_{eq}^2 + t / q_{eq} \tag{3}$$

where k_2 is the adsorption rate constant (g/mg.min). The plot of t/q_t vs. time is shown in Fig. 6.

The values of k_2 were determined by the intercept of the plot and are given in Table 2.

The rate constant for intraparticle diffusion (k_3) is given as [23]:

$$q_t = k_3 t^{1/2} \tag{4}$$

where q_t is the amount adsorbed (mg/g) at time t (min). The plots of q_t vs. $t^{1/2}$ for different adsorbents are shown in Fig. 7. All plots have a similar general trend and initial curved part, followed by a linear one and then a plateau. The initial curved part may be attributed to the bulk diffusion; the linear one to the intraparticle diffusion and the plateau to the equilibrium. This indicates that the transport of Cu(II) ions from the solution through the particle solution interface into the pores of the particles as well as

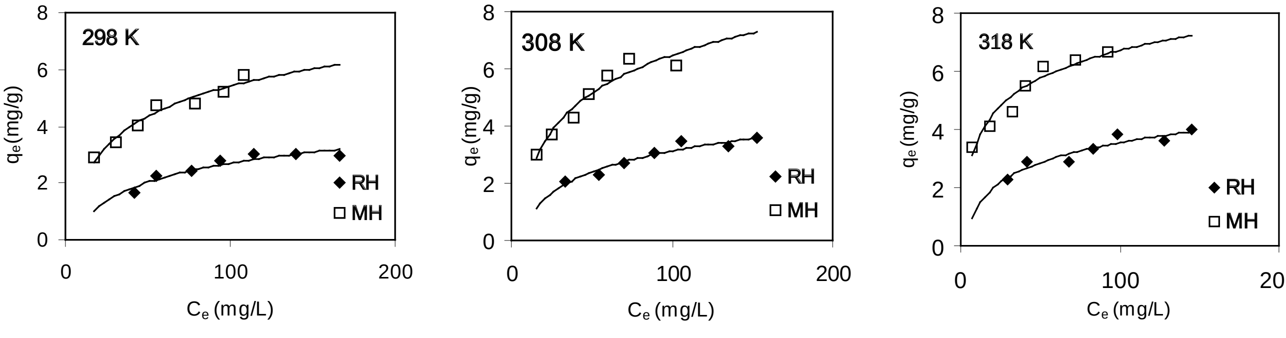

Fig. 4. Effect of modification on adsorption of Cu(II) at different temperatures (C_i 100 mg/L, t 60 min, adsorbent 1.0 g, agitation speed 150 rpm, pH 5.0).

Table 2
Adsorption kinetic parameters of Cu(II) on RH and MH (C_i 100 mg/L, adsorbent 1.0 g, agitation speed 150 rpm, pH 5.0)

Adsorbent	First-order kinetic model				Second-order kinetic model			Intraparticle diffusion	
	T (K)	k_1 (1/min)	q_{eq} (mg/g)	R^2	k_2 (g/mg.min)	q_{eq} (mg/g)	R^2	k_3 (mg/g.min$^{1/2}$)	R^2
RH	298	0.04	2.37	0.976	0.02	3.21	0.991	0.23	0.944
	308	0.03	1.29	0.842	0.07	3.07	0.997	0.09	0.950
	318	0.50	0.86	0.830	0.22	3.63	0.999	0.05	0.897
MH	298	0.04	2.14	0.840	0.05	4.64	0.994	0.15	0.780
	308	0.04	1.95	0.884	0.06	4.66	0.998	0.13	0.969
	318	0.05	1.29	0.783	0.13	4.89	0.999	0.09	0.845

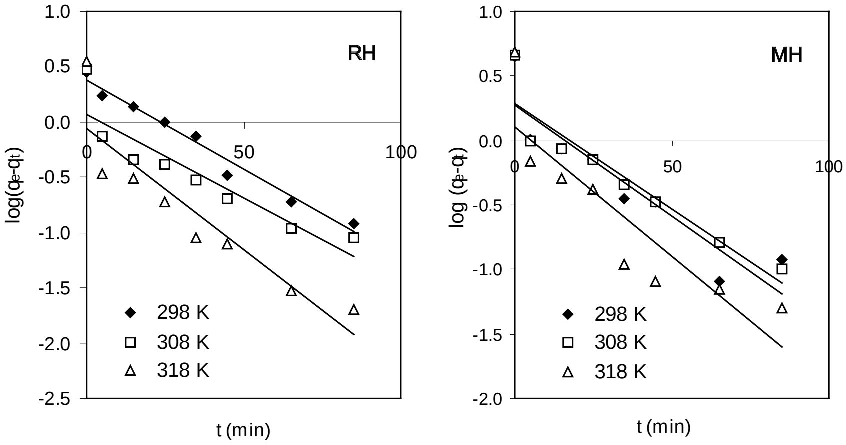

Fig. 5. Pseudo first-order kinetics for adsorption of Cu(II) on RH and MH at different temperatures (C_i 100 mg/L, adsorbent 1.0 g, agitation speed: 150 rpm, pH 5.0).

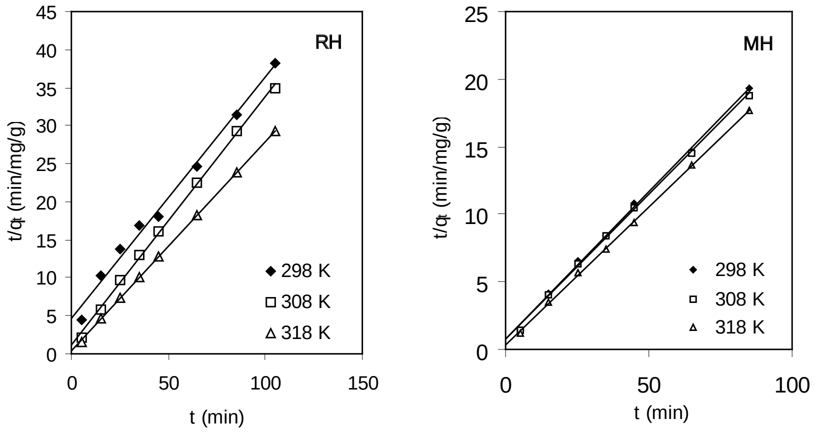

Fig. 6. Pseudo second-order kinetics for adsorption of Cu(II) on RH and MH at different temperatures (C_i 100 mg/L, adsorbent 1.0 g, agitation speed 150 rpm, pH 5.0).

the adsorption on the available surface of adsorbents are both responsible for the uptake of Cu(II) ions [3].

k_3 (mg/g.min$^{1/2}$) is characteristic for the rate of adsorption in the region, where intraparticle diffusion is rate-controlling. The extrapolation of the linear curve parts of the plots back to the axis provides the intercepts, which are proportional to the extent of the boundary layer thickness, i.e. the larger the intercept, the greater the boundary layer effect [26]. The deviation of the curves from the origin also indicates that intraparticle transport is not the

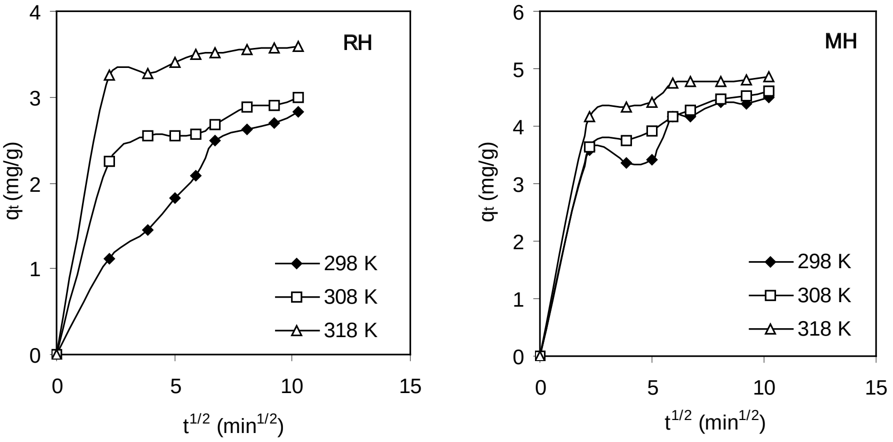

Fig. 7. Intraparticle diffusion plots of Cu(II) on RH and MH at different temperatures (C_i 100 mg/L, adsorbent 1.0 g, agitation speed 150 rpm, pH 5.0).

only rate limiting step [3]. The values of rate constants (k_3) of RH and MH at 298, 308, and 318 K temperature were found to be 0.23, 0.09 and 0.05, 0.15, 0.13 and 0.09 mg/g. min$^{1/2}$, respectively (Table 2).

3.6. Adsorption model

The equilibrium adsorption isotherm is of importance in the design of adsorption systems [7]. In general, the adsorption isotherm describes how adsorbates interact with adsorbents and thus is critical in optimizing the use of adsorbents. Adsorption isotherms expressing the adsorbed amounts as a function of equilibrium concentration for different temperatures are presented in Fig. 8.

Although several isotherm equations are available, two important isotherms are selected for this study: the Langmuir and Freundlich isotherms. The Langmuir adsorption isotherm assumes that adsorption takes place at specific homogeneous sites within the adsorbent, and it has been used successfully for many adsorption processes of monolayer adsorption. The linearized Langmuir equation is represented as follows [22]:

$$C_e / q_e = 1 / bQ_m + C_e / Q_m \tag{5}$$

where b is the equilibrium constant or the Langmuir constant related to the affinity of binding sites (L/mg) or (L/mol) and Q_m represents a partical limiting adsorption capacity when the surface is fully covered with metal ions and assists in the comparison of adsorption performance. Q_m and b are calculated from the slope and intercept of the straight lines of plot C_e/q_e vs. C_e.

The Freundlich isotherm is an emprical equation employed to describe heterogeneous systems. The Freundlich isotherm is given in logaritmic form as [27]:

$$\log q_e = \log K_F + 1/n \log C_e \tag{6}$$

where K_F is roughly an indicator of the adsorption and

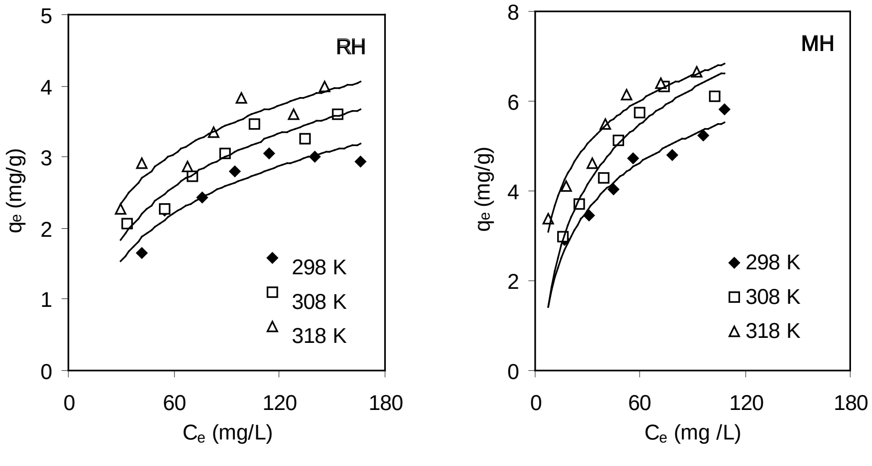

Fig. 8. Isotherm for adsorption of Cu(II) on RH and MH (t 60 min, adsorbent 1.0 g, agitation speed 150 rpm, pH 5.0).

(1/n) of the adsorption intensity. K_F and n can be determined from the linear plot of log q_e vs. log C_e.

Adsorption isotherms were obtained in terms of Eqs. (5) and (6) by using experimental adsorption results in these equations. The values Q_m, b, K_F and n are summarised in Table 3. The isotherm data were calculated from the least square method and the related correlation coefficients (R^2 values) are given in the same table. As seen from Table 3, the Langmuir equation represents the adsorption process very well; the R^2 values were all higher than 0.961, indicating a very good mathematical fit. The fact that the Langmuir isotherm fits the experimental data very well may be due to homogeneous distribution of active sites onto adsorbent surface, since the Langmuir equation assumes that the surface is homogenous [28]. As seen in Table 3, the maximum adsorption capacities for Cu(II) onto RH and MH at 298, 308 and 318 K were 3.95, 4.65, and 4.74; 7.00, 8.12, and 8.61 mg/g, respectively. Maximum adsorption capacities of adsorbents rise with the increase in temperature.

K_F is an Freundlich constant that shows adsorption capacity of adsorbent, n is a constant showing greatness of relationship between adsorbate and adsorbent [7]. The value K_F of RH and MH for Cu(II) at 298, 308 and 318 K are 0.408, 0.514 and 0.801; 1.016, 1.211 and 1.874, respectively. It is generally reported that the values of n in the range 1–10 represent good adsorption [22]. In the present work, the exponent was $1 < n < 10$, indicating favourable adsorption.

The essential features of the Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor R_L which is defined by the following relationships [8]:

$$R_L = 1/1 + bC_i \tag{7}$$

According to the value of R_L the isotherm shape may be interpreted as $R_L > 1.0$ (unfavourable), $R_L = 1.0$ (linear), $1 > R_L > 0$ (favourable) and $R_L = 0$ (irreversible).

The results given in Table 3 show that the adsorption of Cu(II) on RH and MH is favourable. As also seen in Table 3, the maximum adsorption of RH and MH for Cu(II) varied between 3.95 and 4.74 mg/g ; 7.00 and 8.61, respectively.

Previously, some researchers have investigated several adsorbents such as diatomite (27.55 mg/g) and modified diatomite (55.56 mg/g) [17], fly ash (1.54 mg/g) [10], sawdust (1.79 mg/g) [3], peat (12.07 mg/g) [29] and tea-industry waste (8.64 mg/g) [30] for the removal of Cu(II). By comparison of the results obtained in this study with those in the previously reported works on adsorption capacities of various low-cost adsorbents in aqueous solution for Cu(II), it can be stated that our findings are valuable.

3.7. Estimation of thermodynamic parameters

To determine the effect of temperature on the adsorption of Cu(II), the experiments were also conducted at 298, 308 and 318 K, and are shown in Fig. 8. The degree of adsorption increases with increasing temperature, indicating that the adsorption is endothermic [31]. The free energy of adsorption ($\Delta G°$) can be related to the equilibrium constant K (L/mol), corresponding to the reciprocal of the Langmuir constant, b, by the following equation. The values of free energy change ($\Delta G°$), enthalpy change ($\Delta H°$), and entropy change ($\Delta S°$), for the adsorption process were calculated, using the equations [7,31],

$$\Delta G^\circ = -RT \ln b \tag{8}$$

$$\ln b = \Delta S^\circ / R - \Delta H^\circ / RT \tag{9}$$

Thus, a plot of ln b vs. 1/T should be a straight line. $\Delta H°$ and $\Delta S°$ values were obtained from the slope and intercept of this plot, respectively [7]. $\Delta G°$, $\Delta H°$ and $\Delta S°$ were obtained from Eqs. (8), (9) and are given in Table 4.

Negative values of ΔGo indicate the feasibility of the process and spontaneous nature of the adsorption with a high performance of Cu(II) for both RH and MH. Positive value of $\Delta H°$ indicates the endothermic nature of the process, while positive value of $\Delta S°$ reflects the affinity of the adsorbents for Cu(II) ions, suggesting some structural changes in adsorbate and adsorbent[10].

Table 3
Langmuir and Freundlich isotherm constants for adsorption of Cu(II) on RH and MH (t 60 min, adsorbent 1.0 g, agitation speed 150 rpm, pH 5.0)

	T (K)	Langmuir constants				Freundlich constants		
		B (L/mg)	Q_m (mg/g)	R_L	R^2	K_F	n	R^2
RH	298	0.022	3.95	0.313	0.961	0.408	2.456	0.848
	308	0.020	4.65	0.323	0.968	0.514	2.569	0.928
	318	0.030	4.74	0.244	0.971	0.801	3.108	0.882
MH	298	0.033	7.00	0.227	0.979	1.016	2.735	0.965
	308	0.035	8.12	0.222	0.974	1.211	2.338	0.949
	318	0.069	8.61	0.125	0.984	1.874	3.525	0.956

Table 4
Values of thermodynamic parameters for the adsorption of Cu(II) on RH and MH (t 60 min, adsorbent 1.0 g, agitation speed 150 rpm, pH 5.0)

Adsorbent	T (K)	B (L/mg)	B (L/mol)	ΔG (kJ/mol)	ΔH (kJ/mol)	ΔS (J/mol K)
RH	298	0.022	19261	–24.444	11.997	121.592
	308	0.020	17510	–25.021		
	318	0.030	26265	–26.904		
MH	298	0.033	28892	–25.447	28.800	181.162
	308	0.035	30643	–26.452		
	318	0.069	60410	–29.106		

4. Conclusions

- The present work indicates that the hazelnut shells modified (MH) chemically by Reactive Orange 122, exhibits more efficient adsorption of Cu(II) ions than the unmodified one (RH).
- The amount of Cu(II) uptake (mg/g) on adsorbents was found to increase with the increase in contact time, temperature and pH.
- The equilibrium data were fitted to two adsorption models, and Langmuir isotherm model was the best model to describe the data.
- In addition, the kinetic data were best described by the pseudo-second order kinetic model.
- The data obtained from the adsorption isotherms at different temperatures were used to calculate thermodynamic quantities such as $\Delta G°$, $\Delta H°$ and $\Delta S°$. The results indicate that the adsorption of Cu(II) onto RH and MH is spontaneous and physical in nature.

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