



Removal of copper from aqueous solutions by adsorption onto chestnut shell and grapeseed activated carbons

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ABSTRACT

Activated carbons prepared from chestnut shell and grapeseed were used as adsorbent for the removal of Cu (II) ions from aqueous solutions. Adsorption experiments were performed by varying initial metal ion concentration, temperature and pH. Freundlich and Langmuir isotherms were used to analyze the equilibrium data obtained at different adsorption conditions. It was observed that Freundlich isotherm provided better fit to the equilibrium data than Langmuir isotherm. Effects of temperature, pH and adsorbent surface area on the adsorption capacity constant of Freundlich and Langmuir isotherms were statistically investigated by using a two-level factorial design technique and empirical regression equations were developed. It was determined that the adsorption capacities of adsorbents increased with increasing temperature, pH and surface area. The SEM images of adsorbents before and after adsorption were compared.

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1. Introduction

Heavy metal contamination exists in aqueous waste streams of many industries, such as metal plating facilities, mining operations and tanners [1]. Copper pollution especially, arises from copper mining and smelting, brass manufacture, electroplating industries and excessive use of Cu-based agro-chemicals. Copper along with arsenic and mercury, is recognized as the highest relative mammalian toxic and continued inhalation of copper containing sprays is linked with an increase in lung cancer among exposed workers [2]. Hence, the removal of copper from aqueous solutions is extremely important. Adsorption is highly effective and economical method to remove heavy metal ions from aqueous solutions. Activated carbons, with their high surface area, microporous structure and chemical nature of their surface, are potential adsorbents for the removal of different heavy metals from industrial wastewaters [3–7].

There have been many studies to obtain low cost activated carbons from agricultural wastes such as corn cob [8,9], date pits [10], apricot stone [11–13], almond shell, nut shell, peach stone [12,14], oat hulls, corn stover [15], coconut shell [16,17], hazelnut shell [14], grapeseed [12,18], sour cherry stone [12], olive stone [12,19] and rice husk [20].

The copper adsorption capacities of various adsorbents given in literature were summarized in Table 1. Although several studies

have been reported in the literature on the copper adsorption by activated carbons produced from different agricultural wastes, any study on the adsorption of copper by activated carbons produced from chestnut shell and grapeseed does not exist.

The goal of this study was to investigate the copper removal efficiencies of the activated carbons produced from chestnut shell and grapeseed. The adsorption of copper ions onto activated carbons was studied in batch equilibrium conditions. Freundlich and Langmuir isotherms were used to analyze the equilibrium data. The influences of various parameters such as temperature, pH and adsorbent surface area on the adsorption process were also determined statistically.

2. Experimental

Chestnut shell obtained from a chestnut candy factory in Bursa located in the Marmara region of Turkey, and grapeseed obtained from a wine factory in Nevşehir located in the middle Anatolian region of Turkey, was used as raw materials in this study.

Air-dried grapeseed and chestnut shell samples were initially ground and sieved to determine the average particle diameters. Additionally, porosity and surface area measurements were made by using Quantachrome Autoscan-33 Model mercury intrusion porosimeter and Quantachrome NOVA 1200 Model sorptometer and the results were given in Table 2. Beside these physical properties, structural properties of biomass samples were also determined according to the standard methods given in literature [29–31] and the results were summarized in Table 3 [32].

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Table 1
Comparison of adsorption capacity of various adsorbents for Cu (II).

Adsorbent	Adsorption capacity (mg/mg)	pH	References
Hazelnut husk activated carbon	6.64	5.7	[21]
Peanut hulls	10.17	–	[22]
Tea industry waste	8.64	5.5	[23]
Rubber wood sawdust activated carbon	5.72	6	[24]
Bagasse fly ash	2.26	4	[25]
Wheat shell	10.84	5	[26]
Rice hulls activated carbon	3.92	5.3	[27]
Hazelnut shell activated carbon	36.33	6	[28]

For the porosity measurements samples were put into the penetrometer and placed into the filling device to outgas by vacuum application. Then the system pressure increased slowly up to atmospheric pressure to fill the penetrometer with mercury and measure the volume of pores having radii between approximately 200–4 μm . The penetrometer containing the sample and mercury placed into the pressure vessel and system pressure increased up to 227 MPa continuously to measure pore volumes in the range from about 7 to 0.0032 μm radius. In these measurements the pores are assumed to be cylindrical and Washburn Equation [33] was used to calculate the pore radius.

The Brunauer–Emmett–Teller (BET) method [34] is used for the determination of the surface area values of samples. In this method, moisture and atmospheric gases were firstly removed from the sample by application of heat and evacuation. Then the temperature was reduced to that of liquid nitrogen and the adsorbing gas (nitrogen) was admitted in incremental doses. BET isotherm plot which is used to determine the total surface area of the sample was obtained by using the adsorbed gas versus gas pressure data. The specific surface area was calculated by dividing the total surface area to sample weight.

For the production of activated carbons, chestnut shell and grapeseed samples were physically impregnated with ZnCl_2 and then, they were carbonized by heating in nitrogen atmosphere with a rate of 20 K/min up to the temperature of 823 K which corresponds to the activation temperature. These carbonized materials were used as activated carbons after washing several times with diluted HCl solution and hot distilled water and drying at 378 K for 24 h.

Characterization of produced activated carbons were done by performing necessary physical and chemical analysis. For this purpose, beside the porosity and surface area measurements, as described above, the micropore volume percentage of activated carbons was also determined by using a Micromeritics 2010 model ASAP instrument. The Boehm and iodine number analysis of activated carbons were done according to ASTM standards [35,36]. The surface micrographs of activated carbons before and after adsorp-

Table 2
The physical properties of chestnut shell and grapeseed.

Properties	Chestnut shell	Grapeseed
Average particle diameter (mm)	0.377	0.657
Specific surface area (m^2/g)	7.01	10.59
Average pore diameter (nm)	502	313
Porosity (%)	27.64	6.3
Total pore volume (ml/g)	0.3281	0.0756

Table 3
The structural analysis results of biomass samples (dry base).

Material	Extractives (%)	Lignine (%)	Holocellulose (%)
Grapeseed	19.79	41.64	44.40
Chestnut shell	8.71	42.80	58.95

tion were taken by using a Jeol Model JSM–T330 Scanning Electron Microscope which is operated at 20 kV.

In batch adsorption experiments 50 mg activated carbon (adsorbent) was thoroughly mixed with the 2 ml aqueous solutions having the copper ion concentrations of 25, 50, 100, 200, 400, 500, 750 and 1000 ppm. These solutions were prepared by diluting the stock solution having the copper concentration of 1000 ppm. The stock solution was prepared by dissolving a known quantity of metallic copper in HNO_3 solution. The effect of pH and temperature on the adsorption were studied at predetermined optimum adsorption time. pH value of the solution was adjusted by using diluted HCl and NH_3OH solutions. A Unicam model atomic absorption spectrometer with copper cathode lamp and air acetylene flame was used for determining copper concentrations of solutions after adsorption.

3. Results and discussion

3.1. Properties of activated carbons

Important properties of the produced activated carbons which affect their adsorption characteristics were determined and the results were given in Table 4.

It is clearly seen from Table 4 that the chestnut shell activated carbon has higher microporosity, iodine number and larger BET surface area than grapeseed activated carbon. However, the bulk density value of grapeseed activated carbon is higher than the chestnut shell activated carbon. From the pH values it can be concluded that both of the produced activated carbons have acidic character.

The types and amounts of surface functional groups that present in the activated carbon samples were determined by the Boehm analysis and the results were given in Table 5. The amounts of carboxylic, lactonic and phenolic groups were determined by neutralizing them with basic solutions having different base strengths such as, NaHCO_3 , Na_2CO_3 , NaOH , and $\text{C}_2\text{H}_5\text{ONa}$. The basic group content was determined by the method of titration with HCl.

The chemical composition of the precursors influences the chemical properties of the carbons obtained at the same conditions [12]. As can be seen from Table 5 raw materials and activated carbons contain mainly oxygen groups with weakly acidic properties and basic groups. Boehm analysis results clearly showed that an increase in the amount of carboxylic functional groups and a decrease in the amount of basic groups were observed after the activation process applied to raw materials. It is known that the increase in acidic functional group content of adsorbent cause an increase in the amount of copper adsorbed on the surface. Because, the removal of positively charged species positively effected from the acidic functional groups that display ion-exchange properties [37].

Table 4
Important properties of the activated carbons obtained from chestnut shell and grapeseed.

Properties	Chestnut shell activated carbon	Grapeseed activated carbon
Specific surface area (m^2/g)	1319	916
Average pore diameter (nm)	36.5	30.5
Porosity (%)	40.5	36.2
Total pore volume (ml/g)	0.5670	0.3923
Microporosity (%)	58.5	32.1
Iodine number (mg/g)	785	601
Bulk density (g/cm^3)	0.71	0.92
pH	3.33	3.04

Table 5
The Boehm analysis results of activated carbons and raw materials (meq/g).

Material	Basic groups	Carboxylic groups	Lactonic groups	Phenolic groups	Total acidic groups
Chestnut shell activated carbon	0.35	0.45	0.39	0.29	1.13
Chestnut shell	0.41	0.39	0.40	0.31	1.10
Grapeseed activated carbon	0.24	1.28	0.16	0.27	1.71
Grapeseed	0.43	0.25	0.49	0.41	1.15

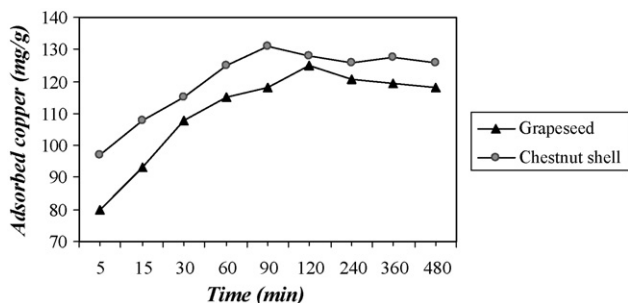


Fig. 1. Effect of contact time on the amount of copper adsorbed by chestnut shell and grapeseed activated carbons.

3.2. Effect of contact time on adsorption

In order to determine the optimum adsorption time for the activated carbons used in this study the effect of contact time on adsorption was determined at 298 K by using the stock solution which has the copper ion concentration of 1000 ppm. As can be seen from Fig. 1, the copper removal increased rapidly at the beginning of adsorption with increasing contact time and thereafter attained to the equilibrium. The minimum contact time required to reach to the equilibrium is found as 90 min for chestnut shell and 120 min for grapeseed activated carbons. Thus for the following batch adsorption experiments the contact time was fixed at these values to make sure that equilibrium was established.

3.3. Adsorption isotherms

Adsorption isotherms are very important for the design of adsorption systems since they represent how the metal ions are

partitioned between the adsorbent and liquid phases at equilibrium as a function of metal ion concentration. Many isotherm models have been proposed to analyze the adsorption equilibrium data. In this study the equilibrium data obtained for the adsorption of copper ions onto activated carbons were analyzed by considering the Freundlich and Langmuir isotherm model equations given below [38,39].

$$\text{Freundlich isotherm equation: } \log q_e = \log k_f + \frac{1}{n} \log C_e \quad (1)$$

$$\text{Langmuir isotherm equation: } \frac{1}{q_e} = \left(\frac{1}{Q_0 b} \right) \frac{1}{C_e} + \left(\frac{1}{Q_0} \right) \quad (2)$$

where q_e (mg/g) and C_e (mg/l) are the equilibrium concentrations of copper in the solid and liquid phases, respectively. k_f [(mg/g)/(mg/l)^{1/n}] is the Freundlich constant related to the sorption capacity of the adsorbent and $1/n$ is the Freundlich constant related to the energy heterogeneity of the system and the size of the adsorbed molecule. The values of k_f and n can be determined from the linear plot of $\log q_e$ versus $\log C_e$. In Eq. (2) Q_0 (mg/g) represents the theoretical monolayer saturation capacity and b (1/g) is an empirical parameter related to the energy of adsorption. A plot of $1/q_e$ versus $1/C_e$ gives a straight line of slope $1/Q_0 b$ and intercepts $1/Q_0$.

The Freundlich and Langmuir isotherms obtained from the equilibrium adsorption data of this study were given in Figs. 2–5. The Freundlich and Langmuir constants which are concluded from these plots for different temperature and pH values were summarized in Tables 6 and 7 along with the regression coefficients. It is observed from isotherms given in Figs. 2–5 that both models indicate a good representation of the experimental results by linear Langmuir or Freundlich isotherm equations. But from the calculated regression coefficients (R^2), it can be calculated that Freundlich

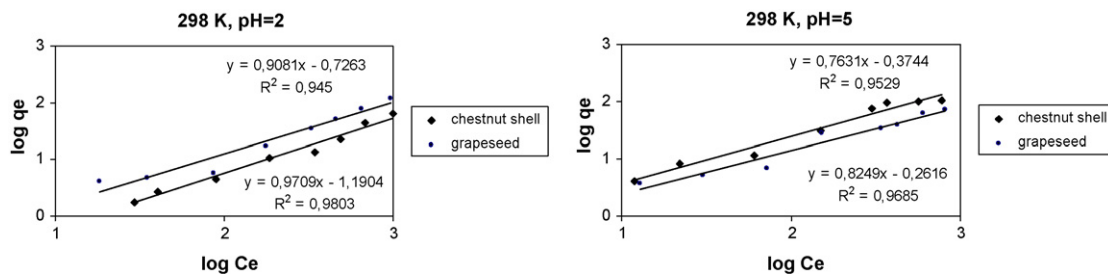


Fig. 2. Freundlich adsorption isotherm for the adsorption of copper ions onto chestnut shell and grapeseed activated carbon at $T=298$ K.

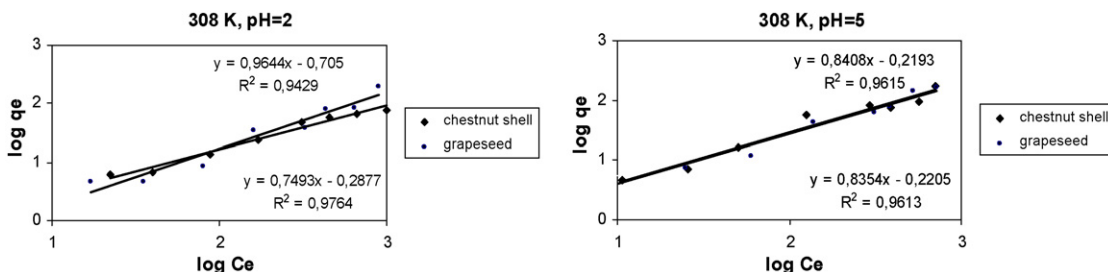


Fig. 3. Freundlich adsorption isotherm for the adsorption of copper ions onto chestnut shell and grapeseed activated carbon at $T=308$ K.

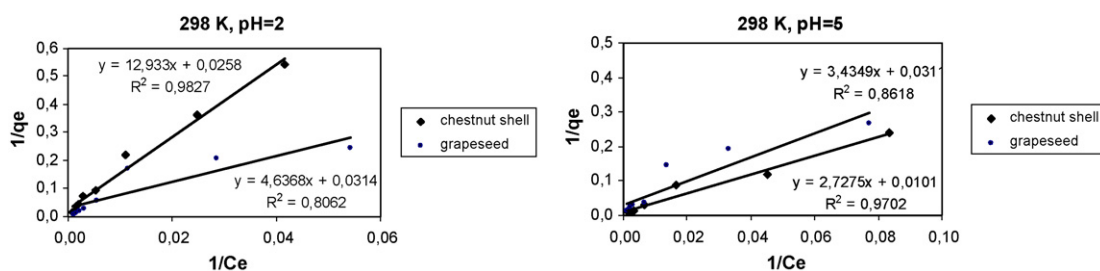


Fig. 4. Langmuir adsorption isotherm for the adsorption of copper ions onto chestnut shell and grapeseed activated carbon at $T = 298$ K.

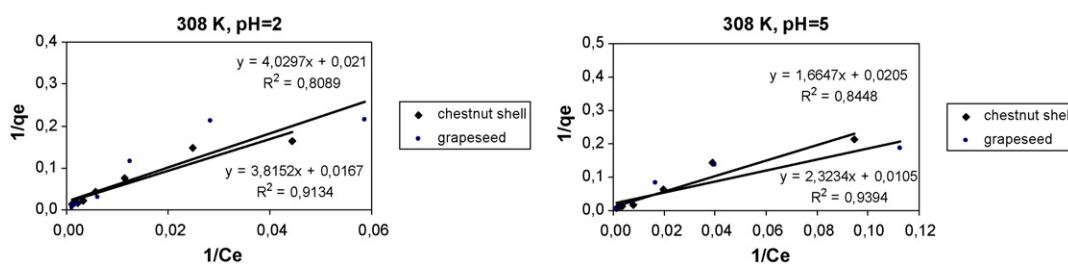


Fig. 5. Langmuir adsorption isotherm for the adsorption of copper ions onto chestnut shell and grapeseed activated carbons at $T = 308$ K.

isotherm provided better fit to the equilibrium data than Langmuir isotherm.

As can be seen from Table 6, the k_f and Q_0 values which are indicating the adsorption capacity were found as 0.06, 38.76 and 0.55, 98.04 at 298 K for the adsorption of copper onto chestnut shell activated carbon at pH values of 2 and 5, respectively. By increasing the adsorption temperature from 298 to 308 K caused to increased these values to 0.52, 59.88 and 0.61, 100 for pH values of 2 and 5, respectively.

As indicated in Table 7, for the adsorption of copper onto grapeseed activated carbon at 298 K, the k_f and Q_0 values which are indicating the adsorption capacity were found as 0.19, 31.84 and 0.42, 32.15 for pH values of 2 and 5, respectively. Similar to chestnut shell activated carbon by increasing the adsorption temperature from 298 to 308 K caused to increase these values to 0.20, 47.61 and 0.60, 48.78 for pH values of 2 and 5, respectively.

The adsorption capacity (Q_0) values of chestnut shell and grapeseed activated carbons obtained at pH=5 (Tables 6 and 7) were found considerably higher as compared with those given in Table 1 for different adsorbents. Since the adsorption experiments were conducted at nearly the same pH this change can mainly be

attributed to the properties of the adsorbents used. It is well known that, the physical properties and the surface functional group content of adsorbent have strong influence on the adsorption capacity. As can be seen from Tables 4 and 5, the adsorbents used in this study have large surface area and acidic functional groups that cause to increase in the amount of copper adsorbed on the surface.

3.4. Effect of temperature on the adsorption capacity of activated carbons

The adsorption isotherms given in Figs. 2–5 and calculated k_f and Q_0 values (Tables 6 and 7) clearly showed that the adsorption capacities for two activated carbons increased with increasing the temperature from 298 to 308 K.

An increase in adsorption capacity with increasing temperature denotes that some kind of endothermic chemical interactions may be taken place during adsorption process [40]. Additionally, an increase in adsorption capacities of the adsorbents at higher temperature may also be attributed to the enlargement of pore size [41].

Table 6

Calculated Freundlich and Langmuir constants and correlation coefficients for the adsorption of copper onto chestnut shell activated carbon at different conditions.

Chestnut shell activated carbon		Freundlich constants			Langmuir constants		
		k_f	n	R^2	Q_0	$b(10^{-4})$	R^2
T = 298 K	pH = 2	0.06	1.02	98.03	38.76	1.99	98.27
	pH = 5	0.55	1.22	96.85	98.04	3.74	97.02
T = 308 K	pH = 2	0.52	1.33	97.64	59.88	4.38	91.34
	pH = 5	0.61	1.19	96.15	100.00	4.30	93.94

Table 7

Calculated Freundlich and Langmuir constants and correlation coefficients for the adsorption of copper onto grapeseed activated carbon at different conditions.

Grapeseed activated carbon		Freundlich constants			Langmuir constants		
		k_f	n	R^2	Q_0	$b(10^{-4})$	R^2
T = 298 K	pH = 2	0.19	1.09	94.50	31.84	0.70	80.62
	pH = 5	0.42	1.31	95.29	32.15	9.05	86.18
T = 308 K	pH = 2	0.20	1.04	94.29	47.61	5.21	80.89
	pH = 5	0.60	1.19	96.13	48.78	12.05	84.48

Larous et al. have been reported that the active surface sites available for adsorption have increased with temperature. Consequently, the adsorption capacity of the adsorbent also increased. However, it is important not to exceed temperature limit, because the increase of the temperature encourages the process of agglomeration in a very determined sense, until a certain temperature limit, beyond which the desorption becomes more important and hence reducing the rate of adsorption, as time goes on [42].

The effect of temperature on the adsorption capacity of grape-seed and chestnut shell activated carbons is in agreement with the previously reported results for adsorption of different chemicals from aqueous solutions by sunflower oil cake activated carbon [43], apricot stone activated carbon [44], coir pith carbon [45], sawdust [46], hazelnut shell [47], different bagasse pith activated carbons [40] and euphorbia rigida activated carbon [48] in the literature.

3.5. Effect of pH on the adsorption capacity of activated carbons

The results given in Figs. 2–5 and Tables 6 and 7 indicate that the adsorption capacity values of the activated carbons are clearly pH dependent and increased with increasing pH value from 2 to 5.

Since the binding of metal ions by surface functional groups was strongly pH dependent, the pH of the aqueous solution is an important controlling parameter in the adsorption process [2]. The pH of solution controls the electrostatic interactions between the adsorbent and the adsorbate. The surface properties of the activated carbon also change with the pH of solution [43]. It is known that increase of pH decreases the competition between the hydrogenium and metal ions for surface sites and results in increased uptake of metal ions by the activated carbon. Carbon samples in aqueous solutions carry a surface charge, which is very much dependent on the pH of the solution and the results might be explained by the changes in the carbon surface charge at different pH values [3,49].

An examination of copper removal in different raw and chemically treated tree barks showed that copper removal at the pH values higher than 5 can be attributed to precipitation [50] and the precipitation of heavy metal ions may contribute to high uptake of the metal ions [21,51]. The precipitation of copper ions as copper hydroxides can be seen such as $\text{Cu}(\text{OH})$, $\text{Cu}(\text{OH})_2$, $\text{Cu}(\text{OH})_3$, $\text{Cu}(\text{OH})_4$. Hence the pH values higher than 5 were not studied in this study.

The effect of pH on the adsorption capacities of grape-seed and chestnut shell activated carbons is in agreement with the previously reported results for adsorption of different chemicals from aqueous solutions by sunflower oil cake activated carbon [43], apricot stone activated carbon [44], coir pith carbon [45], hazelnut husk activated carbon [21], walnut shell activated carbon [52], hazelnut shell [47], different bagasse pith activated carbons [40], euphorbia rigida activated carbon [48] in the literature.

3.6. Statistical evaluation of the results

It is clearly seen from the results given in Tables 6 and 7 that k_f and Q_0 values are changed depending on adsorption temperature, pH value of solution and type of activated carbon used. It is well known that the surface area of the activated carbon is the most important property which affects its adsorption capacity. Therefore, in statistical evaluation, the parameters were selected according to 2^3 two-level factorial design matrix considering the following variables: adsorption temperature (298 and 308 K), pH (2 and 5) and surface areas of the activated carbons (1319 and 916 m^2/g) as summarized in Table 8. In Table 9 the levels of these parameters are given.

The regression equation, used to estimate the values of k_f and Q_0 and to comprehend the effects of experimental variables and their interactions on these parameters, is a multi-factor linear model of

Table 8
Experimental parameters considered for statistical evaluation.

Adsorption parameters			
The surface area of activated carbon samples	Temperature	pH	Experimental code
1319 m^2/g	298 K	2	A1
		5	A2
	308 K	2	A3
		5	A4
916 m^2/g	298 K	2	A5
		5	A6
	308 K	2	A7
		5	A8

Table 9
The levels of experimental parameters.

Parameters	Superior level	Inferior level	Central level
A: specific surface area (m^2/g)	1319	916	1117.5
T: temperature (K)	308	298	303
P: pH	5	2	3.5

the following type:

$$y = a_0 + a_1 \cdot x_1 + a_2 \cdot x_2 + a_3 \cdot x_3 + a_4 \cdot x_1 \cdot x_2 + a_5 \cdot x_1 \cdot x_3 + a_6 \cdot x_2 \cdot x_3 + a_7 \cdot x_1 \cdot x_2 \cdot x_3 \quad (3)$$

where x_1 , x_2 and x_3 are the normalized values of experimental variables. They are calculated by using the following equations:

$$x_1 = \frac{A - \text{central level}}{(\text{superior level} - \text{inferior level})/2} \quad (4)$$

$$x_2 = \frac{T - \text{central level}}{(\text{superior level} - \text{inferior level})/2} \quad (5)$$

$$x_3 = \frac{P - \text{central level}}{(\text{superior level} - \text{inferior level})/2} \quad (6)$$

The design matrix and the values for adsorption capacity constants of chestnut shell and grape-seed activated carbons were listed in Table 10.

The design matrix was analyzed statistically to identify and measure the main and interactional effects quantitatively by using the analysis of variance which is the most effective technique in the factorially designed experiments. As a result of this statistical analysis, the following regression equations were developed for predicting the values of adsorption capacity constants in Freundlich equation (k_f) and Langmuir equation (Q_0).

$$y_{k_f} = 0.394 + 0.0412x_1 + 0.0888x_2 + 0.151x_3 + 0.041x_1 \cdot x_2 - 0.0287x_2 \cdot x_3 - 0.0712x_1 \cdot x_2 \cdot x_3 \quad (7)$$

$$y_{Q_0} = 57.1 + 17x_1 + 6.93x_2 + 12.6x_3 + 12.2x_1 \cdot x_3 - 2.29x_2 \cdot x_3 - 2.50x_1 \cdot x_2 \cdot x_3 \quad (8)$$

Table 10
The design matrix and the values for adsorption capacity constants of chestnut shell and grape-seed activated carbons.

Experimental code	x_1	x_2	x_3	Freundlich constant (k_f)	Langmuir constant (Q_0)
A1	1	-1	-1	0.06	38.76
A2	1	-1	1	0.55	98.04
A3	1	1	-1	0.52	59.88
A4	1	1	1	0.61	100
A5	-1	-1	-1	0.19	31.84
A6	-1	-1	1	0.42	32.15
A7	-1	1	-1	0.20	47.1
A8	-1	1	1	0.60	48.78

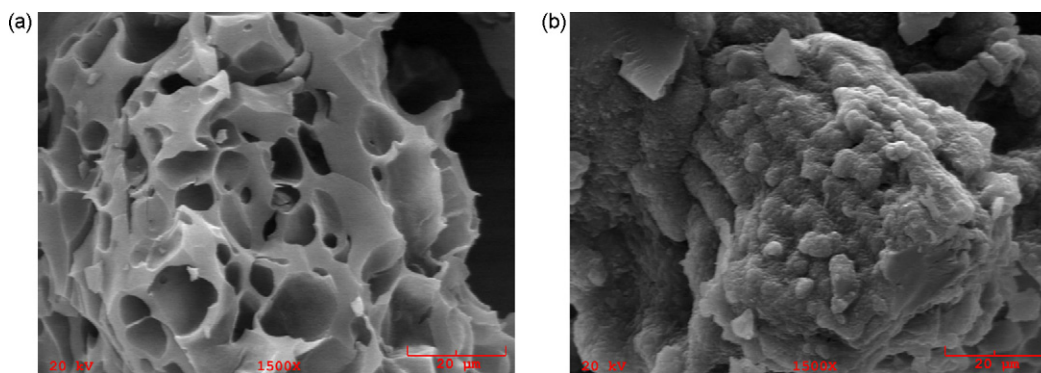


Fig. 6. SEM micrographs of the chestnut shell activated carbon before (a) and after copper adsorption (b).

The coefficient of determination for Eqs. (7) and (8) was determined as 0.999 and 0.986, respectively.

Eq. (7) clearly shows that since the coefficient of pH is the highest among all the variables, the effect of this variable on the adsorption capacity constant of Freundlich adsorption isotherm (k_f) is the strongest. But, in Eq. (8) the coefficient of surface area of activated carbon is the highest among all the variables and therefore, the effect of this variable on the adsorption capacity constant of Langmuir adsorption isotherm (Q_0) is the strongest.

It can be seen from the Eq. (7) that after pH effect, temperature, surface area and interactional effect of $x_1 \cdot x_2$ influence k_f positively; whereas, the influences of the interactional effect of $x_1 \cdot x_2 \cdot x_3$ and $x_2 \cdot x_3$ on k_f is negative.

The regression Eq. (8) shows that after surface area effect, pH, interactional effect of $x_1 \cdot x_3$ and temperature influence the Q_0 positively; whereas, the influences of the interactional effect of $x_1 \cdot x_2 \cdot x_3$ and $x_2 \cdot x_3$ on Q_0 is negative.

The normalized values of experimental variables can be converted to real values by using Eqs. (9)–(11), and the real regression Eqs. (12) and (13) were given as follows.

$$x_1 = \frac{A - 1117.5}{201.5} \quad (9)$$

$$x_2 = \frac{T - 303}{5} \quad (10)$$

$$x_3 = \frac{P - 3.5}{1.5} \quad (11)$$

$$y_{k_f}^* = 4.2 - 0.0121 \cdot A - 0.0146 \cdot T + 1.29 \cdot P + 0.000041 \cdot A \cdot T - 0.000021 \cdot A \cdot P - 0.00383 \cdot T \cdot P \quad (12)$$

$$y_{Q_0}^* = -1044 + 0.293 \cdot A + 3.75 \cdot T + 56 \cdot P - 0.00116 \cdot A \cdot T + 0.0405 \cdot A \cdot P - 0.305 \cdot T \cdot P \quad (13)$$

By taking into account the above results, the optimum adsorption conditions for maximum adsorption capacity constant were determined as $T = 308$ K, $\text{pH} = 5$ and high surface area.

The regression equations (Eqs. (12) and (13)) developed for the calculation of k_f and Q_0 values have a high determination coefficients and these give an advantage to determine adsorption capacity constants of Freundlich and Langmuir isotherms without doing experiments in the investigated parameter range.

3.7. Comparison of the SEM micrographs of activated carbons before and after adsorption

The SEM micrographs of the activated carbons were given in Figs. 6 and 7 for chestnut shell and grapeseed activated carbons, respectively. SEM images are very useful to obtain accurate adsorption details of activated carbons before and after adsorption experiments.

As mentioned previously, physical properties and the surface morphology of activated carbons influence the adsorption capacity. Chestnut shell activated carbon has more porous structure and higher surface area than grapeseed activated carbon (Table 4) and so, it has more adsorption capacity in comparison with grapeseed activated carbon (Tables 6 and 7). Fig. 6(a) also shows that the chestnut shell activated carbon had a porous and high surface area. This observation is supported by the BET surface area ($1319 \text{ m}^2/\text{g}$) and iodine number (785 mg/g) of the activated carbon. As can be seen

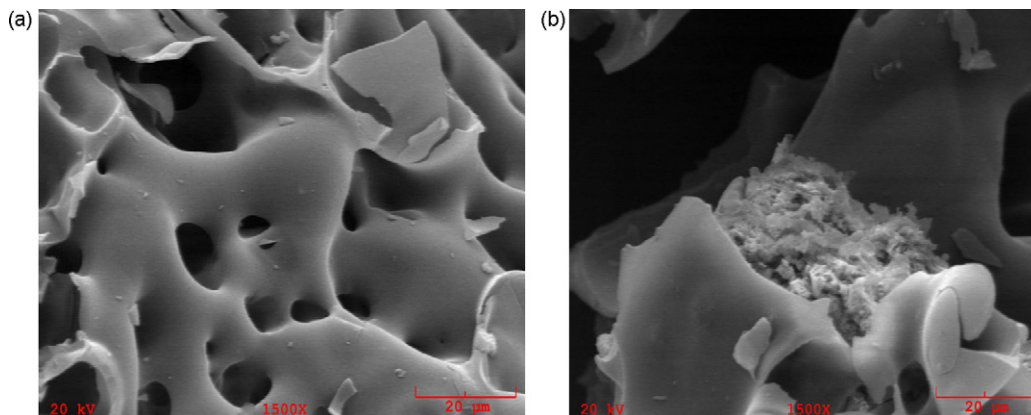


Fig. 7. SEM micrographs of the grapeseed activated carbon before (a) and after copper adsorption (b).

from Fig. 6(b), after the copper removal from solution was achieved the surface of activated carbon was completely covered with copper ions.

It is clear from the SEM micrograph presented in Fig. 7(a), the grapeseed activated carbon adsorbent had also a porous surface. The copper adsorption of grapeseed activated carbon, which has the BET surface area of $916 \text{ m}^2/\text{g}$ and iodine number of 601 mg/g is little different from chestnut shell activated carbon. The reason of more micropore structure of chestnut shell activated carbon is that the chestnut shell raw material has more cellulose content (% 58.95) than grapeseed raw material (% 44.40) [32]. The porosity parameters of the activated carbons obtained from different agricultural residues suggest that the differences in the lignin and cellulose contents of the precursors can influence the porous structure of the activated carbons. Materials with a greater content of lignin develop activated carbons with macroporous structure, while raw materials with a higher content of cellulose yield activated carbon with a predominantly microporous structure [12].

4. Conclusions

The present study has demonstrated that activated carbon prepared from chestnut shell and grapeseed could be used as an effective adsorbent for the removal of copper ions from aqueous solutions.

An increase in temperature leads to an increase in adsorption capacity and also adsorption was increased with increasing pH. The chestnut shell activated carbon has more adsorption capacity than grapeseed activated carbon due to its higher surface area and porosity. Isotherm data fit well to both Langmuir and Freundlich models for two activated carbons. However, generally higher R^2 values were obtained from the Freundlich model for copper adsorption.

Statistical evaluation of the experimental results showed that the pH is the most significant parameter among all the parameters studied that influences the adsorption capacity constant (k_f) of Freundlich isotherm and the surface area of activated carbon is the most significant parameter among all the parameters studied that influences the adsorption capacity constant (Q_0) of Langmuir isotherm.

It was clearly observed from the SEM images of adsorbents taken before and after adsorption, the surface of activated carbon was completely covered with copper ions.

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