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Copper adsorption from aqueous solution by activated carbon of wax beans waste activated by magnetite nanoparticles

Mohsen Arbabi[a] , Nazila Golshani[b], Sara Hemati[b,*], Arman Arbabi[c,d]

[a]*Social Determinants of Health Research Center, School of Health, Shahrekord University of Medical Sciences, Shahrekord, Iran, email: arbabi.m@skums.ac.ir (M. Arbabi)*
[b]*Department of Environmental Health Engineering, School of Health, Shahrekord University of Medical Sciences, Shahrekord, Iran, email: nazi_golshani@yahoo.com (N. Golshani), Tel. (+98)3833333710, Fax (+98)3833334678, email: hemati.sara88@yahoo.com (S. Hemati)*
[c]*Department of Environmental Health Engineering, School of Health, Shahid Beheshti University of Medical Sciences, Tehran, Iran*
[c]*Department of Environmental Health Engineering, School of Health, Isfahan University of Medical Sciences, Isfahan, Iran, email: armanarbabi@gmail.com (A. Arbabi)*

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ABSTRACT

Copper, a heavy metal, causes environmental pollution through a variety of industrial processes in many countries. Adsorption is known as an effective and efficient way of removing heavy metals. The present study was conducted mainly to magnetize the carbon in wax bean waste with magnetite nanoparticles and use it as adsorbent to remove copper from aqueous solution. Carbon was obtained from wax beans waste and activated with magnetite nanoparticles. The characteristics of obtaining adsorbent were studied and analyzed by FE-SEM, BET, and FT-IR. In this study, the effect of pH, adsorbent dose, contact time and copper concentration on the efficiency of copper removal was investigated per full factorial design by the Design Expert Software. The concentration of copper was measured by atomic absorption spectrophotometer (Varian AA240). For statistical analysis of the experiment's data, ANOVA and P-value were used. Copper initial concentration 100 mg/L, adsorbent dose 1 g/L, pH 7 and contact time 40 min were obtained as optimal conditions for copper removal. Investigation of the isotherms indicated that the experimental data of the process were correlated with Langmuir Model. The maximum capacity of copper adsorption of Langmuir Model was 49.75 mg/g. Findings indicated that at optimal conditions, the amount of copper adsorbed from synthetic wastewater and real wastewater was 99.73% and 63%, respectively. Therefore, this method is capable of removing copper effectively and could be used to remove this metal from industrial wastewaters.

Keywords: Copper; Wax bean; Magnetite nanoparticles; Adsorption; Atomic adsorption

1. Introduction

Heavy metals have caused many serious problems for human and other animals in the environment. These metals could not biologically decompose and are highly toxic. Further, they have high mobility and accumulate in the tissues of living organisms [1–3]. Copper (II) is a main element for plant growth and human health and functions as an active center for copper enzymes such as cytochrome C oxidase which is a component of mitochondrial respiratory chain. But the excessive amount of copper is toxic to all living organisms. Human activities including electroplating baths, melting metals, electronic industries, application of sewage and industrial wastewater sludge in farmlands, and use of copper as fungicide and pesticide cause contamination of water and soil with copper. Copper at high concentration could even affect the ecosystem's microbial population [4–7].

Corrosion of copper pipes or fittings, domestic wastewater, combustion processes, wood production, phosphate fertilizer production, the dust blown by the wind and volcanoes, and plant decomposition are some of the sources of copper released into the environment [8,9]. Copper could

*Corresponding author.

cause headache, dizziness, hepatitis, stimulation of mucus secretion, hepatic atrophy, damage to central nervous system, gastrointestinal disorders, Wilson's disease, thalassemia, anemia, tuberculosis, abortion, copperosis, and even lung cancer [10–12].

The conventional methods of removing heavy metals from wastewater include a variety of processes such as precipitation, coagulation, ion exchange, electro dialysis, electro-coagulation, reverse osmosis, evaporation, and filtration [13,14]. Despite various methods of removing metals, most processes suffer disadvantages such as the need for high energy and hence the cost and low efficiency. Since the adsorption process is low cost, environment-friendly, insensitive to toxic compounds, and reclaimable, it is developed as an effective method versus conventional methods for removing heavy metals from aqueous solutions [15]. Therefore, use of agricultural byproducts and waste to adsorb heavy metals from water and wastewater in recent years has been rapidly developing because of containing cellulose compounds and carbon in their chemical structure and hence being highly efficient and cost-effective. In addition to being abundant and available, these substances have no particular usage [16]. Recently the use of magnetic nanoparticles field has been paid extensive attention because this method is inexpensive, relatively fast, and highly efficient for separation. In this regard, various adsorbents are used, including polymer adsorbents, wastes, activated carbon fibers, and even magnetic nanoparticles. Chang and Chen studied the copper adsorption from aqueous solutions using Chitosan-attached magnetite nanoparticles. The findings indicated that the highest copper adsorption was 21.5 mg/g, the adsorption obeyed the Langmuir equation. The pH and temperature effects revealed that the adsorption capacity increased significantly with increasing pH from 2 to 5 [17].

Liu et al. [18] study of arsenate removal from water with Fe_3O_4 and sawdust activated carbon concluded that the highest removal rate was obtained at pH 8, the rise in temperature led to accelerated reaction, and this method was economical due to use of waste. Basu and Dutta [19] studied copper removal from the industrial wastewater of leather factory with microwave and acacia activated carbon and obtained a 99.9% removal rate within 80 min, found that the remaining copper was lower than WHOs' permissible limit (1.5 mg/L), the adsorption rate increased as temperature decreased, and the maximum efficient removal was seen at pH 6.

This study was conducted to examine the possibility of activated wax bean waste with magnetite nanoparticles and its efficiency to remove copper from aqueous solutions.

2. Materials and methods

2.1. Chemicals and materials

Ammonium hydroxide, $CuSO_4$, HCL, NaOH, $FeCl_3\cdot6H_2O$ (P ≥ 96), $FeSO_4\cdot7H_2O$ (P ≥ 99.5), ethanol (C_2H_5OH, P ≥ 96%) was purchased from Merck company, Germany. All other chemicals were used without further purification.

2.1.1. Preparing the wax bean activated with magnetite nanoparticles

Firstly, wax bean waste was washed and rinsed with deionized water and then dried in oven at 105°C for 24 h [20]. To reduce acidity, we left the samples in hydroxide sodium 0.5 M for 4 h at room temperature and then washed them with distilled water twice. For thermal activation, the samples were placed in furnace at 500°C for 2 h. After cooldown, the samples were ground and passed from through sieve having a mesh of 100 µm (0.15 mm) [21–23].

Magnetic magnetite nanoparticles were produced by chemical method of co-precipitation. For this process, chemical sources such as iron chloride of 2 and 3 valences were used as precursors and ammonium hydroxide as a precipitate. By this method, firstly 1.6 g iron chloride with 6 molecules of H_2O and 2.4 g iron sulphate with 7 molecules of H_2O were dissolved with 100 mL of distilled water separately [24].

The two solutions were combined and rapidly mixed with each other at 90°C. 1 g of the already prepared adsorbent was dissolved with 200 mL distilled water, combined with ferric chloride and iron sulphate and then slowly mixed with each other at room temperature for 30 min. Gradually, 10 ml ammonium hydroxide 0.25 M was introduced into the solution until the pH reaches to 10–11. After one-hour slow mixture, the suspension temperature in laboratory gradually declined.

After filtering the solution and repeated washing with distilled water, we left the solution in oven at 50°C for 24 h. Finally, the adsorbent activated with magnetite nanoparticles was pulverized by an electric mill [25,26].

2.2. Adsorption experiment

In this study all the samples were daily prepared using distilled water. All experiments were done at 25°C. Anhydrous copper sulfate ($CuSO_4$) was used to prepare stock solution 1000 mg/L and Erlenmeyer 250 ml was used as experiment container [27].

Adsorption experiments were carried out in a batch system to determine the effect of various factors on adsorption using wax bean waste-magnetite nanoparticles as adsorbent at contact times 40, 80, and 120 min, pH 3, 5, and 7, copper initial concentrations 75, 50, and 100 mg/L, adsorbent doses 1, 1.5, and 2 g/L, and mixed at 150 RPM. For all the samples, after the adsorbent was mixed, the solution was filtered with cellulose acetate filter paper 0.45 µ diameter. Then the concentration of copper was measured by atomic absorption spectrophotometer (Varian AA240). In this study, the percentage of removal efficiency was determined by Eq. (1).

$$R = \frac{(C_0 - C_e)}{C_0} \times 100 \quad (1)$$

where C_0 represents initial concentration, C_e the final concentration of copper in solution, and R removal percentage. To calculate equilibrium capacity of copper ions Eq. (2) was used.

$$q = \frac{(C_0 - C_e) \times V}{M} \quad (2)$$

where C_e represents the equilibrium concentration of the adsorbed substance (mg/L), C_0 the initial concentration (mg/L), V the solution volume (L), and M the adsorbent mass (g) [28,29].

In this study, the experiments were designed and the data were analyzed by the response surface method (RSM), statistical modeling method of full factorial design was done by Design Expert ver. 07, and one-way ANOVA was used for results interpretation. P value < 0.05 was considered as the level of significance. In this study pH, contact time, and adsorbent dose were considered as independent variables and copper removal efficiency as the response variable.

3. Results and discussion

3.1. Adsorbent characteristics

To study the surface and structural characteristics of the prepared adsorbent, several experiments were done. Scanning electron microscopy (FE-SEM) (MIRA3TESCAN-XMU) was used to illustrate the morphology and surface characteristics of the adsorbent (Figs. 1a, b). Fig. 1a depicts the smooth and soft surface of the adsorbent which enhances its ability to absorb the pollutants rapidly [30,31]. The size of nanoparticles is approximately 10–15 nm (Fig. 1b).

Micrograph of EDX (energy dispersive X-ray microanalysis) shows the main elements of the adsorbent activated with iron nanoparticle. As the graph illustrates, the main adsorbent elements are carbon (36.39%), oxygen (29.16%), and iron (28.48%). By means of FT-IR (Fourier Transform Infrared) (JASCO, FT/IR-6300, Japan), the existing groups in the sample were identified to ensure the presence of Fe-O in magnetite nanoparticles (Fig. 2a).

As illustrated in Fig. 2b, the observed peak at 3393.58 cm^{-1} wavelength represents the functional group OH on the iron particles surface. 1626.89 cm^{-1}, 2924.25 cm^{-1} and 510.84 cm^{-1} wavelengths represent the carbonyl functional groups C=O, C–H and Fe–O, respectively. 1013.52 cm^{-1} and 1088.59 cm^{-1} wavelengths confirm the presence of ester groups C–O. Brunaer Emmet and Teller test (BET) (Belsorp mini II, Bel-Japan) was used to measure the adsorption and desorption rates of the adsorbent such as specific surface, diameter, volume, and distribution of pore size. The adsorption rate is generally proportionate to the surface characteristics of the adsorbent. The area of specific surface of wax bean waste carbon and Fe_3O_4-activated wax bean waste carbon was obtained 3.016 and 29.15 m^2/g, respectively.

3.2. Effect of pH change

To study the effect of change in pH on copper removal from the solution at different concentrations by adsorbent,

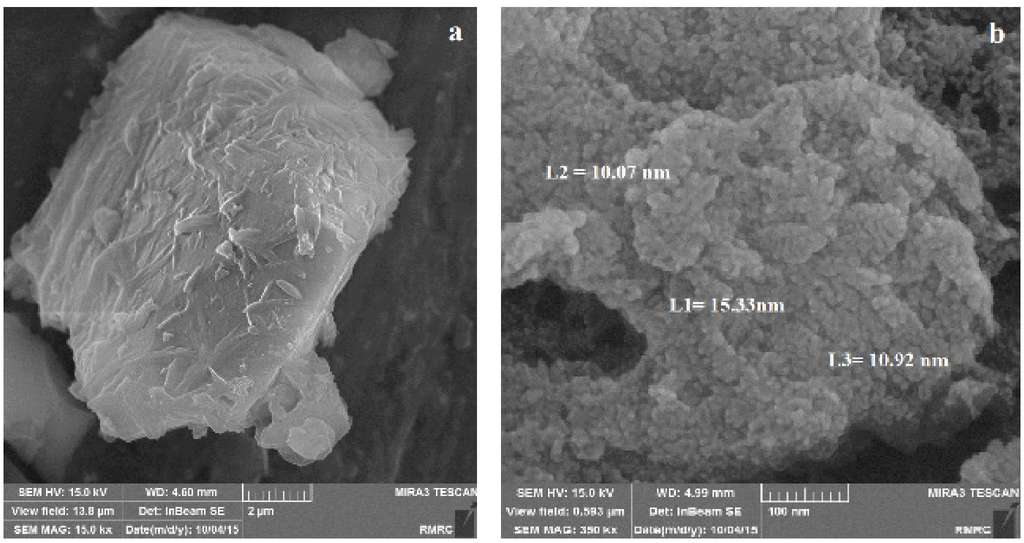

Fig. 1. Micrographs of FE-SEM: (a) carbon waste of wax bean (b) carbon waste of wax bean activated with magnetite nanoparticle.

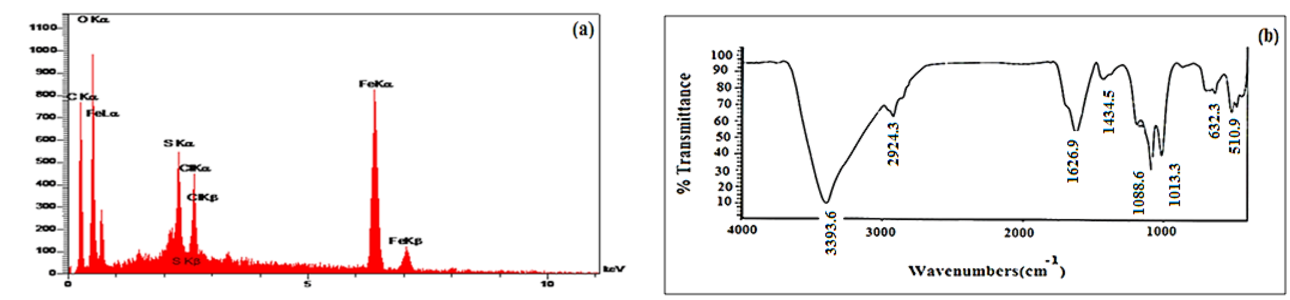

Fig. 2. (a) EDX micrograph and FTIR spectrum (b) of carbon waste of wax bean activated with magnetite nanoparticle.

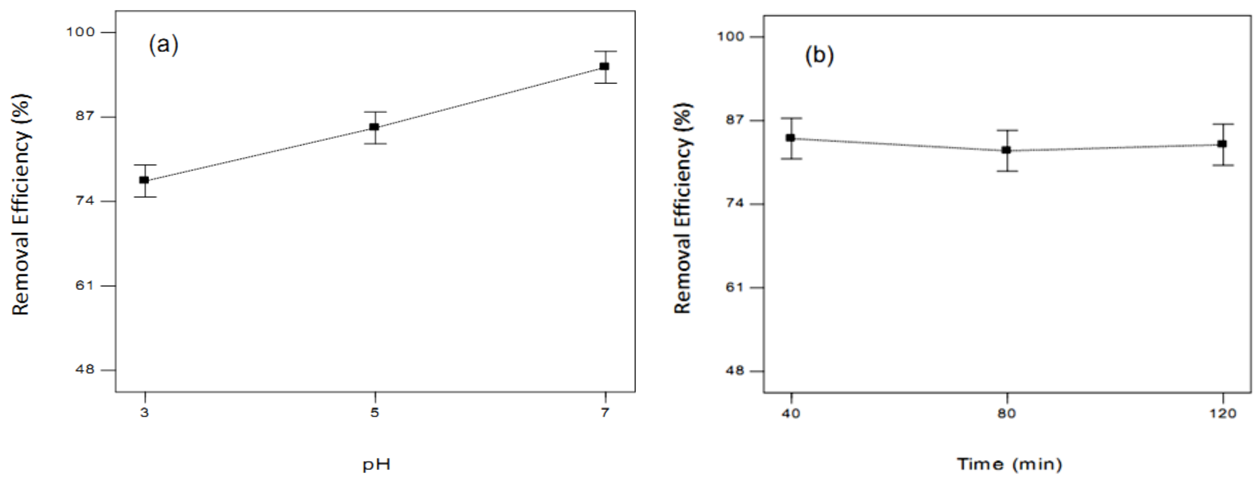

Fig. 3. Effect of pH (a) and contact time (b) on copper removal efficiency (25°C, lab scale).

pH 3, 5, and 7 was used. As Fig. 3a illustrates, when the pH increases from 3 to 7, removal efficiency increases from 77.15% to 94.66%, with the highest removal efficiency at pH 7. Therefore, pH 7 was determined as optimal pH. At lower pH, H^+ ions concentration is high in the solution, which causes copper and hydrogen ions to compete for adsorption with the empty sites of adsorbent surface. The resulted repulsive force causes decrease in the metal cations capable of approaching adsorbent.

3.3. Effect of change in contact time

Contact time is one of the most important effective factors on adsorption processes. The effect of contact time on copper adsorption efficiency at different concentrations is illustrated in Fig. 3b. As seen, the highest removal efficiency of the adsorbent (86.66%) was derived at 40 min and then the removal efficiency declined over time. This finding indicates that at early times of the experiment, the amount of copper ion is high in the solution and hence the effective impacts between copper cations and the effective sites on the adsorbent surface are more frequent. Therefore the adsorption rate increases at a higher speed.

Over time, the amount of cations in the solution decreased and most effective sites on the adsorbent surface were filled and hence the adsorption speed declined. Similar studies have conducted to examine the contact time effect on copper adsorption rate and inconsistent findings were obtained. For example, Dutta and et al. [19] study of copper adsorption from industrial wastewater of leather factory with microwave and the acacia-activated carbon reported the contact time 80 min, and Kongsuwan et al. [19,32] study of copper and lead adsorption reported the optimal contact time in the experiment 45 min.

3.4. Effect of change in adsorbent amount

The adsorbent amount is economically important for determining the capacity of adsorbent-assisted metal adsorption. Fig. 4a depicts the effect of initial amount of adsorbent on copper adsorption efficiency. The effect of adsorbent amount on copper adsorption efficiency was investigated by changing its initial amount (1, 1.5, and 2 g/L).

As observed, mean adsorption percentage (86.62%) was obtained with 1 g/L adsorbent. Banerjee et al. [33,34] study on copper adsorption from aqueous solutions using watermelon skin and Khan et al. [33,34] study on use of bio-adsorbents existing in citrus peel and sawdust for copper adsorption from aqueous solutions demonstrated that the adsorption rate increased with increase in adsorbent. However in the present study, the effect of different amounts of adsorbents on the process of copper ion adsorption was not significant and no considerable difference in adsorption efficiency was seen with change in the adsorbent amount.

3.5. Effect of change in copper initial concentration

The effect of change in copper initial concentration on copper removal efficiency is illustrated in Fig. 4b. As seen, mean adsorption percentage increased from 82.27% to 87.77%. Therefore, the changes in initial concentration had no considerable effect on the process efficiency. As the copper concentration increased, the adsorption efficiency increased because of increased metal ions and saturated adsorption sites. Larous et al. and Kongsuwan reported similar findings [12,32].

3.6. Optimization of conditions for copper adsorption

To determine the optimal conditions for copper adsorption in aqueous solution using carbon wax bean waste activated with magnetite nanoparticles to achieve the optimal removal efficiency, copper adsorption percentage (response), and independent variables were defined in Maximize and in Range, respectively. Table 1 shows optimal conditions to achieve the maximum removal percentage. The actual amount of adsorption in the conducted experiments is 99.73% and the predicted amount by the model is 98.57%. Therefore, an acceptable agreement is seen between the values and the used model is appropriate.

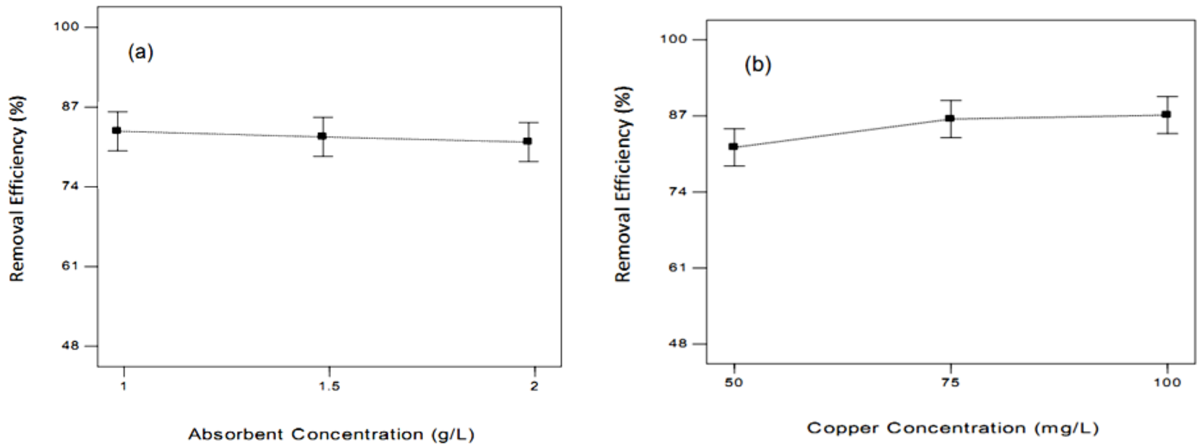

Fig. 4. Effect of absorbent dose (a) and initial concentration of copper (b) on copper removal efficiency (25°C, lab scale).

Table 1
Optimal conditions to achieve the maximum removal percentage of copper

Variable	Value
pH	7
Time (min)	40
Absorbent dose (g/L)	1
Initial concentration of Cu (mg/L)	100
Real amount of adsorption (%)	99.73
Predicted value using the model (%)	98.57

Table 2
Equilibrium isotherm parameters of the copper adsorption process in optimal conditions

Adsorption isotherm	Isotherm equations	Constant and correlation coefficients of isotherm		
Langmuir	$\frac{1}{q_e}=\frac{1}{q_m k_L C_e}+\frac{1}{q_m}$	q_m (mg/g)	K_L	R^2
		49.75	0.092	0.9855
Freundlich	$\text{Log } q_m = \text{Log } k_f + 1/n \text{ Log } C_e$	K	1/n	R^2
		2.12	0.52	0.9438

3.7. Adsorption isotherms and analysis of isotherm data

In this study, Langmuir and Freundlich isotherms were used to investigate the adsorption process. Table 2 shows the results of equilibrium isotherm of copper adsorption process on the magnetite nanoparticles. The results indicated that this process (regression coefficient: 0.985) followed Langmuir isotherm and the maximum adsorption capacity was obtained 49.75 mg/g by this model. Fig. 5 illustrates Freundlich and Langmuir isothermal models.

In the above equations, q_e (mg/g) represents the amount of metal ions adsorbed by adsorbent, C_e (mg/L) the concentration of residual metal ions, and K_L the Langmuir constant, K_f and n Freundlich constants, and q_m (mg/g) the maximum adsorption capacity [35].

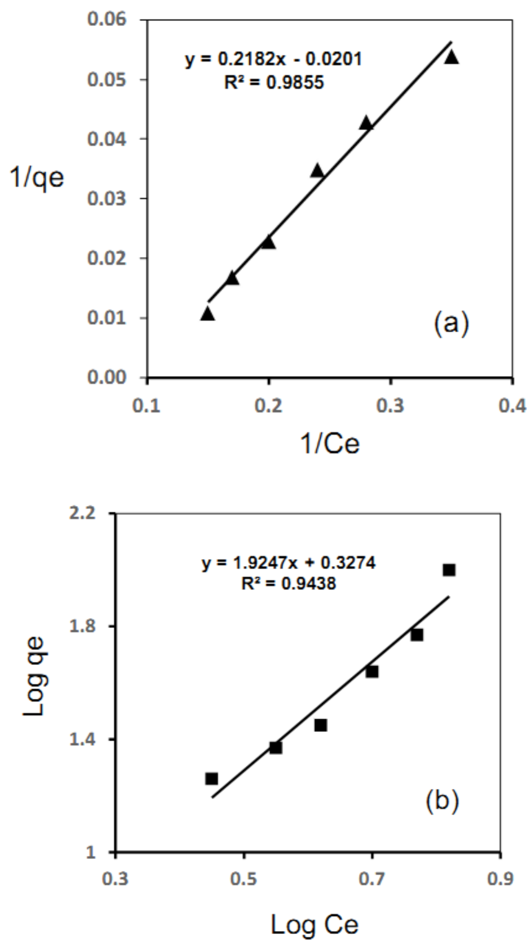

Fig. 5. Isotherm models (a) Langmuir and (b) Freundlich.

3.8. Statistical analysis

In this study, full factorial method and one-way ANOVA were used to study the effect of independent variables on response function (efficiency of copper ion adsorption). Table 3 shows these variables.

Table 3
Levels and values of independent variables

Variable	Symbol	Agent levels		
		3	2	1
pH	A	3	5	7
Time (min)	B	40	80	120
Absorbent dose (g/L)	C	1	1.5	2
Initial concentration of cu (mg/L)	D	50	75	100

Table 4
Analysis of variance (classical sum of squares - Type II)

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F
Model	9124.50	8	1140.56	7.06	< 0.0001
A-pH	8060.01	2	4030.01	24.95	< 0.0001
B-Time	97.32	2	48.66	0.30	0.7404
C-Absorbent Cons.	82.28	2	41.14	0.25	0.7755
D-Cu Cons.	943.30	2	471.65	2.92	0.0570
Residual	24068.65	149	161.53	–	–
Lack of fit	13823.77	72	192.00	1.44	0.0573
Pure error	10244.89	77	133.05	–	–
Cor. total	33193.15	157	–	–	–

According to P values (Table 4), the effect and coefficients obtained for each factor, the regression equation of copper ion adsorption was obtained as Eq. (3). As P value is less than 0.005, so the studied model is significant.

$$Y = 85.71 - 8.56A_1 - 0.38A_2 + 0.95B_1 - 0.95B_2 + 0.91C_1 - 0.032C_2 - 3.45D_1 + 1.38D_2 \quad (3)$$

The level of significance (P value) was considered 0.05. The significance of the studied model is aimed to explain the adsorption of copper ion by synthesized adsorbent and is expressed by F value.

This variable was derived 7.06 in the present study and P value was less than 0.05 ($P < 0.0001$). Therefore, the above model is significant for copper ion adsorption. In this study, R^2 and adjusted R^2 (R^2_{adj}) were derived 27% and 23%, respectively. The adequate precision value represents the difference between the model's predicted response and the mean predicted error. If this difference exceeds 4, as with the obtained results (8.8) in the present study, the model is considered appropriate.

A normal distribution diagram was used to confirm the appropriateness of one-way ANOVA. In Fig. 6a, the studentized residual represents normal distribution, goodness of fit. Ascending diagram of the predicted versus observed values confirms or rejects the hypothesis of constant variance.

The higher density of the spots around the diagram represents the constant variance, the correlation among the values, and the distribution of the observed values around regression (Fig. 6b). The hidden variables affect on response variable are investigated by the diagram of residual values versus the values of the number of experiment steps. Fig. 6c illustrates that the data distribution is small and the rate of constant variance and error percentage is 10% with regard to confidence interval (red lines).

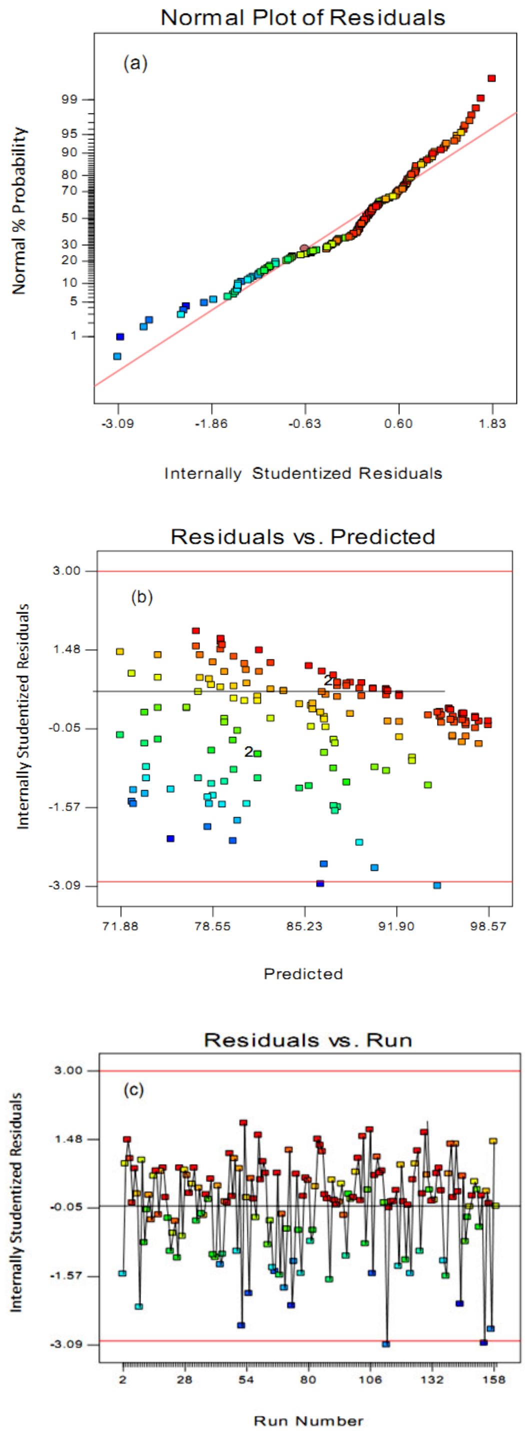

Fig 6. (a) Normal distribution of residuals (b) Predicted vs. residual values and (c) Residuals vs. run.

Table 5
Removal percentages for real wastewater samples

Removal rates (%)			Average removal rate (%)
67.2	62.3	60.35	63

3.9. Real wastewater analysis

Real wastewater samples were taken from effluent of Weir (copper tubes and cables) Manufacturing Company with copper concentration of 3.2 mg/ l. Therefore, firstly the solution was filtered with membrane filter several times. Then optimal conditions of experiments (mentioned in Table 1) performed on it and mixed at 150 rpm. All of experiments repeated thrice and measured by atomic absorption spectrophotometer (Varian AA240). Average removal rate of copper in real wastewater was obtained 63% (Table 5).

4. Conclusions

Finally, the process of adsorption could be considered as a very effective technology for copper adsorption. This study was mainly aimed to examine the possibility of activating wax bean with magnetite nanoparticles and its efficiency for copper adsorption in aqueous solutions.

FESEM images and EDX analysis indicated that absorbent was well activated by magnetic nanoparticles. Results of BET experiment indicated that the area of specific surface of wax bean waste carbon and Fe_3O_4-activated wax bean waste carbon was obtained 3.016 and 29.15 m^2/g, respectively.

The results of the experiments demonstrated that the magnetized activated carbon could function as an effective adsorbent of copper in industries effluent because of considerably efficient adsorption, high adsorption capacity, cost-effective considerations, and highly convenient isolation after adsorption. The optimal adsorption was obtained 99.73% at pH 7, copper initial concentration 100 mg/L, absorbent dose 1 g/L and contact time 40 min. The adsorption rate of copper ion in real wastewater was 63%. Study of isotherms indicated that the process of copper removal follows Langmuir Isotherm equation.

Competing interests

The authors declare that they have no competing interests.

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