

Box-Behnken Design Approach for Optimizing Removal of Copper from Wastewater Using a Novel and Green Adsorbent

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ABSTRACT

The aim of the present research was to apply the Box-Behnken experimental design and response surface methodology for modeling of copper (Cu^{2+}) ions from an industrial wastewater and leachate pre-treated astragalus herbal plant. A three factor, three level Box-Behnken experimental design combined with response surface modeling (RSM) and quadratic programming (QP) was employed for maximizing $\text{Cu}(\text{II})$ removal from aqueous solution based on 17 different experimental data obtained in a batch experimental study. Three independent variables (pH ranging from 2.0 to 8.0, contact time from 10 to 180 minutes, and adsorbent amount from 0.1 to 1 g) were studied. The significance of the independent variables and their interactions were tested by means of the analysis of variance (ANOVA) with 95% confidence limits. The

standardized effects of the independent variables and their interactions on the dependent variable were also investigated by preparing a Pareto chart. The optimum values of the selected variables were obtained by solving the quadratic regression model as well as by analyzing the response surface contour plots. Using the experimental conditions of pH = 5.0, contact time = 92.5 minutes, adsorbent dosage = 0.25 g, the recovery efficiency of $\text{Cu}(\text{II})$ was found to be 100%.

Copper-free and copper-loaded astragalus was analyzed using fourier transform infrared spectrometry (FTIR) which evidenced the functional groups involved in copper uptake. Adsorption equilibrium for copper was described by using the Freundlich and Langmuir adsorption isotherms. This adsorbent was applied to different industrial wastewater and leachate samples for copper removal.

Thus, it becomes vital to reduce and control the permissible heavy metals levels in wastewaters (1, 7). Currently, the removal of toxic metal contaminants from various aqueous waste systems is one of the most important environmental issues. In order to remove heavy metals from contaminated water, especially industrial effluents, a variety of physicochemical methods including chemical precipitation (8), ion exchange (9), nanofiltration, low energy reverse osmosis (10), and ultra filtration have been proposed. Reverse osmosis, although very effective, is a very costly process since it requires frequent membrane replacement. On the other hand, when the pollutants are at trace levels, chemical precipitation is not a suitable method. While ion exchange is expensive and sophisticated, solvent extraction or electrolytic processes are also available but they are not considered to be cost-effective methods (11). Hence, most of these processes are not widely acceptable because of disadvantages such as difficulty in the disposal of sludge, low efficiency, and inapplicability to a wide range of pollutants (12-15).

In recent years, the adsorption technology used for the purification of water has received increasing attention because it is effective, simple, and economical (16-20). To obtain cheaper and effective adsorbents, various materials such as lignocellulosics have been investigated. For this purpose, cheaper and abundantly available adsorbents for the determination of metals in agricultural waste have been used and studied such as tea waste,

INTRODUCTION

The increase in industrial activity has led to environmental contamination from various harmful components due to the lack of strict control of waste quality (1). As is well known, copper is one of the most common and important pollutants in the environment, especially in water and industrial wastewater, and since it is non-biodegradable, its toxic effects have become a pub-

lic health concern. The most toxic or carcinogenic metals are mercury (Hg), cadmium (Cd), lead (Pb), and copper (Cu) (2). Heavy metals pollution, especially from copper, comes from different natural activities and industrial effluents. If these metals enter the ecosystem, they will be easily adsorbed by marine animals and directly enter the human food chain causing serious health problems in the liver, brain, dysfunction of the kidney, the reproductive and the central nervous systems (3, 4). The toxicity of these metals accumulates in living tissues with consequent biomagnification in the food chain (5, 6).

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peanut hull, banana peel, hazelnut shells, saw dusts, pine bark, coconut husk, peanut skins, rice hulls, and almond shells in addition to different agricultural products (21-25).

For metal removal in aqueous systems, ion exchange, reverse osmosis, chemical precipitation, and electrolysis are frequently employed. For effluent treatment, many strategies and techniques have been investigated and reported (26-28). Due to the critical importance of adsorption processes, the development of low cost, effective, and eco-friendly methods is very important and necessary (29-32). There are two different classes in terms of these materials: natural materials include natural zeolites, coal, coir, rice husk, clay, and biosorbents such as fungi, algae, and bacteria (33,34). The astragalus plant can be considered as an effective, natural, and environmentally friendly material for its application in effluent treatment. To our knowledge, this material, in its natural form, has never been applied for this purpose.

In this study, the feasibility of astragalus as an economical and abundantly available adsorbent for the removal of copper from wastewater samples is used in a batch system. For this purpose, the Box-Behnken model experimental design in response surface modeling (RSM) was found to be a beneficial tool to optimize the experimental conditions and to evaluate the multiple analytical factors and their interactions. RSM is a combination of mathematical and statistical techniques used for developing, improving, and optimizing the processes and to evaluate the relative significance of several parameters in the presence of complex interactions. Since RSM provides a mathematical model with the advantages of achieving higher percentage yield, reducing process variability, closer confirmation of

output response to nominal target achievement, and less treatment time with minimum cost. At the same time to understand the adsorption mechanism, the evidence for physicochemical characteristics of astragalus obtained from FTIR analysis was investigated. The optimal experimental conditions were applied to investigate the effects of the parameters and their interactions on copper removal by adsorption. In addition, the adsorption isotherms (Freundlich and Langmuir models) were determined using these conditions. In view of these important characteristics, the aim of this work was to establish astragalus as an alternative and effective biomaterial for removing copper ions from various wastewater samples. Before and after treatment, copper concentration was determined by using flame atomic absorption spectrometry (FAAS).

EXPERIMENTAL

Reagents

Copper nitrate, sodium hydroxide, hydrochloric acid, sodium citrate monohydrate, sodium dihydrogen phosphate, sodium tetraborate and nitric acid were obtained from Merck (Darmstadt, Germany). All chemicals used were of analytical grade.

Preparation of Standard Solutions

A stock solution of 1000 mg L⁻¹ Cu(II) was prepared by dissolving an accurate quantity of Cu(NO₃)₂ in ultrapure water. Other concentrations of 1 mg L⁻¹ to 200 mg L⁻¹ were prepared using the stock solutions by dilution.

Preparation of Adsorbent

The astragalus plant samples were collected at Turusmek (Aktuluk), a local area in Tunceli, Turkey. They were washed with tap and ultrapure water to remove the dirt, then oven-dried at 60 °C until con-

stant weight, then peeled. After drying, the astragalus samples were ground in a blender, sieved to particles of <120 mesh, and stored at room temperature in polyethylene bags until use.

Box-Behnken Experimental Design and Optimization by RSM

The optimum conditions for maximizing the adsorption of Cu(II) by astragalus were determined by means of a three-factor, three-level Box-Behnken experimental design combined with response surface modeling and quadratic programming. According to single-factor experiments, a Box-Behnken design was used to determine three independent variables: pH (X₁), contact time (X₂), and adsorbent amount (X₃) on adsorption of copper onto astragalus (Y). In order to reduce unexplained variability effects on the observed response, randomized experimental order was carried out. Seventeen experimental points including replications of the central points experimental design were used. Table I lists the different parameters such as variable conditions, run order, experimental values, and predicted values. A final equation was obtained from RSM in terms of actual factors:

$$Y = -2.82 + 1.28816X_1 + 0.015X_2 + 3.13488X_3 - 7.42857E-004X_1X_2 - 0.16667X_1X_3 - 1.33333E-003X_2X_3 - 0.12003X_1^2 - 5.26041E-005X_2^2 - 1.81605X_3^2$$

After data analysis by ANOVA in order to determine the lack of fit, other parameters were evaluated including the effects of quadratic, linear, and interaction variables for copper adsorption on astragalus. RSM and data analyses were carried out with Design Expert software program (Design Expert Version 10, Stat-Ease, USA).

All adsorption experiments were performed in Erlenmeyer flasks

containing Cu(II) synthetic solutions and adsorbents at <120 mesh adsorbent particle size were added to the solutions. The effect of pH (2–8), contact time (10 to 180 minutes) and adsorbent mass (0.1–1 g) were studied at room temperature. The pH was adjusted using sodium hydroxide and hydrochloric acid. A model Duo S213 digital pH meter (Mettler Toledo, Switzerland) was used for pH measurements. The adsorbent was separated from the samples by filtering, and the filtrate was analyzed using a PerkinElmer® AAnalyst™ 800 FAAS (PerkinElmer, Inc., Shelton, CT, USA). The instrumental operating conditions are listed in Table II. Three independent replicates were prepared and the average results are presented.

Characterization of Adsorbent

FTIR spectra of the pretreated astragalus were compared with the FTIR spectra of the astragalus

spiked with copper. The spectra were recorded in the frequency range of 4000–500 cm⁻¹ using the Thermo Nicolet iS10 FTIR spectrophotometer (Thermo Scientific, USA). The instrumental operating conditions are listed in Table III. Attenuated Total Reflectance (ATR, diamond crystal) was used for sample analysis.

RESULTS AND DISCUSSION

Second-order Polynomial Model

RSM with a Box–Behnken design and ANOVA was used for copper adsorption on astragalus and the conditions are shown in Table I and Table IV, respectively. The Model F-value of 142.17 implies that the model is significant. There is only a 0.01% chance that a F-value this large could occur due to noise. Values of "Prob>F" less than 0.0500 indicate that the model terms are statistically significant.

TABLE I
Box–Behnken Design and Observed Responses
of Cu Levels on Astragalus (mg g⁻¹)

Run	pH	Contact Time	Adsorbent Amount	Copper (q _e , mg g ⁻¹)	
	X ₁	X ₂ (min)	X ₃ (g)	Experimental Values	Predicted Values
1	2	5	0.55	0.33	0.33
2	5	180	1	1.22	1.27
3	5	180	0.1	1.28	1.22
4	2	180	0.55	0.94	0.94
5	5	5	0.1	0.95	0.90
6	8	92.5	0.1	0.32	0.37
7	8	180	0.55	0.13	0.12
8	5	92.5	0.55	1.82	1.89
9	8	5	0.55	0.30	0.29
10	2	92.5	1	1.10	0.98
11	5	5	1	1.10	1.20
12	5	92.5	0.55	1.98	1.91
13	8	92.5	1	0.15	0.12
14	5	92.5	0.55	1.92	1.91
15	2	92.5	0.1	0.32	0.31
16	5	92.5	0.55	1.90	1.91
17	5	92.5	0.55	1.92	1.91

Because the model coefficient (R²) was 0.9946, it can be said that 99.46% of the model-predicted values matched the experimental adsorbed copper values on astragalus. The "Pred R-Squared" of 0.9382 is in reasonable agreement with the "Adj R-Squared" of 0.9876; i.e., the difference is less than 0.2. "Adeq Precision" measures the signal-to-noise ratio. A ratio greater than 4 is desirable. The ratio of 30.691 obtained in this study indicates an adequate signal. This model can be used to navigate the design space. On the other hand, Lee et al. (35) reported that when R²>0.75, the model is adequate. This study revealed that the lack of fit that measures the fitness of the model was not significant (P>0.05); the "Lack of Fit F-value" of 2.82 implies the Lack of Fit is not significant relative to the pure error. There is a 17.12% chance that a "Lack of Fit F-value" this large could occur due to noise. A non-significant lack of fit is good. In addition, the number of experiments was sufficient to determine the effects of the independent variables for copper adsorption on astragalus.

TABLE II
Instrumental Operating Conditions of AAnalyst 800 FAAS

Parameters	Values
	Cu
Wavelength	324.8 nm
HCL current	30.0 mA
Flow rates:	
Air	17 L min ⁻¹
Acetylene	2 L min ⁻¹
Slit width	0.7 nm

TABLE III
Instrumental Parameters for FTIR Analysis

Wavenumber range	4000–500 cm ⁻¹
Sample to KBr mass ratio	1:100
Spectral resolution	4 cm ⁻¹
Crystal Type	Diamond

The results expressed by using the statistical model were adequate in order to predict the copper levels and were fitted to a second-order polynomial equation. In this case, while X_1 is highly significant ($P < 0.01$), X_2 , X_3 , X_1X_2 , X_1X_3 , X_1^2 , X_2^2 , X_3^2 are significant model terms in terms of copper adsorption on astragalus. The quadratic and linear coefficients affecting the factors on the response of copper adsorption on astragalus follow the order: pH > contact time > adsorbent amount.

RSM Analysis

Two-dimensional (2D) contour plots and three-dimensional (3D) response surface graphs were made because they are useful in determining maximum, minimum, and middle response points. With contour plots, the levels of the variables can be determined and also con-

tribute to a desired response. In addition, the variable levels are plotted in a curve with equal response. Because of these reasons, contour plots are easier to interpret. Figure 1 shows the effect of pH and contact time on copper in astragalus. The adsorbed copper amount increased with an increase in pH until it reaches a plateau at 5, indicating that there are further improvements for copper levels. At the same time, contact time has important effects on copper adsorption on the adsorbent. The effects of pH and adsorbent amount on copper adsorption are shown in Figure 2. The interaction of these two variables had a significant effect on the adsorption process including from the quadratic variables (pH, $P < 0.01$; contact time, $P < 0.05$). As a result, the impact of pH on the copper adsorption level

was more significant than of contact time. The effects of contact time and amount of adsorbent on copper adsorption onto astragalus are shown in Figure 3. The adsorbed copper amount increased with an increase in contact time until it reached a plateau at 92.5 minutes, indicating that there was no further improvement in the adsorbed copper level.

Confirmation Experiments

To support the optimized data given by numerical modeling under optimized conditions, experiments were conducted with the parameters as suggested by the model (pH 5.0, adsorbent dose 0.50 g/100 mL, contact time 92.5 minutes, and stirring speed 150 rpm, temperature 25 ± 1 °C) and the percent removal was found to be 100% (Table V). The effect of pH, Cu(II) concentration, and adsorbent dose were also studied to verify the results.

There are many studies and different results were reported for adsorbents. Yao et al. (36) used a batch experiment system for biosorption of Cu(II) onto food waste adsorbent. The equilibrium data agreed well with the two isotherm models of Redlich-Peterson and Langmuir. The capacity of chestnut shell adsorption was calculated as 12.56 mg g^{-1} at room temperature with a pH ranging from 4–6. Jiang et al. (11) studied kaolinite clay adsorption of Ni(II) and reported that it increased with an increase in pH from 2.0 to 8.0. In another study (37), tea waste was used as the adsorbent and the maximum adsorption of Ni(II) ions was obtained at pH 4.0.

Zuorro and Lavecchia (38) used black and green tea leaves as the adsorbent for Pb removal from aqueous solution. They set the temperature at 25 or 40 °C and the contact time to 2 hours. Under the optimum experimental conditions, they also compared the results

TABLE IV
Analysis of Variance (ANOVA) for the Quadratic Polynomial Mode

Source	Sum of Squares	df	Mean Square	F Value	p-value* Prob > F	
Model	7.56	9	0.84	142.17	<0.0001	significant
X_1 -pH	0.38	1	0.38	64.06	<0.0001	
X_2 -Contact time	0.099	1	0.099	16.76	0.0046	
X_3 -Adsorbent amount	0.053	1	0.053	8.94	0.0202	
X_1X_2	0.15	1	0.15	25.75	0.0014	
X_1X_3	0.20	1	0.20	34.28	0.0006	
X_2X_3	0.011	1	0.011	1.87	0.2142	
X_1^2	4.91	1	4.91	831.68	<0.0001	
X_2^2	0.68	1	0.68	115.61	<0.0001	
X_3^2	0.57	1	0.57	96.39	<0.0001	
Residual	0.041	7	5.908E-003			
Lack of Fit	0.028	3	9.358E-003	2.82	0.1712	not significant
Pure Error	0.013	4	3.320E-003			
Cor Total	7.60	16				
R-Squared	0.9946					
Adj R-Squared	0.9876					
Pred R-Squared	0.9382					
Adeq Precision	30.691					

* $P < 0.01$ highly significant; $0.01 < P < 0.05$ significant; $P > 0.05$ not significant.

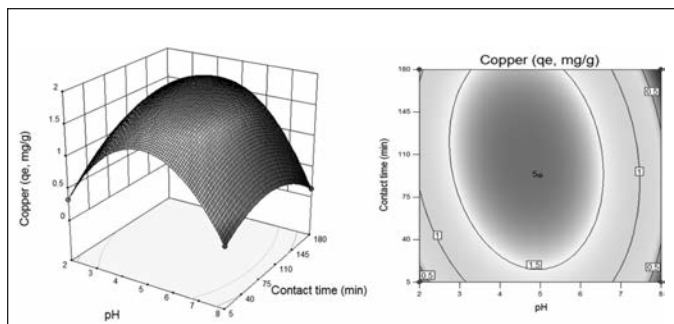


Fig. 1. Response surface and contour plot for copper sorption on astragalus as pH and contact time.

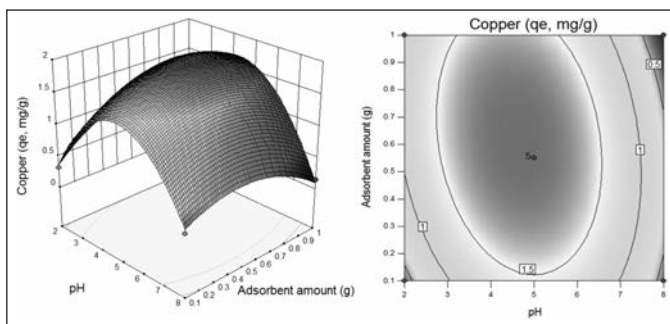


Fig. 2. Response surface and contour plot for copper sorption on astragalus as adsorbent amount and pH.

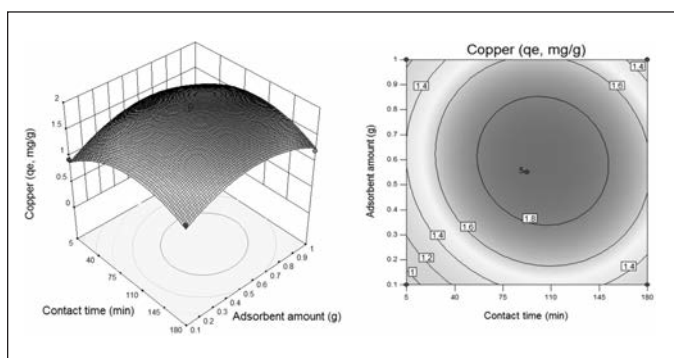


Fig. 3. Response surface and contour plot for copper sorption on astragalus as adsorbent amount and contact time.

using tea leaves and coffee grounds for the removal of lead and found that the efficiency was quite similar for both. The average adsorption capacities were $10.81 \pm 0.42 \text{ mg g}^{-1}$ (at 40°C) and $10.99 \pm 0.11 \text{ mg g}^{-1}$ (at 25°C), respectively. Ince (22) discusses the influence of contact time (10 to 180 minutes) on the adsorption of Ni(II) on low-cost and natural adsorbents such as tea waste and egg shell. The final and best contact time in that study was fixed at 45 minutes for both adsorbents (22).

Ince et al. (23) also used a batch experimental system for the removal of the heavy metals Ni(II), Pb(II), and Cd(II) with banana peel. After investigating the effects of various parameters, the maximum adsorbent amount was 0.1 g for Pb, and 0.25 g for both Cd and Ni.

In another study (24) that performed in an aqueous system, the

adsorbent hydroxyapatite was used for the removal of cadmium. The design experimental methodology and response surface methodology (RSM) was used to optimize some parameters such as pH and adsorbent dosage. RSM indicated that the optimum adsorbent dosage of hydroxyapatite was 0.57 g for the adsorption of Cd(II).

Calculation of Adsorbed Cu Amount on Adsorbent

The amount of metal adsorption was calculated using Equation 1.

$$q_e = ((C_0 - C_e) \times V) / m \quad \text{Eq. (1)}$$

where q_e represents the adsorbed Cu(II) amount by the natural adsorbents (mg g^{-1}); C_0 = metal concentrations in the solution before

TABLE V

Removal of Cu(II) Using Astragalus For Different Wastewater Samples

Sample	Cu(II) (mg L^{-1})		
	SA	Found	%Removal
Industrial Wastewater 1	0.0	12.7 ± 0.3	100.0
	10	22.4 ± 0.4	98.6
Industrial Wastewater 2	0.0	9.8 ± 0.2	100.0
	10	19.8 ± 0.2	100.0
Industrial Wastewater 3	0.0	15.1 ± 0.2	100.0
	10	24.8 ± 0.3	98.8
Leachate 1	0.0	5.9 ± 0.2	100.0
	10	15.3 ± 0.3	96.2
Leachate 2	0.0	7.5 ± 0.2	100.0
	10	17.2 ± 0.3	98.3
Leachate 3	0.0	6.8 ± 0.1	100.0
	10	16.6 ± 0.2	98.8
SRMs	20.0	20.0 ± 0.2	99.0

adsorption (mg L^{-1}); C_e = metal concentrations in the solution after adsorption (mg L^{-1}); V = solution volume (L); m = used adsorbent mass (g).

The natural adsorbent astragalus was used for copper adsorption and the results were calculated under optimum conditions. The q_e was calculated as 1.98 mg g^{-1} . According to the obtained results, astragalus is an excellent adsorbent for copper removal in wastewater samples.

Adsorption Isotherms

The isotherms of adsorption show the data calculated at the equilibrium point of the adsorbent and are represented as positive,

smooth, and concave. The amount of toxic metal increased with the equilibrium concentration of copper in the solutions. Because of the shape of the isotherms, the data of adsorption were calculated according to the Langmuir and Freundlich equations.

Langmuir Model

The Langmuir model states that uptake occurs on a homogenous surface by monolayer adsorption with constant heat of adsorption for all sites and without interaction between adsorbed molecules (39). The Langmuir model is given in Equation 2.

$$q_e = \frac{XmbC_e}{1 + bC_e} \quad \text{Eq. 2}$$

where C_e is the solution metal ion concentration (mg L^{-1}) in the equilibrium, q_e is the adsorbed metal ion amount (mg g^{-1}) at equilibrium, Xm represents the metal ion amount required to form a monolayer, i.e., adsorption capacity of the adsorbent (mg g^{-1}), and b (L mg^{-1}) is the equilibrium constant related to free energy or net enthalpy of adsorption ($b \propto e^{-\Delta H/RT}$). To comply with the Langmuir

model of adsorption, this equation can be linearized and a plot of C_e/q_e versus C_e should be a straight line with the slope $1/Xm$ and intercept $1/Xmb$.

Freundlich Model

The Freundlich model (40) is an empirical equation based on the adsorption on a heterogeneous surface. It does not indicate a finite sorbent uptake capacity and can only be applied to range from low to intermediate concentration. The Freundlich model equation is expressed in Equation 3.

$$q_e = K_f(C_e)^{1/n} \quad \text{Eq. 3}$$

where, while K_f (mg g^{-1}) represents the Freundlich isotherm constants relating to multilayer adsorption capacity, $1/n$ (L g^{-1}) shows the adsorption intensity. If this equation is linearized, the plot of $\log q_e$ versus $\log C_e$ will give a straight line of slope $1/n$ and intercept K_f .

In Equation 3, the slope $1/n$, ranging between 0 and 1, is a measure for the adsorption intensity or surface heterogeneity. K_f is a constant for the system, related to the bonding energy, can be defined as adsorption or distribution coefficient, and represents the general

adsorbed toxic metals capacity on the adsorbent for a unit of equilibrium concentration. The results of the Freundlich and Langmuir isotherms fitted using the data of adsorption capacity from the regression of Equation 2 and 3.

FTIR Analysis of Adsorbent

Before and after adsorption of copper on astragalus material, FTIR spectra within the range of $4000\text{--}500\text{ cm}^{-1}$ were used to determine the frequency changes in the functional groups of the adsorbent and this spectra is given in Figures 4 (a and b).

In light of this information, observed changes and shifts in FTIR bands can be indicated by the dominance of the ion exchange over the Cu(II) sorption on astragalus. For example, the adsorption band at approximately 3330 cm^{-1} is attributable to the hydroxyl groups from the polyphenols originally present in astragalus.

On the other hand, the C-H stretching vibrations of peak characteristic can be seen at approximately 2900 cm^{-1} , while the observed band is around 1730 cm^{-1} of the carboxylic acid group or its

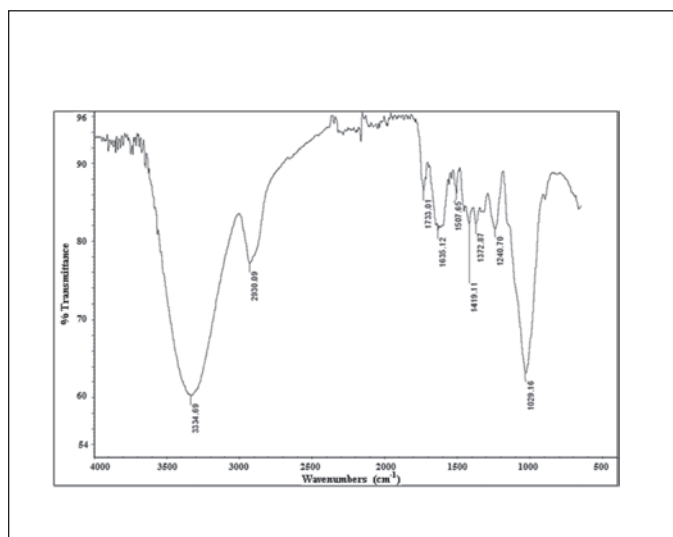


Fig. 4a. FTIR spectra of astragalus.

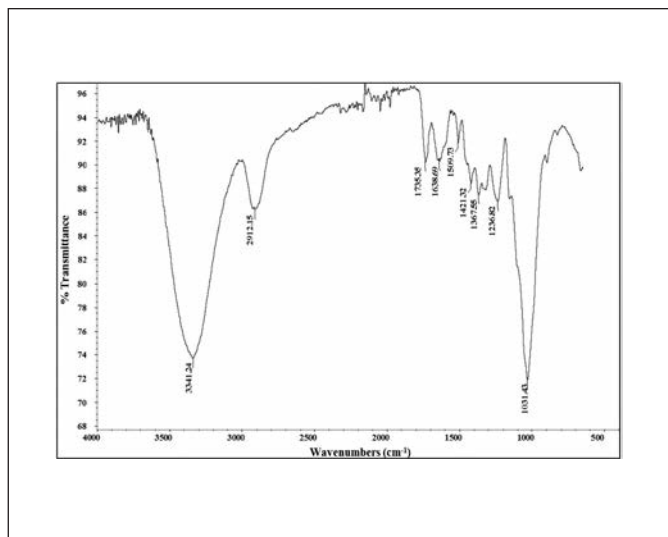


Figure 4b. FTIR spectra of Cu-loaded astragalus.

ester. The band at 1600 symmetric and the asymmetric stretching of C=O or C=C aromatic vibration, in addition to the band at 1400 cm^{-1} , is due to C-(CH₃)₂ bending. When around 1635 cm^{-1} it reflects the carbonyl group stretching (amide), the band around 1240 cm^{-1} represents stretching of OCOC acetate esters. The astragalus sample showed lower intensity peaks at 3330 cm^{-1} , 2900 cm^{-1} , and at 1030 cm^{-1} compared with the copper loaded astragalus sample, suggesting a disruption of some of these groups during treatment. Figure 4 summarizes the shifts and changes in the FTIR bands, especially the ion exchange over the Cu(II) sorption on the adsorbent.

Analytical Application to Real Samples

The analytical applicability of a new and effective adsorbent was tested for the removal of Cu(II) from industrial wastewater and leachate samples obtained from different cities in Turkey. The developed analytical method uses the Box-Behnken experimental design in combination with the response surface modeling (RSM) and quadratic programming. An effective and eco-friendly adsorbent, the astragalus plant was applied to various real samples including industrial wastewater and some leachate samples. Under the optimum conditions, approximate 50 mL of real samples were filtered and adjusted to pH 5. In addition, 50 mL aliquots were spiked with Cu(II) at pH 5. The solutions were agitated with 0.25 g of astragalus at a shaking speed of about 150 rpm for 92.5 minutes. The metal ions were then eluted with 3 mL of HNO₃ and the copper concentration determined using FAAS. The results in Table V clearly show the efficiency of astragalus for the removal of Cu(II) ions from industrial wastewater and leachate samples. The concentrations of Cu in the industrial waste-

water and leachate samples were in the range of 9.8 ± 0.2 - 15.1 ± 0.3 ng mL⁻¹ and 5.9 ± 0.2 - 7.5 ± 0.2 ng mL⁻¹, respectively. The accuracy of the method was verified by examining the standard reference material (SRM) SPS-SW1 Batch 119 Surface waters (Spectrapure Standards AS, Oslo, Norway). The recovery results of 99% were obtained using the standard additions method.

Kaplan Ince et al. (24) used the response surface methodology (RSM) with a quadratic model for the adsorption of cadmium from aqueous solution using eggshell as an effective adsorbent. They optimized the experimental conditions and optimal adsorption of Cd(II) was obtained at 895 mg g⁻¹. Chiban et al. (41) studied a dried plant material in order to remove several heavy metals using the batch adsorption technique and obtained about 99% removal percentage for Pb. Dong et al. (20) reported that hydroxyapatite/magnetite (HAp/Fe₃O₄) was produced as a novel composite adsorbent for removing Pb from aqueous solution and up to 99% of Pb(II). Gupta et al. (42) used a novel rubber tire activated carbon (RTAC) method as the adsorbent for some heavy metals including Pb and Ni from aqueous solutions. They achieved around 96% Pb and 87% Ni removal by RTAC.

CONCLUSION

This study explores the astragalus plant as a new, effective, and inexpensive sorbent and an alternative to costly adsorbents for the removal of copper ions from different aqueous solutions. A batch experimental system was used to investigate the feasibility of this naturally growing plant (astragalus) as a possible adsorbent for Cu(II) from the aqueous medium by using the Response Surface Methodological (RSM) and Box-Behnken design approach. The results prove that this method

is a very effective and time-saving technique for studying the influence of major process parameters on response factor by significantly reducing the number of experiments and hence facilitating optimum conditions. Astragalus was found suitable for Cu(II) removal from aqueous solution.

The astragalus adsorbent is low cost and eco-friendly with high sorption capacity values that are considered among the main advantages. This adsorbent has been shown to have comparable performance with commercial levels. FTIR analysis of the astragalus samples before and after copper adsorption has revealed the presence of adsorbed Cu because of the main functional groups that participate in metal binding such as amino, alcoholic, and ether in the adsorption process.

The Langmuir and Freundlich isotherm models were employed to describe the metal ion adsorption on astragalus. Isotherm data fit well to both the Langmuir and Freundlich models. The Langmuir model is better than the Freundlich model because generally higher R² values were obtained for copper adsorption. The monolayer adsorption capacity (q_c) obtained was 1.98 mg g⁻¹ under optimal conditions. The experimental results showed that under optimized conditions, astragalus can be used as an adsorbent for the removal of Cu(II) at a slightly acidic pH range.

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