CHARACTERIZATION OF ACTIVATED CARBON AND APPLICATION OF COPPER REMOVAL FROM DRINKING WATER

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Summary - In this study, removal of copper ions from aqueous solution by adsorption was investigated. The methods were applied to removal of copper in artificial water and drinking water samples using activated carbon. For this purpose, metal removal from water depends on the pH, initial concentration of metal, amount of activated carbon, and effect of sorption time were investigated. The process parameters were investigated with batch studies. In this study, commercial activated carbon, Chemviron C-1300, has been used. Granular activated carbon were characterized using nitrogen porosimetry, pH titration, Boehm's titration, mercury porosimetry, FTIR and scanning electron microscope measurements. The copper ions were determined by an atomic absorption spectrometry. Optimum conditions were found as concentration of 10 mg l^{-1}, pH: 5, contact time:25 min, and activated carbon amount:750 mg. Optimum condition were applied to drinking water for removal of Cu(II). Furthermore, adsorption isotherm data were fitted to both Langmuir and Freundlich models for finding the optimum conditions.

INTRODUCTION

The presence of heavy metals in the environment can be detrimental to a variety of living species. Heavy metal ions have become an ecotoxicological hazard of prime interest and increasing significance, because of their accumulation in living organisms.[1] Copper is one of the potential contaminant for producing illness in national drinking water. Usually water-soluble copper compounds occur in the environment after release through application in agriculture. The large doses of copper is dangerous to infants and

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people with certain metabolic disorders. It is known that an insoluble complex of copper can cause gastrointestinal problems and, in large doses, copper is dangerous to infants and people with certain metabolic disorders.[2] Copper pollution arises from copper mining and smelting, brass manufacture, electroplating industries and excessive use of Cu based agri-chemicals.[3] Therefore, the undesirable effects of Cu (II) ion can be avoided by treatment of wastewater to protect public health.

A lot of methods have been developed for treatment of water and wastewater. Chemical precipitation, membrane filtration, ion exchange, reverse osmosis, biological treatment, chemical treatment with lime, the use of caustic materials and adsorption are some of the most commonly used processes.[4,5]

Adsorption processes are being effective for heavy metal removal from contaminated water.[6] Commercial activated carbon is being used more than ever as an adsorbent in many applications. Adsorption characteristics of activated carbon are determined by its pore structure (magnitude and distribution of pore volume) and surface chemistry (kind and quality of surface functional groups).[7,8]

Activated carbon has large internal surface area, a porous (micro"0-20 A"– meso "20-500 A"– macro">500 A") structure and high degree of surface reactivity.[9-12] The chemical reactivity of activated carbon is due to the existence of unsaturated valence (active sites) at the edges of aromatic planes i.e., "graphene layers". The ratio of these active sites, in relation to the inert carbon atoms within the graphite layers, increases as the surface area increases. Heteroatoms, such as oxygen, hydrogen or nitrogen also have a strong influence on the mechanisms of the adsorption process. The most important of them is oxygen. It is presented in surface groups or complexes as basic or acidic surface oxides: chromene and pyrone have Lewis base properties, anhydrides, lactones, lactols, carboxyls or phenols have acidic character.[13,14] Therefore, activated carbon is considered as a good adsorbent. The pore structure of activated carbon determines the application. In adsorption from the gas phase mainly micro porous carbon is used whereas mesoporous carbon is applied in liquid phase processes. An application of mesoporous activated carbon includes drinking water purification, wastewater treatment, food and chemical processing.[15]

Many researchers studied the adsorptive removal of Cu (II) ions from aqueous solutions.[9,16-22] Adsorption of copper depends upon adsorbent surface chemistry and adsorption conditions.

The surface chemistry of carbon is determined by the number and the nature of the surface functional groups or complexes. Carbon-oxygen surface compounds are the most important factors on the surface reactions, surface behaviours, hydrophilic and electrical and catalytic properties of carbon.[23] Ionic exchange capacity of carbon is dependent on surface functionality, acidic or basic characteristics.[14] Toles and coworkers[24] observed a direct relationship between copper ion adsorption and surface charge in activated carbon. Copper ion uptake increased with increasing acidic surface charge.

Several investigators reported that the sorption of metal ions depend on pH, temperature of solution, carbon type and concentration of metal ions in solutions.

Researchers found that metal uptake value of Cu (II) ions increased considerably in the pH range 3-4.[5,10,25,26]

In this study, Chemviron C-1300 type granular activated carbon was used as an adsorbent for removal of copper (II) ions from wastewater. The aim of this study was to

investigate the optimum conditions of metal uptake. Optimum conditions were then applied to drinking water and wastewaters. In addition, adsorption isotherm data were fitted to both Langmuir and Freundlich models for optimum conditions.

MATERIAL AND METHOD

The activated carbon used in this study was C-1300, a granular activated carbon (GAC) supplied by Chemviron. Activated carbon was characterized using nitrogen porosimetry, pH titration, Boehm's titration, mercury porosimetry, FTIR and scanning electron microscope measurements. For removal of copper (II) in aqueous solutions the batch method was used. The effects of pH, amount of activated carbon, initial metal concentration and contact time were investigated for determination of optimum conditions. The optimal amount of carbon was contacted with 50 ml of solution containing 10 mgl^{-1} copper (II) at the optimal time. All the operations were conducted at room temperature. After filtration of solid phase, the content of copper in the liquid phase was determined by atomic absorption spectrometry.

A Varian Spectr AA-20 model atomic absorption spectrophotometer with an air-acetylene flame was used for determination of copper amounts in the aqueous phase. All pH measurements were made with a pH-meter (WTW) and a combination pH electrode.

All the chemicals were used analytical-reagent grade. Reference solutions were prepared as required by further dilution with distilled water. The laboratory glassware kept overnight in a 5% nitric acid. Afterwards it was rinsed thoroughly with water and dried. The stock solutions of Cu (II) (1000 mg l^{-1}) were prepared by dissolving $CuSO_4$ (Merck) in 100 ml water. Working standard solutions were prepared by dilution with water.

To application of the method, 250 ml of filtrated drinking water sample was put in a beaker, and then pH of the sample was adjusted to 5 with 0.1 N HCl- 0.1 N NaOH solutions. Then the adsorption method given above was applied. The concentrations of ions in the final solution were determined by AAS.

CHARACTERIZATION OF ACTIVATED CARBON

Surface area and pore structure

Surface area of carbon was determined from nitrogen adsorption isotherms at 77 K measured by Micromeritic-Gemini III 2375 model surface area analyser. Samples were out gassed for an hour at 378 K and determined by amount of liquid N_2 adsorption volume at liquid N_2 temperature (77 K). The Brunauer, Emmet and Teller (BET) equation was used to determine the specific surface area. Total pore volume and average pore diameter of activated carbon samples were determined by using a Quantachrome mercury porosimetry.

Boehm Titrations

The relative concentrations of different surface functional groups in carbons were determined by Boehm's method (27)· 0.2 g of dried carbon particles (size range 75-100 mm) were weighed into 50 ml nominal capacity Erlenmeyer flasks prior to the addition

of 20 ml of base of varying strength e.g., 0.1N solutions of NaOH, Na_2CO_3, $NaHCO_3$. The carbon samples were equilibrated in alkaline solutions for 72 h at 22 ± 2 °C using a shaker. The equilibrated solutions were filtered and 5 ml solutions were titrated with 0.1N volumetric HCl standard using methyl-red as an indicator.

FTIR and SEM analysis of carbon

Major functional groups were analyzed by Fourier transform infrared (FTIR) spectroscopy. In this way, the result of Boehm titration was supported by IR spectrum analysis. Discs were prepared by mixing powdered carbon with KBr in an agate mortar. The activated carbon powder was mixed with KBr by a weight ratio of 1:1500 approximately. Then pressing the resulting mixture successively under a pressure of 10 tons/cm^2 for 5 min. The spectra of the samples were recorded between 4000 and 400 cm^{-1} using a Mattson 1000 spectrophotometer.

A JEOL JSM-5410LV Scanning Microscope was used to visualize the surface morphology and the structure of the activated carbon.

pH titrations

The potentiometer titration allows the determination of the chemical properties of carbons by proton binding adsorption. pH titrations of activated carbon were carried out using the method described by Helfferich.[28] Typically, a number of samples (75 mg each) of carbon were weighed into separate flasks. A set of samples were prepared with successively larger amounts of 0.1 M NaOH or HCl added to the different samples. 10 millilitres of 0.1 M NaCI solutions were added to each flask to keep a high background electrolyte concentration. A total batch volume of 15 ml was made up by adding distilled water to maintain the solution volume to sorbent weight ratio constant. A blank experiment with no carbon was also performed. The batch was equilibrated for 48 h. The equilibrium pH was measured for each sample. Basic titration data were transformed into proton-binding isotherms using a proton balance equation and theorical blank reference.[29] The obtained proton-binding isotherms are positive for the proton-binding process and negative for proton dissociation.[30]

RESULT AND DISCUSSION

Surface properties of carbon

a) Surface area and pore structure.

The results of surface area and pore volume are shown in Table 1.

TABLE 1. - Surface Area and Pore Volume Results

Sorbent	Total Pore Volume (cc/g)	Average Pore Diameter (°A)	BET Surface Area (mm^2/g)
Chemviron C-1300	0.6965	251	824.93

Average pore diameter of activated carbon also indicated that pore structure was in mesoporous region. Mesoporous carbon is a good adsorbent in liquid phase processes.

b) Boehm Titrations

The distributions of surface functional groups at the surface of the carbon are given Table 2.

TABLE 2. - Concentration of Surface Functional Groups of Carbon

Sorbent	Carboxylic groups (meq/g)	Lactones (meq/g)	Phenolic groups (meq/g)	Total (no carbonyl) (meq/g)
Chemviron C-1300	0.0208	0.0275	0.215	0.263
%	7.91	10.45	81.64	100

The Boehm's titration results presented in Table 2 suggest that activated carbon possess oxygen functionalities in the form of carboxylic, lactonic and phenolic groups.
Carboxylic groups are considered to be strongly acidic.[24,31,32] The number of strongly acidic groups neutralised by $NaHCO_3$ (carboxylic groups) corresponds to 7.9% of the total number of acidic non-carbonyl group for Chemviron C-1300 type activated carbon.
Chemviron C-1300 type carbon has not been applied to any oxidation process. Thus, the phenolic groups on carbon surface have higher value than carboxylic groups.

c) FTIR and SEM analysis of carbon

FTIR and SEM analysis of carbon is given in figure 1 and 2.

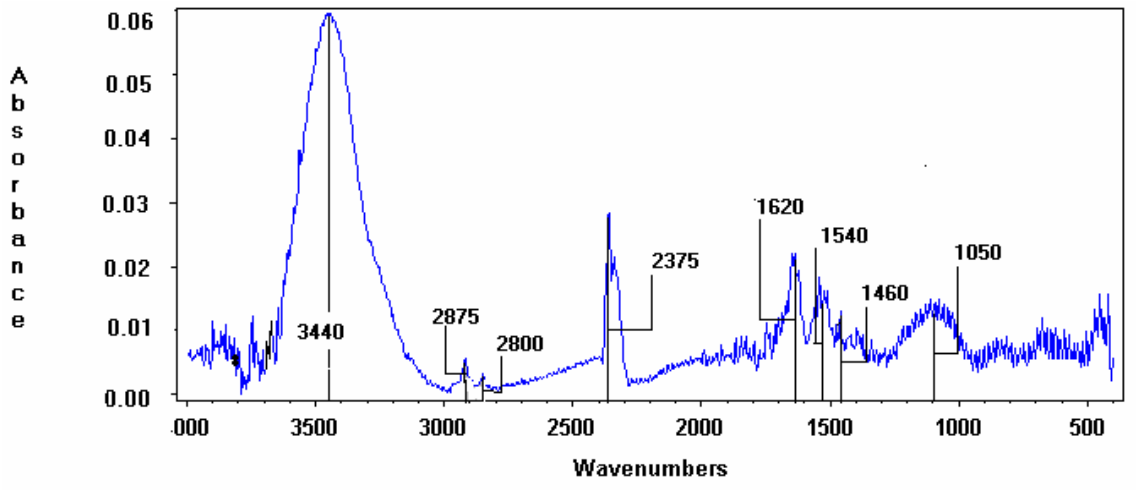


FIGURE 1. - FTIR spectra of granular activated carbon

The FTIR spectra of the Chemviron C-1300 type carbon present bands at 3440 cm^{-1} which can be assigned to the O–H stretching mode of hydroxyl functional groups.[33,34] The bands are shown about 2875 and 2800 cm^{-1} due to the C – H stretching vibrations in aliphatic.[35] The band about 2375 cm^{-1} can be due to C=C structure. The bands around 1620, 1540 and 1460 cm^{-1} (1550-1750 cm^{-1}) can be due to carboxyl groups. The band at 1050 cm^{-1} denotes the presence of primary hydroxyl groups.[34] These results are supported to the Bohem titration results. SEM microphotographs of granular activated carbon are shown in Fig. 2. They indicate the presence of mikro-mezo and macropores for sorbent.

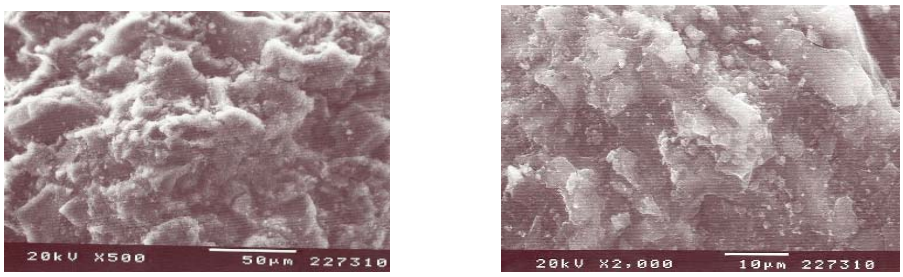


FIGURE 2. - SEM view of granular activated carbon

d) pH titrations

Activated carbon has large internal surface area and porous structure. Thus, it has been used as an adsorbent for heavy metal removal from aqueous solutions. Whereas activated carbon should be deionized to the same pH value of metal ions, it could be used as an ion exchanger. Because of metal ions collapses as a metal hydroxide above pH 5, heavy metals could remove from aqueous solutions up to pH 5. The proton binding pH titration curve for carbon studied are shown in Fig. 3. Basic properties are dominant for carbon up to pH 10.5. The value of proton binding from the titration curve of carbon is very low. However, this carbon displays high anion exchange capacity. In this study, pH titration results indicated that adsorption process was more effective than ion exchange.

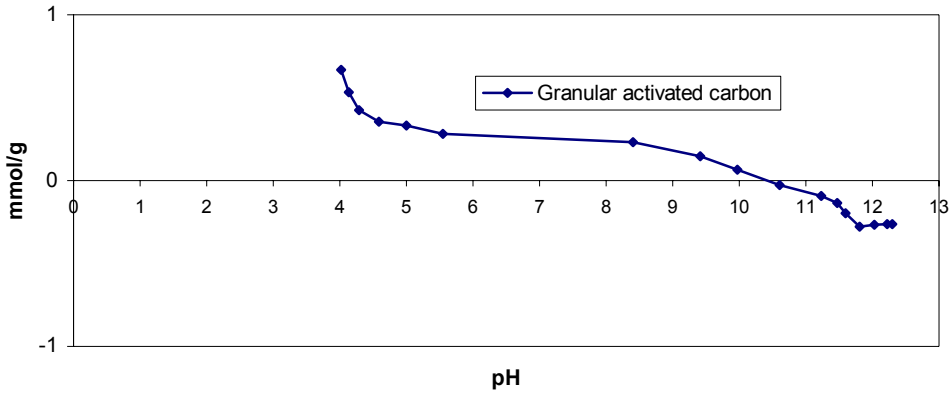


FIGURE 3. - Proton- binding curves for granular activated carbon

Optimum process conditions

a) Effect of pH on the retention of copper

An important parameter in achieving quantitative adsorption and recovery of trace elements on adsorbent is pH. The equilibrium pH of the activated carbon/solution mixture has been shown to be the principal factor controlling the extent of removal of Cu(II) ion from aqueous solutions. In order to optimize the sorption conditions for the retention of copper on activated carbon, the retention of copper was determined by applying the general sorption procedure by changing the pH of the sample solution in the range of 1- 6.

As can be seen in Fig. 4, quantitative retention (92.90%) was obtained for copper at the pH 5.0. An experimental condition studied is concentration 10 mg l^{-1}, activated carbon amount of 750 mg and contact time of 25 min.

At pH 5.0 highest retention of copper was suggested**.**

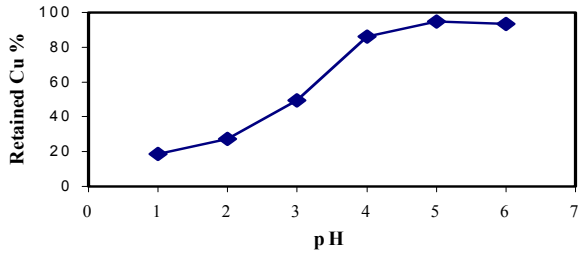


FIGURE 4. - The effect of pH on the retention of copper on activated carbon

b) Effect of activated carbon amount on copper adsorption

The activated carbon amount is the other important parameter for obtaining quantitative retention. Thus, the effect of carbon amount on the sorption of 10 mgl^{-1}, copper, contact time 25 minutes at pH 5 was examined in the range 5 – 750 mg of activated carbon, as given in Figure 5.

It was found that the sorption of Cu (II) increased with increasing amount of carbon. The value of sorption Cu (II) was found 92.90% for 750 mg activated carbon.

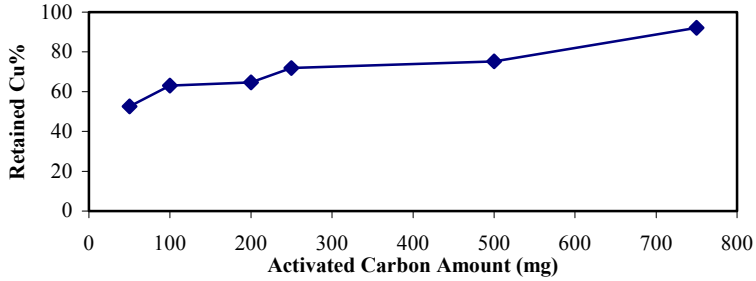


FIGURE 5. - The effect of activated carbon amount of copper on activated carbon

c) Effect of contact time on copper adsorption

The retention of copper on activated carbon, the recovery of copper were determined by applying the general sorption procedure by changing the contact time of sample solution with activated carbon in the range between 15 and 60 min. Thus, the effect of amount of

contact time on the sorption of 10 mg l^{-1}copper at pH 5 resulted to be 25 min. for 750 mg of activated carbon.

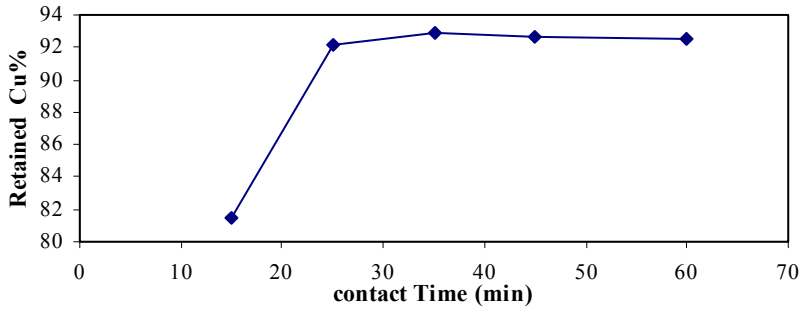


FIGURE 6. - Effect of contact time on copper adsorption

d) Effect of initial concentration on copper adsorption

The effect of initial concentration of copper on the adsorption by 750 mg of activated carbon, at pH 5, and contact time 25 min. was examined in the range between 5 and 100 mg l^{-1} copper (II) concentrations. The results are given in Table 3. The quantitative retention decrease was obtained by increasing concentration of copper. Therefore, in subsequent experiments, 10 mg l^{-1} of copper concentration was taken.

TABLE 3. - Optimal versus of copper adsorption on activated carbon

Copper Concentration	*Retained Cu%*
10	92.90
20	80.50
30	72.70
50	67.26
75	56.72
100	51.80

Application to natural samples

The method was applied to drinking water which was taken İSKİ for the determination of Cu (II). In this study, C-1300, a granular activated carbon (GAC) supplied by Chemviron was used as an adsorbent for removal of copper (II) ions from drinking water. The samples are at pH 5, carbon amount is 2000 mg and contact time is 25 min. The results are based on the average of three replicates.

The proposed procedure was applied and achieved retentions varied from 87.5 to 99.6, which demonstrated that the used method had a good accuracy.

Generally, there is small different between the two sets data. This is associated with colloidal particles or complexed by naturally occurring organic compounds.

TABLE 4. - Copper determination in natural water samples

Drinking water of sample	*Adsorption of % Cu*	
	Raw water	*Treated water*
K.H. Spring	89.6	98.4
K.H Summer	87.9	96.9
B:Ç Spring.	94.6	98.5
B.Ç Summer	87.5	99.6

ADSORPTION ISOTHERMS

The contact time 25 min**,** pH value of 5 and activated carbon amount 750 mg were chosen as the experimental conditions for the determination of adsorption isotherms of copper (II) ions (Fig. 7)

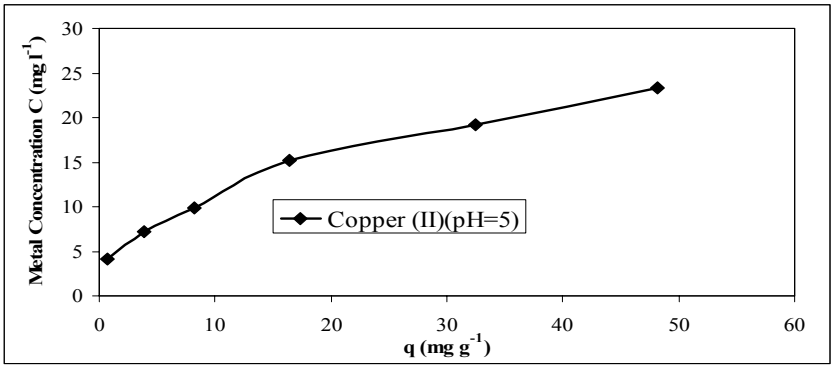


FIGURE 7. - Isotherms for equilibrium binding of metal ions on activated carbon

The adsorption isotherm shows that the amount of metal adsorbed increases as its equilibrium concentration increases in solution.
Analysis of adsorption isotherms of Cu^{+2} was performed by applying the linear Langmuir and Freundlich model equations:

$$\frac{C}{q} = \frac{1}{K_L.q_m} + \frac{C}{q_m} \qquad \text{(Langmuir equation)}$$

$$\text{Log } q = \text{Log } K_F + 1/n \text{ Log } C \qquad \text{(Freundlich equation)}$$

Where q is the amount of the adsorbed metal concentration per unit weight of adsorbent at the equilibrium concentration C, K_L, K_F and n are equation constants and q_m the monolayer capacity of sorbent.

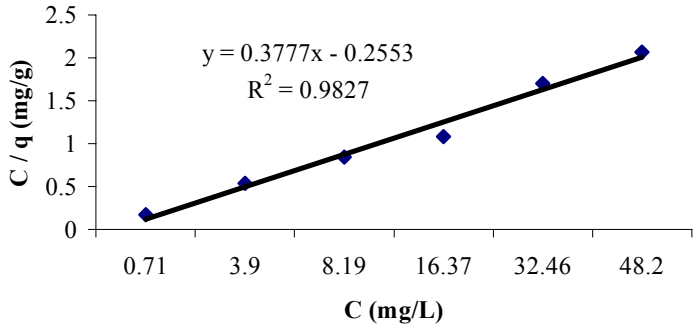


Figure 8. - Langmuir isotherm of Cu (II)

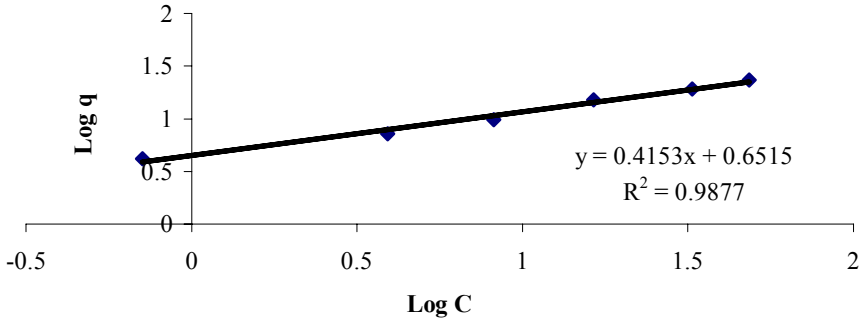


FIGURE 9. - Freundlich isotherm of Cu(II)

Adsorption constants, metal-binding constant and correlation coefficients for the Cu (II) were calculated from Langmuir and Freundlich isotherms and are given in Table 5.

TABLE 5. - Adsorption isotherm parameter for Cu (II) on activated carbon

Langmuir isotherm			**Freundlich isotherm**		
X_m	K_L	R^2	n	K_F	R^2
2.65	1.478	0.9827	2.40	4.422	0.9877

CONCLUSION

In this study we aimed to determine the sorption ability of Chemviron C-1300 type activated carbon for removal of copper (II) by atomic adsorption spectrometry.
In the first part of the study, the structural properties of Chemviron C-1300 type activated carbon were examined:

1. Pore structure of carbon was determined in the range of mesoporous region.
2. Boehm titrations and FTIR analysis results showed that unoxidized C-1300 type carbon possess acidic surface functionalities in a form of carboxylic, lactonic and phenolic groups.
3. pH titrations results were indicated that adsorption process was more effective than ion exchange for Chemviron C-1300 type activated carbon.

In the second part of the study, adsorption behaviour of C-1300 type carbon toward copper (II) from aqueous solution was investigated by batch equilibrium technique.
Optimum conditions were found as concentration 10 mg l^{-1}, pH 5, contact time 25 min, and activated carbon amount 750 mg.
In the third part of the study, the method was applied to drinking water and wastewater. This product exhibits very good adsorption for copper from drinking water and finishing water of plating bath.
At the end of the study, adsorption isotherm data were fitted to both Langmuir and Freundlich models for optimum conditions. The adsorption isotherm data of Cu (II) provides an excellent fit to both Langmuir and Freundlich models. However, higher R^2 values are obtained from Freundlich model for Cu (II) adsorption.

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