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Investigation of Cu metal adsorption using acorn caps obtained from *Quercus robur* L.[#]

Zafer Zeybek[1*], Sukru Dursun[2]

[1] Aydın Public Health Laboratory,09100 Aydın,Turkey
[2] Enviromental Engineering Department, Faculty of Engineering and Natural Sciences, Konya Technical University, 42003 Konya, Turkey

E-Mail: *zaferzeybek70@hotmail.com, sdursun@ktun.edu.tr*

Abstract: Due to population growth in the world and the collective lives of people, natural resources in the world are rapidly depleting or being recycled and becoming polluted. Pollutants can also pollute the atmosphere, especially the soil and water resources. On the other hand, sources contaminated with these pollutants also affect each other. Especially during the processing of mines and the production of new products, many metal derivatives are mixed with soil and water resources. Particularly, there are difficulties in removing the low concentration of metal pollution. In addition to the use of chemical methods in the treatment process, biological processes are also used in some studies. In this present study, the acorn cap which is one of the natural materials and LCAs can be used for the removal of copper ions which can be found in low concentrations in water sources. Furthermore, the adsorption process was investigated with SEM + EDX and XRD studies. Hence, oak acorn cap is a natural material, it has been seen that it can be used in sources that may be drinking water and success has been achieved.

Keywords: Water Pollution, Copper, Adsorption, LCAs, Oak Acorn Cap, Low Concentrations

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INTRODUCTION

One of the environmental problems that threaten the future of humanity in recent years is water pollution. Water pollutant sources are diverse, and metals play a major role in water pollution due to natural and anthropogenic reasons.

Before contaminated waters are discharged to the environment, pollutants are tried to be minimized by various treatment processes. In these procedures, the highest success rate is achieved by using advanced treatment techniques. However, the cost of using such techniques is very high thereby it is not widely available. Adsorption is also an advanced treatment technique, which allows the purification of various pollutants at much lower costs than other techniques.

In adsorption technology, the natural or synthetic material used in the treatment of a specific pollutant is called an adsorbent. Natural adsorbents are much less expensive and common than synthetic adsorbents. In recent years, there has been a large increase in the work with natural adsorbents.

According to Worch [1]; the adsorbents used for water treatment are either of natural origin or the result of industrial production and / or activation. Low cost adsorbents (LCAs); natural materials (e.g., wood, coal, peat, chitin / chitosan, clays, natural zeolites), agricultural wastes and by-products (e.g., husks, stems and kernels of fruit and nuts, sawdust, corncob waste, sunflower stems, straw) and industrial wastes and by-products (e.g., fly ash, blast furnace slag and sludge, pulp, pulp extract and fly ash, palm oil ash, shale oil ash, red sludge). Some researchers [2,3], prefer to call as green adsorbents to draw attention to the eco-friendly aspects. Green adsorbents consist mainly agricultural and forestry wastes and by-products.

Constantly new ones are being added to studies that test the efficiency of LCAs against polluting metals in water. However, generally these studies don't consider the adsorption yield – cost relationship. Especially with the modification applications, the cost of adsorbent can be increased up to hundreds of times. Furthermore, removal studies are carried out with initial concentrations far above the discharge limits and the values allowed for the pollutants to be present in the waters. Whereas, concentrations in metals contaminated waters are reduced due to natural processes such as reactions with different chemicals, precipitation, adsorption and bio-sorption. As a matter of fact, that, legal regulations or guides, on the discharge of pollutants into water or the maximum concentration of metals allowed to be present in water consists lower concentrations. Therefore, metal removal should be examined at low

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[*] *Corresponding E-mail: zaferzeybek70@hotmail.com*

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initial concentrations or in a rational concentration range, especially in stable and flowing water used for drinking water. According to the literature data, the number of such studies is quite low.

One of the aims of this paper was investigation of removal of Cu metal which has low initial concentrations from waters by the oak acorn cap natural adsorbent and determination of adsorption capacity and parameters affecting adsorption. Another aim was to investigation of the topography (surface structures) and morphology (structural properties) of adsorbent and the mechanisms that effected to the adsorption of Cu metal.

Copper health effects

Copper is also toxic to a variety of aquatic organisms even at very low concentrations. Mining, metallurgy and industrial applications are the major sources of copper exposure in the environment. Copper is an essential nutrient, used by biological systems for activation of certain enzymes during photosynthesis, however high doses it shows toxic effect and can cause stomach and intestinal discomfort, liver and kidney damage, vomiting and loss of strength [4]. Bondy and Campbell [5], emphasized that copper has also been shown to be effective in neurodegenerative diseases such as Alzheimer's and Parkinson's disease and that people with Wilson's disease have a high health risk due to copper. There is insufficient evidence that copper has the potential to cause lifetime exposure to drinking water [6] and toxicity studies should be conducted according to populations [7].

Legal regulations and recommendations in water for copper

WHO [8] and USEPA [9] believe that copper is mixed with drinking water due to the corrosion of copper pipes and fittings commonly used in water distribution in drinking water. USEPA [10] treats copper as a class of inorganic chemical pollutants in national primary drinking water standards. USEPA [9] treats copper in secondary drinking water standards. Secondary standards include parameters that cause aesthetic, cosmetic and technical effects in drinking water. In Turkey, official regulation has been made with the Regulation on Water for Human Consumption (TRW) prepared by harmonizing with the European Union (EU) legislation for drinking water. The comparison of the limit values for copper in drinking water is shown in Table 1.

Table 1. Comparison of limit values for copper in drinking water

	WHO	USEPA	EU, TRW
Copper, Cu	2 mg/L	Primary standards: 1.3 mg/L Secondary standards: 1 mg/L	2 mg/L

Tables Although there are differences according to the countries, in determining the limit values for copper in all of the receiving water environment standards; it accepts the consideration of pH, aquatic life elements and other water quality parameters, especially hardness as a precondition. According to some national standards, the comparison of the limit values for copper in receiving water environments is shown in Table 2.

Table 2. Comparison of limit values for copper in receiving water environments

Standards	Receiving water environment (µg/L)	
Australian and New Zealand Anzecc & Armcanz [11]	Freshwater 1.4 For 30 mg/L $CaCO_3$	Marine 1.3 For 30 mg/L $CaCO_3$
Canadian CCME [12]	Freshwater 2 For 0-82 mg/L CaCO3	Marine No data
American USEPA [13]	Freshwater Acute: - Chronic:-	Saltwater Acute: 4.8 Chronic: 3.1

In Turkey, the regulations on copper for wastewater are included in the discharge standards according to the sectors in the annexes of the Regulation on Water Pollution Control (e.g. for metal ındustry 2 mg/L for 2 hours sample, for mining industry 3 mg/L for 24 hours sample).

MATERIAL AND METHODS

Adsorbent

The acorn caps used in this study Karaman / Turkey originate and was obtained from Handle Oak (Quercus robur subsp. robur). Materials falling from the tree were collected, their heads were collected, the heads separated from their stems; washed with pure water and allowed to dry outdoors under the sun. The dried samples were pounded in mortar and sieved to particle sizes. The prepared samples were kept in glass jars to be airtight. The natural adsorbent is briefly named P. The handle oak tree and acorn caps from which the adsorbent was obtained are shown in Figure 1.

Figure 1. Images of Handle Oak: tree, leaves and acorn caps

Experimental (Devices and equipments)

In the experiments, shaking incubator (ZHWY-200B), uv-visible spectrophotometer (Hach Lange Dr.2800 and Dr.3900 models), pH device (WTW multi720), precision balance (Precisa 205A), orbital shaker (Heidolph-unimax 1010), drying oven (NUVE F 500) and vacuum pump (SARTORIUS-Microsart® e.jet) devices were used.

For analysis; automatic pipette (1-5 ml) and tip, pipette (5-10 ml), balloon flask (100-500-1000 ml), flask (250 ml), glass funnel (50-100 mm), graduated cylinder (25-50) -100 ml), flasks (250 ml-500 ml), beaker (100-500 ml), glass tube (25 ml), tube sports, weighing papers, weighing containers, locked nylon bag, parafilm and filter papers (Whatman, 125 mm) equipment were used.

0.1, 0.5, 1.0, 1.5, 2.0 and 2.5 mg / L solutions were prepared from 10 mg / L stock solution using 1000 ppm standard solution for Cu with 0.1 N HCl and 0.1 NaOH solutions for pH adjustments. 1: 1 HNO3-H2O solution was used for cleaning the materials.

Experiments were performed according to the Copper test procedure [14] using Hach Lange reactive tests. For copper tests, the measurement range of 0.04 - 5.00 mg / L and 560 nm wave length were studied by the Bicinchonitate method.

Adsorption experiments and adsorption equilibrium

In order to investigate the removal properties of natural adsorbent, adsorption experiments were performed on the effects of pH, initial concentration, temperature, contact time, adsorbent dose, mixing speed and adsorbent size.

To determine equilibrium data, batch adsorption method was applied. In this method, a set of flask is used determine adsorption isotherm points. Each flask is filled with the adsorbate solution which known volume and initial concentration. Then, a certain amount adsorbent is added to adsorbate solution and is shaken until the state equilibrium is reached in a certain contact time.

To calculate the percentage of removal (removal %) and adsorption capacity (*qe*), we have used the following equations in batch adsorption experiments [15].

$$Removal\,\% = \left[\frac{Co-Ce}{Co}\right] x\ 100 \qquad \text{(Equation 1)}$$

$$qe = [\ (Co - Ce)xV\ ]/\ m \qquad \text{(Equation 2)}$$

Here, Co (mg/L) is the initial metal concentration, Ce (mg/L) is the metal concentration in equilibrium, qe (mg/g) adsorption capacity, V (L) is the volume of adsorbate used and m (g) is the amount of adsorbent used.

Characterization studies with SEM+EDX and XRD

For the surface morphology and topography of P natural adsorbent, XRD and SEM + EDX analyzes were taken from Karamanoğlu Mehmet Bey University Scientific and Technological Researches Application and Research Center. In the experiments, "BRUKER D8 ADVANCE with DAVINCI" X-Ray Diffractometer (XRD) device and "HITACHI SU5000" EDX equipped field emission scanning electron microscope (SEM + EDX) device were used.

RESULTS AND DISCUSSION

pH effect

The pH effect on the removal of Cu metal with P adsorbent is shown in Figure 2. The pH experiments were carried out at 25 ºC, 2 mg / L metal initial concentration, 5 g / L adsorbent dose, 60 min contact time, 300 µ adsorbent size, 100 rpm mixing speed and pH 4-8 range in the initial conditions.

All chemical reactions are controlled by pH and the ions dissolved in solution at a certain pH form some compounds with greater willingness. Since adsorption is also basically an equilibrium reaction, from the moment the solution is brought into contact with the adsorbent at an appropriate pH, the metal ions desired to be removed in the solution will be reduced and the concentration in the solution will be expected to remain unchanged after equilibrium is established.

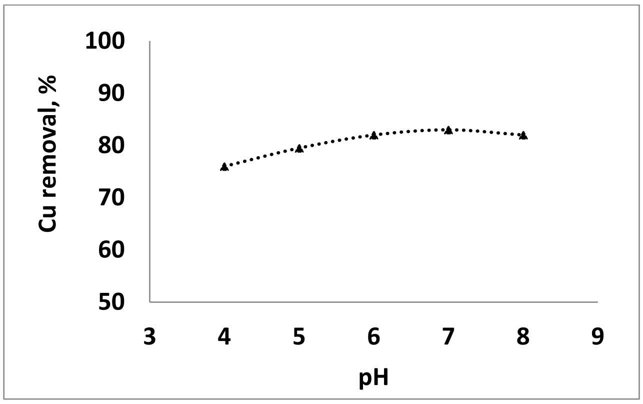

Figure 2. The pH effect of Cu removal

Many researchers [16-18] pH of adsorption event; They think that the surface load of the adsorbent in the aqueous solution with adsorbate, the properties of metal ions, the degree of ionization and the functional groups on the adsorbent surface affect the chemical efficiency of ion exchange and complexation.

When Figure 2 is examined; the highest removal in Cu removal was 83% at pH 7. The removal efficiency for P increased in the range of pH 4-7, slightly decreased after pH 7. Ashwini et al. [19], in their study of Cu (II) adsorption on unmodified sawdust, they achieved a continuous increase between pH 2-7 and the highest removal rate at pH 7 similar to our study. They reported that maximum adsorption efficiency may be caused by the interaction of Cu^+, $Cu(OH)^+$ and $Cu(OH)_2$ with functional groups on the surface of raw oak sawdust, and that the reduction of removal efficiency at higher pH levels may result from soluble hydroxyl complexes. Chakravarty et al. [20], using the newspaper paper pulp Cu adsorption studies; in a similar way with us, they have achieved a result which increases continuously up to pH 7 and reaches maximum removal efficiency at pH 7. Chen et al. [21], using palygorskite Cu (II) removal pH in the range of 2-7 examined, until the pH 7 constantly rising and reached the highest removal efficiency at pH 7 observed a pH effect.

P is an organic adsorbent and it is thought that electrostatic interactions of functional groups such as amine, tannin on the surface are effective in adsorption process.

Effect of initial metal concentration

The initial metal concentration effect on the removal of Cu metal with P adsorbent is shown in Figure 3. The experiments were carried out at pH 7, 25 ºC, 5 g / L adsorbent dose, 60 min contact time, 300 μ adsorbent size, 100 rpm mixing speed and 0.1 – 2.5 mg/L initial Cu concentration range in the initial conditions.

One of the based main points of this study is to examine the studied metal at low initial concentrations. Since, metals are in lower concentrations by various mechanisms in water, and considering this situation, lower concentrations are present in the legal regulations on the discharge of various pollutant metals to the waters and the permissible concentrations in the waters. This is explained in detail in section -Legal regulations and recommendations in water for copper- and shown in Table 1 and 2. In some studies, adsorption processes at very high concentrations (e.g. 100 mg/L) have been investigated with various adsorbents, and the results obtained are far from rationality. Therefore, we preferred to work at the initial concentration in the range of 0.1-2.5 mg Cu / L.

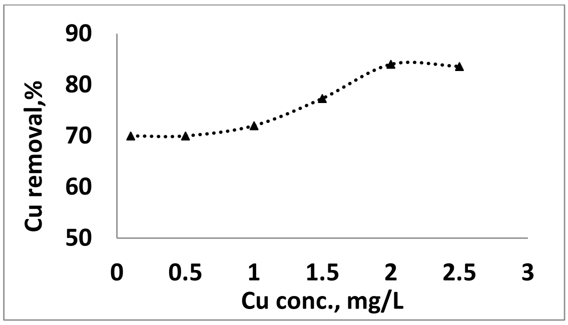

Figure 3. The effect of initial Cu metal concentration

When Figure 3 is examined; removal efficiencies increased continuously and reached maximum values at 2 mg / L and reached 84% values, while some decrease was seen in 2.5 mg / L. In other words, the system reached equilibrium at 2 mg / L level. When the initial concentration in Cu removal was gradually increased from 0.1 mg / L to 2 mg / L, the removal efficiency increased. This is due to the fact that the porous structures and functional groups on the adsorbent surface are not yet saturated with metal ions.

Effect of temperature

The effect of temperature on the removal of Cu metal with P adsorbent is shown in Figure 4. The experiments were carried out at pH 7, 2 mg / L initial Cu concentration, 5 g / L adsorbent dose, 60 min contact time, 300 μ adsorbent size, 100 rpm mixing speed and 25 ºC, 35 ºC, 45 ºC in the initial conditions. Solution temperature plays an important role on adsorption by affecting the equilibrium and removal rate in adsorption processes. In general, increased adsorption capacity with increasing temperature is known as an endothermic process, and the adsorption capacity decreasing with increasing temperature of the solution is called exothermic adsorption [17]. The effect of temperature on adsorption processes is also related to the shape of the adsorption process. Physical sorption occurs at low temperatures and chemical sorption occurs at wider temperature ranges [22].

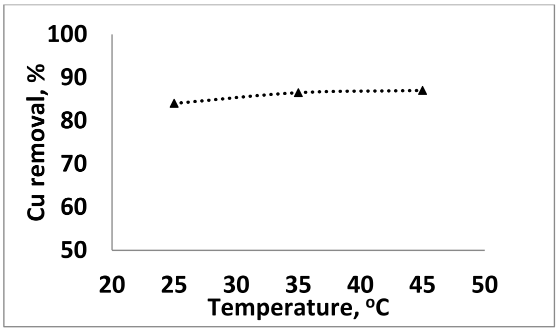

Figure 4. The effect of temperature

When Figure 4 is examined; in the removal of Cu (II) with adsorbent P, the removal yield increased from 84 to 87% when the temperature was increased from 25 °C to 45 °C. This is due to fact that the increase in the frequency of collision between adsorbent and metal ions and the increase in the surface activity of the adsorbent and the kinetic energy of the adsorbate [23,18]. The increase in the adsorption capacity with the increase in temperature indicates that the adsorption process is endothermic.

Effect of contact time

The effect of contact time on the removal of Cu metal with P adsorbent is shown in Figure 5. The experiments were carried out at pH 7, 2 mg / L initial Cu concentration, 5 g / L adsorbent dose, 25 ºC, 300 μ adsorbent size, 100 rpm mixing speed and 0- 120 min contact time range in the initial conditions.

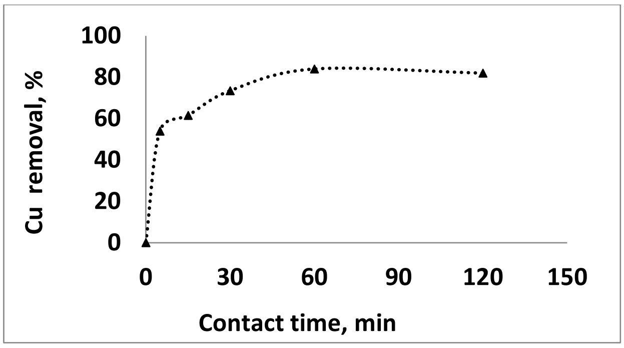

Figure 5. The effect of contact time

In laboratory studies, different contact times have been tried during preliminary trials and findings related to removal efficiencies have been obtained. According to these results, up to 120 minutes of contact time can be obtained with efficient results related to adsorption kinetics. Therefore, the contact time interval is given between 0 - 120 min.

When Figure 5 is examined; adsorption was observed to be quite rapid in Cu removal. At the end of the first 15 min, 61.5% removal efficiency was achieved with P adsorbent. At the end of the 60th minute, it was found that equilibrium was reached with the highest removal efficiency (84%) and adsorption capacity (0.336 mg/g). There was little reduction in removal efficiency at 120 min (82%).

Adsorption under these conditions is rapid adsorption, and there are many studies in the literature. Hossain et al. [24], using banana peels, 10 - 200 mg Cu / L in the initial dose of the effect of contact time study in the first 30 minutes of adsorption occurred in the majority of the first 60 minutes and reached equilibrium at the end of the determined. They attributed this to the rapid depletion of the mass transfer between the liquid phase and the solid phase by the rapid filling of the active zones in the initially empty banana peel by Cu ions, the saturation of the mesopores and the formation of repulsive forces between the Cu ions in the solution and the Cu bound in the solution.

Effect of adsorbent dose

The effect of adsorbent dose on the removal of Cu metal with P adsorbent is shown in Figure 6. The experiments were carried out at pH 7, 2 mg / L initial Cu concentration, 25 ºC, 60 min contact time, 300 μ adsorbent size, 100 rpm mixing speed and 0.1- 1.0 mg/100 ml adsorbent dose range in the initial conditions.

In the laboratory studies, different initial doses of adsorbent were tried during the preliminary trials and the maximum dose level was 1 g / 100 ml for reasons such as coloration and turbidity during the experiments and the minimum dose level associated with the amount of adsorbent that could be filtered during the experiments was determined as 0.1 g / 100 ml.

When Figure 6 is examined; it was seen that the highest yield in Cu removal occurred in 1 g dose and was 89%. Hossain et al. [24], in the study of the effect of adsorbent dose in Cu removal using banana peels using different Cu concentration and adsorbent doses, they determined the adsorbent dose of 5 g / L and 88% removal efficiency at 10 mg Cu/ L concentration. In our study, 5 g / L adsorbent dose and 2 mg / L Cu initial concentration yielded 84% removal efficiency with P removal of Cu.

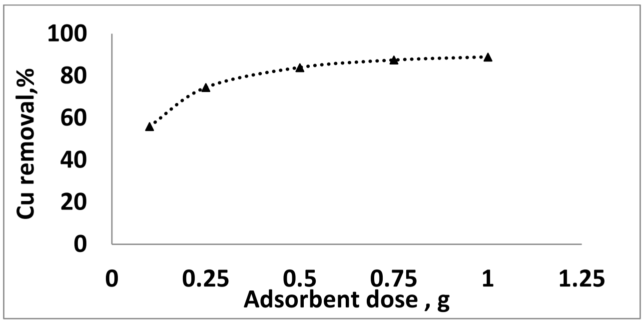

Figure 6. The effect of adsorbent dose

Once the maximum equilibrium value is reached, the removal value does not change by the addition of adsorbent. This result means that the relationship between adsorbent dosage and removal efficiency is related to the increase in the number of adsorption zones and that increasing this number will not affect removal after reaching equilibrium [15].

As a result of this study in which the adsorbent dose was examined, very little removal increases were eliminated for healthy working conditions; It was seen that 0.5 g/100 ml adsorbent dose would be sufficient instead of 1 g/ 100 ml adsorbent dose and these doses were used in the following studies.

Effect of shaking speed

The effect of shaking speed on the removal of Cu metal with P adsorbent is shown in Figure 7. The experiments were carried out at pH 7, 2 mg / L initial Cu concentration, 25 ºC, 60 min contact time, 5 g/L adsorbent dose, 300 µ adsorbent size, 50 – 300 rpm shaking speed range in the initial conditions.

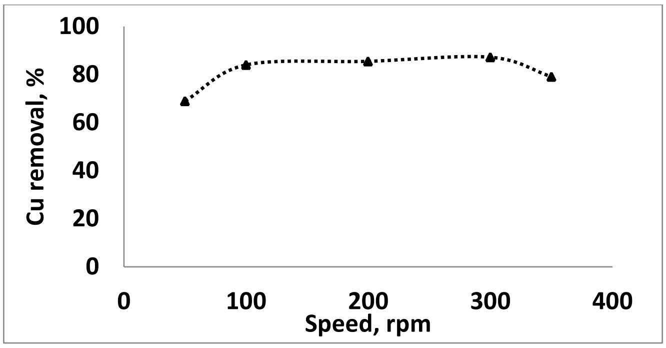

Figure 7. The effect of shaking speed

When Figure 7 is examined; when the stirring speed in Cu removal was increased from 50 rpm to 300 rpm, the removal efficiency increased from 69% to 87.2%. When the mixing speed was increased to 350 rpm, the removal efficiency decreased to 79.1%.

Optimizing the shaking speed is one of the most important adsorption parameters and has a direct impact on the adsorbent cost. Vreysen et al. [25] emphasized that electricity is mostly used in the adsorption-flocculation process to pump water and mix the adsorbent suspension. On the other hand, Argun et al. [15] mentioned the importance of determining the optimum speed to be used in wastewater treatment, since the shaking energy consumes and affects the adsorption efficiency. Generally, increasing mixing speed increases metal removal, but higher mixing speeds cause aggregate deterioration. Therefore, the mixing speed should be chosen to provide rapid adsorption kinetics as well as good adsorbent flocculation [25].

Therefore, a mixing speed of 100 rpm can be used instead of 300 rpm to reduce the energy cost during agitation. Hence the effect on removal efficiency is only 3.8%.

Effect of adsorbent size

The effect of adsorbent size on the removal of Cu metal with P adsorbent is shown in Figure 8. The experiments were carried out at pH 7, 2 mg / L initial Cu concentration, 25 oC, 60 min contact time, 5 g/L adsorbent dose, 100 rpm shaking speed and 300 - 1000 µ range in the initial conditions.

When Figure 8 is examined; when the adsorbent size increased from 300 to 600 μ, the removal efficiency decreased from 84% to 60% and when it increased to 1000 μ, it decreased to 43%.

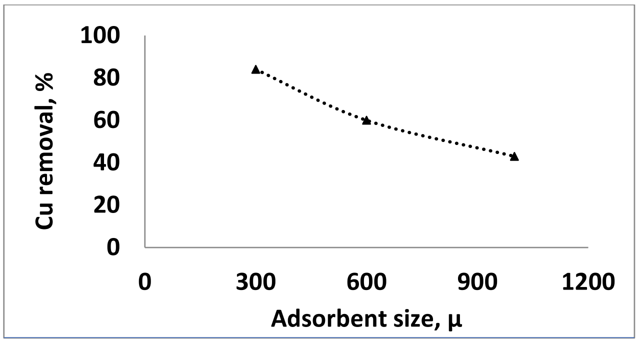

Figure 8. The effect of adsorbent size

As particle size decreases, removal efficiency increases with increasing surface area. Since adsorption occurs through interactions and reactions at the liquid-solid interface, the size of the surface area of the adsorbent increases the adsorption capacity and this is a basic rule. As adsorbent particle size decreases, removal efficiency [26,24] and adsorption rate [15,27-28] studies are available.

Adsorbent characterization studies

In this section, topography (surface structure) and morphology (structural properties) of P adsorbent; the changes after adsorption with Cu used as pollutant metal were examined according to SEM + EDX (Scanning Electron Microscopy and Energy Dispersive X-ray Spectroscopy) and XRD (X-ray Diffraction) analysis results. In addition, EDAX data obtained with SEM + EDX and chemical compositions were given.

Energy Dispersive X-ray Spectroscopy (EDS) is a chemical analysis method that can be coupled with the two major electron beam based techniques of Scanning Electron Microscopy (SEM). X-rays generated by the interaction of the electron beam with the sample are collected by an EDS detector and used in Energy-Distributed X-Ray Spectroscopy (EDX). With EDX, the composition and percentage of each element can be determined, and XRD can be used to learn crystal structures and crystal information. SEM, EDX and XRD analyses was carried out by BILTEM laboratories of Karamanoğlu Mehmet Bey University in Karaman/Turkey.

SEM and EDX analysis results

EDS results from different points of P adsorbent was presented as EDAX with APEXTM software. EDAX results are given in Table 3 and SEM images in Figure 9.

Table 3. EDAX results from different areas for P adsorbent

Area	Area 361			Area 321		
Elm	**%,W**	**%,A**	**%,E**	**%,W**	**%,A**	**%,E**
CK	30.41	37.71	6.26	34.28	42.1	7.16
OK	65.77	61.24	8.71	60.2	55.2	9.39
MgK	-	-	-	0.56	0.34	15.5
AlK	0.38	0.21	9.59	0.75	0.41	11.4
IrM	1.48	0.11	11.2	-	-	-
CaK	1.97	0.73	2.03	2.53	0.93	4.00
SiK				0.87	0.46	8.79
YL				0.82	0.14	8.70

Elm: Elements, W: Weight, A: Atomic, E: Error

Moseley's Law is the basis for elemental analysis with EDS. If the energy of a given K, L or M line is measured, then the atomic number of the element producing that line can be determined. The K, L and M series X-rays increase in energy with increasing atomic number [29]. According to EDAX results (Table 3), adsorbent is heterogeneous. Ir, Y, Mg and Si elements were determined in different regions of adsorbent except fellow elements (C, O, Al, Ca). As weight percentage of P adsorbent elemental structure, the dominant elements are O and C, and less found elements Al and Ca.

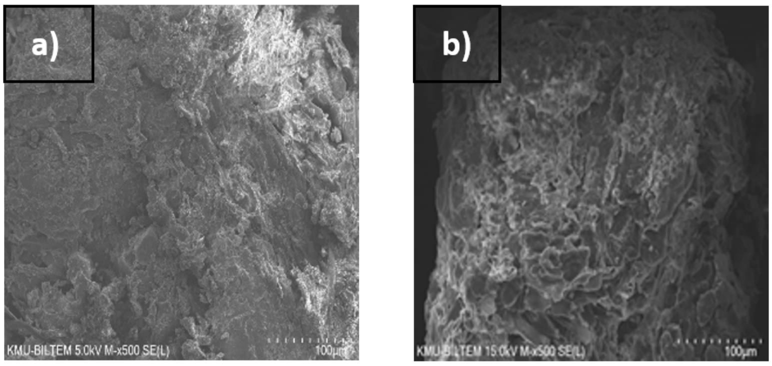

Figure 9. SEM images of P adsorbent: a) P raw-500x, 100 µm, b) P-Cu 500x, 100 µm,

Table 4. EDAX results before and after with Cu adsorption

Area		Area 321			Area 327	
Elm	**%,W**	**%,A**	**%,E**	**%,W**	**%,A**	**%,E**
CK	34.28	42.1	7.16	23.25	32.88	3.25
OK	60.2	55.2	9.39	55.94	59.39	2.97
MgK	0.56	0.34	15.5	-	-	-
AlK	0.75	0.41	11.4	2.43	1.53	6.44
CaK	2.53	0.93	4.00	10.78	4.57	6.39
.SiK	0.87	0.46	8.79	-	-	-
YL	0.82	0.14	8.70	5.24	1.00	7.36
CuK	-	-	-	2.35	0.63	17.1

Elm: Elements, W: Weight, A: Atomic, E: Error

Cu metal examined after adsorption are samples of the studies under 2 mg / L initial concentration, 60 min contact time and pH 7 conditions. Cu metal EDAX results calculated after adsorption is given in Table 4 and SEM images Figure 9. When the Figure 9 examined; according to SEM images taken at 500x magnification, 100 µm dimension, the surface structure of P adsorbent has changed after adsorption with Cu metal. Furthermore, Cu was retained on adsorbent surface according to EDAX results (Table 4) and EDS spectrum plot (Fig 10.b). EDS plots are given Figure 10 for Area 321 and Area 327.

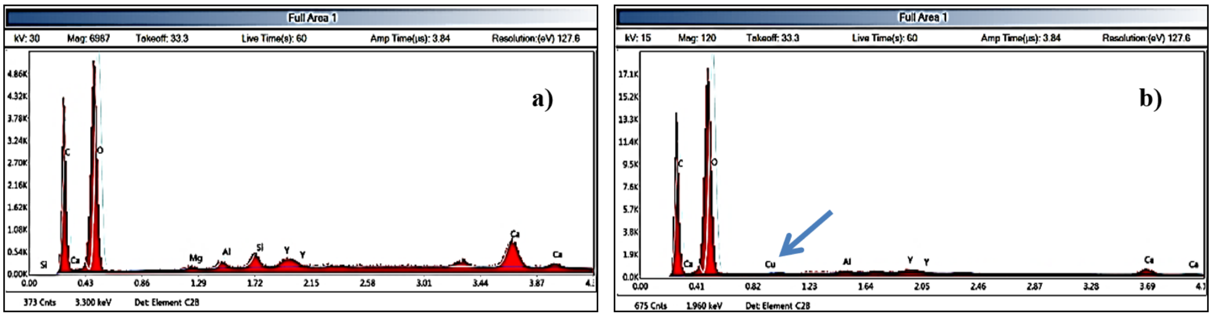

Figure 10. EDS spectrum plots: a) P raw, b) P-Cu

XRD analysis result

XRD patterns for P raw and P-Cu are given Figure 11. MATCH! Version 2 program was used to create the patterns. When XRD patterns were examined; changes in XRD pattern were observed after Cu adsorption (Figure 11.b).

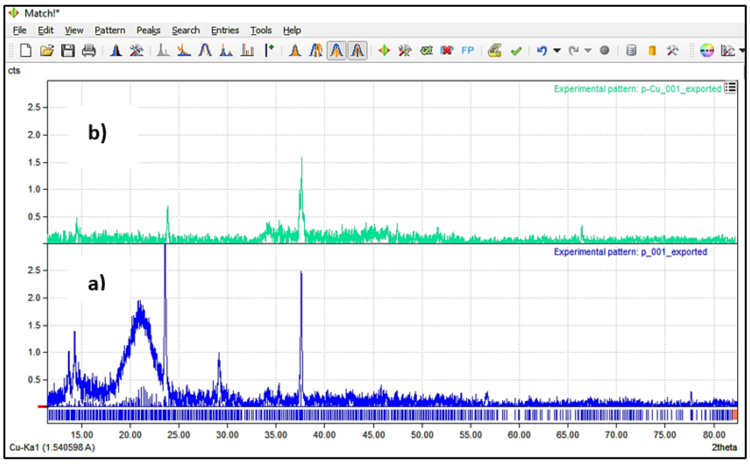

Figure 11. XRD patterns: a) P raw, b) P-Cu

P adsorbent is an organic structure, according to EDAX results did not show a significant reduction in the amount of any element (Table 4). However, when XRD patterns were examined; there were changes in the peak structure of the raw P adsorbent after adsorption with Cu. (Figure 11.a and 11.b).

According to EDAX results after adsorption with Cu, the value of 2.35 %W for Cu confirms this result. It is therefore thought that Cu can be retained by functional groups such as condensed tannins on the adsorbent surface by forming or complexing.

CONCLUSIONS

It was investigated Cu metal adsorption mechanisms with adsorption isotherms and characterization studies using acorn caps which obtained by Quercus robur L. in this study. Studies were conducted without modification and at low initial concentrations. Thus, low-cost adsorbent was obtained, and the more rational results obtained according to the discharge limits and the values allowed for the pollutants to be present in the waters. It was found the percentage of removal efficiency, 84 and adsorption capacity 0.336 mg/g. SEM+ EDX and XRD were carried out for P adsorbent characterization. According to SEM, EDS and EDAX results, P adsorbent was heterogeneous and Cu was retained adsorbent surface. P adsorbent's XRD pattern was changed after adsorption by Cu. Functional structures such as tannins and amines in the P adsorbent structure may have been influenced by ion exchange, complexation and interactions between ions and adsorption mechanisms.

Consequently, P adsorbent can be classified in LCAs and natural adsorbents class. It can be used successfully in the treatment of low concentrations of copper in water by adsorption.

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