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DEVELOPMENT OF NEW NATURAL SORBENT FOR THE REMOVAL OF COPPER FROM INDUSTRIAL WASTEWATER

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Abstrac. The general objective of this study was to investigate the removal of Cu (II) from wastewater by adsorption using adsorbent materials produced by pyrolysis of ago-industrial wastes. So in this day and age heavy metal pollution in environment has unavoidably increased. It is the result of no other than human activities. Heavy metals are among the most harmful pollutants released into the environment. Adsorption is the technique of removing heavy metals from wastewater. There have been several studies done to remove heavy metals using various materials. In particular, those heavy metal ions that are toxic to humans have been removed from wastewater using a variety of adsorbents. The most widely utilized adsorbents include activated carbons, plant or lignocellulosic wastes, clays, and biopolymers. Spent coffee-based sorbent synthetized by pyrolysis was used in this study as an adsorbent to extract copper from wastewater. To carry out the experiments, a synthetic wastewater was prepared in the lab. The best conditions for copper removal were determined through batch tests. It was also established the effect of various parameters including pyrolysis temperature, contact time, and metal ion concentration. The optimum conditions obtained were 400°C highest yield of sorbent and maximum adsorption, 1-hour optimal contact time.

Keywords: *adsorption, pyrolysis, heavy metal,copper, wastewater, spent coffee.*

Аннотация. Общей целью работы было изучение удаления Cu(II) из сточных вод путем адсорбции с использованием адсорбирующих материалов, полученных пиролизом отходов агропромышленного комплекса. Таким образом, в наши дни загрязнение окружающей среды тяжелыми металлами неизбежно возросло. Это результат не что иное, как деятельность человека. Тяжелые металлы являются одними из наиболее вредных загрязнителей, попадающих в окружающую среду. Адсорбция – это метод удаления тяжелых металлов из сточных вод. Было проведено несколько исследований по удалению тяжелых металлов с использованием различных материалов. В частности, из сточных вод с помощью различных адсорбентов удалось удалить те ионы тяжелых металлов, которые токсичны для человека. Наиболее широко используемые адсорбенты включают активированные угли, растительные или лигноцеллюлозные отходы, глины и биополимеры. В качестве адсорбента для извлечения меди из сточных вод в работе использовался отработанный сорбент на основе кофе, синтезированный методом пиролиза. Для проведения экспериментов в лаборатории готовили синтетические сточные воды. Наилучшие условия для удаления меди были определены посредством серийных испытаний. Также было установлено влияние различных параметров, включая температуру пиролиза, время контакта и концентрацию ионов металлов. Оптимальными условиями были 400°C, максимальный выход сорбента и максимальная адсорбция, оптимальное время контакта 1 час.

Ключевые слова: *адсорбция, пиролиз, тяжелые металлы, медь, сточные воды, отработанный кофе.*

Introduction

Water without any flavour, colour or odour was long believed to be pure and unpolluted. Thoughts regarding water pollution have entirely changed, though. Even if the water is pure, dissolved contaminants including radioactive nuclides, organic pollutants, heavy metals, and new poisons can lead it to become polluted.

Several in-situ treatment techniques have been developed for the bioremediation of contaminated surface water, including artificial wetlands and floating-bed biological systems. Ecological floating beds are renowned for their accessibility, high levels of efficacy, and perfect growing environments for plants. However, many of these methods have a lot of disadvantages, such as high prices, protracted preparation periods, and the need for a huge space. The field of environmental preservation is focusing more and more on approaches that rehabilitate badly damaged streams by combining microbiological and technological tools. One of the key benefits of treating contaminated river water over alternative technologies is the effective overall treatment that results from the integration of several technical and biological processes. In reality, selecting a particular water treatment process should take into account not only its effectiveness but also the environment and the economy [1].

The elements with a specific gravity greater than five times that of water are known as heavy metals. One of the most dangerous categories of water pollution is heavy metals. Heavy metal pollution in aquatic environments has unavoidably risen as a result of the massive rise in heavy metal consumption over the past few decades. Heavy metals are present in larger concentrations in industrial effluent, which can contaminate water when released into the environment. The toxic heavy metals such as zinc, copper, nickel, mercury, cadmium, lead, and chromium are of particular concern when treating industrial wastewaters.

Metals often build up in living things, as opposed to organic contaminants, which biodegrade. Additionally, connected to risk or cancer are several heavy metal ions. Heavy metals in drinking water provide a concern to consumers since they can damage their nerves, liver, and bones in addition to obstructing the action of key enzyme functional groups. Both natural and manmade sources, such the processing of solid waste and industrial effluents, can result in the production of metal ions in water. Mineral deposits can also be leached to provide natural sources. Heavy metal levels in the water system have significantly grown over time as a result of the recent fast expansion of industrial activities. Because employing some metals can be dangerous, they are under regulation [2-5]. Because of its widespread usage for several engineering applications, copper is a significant engineering metal. Copper is utilized in the production of wires in several sectors, including those that deal with electrical appliances, electronics, automobiles, and white goods. Fungicides, algicides, insecticides, and wood preservatives all contain chemicals containing copper. In the production of dye and electroplating, it is employed. Fertilizers and animal feed are supplemented with copper compounds as a nutrient to boost the development of plants and animals [6-8]. Both natural and human-made sources introduce copper into the environment.

Copper may be toxic if consumed in excess through food, drink, or the air. Gastrointestinal disorders might result from copper intake of 15–75 mg. Copper levels in drinking water must not exceed 0.05 mg/L.

Copper Removal Techniques. Several methods may be used to extract copper from wastewater, including adsorption using natural and engineered adsorbents, cementation, membrane filtering, electrochemical processes, and photocatalysis. The removal of copper from wastewater is the common goal of all these procedures, which operate in various ways. The effectiveness of the approach and the parameters that must be taken into account while utilizing it are only two of the numerous factors that cause different procedures to produce varied outcomes. Due to the complexity of the effluents, there is currently no one technology that can offer totally

Figure 1. Oil polluted areas in the Baku city.

suitable treatment. In order to achieve the required water quality in the most economical way, a combination of procedures is typically used [9].

Low-Cost Bio Sorbents as Adsorbents. Recent years have seen significant advancements in the study of the removal of heavy metals from industrial wastewater using adsorbents made from agricultural wastes, sometimes known as "bio-sorbents." One of the inexpensive biosorbents that may be used for the adsorption process is waste grain. It has been demonstrated to be an effective bio-sorbent for the remediation of wastewater polluted with copper that is both safe and biodegradable. The investigation also revealed that the pH of the starting solution must be maintained above pH 3.6 in order to prevent competitive inhibition by protons or the desorption of Cu^{2+} ions by ion exchange. In general, flow rate had no impact on the overall amount of Cu^{2+} ions adsorbed by discarded grain, although Cu^{2+} ion concentration did. Also, sawdust, which has a high retention capacity upon chemical activation, might be utilized as a useful adsorbent for the separation of copper from wastewater [10].

Materials and Methods

Chemicals. All the chemicals used were of analytical reagent grade. Copper sulphate pentahydrate were used for preparation of stock solutions. Hydrochloric acid for washing biochar. Demineralized water was used throughout the experimental studies.

Equipment. The table below provides a list of the equipment used in the adsorption experiments along with information on how they were utilized (Table 2).

Instrument	Maker	Function
Analytical balance	RADWAG	Weight Measurement
Atomic absorption spectrometer	Perkin Elmer	Estimation of metal ion concentration
Shaker	OHAUS	Batch adsorption studies of heavy metals
ICP-MS spectrometer	Perkin Elmer avio 220	Estimation of metal ion concentration
Muffle	STEM	Pyroliysis
Centrifuge	SUNSHINE SCIENTIFIC EQUIPMENTS	Separate solid from fluid
Water system	DragLab	Preparation of the stock solution

Stock solution preperation. Stock solution of 100 ppm of Cu (II) ion is prepared dissolving copper sulphate pentahydrate ($CuSO_4$ x $5H_2O$). For preparing this concentration 0.0392 g $CuSO_4.5H_2O$ is added in demineralized water contained in 100 ml volumetric flask. Other concentrations solutions of Cu (II) are made according to this. Stock solution of 1mol HCl is made from using its 6 mol solution. For preparing this concentration 16.6 ml initial HCl is diluted. Demineralized water was used throughout the experimental studies.

Preparation of Biochar. For preparing biochar 500 g initial spent coffee is used for preparation of initial product. Spent coffee grounds were collected from some local cafeterias. The product was first cleaned from extra fractions then washed under tap water and dried 60 C for 1 day.

Figure 2. Initial spent coffee.

Figure 3. Stainless steel Autoclave.

After 24 hours, the dried coffees ground were collected to autoclave and pressed maximum so there was no air left. Then autoclave was put into muffle.The experiment leaded in a different range of temperatures (from 400 to 700) and the pyrolysis process went for 1 hour.

After carbonization of spent coffee for 1 hour the muffle turned off and keeped for cooling down for a while. Then autaclave was taken from muffle carefully and keeped till the temperature become same as room temperature.

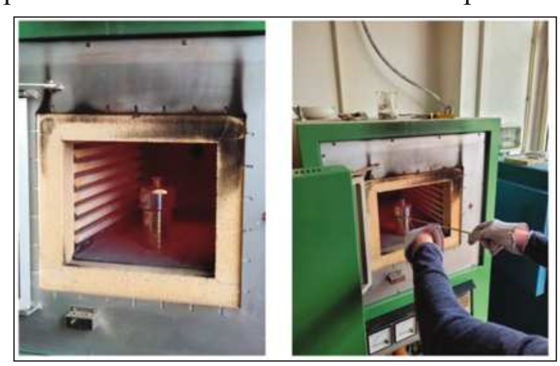
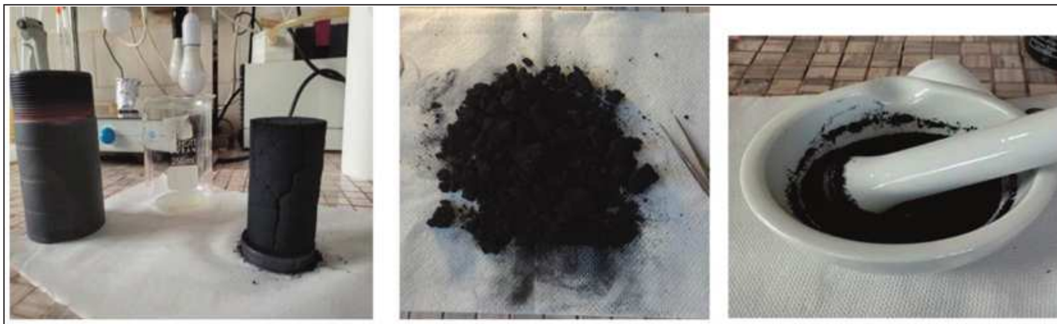


Figure 4. After pyrolization process autoclave in muffle and removal of it form muffle.

After cooling down of autaclave carbonized simples taked from autoclave [fig.5 (a)]. Hard pices broked little pices [fig.5(b)] then crushed in the laboratory ceramic mortar [fig.5 (c)] until it becomes like soft powder. This process was done for all temperature intervals.



a) b) c

Figure 5. Treatment of pyrolysed coffee.

Followingly the 1 g of product was taken and washed with 1 mol 100 ml of HCl.The washing of biochar leaded for 1 hour in normal room temperature and the process carried by stirring .After 1 hour biochar filtirated and for removing the HCl remowed by washing with demineralized water until there was no HCl left. Whole operation was leaded by using vacuum filtratone pump.

a) b)

Figure 6. Washing biochar by HCl (a) and vacuum filtration process (b) Absorption tests

Absorption tests was performed by using 30 mg of biochar and 30 ml of different concentrations of copper solution (1:1). Whole process was undertaken in the dark and by stirring for various time intervals. After test the solution was separated from solid particles by using vacuum filtration and centrifuging.

Figure 7. Samples after filtration.

Results and Discussion

Effect of Pyrolysis Temperature on Sorbent Yield. The table below (Table 3) illustrates the effect of different pyrolysis temperature on the final yield of biochar. So, it illustrates each time initial and final mass after pyrolysis process.

Table 3

Temperature pyrolysis (°C)	Initial weight (g)	final weight(g)
400	119.8	37.4
500	106.4	26.2
600	102.7	23.5
700	105.0	22.8

As it is described in obviously seen from the table highest biochar was gotten at the temperature of 400°C comparing with higher temperatures.

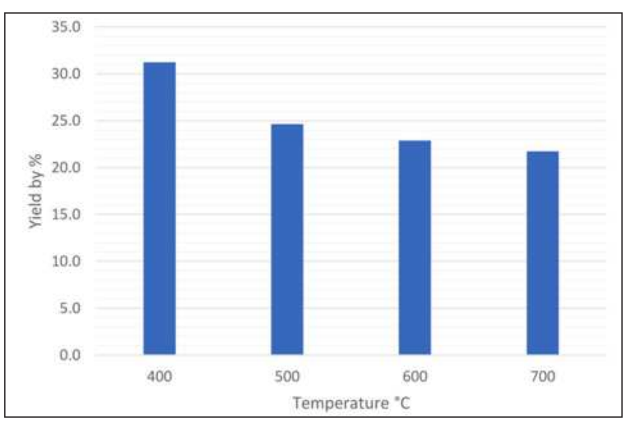


Figure 8. Effect of different pyrolysis temperature on biochar yield by %.

The bar chart (Figure 8) shows that it is more efficient to use 400°C for getting biochar because firstly it is economically suitable, so it uses less energy for obtaining adsorbent secondly in this temperature more final product is gotten in this temperature. From economical and yield side we can say that this temperature is better for obtaining biochar.

Effect of pyrolysis temperature on adsorption capacity of material. The table below (Table 4) illustrates the temperature final biochar effectivity on adsorption of Cu (II) from synthetic solution. As it is seen from the table the highest removal was on the sample marked as (a). This biochar was obtained at the temperature of 400°C which is the lowest test temperature for this test. In the initial solution the concentration was 110 ppm from this 44.6 was adsorbed by the biochar of coffee. It means 49.6% of copper removed from solution. All this test leaded for 1 hour and at the same condition so for being sure that other factors not effect on test. The second highest removal percentage was the following temperature. More detailly it was the sample indicated as (b) which is at the temperature of 500°C.

Table 4.

Sample	Dilution	Concentration ICP (mg/L)	Concentration (mg/L)
a	110	0.554	55.4
b	110	0.618	61.8
c	110	0.634	63.4
d	110	0.659	65.9

a-400°C, b-500°C, c-600°C, d-700°C

To cut long story to short there is linear relationship between temperature and adsorption capacity of biochar. The line graph shows this relationship more detailly (Figure 9).

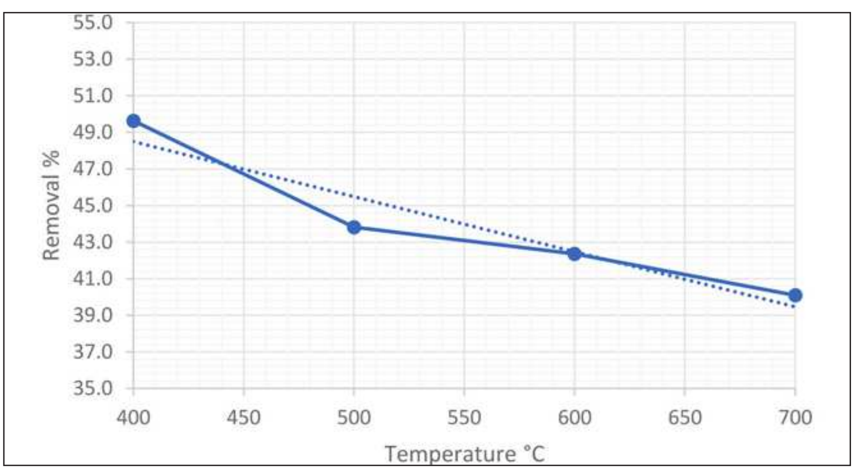


Figure 9. The dependence of sorbent production from temperature by %.

From the literature the biochar is produced from spent coffee were in the interval of 200 to 700°C. The final yield also changing according to the temperature as in our work.

Effect of concentration

The concentration of Cu (II) in initial solution was studied by us during these testes. As it is seen from the result of pyrolysis temperature on adsorption we decide to use the yield we got at the temperature of 400°C because the luck of time and for the future test this temperature's biochar was used (Figure 10). During initial test for the studies of pyrolysis temperature's effect on adsorption lower concentrations of copper was used. For this analysis stuck solution of Cu (II) was chosen with the concentration of 10 ppm. But after leading adsorption process for 1 day in normal room temperature the AAS test result showed partially there was no considerable concentration of Cu (II) left in the initial solution. The test was leaded for five times higher concentration of copper solution for the test. Same test leaded again but same result was obtained so after test there was no considerable copper left. Finally, from the 10 times more than initial concentration of Cu (II) initial concentration was chosen for future tests. From literature for other metals and organic compounds 50-100 ppm for used for some metals. In our future analysis and test we made coppers 100 ppm solution.

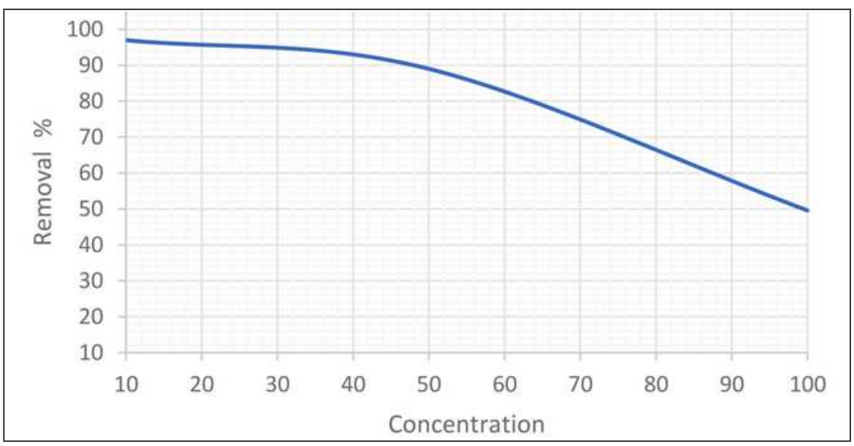


Figure 10. Effect of concentration on removal of Cu (II) by %.

Effect of time

The results of test for one and six days are shown in the table below (Table5).

Table 5.

Time (h)	a	b	c	d
24	0.723	0.717	0.728	0.883
144	0.651	0.678	0.675	0.657

a-400°C, b-500°C, c-600°C, d-700°C

As it mentioned above so it is better to work with the higher concentration of copper solution this test also was proceeded by using 110 ppm concentrated solution of copper. For the initial tests one day was chosen. But it was observed that for the all 4 different temperature biochars there were considerable high percentage of adsorption. Future test proceeded for six (144 hours). But the sorption percentage was increased more. From this result we can say that for a long time period sorption process was continued. That results are same for all four sorbents.

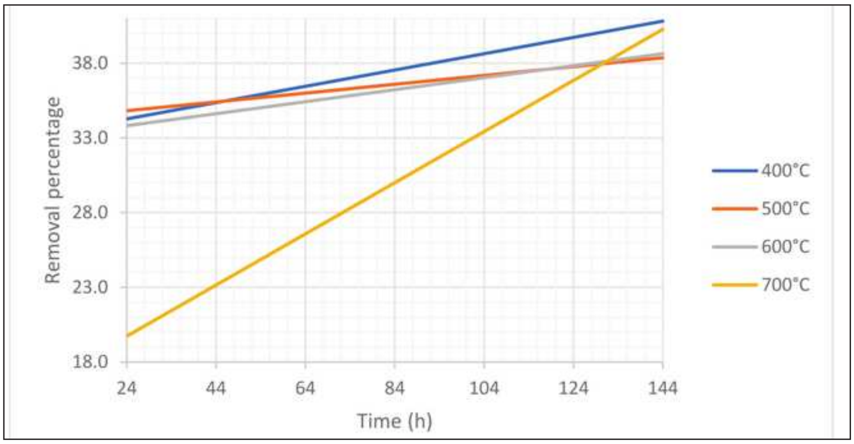


Figure 11. Effect of time on removal percentage.

Future test was operated for considerably short times comparing with initial time intervals for observing action of sorbents for short time intervals. For 1 hour and half hour the adsorption percentage was higher comparing 1 day and 6 days. This tendency was observed for all four biochar. But for biochar that obtained at the temperature of 400°C had better adsorption rate comparing with other biochar. The table below shows result of analysis.

Table 6.

Time (h)	a	b	c	d
0.5	0.663	0.654	0.666	0.691
1	0.554	0.618	0.634	0.659

a-400°C, b-500°C, c-600°C, d-700°C

The tests for an hour and 30 minutes had better results comparing with initial test but the biochar marked as d had almost same results for all time intervals. It shows biochar that obtained at the temperature of 700°C reaches its plateau after 30 minutes and no future adsorption goes. The chart shows the percentage of sorption.

As it is obvious from the line graph again the highest performance of adsorption was done by the biochar that obtained at the temperature of 400°C. For that reason, following test were done only for that temperature.

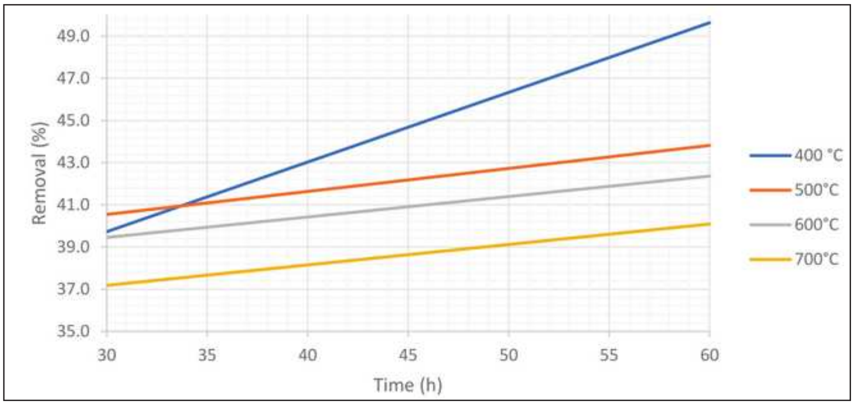


Figure 11. Effect of time (30 min to 1 hour) on removal percentage.

For testing adsorption capacity of lesser time interval, we used only 400°C because of above-mentioned reason.

Table 7.

Time (h)	a
0.08	0.759
0.17	0.754
0.25	0.831

a-400°C

The result of the test shows that the biochar that obtained at the temperature of 400°C works very well in a short time. Initially high percent of copper was adsorbed by sorbent in 5 minutes. After five minutes the solution was sustained almost same percentage because in 10-minute test shows 31.5% of Cu (II) from initial solution was removed. This result differs from previous 5 minutes test only 0.5%. More detailly next 5 minutes less amount of copper was adsorbed by coffee based new sorbent. Yet in 15 minutes the rate of sorption was decreased to 24% so desorption happened in solution.

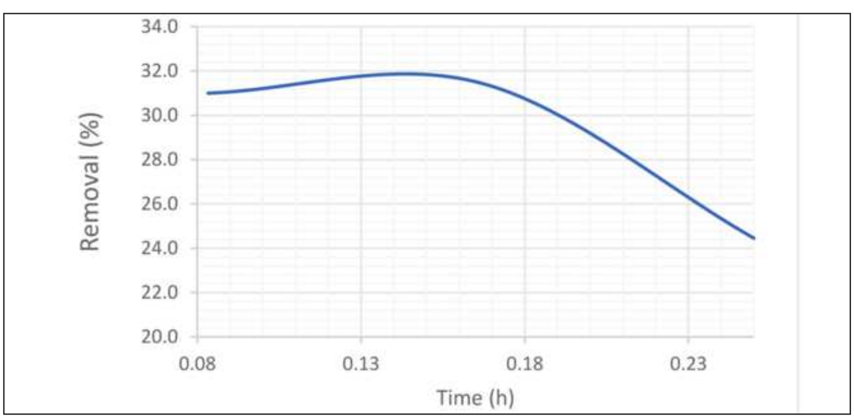


Figure 11. Effect of time (5-15 min) on removal percentage.

Conclusions and Perspectives

As promising and complete this study was there were some future developments. Concerning the possibility to begin all the processes from wastewater, the other test can be done for all four types of biochar,the sorption capacity's dependance of pH and temperature can be studied. All this did not done becouse of time shortage.For three month as much as possimle tests were done.In the future more complete and complex test can be done as we take into acout that in our times low cost sorbents and investigating their application on waste water.

Considering the outcomes performed in this study, the following conclusion can be drawn:

▪ The present investigation is carried out to study the suitability of a novel indigenous adsorbent, spent coffee for the removal of copper (II) from the wastewater.

▪ Influence of process parameters such as adsorbent dosage, contact time, initial metal ion concentration were at moderate levels such that they can affect the removal efficiencies of the heavy metals were concerned.

▪ The optimum pyrolysis temperature for the higest sorbent yiel was found to be 400°C.

▪ The optimum pyroysis time for spent coffee for obtainin biosorbent was found to be 60 min.

▪ The optimum time for adsorption of copper was found to be 60 min.

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