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Removal of Heavy Metal of Copper Using Microbial Nano Cellulose from Industrial and Hospital Wastewater

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Abstract

Industrial and municipal wastewater typically contains metal ions. When these metal ions are more than allowed, they can be harmful to aquatic organisms and human health. Environmental pollution by heavy metals is one of the main environmental problems. In this study, microbial nano cellulose was used as adsorbents in removing copper from wastewater. The purpose of this study was to study the possibility or impossibility of removing heavy metal copper by microbial nano cellulose under various environmental conditions. Removal of copper under different conditions was investigated by microbial and dry microbial nano cellulose adsorbent, contact time of 30 and 60 min and ambient temperature and temperature of 60℃. For further investigation, flame atomic absorption spectroscopy and infrared spectroscopy as well as scanning electron microscopy were used to illustrate the structure of microbial nano cellulose. The results showed that microbial nano cellulose are suitable for the development of economical and efficient adsorbents to remove heavy metals from the aquatic environment. According to the results, the initial metal content in the solution was 1.83 ppm, which increased with increasing temperature and time of absorption. Comparison between microbial nano cellulose and dry microbial nano cellulose. The results showed that absorption in the microbial cellulose nanoparticles is more than dry, due to the microbial cellulose structure. Also, using infrared spectroscopy, microbial nano cellulose absorption bands alone and dried microbial nanoclayers were compared with each other in a heavy metal solution, and no new absorption bar was created. As a result, the absorption of microbial cellulose nanoparticles was better at higher temperatures and more time than the rest.

Keywords: Copper; Nano; Microbial cellulose; Adsorption; Wastewater; SEM.

1. Introduction

Heavy metals are among the environmental pollutants that enter the environment today through industrial activities. The mechanism of toxicity of heavy metals is biochemically due to the intense tendency of these cations to react with sulfur. Heavy metal cations or molecules that contain these metals enter the body through swallowing and are easily attached to the sulfate groups that are found in the human body abundantly. Sulfur-derived metal grafts usually affect enzymes that control the speed of important metabolic reactions in the body, therefore, these enzymes cannot perform their normal task, and human health is compromised, and sometimes Death ends [1]. Copper in nature is found in 4 states: CU is a copper element (metal Solid) $Cu^{+}$and Cu^{2+} And rarely ion Cu^{3+}. [2] Mining and melting of minerals and metals, production of energy and fuel, industrial fertilizers and pesticides, coating, electrolysis, brain osmosis, leather work, photography, electrical power generation, painting, printing operations, energy and energy utilities, etc ,the main sources of metal contamination are copper to the environment [3]. The presence of copper in the environment disrupts the mechanism of chemical sensors in aquatic plants. In studies, the concentration of total water-soluble copper in the range of 0 to 20 ppm affected the sensory ability and fish behavior in salmon [4]. At higher concentrations, copper can damage the tissue of the sensory organs [5]. Due to environmental concerns and the demand for high quality water, there has been consistent control over the discharge of effluent and toxic compounds into the water. Identification and purification of toxic chemicals is an essential element of environmental protection. In this regard, secondary effluent treatment is not enough to remove heavy metals from wastewater, so we need advanced wastewater treatment methods. Nanotechnology is undoubtedly the most important technology of the twenty-first century. The connection between the new technology and the complex environment. Nanotechnology is the ability to produce new materials, tools and systems by taking control of the molecular and atomic levels and using the properties at which the levels appear. Research shows that the use of nanotechnology in water and wastewater treatment can greatly reduce the cost of refining. Cellulose is one of the most widely used biopolymers for the production of paper, textiles and medical materials. Due to the limitation of the main source of cellulose and the preservation of natural resources, one of the most interesting aspects of cellulose production is the microbial method. On the other hand, because of the lack of pure cellulose and the combination of lignin and hemicellulose, it is preferable to use bacterial cellulose that is pure polymer. Cellulose is a polysaccharide composed of a large number of beta-glucose monomers. This natural polymer is tissue tissue in the cell wall of the plant. Cellulose is the main combination of plant cell walls, algae and fungi, which has become the most abundant source of earth bioplimate in the world today. Cellulose comes from some plants, such as forest trees and cotton,

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through the photosynthesis of living plant cells from glucose. Cotton with 94% and wood with 50% cellulose are the main sources for cellulose in commercial and industrial areas. In recent years, the use of natural adsorbents to remove contaminations such as oil and textile industries, as well as the removal of heavy metals has been proposed and good results have been achieved [6].

The adsorption of heavy metals by lignocellulosic material may be due to the presence of carbohydrates and phenolic compounds which, by having carboxyl, hydroxyl, sulfate, phosphate and amine groups attached to their structures with metal ions, leads to the removal of these elements from the sewage [7]. Come back Kadrilo and colleagues found heavy metal wastewaters with cellulosic and non-cellulosic compounds (such as lignin and tannins) that heavy metals are absorbed by cellulose compounds and their absorption by non-cellulosic compounds is negligible [8]. Studies on the removal of heavy metals by cheap and natural adsorbents began largely from the 1970s. Larsen and Shaw studies can be mentioned in this regard [9]. Microbial cellulose was first obtained by Brown in 1886 at the time of vinegar production at the vinegar level in the form of a gelatin material. Bacterial cellulose is produced from four types of bacteria, stubacter, rhizobium, agrobacterium and alcohol in a static culture medium [10].

In 1976, independent and independent absorption of fungi and yeasts by Tobin-Avery-Duncan was established in 1992 and later by Brady in 1994 [11] Since the early 1980s, with the intensification of the use of Biological absorbers, bacteria were also considered. Most of the work done by researchers in the field of biological absorption has been on artificial wastewater [12] In 2007, Padmawati examined the absorption of nickel ions by bakery yeast. Most studies have also been conducted to remove an ion using fungi and algae. Therefore, studies on natural wastewater, especially acidic wastewater from mines containing heavy metal ions, appear to be necessary using less absorbent adsorbents. Chen and colleagues also removed copper and nickel ions in 2008 using algae. [13]

In 2004, Park and his colleagues investigated the removal of 6-chromium ions using Aspergillus niger's fungal mass [14] Lim and et al in 2012 used copper and cadmium metal ions to absorb the core from a tree species, respectively, with an absorption efficiency of 51% and 78%, respectively [15]. Excessive amounts of heavy metals such as cadmium, lead, copper and chromium, which are commonly found in contaminated soils, can also be harmful to germs and plants. So that they can exacerbate the symptoms of iron deficiency and, as a result, reduce their growth. See Table 1 for drinking water standards and the United States Environmental Protection Agency's Health Guidance Environmental States United: EPA US‹For some heavy metals and their important effects on human health is brought. In addition, heavy metals can be combined with sulfoidril groups, which can also reduce enzymatic activity. The permanent presence of heavy metals in aquatic ecosystems is a permanent threat to the health of human societies. [16] Microorganisms absorb heavy metals (or adsorption) inactive (or inactive), the cell wall, which is mainly composed of polysaccharides, lipids and proteins, has a variety of functional groups for bonding with heavy metals They include carboxylate, hydroxyl, amino, and phosphate groups [17].

2. Materials and Methods

Microbial cellulose from the University of Tarbiat Modarres, Copper nitrate produced by Merck Germany, distilled water, acetic acid produced by Merck Germany, SDS powder produced by Merck Germany, NaOH from Merck Germany. In this study, the LEO1455VP SEM machine in England and the Perky elmer 2133 flame atomic absorption device were used.

2.1. Preparation and Preparation of Adsorbent

One of the most famous Cellulose culture medium used in many studies to produce microbial cellulose is Hestrim. Various combinations of this culture medium are presented in Table 2. For the production of cellulose, this medium was used at pH = 5.

Table-1. EPA US legal restrictions for some heavy metals and their concentration in drinking water and their important impacts on human health. [18]

Name of metal	Maximum allowed concentration	Effects
Bohrium	2	Respiratory failure, Gastrointestinal Disorders
Cadmium	0.005	Carcinogenic, Damage to the lungs
Copper	1.3	Kidney damage, Brain damage
Lead	0.015	Reduce intelligence, Heart disease risk

Table-2. Various media combinations

Type of Material	The amount of W/V%
Glucose	2
Peptone	5
Yeast extract	6
Disodium phosphate without water	27
Citric Acid Monohydrate	71

The ability to produce cellulose was evaluated by a bacterium in a culture medium of HS, which is the formation of cellulosic cell at the level of the culture medium that emphasizes Acetaborxylinome. I used to study the production efficiency of cellulose microbial from Acetaborxylinome instead of glucose from other carbohydrate sources including glycerol, fructose and sucrose to determine the most efficient source of carbohydrates.

2.2. Complex Microbial Cellulose

After separating the base solution in distilled water, rinse the microbial cellulose and then place it on a filter to remove the excess solution. In this test, bleached cellulose is used for penetration and SDS bleaching. Put cellulose in 1000 ml container and add 3% by weight of SDS and place it in boiling temperature for 3 hours. After harvesting, microbial cellulose was washed several times with distilled water. After washing, re-enter the microbial cellulose and add 3-4% of the weight to the precipitate and place it at boiling point for 3 hours. Then washed with distilled water. Due to the alkaline pH of the cellulose, pH should be neutralized and acetic acid was used. Acetic acid and distilled water were combined with microbial cellulose for 30 minutes and then neutralized, and then the solution was drained and washed with distilled water, and used for this bleached cellulose in the experiments.

3. Material and Methods

3.1. Solubilizing Heavy Metals

In this study, copper nitrate with a molecular mass of 241.6 and an atomic mass of 63.546 was used. To test the flame atomic absorption, a concentration of about ppm is required. The following formula was used to prepare the solution.

Calculating formula for example number (1)

$$100\text{mg}/m^2 \times 100\text{ml} \times M_w(\text{Pb}(No_{3)2})/\text{Mw}Pb_2 \times 1\text{gr}/10^6 = \text{X} \quad (1)$$

In order to know how much copper should be used, the formula (atomic mass / molecular mass × 0.1) should be used to obtain a solution of 1000 ppm of copper, then 3 cc of solution was dissolved in a 100 cc balloon and the volume was 100 cc.

3.2. Scanning Electron Microscopes (SEM)

Non-conductive materials are usually coated with a thin layer of carbon, gold, or gold alloys. There must be a bond between the sample and the base of the electrical connection, and fine samples such as powders should be spread on a conducting film such as aluminum paint and thoroughly dried. Samples should be free from high pressure vapor, such as water, organic detergent and oily films. To see images of microbial cellulose nanoparticles, a thin layer of gold alloy was used to determine the structure of the electron microscopy (SEM).

3.3. Infrared Spectrometers

Infrared spectroscopy is a superior method in spectroscopy or infrared spectroscopy. In the infrared spectroscopy, the IR beam passes through the sample. Part of it passes through the sample and another part inside it. The resulting spectrum represents the molecular absorption and passage and creates the molecular effect of the sample. Similar to the fingerprint, the molecular structure of the material is also quite unique. This index makes infrared spectroscopy useful for analyzing various types of materials.

3.4. Flame Atomic Absorption Test

Infrared spectroscopy is a superior method in spectroscopy or infrared spectroscopy. In the infrared spectroscopy, the IR beam passes through the sample. Part of it passes through the sample and another part inside it. The resulting spectrum represents the molecular absorption and passage and creates the molecular effect of the sample. Similar to the fingerprint, the molecular structure of the material is also quite unique. This index makes infrared spectroscopy useful for analyzing various types of materials.

3.5. Flame Atomic Absorption Test

Measurement of copper was carried out using the Atomic Absorption Flame Model ALS2300C made by Perkin elmer. In order to prepare the device, after adjusting the bulb, for standard calibration line, standard solutions with different concentrations, prepared from standard mother solution at a concentration of 1000 ppm, were used.

3.5.1. Investigation of Heavy Metal Adsorption by Cellulose

The amount of 4 grams of microbial cellulose and 20 cc of metallic copper was injected into the human 50 cc and placed at 30-60 min and ambient temperatures of 60℃; adsorption was investigated in different conditions.

3.5.2. Investigation of Heavy Metal Adsorption by Dry Cellulose

The microbial cellulose was placed into the oven and after drying, then weighing 0.7 g of it using a weighing instrument and weighing 20 cc of metal carbide in the manure and various tests were done. The test variables included 30-60 minutes at ambient temperature and60℃, after which the cellulose was dissolved and the solution was prepared for testing.

- Initially, the time was kept constant and at 2 different temperatures with nanosilver adsorbent, the microbial cellulose was investigated.
- In this test, the temperature was kept constant and with two different time periods, nanosilver absorption of microbial cellulose was investigated.

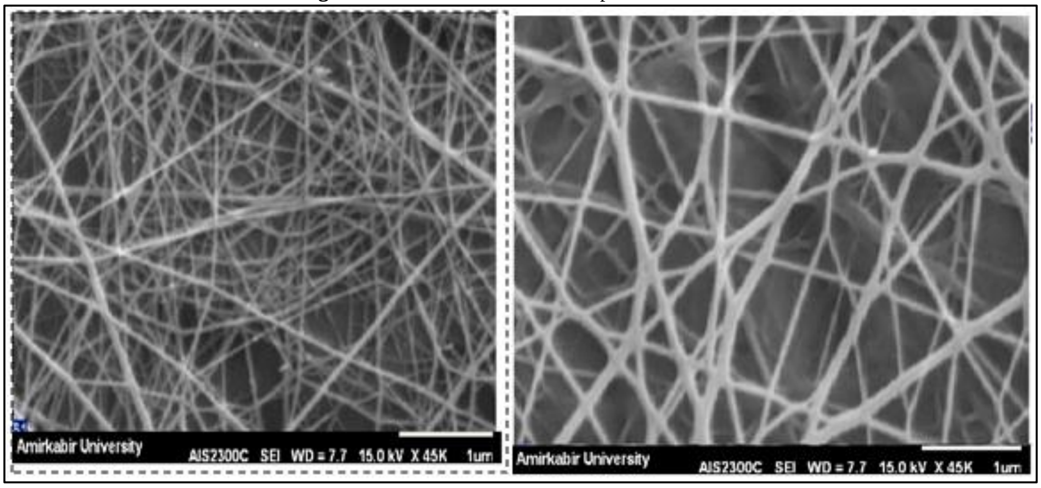
- In the next test, in a constant temperature constant, nanosilver absorption of microbial cellulose was investigated

4. Results and Discussion

4.1. Results of Scanning Electron Microscopy

Images of microbial cellulose nanoparticles in figure 1 were determined using an electron microscope. As it is known, the microbial cellulose structure consists of nano-sized strands. One of the nano properties is that their contact surface has become larger. The more this level of contact is the result of more absorption.

Figure-1. Microbial cellulose nanoparticle structure



4.2. Infrared Spectroscopy Results

Fig. 2 is related to the infrared spectroscopy of microbial cellulose, and Fig. 3 is related to the more microbial cellulose in a heavy metal copper solution, and the following results can be obtained from the spectral characteristics of the cell.

A) The presence of a strong and wide absorption band in the region of 3500 - 3200cm^{-1} indicates the presence of a tensile O-H alcohol factor in the composition, which is justified by the fact that cellulose is also a polyalcohol. In addition, the presence of a broad beam in this region demonstrates the existence of a hydrogen bond in the composition, which is due to the multiplicity of the alcoholic action along the cellulose chains.

B) The absorption band obtained in the range of 1200-1100 cm^{-1} refers to the etheric bonds in the building of this biopolymer located between the molecules of -β and the glucose molecule itself.

C) The absorption band in the region of 300-2800cm^{-1} is due to the elongation of the C-H alkanic bond that shows strong absorption in this region, or more generally refers to the aliphatic bonds in the material.

D) The absorption band in the region of 1470 to 1340 cm^{-1} corresponds to the C-H- flexing spectrum.

E) The presence of absorption band in the 1650 cm^{-1}region is related to the C = o functional group.

F) The absorption band in the 900 to 690cm^{-1} range refers to the outer-plate flexural C-H spectrum, which is located in the cyclohexane ring.

G) The absorption band obtained at 1060-1060 cm^{-1}indicates a cyclohexane ring in the composition.

Figure-2. Infrared spectroscopy related to microbial cellulose

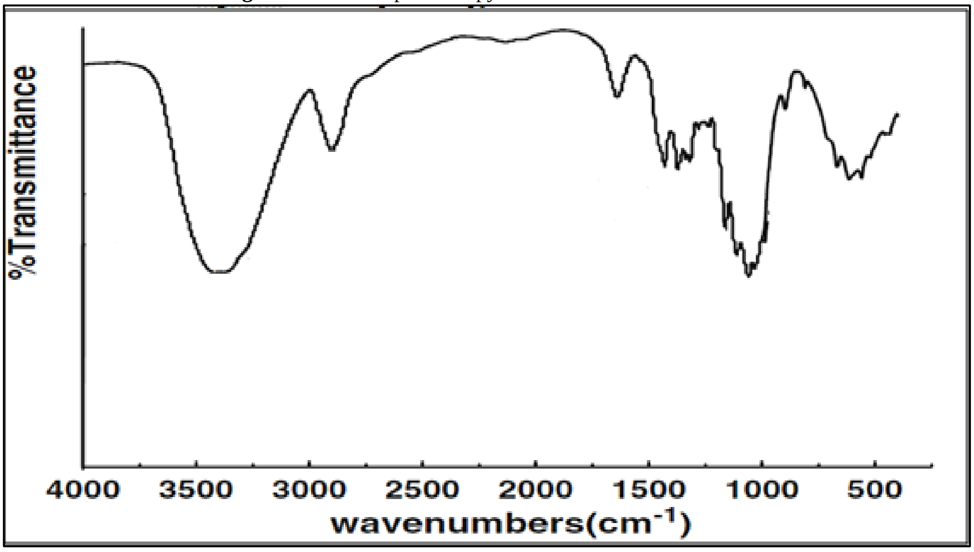
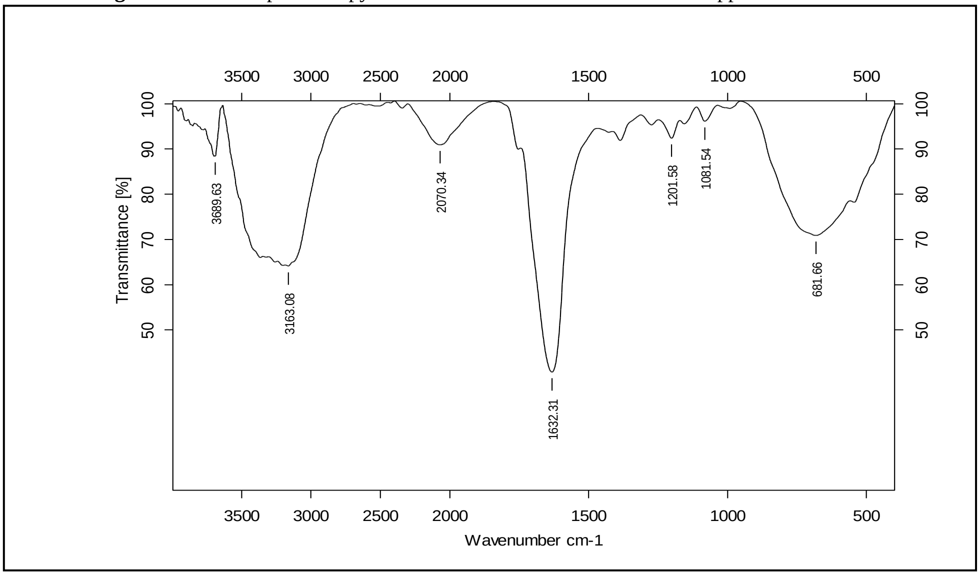


Figure-3. Infrared spectroscopy related to microbial nano cellulose in copper metal solution



4.3. Flame Atomic Absorption Test Results

The amount of copper in the initial solution of 1.83 ppm was determined as a control sample by a flame atomic absorption device. At present, changes in parameters such as temperature and time of copper metal adsorption were investigated.

A. In table (3), the adsorption of copper heavy metal by dry cellulose adsorbio biocides has been reported at ambient temperature and temperature of 60℃ and constant time of 30 minutes. As it turns out, the rate of absorption has also increased with increasing temperature. . The initial metal content without adsorbent was 1.83 ppm, which was reduced to 1.63 ppm at ambient temperature and 0.897 ppm at 60℃.

B. Table 4, in contrast to Table 3, kept the temperature constant but increased the contact time and the solubility of contact from 30 minutes to 60 minutes. In this experiment, it was also found that increasing absorption time increased the absorption rate by increasing the time

C. In Table (5), the adsorption of copper heavy metal with a cellulose bioavailable agent was reported at ambient temperature and at a temperature of 60℃ and a constant time of 30 minutes. As it turns out, the rate of absorption has also increased with increasing temperature

D. The initial metal content without adsorbent was 1.83 ppm, which at 0.897 ppm at ambient temperature dropped to 0.165 ppm at 60℃.

E. Comparison between the two tables (3) and (5), at different temperatures and times, but different adsorbents have been used, such as dried microbial nano cellulose and more microbial nano cellulose. As it is known, removal of metals with more microbial nano cellulose and its structure can be as long as the cellulose is more microbial, the distance between it and the dry microbial cellulose (which, due to the drying distance, becomes less and less blurred as a result of the possibility for Absorption and penetration is less).

Table-3. Results of heavy metal adsorption by dry cellulose in a constant time of 30 minutes and at 60℃ and ambient temperatures

Name of metals	Absorbent type	Temperature (celsius)	Time (min)	The amount of money is left
copper	Dry cellulose	environment temperature	30 minutes	**1.63**
Copper	Dry cellulose	60 degrees	30 minutes	**0.897**

Table-4. shows the results of heavy metal adsorption by cellulose at a constant temperature of 60 ° and at 30 and 60 minutes

Name of metals	Absorbent type	Temperature (celsius)	Time (min)	The amount of money is left
copper	Dry cellulose	60 degrees	30 minutes	**0.897**
Copper	Dry cellulose	60 degrees	60 minutes	**0.563**

Table-5. Atomic Absorption Atomic Tests Results by Cellulose Temperature and Time of 30 Min

Name of metals	Absorbent type	Temperature (celsius)	Time (min)	The amount of money is left
copper	cellulose	environment temperature	30 minutes	**0.505**
copper	cellulose	60 degrees	30 minutes	**0.247**

Chart-1. Comparison of residual metal content with dry microbial cellulose in a constant time of 30 minutes and ambient temperature, 60 ° C

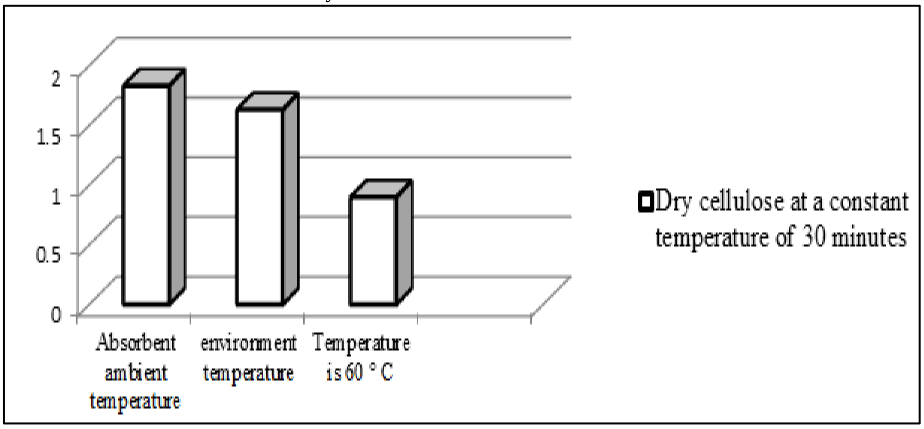


Chart-2. Comparison of the residual metal content with dry microbial cellulose at a constant temperature of 60 ° C and 30, 60 minutes

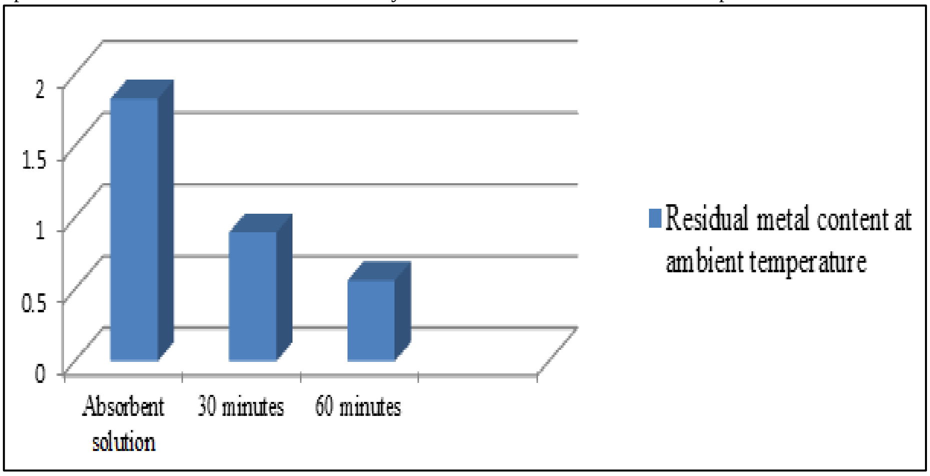
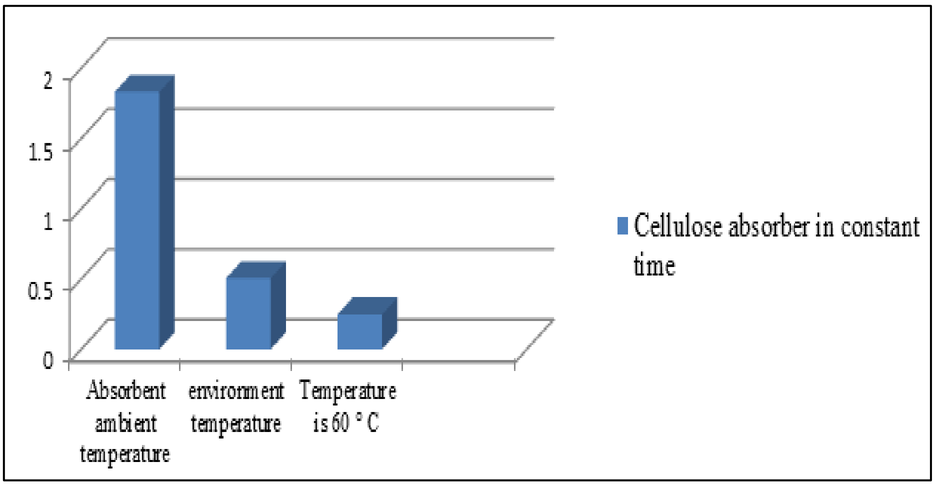


Chart-3. Comparison of the residual metal content with the aid of a more abundant cellulose in a constant time of 30 minutes Environment and 60 ° C



5. Conclusion

The purpose of this research is to remove metal copper in an economical way, as well as to investigate the rate of adsorption by means of microbial nanoclayers as adsorbent adsorbent adsorbents. The effective parameters in removing this heavy metal include changing temperature or time, as well as microbial nanoclayers adsorbent in dry or dry conditions. In this study, the biological absorption process and bioavailable adsorbents such as microbial nanoclayers were used. Nanoparticles of microbial cellulose particles were depicted by Scanning Electron Device in Figure 1.

By increasing the contact time of the adsorbent particles with a solution containing metal ions, the percentage of adsorption also increases, and then gradually increases with time. This is due to the fact that, at the earliest times of contact, there are vacant spaces on adsorbent surfaces for absorption of metals, and gradually occupies these sites, resulting in the removal of metal from the adsorbent surface and the reduction of the absorption process. As the contact time increases, the efficiency of the removal of metal ions increases, and at the initial contact times, the highest adsorption rate occurs and then it will slowly increase, which is probably due to the removal of metal ion by adsorbent [19-21].

In the absorption spectroscopy of infrared absorbent nanoclayers and microbial nanoclayers in a heavy metal solution of cobalt, absorption in the range of 1100-100 cm -1 returns to the etheric links in the building of this biopolymer, which occurs between the β-glucose molecules and also within the molecule itself is located. In the 1650 cm-1 region, the factor group is C = o

The presence of a strong and wide absorption band in the cm-1 3500 - 3200 range indicates the presence of a tensile O-H alcohol in the composition, since cellulose is also a polylactic. In addition, the presence of a broad beam in this region indicates the presence of a hydrogen bond in the composition, which is due to the fact that the alcohol factor is multiplied throughout the cellulose chain. As you know, a new courier was not created. The flame atomic ray absorption test showed that by increasing the time, more permission was allowed for the formation of the complex and eventually absorbed more. So that the amount of initial metal without adsorbent as control is 1.83, when it is dry microbial cellulose absorbent, it decreases by increasing the time to 0.897 ppm and remaining in solution for 30 minutes to 0.563 ppm. The same amount of metal was reduced by increasing the temperature. At ambient temperature, the metal content was 1.63 ppm, but the temperature dropped to 6063 ppm (0.563 ppm).

The comparison between the two adsorbents shows that most of the microbial cellulose has a higher absorption of dry microbial cellulose, and the dry microbial cellulose is compressed due to its structure after drying and penetration into the metal due to its structure.

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