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Copper Removal by Eucalyptus Sawdust and Determination of Isotherms and Kinetic of Adsorption Process

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ABSTRACT

Background: Sawdust is considered as a biological absorbent for removing and measuring heavy metals. **Objective:** The objective of this study is analyzing the use of Eucalyptus sawdust as an economical adsorbent for the removal of copper from effluents. The experiments were conducted in batch system and the effect of pH, the amount of adsorbent, contact time and the initial concentration of copper were examined. The most common isotherms and kinetics of adsorption were applied to analyze copper adsorption and the reaction rate; also the morphological characteristics of Eucalyptus sawdust were determined before and after the process by using scanning electron microscope (SEM). **Results:** According to the results, the maximum efficiency of copper adsorption was 98.23% which was obtained in pH of 7 and contact time of 90 minutes and 10 g/L of adsorbent. With the increase of initial concentration of copper, the amount of the adsorbed metal increased, but the removal percentage decreased. The data of this study showed sufficient agreement with both the Langmuir and Freundlich isotherm. The analysis of kinetic indicated that copper adsorption is consistent with the second-degree kinetic adsorption model (R^2=0.9994). **Conclusion:** According to the high efficiency of copper removal by the sawdust of Eucalyptus, this method can be used as an efficient and low cost way for the removal of copper.

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INTRODUCTION

In 1969, water pollution was defined as the increase of any material including chemical, physical or biological type that changes quality and plays a crucial role in its particular application [1]. Copper diffuses into the environment through natural sources and human activities [2]. Copper will not degrade in the environment and therefore will remain in soil, plants and animals by accumulation in organs. Soils that contain large amounts of copper will cause only a limited number of plants to have a chance of survival [3]. In some studies, a direct correlation between the level of free copper in the blood and Alzheimer's disease has been noted [4]. According to potable water standard offered by United States Environmental Protection Agency (U.S.EPA) and the World Health Organization, the permissible quantity of copper in drinking water is 1.3 mg/L [5]. These facts and considering the amount of copper in food and beverages, Factor for the increasing number of studies that have dealt with the determination of copper in samples [6].

Now, many companies have been developed and produce chemical products for removing heavy metals from sewage systems. Furthermore, some of these products have been used in order to remove heavy metals from water resources and groundwater [7]. According to some sources, wastewaters from old mines and areas where solid waste is buried are the biggest cause of heavy metal pollution [8]. Now, there are many methods for reduction of pollution from water and soil including filtration, coagulation, oxidation and ion exchange [9], but most of these methods are often time-consuming, high-cost and low efficient. Today, the trend is finding simple and cheap methods, which have the same efficiency for sewage treatment, particularly in the developing countries that are unable to use high-cost methods. Among these methods, the technology of adsorbents based on the process of ion exchange, physical and chemical adsorption has increasing application in the recent years. Sawdust is a cheap by-product, which is produced widely in the woodcutting industries and has adsorption and ion exchange characteristics. Studies show that there is a feasible application of Sawdust for adsorption of various metal ions. Among the previous conducted research, Raji and Anirudhan used a mixture of sawdust and

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poly acrylic amid to remove chromium (VI) from aqueous solutions. They achieved an absorption percentage of 91% for solutions with the initial concentration of 100 mg/L, temperature of $30^{O}C$, and pH=3. Adsorption capacity was measured using the Freundlich model, with chromium (VI) adsorption following the first order equation [10]. Sima et al. used tree sawdust to remove thallium (I) from aqueous solutions. This process followed the Langmuir, Freundlich, and Temkin isotherms, with thallium absorption standing at 98% for an eight-minute contact time [11]. Gupta and Babu also used sawdust to remove chromium from aqueous solutions. Their results had an excellent correspondence with the Langmuir isotherm, and chromium adsorption followed the second order equation. This absorbent had a capacity of 41.5 mg/g and showed good results with respect to removing chromium in the spectrum of pH: 6-9 [12]. Finally, Srinivasa et al. used modified sawdust to remove nickel and copper from industrial wastewater. Optimal pH was 5 for copper and 4 for nickel. Also, optimal contact time was 150 minutes for copper and 180 minutes for nickel [13].

In this paper, we report on using Eucalyptus sawdust as a low cost adsorbent for the removal of copper from effluents. This is significant because Sawdust is a inexpensive by-product which is produced widely in the woodcutting industries and has valuable adsorption and ion exchange characteristics. The paper should be of interest to readers in the areas of industrial wastewater. Studies show that there is a feasible application of Sawdust for adsorption of various metal ions . This capability of sawdust depends on its combination and structure [14]. The aim of this research is achieving an efficient and economical method for removing heavy metal of copper from the wastewater of various industries. For the same reason, it is intended to measure the removal capability and analyze the sawdust of Eucalyptus which is a native species in Khuzestan province.

MATERIALS AND METHOD

2.1 The preparation of adsorbent:

After collection of sawdust adsorbent of Eucalyptus, the particles were homogenized by mesh 35, then it was washed with distilled water to remove dust and other pollution, then was dried in oven at $30^{O}C$.

2.2 The preparation of synthetic solutions:

Copper nitrate was used to make synthetic solution. For this purpose, at first the copper solution with concentration of 25 mg/L was prepared, then the other concentrations were prepared by diluting the main solution. All the applied chemicals supplied from Merck Company. The experimental stages were conducted at $20^{O}C$ and the remained concentration of the metal was determined by atomic absorption spectrophotometer. It is important to note that all the experiments were replicated three times and the mean of data and the results were determined.

2.3 The effect of pH on the efficiency of copper removal:

For determination of optimum pH, it was selected in range of 3 to 10. After adjustment of pH using Hydrochloric acid and 0.1N NaOH solution, considering other fixed parameters, 0.5 g of sawdust was added to 50 ml of the copper sample with concentration of 10 mg/L. After 30 minutes, the concentration of remained copper was determined.

2.4 The effect of adsorbent quantity on the efficiency of copper removal:

In this step, in order to determine the optimum quantity of adsorbent with consideration of other fixed parameters, 0.15, 0.3 and 0.5 g of sawdust were added to the 50 ml solutions with the initial copper concentration of 10 mg/L and with the optimum obtained pH quantity from the previous stage. After 30 minutes of contact time, the concentration of the remained copper in the solution was determined.

2.5 The effect of contact time on the quantity of copper adsorption:

In the examination of time effect with consideration of other fixed parameters, after the preparation of 50 ml solutions with the initial copper concentration of 10 mg/L, the optimum quantities of sawdust and pH were added and adjusted to the solutions and the samples were brought out from the mixer at intervals between 15 to 120 minutes and were analyzed.

2.6 The effect of initial concentration of copper on efficiency of copper removal:

In order to examine the effect of initial concentration of copper on the adsorption quantity, considering initial concentration as variable and the other fixed parameters, 50 ml solutions were prepared with the initial concentrations of 5, 10, 15, 20, 25 mg/L and were analyzed after adjustment and adding the optimum quantity of pH and sawdust in the optimum contact time obtained in the previous stage.

2.7 The morphological study of sawdust:

The scanning electron microscope (SEM) photomicrograph of adsorbent using particle size analyzer revealed the considerable variation in particle size. In this stage, SEM was used in order to identify the morphology and it showed how copper is adsorbed on the Eucalyptus sawdust.

RESULTS AND DISCUSSION

3.1 The examination of pH effect on copper removal:

Fig. 1 shows the results of effect of various pH on the adsorption percentage. Based on the obtained results, with the increase of pH up to 7, the removal efficiency is increased and would be decreased after that. According to the conducted studies, in acidic pH, the concentration of H^+ ion is high in the solution and this cation compete with copper for setting on the adsorption places and copper adsorption would be decreased and in higher pH, concentration of OH^- ion will be high and copper deposits are being observed and adsorption rate would be decreased.

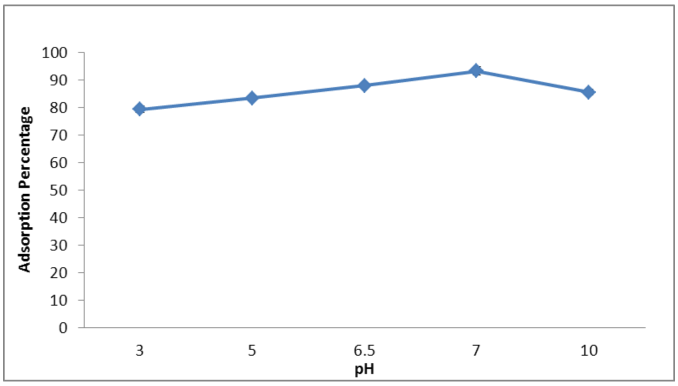

Fig. 1: Effect of various pH on the adsorption percentage of copper (Adsorbent quantity =10 g/L,Contact time=30 min, Initial concentration of copper=10 mg/L).

3.2 The examination of the effect of adsorbent quantity on the adsorption rate of copper:

The results of the effect of adsorbent quantity on the adsorption of copper are presented in Fig. 2. The results showed that the removal percentage of copper by sawdust of Eucalyptus increases with the increase of adsorbent quantity, because with the increase of adsorbent quantity, the quantity of contact surface of adsorbent with copper increases, therefore the efficiency of adsorption increases.

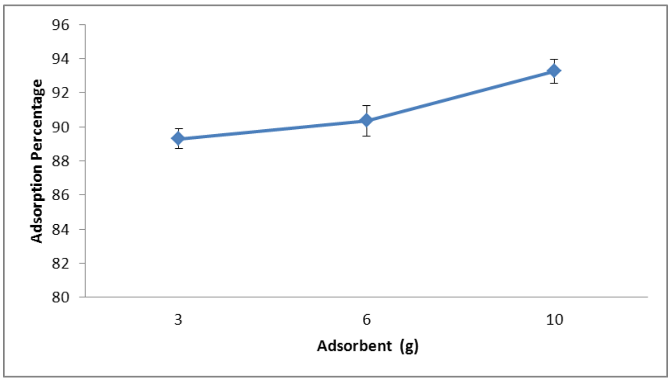

Fig. 2: Effect of different adsorbent quantity on adsorption percentage of copper (pH=7, Contact time=30 min, Initial concentration of copper=10 mg/L).

3.3 The effect of contact time on the adsorption rate of copper:

The results of different contact time on the adsorption rate of copper are shown in Fig. 3. According to the results, removal efficiency increases with the increase of contact time, but after 30 minutes, with the increase of time, at 60 minutes, adsorption rate decreases and with more passing time, adsorption rate again increases and at 90 minutes, its reaches to maximum removal, that the cause of this issue is the reversibility of adsorption process that at first with passing time, adsorption reaction would be started and with more passing time, the reverse reaction would occur. Finally, after passing certain time, this cycle increases and the decrease of concentration would be fixed, that this behavior does not signify the cease of forward and backward reactions, but these reactions are still current and with equal velocities, thereby maintaining the concentration, that in this case, the reaction has reached dynamic equilibrium (not static).

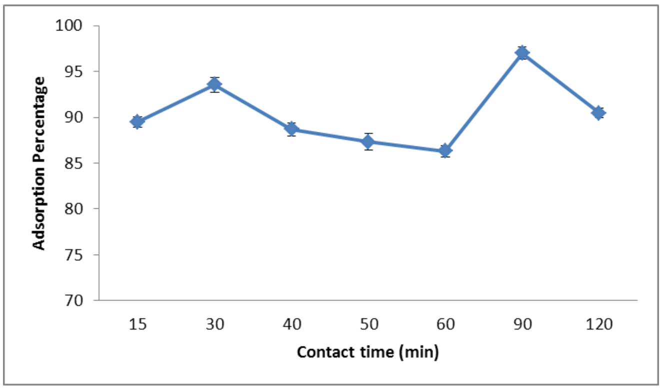

Fig. 3: Effect of different contact times on the adsorption percentage of copper (pH=7, Adsorbent quantity =10 g/L, Initial concentration of copper=10 mg/L).

3.4 The effect of initial concentration of copper on the removal percentage and adsorption capacity of copper:

The quantity of adsorbed substance (adsorption capacity) is defined as follows:

$$q_e = (C_o - C_e) \times \frac{V}{W} \quad (1)$$

Where C_0 is the initial concentration of adsorbed substance (mg/L), C_e is the concentration of the adsorbed substance after adsorption (mg/L), V is the volume of the solution (L) and W is the weight of adsorbent substance (g).

The results of examination of the initial concentration effect of copper on adsorption are shown in Fig. 4. The results showed that with the increase of initial concentration of copper, the quantity of adsorbed substance (adsorption capacity) increases, but the adsorption percentage decreases, in a way that with the increase of initial concentration of copper from 5 to 25 mg/L, adsorption capacity increases from 0.491 to 2.122 mg/g, but removal percentage decreases from 98.23% to 84.89%. This issue can be concluded from having more free bands of adsorbent and bands of ion exchange in low concentrations of copper. Furthermore, in batch adsorption systems, the input concentration of copper in the solution plays a crucial role as the motivative force for overcoming the resistance from the mass transfer between liquid and solid phases. Therefore, with the increase of copper concentration in the solution, the adsorption capacity of copper increases.

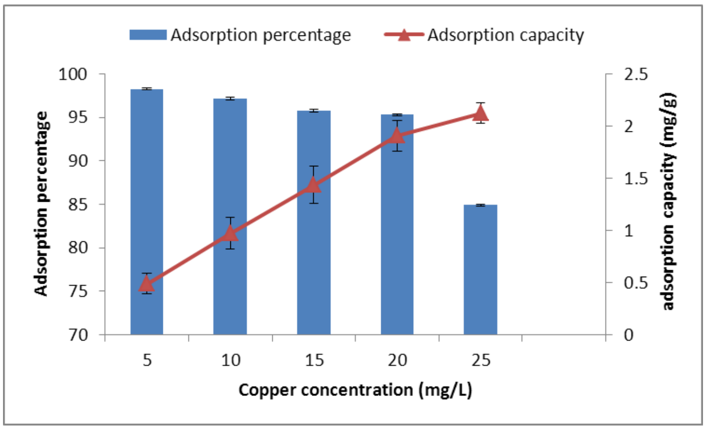

Fig. 4: Effect of the quantity of different initial concentration on the capacity and percentage of copper (pH=7, Adsorbent quantity =10 g/L, Contact time=90 min).

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3.5 Isotherms studies of copper adsorption by Eucalyptus sawdust:

Analytical information was obtained from isotherms in order to develop equation which is necessary for designing. Furthermore, adsorption isotherm can be used to describe how the reaction of adsorbing substance with adsorbent is as well as optimizing the quantity of adsorbent application [15].

3.5.1 Langmuir isotherm:

The linear form of Langmuir equation is as follows [16, 17]

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{q_m \times K_1 \times C_e} \quad (2)$$

Where q_e is the amount of adsorbed substance (mg/g), q_m and K_1 are Langmuir parameters that are related to the maximum adsorption capacity and the correlation energy of adsorption respectively. The quantities of q_m and k_1 can be determined by drawing the changes of $1/q_e$ based on $1/C_e$. The main characteristic of Langmuir equation is a dimensionless constant which is called equilibrium parameter that is defined as follows [18]:

$$R_L = \frac{1}{1 + K_1 \times C_o} \quad (3)$$

R_L indicates type of isotherm. $0<R_L<1$ for optimum adsorption, $R_L>1$ for non-optimum adsorption, $R_L=1$ for linear adsorption and RL=0 for irreversible adsorption [19]. The results of Langmuir isotherm analyzing are shown in Fig. 5 and Table 1, according to the obtained results of R_L=.0126 and correlation coefficient of R^2=0.9925, achieved data is conformed with Langmuir isotherm.

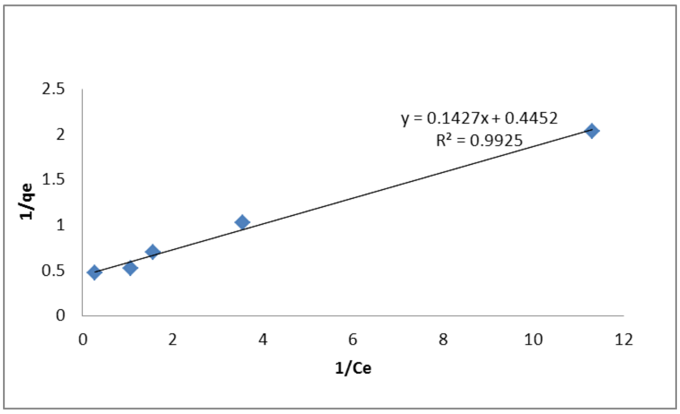

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Fig. 5: Langmuir isotherm model for copper adsorption.

Table 1: Results of Langmuir isotherm calculations.

qm	K_1	R_L
2.247	3.133	0.0126

3.5.2 Freundlich isotherm:

The linear form of Freundlich equation is as follows [20, 21].

$$\text{Log } q_e = \text{Log } K_F + \frac{1}{n} \text{Log } C_e \quad (4)$$

Where K_F is adsorption capacity (mg/g), 1/n is the intensity of adsorption, C_e is the equilibrium concentration (mg/L) and q_e is the adsorbed substance (mg/g). From the linear diagram $\log(q_e)$ against $\log(C_e)$, K_F and 1/n are determined that 1/n indicates type of adsorption process, if 1/n=0 it shows irreversible process, $0 < 1/n < 1$ shows optimum adsorption state and if 1/n >1 indicates non-optimum adsorption [22]. The results of Freundlich isotherm analyzing are shown in Fig. 6 and Table 2 that according to 1/n, the adsorption process is optimum and achieved data is conformed with Freundlich isotherm.

Table 2: Results of Freundlich isotherm calculations.

K_F	1/n
1.555	0.395

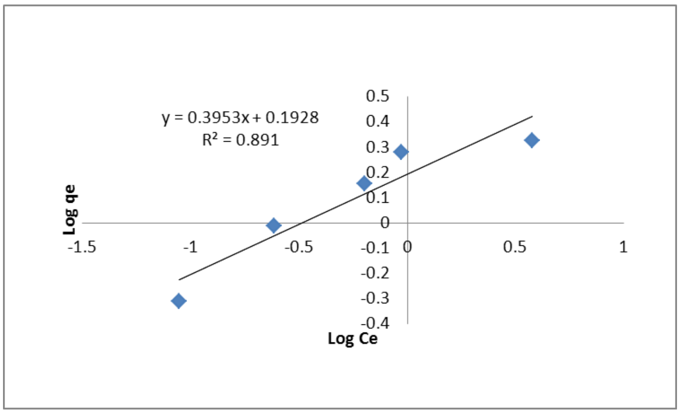

Fig. 6: Freundlich isotherm model for copper adsorption.

3.6 Kinetic studies of copper adsorption by Eucalyptus sawdust:

One of the most important factors for adsorption process is prediction of adsorption rate. The adsorption kinetic depends on the physical and chemical properties of adsorbent that affects adsorption mechanism.

3.6.1 The kinetic model of the first-degree adsorption:

The first-degree adsorption kinetic can be described as follows [23, 24, 25]

$$\text{Log}\,(q_e - q_t) = \text{Log}\,q_e - \frac{K_1}{2/0303}t \quad (5)$$

In this equation, q_e is the adsorption capacity of sawdust in equilibrium condition (mg/g), q_t is the quantity of adsorbed copper in time (mg/g) and k_1 is a constant of first-degree equilibrium velocity (1/min). The first-degree kinetic model is obtained by linear drawing of log(q_e-q_t) on the basis of t, that k_1 and q_e are drawn from slope and intercept and correlation coefficient R^2 also can be obtained from the diagram. The results of the first-degree adsorption kinetic are shown in Table 3 and Fig. 7. According to the parameters and diagram, it can be concluded that the data does not follow the first-degree adsorption kinetic model because the quantity of R^2 is not optimum and quantities of q_e from the experiment are not equal with calculated q_e from the diagram.

3.6.2 The kinetic model of the second-degree adsorption:

The second-degree abdsorption kinetic model is also one of the most common models for analyzing the kinetic of adsorption reactions, which are as follows [26, 27]:

$$\frac{t}{q_t} = \left[\frac{1}{q_e}\right]t + \left[\frac{1}{K_2 \times q_e^2}\right] \quad (6)$$

In a way that, q_e is the adsorption capacity of sawdust in equilibrium condition (mg/g), q_t is the adsorbed copper quantity in time (mg/g) and k_2 is a constant of second-degree equilibrium velocity (g/mg/min). the second-degree kinetic model is obtained by linear drawing of t/q_t on the basis of t that q_e and k_2 are drawn from slope and intercept and correlation coefficient R^2 also can be obtained from the diagram. The results of the second-degree adsorption kinetic are shown in Table 4 and Fig. 8. According to the parameters and diagram, it can be concluded that the data follow the second-degree adsorption kinetic model because the quantity of R^2 is optimum and obtained q_e quantities from the experiment are equal with calculated q_e from the diagram.

Table 3: Kinetic results of the first-degree adsorption.

K_1	qe (calculated)	qe (experiment)	R^2
-0.0102	0.0526	0.9742	0.3256

Table 4: Kinetic results of the second-degree adsorption.

K_2	qe (calculated)	qe (experiment)	R^2
-0.956	0.8453	0.9742	0.9994

3.7 Morphological study of Eucalyptus sawdust:

Figs. 9 and 10 show images from the surface of sawdust by scanning electron microscope (SEM). Fig. 9 show the images before the adsorption of sawdust in different magnifications, that show porous structure. Fig.

10 show the images after the adsorption of sawdust in different magnifications that metals have filled pores and the adsorption process is conducted.

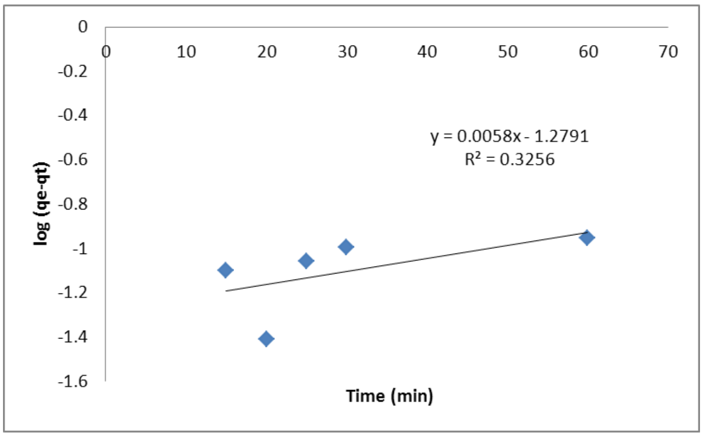

Fig. 7: First-degree adsorption kinetic model.

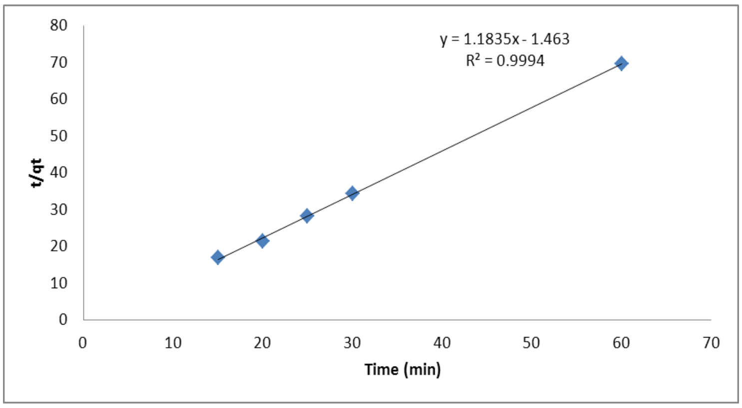

Fig. 8: Second-degree adsorption kinetic model.

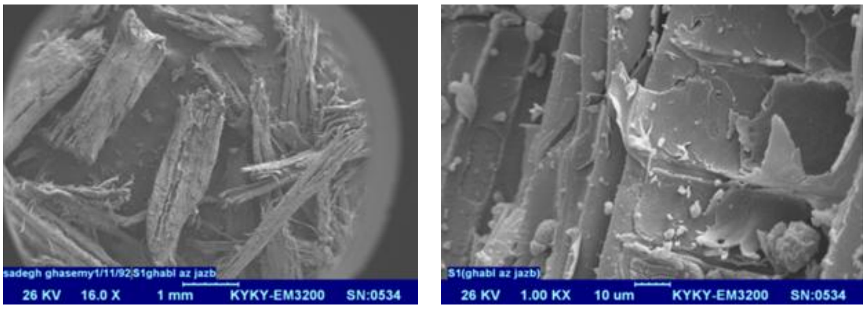

Fig. 9: SEM images before adsorption of metal by Eucalyptus sawdust with 16X and 1KX magnifications.

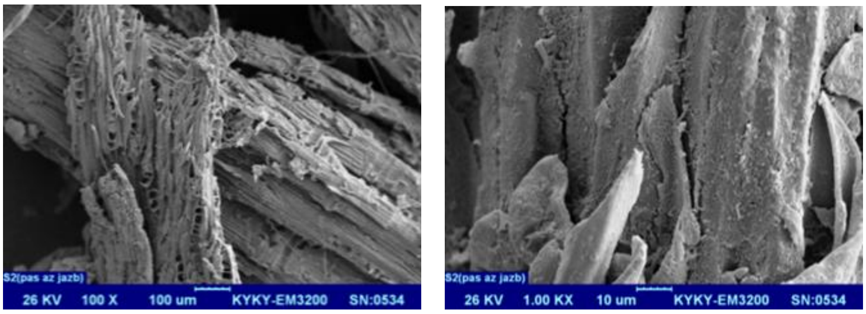

Fig. 10: SEM images after adsorption of metal by Eucalyptus sawdust with 100X and 1KX magnifications.

4. Conclusion:

The results of this study indicated that the highest adsorption efficiency is 98.23% that was conducted in optimum conditions of pH =7, adsorbent quantity of 10 g/L, 90 minutes of contact time and the initial copper concentration of 5 mg/L. According to the considerable removal percentage of Eucalyptus sawdust in removing of copper, this method can be considered as an effective method in heavy metals removing. Ion exchange and/or formation of hydrogen bonds could be among the principles of mechanisms for separating metal ions [28].

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