



ORIGINAL ARTICLE

Kinetic and Isotherm Study of Lead Adsorption from Synthetic Wastewater by Myrtaceae Sawdust

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ABSTRACT

The objective of this study is the analysis of using myrtaceae sawdust as a cheap adsorbent for the removal of lead 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 lead were examined. The most common isotherms and kinetics of adsorption were applied to analyze lead adsorption and the reaction rate, also the morphological characteristics of myrtaceae sawdust were determined before and after the separation process by using scanning electron microscope (SEM). According to the results, the maximum efficiency of lead adsorption was 97.49% which was obtained in pH of 7 and contact time of 30 minutes and 10 g/L of adsorbent. With the increase of initial concentration of lead, the adsorbed metal and removal percentage increased. Achieved data from this study indicated a good correspondence with both isotherms of Langmuir and Freundlich. The analysis of kinetic indicated that lead adsorption is consistent with the second-degree kinetic adsorption model ($R^2=1$). According to the high efficiency of lead removal by the sawdust of myrtaceae, this method can be used as an efficient and cheap way for the removal of lead.

Keywords: Lead Removal, adsorption, Sawdust of Myrtaceae, Kinetic and Isotherm of Adsorption

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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]. Lead is a toxic metal that has a poor electrical conductivity [2]. This metal can be dangerous and poisonous even in low concentration [3]. disorders of Learning and behavioral in children, damage to organs, liver, kidney and heart are the consequences of lead contamination [4]. 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 [5]. Lead metal ion is found mainly in industrial wastewater [6]. Now, there are many methods for reduction of pollution from water and soil including filtration, coagulation, oxidation and ion exchange [7], 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, the removal of metals (lead, Chromium and cobalt) from the aqueous solution by a mixture of sawdust adsorbents and the stalk of Persian turpentine tree was conducted by Hashemi Sharaf Abad, The highest rate of metals removal for lead, Chromium and cobalt in solution with concentration of 10 ppm were 67.43%, 46.57% and 17.70%, that the rate of lead removal is higher than the other metals [8]. In research titled "the adsorption of cobalt from aqueous solution by active coal produced from the wood of fig tree conducted by Miri Tarhan, the results showed that this adsorbent has a high-capacity for removing cobalt from the

polluted aqueous solutions [9]. Finally, in research titled “the analysis of the efficiency of wood ash in removing cadmium from the sewage of color-producing industries (Binalood of Kerman) which was conducted by Malakootian, the results showed that wood ash has high efficiency of 97% to 98% in removing cadmium with the increase of the quantity of adsorbent about 100 g/L [10]. The aim of this research is achieving an efficient and cheap method for removing heavy metal of lead from the wastewater of various industries. For the same reason, it is intended to measure its removal capability and analyze the sawdust of myrtaceae which is a native tree of Khuzestan province for removing lead from synthetic wastewater are examined.

MATERIALS AND METHODS

The preparation of adsorbent

After collection of sawdust adsorbent of myrtaceae, 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°C .

The preparation of synthetic solutions

Lead nitrate was used to make synthetic solution. For this purpose, at first the lead solution with concentration of 25 mg/L was prepared . then the other concentrations were prepared by diluting the main solution. All the applied chemicals were from Merck Company. The experimental stages were conducted at 20°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.

The effect of pH on the efficiency of lead 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 lead sample with concentration of 10 mg/L. After 30 minutes, the concentration of remained lead was determined.

The effect of adsorbent quantity on the efficiency of lead 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 lead 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 lead in the solution was determined.

The effect of contact time on the quantity of lead adsorption

In the examination of time effect with consideration of other fixed parameters, after the preparation of 50 ml solutions with the initial lead 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.

The effect of initial concentration of lead on efficiency of lead removal

In order to examine the effect of initial concentration of lead 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.

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 lead is adsorbed on the myrtaceae sawdust.

RESULTS AND DISCUSSION

The examination of pH effect on lead removal

Figure 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 lead for setting on the adsorption places and lead adsorption would be decreased and in higher pH, concentration of OH⁻ ion will be high and lead deposits are being observed and adsorption rate would be decreased.

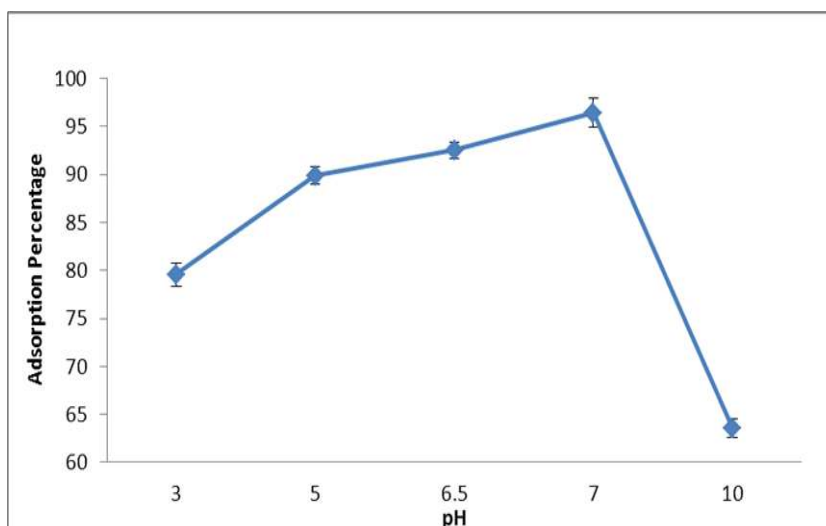


Figure 1. Effect of various pH on the adsorption percentage of lead (Adsorbent quantity =10 g/L, Contact time=30 min, Initial concentration of lead=10 mg/L)

The examination of the effect of adsorbent quantity on the adsorption rate of lead

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

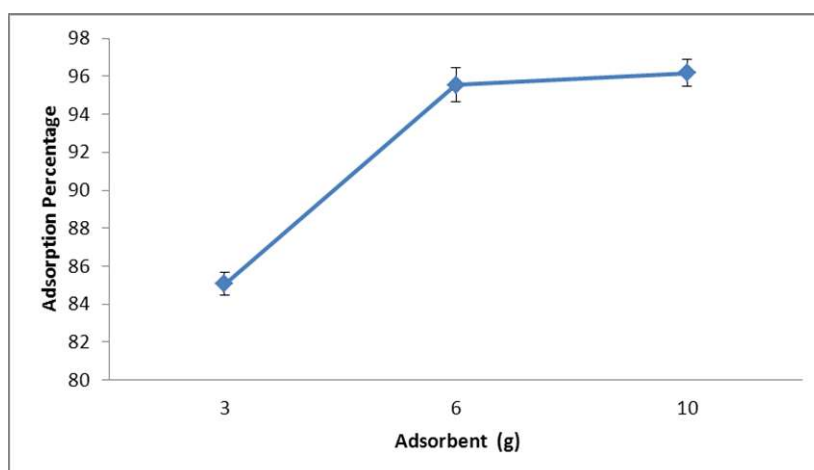


Figure 2. Effect of different adsorbent quantity on adsorption percentage of lead (pH=7, Contact time=30 min, Initial concentration of lead=10 mg/L)

The effect of contact time on the adsorption rate of lead

The results of different contact time on the adsorption rate of lead are shown in figure 3. According to the results, removal efficiency increases with the increase of contact time up to 30 minutes, but with the increase of time, at 60 minutes, adsorption rate decreases and with more passing time, adsorption rate again increases, 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). According to the results at the contact time of 90 minutes, we saw the highest rate of absorption but as the adsorption quantity at 90 minutes was not very different with the adsorption quantity at 30 minutes, considering the time importance at adsorption process, the optimum contact time of lead, 30 minutes was determined.

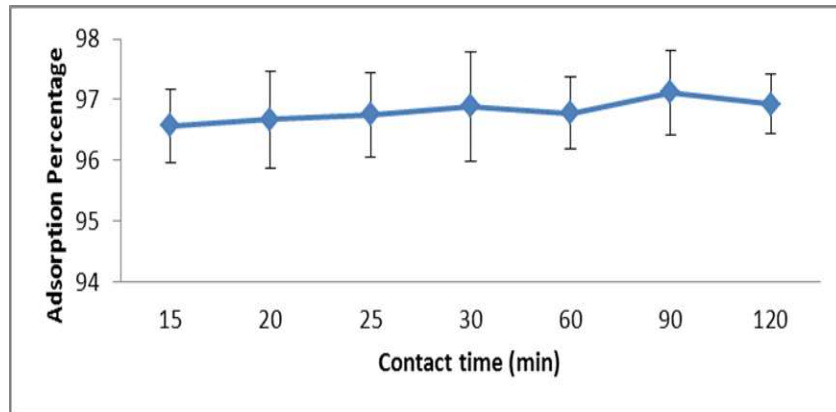


Figure 3. Effect of different contact times on the adsorption percentage of lead (pH=7, Adsorbent quantity =10 g/L, Initial concentration of lead=10 mg/L)

The effect of initial concentration of lead on the removal percentage and adsorption capacity of lead

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

$$q_e = (C_0 - C_e) \times \frac{V}{W} \quad (1)$$

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 lead on adsorption are shown in figure 4. The results showed that with the increase of initial concentration of lead, the quantity of adsorbed substance (adsorption capacity) and adsorption percentage increases. This issue can be concluded from having more free bands of adsorbent and bands of ion exchange in high concentrations of lead. Furthermore, in batch adsorption systems, the input concentration of lead in the solution plays a crucial role as the motive force for overcoming the resistance from the mass transfer between liquid and solid phases. Therefore, with the increase of lead concentration in the solution, the adsorption capacity of lead increases. It is important to note that with the increase of concentration from 20 to 25 mg/L, the adsorbed substance (q_e) increases slightly and adsorption percentage decreases that shows the saturation of sawdust.

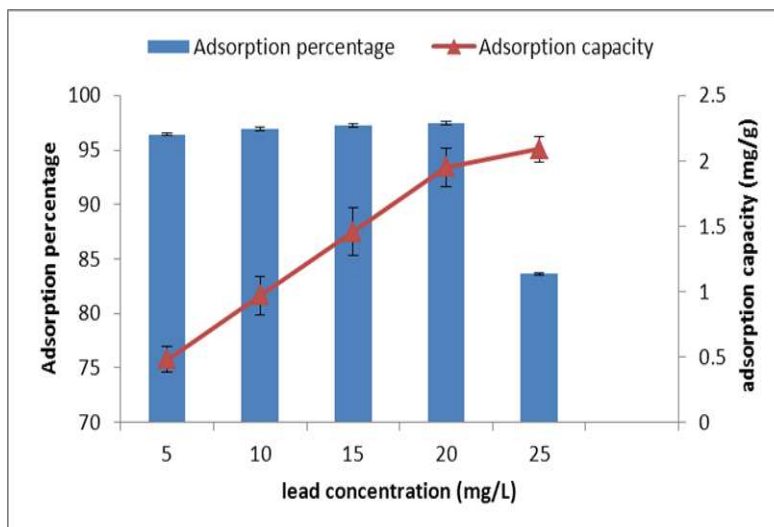


Figure 4. Effect of the quantity of different initial concentration on the capacity and percentage of lead (pH=7, Adsorbent quantity =10 g/L, Contact time=30 min)

Isotherms studies of lead adsorption by myrtaceae 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 [11].

Langmuir isotherm

The linear form of langmuir equation is as follows [12&13]

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

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:

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

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 $R_L = 0$ for irreversible adsorption [14]. The results of Langmuir isotherm analyzing are shown in figure 5 and table 1, according to the obtained results of $R_L = 0.112$ and correlation coefficient of $R^2 = 0.8717$, achieved data is conformed with langmuir isotherm.

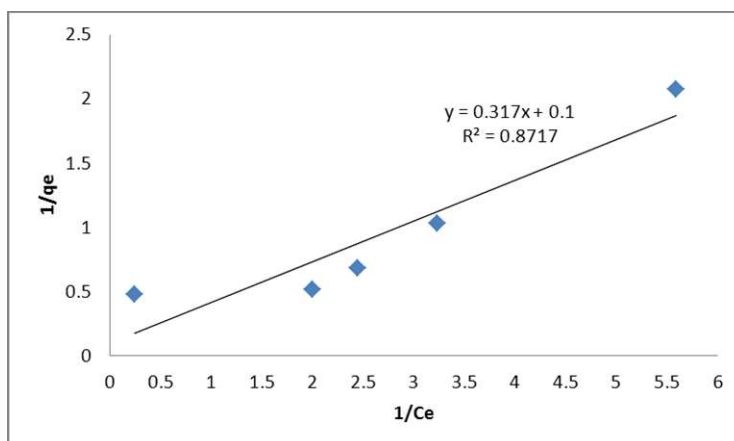


Figure 5. Langmuir isotherm model for lead adsorption

Table 1. Results of Langmuir isotherm calculations

q_m	K_1	R_L
10	0.315	0.112

Freundlich isotherm

The linear form of freundlich equation is as follows [15&16] :

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

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 [17]. The results of Freundlich isotherm analyzing are shown in figure 6 and table 2 . according to the obtained results of $1/n=0.377$ and correlation coefficient of $R^2=0.9989$, achieved data is conformed with freundlich isotherm.

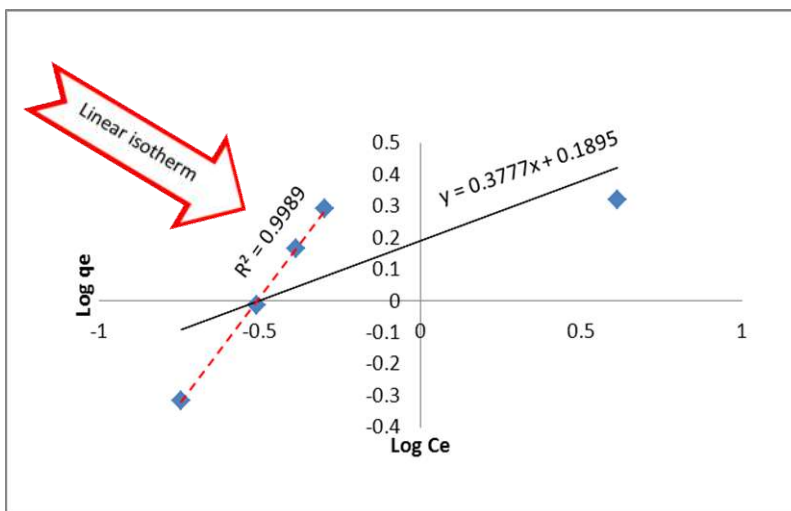


Figure 6. Freundlich isotherm model for lead adsorption

Table 2. Results of Freundlich isotherm calculations

K_F	$1/n$
1.547	0.377

kinetic studies of lead adsorption by myrtaceae 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.

The kinetic model of the first-degree adsorption

The first-degree adsorption kinetic can be described as follows [18&19] :

$$\text{Log } (q_e - q_t) = \text{Log } q_e - \frac{K_1}{2.303} t \tag{5}$$

In this equation, q_e is the adsorption capacity of sawdust in equilibrium condition (mg/g), q_t is the quantity of adsorbed lead 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 figure 7. According to the parameters and diagram, it can be concluded that the data does not follow the first-degree adsorption kinetic model because in spite of optimum R^2 , quantities of q_e from the experiment are not equal with calculated q_e from the diagram.

The kinetic model of the second-degree adsorption

The second-degree adsorption kinetic model is also one of the most common models for analyzing the kinetic of adsorption reactions, which are as follows [20]:

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

In a way that, q_e is the adsorption capacity of sawdust in equilibrium condition (mg/g), q_t is the adsorbed lead 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 figure 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	q_e (calculated)	q_e (experiment)	R^2
0.0728	0.0112	0.9689	0.9971

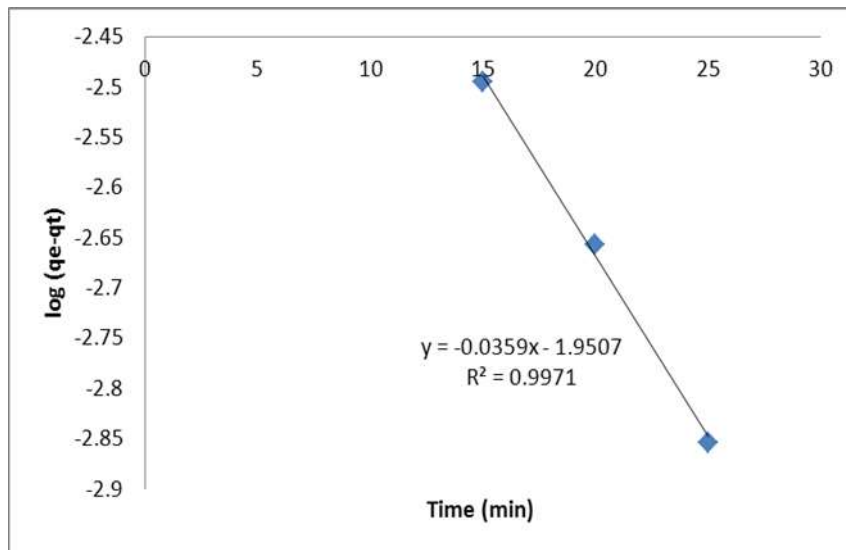


Figure 7. First-degree adsorption kinetic model

Table 4. kinetic results of the second-degree adsorption

K_2	q_e (calculated)	q_e (experiment)	R^2
14.5327	0.9702	0.9689	1

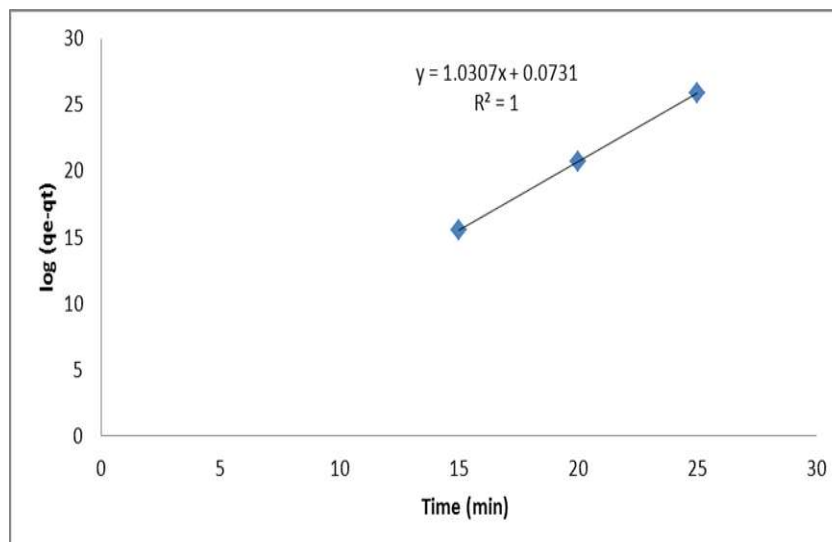


Figure 8. Second-degree adsorption kinetic model

Morphological study of myrtaceae sawdust

Figures 9 and 10 show images from the surface of sawdust by scanning electron microscope (SEM). Figure 9 show the images before the adsorption of sawdust in different magnifications, that show porous structure. Figure 10 show the images after the adsorption of sawdust in different magnifications that metals have filled pores and the adsorption process is conducted.

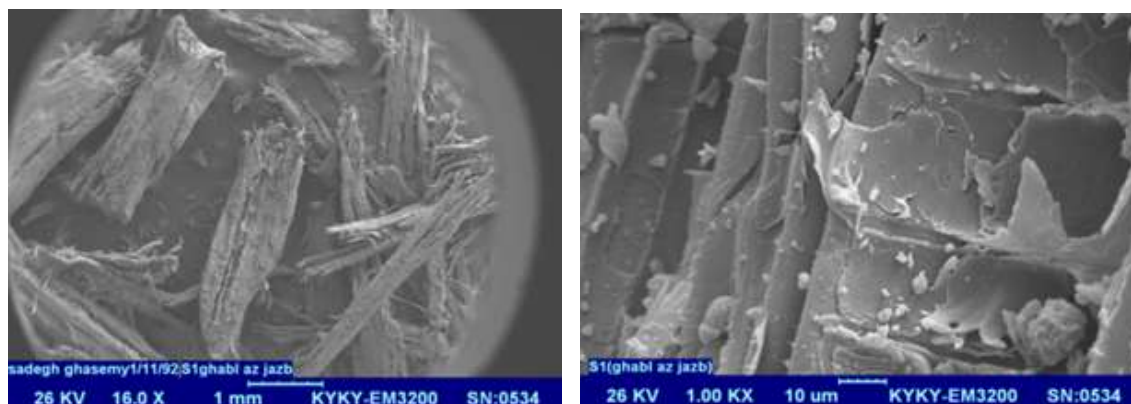


Figure 9. SEM images before adsorption of metal by myrtaceae sawdust with 16X and 1KX magnifications

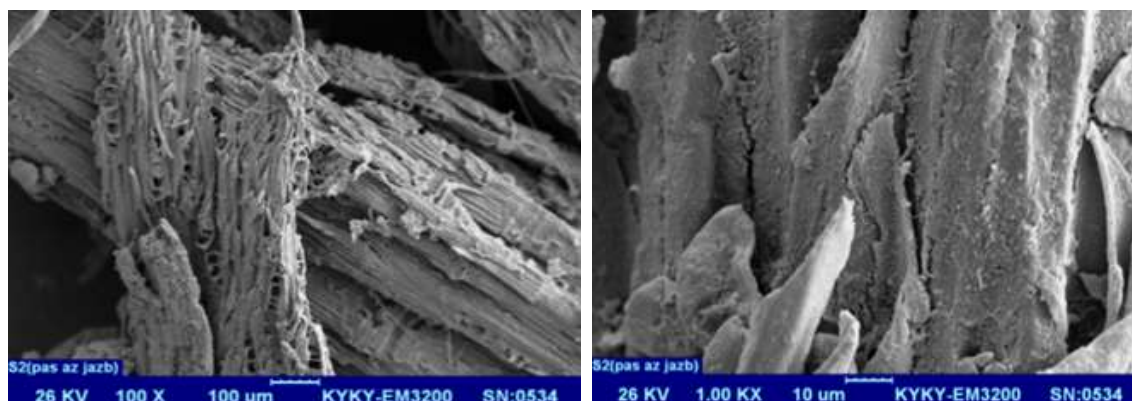


Figure 10. SEM images after adsorption of metal by myrtaceae sawdust with 100X and 1KX magnifications

CONCLUSION

The results of this study indicated that the highest adsorption efficiency is 97.49% that was conducted in optimum conditions of pH =7, adsorbent quantity of 10 g/L, 30 minutes of contact time and the initial lead concentration of 20 mg/L. According to the considerable removal percentage of myrtaceae sawdust in removing of lead, this method can be considered as an effective method in heavy metals removing.

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