

Removal of Pb (II) from Wastewater Using Henna: Optimization of Operational Conditions

M. Shafiee*, A. Akbari, B. Ghiassimehr

Department of Chemical Engineering, Jundi-Shapur University of Technology, Dezful, Iran

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ABSTRACT

This paper studies the removal of Pb (II) using *Lawsonia inermis* (Henna). In recent years, the use of low price adsorbent has received much attention. Adsorption experiments were performed in the batch system at ambient temperature (25 °C). The effects of some parameters, such as time, initial metal concentration, pH, and adsorbent dose, were investigated. The optimum conditions were obtained at pH of 6, initial metal concentration of 10 ppm, contact time of 80 min, and adsorbent dose of 0.75 g/L. To study the adsorbent morphology, Scanning Electron Microscope (SEM) and Fourier transform infrared spectroscopy (FTIR) were used before and after adsorption of Pb (II) ions. Sorption of Pb (II) was evaluated by Freundlich and Langmuir isotherms. The results indicate that the Freundlich isotherm model describes the adsorption of Pb (II) better than the Langmuir isotherm model. Also, it is observed that the pseudo-second-order kinetic model fits well with the experimental data.

1. Introduction

Industrial processes are the main resource of wastewaters that usually discharge to the environment. Heavy metal ions, solvents in organic compounds, and petroleum products are considered as the most serious contaminants [1]. The adverse impact of heavy metals, especially Lead, on the environment and living organisms was studied by many researchers [2-7]. Adsorption is an effective and economical method for removing heavy metals from industrial wastewaters. Due to the reversibility of adsorption, adsorbents can resuscitate by a simple process. Activated Carbon is a common adsorbent that is widely

used for wastewater treatment [8-11]. Activated Carbon is the most usable adsorbent while it can be classified as an approximately high-cost adsorbent. Finding a low-cost adsorbent with an easy access for removing heavy metals has become the main priority of researchers. Many low-cost adsorbents, such as orange peel [12-14], Olive leaf ash [15-16], and Bengal Gram Husk [17-18], have been used to remove metal ions. In the present study, *Lawsonia inermis* (Henna) was used to remove Pb (II) from wastewater. Henna is a plant adsorbent that can adsorb metal ion from wastewater [19]. The effects of operational conditions, such as contact time, pH, adsorbent dose, and initial metal

*Corresponding author: shafiee@jsu.ac.ir

concentration, were investigated. Thereafter, the adsorbent was characterized by (FTIR) and (SEM) analysis. Finally, to describe the adsorption process, isotherms and kinetic models were investigated.

2. Experimental

2.1. Materials

Lead Nitrate was purchased from Merck chemical Co. (99 %). Henna Leave Powder was supplied from Golbedastan Co. (Yazd, Iran). NaOH (37 %) and HCl solution (37 %) were supplied from Dr. Mojallali Industrial Chemical to pH adjustment.

2.2. Adsorbent characterization

To analyze the surface morphology of Henna, Scanning Electron Microscope (SEM) was carried out. The surface functional groups of adsorbent were characterized by Fourier transform infrared spectroscopy (FTIR). Also, a flame atomic adsorption spectroscopy (AAS) was used to determine the number of metal ions in aqueous solution.

2.3. Adsorption experiments

The experiments were carried out in a 250-cc flask at a temperature of 25 °C, pH (2-9), adsorbent dose (0.15-1.5 g/L), initial metal concentration (10-100 ppm), and contact time (20-200 min). First, the Henna leave powder was washed with distilled water and dried in the oven at 100 °C for 24 h. Afterward, the powder passed through the mesh screen (mesh100). Then, 100 ml of diluted stock solution was added to the flask. NaOH (0.1 M) and HCl (0.1 M) solutions were used to adjust pH. Then, a certain dose of adsorbent was inserted into the aqueous solution. Thereafter, the mixture was stirred at 600 rpm for a specified contact time. At the end of the process, the mixture was filtered using a filter paper, and residual metal concentration was

measured by a flame atomic adsorption spectroscopy (Shimadzo, Japan).

3. Results and discussion

3.1. The effect of pH

To investigate the impression of pH, adsorption was performed at the initial metal concentration of 10 ppm, contact time of 100 min, adsorbent dose of 1g/L, and pH in the range of (2-9). Fig. 1 indicates the adsorption as a function of pH. As observed, with an increase in PH from 2 to 6, the adsorption increased from 57 to 90 %. Then, with a further increase in pH up to 9, the removal of Pb (II) decreased. PH is an effective insolubility parameter of metal ions in aqueous solution. In addition, Lead can appear in the form of $Pb(OH)^+$, $Pb(OH)_2$, and $Pb(OH)_3^-$ at different pHs. In an acidic condition, the adsorbent surface protonated; due to the competition between hydrogen and Pb (II) ions, the adsorption decreased [20]. In the alkaline condition, by increasing OH concentration, the adsorbent surface is charged negatively [21]. Furthermore, lead is probably in the form of $Pb(OH)_3^-$. In addition, at a higher pH, due to the repulse forces between $Pb(OH)_3^-$ and surface, the Pb (II) ions' tendency to precipitation is more than adsorption.

3.2. The effect of adsorbent dose

Adsorbent dose is an effective parameter in adsorption processes. To determine the optimum adsorbent doses, the experiment was carried out in the range of (0.15-1.5 g/L) at pH of 6, the initial metal concentration of 10 ppm, and contact time of 100 min. Fig. 2 indicates that with an increment in adsorbent dose from 0.15 to 0.75 g/L, the adsorption increased from 61 % to 89 %. As seen, at a low level of adsorbent dose, the removal was

not efficient due to the deficit of accessible unloaded sites on the adsorbent. Then, with an increment in adsorbent dose, the sites on the surface increase and, subsequently, adsorption increases. With a value of adsorbent dose higher than 0.75 g/L, a

significant increment in adsorption was not obtained, and adsorption was found 90 % at 1.5 g/L of adsorbent dose, corresponding to the overlapping of unloaded sites on the adsorbent surface [22].

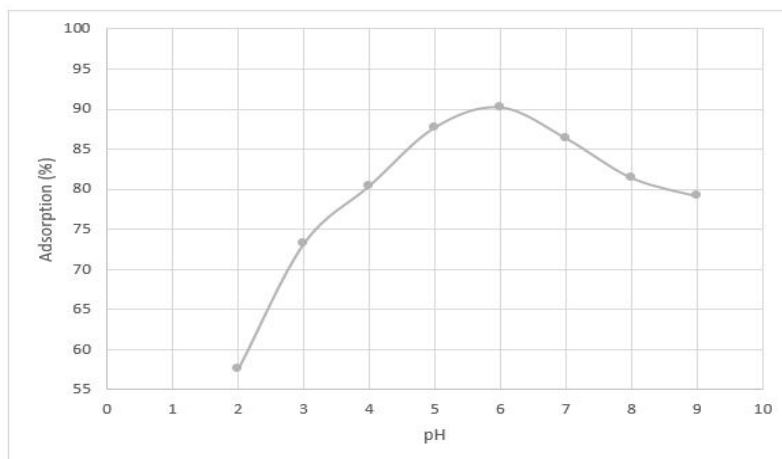


Figure 1. Adsorption as a function of pH.

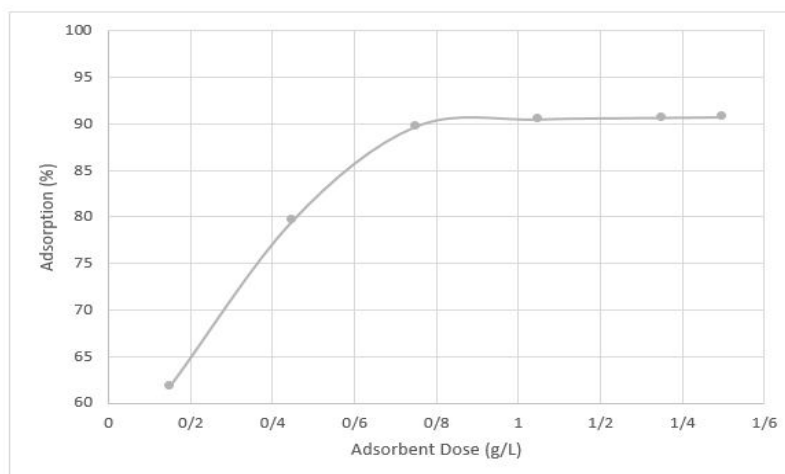


Figure 2. Adsorption as a function of adsorbent dose.

3.3. The effect of initial metal concentration

To determine the optimum initial concentration, adsorption was performed at pH of 6, adsorbent dose of 1 g/L, contact time of 100 min, and the initial concentration in the range of 10 to 100 ppm. Fig. 3 shows the adsorption efficiency as a function of initial metal concentration. As observed, the highest adsorption efficiency (89.98 %) occurred at

the initial concentration of 10 ppm. As observed, by increasing metal concentration from 10 to 20 ppm, the adsorption decreased from 89.98 to 86.24 %; in addition, with a further increase in metal concentration, adsorption was obtained 72.95 % at 100 ppm, which can result from the lack of unloaded sites on adsorbent surface at a higher value of the initial metal concentration.

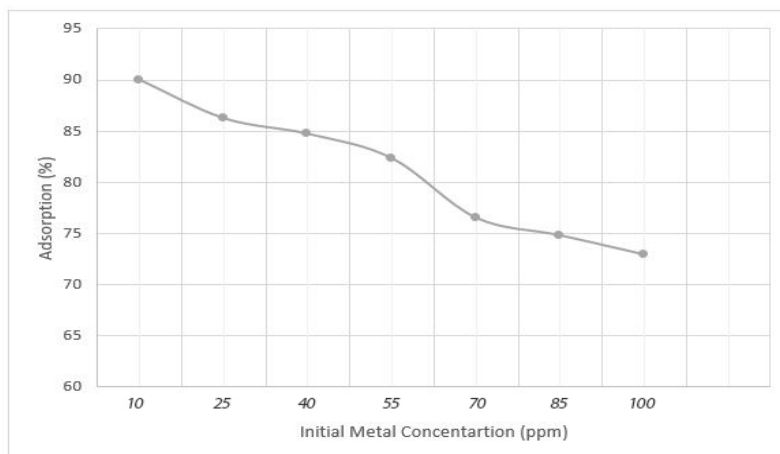


Figure 3. Adsorption as a function of initial metal concentration.

3.4. The effect of contact time

Contact time is an effective parameter in adsorption efficiency. The adsorption was carried out in operational conditions such as pH of 6, the initial metal concentration of 10 ppm, adsorbent dose of 1 g/L, and contact time in the range of 20-200 min. Fig. 4 shows adsorption as a function of contact time. The adsorption process can be divided into two steps of Fast and Slow. According to Fig. 4, the adsorption is rapid in the first 80 min and

increases from 61.59 to 88.37 %; then, it gradually achieves equilibrium. As seen, with a further increase in contact time, a considerable increment was not found; thus, the adsorption was obtained 91.18 % at 200 min. In the beginning of the process, the number of vacant sites on the adsorbent surface was high; thereafter, by occupying the sites, the number of vacant sites decreased and, subsequently, adsorption did not occur.

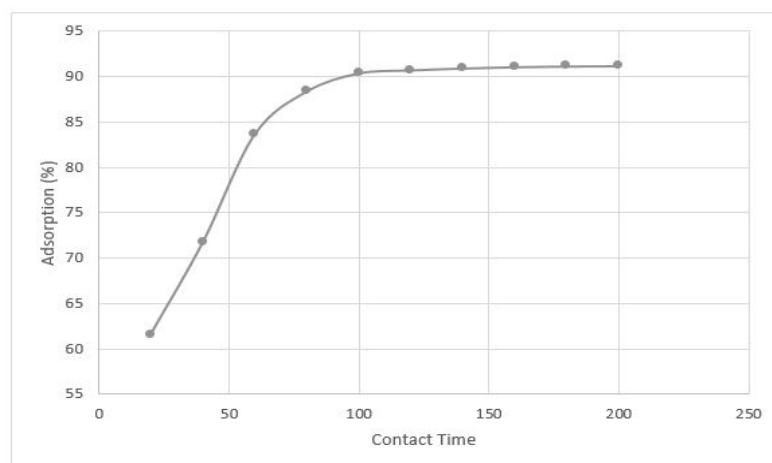


Figure 4. Adsorption as a function of contact time.

3.5. Morphology studies

The morphology of the adsorbent was investigated using SEM analysis (Tescan Vega 2 xmu). Fig. 5(a-b) shows the SEM images of adsorbent before and after the adsorption process, respectively. According to

Fig. 5(a), the porous surface of Henna with a uniform distribution of pores is obvious. Fig. 5(b) indicates the presence of Pb (II) ions on the surface of Henna after the adsorption process; in addition, it is shown that the adsorption process has been efficient.

FTIR (Bruker Optics, Germany) analysis was used to characterize the surface functional groups on Henna surface before and after adsorption of Pb (II). Figs. 6 and 7 show the results of FTIR analysis. The peaks at 3409.87 cm^{-1} correspond to (O-H) stretching vibration on the adsorbent surface. The characteristic peak at 2927.68 cm^{-1} can be attributed to (C-H) stretching vibration. The band appeared at 1632.91 cm^{-1}

corresponding to (C=O) stretching vibration. Also, the bands observed at 1438.57 cm^{-1} are associated with the presence of (S=O) stretching vibration. The peak at λ value of 1243.35 cm^{-1} results from the presence of (C=N). The characteristic peak at 1055.84 cm^{-1} demonstrated the presence of (C-O). Furthermore, the vibration at 518.46 cm^{-1} corresponds to (C-Br) stretching vibration on the Henna surface.

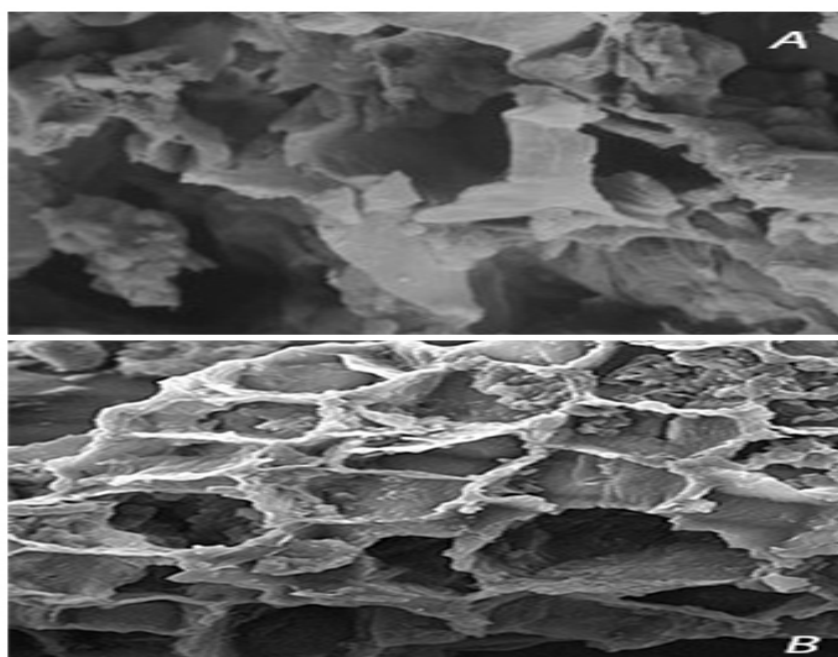


Figure 5. SEM images of Henna (a) before adsorption and (b) after adsorption of Pb (II).

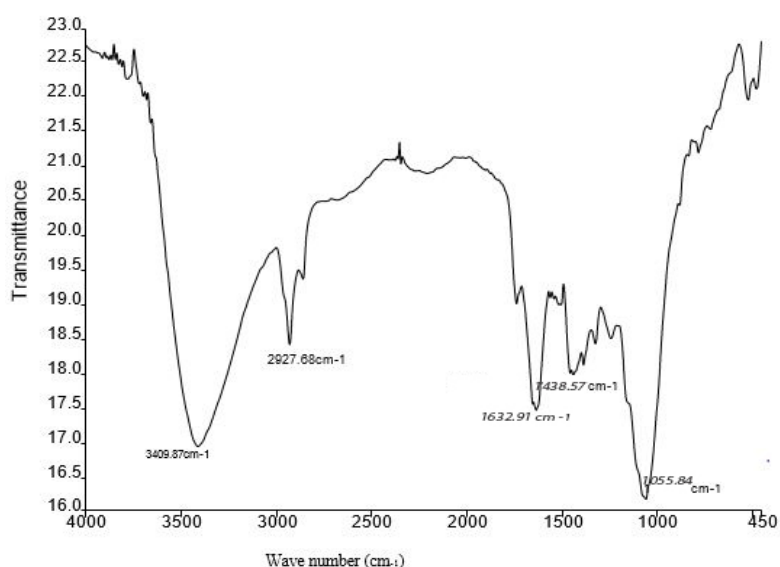


Figure 6. FTIR spectrum of Henna before adsorption of Pb (II).

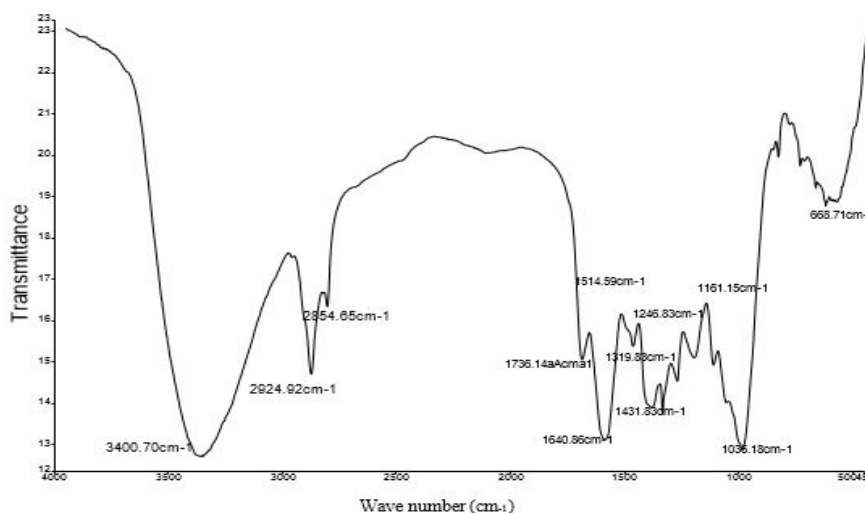


Figure 7. FTIR spectrum of Henna after adsorption of Pb (II).

3.6. Adsorption isotherms

To investigate the adsorption isotherm, Langmuir (Eq. 1) and Freundlich (Eq. 2) adsorption isotherm models were used to describe the adsorption of Pb (II) using Henna.

$$\frac{q_e}{C_e} = \frac{1}{q_{\max}K_L} + \frac{C_e}{q_{\max}} \quad (1)$$

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (2)$$

where C_e is the equilibrium concentration of the solution (mg/L); q_e is the value of adsorption at equilibrium (mg/g); q_{\max} is the maximum adsorption capacity (mg/g); K_L is the Langmuir constant, which indicates the interdependence of the solute and the adsorbent (L/mg); K_F and n are the Freundlich constants relevant to the

adsorption capacity and intensity, respectively.

Figs. 8 and 9 show the plots of Langmuir and Freundlich adsorption isotherm models. Isotherm parameters calculated with simulations are shown in Table 1. The correlation coefficients of Langmuir and Freundlich models were obtained as 0.9784 and 0.9879, respectively, showing that the Freundlich model could describe the experimental data better than the Langmuir model. As observed, correlation coefficients of two models indicate that the models closely fit the experimental data. Also, the calculated values of R_L ($0 < R_L < 1$) and n ($0 < n < 10$) show that the sorption of Pb (II) using Henna has been efficient.

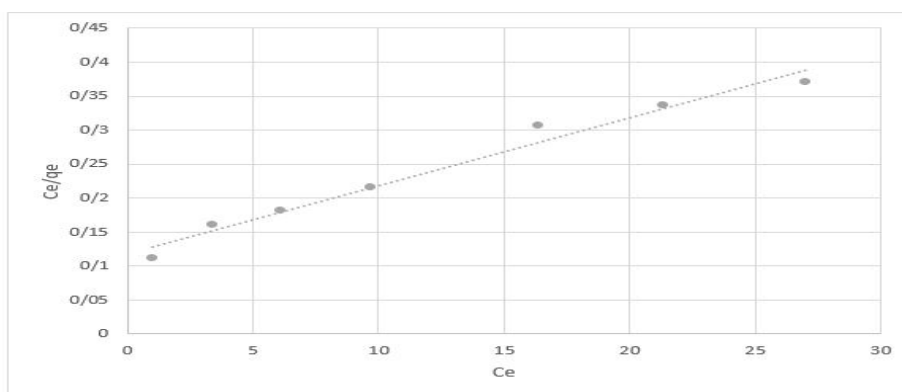


Figure 8. The plot of the Langmuir adsorption isotherm model.

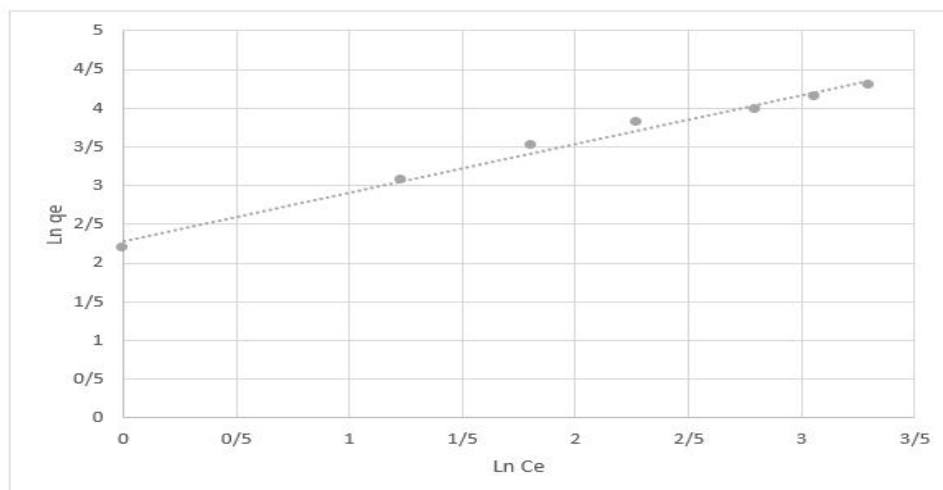


Figure 9. The plot of Freundlich adsorption isotherm model.

Table 1

Langmuir and Freundlich isotherm models parameters.

| | Parameters | Pb (II) |
|------------|-------------------------------------|--------------|
| Langmuir | q_{\max} (mg/g) | 100 |
| | K_L | 0.0845 |
| | R_L | 0.1058-0.542 |
| | R^2 | 0.9784 |
| Freundlich | n | 1.5959 |
| | K_F (mg/g (L/mg) ^{1/n}) | 9.7689 |
| | R^2 | 0.9879 |

3.7. Adsorption kinetics

To analyze the kinetic experimental results, Pseudo-first-order model (Eq. 3) and pseudo-second-order model (Eq. 4) were used.

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (3)$$

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} \quad (4)$$

where q_t is the amount of metal ions adsorbed, q_e is the value of adsorption in equilibrium (mg/g), K_1 is the rate constant of the pseudo-first-order model ($g/mg^{-1}min^{-1}$), and K_2 is the rate constant of

the pseudo-second-order model ($g/mg^{-1}min^{-1}$).

Figs. 10 and 11 show the plots of pseudo-first-order model and pseudo-second-order model, respectively. The calculated relevant parameters are given in Table 2. The results indicate that the calculated adsorption capacities ($q_{e.cal}$) from the pseudo-first-order model for adsorption of Pb (II) are closer to the experimental adsorption capacities ($q_{e.exp}$), while the correlation coefficient of the pseudo-second-order model ($R^2 = 0.9986$) is more than that of pseudo-first-order model ($R^2 = 0.9931$).

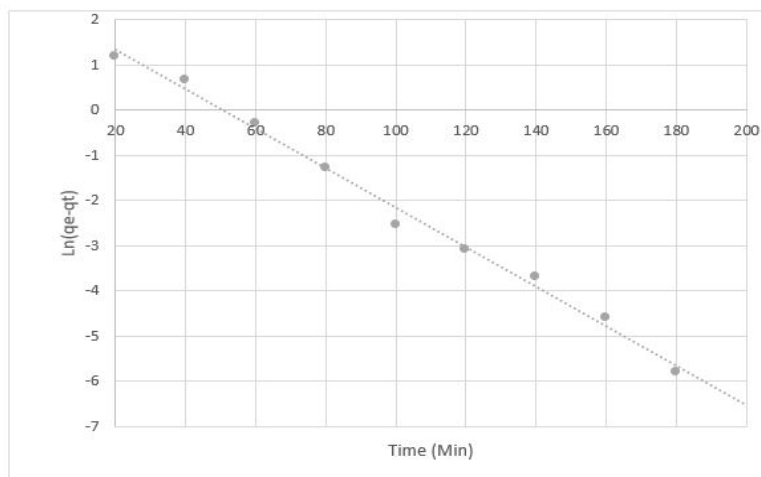


Figure 10. The plot of the pseudo-first-order kinetic model of Pb(II) adsorption.

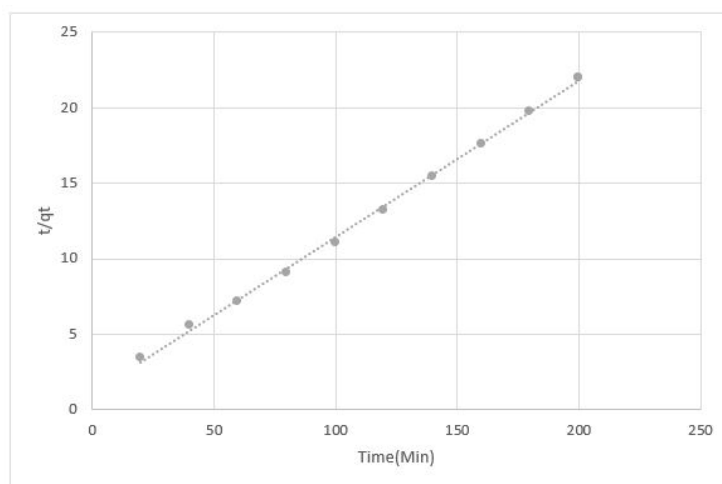


Figure 11. The plot of the pseudo-second-order kinetic model of Pb(II) adsorption.

Table 2

Adsorption kinetic models' parameters.

| Pb (II) | Temperature (°C) | $q_{e.exp}$ (mg/g) | Pseudo-first-order model | | | Pseudo-second-order model | | |
|---------|------------------|--------------------|--------------------------|--------------------|--------|---------------------------|--------------------|--------|
| | | | K_1 | $q_{e.cal}$ (mg/g) | R^2 | K_2 | $q_{e.cal}$ (mg/g) | R^2 |
| | 25 | 9.118 | 0.0437 | 9.144 | 0.9931 | 0.00989 | 9.6805 | 0.9986 |

4. Conclusions

This study investigated the removal of Pb (II) ions using Henna. The effects of the operational conditions, such as pH, contact time, initial metal concentration, and adsorbent dose, were investigated. The optimum condition was provided at pH of 6, contact time of 80 min, the initial metal concentration of 10 ppm, and the adsorbent dose of 0.75 g/L. The adsorption isotherm and

kinetic models were used to describe the sorption of Pb (II) ions. The results showed that the Langmuir isotherm and pseudo-second-order kinetics model highly fitted experimental data. Also, the morphology studies demonstrated the porous surface of the adsorbent with a homogeneous distribution of pores, making it efficient in adsorption of metal ions.

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