Investigation of Affecting Parameters on the Adsorption of Lead (II) from Aqueous Solutions on Henna Powdered Leaves

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ABSTRACT: *In the present study, the removal of lead (II) ions from aqueous solutions was investigated by powdered Henna. Henna is a herbal material that can dramatically adsorb metal ions. Adsorption experiments were carried out in a batch system at room temperature. Then, the equilibrium concentration of each sample was analyzed by atomic adsorption device. The effects of various parameters such as time, initial concentration, adsorbent amount, and pH were investigated. pH, initial concentration, and adsorbent amount showed sharp effects on the adsorption rate. The effect of time on the process was not considerable, as well. The optimum operating conditions were found at pH of 4.78, time of 49.47 min, lead (II) initial concentration of 93.5 mg/L, and adsorbent amount of 1 g led to 97.8% removal of lead (II). Furthermore, Langmuir and Freundlich adsorption isotherms were investigated for the lead (II) adsorption process on Henna. The results showed that Langmuir's isotherm model is more suitable for this process (R^2=0.947).*

KEYWORDS: *Adsorption; Biomass; Henna leaves; Optimization; Pb(II).*

INTRODUCTION

Lead is a non-biodegradable hazardous heavy metal that easily accumulates in the human body. The major source of lead in the human body is the drinking water containing substantial amounts of lead.

It can initially enter the body through the digestive tract and lungs and spread by blood inside the body. Large amounts of lead in the drinking water may cause anemia, cancer, renal kidney disease, nervous system damage, and mental retardation [1-5]. Lead is dangerous for the human body when its amount is more than 15 µg/L

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in the drinking water. The permissible limit for Pb (II) in wastewater given by Environmental Protection Agency (EPA) is around 0.05 mg/l [6, 7]. Since the lead ions concentration in wastewaters exhausted from most of industries is in 200-500 mg/l, it should be reduced up to the EPA protocol before discharging to the ecosystem [7-9].

Various techniques are in progress for the separation and removing the heavy metals [10]. Each of these methods has practical advantages and some disadvantages. Nowadays, adsorption is known as an effective and economical method to treat wastewater from the heavy metals. The adsorption process is flexible in terms of design and operation. It also produces a high-quality refined flow [11]. However activated carbon is an effective adsorbent for the heavy metals removal from wastewaters but, it is expensive and requires chelating agents to enhance its performance. Therefore, it will increase the costs [12]. For the past two decades, there are some researchers focused on using low-cost and efficient adsorbents for the heavy metals removal. Furthermore, the adsorption behavior of several natural materials and biomasses such as clay [16, 17], agricultural by-products [18, 19], some aquatic plants [20, 21] and microorganisms [22, 23] were investigated for the heavy metals removal.

Persimmon leaves contain a large number of hydroxyl groups, and it is very suitable for adsorbing the heavy metals [24]. Georgescu et al. examined the properties and ability of chlorine-pillared clay adsorbent for adsorbing lead ions from aqueous solutions [25].

Sani et al. used ZnO nanocomposite to remove lead and copper from aqueous solutions. They studied the effect of various parameters such as contact time, dose, initial concentration and pH [11]. *Ghosh et al.* studied the separation of copper by the modified tea leaves [26].

Deepa et al. optimized various parameters for copper removal from aqueous solutions by Araucaria [27]. Krishna and Sree removed copper from aqueous solutions using the Flabellifer herb [28]. Kumar et al. conducted a series of batch experiments to investigate the ability of Bengali peel skin to adsorb iron (III) from aqueous solutions [29]. Liu et al. studied Pb (II) removal from an aqueous solution using dithiocarbamate modified chitosan beads with Pb (II) as imprinted ions [30].

The appropriate adsorbent selection with the maximum capacity and minimum consumption has been the subject of a lot of researches in the last decade. Adsorption with natural adsorbent has attracted a lot of attention due to its excellence in terms of separation. Existence of a wide surface per mass unit is a necessary item for an adsorbent selection [31].

In the present study, Henna leaves powder (as a natural, cheap, abundant and non-nutritious material) was applied for lead (II) ions removal from aqueous solutions because there were some researches on the heavy metals adsorption by Henna as a biosorbent [32-36]. This plant originally grows up in Mediterranean countries, Asia (Iran), north and east of Africa, north of India and Madagascar. This process operating conditions were statistically and experimentally considered and discussed, as well.

EXPERIMENTAL SECTION

Materials

Lead nitrate salt (with purity of 99.9% supplied by Merck Company), Henna leaves (purchased from a local grocery), sodium hydroxide and hydrochloric acid (Merck grade) were prepared. The atomic adsorption technique (with a Shimadzu equipment, model: AA-680 Japan) was used to determine the residual Pb (II) in the solutions after each run.

Furthermore, Infrared Spectrometer (FT-IR) (model: Unicam 5000) was used to consider the adsorbent functional groups. The Scanning Electron Microscopy (SEM) (model: JDM35) was used to see the adsorbent morphology before and after adsorption process.

Adsorbent preparation

The purchased Henna leaves were washed twice with deionized distilled water to remove the possible impurities. Then, they were dried in an oven at 100 °C for 24 h. The dried leaves were grinded and passed through the standard screens (Tyler sieves). The particles sizes were around 70-100 µm [32-36].

Experiment procedure

According to the literature, these operating ranges (pH of 2-9, time of 20-200 min, adsorbent dosage of 0.1-1 g and lead (II) initial concentration of 10-100 mg/L) should be suitable and considerable for a heavy metal adsorption on a biomass [36]. 0.16 g of $Pb(NO_3)_2$ (with purity of 99.9%) was dissolved

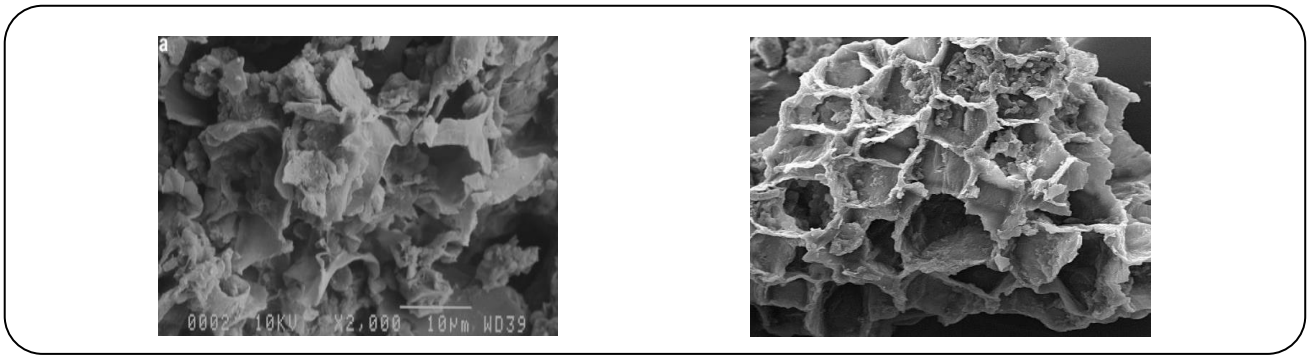

Fig. 1: (a) Henna SEM before adsorption, (b) Henna SEM after adsorption.

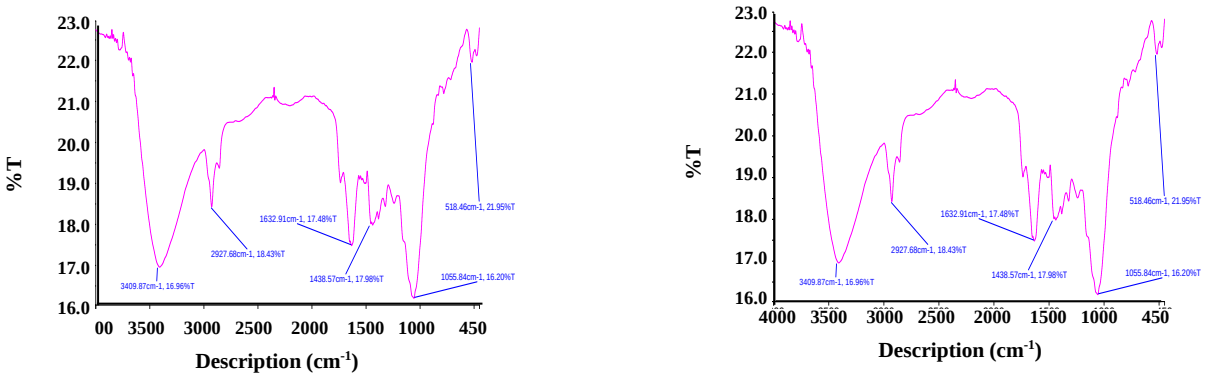

Fig. 2: (a) Henna adsorbent IR spectrum before adsorption process, (b) Henna adsorbent IR spectrum after adsorption process.

in 1000 mL of deionized distilled water. Therefore, a stock solution with concentration of 100 mg/L was produced. This solution was diluted to obtain different solutions with various concentrations as applied in the experiments. The batch experiments were performed in a 250 cm^3 beaker at ambient temperature (25 ± 1 °C). A magnetic stirrer with a constant speed of 600 rpm (without any vortex) was used to mix the adsorbent in the solution.

The pH effect on the adsorption of Pb (II) was considered by adding NaOH (0.1 M) and HCl (0.1 M). The adsorbent was separated from solution by filtering through a cellulose filter (with 0.4 µm pore diameter). Several drops of concentrated HCl were added to the samples to prevent lead deposition. Then, it was stored at temperature of 4 °C. After performing the experiments, the residual lead (II) concentration was measured using a flame atomic absorption spectroscope.

Henna structure consideration

The Scanning Electron Microscopy (SEM) is one of the most famous microscopic methods which can be used for the solids morphological structure consideration. As shown in Fig. 1(a), Henna before adsorption has a heterogeneous and irregular surface where can properly adsorb the metal ions while a very dense structure can be observed after lead (II) adsorption [Fig. 1(b)].

RESULTS AND DISCUSSION

The heavy metals adsorption on the biomasses has direct relation with the functional groups in the plants. Furthermore, the cellular wall of plants is mainly composed of polysaccharides, proteins and lipids, which include many functional groups such as carboxyl, carbonyl, hydroxyl and amino. These functional groups can be joined metal ions and remove them [37]. Henna IR images [before and after lead (II) adsorption] are shown in Figs. 2(a) and 2(b), respectively.

The IR peaks are summarized in Table 1.

IR analysis indicates that there is a difference in the position of some peaks during the adsorption process. In order to recognize the characteristics of the adsorbent functional groups, the infrared spectroscopy (FT-IR) was carried out. According to FTIR tests, the Henna contains

Table 1: IR spectra characteristics before and after adsorption process.

IR peak	Adsorption bands (cm^{-1})			Functional groups
	Before adsorption	After adsorption	Difference	
1	3409.87	3400.70	-9	O-H
2	2927.68	2924.92	-3	C-H
3	1632.91	1796.14	164	C=O
4	1438.57	1431.83	-7	S=O
5	1243.35	1246.83	3	C=N
6	1055.84	1035.18	-20	C-O
7	518.46	663.71	145	C-Br

many active functional groups which are able to adsorb metal ions such as Pb (II). The bands at 3409-3400 cm^{-1} are related to O-H functional group. The broad peaks at 2927-2924 cm^{-1} are related to the functional group of –CH. The bonds observed at 1632-1796 cm^{-1} belong to the functional group of C=O while the bands at 1438-1431 cm^{-1} are related to the functional group of S=O. The peaks at 1243-1246 cm^{-1} are related to the C=N functional group. The bands at 1055-1035 cm^{-1} are related to the functional group of –C-O. The functional groups of -O-P-O, $–PO_4$ and C-Br appear in the range of 518-663 cm^{-1}. The functional groups provide an electron which increases Pb (II) adsorption tendency. FTIR analysis shows that there are some changes in the adsorption peaks after adsorption. It seems that C=O functional group (at 1796 cm^{-1}) is the most effective functional group [38-40].

Effect of initial pH

pH of aqueous solution is an important parameter in the adsorption process. This directly depends on the competitive ability between hydrogen ions and metal ions on the active sites of adsorbent. In fact, hydrogen of hydroxyl functional group (from Henna) is replaced by Pb^{2+} and H^+ is then released in the solution. This will decrease pH of solution. Furthermore, the functional groups generally are in the segregated status and can exchange H^+ with the metal ions (Pb^{2+}) when solution pH is more than pka (acidic segregation constant). In the other words, the metal cations cannot be connected to the functional groups due to lacking the functional groups in the solution with low pHs. Therefore, there is limitation in the metal ions removal from a solution with low pH (as Pb^{2+} removal was low for the solutions with $pH \leq 2$) [41, 42]. Therefore, the adsorption process increases by increasing pH. It is due to the competition reduction between protons and metal ions for detection of active sites (positive charge loss).

The effect of pH on lead (II) adsorption by Henna was investigated in the range of 2 to 9. As shown in Fig. 3, the final concentration of lead (II) rapidly increased in the pH range of 2 to 5.5 while further increment in pH (up to 9) decreased the adsorption efficiency. This reduction reason (above 5.5) may be due to the competition between hydroxide ions in the solution and the adsorbent sites for the metal ions detection [42].

Adsorbent mass effect

The adsorbent amount is an important parameter in the metal adsorption by an adsorbent. In fact, the adsorbent optimum amount can reduce the treatment cost, contamination and sludge amounts. Fig. 4 shows the effect of Henna amount on the removal rate of lead (II). As shown in this figure, the lead (II) removal increased by Henna amount increment. It is due to existing greater number of active sites [43].

Initial concentration effect

According to Fig. 5, adsorption amount sharply increases when the initial concentration rises. This behavior is properly supported by literature [43].

Contact time effect

As shown in Fig. 6, the adsorption process can generally divide in two steps. First step is a low rate one.

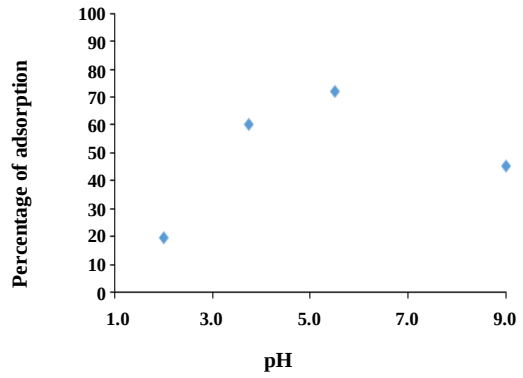

Fig. 3: pH effect on the lead (II) adsorption by Henna.

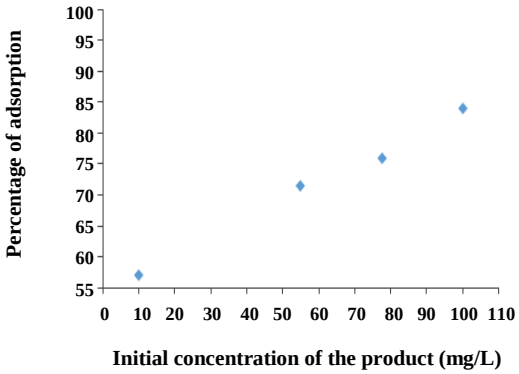

Fig. 5: Effect of initial concentration on the adsorption by Henna adsorbent.

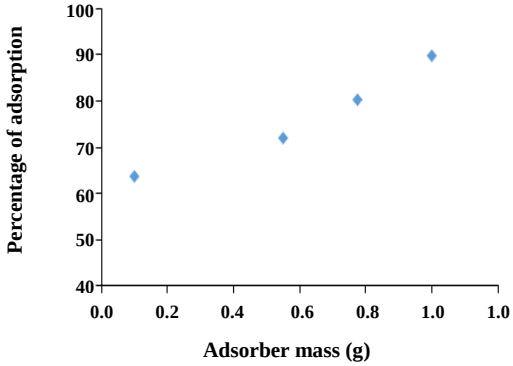

Fig. 4: Effect of adsorbent amount on lead adsorption by Henna adsorbent.

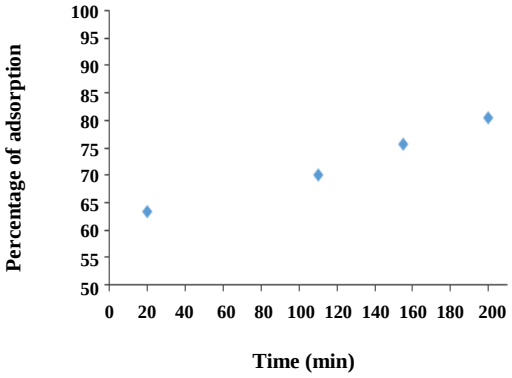

Fig. 6: Effect of time on the adsorption by Henna adsorbent.

It is related to the internal diffusion of metal ions. Second step is rapid rate one. In fact, the functional groups are located in the adsorbent cell wall in this step. The active sites frequency reduction decreases the adsorption rate while the presence of plenty of porosity and the structure of the cavities in the adsorbent allow fast diffusion for the metal ions in the bonded sites [44].

Optimization procedure

The Pb (II) removal percentage obtained from the experiments were transferred in a statistical software (DoE: version 7) for each run and maximum lead (II) removal was targeted. The optimum operating conditions were statistically found at pH of 4.78, time of 49.47 min, lead (II) initial concentration of 93.5 mgL^{-1} and adsorbent amount of 1 g for 100% removal of lead (II). Then, these conditions were experimentally provided and 97.8% removal of lead (II) was found and validated in an individual experiment (optimized one).

Isotherm models

One of this work aims was to find a model that describes the experimental data behavior. For this purpose, Freundlich and Langmuir isotherm models were used to justify adsorbent-adsorbate behavior. Two linear and nonlinear regression methods were applied to investigate a suitable model. The linear regression normally is simpler and easier due to its assumptions [45]. Figs. 7 and 8 show Freundlich and Langmuir isotherm models, respectively.

As shown in Table 2, the determination coefficient data for Freundlich and Langmuir models are 0.818 and 0.947,

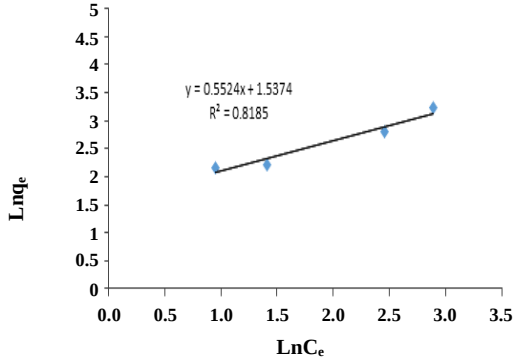

Fig. 7: Freundlich isotherm model for Pb (II) adsorption on Henna. [q_e which is equilibrium adsorption capacity of Henna (mg adsorbate/g adsorbent) and C_e which is equilibrium concentration of Pb(II) in solution (mgL^{-1})]

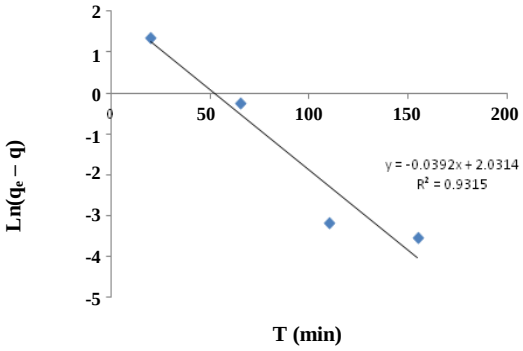

Fig. 9: Pseudo-first-order kinetic model. [ln (q_e-q) which is natural logarithm of difference between equilibrium adsorption capacity of Henna (mg adsorbate/g adsorbent) and adsorption capacity of Henna as a function of time vs. time (min)].

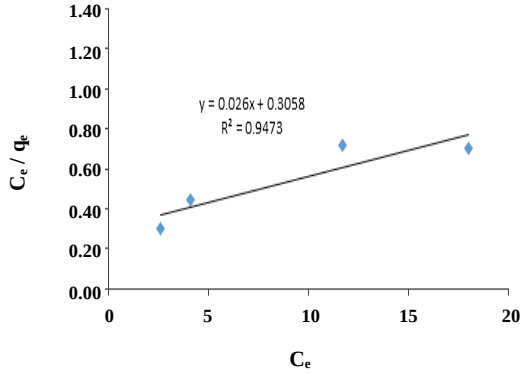

Fig. 8: Langmuir isotherm model for Pb(II) adsorption on Henna. [q_e which is equilibrium adsorption capacity of Henna (mg adsorbate/g adsorbent) and Ce which is equilibrium concentration of Pb(II) in solution (mgL^{-1})].

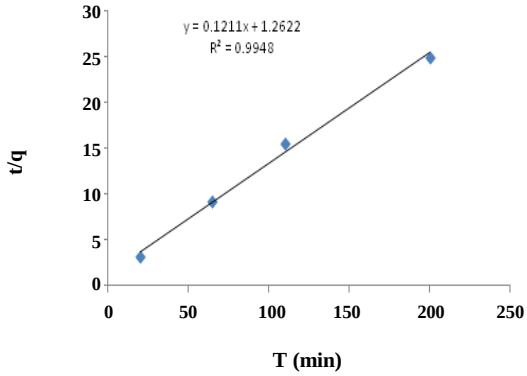

Fig. 10: Pseudo-second-order kinetic model. [t/q which is time per adsorption capacity of Henna as a function of time vs. time (min)].

respectively. Therefore, the Langmuir model is more consistent with the experimental data [36].

Kinetic study

The adsorption kinetic models are shown in Figs. 9 (pseudo-first-order kinetic model) and 10 (pseudo-second-order kinetic model).

According to these two models data illustrated in Table 3, pseudo-second-order kinetic model can properly applied for this process (R^2=0.994). Furthermore, thermodynamic parameters for Pb(II) adsorption on Henna were shown in Table 4. As shown in this table, the adsorption process was physisorption and exothermic one (ΔH=-25.166 kj/mol) [36].

CONCLUSIONS

In this study, Henna herbal as an adsorbent was used for lead (II) ions removal from aqueous solutions. The results showed that the adsorption increased with increasing pH and adsorbent amounts. Moreover, the adsorption increased with increasing contact time and initial concentration of Pb(II). The optimum operating conditions were statistically and experimentally found. Langmuir isotherm model was more appropriate

Table 2: Two applied isotherm models data.

Isotherm	Freundlich	Langmuir
	$\ln q_e$ vs. $\ln C_e$	$\frac{C_e}{q_e}$ vs. C_e
Equation	$\ln q_e = 0.552 \ln C_e = + 1.537$	$\frac{C_e}{q_e} = 0.26C_e + 0.306$
R^2	0.818	0.947
Isotherm adsorption parameters	K_f = 4.65	K_L = 0.085
	n = 1.81	q_{max} = 38.46

Table 3: Two kinetic models data.

Pseudo-first-order data			Pseudo-second-order data		
q_e-Calculated	K_1	R^2	q_e-Calculated	K_2	R^2
7.624	0.039	0.931	8.25	0.01	0.994

Table 4: Thermodynamic parameters for Pb(II) adsorption on Henna

T(K)	ΔG (kj/mol)	ΔH (kj/mol)	ΔS (j/mol.k)
298	8.66-	25.166-	55.146+
308	8.38-		
318	7.65-		
328	7.03-		

than the Freundlich one for this process. It was concluded that Henna is a suitable bio-adsorbent for lead (II) removal.

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