Removal of lead ion from Industrial Wastewater by using Date Palm Seed as a Low-Cost Adsorbent

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Abstract

Date palm seed (*Phoenix dactylifera L.*) was using as an adsorbent product to remove lead ions from aqueous solutions through the batch adsorption process. In this study, the optimum condition used to determine the adsorption of industrial wastewater were including pH, temperature, agitation speed and contact time. The results were evaluated by using seeds of two date palm cultivars (Hillawi and Zahdi) The results showed that, the highest removal ratio of lead ions from industrial wastewater samples achieved by Hillawi seeds was $0.598\,mgg^{-1}$, 79.81% at Time 90 min., pH 6.5, agitation speed 50 rpm and Temp. 25°C. While Zahdi seeds were shown the results $0.349\,mgg^{-1}$, 43.65% at Time 90 min., pH 4.5, agitation speed 200 rpm and Temp.35°C. Surface morphology and functional surface groups determined by used the scanning electron microscopy and infrared spectroscopy (FT-IR) respectively.

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Keywords: Adsorption, Date Palm Seed, Lead Removal, FT-IR, SEM.

Introduction

The wastewater of industrial processes is conceder as an important source of heavy metal pollution. If discharged without treatment, these effluents may cause harm to human health and the environment. The Heavy metal ions like lead, chromium, zinc, cadmium, copper, nickel, etc. should be removed from the wastewater of industrial (Danish *et al.*, 2011).

The rise of industrialization and human activities has become a large issue nowadays, as large amounts of waste of heavy metals are directed throwing to surface waters, rivers and ponds, That will disturb the ecosystem and make it inappropriate for the consumption of humans (Bayuo . 2019).

Heavy metals pose a high toxicity to humans and the environment, because they non-degradable, thus tend to accumulate in the tissues of humans, plants, and animals (Alatabe and Kariem, 2019).

Lead has a strong effect and may lead to harm to the livers, kidneys, and reproductive system, as well as brain functions and basic cellular processes. The symptoms of lead poisoning are dizziness, Anemia, insomnia, muscle weakness, headache, kidney damage, irritability and hallucinations (Mansour *et al.*, 2016).

Among all the techniques involving the recovery of industrial and municipal wastewater, adsorption is generally very appropriate through its high effectiveness and whole elimination of metal ions even at cost is low, concentration is less, separation of sorbents and ease of adjustment. From the phase of aqueous after the completion of the treatment (Sulyman *et al.*, 2017).

The adsorption considered an integral technique of water treatment and recovery. Also can use to eliminate organic, inorganic and biological contaminants with an elimination efficiency of up to 99%. Therefore, the technique has attracted attention to the treatment of industrial wastewater (Shafiq *et al.*, 2018).

The seed of the date is the main by-product of the date fruit and represents around 10% of the date fruit. In addition, it's contain a high percentage of the ashes (1.12-1.15)%, proteins (5.17-5.56)%, carbohydrates (81.0-83.1)%, oleic acid (41.3-47.7)%, oil (10.19-12.67)%, and the seeds of Date

contain also total phenols and flavonoids, which, unlike the accumulation of heavy metals play a chelating role (Mohammadi *et al.*, 2016).

The aim of the current study evaluating the capability of date palm seeds to adsorb pb (II) ions of aqueous solutions by using various conditions.

Materials and Methods

Experimental Part

Chemicals

The stock solution prepared by dissolving 1g of lead nitrate in 1000 ml of deionized water. Then has made a serial dilution by using deionized water to concentrate the aqueous solution to 25 mg l^{-1}. The pH of the solution adjusted into 4.5-8.5 by adding the diluted solution (0.1M) of HCl or NaOH.

Adsorbent

Approximately 4000g of two kinds of date palm seeds (Hillawi and Zahdi) collected from Basrah-Iraq, during 2017. Date palm seeds (DPS) repeatedly rinsed with running water to clean then dried in the sun for 24h. The DPS crashed by an electric grinding machine and screening at 63 microns (Retsch, Germany) after that the powder dried at 100°C for 2h (Bingöl *et al.*, 2013; Mohammadi *et al*., 2017).

Adsorption experiments

Added 0.5 g of DPS powder into 15ml of lead solution (25 mgl^{-1}) in Erlenmeyer flasks. Subsequently, the flasks were incubated on various conditions which including shaking at 50-200 rpm, temp (15-55)°C, pH (4.5-8.5)and time(0-180) min until an equilibrium. The solution was filtered using Whatman filter paper No. 40 and analyzed the content of Pb by an Atomic Absorption Spectrophotometer (AA7000-Shimadzu) (Bingöl *et al*., 2013; Mohammadi *et al*., 2017).

According to the following equation was calculated the percentage of metal adsorption:

Removal % = {(C_i-C_e) /C_i}*100

Where C_i and C_e are the initial and equilibrium concentration of metal ions (mgl^{-1}) in solution.

 Equation for the adsorbent:

$q_e = (C_i-C_e)$ V/W

Where q_e is the adsorption capacity (mgg^{-1}), V is the volume of the metal ion solution (L), and W is the weight of the adsorbent (g).

FT-IR analysis

The analysis of Fourier Transform Infrared (FT-IR) achieved with a Shimadzu spectrometer (FT-IR-8 400).

SEM

The characterization of DPS Hillawi and Zahdi (1-50µm) before and after the adsorption of lead ions was through scanning electron microscopy (SEM). The samples attached to pieces of brass with double-sided tape. The SEM images taken with a scanning electron microscope (TESCAN MERA III, Czech Republic) at magnifications of 800 to 7500. The working distance of 4 to 5mm maintained and the images taken by 100X acceleration waves for the Hillawi and 50X for the Zahdi using a secondary electron detector.

Results and Discussion

Effect of Contact Time on Lead Adsorption

The experiments performed in triplicate to determine the required time for the balance of lead adsorption in DPS to reach equilibrium at pH 6.5, agitation speed 200 rpm and temperature 20°C. Slower adsorption of lead observed during the first 60 min, after that a high adsorption for about 90 min, and a high constant adsorption capacity observed between 90 to 180 min. The results showed that the higher adsorption capacity was 0.668mgg^{-1}, 82.56% for DPS cultivar Hillawi after 90 min. While, was 0.122mgg^{-1}, 16.21% for DPS type Zahdi at the same time (Table 1). Yadav et al., (2013) reported that the Pb case of the adsorption process was rapid and the optimum established in 120 min. Mohammad et al., (2017) discovered that greater adsorption achieved by increasing contact time. That is the initial stage a high number of free surface sites for adsorption are available and

that the remaining free surface is difficult to fill after some time during to the repulsive forces between the molecules dissolved in the solid phases and volumetric (Danish *et al.*, 2011a).

Table 1: The effect of contact time on the removal efficiency of lead.

Time	Weight capacity of Adsorption mgg^{-1} (q_e)	Adsorption %
Hillawi		
0	0.010	1.86
5	0.256	34.57
10	0.298	39.29
20	0.349	43.97
30	0.258	34.94
40	0.330	41.93
50	0.381	50.87
60	0.361	48.24
90	**0.668**	**82.56**
120	0.666	82.14
180	0.660	80.72
Zahdi		
0	0.004	0.59
5	0.055	7.39
10	0.076	10.15
20	0.037	4.92
30	0.044	5.85
40	0.047	6.21
50	0.034	4.47
60	0.027	3.54
90	**0.122**	**16.21**
120	0.122	16.21
180	0.122	16.21

Effect of pH on Lead Adsorption

The results of pH (4.5-8.5) on the adsorption of lead shown in Table (2) at time 90 min, agitation speed 200 rpm and temperature 20°C. The percentage of adsorption of Pb in DPS Hillawi increased at pH 4.5 and 6.5 and the maximum elimination was achieved at pH 6.5(0.680 mgg^{-1}, 90.67%). A similar trend observed in lead adsorption at pH 6.5 (Danish *et al.*, 2011b).

The efficiency of the Pb adsorption in DPS of Zahdi type increased at pH 4.5 and the elimination decreased slightly from pH 5.5 to 7.5 (0.360 mgg^{-1}

, 48.01%), because of the increase of pH in solution more than 7 lead to deposits of Pb (Alatabe and Kariem, 2019). The adsorption under acidic conditions confirms the competition of H^+ ions with lead ions, which makes adsorption of lead ions difficult on the surface. In addition, the protonation of groups functional on the surface of the adsorbent results in the electrostatic repulsion of metal ions, thus minimizing their adsorption (Amin *et al.*, 2017).

Table 2: The pH effects on the removal efficiency of Lead.

pH	weight capacity of Adsorption mgg^{-1} (qe)	Adsorption %
Hillawi		
4.5	0.656	87.44
5.5	0.670	89.20
6.5	**0.680**	**90.67**
7.5	0.698	92.95
8.5	0.702	93.63
Zahdi		
4.5	**0.360**	**48.01**
5.5	0.141	18.80
6.5	0.018	2.45
7.5	0.503	67.01
8.5	0.677	90.23

Effect of Temperature on Lead Adsorption

Adsorption experiments were carried out to investigate the temperature effect was (15-55)°C on the lead ions adsorptions at time 90 min, agitation speed 200 rpm , pH (6.5 for Hillawi and 4.5 for Zahdi). Into table (3), the capacity of adsorption of Pb in DPS Hillawi appeared increasing at 25°C (0.645 mgg^{-1}, 85.99%). Samra et al., (2014) recorded high adsorption to Pb at 25°C. While in DPS Zahdi, the adsorption rate of the Pb ion was relatively high at 35°C (0.019 mg g^{-1}, 2.45%). (Rajamohan *et al.*, 2014) found the adsorption increased when the temperature increased from 25 to 35°C. According to the theory of adsorption, the adsorption process decreases with increasing temperature, and molecules previously adsorbed on a surface tend to desorb from the surface at high temperatures. The reduction in adsorption with the rising of temperature indicates a weak adsorption interaction between the surface of biomass and the ion of metal (Horsfall and Spiff, 2005).

Table 3: The temperature effect on the removal efficiency of Lead.

Temperature °C	weight capacity of Adsorption mgg^{-1} (q_e)	Adsorption %
Hillawi		
15	0.642	85.66
25	**0.645**	**85.99**
35	0.640	85.40
45	0.567	75.66
55	0.569	75.96
Zahdi		
15	0.005	0.74
25	0.010	1.30
35	**0.019**	**2.45**
45	0.006	0.86
55	0.006	0.86

Effect of agitation speed on Lead Adsorption

The mixed speed effects of Pb removal efficiency was investigated during the varying stirring speed (50-200) rpm at time 90 min, pH (6.5 for Hillawi, 4.5 for Zahdi) and temperature (25°C for Hillawi, 35°C for Zahdi). The adsorption efficiency of Pb in DPS Hillawi generally increased in 50 rpm (0.680 mgg^{-1}, 90.68%), whereas in DPS Zahdi the adsorption of Pb is effective when the agitation rate increases (0.100 mgg^{-1}, 13.39 %) since the mixed speed increased from 50 rpm to 200 rpm (Table 4). Nomanbhay and Palanisamy (2005) found that the removal efficiency of Cr from the adsorbent of chitosan-coated acid beads increased as the mixing speed rise from 50 rpm to 100 rpm. This indicates that agitation speed in the range of 100-200 rpm is sufficient to ensure that all the binding sites of the surface are readily available for absorption. However, other studies have shown that higher agitation speed leads to a decrease in adsorption capacity (Jamil et al., 2011, Omri *et al.*, 2012). As described by Jamil *et al.*, (2011) this is due to a very high agitation rate, the energy kinetic of both adsorbate molecules and adsorbent particles increased enough to collide sharply; releasing adsorbate molecules caused by the separation of adsorbate the particles.

Table 4: The agitation speed effects on the removal efficiency of Lead.

agitation Speed (rpm)	weight capacity of Adsorption mgg^{-1} (q_e)	Adsorption %
Hillawi		
50	**0.680**	**90.68**
100	0.651	86.75
150	0.652	86.89
200	0.006	0.86
Zahdi		
50	0.033	4.44
100	0.037	4.90
150	0.047	6.31
200	**0.100**	**13.39**

FT-IR

FT-IR spectroscopy has high importance in the diagnosis of different functional groups, the infrared spectrum appear a variety of packages indicating that there are multiple effective groups responsible for the adsorption of the elements under study. The FT-IR spectrum of Hillawi seeds powder was measure as shown in figure (1). The band of the hydroxyl groups (OH) showed at 3336 cm^{-1}. This group is found in glucose, which is the basic unit of cellulose structure, as well as the bands at 2927 and 2854 cm^{-1} belonged to aliphatic C-H group, and the band, which appeared at 1743 cm^{-1} might be attributed to the presence of carbonyl group (C = O). On another hand, the group C = C and C = N were appeared at 1612 cm^{-1}, while the bands at 1249 cm^{-1} and 1373 cm^{-1} might be due to C-O and C-N group, respectively. All these groups have the ability to bind to the element under study by the process of physical or chemical adsorption. The presence of acid functional groups is responsible for their adsorption property. The biochemical properties of acidic functional groups are responsible for their adsorption of metal ions according to their studies on natural plant substances (Alatabeand Kariem, 2019).
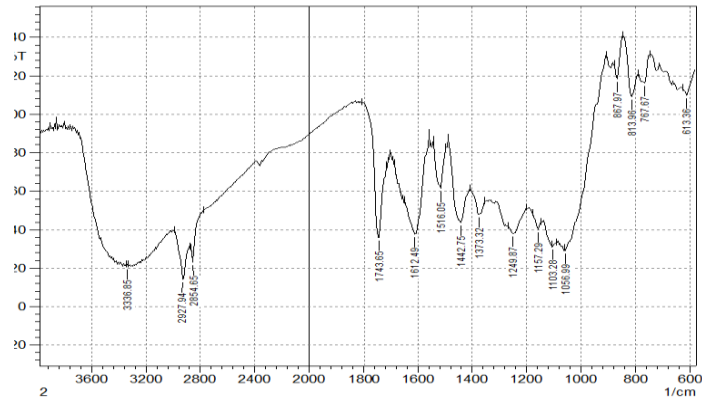
Fig.1: FTIR study of DPS Hillawi adsorption

Figure (2) represents the infrared spectrum of the Zahdi seeds powder, where all the measurement of FT-IR spectroscopy carried out by using the KBr disk and at the range between 4000-400 cm^{-1}. The infrared spectrum shows a strong band at 3302 cm^{-1}, which might be due to the presence of OH group, while the band at 1747 cm^{-1} might be attributed to the carbonyl group. The bands appeared at 1662 cm^{-1} and 1608 cm^{-1}, which might be attributed to the $C = C$ and $C = N$ group, which is included in the cellulose composition, whereas the C-O and C-N bands showed at 1246 and 1373 cm^{-1} and the C-H group appeared at 2924, 2854 cm^{-1}. It was also described in activated date stone by Danish et al., (2011) whose pure spectrum has bands at 2923.29 cm^{-1} (due to the asymmetric stretching of C-H of methylene groups in aliphatic compounds or fragments) and 2855.79 cm^{-1} (vibration has symmetric C-H of methylene groups in aliphatic compounds or fragments).
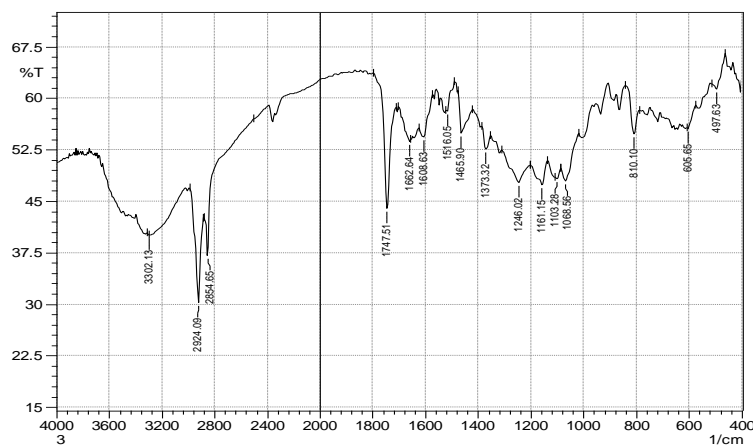

Fig.2: FTIR study of DPS Zahdi adsorption

SEM

The specific surface area of the solid adsorbent is important because the adsorption capacity generally increases with an increase in the specific surface area. Natural materials are available in large amounts and have a big surface area and high cation exchange capacity, which are the necessary properties of an adsorbent. Therefore, a larger internal surface results in a greater adsorption capacity (Shafiq *et al.*, 2018).

The SEM images present asymmetric pores that were rough and cylinders on the DPS surfaces before the lead ions adsorbed. The rough surface of these asymmetric pores helps improve interaction with heavy metal ions (Fig.3 a, c). After lead adsorption, the surface of the DPS becomes bright and smooth and closed the pore structures. (Fig.3 b, d) possibly due to the physicochemical interaction between the functional groups present on the surface of the DPS and the lead ion (Amin, 2017).
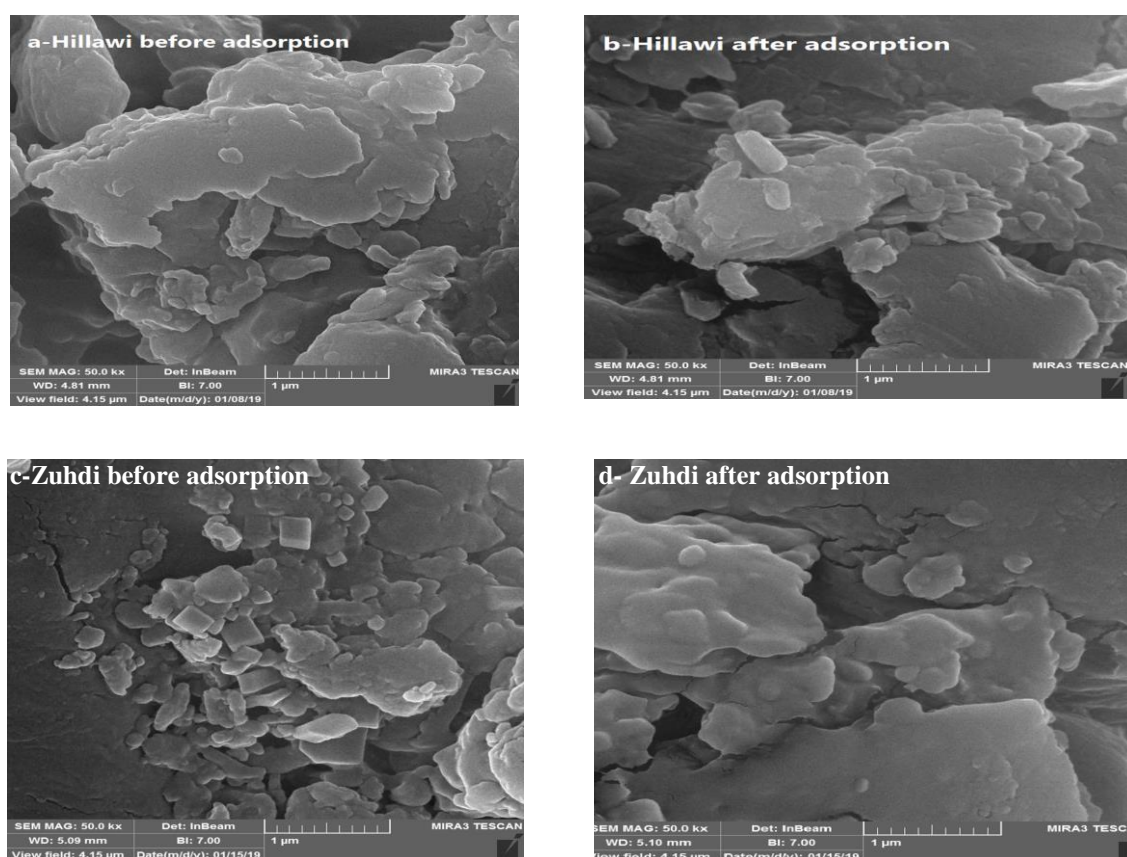

Fig.3: SEM images of DPS before and after pb adsorption

Application of the suggested method to real samples

The percentage and capacity of lead ion adsorption in the optimal condition of DPS Hillawi was 0.680mgg^{-1}, 90.67% and DPS Zahdi 0.360mgg^{-1}, 48.01% has shown in (Table 5).

Table 5: Adsorption of lead in the aqueous solution by DPS

Adsorbent	pH	Time (min)	Temperature °C	agitation speed	Weight capacity of Adsorption mgg^{-1} (qe)	Adsorption%
Hillawi	6.5	90	25	50	0.680	90.67
Zahdi	4.5	90	35	200	0.360	48.01

Under the same optimized conditions of lead ion adsorption on the aqueous solution in this experiment has applied to the real wastewater sample to get a suitable result. The industrial wastewater samples results summarized in table (5). The industrial wastewater sample collected from site of Nahr Binomar in Basrah governorate Southern of Iraq.

Table 6: Adsorption lead in the industrial sample by DPS

Adsorbent	pH	Time (min)	Temperature °C	agitation speed	Weight capacity of Adsorption mgg^{-1} (qe)	Adsorption%
Hillawi	6.5	90	25	50	0.598	79.81
Zahdi	4.5	90	35	200	0.349	43.65

The agricultural wastes generally contain cellulose, hemicellulose and lignin polysaccharides in their cellular components as main structural components. Therefore, they are called lingo cellulosic substances. The biochemical substances structures are partially linked to several functional groups like carbonyl groups, hydroxyl, and methyl. As sorbents for the sorption of lead ions (Sulyman *et al.*, 2017).Date palm is considered the best biosorbent to remove all types of wastewater from industrial effluents, but it is especially effective for removing heavy metals (Shafiq *et al.*, 2018).

Conclusions

In summary, we have used an adsorbent consisting of date palm seeds from two cultivar of the Date palm fruit. The result showed an efficient removal

of lead from the industrial water and we determined the rapid adsorption rate, high adsorption capacity, optimum pH, the contact time, temperature and the optimum mixing speed. The capacity of adsorption in the following order: Hillawi ($0.598 mgg^{-1}$, 79.81%)> Zahdi ($0.349 mgg^{-1}$, 43.65%).As a result, it can conclude the DPS is an appropriate adsorbent for the removal of lead ions from industrial wastewater. Moreover, DPS is a natural, economical and abundant material. Other studies on the adsorption of other metals with activated date palm seeds will also optimize the treatment of industrial wastewater containing a variety of several metal ions.

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إزالة أيون الرصاص من مياه الصرف الصناعية باستخدام نواة نخيل التمر كمادة ممتزة ومنخفضة الكلفة

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الخلاصة

تم استخدام نواة نخيل التمر (.Phoenix dactylifera L) كمادة ممتزة لإزالة أيون الرصاص من المحاليل المائية. في هذه الدراسة، كانت الظروف المثلى المستخدمة لتحديد امتزاز مياه الصرف الصناعي تشمل درجة الحموضة ودرجة الحرارة وسرعة الدوران ووقت الاتصال ، من خلال تجربتها اولا على محلول قياسي تم تحضيره مختبريا. وبعدها استخدمت الظروف ذاتها على العينة الحقيقية لمياه الصرف الصحي لغرض الحصول على النتائج المناسبة لامتزاز ايون الرصاص. تم تقييم النتائج باستخدام نواة صنفين من نخيل التمر (الحلاوي والزهدي) حيث أظهرت النتائج أن أعلى نسبة إزالة لأيون الرصاص من عينات مياه الصرف الصناعي التي حققتها نواة الحلاوي كانت 0.598ملغم /لتر، ونسبة مئوية 79.81% خلال 90 دقيقة واس هيدروجيني 6.5، وسرعة دوران 50 دورة / الدقيقة وبدرجة حرارة 25 درجة مئوية. بينما أظهرت نتائج استخدام نواة الزهدي قابلية امتزاز 0.349ملغم/لتر، ونسبة مئوية 43.65٪ خلال 90 دقيقة، وأس هيدروجيني 4.5، سرعة دوران 200 دورة / الدقيقة، ودرجة حرارة 35 درجة مئوية. وتم تقييم الشكل الخارجي للأسطح الممتزة والمجاميع الفعالة التي لها القابلية على الامتزاز باستخدام فحص المجهر الإلكتروني (SEM)ومسح الأشعة تحت الحمراء (FT-IR) على التوالي.

الكلمات المفتاحية: امتزاز، نوى التمر، إزالة ايون الرصاص، FT-IR، SEM