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Removal of lead (II) and cadmium (II) from aqueous solutions by adsorption on date pits modified by DTPAD

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ABSTRACT

The objective of this work is to study the adsorption of lead and cadmium on raw date pits. In a second phase we cross linked carboxylic functions from Diethylenetriaminepentaacetic dianhydride (DTPAD) on raw date pits in order to evaluate any improvement of the adsorption capacity of the adsorbent. We used mathematical models of Langmuir, Freundlich, Temkin and Dubin-Radushkevich to represent the adsorption isotherms and evaluate which model fits correctly the adsorption mechanism. It was observed that the adsorption capacity of raw date pits (RDP) was increased after the functionalization of RDP with DTPAD. According to Langmuir isotherm, the maximum uptake capacities (q_{max}) were 15.625 mg and 59.17 mg of lead(II) per gram of RDP and modified-RDP respectively, while they were 8.55 mg and 89.3 mg of cadmium(II) per gram of RDP and modified-RDP respectively. The adsorption energy for RDP powder was 22 kJ/mol and 10 kJ/mol for Pb^{2+} and Cd^{2+} respectively, suggesting that the process of the adsorption of Pb^{2+} is a chemisorption while an ion exchange process is dominant in the adsorption of Cd^{2+}. The adsorption energy was around 8.45 kJ/mol and 7.07 kJ/mol on modified-RDP powder for Pb^{2+} and Cd^{2+} respectively; inducing that an ion exchange reaction occurs for Pb^{2+} and a physisorption takes place for Cd^{2+}. We performed FT-IR spectroscopy to characterize the raw and the modified powder. The analysis of the powder via scanning electronic microscopy indicates the formation of linking bridges.

Keywords: Date pits; Heavy metals; Adsorption; Lead; Cadmium; Langmuir; Freundlich; Temkin; Dubinin-Radushkevich

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1. Introduction

Contamination of wastewaters with metal ions such as cadmium, lead, chromium, arsenic, nickel and zinc, due to their toxicity, and non-biodegradability [1–2] stands as a critical problem for the environment, the human health, and most living organisms. This contamination is carried through the wastewaters network [3], from the industrial areas, where industrial processes, such as batteries, electrical accumulators, and dyes manufacturing units discharge aqueous effluents containing heavy metals.

The wastewaters of the industrial areas of Rouiba and Reghaïa, in the district of Algiers are treated on a dedicated treatment plant situated along the Reghaïa river.

Various methods have been developed to remove toxic metal ions from aqueous solutions, such as reverse osmosis, ion exchange, precipitation, electro dialysis and adsorption. Adsorption is the most widely used one [4].

Our research is part of the so called Green chemistry, an environment respectful chemistry that aims to develop natural and cheap adsorbents. In recent years, a great interest has been devoted to the use of lignocellulosic materials such as agricultural wastes or by products for the removal of metal ions, due to their low cost and abundance [5].

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Algeria is a country located in North Africa known for its variety of dates, and according to the UN Food & Agriculture Organization (FAO), Algeria produces about 690 000 metric tons of dates per year. "Ghers" is a variety of dates largely processed and marketed as paste. Manufacturers of date juice and paste of dates reject high quantities of pits. On average a date pit is about 10% of the date's fruit weight [6].

According to previous researches, raw and activated date pits have been found to be an effective adsorbent for the removal of iodine, phenols, methylene blue [7], dyes [8–10], heavy metals [11–15], pesticides [16], as well as adsorption of aluminum [17], gold [18], and cobalt [19].

As will be discussed in more details later, both modified, and unmodified powder of date pits have an adsorption capacity worth considering, as a cost effective and economical alternative for decontamination of wastewaters.

In today's world, technologies such as enzyme processing, and fermentation are used to leverage date waste by products by transforming them into bio-fuels, biopolymers, bio -surfactants, organic acids, antibiotics, industrial enzymes and others, hence turning date waste into a valuable commodity [6].

Other researchers have used activated carbon of raw date pits, and tested it in the field of wastewater treatment, but due to its high operating cost, they are looking for a low cost vegetal biomass, with the capacity to remove heavy metal ions [20]. A chemical modification of this vegetal biomass may eventually improve its adsorption efficiency [21].

In our study, we developed a biomass based on the powder of date pits. As the date stones powder is mainly composed of cellulose, hemicelluloses, pectin and lignin [22], we thought to test this biomass as adsorbent of heavy metals, as was the case with other plant materials such as mongo stones [23] and Douglas fir barks [24] in others studies. Mongo stones adsorb lead and cadmium with a q_{max} of 1.9 mg/g and 21.05 mg/g respectively [23]. Whereas Douglas fir barks adsorb lead with a q_{max} of 24.65 mg/g and cadmium with a q_{max} of 12.36 mg/g [24].

In a previous research [25], after the oxidation of primary alcohols of hemicelluloses and cellulose with NaOBr catalyzed by TEMPO(2,2,6,6-tetramethylpiperidin-1-oxy) radical, the adsorption capacities are improved (59.17 mg/g for lead and 8.65 mg/g for cadmium compared to those of native date pits, which are 15.62 mg/g for lead and 6.55 mg/g for cadmium. This physiochemical process of elimination of TM (Trace Metal) in the presence of a biomass is known as the biosorption.

We call a biomass, a set of live or dead vegetal compounds such as bacteria, yeasts, mushrooms, algae, and other agricultural and alimentary (food) waste. The surface onto which the fixation of the pollutant happens is named the biosorbent [26].

Given the availability of the biosorbent (adsorbing biomass) at economical cost, and that it is chemically stable, with a remarkable selectability *vis-à-vis* the TM and organic compounds, along with the possibility of regeneration, the biosorption became an economical alternative.

The complex structure of the biosorbent, and its specific characteristics, such as the presence of complexing groups, a reduced specific surface, and a slight porosity make the biosorption mechanism particular [27].

Biosorption is about an equilibrium state on the interface between the biosorbent and the solution containing the metallic cation. The adsorption sites present in the biomass favor the ion exchange between the proton on the surface of the adsorbent and the metallic cation in the solution. This mechanism is rendered possible due to the adsorbent sites that are the phenols functions within the condensed tannins, the lignin, and the pectins. In addition the hydroxyl groups found in hemicelluloses, cellulose and carboxylic acids groups of pectin represent the adsorption sites.

We have evaluated the increase of this adsorption capacity by adding some carboxylic acids groups of Diethylenetriaminepentaacetic dianhydride (DTPAD). The assumption being that the adsorption takes place on hydroxyl and carboxylic acids groups.

The DTPAD is a strong chelator reagent; it reacts with hydroxyl groups of cellulose, hemicelluloses or lignin in order to release chelating groups on solid support as carboxylic acid and amino groups.

This adsorption study of the raw date pits modified with DTPAD, is an original research topic. No previous report has been published on this matter.

2. Experimental

2.1. Materials

2.1.1. Dates of Ghers category were used for this experiment

The raw date pits (RDP) were collected from Ghardaia palm grove located in the southern Algeria. The raw date pits were washed with distilled water to eliminate all dirt and inherent pulp, dried in a ventilated oven at 105°C for 2 h; then crushed and sieved to 250 µm size particles. The powder was stored in a desiccator at room temperature for further use.

Stock solutions of metal ions were prepared from $Pb(NO_3)_2 \cdot 4H_2O$ and $Cd(NO_3)_2 \cdot 4H_2O$ at 1000 ppm. Milli-Q deionized water (Millipore system) was used to prepare all the solutions and suspensions. The solvents and reagents were supplied by (Sigma, VWR).

2.2. Material functionalization

To improve the adsorption capacity of date pits, we functionalize this raw material with DTPAD, as shown in Fig. 1. A quantity of DTPAD (2.03 g, 5.68 mmol) were dissolved in 8 ml of Dimethyl Sulfoxide (DMSO). Then this solution was added to 4 g of RDP into a 25 ml flask. Two treatments were carried out:

(i) Vacuum impregnation was applied for 30 min.
(ii) The mixture was directly heated in an oil bath at 75°C under stirring conditions for 24 h.

Once the reaction was completed, it was filtered out through a glass frit of porosity 3, and the solid obtained was washed with ethanol, then with deionized water until a pH of 7 was reached for the filtrate [28,29]. This solid was freeze-dried and weighed. The mass yield of the synthesis is 72.68%.

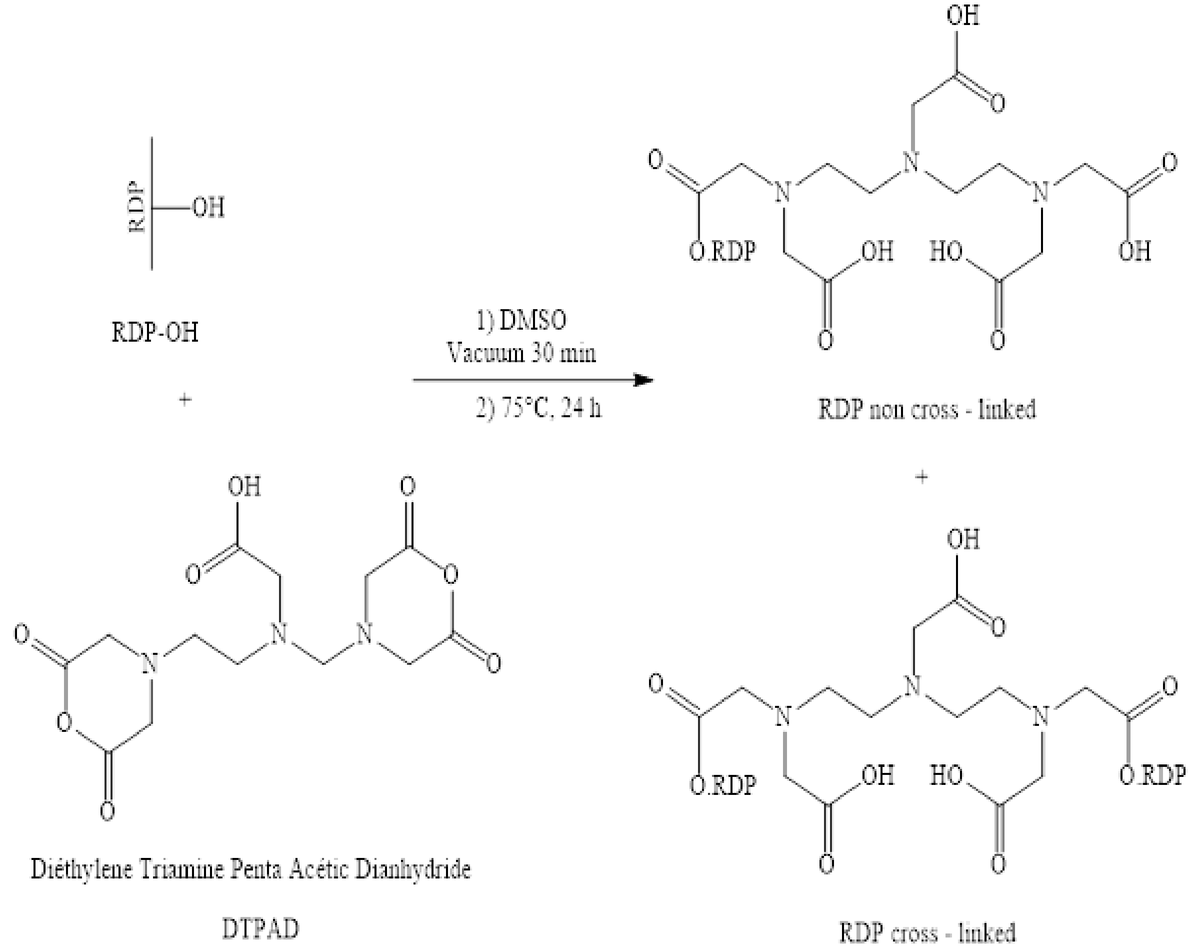


Fig. 1. Synthesis process for the functionalization of raw date pits with DTPAD.

2.3. Batch adsorption studies

Aqueous solutions of the heavy metals were prepared in initial concentrations of 20 ppm to 500 ppm of Pb^{2+} and from 10 ppm to 250 ppm of Cd^{2+}. The solutions were prepared with HNO_3 acid at 3%, the pH was adjusted with HCl 0.01 mol/l and NaOH 0.01 mol/l.

Batch experiments were performed at 22 ± 2°C and carried out at pH of 5.6; then 50 mg of RDP/ modified-RDP was added to 50 ml of metal ions solution. The mixture was stirred for 2 h. After that, the suspension was filtered out using a glass frit of porosity 3. The concentration of residual heavy metals in the filtrate was determined by flame atomic spectrometry at 283.6 nm in the concentration range 0–10 ppm for lead and at 228.8 nm in the concentration range 0–3 ppm for cadmium, with a Perkin Elmer Analyst 400 spectrophotometer.

The quantity of metal adsorbed by the adsorbent was calculated according to the below Eq. (1).

$$q_e = \left(C_e - C_0\right)\frac{V}{m} \tag{1}$$

where q_e (mg/g) is the adsorbed quantity of metal ions at equilibrium; C_0 (mg/l) is the initial concentration of the metal ions solution; C_e (mg/l) is the concentration of residual heavy metal at equilibrium; V (ml) is the volume of the solution.

2.4. Adsorption isotherms

Four mathematical models, with two parameters, namely Langmuir, Freundlich, Temkin and Dubin-Radushkevich models were tested to study the adsorption isotherms of lead and cadmium on raw date pits (RDP) and modified date pits (modified-RDP). The linear form of the models allowed us to determine their parameters and then recalculate the amount of heavy metal adsorbed at equilibrium by the powder of date pits (raw/modified) according to the heavy metal equilibrium concentrations.

2.4.1. The Langmuir isotherm

This model is widely used for adsorption studies. It represents the equilibrium distribution of metal ions between solid and liquid phases. The following Eq. (2) is used to model the adsorption isotherm.

$$q_e = q_{\max}\frac{bC_e}{1 + bC_e} \tag{2}$$

where q_e is the quantity (mg) of metal adsorbed per gram of the biosorbent material; C_e is the metal concentration in solution at equilibrium; q_{max} is the maximum uptake corresponding to the site saturation, i.e. the formation of the monolayer on the surface of the adsorbent and b is the Langmuir constant related to the energy of adsorption [30].

The Langmuir isotherm is based on these assumptions: metal ions are chemically adsorbed at a fixed number of sites; each site can hold only one ion; all sites are energetically equivalent and there is no interaction between the ions.

When the initial metal concentration rises, adsorption increases as long as the binding sites are not saturated.

The following equation represents the linear form of the Langmuir isotherm. It allows the calculation of the adsorption capacities and the Langmuir constant.

$$\frac{1}{q_e} = \frac{1}{b\, q_{\max}} \frac{1}{C_e} + \frac{1}{q_{\max}} \tag{3}$$

The q_{max} and b are obtained from the slope and intercept of the plots [31].

The dimensionless constant separation factor or equilibrium parameter R_L is the essential characteristic of the Langmuir isotherm and is defined as:

$$R_L = \frac{1}{1 + bC_0} \tag{4}$$

where b is the Langmuir constant and C_0 is the initial concentration of the metal ions solution. An R_L value between 0 and 1 indicates a favorable adsorption, whereas the adsorption is unfavorable if R_L is greater than 1. Also R_L value equal to 0 indicates an irreversible absorption and $R_L = 1$ means that the adsorption is linear [32].

2.4.2. Freundlich isotherm

Freundlich model is an empirical model. It is applied to heterogeneous surfaces sorption or surfaces supporting sites of varied affinities. It supposes that the stronger binding sites are occupied first and that the binding strength decreases with the increasing degree of sites occupation [33].

The general Freundlich equation is:

$$q_e = K_F C_e^{1/n} \tag{5}$$

where C_e is the concentration (mg/l) of the adsorbate in liquid phase at equilibrium; q_e: the amount adsorbed at equilibrium (mg/g); K_F: the adsorption capacity; n: the adsorption intensity.

The linear form of the Freundlich adsorption isotherm was used to evaluate the adsorption data and is represented as:

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \tag{6}$$

The values of K_F and n are calculated from the intercept and the slope of the Freundlich plots respectively. According to Kadirvelu and Namasivayam [34], n value between 1 and 10 represents a beneficial adsorption. The parameter n is usually greater than unity. A larger n value means that the system is more heterogeneous; indicating a multilayer adsorption [35].

2.4.3. Temkin isotherm

Temkin isotherm model [36] considered the effect of adsorbate - adsorbent interactions on adsorption isotherms and supposed that (i) the heat of adsorption of all the molecules in the layer would decrease linearly with coverage; (ii) the distribution of binding energies adsorption is uniform, up to some maximum level. The Temkin isotherm is expressed in the following form:

$$q_e = \frac{RT}{b_T} \ln\left(K_T C_e\right) \tag{7}$$

The linear form of Eq. (7) is given by Eq. (8) below

$$q_e = B \ln K_T + B \ln C_e \tag{8}$$

where q_e is the adsorbed amount at equilibrium (mg/g), C_e is adsorbed equilibrium concentration (mg/l). b_T (J/mol) is the Temkin constant related to adsorption heat; $B = RT/b_{T;}$ K_T (l/g) is the equilibrium binding constant corresponding to the maximum binding energy.

The adsorption energy variation ΔQ (J/mol) is calculated with the Eq. (9), where q_{max} is the highest quantity adsorbed given by the Langmuir model.

$$\Delta Q = b_T \cdot q_{\max} \tag{9}$$

2.4.4. Dubinin–Radushkevich isotherm

The adsorption isotherm is given as:

$$q_e = q_D e^{-B} D^{\left[RT \ln\left(1 + \frac{1}{C_e}\right)\right]^2} \tag{10}$$

where B_D is related to the free energy of sorption per mole of the adsorbate as it migrates to the surface of the adsorbent from infinite distance in the solution (kJ/mol^2); q_D (mg/g) is the Dubinin–Radushkevich isotherm constant related to the degree of adsorbate sorption by the adsorbent surface; q_e(mg/g) the amount adsorbed at equilibrium; R is the gas constant (J/mol·K) and T is the absolute temperature in Kelvin.

The linear form of D-R Eq is:

$$\ln q_e = \ln q_D - B_D \left(RT \ln\left(1 + 1/C_e\right)\right)^2 \tag{11}$$

The D-R equation has the advantage of estimating the mean free energy of adsorption E (kJ/mol) from the appropriate parameter B_D as:

$$\mathrm{E} = \frac{1}{\sqrt{2\mathrm{B_D}}} \tag{12}$$

The Polanyi adsorption theory postulates that a fixed volume of adsorption sites are close to adsorbent surface and the existence of an adsorption potential over these sites. The adsorption potential is related to an excess of adsorption energy over the condensation energy and is independent of temperature [13].

Polanyi adsorption potential can be expressed as:

$$\varepsilon = RT \ln(1 + 1/C_e) \quad (13)$$

The average adsorption energy calculated from D-R isotherm provides important information about its properties: E < 8 kJ/mol means that the physisorption dominates the adsorption mechanism, when 8 < E< 16 kJ/mol ions exchange is the dominant factor; whereas when E >16 kJ/mol the adsorption is dominated by the intraparticle diffusion [37].

3. Results and discussion

3.1. Determination of equilibrium time

Fig. 2 shows that the kinetic of cadmium adsorption on the RDP powder is rapid. The adsorbent is saturated at 99% after 40 min. Thus, we choose a contact time of 2 h to ensure that adsorption reached equilibrium.

3.2. Determination of zero point charge pH_{zpc}

The pH_{ZPC} is an important parameter to be determined. At this value, acidic or basic functions on the surface of the adsorbent do not contribute to the pH of the solution; so at $pH \geq pH_{ZPC}$ the surface is charged negatively, consequently the adsorption of cations will be more favorable.

The pH_{ZPC} is the point where the curve of final pH vs. initial pH crosses the line that correspond to the equation final pH=initial pH.

To evaluate pH_{ZPC}, 0.01 M NaCl solutions with a pH between 3 and 9 were prepared; then 0.15 g of the raw date pits powder is brought into contact with 50 ml of each solution. The suspensions are stirred for 24 h at room temperature. Each solution was then filtered out and the final pH was measured. As we can see in Fig. 3, $pH_{zpc} = 5.6$

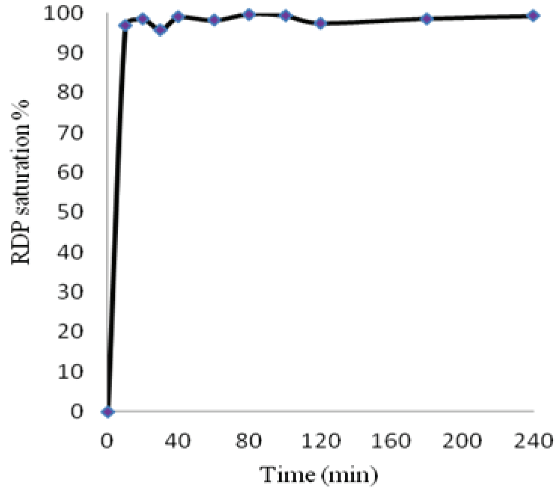


Fig. 2. Effect of time on removal percentage of Cd^{2+} by RDP. Test conditions: 50 ml of cadmium solution, RDP dose 1 g/l, shaking speed 350 rpm, temperature 22°C.

3.3. Determination of adsorbent mass

The effect of the mass of adsorbent and the adsorption performance was studied by varying the mass of the RDP powder from 0.05 to 1 g in 50 ml of cadmium solution, i.e. a ratio of 1 to 20 g/l.

As shown in Fig. 4, when the weight increases from 0.05 g to 1 g the adsorbed amount decreases from 6.7 mg Cd^{2+}/g adsorbent to 3 mg Cd^{2+} /g adsorbent.

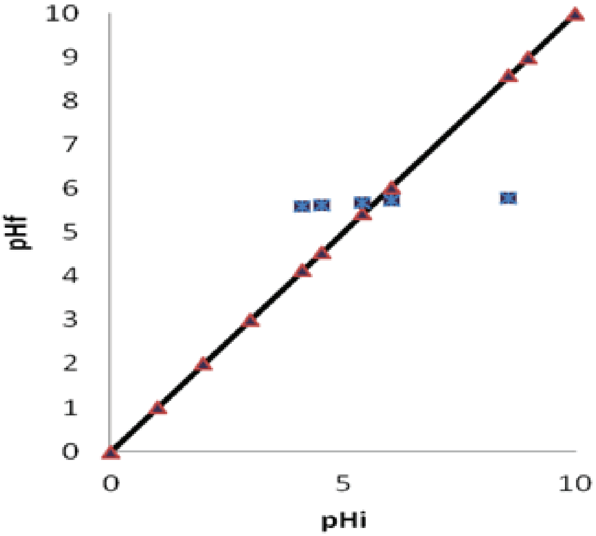


Fig. 3. Determination of zero point charge pH_{ZPC}.

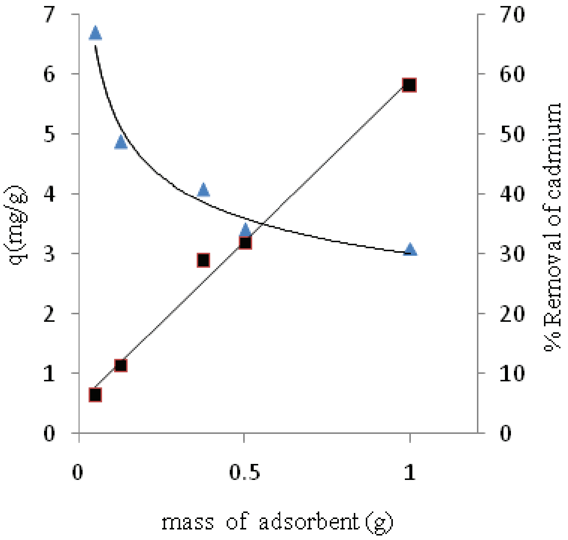


Fig. 4. The effect of RDP weight on the uptake (mg/g) and percentage removal of cadmium: initial concentration cadmium ions: 100 mg/l, temperature 22°C, pH 5.6.

The adsorption efficiency increases from 6.3% to 56%. So the optimal adsorbent weight is 0.5 g. This result is similar to that found in the work of N.M. Hilal [13]. For our batch experiences, we chose to use a mass of 50 mg RDP powder.

3.4. Isotherms

The results for each model are presented in Table 1. The adsorption isotherms of date pits towards Pb^{2+} and Cd^{2+} ions, as shown in Fig. 5, indicate that when the concentration of metal ions increases, the adsorption capacity increases.

The determination coefficient R^2 and the absolute error average were calculated to compare the four isotherms models. As it can be seen from Table 1, high correlation coefficients of Langmuir, Freundlich, Temkin and Dubinin-Radushkevich linear form, indicate that these models described correctly the adsorption process of Pb^{2+} and Cd^{2+}, in the range of the concentration of these ions in the present study.

Langmuir model can represent experimental points with the correlation coefficient $R^2 = 0.93$ and $R^2 = 0.98$ for Pb^{2+} and Cd^{2+} respectively.

The monolayer values (q_{max}) found for the powder modified by DTPAD are 59.17 mg/g for Pb^{2+} and 89.3 mg/g for Cd^{2+} ; while the q_{max} values of unmodified date pits powder were 15.62 mg/g for Pb^{2+} and 8.55 mg/g for Cd^{2+} . Comparison between q_{max} values shows that powder modified by DTPAD can absorb Pb^{2+} nearly 4 times more than raw powder; and can absorb Cd^{2+} 10 times more than raw powder. These results reveal that the functionalization of the date pits powder with DTPAD improves the adsorption capacity, producing an interesting material in terms of its chemical functionality and application.

As can be seen, the calculated R_L values are between 0 and 1, indicating that the adsorption of Pb^{2+} and Cd^{2+} onto raw and the modified powder is favorable within the range of the concentrations used.

For the Freundlich model, n calculated is greater than 1 for the adsorption of Pb^{2+} /Cd^{2+} on RDP and modified RDP, and over the entire range of concentrations studied, this means that adsorption is favorable, and that the sorption intensity is good at high concentrations but weak at lower concentrations. The high value of n indicates the heterogeneity of the surface of the adsorbent and a high value of the intercept K_F is indicative of high sorption capacity.

The correlation coefficients show that the model of Temkin gives the best fit of the experimental points. In addition, we noted that the energy of adsorption of lead and cadmium are similar to those calculated by D-R model.

The plots of ln q_e versus RT ln(1+1/C_e), gave straight lines with $R^2 > 0.96$, inducing that the Dubinin-Radushkevich isotherm was adequate for the adsorption process.

The values of q_D and B_D calculated from the intercepts and slopes of the plots respectively shown in Table 1 indicate: (i) the higher values of q_D, the higher is the adsorption capacity. (ii) the values of q_D are higher for the modified-RDP powder than for the RDP powder, showing that the modified powder exhibited higher adsorption capacity than the unmodified powder.

After using the D-R model, it was found that irrespective of using raw or modified-material the values of energy of adsorption E for Pb^{2+} are always greater than those for Cd^{2+}.

Since the value of E is the energy required to transfer one mole of adsorbate to the adsorption sites of adsorbent from the bulk solution, therefore the highest energy values have shown that it needs more energy to transfer Pb^{2+} onto the surface of adsorbent than Cd^{2+} , and this resulted

Table 1
Isotherm constants of Pb^{2+} and Cd^{2+} biosorption by raw and modified biosorbent

Model	Parameters	Raw adsorbent		Modified adsorbent	
		Pb^{2+}	cd^{2+}	Pb^{2+}	cd^{2+}
Langmuir	Q_{max} (mg/g)	15.625	8.55	59.17	89.3
	b (l/mg)	0.2873	0.0249	0.00357	0.00086
	R^2	0.9369	0.9874	0.9906	0.9918
	R_L	0.01–0.15	0.14–0.89	0.31–0.92	0.82–0.99
Freundlich	K_F	8.97	0.71	1.32	0.14
	n	8.88	2.2	1.844	1.173
	R^2	0.984	0.9434	0.9749	0.9843
Temkin	B	1.51	1.93	13.48	8.64
	b_T (J/mol)	1631.70	1280.80	183.14	285.93
	K_T (l/g)	213.050	0.229	0.0322	0.02
	ΔQ (J/mol)	25495.4	10947	10836.6	25529.7
	R^2	0.9829	0.9551	0.993	0.9992
D-R	q_D (mg/g)	22.06	25.34	162.75	176.34
	B_D	6.10^{-6}	5.10^{-9}	7.10^{-9}	1.10^{-8}
	E (J/mol)	22361	100000.99	8451.54	7071
	R^2	0.99	0.9622	0.9835	0.9888

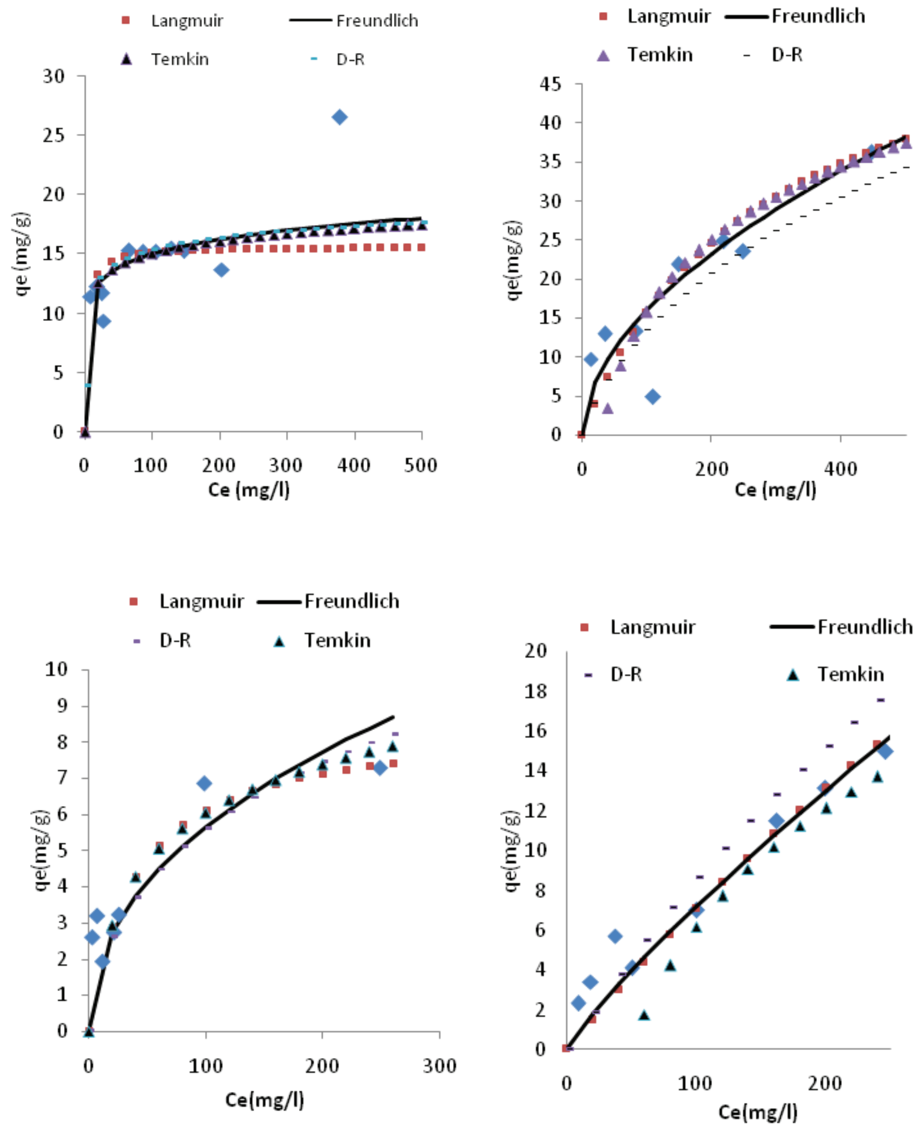


Fig. 5. Isotherms adsorption of Pb^{2+}/Cd^{2+} onto RDP and modified RDP. Pb^{2+} - RDP (a) Pb^{2+} - modified RDP (b) Cd^{2+} - RDP (c) Cd^{2+} - modified RDP (d).
Conditions: Adsorbent 50 mg, solution volume 50 ml, T = 22°C, pH = 5.6.

in stronger adsorbing tendency toward Cd^{2+} than Pb^{2+} [38]. The adsorption energy for RDP powder was 22 kJ/mol and 10 kJ/mol for Pb^{2+} and Cd^{2+} respectively, and this suggests that the adsorption process of Pb^{2+} is a chemisorption (E > 16 kJ/mol), whereas the ion exchange process is dominant in the adsorption of Cd^{2+} (8 kJ/mol < E < 16 kJ/mol).

The adsorption energy was around 8.45 kJ/mol for Pb^{2+} and 7.07 kJ /mol for Cd^{2+} using modified-RDP powder; this supposes that an ion exchange reaction occurs for Pb^{2+} and a physisorption for Cd^{2+}; we can infer from this that the structure of the adsorbent is modified. In fact, it indicated that the adsorption of Cd^{2+} was different from that of Pb^{2+} i.e. the shrinking of the polymer chain changes the surface properties of date pits powder.

Error estimation: An absolute error average Δq_e is calculated as follows:

$$\Delta qe = \frac{1}{n}\sum_{1}^{n}\left(qe\ exp. - qe\ calc.\right) \tag{14}$$

Major values reported in Table 2 are less than 2 mg/g.

Some adsorption results obtained with other vegetal by products were given in (Table 3), except that the experimental conditions were not similar for all.

3.5. Structural characterization by infrared spectroscopy analysis

The characterization of the modified raw powder with DTPAD, shows that the intensity of the bands increased (Fig. 6); this is an indication that the modification has taken place. The analysis of FTIR spectra shows, an increase in the intensity of the band OH of the carboxylic acids at 3374 cm^{-1}.

Table 2
Absolute error average Δq_e (mg/g)

Model	RDP		Modified-RDP	
	Pb^{2+}	Cd^{2+}	Pb^{2+}	Cd^{2+}
Langmuir	0.60	1.20	2.60	1.02
Freundlich	0.80	1.20	2.06	0.90
Temkin	0.80	1.40	4.90	5.20
D-R	1.00	1.20	3.50	1.80

Table 3
Comparative evaluation of RDP, modified RDP and some agricultural products as biosorbents for lead and cadmium reported by other studies

Biosorbent	q_{max} (mg/g) Pb^{2+}	q_{max} (mg/g) Cd^{2+}	Reference
Date pits	2.891	–	[12]
Date pits	7.40	6.02	[13]
Activated date pits	33.44	17.24	[13]
Date pits	–	39.57	[11]
Mongo stones	1.90	21.05	[23]
Cocoa pod	5.31	12.15	[23]
Banana peel	7.97	–	[21]
Orange peel	7.75	–	[21]
Douglas fir barks	24.65	12.36	[24]
Activated carbon cashew nut shells	28.90	17.29	[39]
Sugarcane bagasse mod. by EDTAD	333.0	149.0	[28]
Cellulose modified by EDTAD	232.0	112.0	[28]
RDP	15.62	8.55	This study
Modified-RDP	59.17	89.3	This study

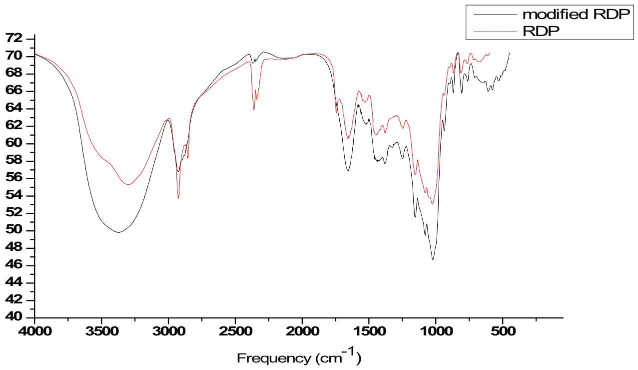


Fig. 6. FTIR spectra of RDP and modified-RDP.

Table 4
FTIR spectra assignment for RDP and modified-RDP

IR peak of RDP (cm^{-1})	IR peak of modified RDP (cm^{-1})	Difference	Assignment
3360	3374	+14	–OH groups
2930	2924	–6	aliphatic C–H group
1740	–		carbonyl stretch of carboxyl
1646	1656	+10	protein C=O stretching, C=O carboxylates
1518	1516	–2	C=C in aromatic ring
1436	1430	–6	C–O carboxylates
1370	1372	–2	C–H deformation in hemicelluloses and celluloses
1238	1240	+2	syringyl ring and C–O stretch in lignin, C–O carboxylic acid group, C–N stretch group
1148	1150	+2	C–O–C stretch in cellulose and hemicelluloses
1072	1088	+16	C–O stretching of primary alcoholic groups, Tertiary amines

The carboxylic acids band C=O at 1740 cm^{-1} is not visible after the chemical modification of RDP, this is due to overlap with the band C=O conjugated to NH_2 of the proteins at 1656 cm^{-1} (Table 4) [40] and to COOH supplied by DTPAD and the increase in the band at 1088 cm^{-1} is attributed to tertiary amines function.

3.6. Measurement of carboxylate content by conductimetry

The carboxyl content of RDP and modified-RDP is determined by conductimetric titration. 50 mg of RDP or modified-RDP are suspended into 15 ml of 0.01 M hydrochloric acid solution. After 30 min of stirring, the suspensions are titrated with 0.01 M NaOH (Fig. 7).

The degree of oxidation DO is calculated per-below the equation:

$$DO = \frac{162C\left(V_2 - V_1\right)}{m - 36C\left(V_2 - V_1\right)} \tag{15}$$

where C is NaOH concentration (mol/l), V_1 and V_2 are the volumes of NaOH (l) and m (g) the mass of RDP or modified-RDP, 162 is the molar mass of the glucose unit present in glycoside bond, whereas 36 represents the difference between the molecular weight of an AGU and that of the sodium salt of glucuronic acid moiety [41].

The first part of Fig. 7 corresponds to the neutralization of the excess of H^+. The second one corresponds to the neutralization of carboxyl groups of the RDP/modified-RDP. The third stage corresponds to the excess of OH^-. V_1 is the equivalent point between the first and the second part, V_2 is the equivalent point between the second and the third portion.

Thus, $(V_2–V_1)$ is the amount of NaOH necessary to neutralize the carboxyl groups in the sample. The degree of oxidation of the raw powder is equal to 16.70% and increases to 25.53% for the modified powder.

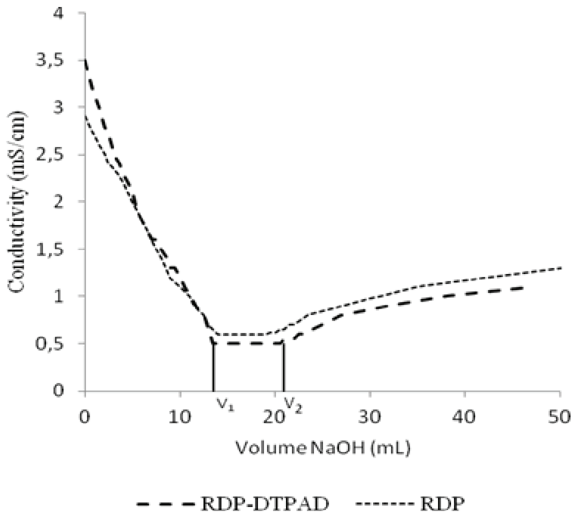


Fig. 7. Conductimetric titration curves of RDP and modified-RDP.

3.7. Scanning electron microscopy (SEM)

The raw date pits powder observed by using scanning electron microscopy, shows a texture in the form of heterogeneous aggregates (Fig. 8 a and b). The powder modified by the DTPAD has a more homogenous and dense matrix structure, and more pores appear (Fig. 8 c and d).

It seems that cross linking of the powder by the carboxylic acid functions of DTPAD lead to the formation of linking bridges.

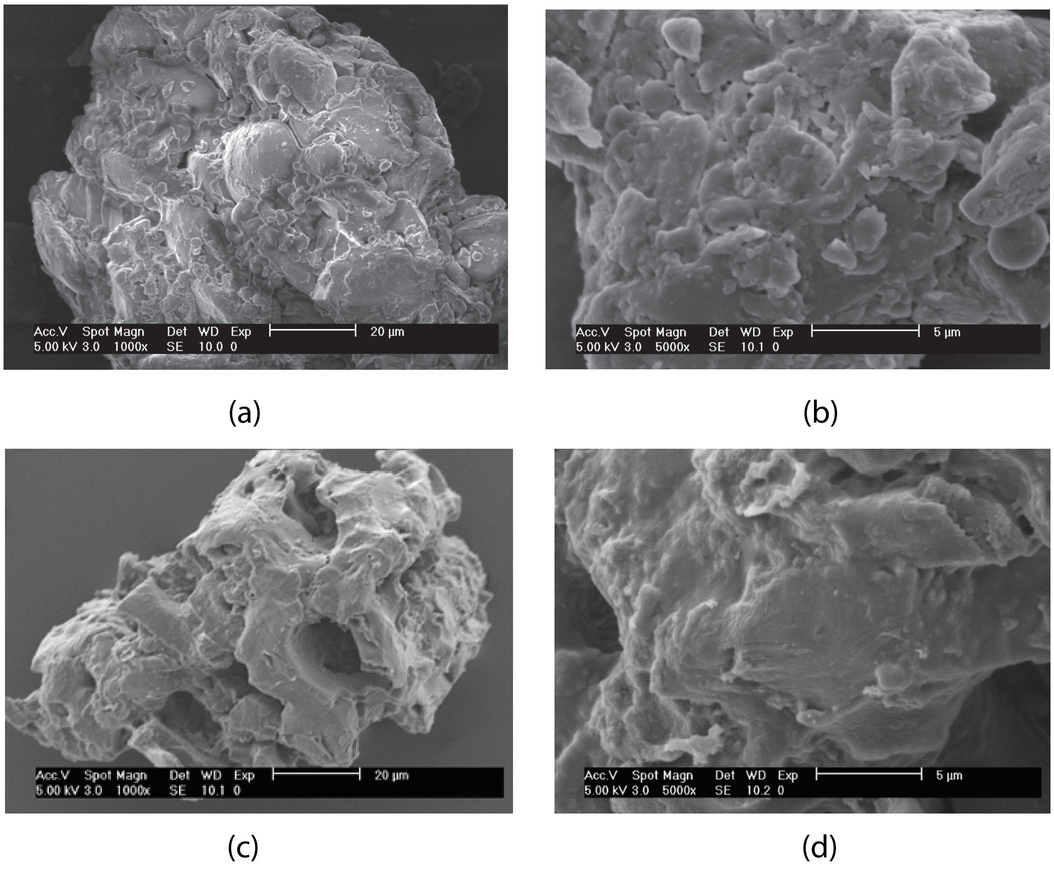
3.8. Surface area of adsorbents

Surface area is calculated by B.E.T (Brunauer, Emettet, Teller) method. The raw powder has a surface of 0.7016 m^2/g and the powder modified by DTPAD has a surface of 0.8696 m^2/g.

4. Conclusion

The present study provided a great deal of significant information on the adsorption phenomena. The study of the adsorption isotherms of the two heavy metals, lead and cadmium on the native powder of date pits and the powder modified by diethylenetriaminepentaacetic dianhydride, is conducted under the following experimental conditions: 50 mg of RDP/modified-RDP, concentration of Pb^{2+} (20–500 ppm) and (10–250 ppm) for Cd^{2+}, pH = 5.6, with the temperature of 22°C, and continuous two hours stirring at 350 rev/min (revolution per minute).

Our results show that raw date pits, the "Ghers" variety has a capacity of adsorption of 15.625 mg/g of lead and



(a) (b)

(c) (d)

Fig. 8. SEM micrographs for RDP (a, b) and modified-RDP (c,d).

8.55 mg/g of cadmium, which are acceptable values compared to other values found using different varieties of date pits mentioned in the literature (reference section).

The chemical modification by attaching new groups of carboxylic acid from DTPAD to the raw powder improves its degree of oxidation with an increase from 16.17% to 25.53%, therefore the adsorption capacity of lead reaches 59.17 mg/g and that of cadmium 89.3 mg/g .

Considering the results calculated by using the different models, and the experimental figures, we find the acceptable level of the average errors is the Freundlich isotherm model followed by Langmuir, Dubinin-Radushkevich and then Temkin isotherms.

Regarding the level of the error average, between the experimental figures and the results calculated by the models, we consider that the Freundlich isotherms gave the best fit, followed by Langmuir, Dubinin-Radushkevich and then Temkin isotherms,

We conclude that the raw and the DTPAD modified date pits have the capacity for the retention of lead and cadmium. Considering their availability at a low operating cost, they can stand as an alternative biomass to remove these heavy metals from the industrial wastewaters.

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