

## ADSORPTION OF LEAD (II) AND CADMIUM (II) ON RAW AND MODIFIED DATE PITS BY TEMPO/NaBr/NaOCl AS ADSORBENT

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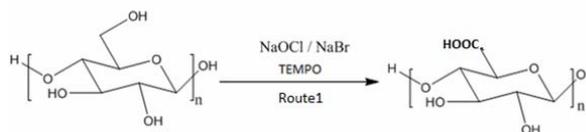
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The principal objective of this study was to remove lead and cadmium on raw date pits (RDP) as adsorbent from wastewater. In order to improve the adsorption capacity of RDP, a chemical modification consisting in oxidation of primary alcohols with NaOBr catalyzed by TEMPO (2,2,6,6-tetramethylpiperidin-1-oxyl) radical is investigated.

The experimental data of adsorption of lead and cadmium were correlated with the widely known isotherms models as Langmuir, Freundlich, Temkin and Dubin-Radushkevich, in order to know how each one fits the adsorption process. The raw powder and the modified one are characterized by FT-IR spectroscopy and the degree of oxidation is measured by conductimetry titration. The analysis of the modified-RDP by scanning electronic microscopy indicates the formation of compact structure and some porosities appear. Adsorption capacities were found better for lead than cadmium before and after the chemical modification.



### INTRODUCTION

The date-palms (*Phoenix dactylifera* L.) grown in Arab countries and North Africa, including Algeria, have an important place in the diet. Dates have an economic and environmental impact on the population life of some producing countries

The high consumption of dates and their use in the food industry for making pulp of dates or date juice, generates a significant amount of pits; representing a waste for the environment and apparently without interest.<sup>1</sup>

Raw date pits (RDP) have some applications as additive in animal alimentation,<sup>2</sup> oil extracted from RDP<sup>3</sup>. Raw and activated date pits are generally used as an adsorbent to eliminate iodine, phenols, methylene blue,<sup>4</sup> dyes,<sup>5,6</sup> heavy metals,<sup>7-10</sup> pesti-

cides,<sup>11</sup> aluminum,<sup>12</sup> gold,<sup>13</sup> and cobalt,<sup>14</sup> Activated raw date pits powder was used as adsorbent in many researches but it remains still an expensive material.<sup>9</sup> In another hand, environmental pollution by heavy metals is a serious problem which has a harmful effect on the human health and aquatic flora and fauna. Several heavy metals have been studied including lead, cadmium, chrome, zinc and nickel because they are toxic and non biodegradable.<sup>15</sup>

Various process are used to remove these toxic metal ions from aqueous solutions as reverse osmosis, ion exchange, precipitation, coagulation, flocculation, electro dialysis and adsorption. The adsorption is the mostly used due to its low cost compared to other processes, easy to implement, and using agricultural by products, the actual new challenge.<sup>16</sup>

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Many industrial processes, such as batteries, paints, electrical accumulators, and dyes manufacturing discharge effluents contaminated with toxic metals.<sup>17</sup>

Other researchers are focused on the treatment of wastewater contaminated by heavy metals by entrant adsorbents such as agricultural by-products and industrial by-products. In this study we invest in the ability to use the raw date pits powder (RDP) as a natural adsorbent, available in large quantities at low cost and as date pits are rich in hemicellulose, cellulose, lignin which are composed of hydroxyl groups, and carboxyl groups responsible for adsorption of heavy metals.<sup>18</sup>

Although activated carbons prepared from those agricultural materials are suitable and show their performance for the adsorption of heavy metals in many studies, their high operating cost conducted many researchers to take vegetal biomass as a new challenge, due to its capability to remove heavy metal ions.<sup>19</sup> The adsorption capacity of vegetal biomass mostly rises after a chemically modification.<sup>20</sup>

The objective of our study is to develop a biomass based on date pits to remove heavy metal ions from wastewaters and particularly test its capacity to eliminate lead and cadmium. We aim also to test the improvement of this adsorption capacity by adding some carboxylic acids groups by oxidation of alcoholic primary groups to acidic groups by TEMPO/NaBr/NaOCl system because we suppose that the adsorption takes place on hydroxyl and carboxylic acids groups.<sup>21-23</sup>

To obtain the adsorption equilibrium isotherms of lead and cadmium on raw date pits (RDP) and modified date pits (modified-RDP), we test four mathematical models, with two parameters such as Langmuir, Freundlich, Temkin and Dubinin-Radushkevish (D-R) model. The linear form of these models was applied in order to determine their parameters and then recalculate the amount of heavy metal ions adsorbed at equilibrium by the powder of date pits (raw/modified) according to the heavy metal ions equilibrium concentrations.

## MATERIALS AND METHODS

The dates were provided from date-palms (*Phoenix dactylifera*) of variety Ghars from Ghardaia palm grove situated in the south of Algeria. The date pits were removed from dates, washed with distilled water to remove dirt particles and inherent pulp, dried in ventilated oven at 105°C for 2 hours; then crushed and sieved to particles size 250µm. The powder of the raw date pits (RDP) is stored in a desiccator at room temperature for further use as adsorbent.

Stock solutions of metal ions were prepared from their nitrates  $Pb(NO_3)_2 \cdot 4H_2O$  and  $Cd(NO_3)_2 \cdot 4H_2O$  at 1000 mg/L. Milli-Q deionized water (Millipore system) was used to prepare all solutions and suspensions. 2,2,6,6-Tetramethylpiperidine-1-oxy radical (TEMPO), sodium bromide NaBr were purchased from Alfa Aesar and the NaOCl (9.6%) is a commercial sodium hypochlorite. Nitrate of lead (99%) and nitrate of cadmium (98.5%) were purchased from Sigma and Alfa Aesar respectively.

### Material functionalization

A quantity of 1 gram of the date pits powder is stirred in 100 mL of Milli-Q deionized water, then 12.34 mg of TEMPO (2,2,6,6 - tetramethylpiperidin-1-oxy radical), and 125 mg of NaBr were added to the suspension. TEMPO-mediated oxidation was initiated by adding 28.2 mL of 9.6% NaOCl added in small drops; every time the pH was adjusted to 10 by addition of aqueous NaOH (0.1M).

When the pH is stabilized at 10, it was adjusted again to a value of 7 with a hydrochloric acid solution (0.1M) and then the mixture was stirred for 85 hours. The suspension was filtered through a glass frit (porosity 3) and the solid obtained was washed with water deionized until a pH 7 is reached for the filtrate. The powder is dried in an oven at 40 ° C. The recovered mass ratio of the modified -RDP was 58.45%.

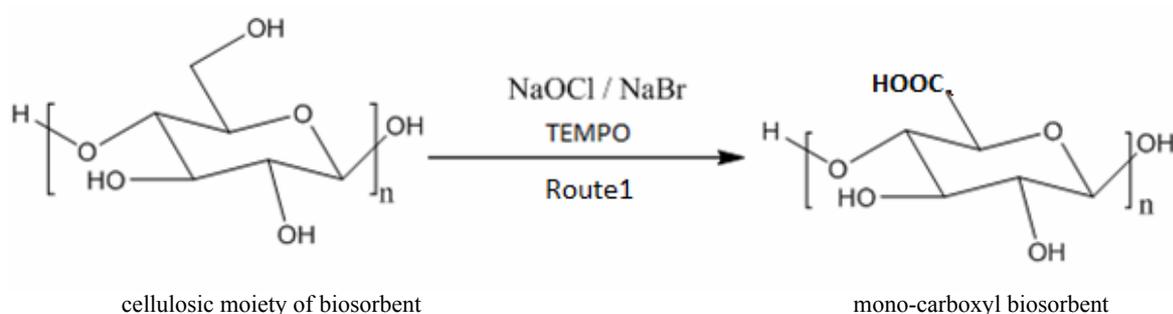


Fig. 1 – Scheme route of selective oxidation of primary alcohol by NaOBr catalyzed by TEMPO.

### Aqueous solution of heavy metals

The solution of  $Pb^{2+}$  and  $Cd^{2+}$  necessary for batch experiments are prepared from their nitrates  $Pb(NO_3)_2 \cdot 4H_2O$  and  $Cd(NO_3)_2 \cdot 4H_2O$  at 1000 mg/L and acidified with  $HNO_3$  (3%). The pH is adjusted to 5.68 with  $HCl$  0.01mol/L and  $NaOH$  0.01 mol/L. The stock solution for each metal are diluted to obtain the initial concentrations from 20 mg/L to 500 mg/L for  $Pb^{2+}$  and from 10 mg/L to 250 mg/L for  $Cd^{2+}$ .

### Biosorption isotherms

Batch mode is used to study the equilibrium experiments, all experiments are conducted at  $22 \pm 2^\circ C$  temperature. To study adsorption of  $Pb^{2+}$  and  $Cd^{2+}$  a fixed amount of RDP or modified -RDP (50 mg) are placed in 50 mL of initial metal ions solutions of  $Pb^{2+}$  and of  $Cd^{2+}$  and they are shaking for 2 hours, the equilibrium time. After that the suspension was filtered on glass frit of porosity 3. Atomic adsorption spectrophotometer (Perkin Elmer Analyst 400 spectrophotometer) was used to quantify the concentration of metal ions in the filtrate. The wavelength was used is 283.6 nm in the concentration 0-10 mg/L for lead, and 228.8 nm in the concentration range 0-3 mg/L for cadmium.

The amount of metal ions uptake by the adsorbent is calculated according to this equation (1).

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

where  $q_e$  ( mg/g) is the adsorbed quantity of ions metals 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): the volume of the solution

### Analyses

RDP and modified-RDP were characterized by FT-IR spectroscopy with a Perkin Elmer Spectrum 1000 FT-IR spectrometer in  $500-4000\text{ cm}^{-1}$  range, to identify the chemical groups present in the raw material and after the chemical modification.

Carboxylate content was measured by conductimetric titration with CDM 210 conductimeter (Meterlab).

## RESULTS AND DISCUSSION

### Chemical modification of biosorbent

RDP oxidized with TEMPO/NaBr/NaOCl system leads to a mass yield of 58.45%. A mass loss of about 41.55% may be the consequence of the parietal polysaccharides extraction, lignin and organic compounds during the oxidation, pointing to the fragility of the natural material during the reaction. The same observation was noticed for the oxidation of date palm lignocellulosic fibers.<sup>24</sup>

### Adsorption isotherms

#### Adsorption capacity versus initial concentration

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. 2 indicates that when the concentration of metal ions is higher, the adsorption capacity is higher.

The determination coefficients  $R^2$ , and absolute error average (Table 2) were used to compare the four isotherms models and to evaluate which one explain better the adsorption process and fit the experimental data. As can be seen from Table 1, high correlation coefficients of linearized Langmuir, Freundlich, D-R and Temkin isotherms indicate that these models can explain the adsorption of  $Pb^{2+}$  and  $Cd^{2+}$  in the range of the concentration of these ions in this study.

#### Langmuir isotherm

The Langmuir model is the most used for adsorption studies, represented by equation (2), it supposes that sorption occurs at the surface of the sorbent in homogeneous way with formation of a monolayer.

$$q_e = q_{\max} \frac{bC_e}{1+bC_e} \quad (2)$$

where  $q_e$  is the amount (mg) of metal ions adsorbed per gram of the biosorbent material;  $q_{\max}$  is the monolayer sorption capacity ;  $C_e$  is the metal ions concentration in solution at equilibrium, and  $b$  is Langmuir constant related to the energy of adsorption.<sup>25</sup>

The Langmuir isotherm supposes that metal ions are chemically adsorbed at a fixed number of sites and each site can be occupied by one ion; moreover all sites are energetically equivalent and there is no interaction between the ions.

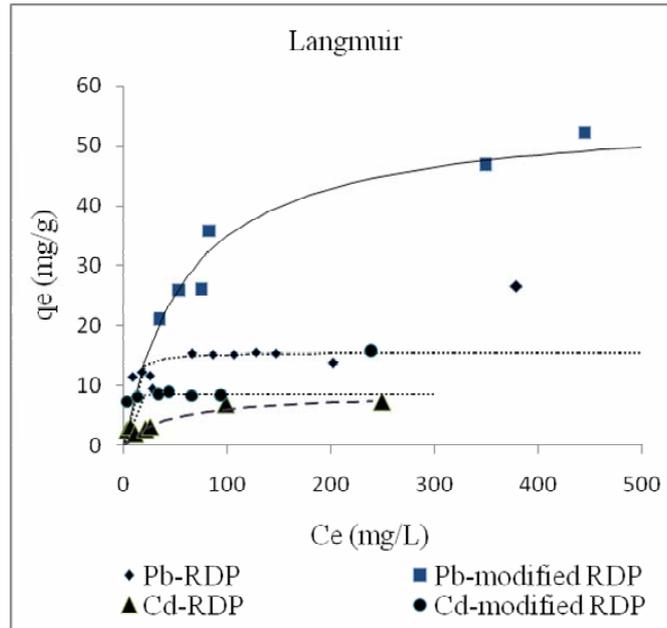


Fig. 2 – Langmuir adsorption isotherms of  $Pb^{2+}$  and  $Cd^{2+}$  on RDP and modified-RDP.

When the initial metal concentration rises, adsorption increases as long as the binding sites are not saturated. The linearized form of Langmuir isotherm is represented by the equation (3). It permits the calculation of the adsorption capacities and the Langmuir constant.

$$\frac{1}{q_e} = \frac{1}{b q_{max}} \frac{1}{C_e} + \frac{1}{q_{max}} \quad (3)$$

where  $q_{max}$  and  $b$  are determined from the slope and intercept of the plots.<sup>26</sup>

Equilibrium parameter or the dimensionless constant separation factor  $R_L$  is the main characteristic of the Langmuir isotherm and it is represented by the following equation:

$$R_L = \frac{1}{1 + b C_0} \quad (4)$$

where  $b$  is the Langmuir constant and  $C_0$  the initial concentration of the metal ions. We note that a value of  $R_L$  between 0 and 1 indicates favorable adsorption, but if  $R_L > 1$  the adsorption is unfavorable. Also  $R_L$  value equal to 0 indicates irreversible adsorption and  $R_L = 1$  means that the adsorption is linear.<sup>27</sup>

The chemical modification of the raw date pits by TEMPO/NaBr/NaOCl system has allowed the increase of the capacity of adsorption of RDP: It reaches 55.58 mg/g for  $Pb^{2+}$  and 8.65 mg/g for  $Cd^{2+}$  onto modified - RDP; while the  $q_{max}$  values of unmodified date pits powder were 15.62 mg/g for  $Pb^{2+}$  and 8.55 mg/g for  $Cd^{2+}$ . These results

show that RDP after oxidation of primary alcohol functions to acidic groups can absorb nearly 3.5 times more  $Pb^{2+}$  than raw powder. The modification has no significant impact for  $Cd^{2+}$ .

As shown in Table 1, it can be found that the values of linear regression coefficient ( $R^2$ ) are mostly equal to 0.92, suggesting that isotherm doesn't provide a good fit with these experimental data. This indicates that  $Pb^{2+}$  and  $Cd^{2+}$  adsorption on RDP and modified-RDP does not follow the Langmuir monolayer adsorption. Despite the separation factor  $R_L$  values, calculated for all initial  $Pb^{2+}$  and  $Cd^{2+}$  concentrations are between 0 and 1, indicating that the sorption process is favorable in the range of the concentrations used.

### Freundlich isotherm

Freundlich model is applied to heterogeneous surfaces sorption or surfaces supporting sites of varied affinities. It assumes that the stronger binding sites are occupied first and that the binding strength decreases with the increasing degree of sites occupation.<sup>28</sup>

The general Freundlich equation is:

$$q_e = K_F C_e^{1/n} \quad (5)$$

where

$C_e$ : concentration (mg/L) of the adsorbate in liquid phase at equilibrium

$q_e$ : the amount adsorbed at equilibrium (mg/g)

$K_F$ : adsorption capacity

$n$ : adsorption intensity.

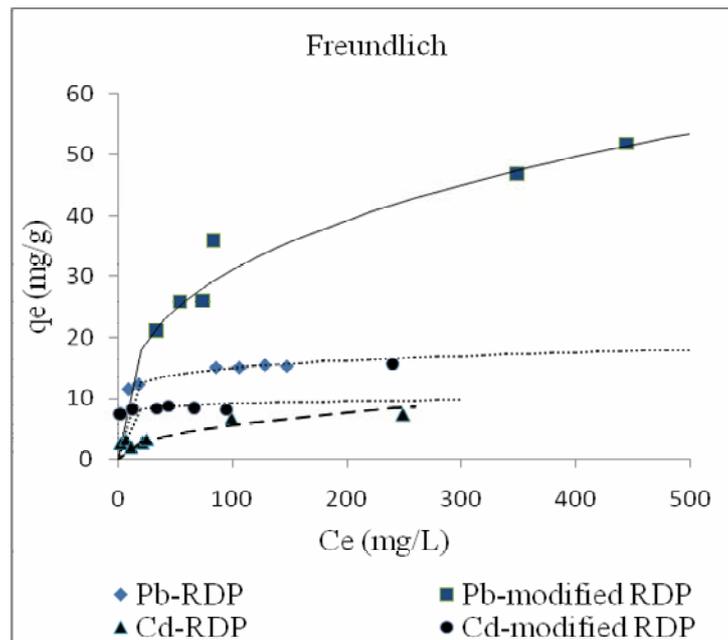


Fig. 3 – Freundlich adsorption isotherms of Pb<sup>2+</sup> and Cd<sup>2+</sup> on RDP and modified-RDP.

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

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (6)$$

The values of  $K_F$  and  $n$  are calculated from the intercept and slope of the Freundlich plots respectively.<sup>29</sup>

The parameter  $n$  is usually greater than unity.  $n$  value between 1 and 10 represents a beneficial adsorption, according to Kadirvelu and Namasivayam,<sup>30</sup> A larger  $n$  value means that the system is more heterogeneous and indicates a multilayer adsorption.<sup>31</sup>

For Freundlich model,  $n$  calculated is greater than 1 for the adsorption of Pb<sup>2+</sup>/Cd<sup>2+</sup> on RDP and modified-RDP. That means favorable adsorption conditions, and that sorption intensity is good at high concentrations but weak at lower concentrations. The large value of  $n$  indicates the heterogeneity of the surface of the adsorbent. A high value of the intercept,  $K_F$ , is indicative of high sorption capacity.<sup>26</sup>

#### Dubin–Radushkevish isotherm

This isotherm model is useful to estimate the characteristic porosity of the biomass and the apparent energy of adsorption.

The adsorption isotherm is given as:

$$q_e = q_D \exp\left[-\frac{B_D}{\sqrt{2}B_D} \left(1 + \frac{1}{C_e}\right)\right] \quad (7)$$

where,  $q_e$ (mg/g) is the amount adsorbed at equilibrium;  $q_D$  (mg/g) is the Dubinin–Radushkevish isotherm constant related to the degree of adsorbate sorption by the adsorbent surface and  $B_D$ , 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<sup>2</sup>) and;  $R$  is the gas constant (J/mol.K) and  $T$  is absolute temperature in Kelvin. The linear form of D-R model is:

$$\ln q_e = \ln q_D - B_D (RT \ln(1+1/C_e))^2 \quad (8)$$

We can estimate the mean free energy of adsorption  $E$  (Kj/mol) from the fitted parameter  $B_D$  as:

$$E = \frac{1}{\sqrt{2B_D}} \quad (9)$$

The Polanyi adsorption theory postulates that a fixed volume of adsorption sites is close to adsorbent surface and existence of 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.<sup>9,32</sup>

Polanyi adsorption potential can be expressed as:

$$\varepsilon = RT \ln(1+ 1/C_e) \quad (10)$$

The D-R isotherm affords important information about adsorption properties with calculating the average adsorption energy: so if

$E < 8$  KJ/mol it means that the physisorption dominates the adsorption mechanism, but 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.<sup>33,34</sup>

From the D-R model equation, the values of  $q_D$  and  $B_D$  calculated from the intercepts and slopes of the plots respectively are summarized in Table 1. So we noted that the higher values of  $q_D$ , the higher adsorption capacity unless for  $Cd^{2+}$ . Showing that the modified powder exhibited higher adsorption capacity than the unmodified powder, which means that oxidation strategy is aimed to increase the acidity of RDP and improve his ability to bind more heavy metal ions.

The value of  $E$  indicated the energy required to transfer one mole of adsorbate to the adsorption sites of adsorbent from the bulk solution. According to D-R model, the values of adsorption energy  $E$  for  $Cd^{2+}$  are greater than those for  $Pb^{2+}$ , in the case of the adsorption on modified-RDP. Therefore, the higher energy values revealed it needs more energy to transfer  $Cd^{2+}$  onto the surface of adsorbent than  $Pb^{2+}$ , which resulted in stronger adsorbing tendency toward  $Pb^{2+}$  than  $Cd^{2+}$ .<sup>35</sup> The free energies of sorption of  $Pb^{2+}$  and  $Cd^{2+}$  onto RDP powder were 22 KJ/mol and 10 KJ/mol respectively, suggesting that the former proceeded by chemisorption ( $E > 16$  KJ/mol)

whereas the later proceeded by ion exchange reaction ( $8KJ/mol < E < 16$  KJ/mol).

By the same way, the adsorption energies obtained 11.49 KJ/mol and 28.9 KJ/mol on modified-RDP powder for  $Pb^{2+}$  and  $Cd^{2+}$  respectively; supposed that an ion exchange reaction occurred for  $Pb^{2+}$  and chemisorption for  $Cd^{2+}$ ; which means that the structure of the adsorbent is modified. This indicated that the adsorption of  $Cd^{2+}$  was different from that of  $Pb^{2+}$  may be due to the shrinking of the polymer chain changes the surface properties of date pits powder.

### Temkin isotherm

The Temkin isotherm is given in the following form:

$$q_e = RT/b_T \ln(K_T C_e) \quad (11)$$

The linearized form of the equation (11) is denoted by the equation (12)

$$q_e = B \ln K_T + B \ln C_e \quad (12)$$

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 Temkin parameter related to the equilibrium binding energy.

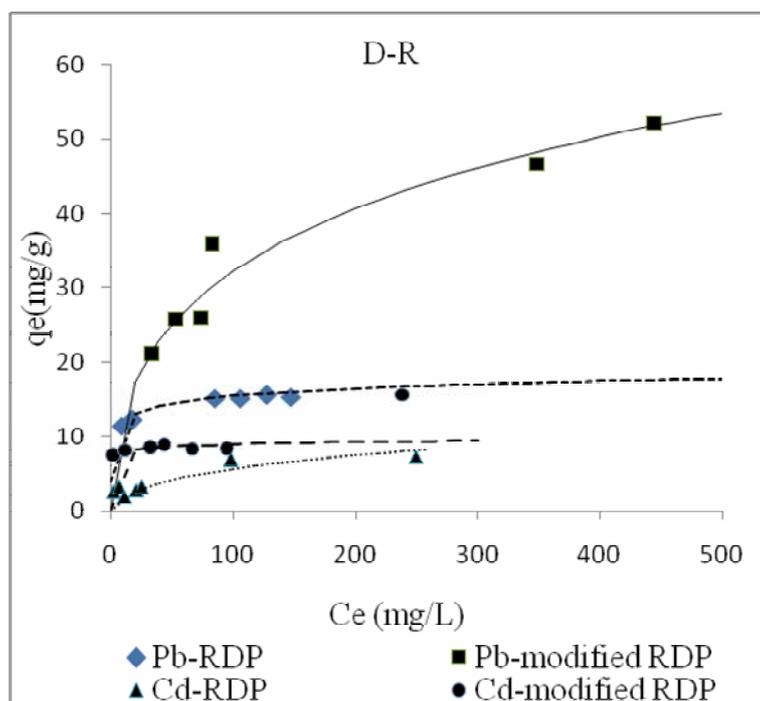


Fig. 4 – Dubinin-Radushkevich adsorption isotherms of  $Pb^{2+}$  and  $Cd^{2+}$  on RDP and modified- RDP.

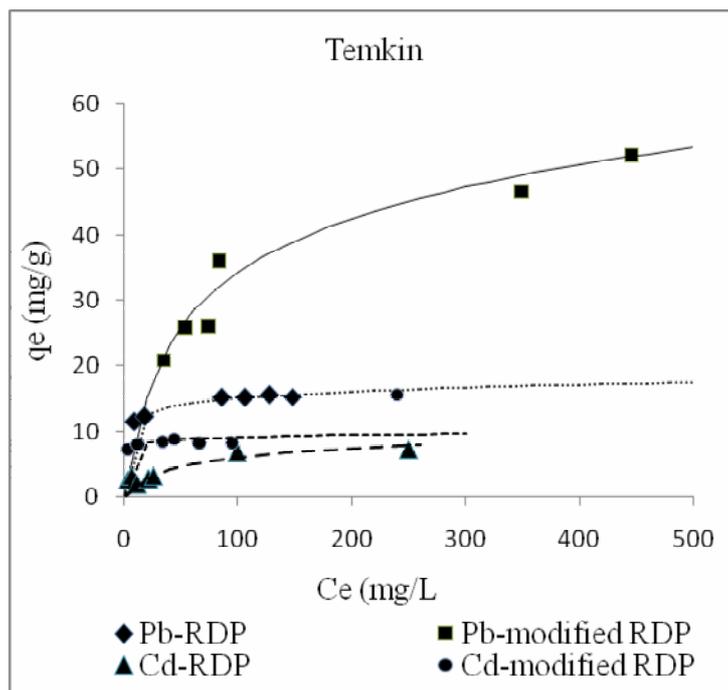


Fig. 5 – Temkin adsorption isotherms of  $Pb^{2+}$  and  $Cd^{2+}$  on RDP and modified-RDP.

Temkin isotherm model went on the effect of adsorbate-adsorbent interactions on adsorption isotherms and was based on these assumptions (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.<sup>36,37</sup>

As the values of  $R^2$ , in Table 1, are situated in the range 0.95 – 0.98 we consider that the fit between the experimental data and the model is fairly good for the adsorption of  $Pb^{2+}$  and  $Cd^{2+}$  on the adsorbents.

The energy of adsorption calculated by Temkin model in the case of the adsorption of lead and

cadmium are the same as the adsorption energy calculated by D-R model.

Generally, Temkin, D-R and Freundlich have the same correlation coefficients for raw RDP or modified-RDP which means that they present very well experimental points than Langmuir model. This results confirm that surface of adsorbents are heterogeneous.

The D-R showed a higher determination coefficient than Freundlich, Temkin and Langmuir for the adsorption of  $Pb^{2+}$  while in the case of  $Cd^{2+}$  the following order was observed: the Langmuir > D-R > Temkin > Freundlich.

Table 1

Isotherm constants of  $Pb^{2+}$  and  $Cd^{2+}$  biosorption by raw adsorbent and modified adsorbent

Model	Parameters	RDP		Modified-RDP	
		$Pb^{2+}$	$Cd^{2+}$	$Pb^{2+}$	$Cd^{2+}$
Langmuir	$Q_{max}$ (mg/g)	15.625	8.55	55.56	8.65
	$b$ (L/mg)	0.2873	0.0249	0.0169	1.8858
	$R^2$	0.9369	0.9874	0.92	0.9237
	$R_L$	0.01-0.15	0.14-0.89	0.11-0.76	0-0.05
Freundlich	$K_F$	8.97	0.71	6.593	6.891
	$n$	8.88	2.2	2.9674	16.103
	$R^2$	0.984	0.9434	0.93	0.9709
Temkin	$B$	1.51	1.93	11.81	0.5
	$b_T$ (J/mol)	1631.70	1280.80	209.08	4967.33
	$K_T$ (L/g)	213.050	0.229	0.183	916229

Table 1 (continued)

	$\Delta Q$ (J/mol)	25495.4	10947	11614.5	42967.4
	$R^2$	0.9829	0.9551	0.947	0.9673
D-R	$q_D$ (mg/g)	22.06	25.34	123.84	10.69
	$B_D$	$6.10^{-6}$	$5.10^{-9}$	$3.79.10^{-9}$	$6.10^{-10}$
	$E$ (J/mol)	22361	10000	11492	28900
	$R^2$	0.99	0.9622	0.93	0.9706

**Error estimation:** An absolute error average  $\Delta q_e$  is calculated as below:

$$\Delta q_e = \frac{1}{n} \sum_{i=1}^n |q_e \text{ exp.} - q_e \text{ calc.}| \quad (13)$$

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

Table 2

Absolute error average  $\Delta q_e$  (mg/g)

Model	RDP		Modified-RDP	
	$Pb^{2+}$	$Cd^{2+}$	$Pb^{2+}$	$Cd^{2+}$
Langmuir	0.60	1.20	3.00	0.82
Freundlich	0.80	1.20	2.00	0.80
Temkin	0.80	1.40	2.70	0.80
D-R	1.00	1.20	2.10	0.79

Table 3

Comparative evaluation of RDP, modified-RDP and 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	7.40	6.02	[9]
Rice husk	58.10	/	[38]
Olive cake	/	10.56	[39]
Coffee husk	/	6.90	[40]
Olive tree punning waste	27.40	/	[41]
Argan barks	16.78	6.52	[42]
Modified argan barks with TEMPO	26.52	8.06	[42]
Douglas fir barks	24.65	12.36	[42]
Modified Douglas fir barks with TEMPO	199.84	67.32	[42]
RDP	15.62	8.55	This study
Modified-RDP	55.56	8.65	This study

## Analysis techniques

### Structural characterization by infrared spectroscopy analysis

Infrared spectroscopy was used to obtain information about the chemical structure and functional groups of the raw material RDP and the modified- RDP. The FTIR spectrum of the RDP is shown in Fig. 6. The band located  $3366 \text{ cm}^{-1}$  corresponds to the -OH vibrations of carboxylic acids, phenols and alcohols.

The band at  $1740 \text{ cm}^{-1}$  corresponds to carbonyl C= O groups. Then the C=O of protein, C=O of carboxylates appears at  $1646 \text{ cm}^{-1}$ , while the skeletal C=C vibrations in aromatic is defined by the band at  $1518 \text{ cm}^{-1}$ . And the band at  $1436 \text{ cm}^{-1}$  corresponds to C-O carboxylates and  $1370 \text{ cm}^{-1}$  to C- H deformation.

After oxidation of the primary alcohol by NaOBr catalyzed by TEMPO, the intensity of the band of -OH at  $3374 \text{ cm}^{-1}$  has increased which means that the oxidation of primary alcohol to carboxylic groups was successful. Otherwise, a shoulder at  $1735 \text{ cm}^{-1}$  appears, because of the overlap with the band at  $1650 \text{ cm}^{-1}$  of carboxylates groups which was increased. The band of C-O carboxylates was shifted to  $1412 \text{ cm}^{-1}$ . The spectrum of modified-RDP powder treated with HCl (1N) has permitted the appearance of the band of COOH at  $1732 \text{ cm}^{-1}$  and the band C=O carboxylates was shifted to  $1650 \text{ cm}^{-1}$ .

We also noticed the disappearance of the bend at  $1518 \text{ cm}^{-1}$  which is supposed to correspond to lignin, which explain the loss of weight of RDP after fonctionnalization and the modified-RDP powder has a clear color.

### Measure of carboxylate content by conductimetry

The carboxyl content of RDP and modified-RDP was obtained by conductimetric titration. The amount of 50 mg of RDP or modified-RDP, were suspended into 15 mL of 0.01M hydrochloric acid solution. After 30 minutes of stirring, the suspensions were titrated with 0.01M NaOH (Fig. 7). The degree of oxidation is calculated as:

$$DO = \frac{162 C (V_2 - V_1)}{m - 36 C (V_2 - V_1)} \quad (14)$$

where C is NaOH concentration (mol/L),  $V_1$  and  $V_2$  are the volume of NaOH (L) and m (g) the mass of RDP or modified-RDP, 162 is the molar mass of glucose unit engaged in glycoside bond, 36 represents the difference between the molecular weight of an AGU and that of the sodium salt of glucuronic acid moiety.<sup>43</sup>

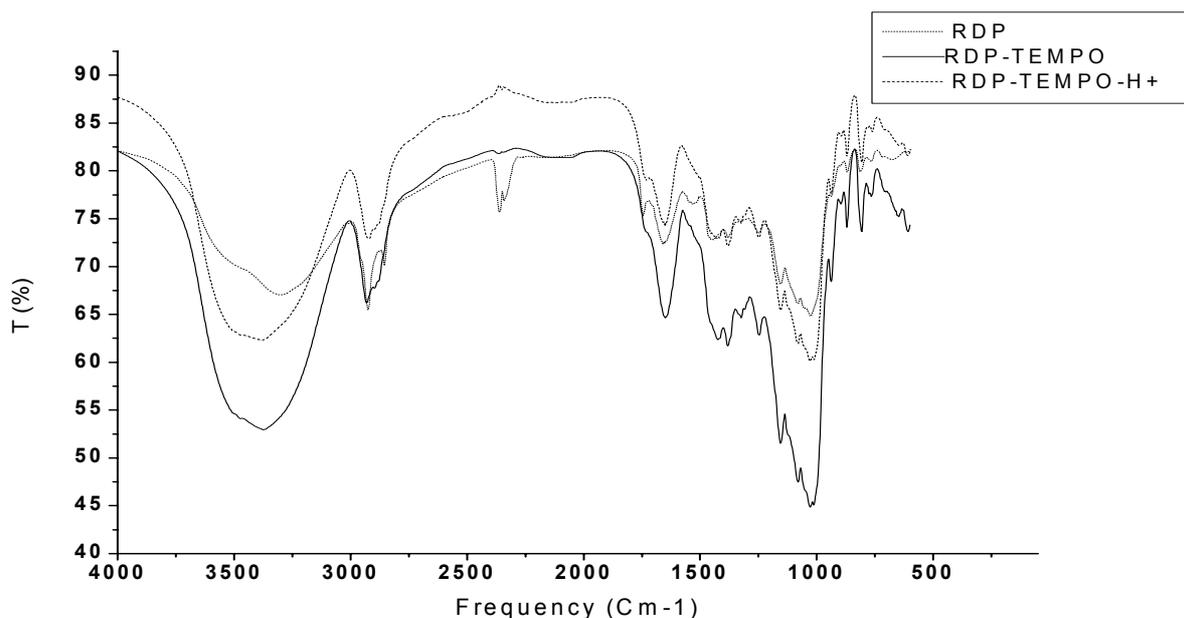


Fig. 6 – FTIR spectra of RDP and modified-RDP with TEMPO/NaBr/NaOCl.

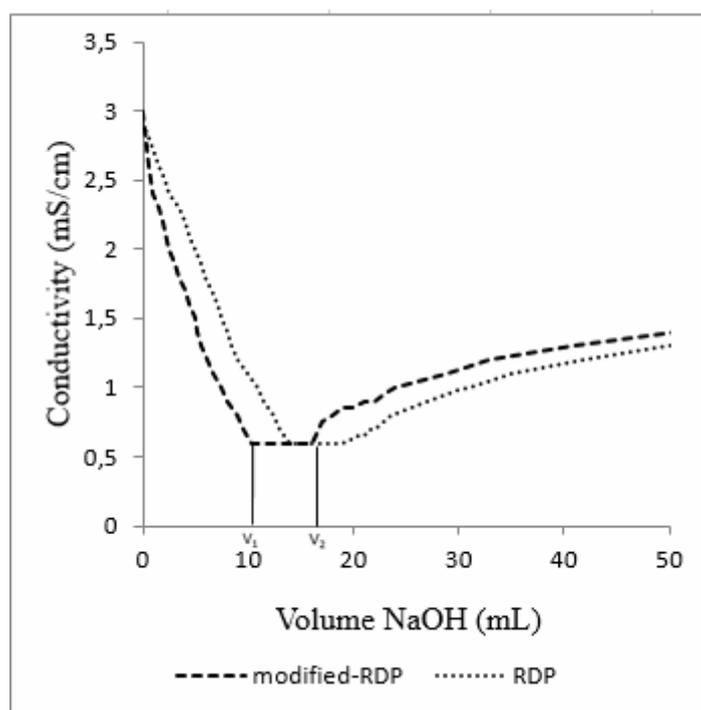


Fig. 7 – Conductimetric titration curves of RDP and modified- RDP.

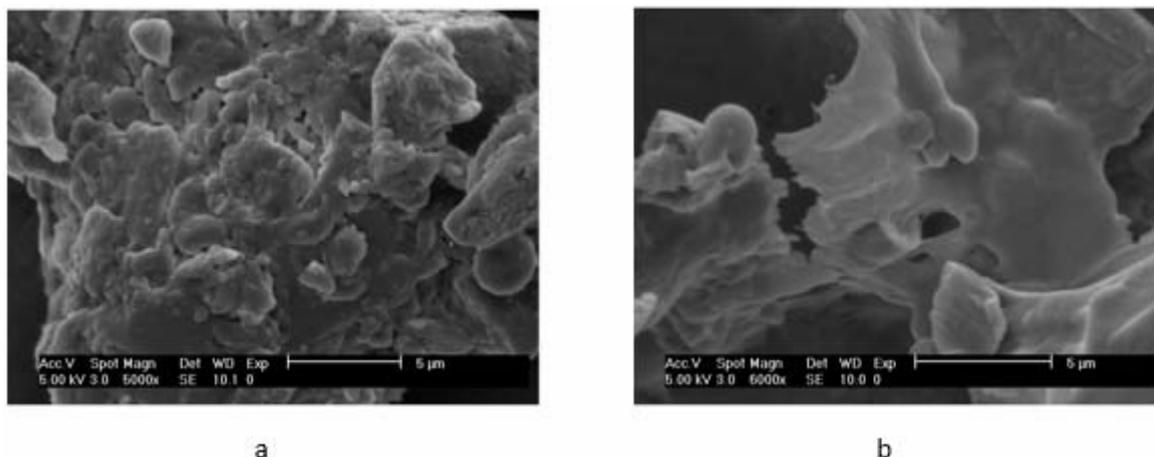


Fig. 8 – SEM micrographs for RDP (a) and modified -RDP (b).

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 that 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 19.14 % for the modified raw date pits. This means that oxidation of primary alcohol groups to carboxylic groups was successful.

#### Scanning electron microscopy (SEM)

The scanning electron microscopy of the raw date pits powder (Fig. 8, a) shows a texture in form of heterogeneous aggregates and low porosity.<sup>44</sup> After the chemical modification (Fig. 8, b) the powder has more homogeneous structure, compact structure then some porosities appear.

#### CONCLUSIONS

This study demonstrates that raw date pits can be a potential adsorbent of lead and cadmium and contributes to the valorization of agricultural waste by-products and the treatment of wastewater. The chemical modification of this raw adsorbent is a successful way to improve the adsorption uptake without using organic toxic solvents.

The RDP treated with TEMPO/NaBr/NaOCl system was found to be efficient to raise the uptake

of  $Pb^{2+}$  ions by 3.5 times and has a small effect on  $Cd^{2+}$  ions elimination. It was observed that the affinity of adsorption on RDP or modified -RDP is in this order  $Pb^{2+} > Cd^{2+}$  which is due to the effect of the both electronegativity and ionic radius.

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