

Using a New Lignocellulosic Material Based on Palm Stems for Hexavalent Chromium Adsorption in Aqueous Solution

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Received 2 Jan. 2015;

Revised 24 June 2015;

Accepted 2 July 2015

ABSTRACT: The objective of this work was focused on the use of a new natural lignocellulosic material based on palm stems for adsorbing of hexavalent chromium (Cr(VI)) in water. The palm stems powder (PSP) was characterized using different techniques. The effects of different operating parameters on the adsorption of Cr(VI) ions were investigated. The results show that the increase of the temperature and the initial Cr(VI) concentration leads to increase the adsorption quantity of Cr(VI) on PSP up to the a maximum in the range of 1.5-2.5 mg/g. On the other hand, the results of the adsorption isotherms follow the Freundlich model and the kinetic adsorption follows the pseudo-second order reaction. In addition, the thermodynamic study indicates that the adsorption process which depending the solution pH, is an endothermic and spontaneous phenomenon. Overall, our results show the adsorption behavior of this raw material that can be used as a low-cost alternative to commercial materials.

Key words: Hexavalent chromium, Lignocellulosic material, Palm stems, Adsorption; Water.

INTRODUCTION

Hexavalent chromium (Cr(VI)) is one of the most toxic heavy metals that exists in contaminated wastewaters discharged from pigment and paint production, leather tanneries and textile industries etc... (Elovitz and Fish 1995; Walsh and O'Halloran 1996, Anirudhan *et al.*, 2013). It is known as a notoriously toxic and potential carcinogen (Palmer and Wittbrodt 1991; Costa 2003). Of the classical techniques have been used for removing of Cr(VI) from wastewater, the adsorption is considered as one of the most advantageous processes due to its efficiency, low cost and much more practical. Even the granular activated carbon recognized as the best available adsorbent for water treatment, it is still considered more expensive. Furthermore, both chemical and thermal regeneration of used granular activated carbon is costly, impractical on a large-scale, and can produce additional effluents and results in considerable loss of the adsorbent. Recently, many researchers have interested to cheaper natural alternative adsorbents like lignocellulosic materials such as olive pits/stones (M. Isidora Bautista-Toledo *et al.*, 2013), date stones (Ziati *et al.*, 2012) peach pits and almond shells (Amit and Mika., 2010). As consequently, this strategy reduces significantly the treatment cost and contributes to sustainable development. In the

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present work, we have used the raw palm stems, an agricultural waste abundantly available in the south of Algeria (Oued-Souf region) as an adsorbent to remove hexavalent chromium from water. For well-understating the adsorptive capacity of this material, its characterization and the Cr(VI) adsorption experiments have been achieved. The characterization of this material was concerned: the surface functions, the material composition, the specific surface area and the morphology. For the adsorption optimization, the influence of some parameters namely adsorbent mass, Cr(VI) concentration, pH, temperature, ionic strength have been investigated. Finally, a modeling of adsorption isotherms has been studied.

MATERIALS & METHODS

The palm stems collected from a local farmland in Oued-Souf region (Algeria) was used in this study. This material was cut into small pieces and was washed several times by double-distilled water in order to eliminate the impurities like sand and dust. After that, the material was dried at 105°C for 24 h to evaporate the humidity. The obtained material was ground using grinder of type Janke and Kunkel IKA labortechnik in order to improve its specific area. Finally, the powder was sieved at a diameter of 1 mm.

The characterization was realized for exploring the structure and the texture of the material. The surface functions of the material were determined using the method described by Boehm 1966. The BET specific surface area was measured by N₂ adsorption isotherm at 77 K using Thermo Quest Sorptomatic 1990. The surface morphology of the material was carried out using Scanning Electron Microscope (SEM) model XL-3 CP, Philips. The chemical composition of PSP by elements was determined by humid mode (AFNOR 1979). Sugars species are measured and identified by HPAEC-PAD. The analyses are performed on a chromatograph Dionex ICS-3000 equipped with a column Carboxyl PA20 Dionex (3x150 mm) and a guard column (3x50 mm) as stationary phase to separate and identify sugar molecules depending to their sizes. The mobile phase was prepared by diluting a NaOH solution of 46-48% in ultrapure water. Monosaccharides and uronic acids are separated respectively in isocratic conditions and using a linear elution gradient. X-ray analysis (XRD) was carried out on X-ray diffractometer (Philips X'PERT PANalytical, Almelo, the Netherlands) using monochromatized CuK α radiation at $\lambda = 1.54 \text{ \AA}$.

All chemicals used in this study have an analytical grade. The chromium stock solution was prepared by dissolving of 2.828 g of potassium dichromate (98% Aldrich) in 1L of ultrapure water with a resistivity of 18 M Ω .cm. From this stock solution, working solutions with different concentrations were prepared by dilutions. The adjustment of the pH of solution was achieved with HCl (Aldrich) or NaOH (Aldrich) and monitored by a pH-meter (HANNA HI 9812-5).

The determination of Cr(VI) adsorption capacity on PSP required in first the optimization of two important parameters : the mass of PSP and the contact time. In order to accomplish this, masses of PSP varying from 0.05 to 3 g, previously dried at 105°C until a constant weight, were mixed with 50 mL of a Cr(VI) solution at 15 ppm in a set of Erlenmeyer flasks with a capacity of 100 mL. After having been agitated for 3 h at a maintained constant temperature in water-bath of 20°C in a solution pH of 5.4, the samples are filtrated in order to measure the residual concentration of Cr(VI) using a UV-Vis spectrophotometer (JENWAY 6405) at a wavelength of 540 nm via the 1,5-diphenylcarbazide standard method (ASTM., 2009).

The adsorption rate of Cr(VI) was calculated using equation (1):

$$R(\%) = \frac{(C_0 - C_e)}{C_0} \cdot 100 \quad (1)$$

The adsorbed quantity of Cr(VI) ions was calculated by the method of rest (equation 2):

$$Q_e = \frac{(C_0 - C_e) \cdot V}{m} \quad (2)$$

Where, C₀ and C_e are the concentrations of initial Cr(VI) solution and at the equilibrium respectively (ppm); Q_e is the equilibrium adsorption capacity (mg/g); V is the solution volume (L); m is the adsorbent dose (g). The effect of solution pH was tested in the range of 1.5-11 under the following conditions: [Cr(VI)] = 15 ppm; [PSP] = 2 g; temperature = 20°C; contact time = 3 h. The effect of Cr(VI) concentration was realized with concentrations from 5 to 50 ppm under these conditions: [PSP] = 2 g; pH = 5.4; temperature = 20°C; contact time = 3 h. The influence of the temperature was tested with values 20; 30; 40 and 50°C under these conditions: [PSP] = 2 g; [Cr(VI)] = 15 ppm; pH = 5.4 and contact time = 3 h. The study of the effect of ionic strength was carried out with different concentrations of NaCl (0; 0.05; 1 and 2 mol/L) on different solutions of Cr(VI) at different concentrations from 5 to 50 ppm, pH = 5.4, contact time 3 h and 2 g of PSP.

RESULTS & DISCUSSION

The determination of different physico-chemical properties of adsorbent is an important point for well understanding the adsorption process. From table 1, it can be noticed that both carbon and oxygen elements represent a major part of this material with mass ratios of 42.3 and 46.6 % respectively, followed by the hydrogen with a ratio of 6.4 %. However, only 0.2 % of nitrogen was detected in the material. This is consistent with the fact that the important PSP constituents are cellulose and lignin. Ying-Shui Shen *et al.*, (2012), have found similar observation in the coir fibers. The cellulose and lignin amounts represent 14.87 and 20.78 % respectively. For the monomer composition of the polysaccharide, the Glucose and Xylose consist the major composition of monosaccharides with 26.68 and 12.48 % respectively. The BET specific surface area of PSP sample determined from the adsorption-desorption isotherm of nitrogen at a liquid temperature of 77 K is 5.9 m²/g. The total pore volume is 0.07 cm³/g. The total acidity of the material surface is 3.2 meq/g with a maximum fraction of lactone groups (2.1 meq/g), traces of carboxyl groups (0.01 meq/g) and phenolic (0.4 meq/g). This acidity of the PSP surface is well correlated with the acidic water extracted from the material, which is 6.02, and with the important rate of oxygen found in the material. Several authors have confirmed the strong relationship between the surface acidity and the rate of the structure oxygen of the material (Hazourli *et al.*, 1994).

In general, XRD result (Fig. 1.a) shows that the PSP is an amorphous material. It is worth noting that

Table 1. Principal physico-chemical characteristics of PSP material.

Element:	N	C	H	O	S	Ca	Mg	Al	Fe	Na	K
(%)	0.25	42.31	6.44	46.6	0.98	0.16	1.20	0.25	0.05	0.38	0.57
Monosaccharides :	Glucose		Mannose		Xylose		Rhamnose		Galactose		Arabinose
(%)	26.68		1.35		12.68		0.43		1.33		0.34
Functions acid groups (m ² /g):	Total : 3.2			Carboxylic : 0.01			Phenol: 0.4			Lactone : 2.1	
Cellulose- Lignin content (%):	Cellulose: 14.87				Lignin: 20.78						
Texture properties:	Specific surface area: 5.9 m ² /g						Pore volume: 0.07 cm ³ /g				

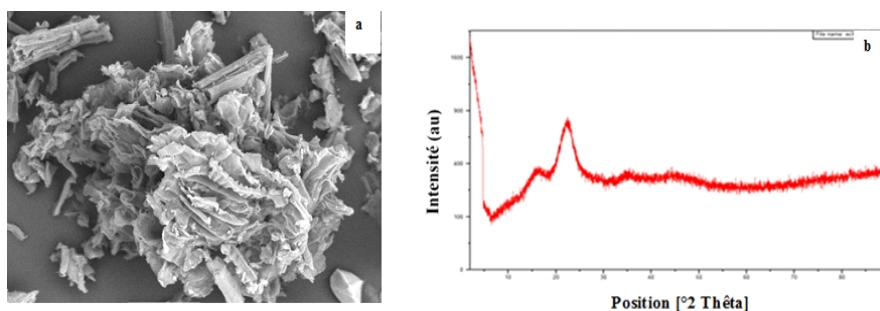


Fig. 1. XRD pattern (a) and SEM picture (b) of PSP sample.

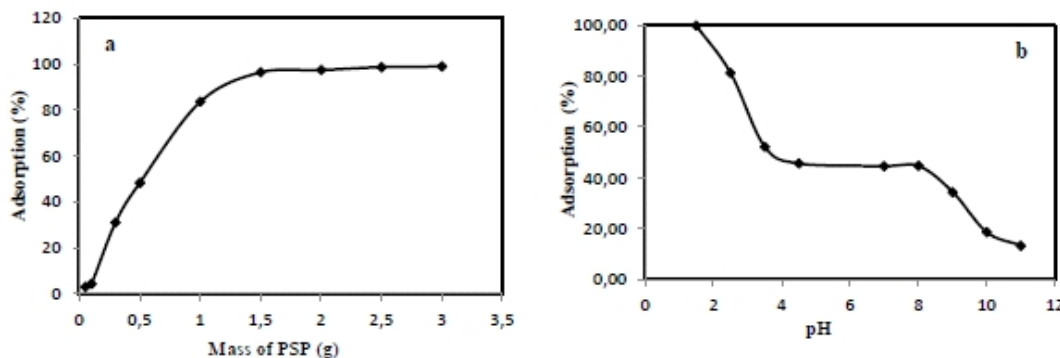


Fig. 2. Effect of PSP mass (a) and pH solution (b) on the adsorption of Cr(VI). Conditions: (a) [Cr(VI)]: 15 ppm, pH solution: 5.4, temperature: 20°C and contact time: 3h. (b): [Cr(VI)]: 15ppm, mass of PSP: 2 g; temperature: 20°C and contact time = 3 h.

the broad band at around 22° in the halo-pattern may be represented some crystalline phases in the material. The morphology of the material described by SEM analysis is shown in Fig. 1.b. From this figure, it is clear that the material has a quasi-spongy structure which facilitates the fixation of different pollutants into its pores. This specific perforated surface is consisted by the ùbers containing in these kinds of materials.

The effect of adsorbent mass on the Cr(VI)adsorption (15 ppm) was studied in the range of 0.05-3 g. The results are shown in Fig.2.a. From this figure, it can be seen that the adsorption rate of Cr(VI) increases proportionality with the increase of PSP mass in the range of 0.5-1.5 g which varies from 3 to 96.3 %. Above this value, there is a slight increase on the adsorption rate for the values 2 g (98 %), 2.5 g (98.6 %) and 3 g (98.9 %). The increase on the adsorption rate

in the range of 0.5-1.5 g is due to the availability of enough active sites on the adsorbent surface which facilitates the Cr(VI) ions fixation. After that, the mass of PSP does not affect the adsorption rate as the number of adsorptive sites is as much as necessary for the immobilization of Cr(VI) ions at 15 ppm from the value 2 g. Also, the adding of higher adsorbent mass above the saturation, results a lower adsorption capacity value as the availability of higher energy sites decreases with a large fraction of lower energy sites occupied (Gupta and Rastogi., 2008). Based on these results, the mass of 2 g was selected for the study of the subsequent experiments.

The pH of the solution is an important parameter for the adsorption process of metallic ions. It can change the ionization of the adsorbent surface and the metallic cation species in the aqueous solution.

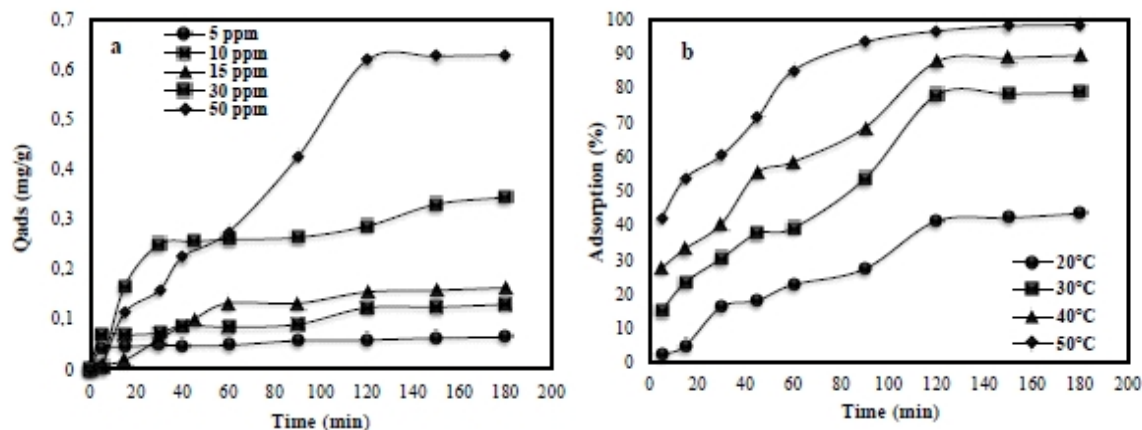


Fig. 3. Effect of initial Cr(VI) concentration (a) and temperature (b) on the adsorption of Cr(VI). Conditions: (a): pH solution: 5.4, temperature: 20°C, mass of PSP: 2 g. (b): [Cr(VI)] : 15 ppm, pH solution: 5.4, mass PSP: 2 g and contact time: 3 h.

Furthermore, it can also affect the biosorption mechanism of different ions on the biomaterials surface. The adsorption effectiveness of Cr(VI) ions at 15 ppm as a function of the initial pH of the solution was studied from 1.5 to 11. The results are represented in Fig. 2. b. From these results, it is clear that the adsorption of Cr(VI) depends strongly on the pH. The removal of Cr(VI) from the solution is highly observed in low pH values and it decreases at basic solutions. This behavior is explained by the role which has the acidic pH, the functional groups presented in the PSP surface (*i.e.* carboxyl groups, lactones, phenols) undergo a strong protonation which gives the material a global positive charge. Furthermore, the ionic forms of Cr(VI) presented in the solution have an anionic nature such as HCrO_4^- and $\text{Cr}_2\text{O}_7^{2-}$ at pH between 1 and 6 and CrO_4^{2-} at pH above 6 (Batista *et al.*, 2009). However, at lower pH less than 1, H_2CrO_4 is the predominant form. At basic pH, the adsorption decreases by the effect of hydroxyl ions (OH^-) which can adsorb on the PSP surface leading to decrease the adsorption of anionic Cr(VI) by the repulsion of charges. The same tendency of the effect of pH has been reported for other materials (Araújo *et al.*, 2013; Taha *et al.*, 2012; Shi *et al.*, 2011). In general, the distribution of chromium species is dependent on the pH of the solution (Mohan and Pittman, 2006; Taha *et al.*, 2012). Between pH 2 and 6, HCrO_4^- and the orange red dichromate ion $\text{Cr}_2\text{O}_7^{2-}$ are in equilibrium. Above pH 6, Cr(VI) forms tetrahedral yellow chromate ion CrO_4^{2-} . For the mechanism of Cr(VI) ions biosorption, there are four suggested models (Bidyut and Chris, 2010; Cerqueira *et al.*, 2012): anionic Cr(VI) adsorption, adsorption-coupled reduction, anionic and cationic adsorption and reduction and anionic adsorption. All of these models are dependent on the pH of the solution. The first model (anionic adsorption) based on the adsorption of negatively charged Cr(VI)

ions (chromate and dichromate) onto the positively charged surface of biosorbent (PSP). This suggestion is in accord with our results that at low pH of Cr(VI) solution, the adsorption increases and at high pH it decreases. This is due to the protonation of the biosorbent surface at low pH leads to attract more negatively charged Cr(VI) ions. However, at high pH, the surface becomes less or non-protonated where a repulsion between the negative chromium species and the biosorbent surface takes place. The second mechanism which can take place on the surface of biomass for removing Cr(VI) from solution is the adsorption-coupled reduction. According to this mechanism Cr(VI) is completely reduced to Cr(III) by functional groups in the biomass surface in acidic medium. Then dependent on the nature of biosorbent, a part of obtained Cr(III) is adsorbed in the surface and a part is released from the surface to the solution. This suggestion is also according to our results as the reduction reaction of Cr(VI) occurs in acidic solution. The third mechanism is almost similar to the second except that it is suggested that not all Cr(VI) is reduced but only a part from it. Then, the obtained trivalent chromium (cationic) and the rest of hexavalent chromium (anionic) are adsorbed to the biomaterial surface. In this case, the pH of the solution affects in the same time the adsorption and the reduction of chromium species. The fourth proposed mechanism is based on the reduction of hexavalent chromium to trivalent chromium by biosorbent and mainly of hexavalent chromium is adsorbed while trivalent chromium remains in the solution. The desorption of Cr(III) from the surface is due to the repulsion between these cationic charge and protonated biomass surface at acidic medium. From all these explanations, we can conclude that the pH of the solution has a strong effect on the adsorption of Cr(VI) in the biomaterial surface by different mechanisms.

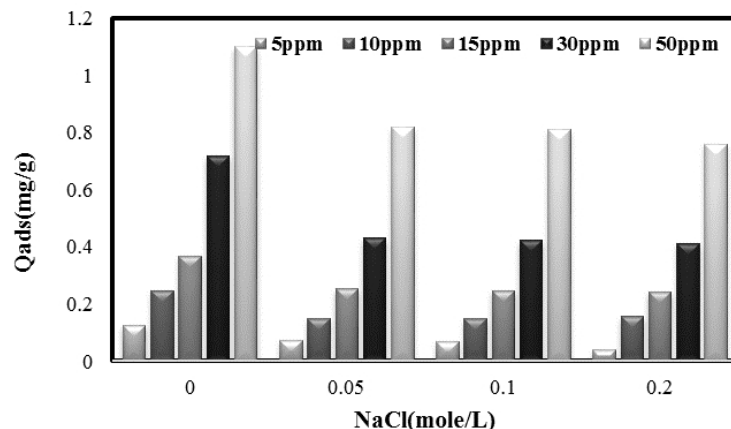


Fig. 4. Effect of ionic strength on the Cr(VI) adsorption. Conditions: [PSP]: 2 g, pH solution: 5.4 and contact time: 3 h.

The influence of Cr(VI) concentration on the adsorption capacity of PSP was investigated with different Cr(VI) concentrations from 5 to 50 ppm. The results are illustrated in Fig.3.a. From this figure, the adsorption capacity increases from 0.12 to 0.62 mg/g when the Cr(VI) increases from 5 to 50 ppm after 3h. This increase can be explained the availability of more Cr(VI) ions around the PSP surface when the concentration is increased which facilitates the fixation of more Cr(VI) ions. The same phenominal was observed for others materials (Ucun *et al.*, (2002) and Park *et al.*, (2006) and Gupta *et al.*, 2013). For the contact time or the equilibrated time of the Cr(VI) with the PSP, under the studied experimental conditions, it was considered as 180 min. However, 60 min was acceptable for Cr(VI) initial concentrations of 5 to 30 ppm. Usually, the contact time is selected at the material saturation or above, because these times correspond to pseudo-equilibriums. For example, under certain conditions and using activated carbons, these times are longer and can reach 72 h (Hazourli *et al.*, 1996).

The study of the effect of temperature on the Cr(VI) adsorption on PSP surface is illustrated in Fig. 3.b. It can be noticed that there is a clear improvement in the adsorption rate with the increase of the temperature. The adsorption rate increases from 43 to 98 % as the temperature increases from 20 to 50°C after 3h. Therefore, the adsorption of Cr(VI) by PSP seems to be an endothermic phenomenon. It can progress the mobility of Cr(VI) ions in the solution which leads to a fast adsorption on the active sites of PSP. Similar results have been reported by other groups such as Arica and Bayramoglu (2005) and Tewari *et al.*,(2005).The endothermic adsorption phenomenon of Cr(VI) on PSP surface will be confirmed in the thermodynamic study (section 3.9.). The presence of interfering ions with Cr(VI) in wastewaters is unavoidable. In order to investigate their effects on

the Cr(VI) adsorption on PSP surface, NaCl salt has been chosen as an electrolyte which can increases the ionic strength and interferes in aqueous solution by the presence of its ions. The study was realized by the application of different concentrations of NaCl on the different concentrations of Cr(VI). The results are shown in Fig.4. From this figure, the increase of ionic strength decreases the Cr(VI) adsorption on PSP. This is may be attributed to the competitive adsorption of these ions (Na⁺, Cl⁻) on the surface of PSP and blocked its sites which can reduce the coulomb attraction between the PSP surface and the Cr(VI) ions. This repulsive behavior has been observed by Albadarin *et al.*, 2013 for the ions CO₃²⁻ on the date-pits/tea-waste biomaterials and by Gupta *et al.*, 2013 using acrylic acid grafted lignocellulosic adsorbent and HCO₃⁻ as interfering.

In the present study, the adsorption equilibrium of Cr(VI) on PSP surface was described by two models such as Langmuir and Freundlich. The nonlinear and linear forms of Langmuir isotherm (Langmuir, 1918) are represented in the following equations respectively:

$$Q_e = \frac{Q^0 \cdot K_L \cdot C_e}{1 + K_L \cdot C_e} \quad (3)$$

$$\frac{C_e}{Q_e} = \frac{1}{K_L \cdot Q^0} + \frac{C_e}{Q^0} \quad (4)$$

Where, Q_e is the adsorbed quantity of the pollutant on the adsorbent surface at the equilibrium (mg/g); Q⁰ represents the maximal quantity of adsorbate (mg/g); K_L is the relative constant of adsorption energy (L/mg). The graphic representation of the rapport variation (C_e/Q_e) as a function of (C_e) gives a linear. From this latter, the theoretic values such as Q⁰ and K_L are calculated.

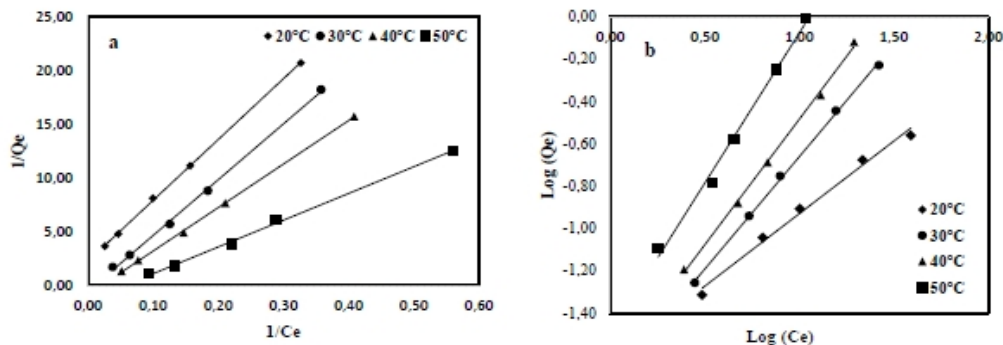


Fig. 5. Isotherms of Langmuir (a) and Freundlich (b) models for Cr(VI) adsorption on PSP.

Table 2. Constants of Langmuir and Freundlich for Cr(VI) adsorption on PSP

Models	Parameters	20°C	30°C	40°C	50°C
Langmuir isotherm	Q°(mg/g)	0.44	0.70	1.17	1.70
	K _L	0.1	0.2	0.4	0.6
	R ²	0.989	0.988	0.995	0.992
	D (%)	2.04	2.2	2.5	2.8
	n	0.91	0.93	0.97	1.18
Freundlich isotherm	K _F	0.19	0.21	0.24	0.32
	R ²	0.999	0.998	0.999	0.997
	D (%)	0.07	0.09	1.2	1.8

The nonlinear and linear forms of Freundlich isotherm (Freundlich., 1906) are represented by the following equations respectively:

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

$$\text{Ln}Q_e = \text{Ln}K_F + \frac{1}{n} \text{Ln} C_e \quad (6)$$

Where, K_F is the Freundlich constant; n is a relative factor of adsorption intensity, it can be also named a heterogeneity factor. The graphic representation of LnQ_e as a function of LnC_e leads to a linear regressions from where the theoretic values n and K_F are calculated. The best adjustment of each isotherm model is estimated from both the correlation coefficient (R²) and the percentage of error deviation (% D). Furthermore, the results of modeling are considered as appropriate for describing the biosorption process if the error deviation is less than 5% and the coefficient R² is more than 95 %. The percentage of error deviation (% D) is calculated from this formula:

$$D = \frac{1}{N} \sum_{i=1}^N \left| \frac{Q_e - Q_{cal}}{Q_e} \right| \cdot 100 \quad (7)$$

Where, N is the number of experimental points; Q_{cal} is the calculated quantity of Cr(VI) adsorbed (mg/g).

The results of correlation coefficients and percentage of error deviation constants for both models for a temperature of 20°C are shown in Table 2.

The obtained experimental adsorption capacity data were compared with the theoretical values obtained from the linear model constants derived from the empirical non-linear equations of the Langmuir and Freundlich isotherms (Eqs. (3) and (5) respectively). The adsorption data were best fitted using the Freundlich model (Table 2 and Fig.5 b), with a good linear correlation for the concentration range used (5-50 mg/L). The R² value obtained for the Freundlich model applied to adsorption of Cr(VI) on palm stems was compared to a value of R² obtained using the Langmuir model. Furthermore, both the obtained calculated percentage of error deviation of Freundlich and Langmuir are lower than 5%. These results indicate that the adsorption process involved multiple layers, a heterogeneous surface, and active sites with different bonding energies (Ismadji *et al.*, 2009).

According to Febrianto *et al.*, (2009), a favorable adsorption is normally indicated by a Freundlich constant (n) between 1 and 10. A higher value of n (smaller value of 1/n) implies strong interaction between adsorbate and adsorbent, while n equals to 1 indicates a linear adsorption process, with constant energy on the entire surface. Application of the linear Freundlich

Table 3. Cr(VI) adsorption by lignocellulosic materials.

Adsorbent material	Qmax (mg/g)	pH	References
Palm stems	2.44	2.0	This study
Neurosporacrassa	0.43	1.0	Tunaliet <i>et al.</i> , 2005
Crust of soybean	0.28	1.0	Daneshvaret <i>et al.</i> ,2002
Sugarcane	0.28	2.0	Garg <i>et al.</i> , 2007
Cake Oil cake	0.63	2.0	Garg <i>et al.</i> , 2007
Maize corn cob	0.82	2.0	Garg <i>et al.</i> , 2007
Soya cake	0.28	<1.0	Daneshvar <i>et al.</i> , 2002
Pine	0.47	2.0	Aliabadi <i>et al.</i> , 2006
Oak tree (treated)	1.74	3.0	Argun <i>et al.</i> , 2007
Almond	3.40	3.2	Pehlivan and Altun 2008
Walnut	2.28	4.0	Agarwal <i>et al.</i> , 2006
Palm flower	4.90	4.50	Elangovan <i>et al.</i> , 2008
Volcanic rocks-pumice	0.046	2.0	Alemayehu <i>et al.</i> , 2011

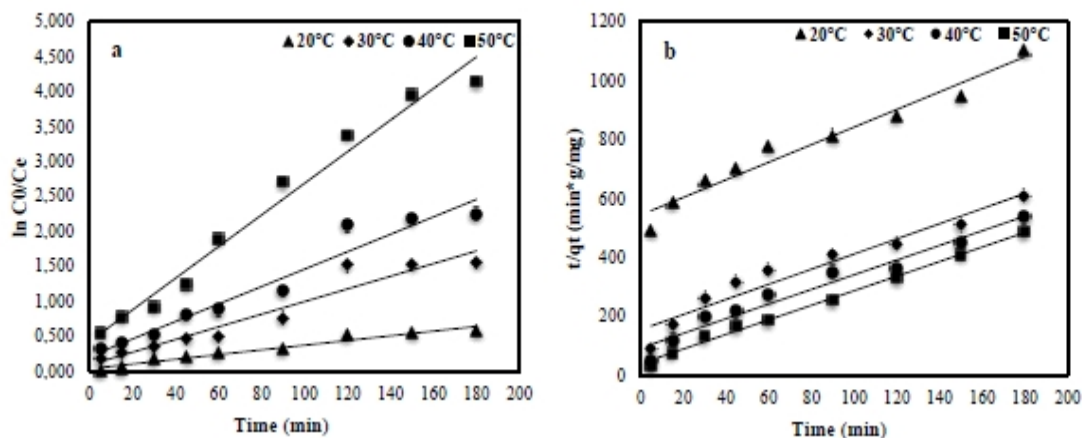


Fig. 6. Slopes of Pseudo-first order (a) and Pseudo-second order (b) kinetics for Cr(VI) adsorption on PSP.

model gave a value of n equals to 1.91, reflecting a favorable adsorption process and satisfying the condition of heterogeneity ($1 < n < 10$ and $0 < 1/n < 1$) (Srihari and Das, 2008), as required by the model. Similar conclusions were found by Albadarin *et al.*, (2013), Araújo *et al.*, (2013), Albadarin *et al.*, (2011). Moreover, as shown in table 3, we made a comparison between our experimental results of Cr(VI) adsorption on PSP surface with others studies reported in the literature using some lignocellulosic materials. From this table, the results of our new raw adsorbent (PSP) show that it has an acceptable potential for removing of Cr(VI) from water with a maximum adsorption capacity of 2.44 mg/g compared to several materials shown in this table. However, others lignocellulosic materials applied in others studies have been shown much higher adsorption capacities such as Bengal gram husk: 91.64 mg/g (Ahalya *et al.*, 2005) and Rice: 285.71 mg/g (Singh *et al.*, 2005). These differences of adsorption capacity of Cr(VI) ions may be attributed to the adsorbent properties like the structure, the functional groups and the specific surface area. Furthermore, the chemical

and thermal treatments usually applied for these materials in order to increase their adsorptive behaviors can be envisaged.

$$\ln \frac{C_0}{C_e} = -k_1 t \tag{8}$$

Where C_0 and C_e represent the Cr(VI) concentration (ppm) before and after adsorption, t is the contact time (min), and k_1 is the adsorption rate constant of pseudo-first order (min^{-1}).

$$\frac{dQ_t}{dt} = k_2(Q_e - Q_t)^2 \tag{9}$$

Where Q_e and Q_t are the adsorption capacity at equilibrium (mg/g), respectively, k_2 is the adsorption rate constant of the pseudo-second order (g/mg.min). For the boundary conditions $t = 0$ to $t = t$ and $Q_t = 0$ to $Q_t = Q_e$, the integrated form of equation (9) will be as follows:

$$\frac{1}{Q_e - Q_t} = \frac{1}{Q_e} + k_2 t \tag{10}$$

Table 4. Kinetic constant parameters obtained for Cr(VI) adsorption on PSP

T (°C)	Pseudo-first order		Pseudo-second order		
	k_1 (min ⁻¹)	R ²	k_2 (g/mg.min)	H (g/mg.min)	R ²
20	0.003	0.9489	0.006	0.0017	0.9589
30	0.008	0.9295	0.02	0.006	0.9337
40	0.011	0.9512	0.03	0.011	0.9616
50	0.021	0.9787	0.06	0.025	0.9939

Table 5. Thermodynamic parameter values for Cr(VI) adsorption equilibrium on PSP.

ΔG° (J/mol.K)				ΔH° (kJ/mol)	ΔS° (J/mol.K)
20°C	30°C	40°C	50°C	21.46	-54.87
-504	-435	-330	-270		

Equation (10) can be rearranged to obtain equation (11), which has a linear form:

$$\frac{1}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{t}{Q_e} \quad (11)$$

The initial adsorption rate, h (mg.g⁻¹ min⁻¹) is given as:

$$h = k_2 Q_e^2 \quad (12)$$

Furthermore, equation (11) can be written as:

$$\frac{t}{Q_t} = \frac{1}{h} + \frac{t}{Q_e} \quad (13)$$

The results of the application of both model equations are shown in Fig. 6 and the kinetic constants deduced from these figures are presented in table 4. The comparison allows to concluded that the Cr(VI) removal follows the pseudo-second order model with correlation coefficients (R²) of 0.95 to 0.99. The increase of the rate constant k_2 as a function the temperature signifies the increase of interactions between Cr(VI) ions and PSP surface. Similar results have been reported by Dakiki *et al.*, 2002 for removing of Cr(VI) using different lignocellulosic adsorbents at temperature of 30°C and pH 2, and by Li *et al.*, 2007 for Cr(VI) adsorption on modified sawdust and bark peanut for temperature values of 20, 25, 30 and 40°C. These results indicate that the process governing the Cr(VI) adsorption on PSP surface is a chemisorption which involves forces and electron exchanges between the adsorbent and the adsorbate. This hypothesis has been described by several authors in the case of pseudo-second order kinetics (Mohan *et al.*, 2006; Suhas *et al.*, 2007; Albadarin *et al.*, 2013).

The determination of different thermodynamic parameters such as Gibbs free energy ΔG° (J/mol), Entropy variation ΔS° (J/mol.K) and Enthalpy adsorption ΔH° (Kj/mol) is useful to identify the

biosorption process nature (endothermic or exothermic and spontaneous). These parameters can be calculated from these equations:

$$\Delta G^\circ = -RT \cdot \ln(K_d) \quad (14)$$

$$\ln(K_d) = \frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \quad (15)$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (16)$$

Where R is the gas constant (8.3145 J/mol.K); T is the temperature (K); K_d (L/g) is the adsorption equilibrium constant calculated from the slope of the graph $\ln(Q_e)/C_e$.

From the thermodynamic data results illustrated in table 5, the negative value of ΔS° indicates the favorable nature of the adsorption phenomenon. The negative values of ΔG° show that the Cr(VI) adsorption process is spontaneous. The increase in ΔG° with increasing temperature showed that the adsorption was more favorable at high temperature. Furthermore, the positive value of ΔH° proves the endothermic nature of this process. Other workers have also reported similar results for the adsorption of Cr(VI)(AL-Othman *et Naushad*, 2012 ; Gonzalez *et al.*, 2005 ; Tazerouti *et Amrani*, 2010).

CONCLUSIONS

In the present work, we showed the adsorption capacity of a new natural lignocellulosic material based on the palm stems. The most remarkable results of the characterization of this material are the BET surface area (about 5.4 m²/g) and the pore volume (about 0.07 cm³/g), the amorphous structure of this material and the presence of surface oxides mainly acids. The study of the effects of different operating parameters shows that the adsorption capacity of Cr(VI) on PSP surface is between 1.5 to 2.5 mg/g. The Cr(VI) adsorption effectiveness depends strongly the pH of the solution where it is more important at low pH values. The ad-

sorption capacity of PSP increases with the increase of the initial Cr(VI) concentration and temperature. The effect of ionic strength study shows that the presence of NaCl with Cr(VI) inhibits the adsorption process. On the basis of the results obtained, it can be concluded that the palm stems materials can be used alternative successful to the commercial granular activated carbon for Cr(VI) removing from wastewaters.

ACKNOWLEDGEMENTS

The authors acknowledge the financial support of the Ministry of Higher Education and Scientific Research of Algeria.

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