ORIGINAL ARTICLE

Removal of Chromium (VI) from Wastewater by Palm Kernel Shell-based on a Green Method

Maryam Razavi Mehr[1], Mohammad Hossein Fekri[*1], Faezeh Omidali[1], Noushin Eftekhari[1], Behrouz Akbari-adergani[2]

[1]*Department of Chemistry, Ayatollah Boroujerdi University, Borujerd, Iran*

[2]*Food and Drug Laboratory Research Center, Food and Drug Administration, Ministry of Health and Medical Education, Tehran, Iran*

ABSTRACT: The potential of palm kernel shell, as agricultural waste, to remove Cr (VI) from aqueous solution was evaluated. Effective parameters such as pH (2–8), temperature (20–80 °C), contact time (10-120 min), adsorbent concentration (0.1–1 g/L), and initial Cr (VI) concentration (10-100 mg/L) were all studied to attain the maximum removal efficiency. Results show the adsorption capacity increases as pH value decreases and the optimum pH value is pH= 2.0. The other optimal conditions are temperature 40 °C, contact time 45 min, adsorbent concentration 0.5 g/L and initial Cr (VI) concentration 10 mg/L. The equilibrium data for chromate adsorption well fitted to Freundlich equation, with maximum adsorption capacity of 125 mg/g. This novel activated carbon derived from palm shell powder has been found to be effective for the removal of Cr (VI) and not noxious to the ecosystem.

INTRODUCTION

The expansion of industries near the suburbs has led to the entry of high levels of heavy metals such as chromium, lead, mercury, cadmium and cobalt into groundwater and municipal sewage. These metals are stable and can have a damaging effect on our ecosystem and our general health [1, 2]. Chromium is one of the most abundant water pollutants in the oxidation states of II to VI. The most important steady state of this element is Cr, Cr (III) and Cr (VI) capacity that can be transferred from human resources to the environment. This metal can cause acute and chronic side effects in blood warming organs. Researchers believe that chromium is likely to be in the human's biological system at state III, which is derived from the diet [3, 4]. Cr (VI) typically comes from sewage produced by the cement,

mining, electroplating, leather tanning, dyeing and environmental industries [5]. Chromium concentration in industrial wastewater is 0.5 - 270 mg/L, and even reaches 1300 to 2500 mg/L in tannery [6]. This is while the European Union (EU) and United States Environmental Protection Agency (USEPA) have set the limit below 0.05 mg/L and the final limit of chromium III and VI recommended below 2 mg/L [7]. There are many ways to remove these ions in aqueous solutions that can have chemical, physical or biological approaches [8]. Physicochemical methods for chromium removal include of electrochemical reactions, ion exchange, membrane technology, chemical treatments, or adsorption by activated carbon [9-14]. The use of activated carbon as an adsorbent

can improve the quality of water. Also due to the high surface area, mesoporous cavities and the active level of carbon have a high potential for chromium removal as a contaminant in aqueous media [15].

Recently, the use of activated carbon from agricultural waste and biomass materials as Cr (VI) adsorbent has attracted many researchers due to the economic cost and availability. Among these lesions are rice and straw, olive bagasse, eichhornia crassipes, peanut shells, jatropha wood, longan seed and date palm seeds all have been used to remove heavy metals [16-21]. Among plant sources, palm kernel is a substance that is rich in fiber, in addition to its frequency and low cost. As regards that Iran produces 1017 million tons of dates annually, it has the second rank of world in production of this product [22] and the palm kernel is disposed of without any processing. So, we tried to use this agricultural product to adsorb chromium.

The palm kernel forms about 10-15% of the date weight and, on average, contains 73.2% cellulose [23]. The physicochemical properties of palm kernel fiber have been investigated [24] which are showed that the nucleus of the palm consists of two parts, shell and the brain that were interchangeable in terms of materials. The purpose of this study was prepared the activated carbon by termochemical method from the crust of the palm kernel. That this process involves two steps, carbonization of the raw material by heat and chemical activating by a mixture of potassium and sodium hydroxide. In continues, we study the effects of activated carbon on the adsorption of Cr (VI). Then, we examined the effect of effective parameters on the adsorption including pH, temperature, contact time, absorbent dose and Cr (VI) concentration. In addition, by linear regression analysis, we investigated the patterns of adsorption isotherms. However, no research has ever been done to show using of the palm kernel shell (PKS), specifically effects on the absorption of Cr (VI).

MATERIALS AND METHODS

Chemicals

The palm kernels were prepared from a palm grocery store in Borujerd City, Lorestan, Iran. This city is a producer of date syrup in Iran. The date type was Mazafati of Bam. In all experiments, distilled water was used for preparation. Potassium dichromate ($K_2Cr_2O_7$), hydrochloric acid (HCl), sodium hydroxide (NaOH) and Potassium hydroxide (KOH) were purchased from merck. A stock solution containing chromium 0.5 g/L was prepared by dissolving 1.404 g of potassium dichromate in 500 ml of distilled water. The desired concentrations 1-100 mg/L obtained by diluting the stock solution. HCl (0.1 N) and NaOH (0.1 N) are used for regulation of pH.

Characterization study

The BET surface area of the prepared activated carbon was measured with surface area analyzer (Quantachrome AS1Win). Morphological study was carried out with a scanning electron microscopy (SEM) (HITACHI model, S-3400N, Japan). The concentration of Cr (VI) in the supernatant solution before and after adsorption was determined using a double beam UV-Vis spectrophotometer (Unico, Japan). The pH of solution was measured with an Ohaus pH meter using a combined glass electrode. (Model ST2100, USA).

Experimental

Core and shell separation of palms

The palm kernels were first washed with distilled water for decontamination and exposed to sunlight for 5 days. Then they were crushed by a mill (mesh 2 mm). The cores consist of two outer and inner parts are separated by a sieve 400 μ. The powder that passed through the sieve was the same as PKS, which was kept in the dark container until the experiments were carried out.

Carbonization of palm kernel shell (PKS)

To prepare the biomass from the date palm, 50 g of palm kernel powder was weighed and sieved by mesh 100 μm. The shells were washed by distilled water and placed in an oven at 110 °C for 3 hours. It was then placed in a furnace at 600 °C for 3 hours. The biochar was cooled down to

reach the ambient temperature and again sifted through a 100 μ sieve.

Preparation of Activated carbon palm kernel shell (AC-PKS)

A solution was prepared by dissolving potassium and sodium hydroxide in a 1:1 weight ratio in distilled water. Then the biochar was immersed in the solution. Until the mixture begin to boil, heated and stirred. The heat stalled and abandoned for 24 hours. The resulting mixture was filtered to obtain activated charcoal. The charcoal was immersed in a crucible and is calcified at 450 °C for 3 hours in the furnace. (At a temperature of 5 degrees per minute), activated carbon is produced. It was washed with 0.1 M HCl to remove residual chemicals, such as salts KCl and NaCl. The CPKS is dried in an oven 110°C for 24 hours.

Adsorption Experiments

The residual chromium concentration in the reaction mixture was analyzed by centrifuging and then measuring the absorbance of the supernatant at the maximum wavelength. The λ_{max} value of the Cr (VI) ion is 370 nm. Chromium concentration in the reaction mixture was calculated from stoke curve. The amount of adsorbed Cr (VI) onto the CPKS (Adsorption capacity), q_e (mg/g), was calculated by relationship (1):

$$q_{e=\frac{(c_i-c_e)V}{m}} \qquad (1)$$

Where C_o and C_e are the initial and equilibrium liquid-phase concentrations of chromium, respectively (mg/L), V, the volume of the solution (L), and m is the mass of the used AC-PKS (g). Removal percentage (A %) were calculated from equation (2)

$$A(\%) = \frac{C_0 - C_e}{C_0} \qquad (2)$$

Effective parameters onto Cr (VI) adsorption by AC-PKS

To find optimal pH for Cr (VI) adsorption, 100 ml solution 100 mg/lit Cr (VI) solution was placed in an erlenmeyer and its pH was adjusted in range of 2-8 by 0.1 and 1 M HCl and NaOH. Then 0.05 g, AC-PKS was poured out, the solution was filtered after 30 min at 30±2 °C and the absorption of the remaining potassium dichromate solution was measured. In order to determine the best mixing time, to several Erlenmeyers containing 100 ml of Cr (VI) solution with concentration of 100 mg/L at pH=2, 0.05 g of absorbent are added and mixed at different times of 10-120 min. The effect of solution temperature on removal of Cr (VI) was investigated in 20-80 °C. In this experiments, 0.05 g absorbent was added to 100ml of 100 mg/L Cr (VI) solution at pH=2. The absorbance equilibrium assessment experiments onto AC-PKS were performed by adding 0.05 mg of adsorbent containing 100 ml of potassium dichromate solution at various concentrations of 1-100 mg/L at pH = 2. at 30 min. To detect the best dose of the absorbent, 100 ml of Cr (VI) solution (100 mg/L) was poured into 8 erlene and 10-100 mg of absorbent, respectively, was added to each of them. At the end of each experiment, 5 ml of each sample were centrifuged and the concentration of the residual solution was measured. Characteristic of effective parameters on adsorption of Cr (VI) onto AC-PKS is shown in Figure 1.

Adsorption isotherm investigation

Freundlich and Langmuir kinetic adsorption models are commonly used in the removal of pollutants.

Langmuir Absorption Model

Langmuir isotherm [25] is one of the most prestigious physical absorption laws, which is true in many cases. To attract a mono layer on surfaces with a limited number of absorption positions is used. The relationship is as following:

$$q_{e=\frac{Q_{max}k_lC_e}{(1+k_lC_e)}} \qquad (3)$$

Where q_e, is the concentration of the adsorbed pollutant in mg/g at any moment, Q_{max}, is the maximum adsorption apacity by adsorbent in mg/g. The equilibrium constant k_l or b, which is depends on the amount of adsorbent-

adsorbate tendency, and C_e is the concentration of equilibrium pollutant or not absorbed in mg/g. The diagram C_e/q_e in terms of C_e is a homogeneous function obtained according to (4).

$$\frac{C_e}{q_e} = \frac{1}{q_{max}b} + \frac{C_e}{q_{max}} \qquad (4)$$

$$\frac{1}{q_e} = \left(\frac{1}{bq_{max}}\right)\frac{1}{C_e} + \frac{1}{q_{max}} \qquad (5)$$
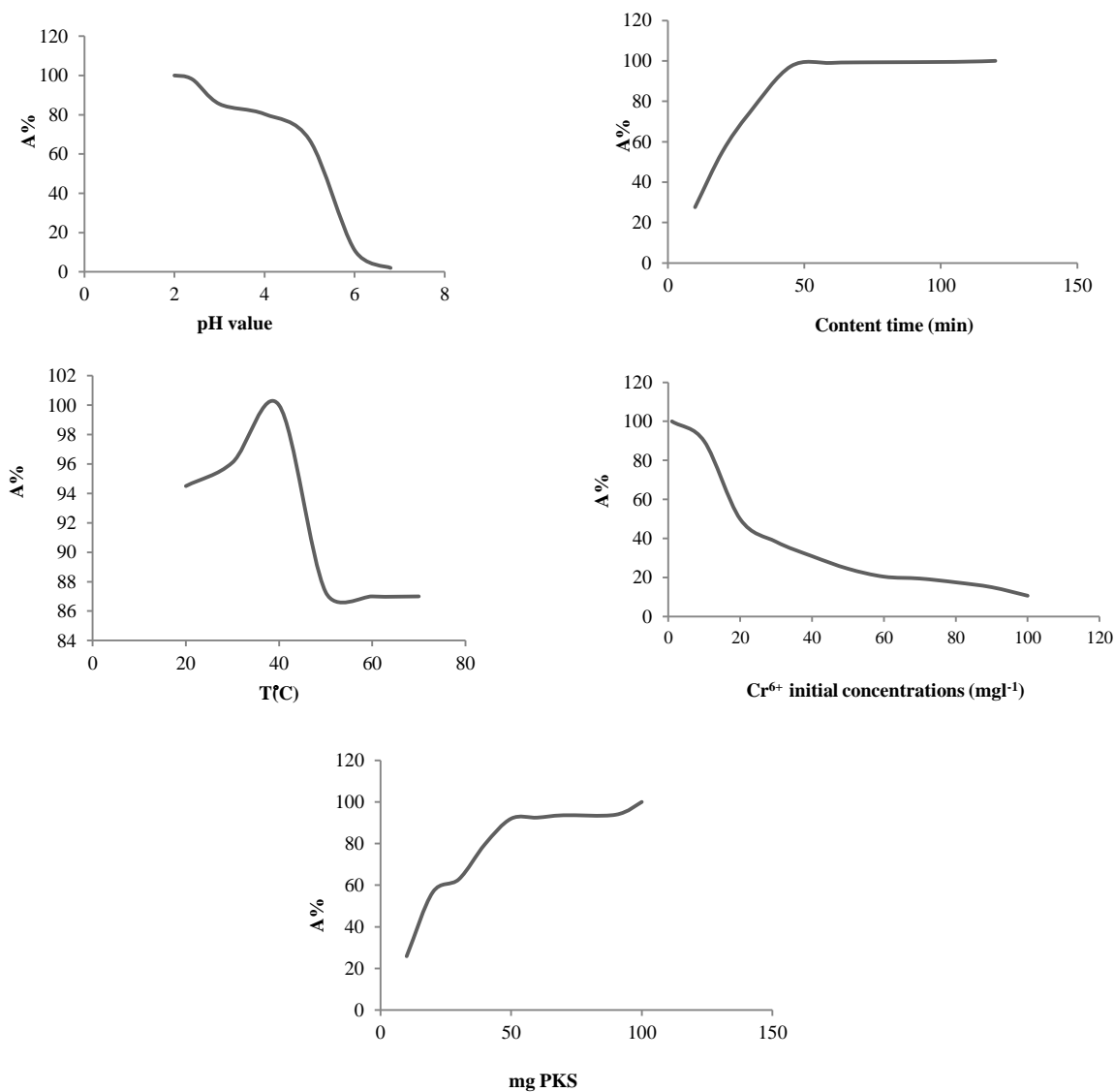

Figure 1. The effective parameters graphs of adsorption of Cr (VI) onto PKS.

The values of q_{max} and b can be obtained from the intercept and slope, respectively. The equation (4) can also be expressed as equation (5). In this case, with the drawing of the linear diagram $1/q_e$, relative to $1/C_e$ constant values obtain. The Dimension Index (R_l) is also used to test the usability of the Langmuir equation and is expressed as (6).

$$R_l = \frac{1}{1 + bC_0} \qquad (6)$$

Where C_0 is the initial concentration of the solution and b is Langmuir constant. If the value is $R_l > 0$, model is inappropriate, if $R_l = 1$, is appropriate as the linear model, if $0 < R_l < 1$, the model is suitable and if $R_l = 0$, the model is inefficient [26]. Also, the four linear forms of Langmuir isotherm model are listed in Table 1.

Table 1. The four linear forms of Langmuir isotherm model.

Langmuir isotherm forms	Equation	Plot
Langmuir-1	$\frac{C_e}{q_e} = \frac{1}{q_{max}b} + \frac{C_e}{q_{max}}$	$\frac{C_e}{q_e}$ vs. C_e
Langmuir-2	$\frac{1}{q_e} = (\frac{1}{q_{max}b})\frac{1}{C_e} + \frac{1}{q_{max}}$	$\frac{1}{q_e}$ vs. $\frac{1}{C_e}$
Langmuir-3	$q_e = q_{max} - (\frac{1}{b})\frac{q_e}{C_e}$	q_e vs. $\frac{q_e}{C_e}$
Langmuir-4	$\frac{q_e}{C_e} = bq_{max} - bq_e$	$\frac{q_e}{C_e}$ vs. q_e

Freundlich absorption model

Freundlich absorption isotherm [27] is valid for adsorption on the heterogeneous surface, and its equation is in the form of relation (7).

$$q_e = k_f . C_e^{1/n} \qquad (7)$$

Where q_e and C_e are the same as those mentioned in the Langmuir relationship. k_f and n are the Freundlich model constants, which represent adsorption capacity and absorption intensity respectively, and is obtained from the slope and intercept of the linear derivative of equation 8.

$$\log q_e = \log k_f + \frac{1}{nf} logC_e \qquad (8)$$

RESULTS AND DISCUSSION

This research was conducted to absorb Cr (VI) by activated carbon from palm kernel shells. For increase of confidence, correctness and accuracy of the tests, sampling and analysis of samples were repeated several times. All of charts were drafted in the excel software under windows. The specific surface area of the activated carbon was calculated by BET equation within a relative pressure range 0.05–0.35 atm.

The BET surface area, pore total volume and pore median diameter of the PKS were found 121.82 m²/g, 0.826 m³/g and 27.14 nm, respectively. According to the category of IUPAC where micropores (< 2 nm), mesopores (2–50 nm), and finally macropores (> 50 nm); therefore, it can be concluded that the high adsorption capacity of activated carbon despite the low surface area BET can be interpreted by the presence of a large distribution of mesopores that adsorbed chromium ions. The textural characteristics of the prepared PKS activated carbon (AC-PKS) are presented in Table 2. Figure 2 shows the SEM micrograph of AC-PKS sample before and after Cr (VI) adsorption. The surface of AC-PKS- loaded Cr (VI) adsorbent (Figure 2(b)) is different from the surface of adsorbent before adsorption (Figure 2(a)).This is clear that SEM micrograph before adsorption, indicated a uneven and typical surface with a prominent gloomy stains of holes and hollows extending that there was a probability for Cr (VI) metal ions to be trapped and adsorbed onto the surface. Figure 2(b) shows after adsorption, pores were exactly filled and AC-PKS surface more regular and rather smoother with several accumulation and agglomeration that Cr (VI) ions have been associated to surface.

Table 2. Textural characteristics of the prepared PKS activated carbon (PKS-AC).

Physical properties	Volume
BET surface area (m^2/g)	121.82
Total volume (cm^3/g)	0.826
Median pore diameter (nm)	27.14

Figure 1 shows the percentage of removed Cr (VI) at different levels pH, initial concentration of chromate, contact time, temperature and adsorbent amount. Due to this fact that maximum adsorption (100%) was obtained at pH = 2, this pH was considered as optimal pH. When the initial pH of the solution increases from 2 to 5, the adsorption rate decreases from 100 to 67 and with increasing pH from 5 to 7, adsorption changes will be faster to 2, which may be due to coagulation or deposition of Cr(VI). These absorption changes can be explained by soluble chromium species and superficial PKS groups. Acidic conditions change surface charge of adsorbent, degree of ionization of adsorbate, separation of active agent groups in active sites, and also soluble chemistry. At pH higher than 8, dominant form is CrO_4^{2-}. With increasing acidity, equilibrium progresses to the formation of dichromate and the dominant chromium species in the acidic pH include of $Cr_2O_7^{2-}$, $HCrO_4^-$, $Cr_3O_{10}^{2-}$, $Cr_4O_{13}^{2-}$ [28; 29]. On the other hand, under acidic conditions, the surface of the adsorbent is very protonated, which causes to absorb Cr (VI) onto PKS in form of anionic. Increasing of the amount of pH reduces the surface protonation, which in turn leads to a decrease in the adsorbent positive surface potential and thus reduces the electrostatic force between the absorbent and the adsorbate. In addition, when the pH is alkaline, competition between OH^- and CrO_4^{2-} arises for adsorption onto the absorbent surface [30].

a

b
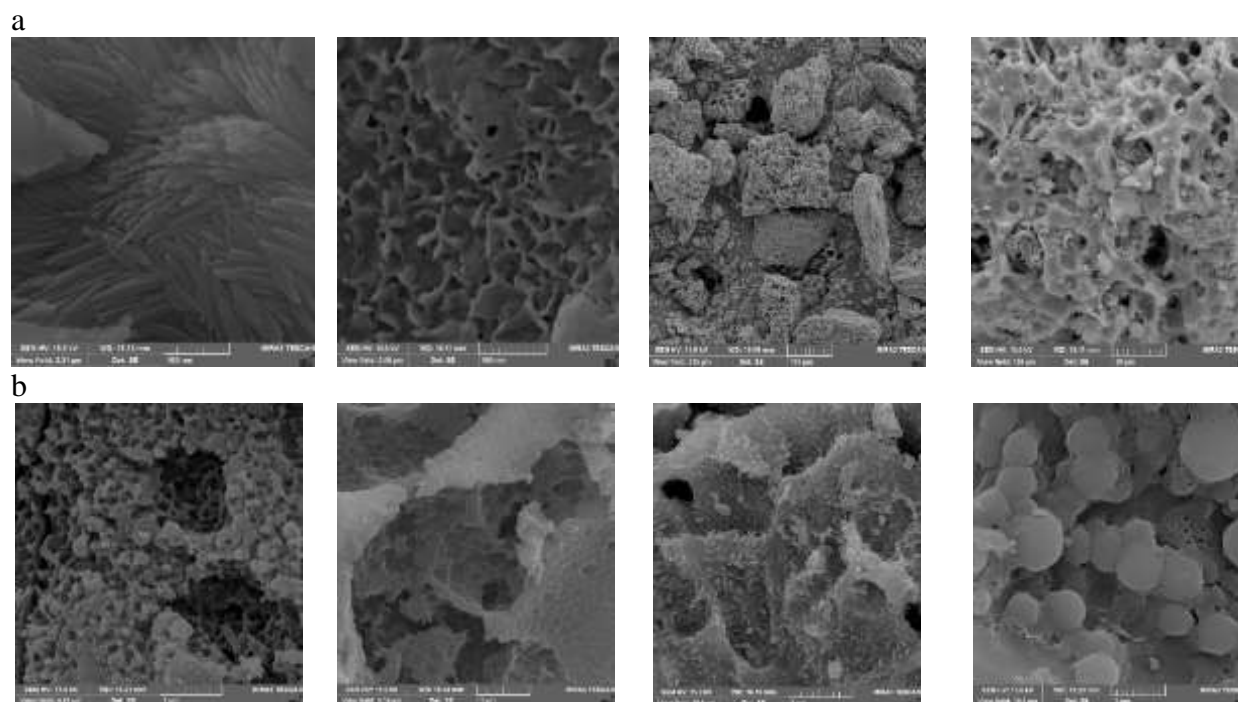
Figure 2. SEM micrograph of the particles of AC-PKS (a) before (b) after Cr (VI) adsorption

The relationship between the amount of removed chromium by PKS and contact time was investigated for studding the rate of absorption. Fig. 1 shows the absorption Cr (VI) onto PKS that the initial concentration of chromate was considered 100 mg/L and pH = 2. The figure shows that more than 50% of the absorption took place in less

than 20 minutes, and after this time, the absorption rate decreases. Also, as it is known, about 97% of chromium has been removed by PKS up to 45 min. The absorption rate is almost constant from 45 to 120 min. Thus, the optimal contact time was selected 45 min. Thus, it can be concluded that the amount of binding Cr (VI) to the adsorbent is high in the initial stages and gradually decreases and finally remains constant. At the beginning of the adsorption process, the absorption rate increases due to the large number of adsorption sites, the difference in concentration between the adsorbed substance in the solution and its amount on the adsorbent surface. But with lapse of time, the slope is very gentle and calm. This is due to the presence of a layer of absorbent on the surface of PKS. Also it is difficult to occupy the remaining surface areas [31].

The results of the temperature effect at optimal pH=2, contact time of 45 minutes for PKS are presented. Regarding the diagram, it can be said that for PKS at 40°C, Cr (VI) absorption is greatest. So that removal efficiency is 99% in this temperature. The rate of chromium ion penetration onto the adsorbent surface increases with increasing temperature. This phenomenon can be attributed to the distribution of chromium ions and the increase in the number of absorption sites that at low temperatures, due to the reduction of the kinetic energy of Cr (VI), the conduction of these ions to active absorbent positions decreases. As a result, absorbent and adsorbate community is minimized [32].

Also, absorption experiments were carried out at initial concentrations of chromium 1-100 mg/L with a dose of 5 mg/100ml of PKS and its results are presented in Figure 1. The results showed that when initial concentration of Cr (VI) increases, removal percentage reduces. This can be explained by the fact that all adsorbents have a limited capacity of active positions. They also are saturated at a certain concentration [32]. By increasing the chromium concentration up to 20 mg/L, the absorption rate reaches about 50%. Afterwards, the slope of the absorption curve decreases.

In the following, for investigation adsorbent amount onto Cr (VI) removal, experiments were carried out that adsorbent amount was changed from 10 to 100 mg in 100 ml of solution and initial chromate concentration was considered constant. The results showed that, generally with increasing amount of adsorbent, the removal percentage increases and the maximum absorption occurs at an absorbent dose of 0.01 g that in this amount, the removal efficiency is 100%. With increasing the absorbent dose increases the absorption site that its result is an increase in removal percentage. Also, increasing the dose from 0.05 to 0.1 g had a slight effect on removal percentage. This can be attributed to a decrease in the area of the effective absorbent surface at higher absorbent doses [33]. Due to economic issues; 0.05 g of PKS was selected as the optimum dose to remove chromium. Absorption percentage is 92% in this dose of PKS.

The adsorption isotherm indicates how the adsorbate molecules are distributed between the liquid phase and the solid phase when the adsorption process reaches an equilibrium state. The analysis of the isotherm data by fitting them to different isotherm models is an important step to find the suitable model that can be used for design purpose. Calculations were performed for Langmuir and Freundlich linear models. Also the parameters and constants of these isotherms were measured (Table 3). The numerical value of the calculated constants for describing the Cr (VI) adsorption behavior onto PKS and the determination coefficients of R^2 for each of the Langmuir1 and Freundlich isotherms have plotted at different temperatures (Fig. 3 and 4). Comparison of correlation coefficient obtained from graphs for any isotherms can be a suitable measure for the matching of the data and mentioned isotherms. As results show, Freundlich isotherm has more adjustment with data than Langmuir isotherms. Correlation coefficients for Freundlich model in 40, 50 and 60°C are R^2 = 0.997, 0.991 and 0.964 which is more suitable than the Langmuir model and the $n_f > 1$, indicating that adsorption of Cr (VI) onto PKS is a favorable physical process [34]. Table 4 shows the comparison of maximum monolayer adsorption capacity of Cr (VI) onto various adsorbents. It is clear that PKS used in this work has a relatively suitable adsorption capacity of 125 mg/g compared to other adsorbents found in literature. The

remarkable thing is that with the least dose of adsorbent, we will have a maximum absorption (125 mg/g).

Table 3. Isotherm parameters obtained from the four linear forms of Langmuir model and Freundlich model for removal of Cr (VI) by PKS at 40, 50, 60 $^{\circ}$C

| Model	Parameters	40 $^{\circ}$C	50 $^{\circ}$C	60 $^{\circ}$C
Langmuir isotherm1	Q_{max} (mg/g)	125	125	111
	b (L/mg)	0.0548	0.0503	0.0625
	R^2	0.954	0.960	0.956
Langmuir isotherm2	Q_{max} (mg/g)	100	100	100
	b (L/mg)	0.1063	0.0893	0.084
	R^2	0.905	0.942	0.994
Langmuir isotherm3	Q_{max} (mg/g)	98.81	100	96.38
	b (L/mg)	0.0972	0.0839	0.0875
	R^2	0.764	0.800	0.883
Langmuir isotherm4	Q_{max} (mg/g)	115.18	109	102
	b (L/mg)	0.07	0.0670	0.077
	R^2	0.764	0.800	0.883
Freundlich isotherm	n	2.45	2.87	2.87
	K_f [(mg/g)(L/mg)^n]	17.57	20.99	20.99
	R^2	0.997	0.991	0.964
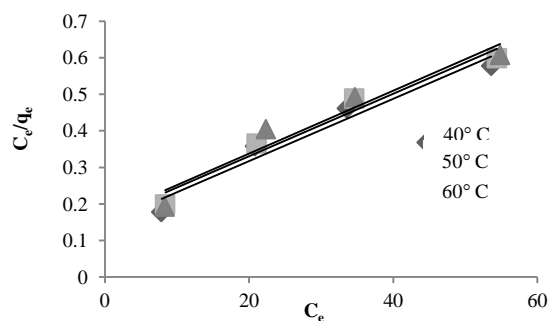
Figure 3. Langmuir1 isotherm model of Cr (VI) adsorbed onto PKS.
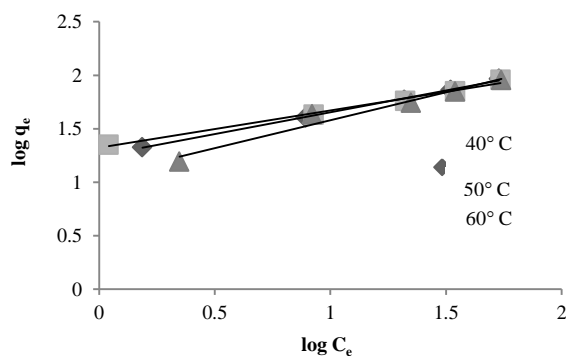

Figure 4. Freundlich isotherm of Cr (VI) adsorbed onto PKS.

Table 4. Comparison of the maximum monolayer adsorption of Cr (VI) onto various adsorbents.

absorbent	Absorbent dose	Maximum monolayer adsorption capacity (mg/g)	References
AC-PKS	0.5 g/L	125	This work
Longan seed	6	35.02	[20]
date palm seed	4 g/L	120.48	[31]
Ziziphus jujuba cores	1 g/L	196.38	[32]
Pistacia terebinthus	2	9.97	[35]
olive stones	0.5	71	[36]
apple peels	1	36.01	[37]
mango kernel	25	7.8	[38]

Thermodynamic parameters such as enthalpy (ΔH^0, kJ/mol), standard entropy (ΔS^0, J/molK), and changes in the Gibbs free energy (ΔG^0, kJ/mol) were calculated in order to understand adsorption process; the following equations have been taken into account:

$$k_c = \frac{C_0 - C_e}{C_e} \qquad (9)$$

$$\ln k_c = -\frac{\Delta H^0}{RT} + \frac{\Delta S^0}{R} \qquad (10)$$

$$\Delta G^0 = -RT \ln k_c \qquad (11)$$

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \qquad (12)$$

Where K_c is the equilibrium constant, R (8.134 J/molK) is the gas constant, and T (K) is the absolute temperature. The data of $\ln K_c$ versus 1/T were fitted using the Van't Hoff plot at different temperatures and initial concentrations of Cr (VI) (Fig. 5); from this plot, values of ΔH^0 and ΔS^0 were obtained from the slope and the point of intercept. The straight line, which does not pass through origin, shows a good linear relationship for optimal initial concentration of Cr (VI) (10 mg/L) with both values of slope and point of intercept determined at 7464.9 and -21.1 and the correlation coefficient $R^2= 0.994$.

The thermodynamic values (ΔH^0, kJ/mol), (ΔS^0, J/molK), and (ΔG^0, kJ/mol) for the adsorption of Cr (VI) ions onto "AC-PKS" were calculated using the equations 9-12. The results are summarized in Table 5. ΔH^0, ΔS^0 and ΔG^0 values were observed as negative for studied three temperatures. The negative values of ΔG^0 show that adsorption process onto AC-PKS is spontaneous. It can be seen for table 6 that ΔG^0 values become more negative with the decreasing of temperature so, decreasing temperature favors the adsorption process. The importance of temperature in the adsorption of Cr (VI) ions onto activated carbon has been clearly illustrated. The negative values of ΔH^0 indicated that the adsorption of Cr (VI) ions onto activated carbon is an exothermic process. The ΔS^0 values play an important role in reflecting whether the order of adsorbate at the solid/ solution interface during the adsorption process becomes less random $\Delta S^0<0$ or more random $\Delta S^0 > 0$ [39]. Moreover, negative ΔS^0 value involves decreasing in degree freedom of Cr (VI) ions in the solution. Also, the sign of ΔS^0 show whether the adsorption reaction is an associative or dissociative process. So, since ΔS^0, has a negative value, it can be an associative mechanism [40].

Table 5. Thermodynamic parameters for the adsorption of Cr (VI) ions onto

AC-PKS at different temperatures (C_0= 10mg/L).

T (K)	K_c	ΔG^0 (kJ/mol)	ΔH^0 (kJ/mol)	ΔS^0 (J/molK)	R^2
313	14.3846	-7.14			
323	8.0909	-5.40	-62.06	-175.53	0.994
333	3.4944	-3.66			
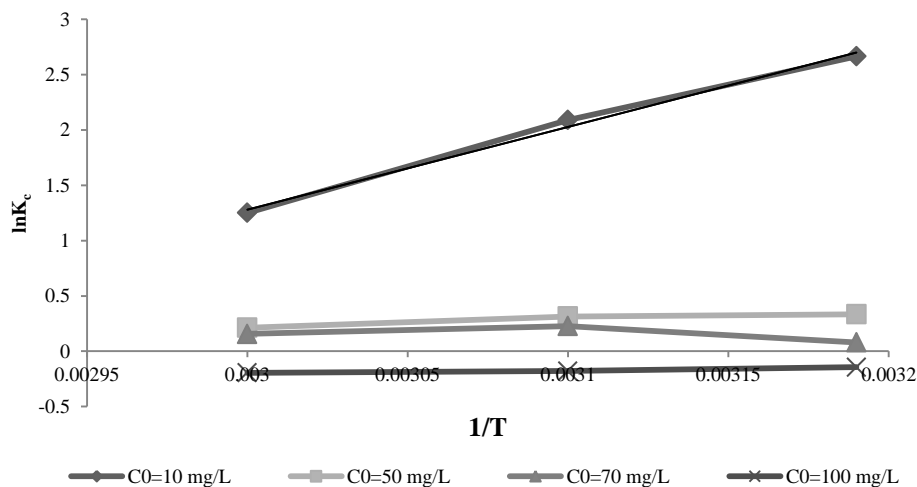
Figure 5. Relationship between thermodynamic constants and temperature of Cr (VI) onto PKS.

CONCLUSIONS

In this study, "AC-PKS," was prepared from palm kernel shell powder, a naturally abundant medicinal plant widely is used in Iran for the purposes of food and agriculture treatment, wich was successfully used to remove Cr (VI) from wastewater. Experiments were performed to identify the nature of adsorption. The following characteristics were found:

•Palm Kernel Shell, an inexpensive and easily available material, was found very effective to remove Cr (VI) from aqueous solutions.

•.The operating parameters for the maximum sorption were pH= 2, initial Cr (VI) solution concentration (10 mg/L), adsorbent dosage (0. 5 g/L), contact time (45 min) and temperature (40 ^{o}C).

•The amount of AC-PKS absorption (mg/g) increases with increase in adsorbent dosage and decreases with increase in initial solution concentration.

•Adsorption behavior is described by a Freundlich isotherm. This model appears to provide the best correlation of experimental data for the adsorption of Cr (VI) than the Langmuir isotherm.

•The tested activated carbon in the present study showed higher adsorption capacities Q_{max}, (125 mg/g) compared to those of some chars and activated carbons reported in the literature.

REFERENCES

1. Farhadkhani M., Nikaeen M., Akbari-adergani B., Hatamzadeh M., Hassanzadeh A., 2014. Assessment of drinking water quality from bottled water coolers. Iranian Journal of Public Health, 43, 674-681.

2. Akbari-adergani B., Memarzadeh N., Ghoreyshi A.A., Pirzadeh K., 2017. Highly Concentrated Ferrus Removal

from Groundwater Using Powdered Activated Carbon as Adsorbent. Journal of Chemical Health Risk, 7(4) 273-284.

3. Nabi S.A., Bushra R., Al-Othman Z.A., 2011. Synthesis, characterization and analytical applications of a new composite cation exchange material acetonitrile stannic (IV) selenite: Adsorption behavior of toxic metal ions in nonionic surfactant medium. Sep Sci Technol. 46, 847–857.

4. Khezami L., Capart R., 2005. Removal of Chromium(VI) from aqueous solution by activated carbons: Kinetic and equilibrium studies. J Hazard Mat B. 123, 223–231.

5. Demirbas E., Kobya M., Senturk E., 2004. Adsorption kinetics for the removal of Chromium (VI) from aqueous solutions on the activated carbons prepared from agricultural wastes. Water SA. 30, 533–539.

6. Liu C.C., Wang M.K., Chiou C.S., 2006. Chromium removal and sorption mechanism from aqueous solutions by wine processing waste sludge. Ind Eng Chem Res. 45, 8891-8899.

7. Park D., Yun Y.S., Kim J.Y., 2008. How to study Cr(VI) biosorption: Use of fermentation waste for detoxifying Cr(VI) in aqueous solution. Chem Engin J. 136, 173–179.

8. Fekri M.H., Banimahd keivani M., Darvishpour M., Banimahd keivani H., 2012. Application of Electroactive Nano Composite Coated onto Wood Sawdust for the Removal of Malachite Green Dye from Textile Wastewaters. J Phys Theor Chem. 9(2), 95-102.

9. Beltrame K.K., Cazetta A.L., de Souza P.S.C., Spessato L.T., Almeida V.C., 2018. Adsorption of caffeine on mesoporous activated carbon fibers prepared from pineapple plant leaves. Ecotoxicol Environ Saf. 147, 64–71.

10. Yang J., Qiu Yu.T., 2014. Adsorption thermodynamics and kinetics of Cr(VI) on KIP210 resin. J Ind Engin Chem. 20, 480–486.

11. Hafez A.I., El-Manharawy M.S., Khedr M.A., 2002. RO membrane removal of unreacted chromium from spent tanning effluent. A pilot-scale study, Part 2. Desalination. 144, 237–242.

12. MonserL., Adhoum N., 2002. Modified activated carbon for the removal of copper, zinc, chromium and cyanide from wastewater. Sep Purif Technol. 26, 137–146.

13. Deveci H., Kar Y., 2013. Adsorption of hexavalent chromium from aqueous solutions by bio-chars obtained during biomass pyrolysis. J Ind Engin Chem. 19, 190–196.

14. Suksabye P., Thiravetyan P., 2012. Cr(VI) adsorption from electroplating plating wastewater by chemically modified coir pith. Journal of Environmental Management 102, 1–8.

15. Kadirvelu K., Namasivayam C., 2003. Activated carbon from coconut coir pith as metal adsorbent: Adsorption of Cd (II) from aqueous solution. Adv Environ Res. 7, 471–478.

16. Bishnoi N.R., Bajaj M., Sharma N., 2004. Adsorption of Cr(VI) on activated rice husk carbon and activated alumina. Bioresour. Technol. 91, 305–307.

17. Demiral H., Demiral I., Tumsek F., 2008. Adsorption of Chromium(VI) from aqueous solution by activated carbon derived from olive bagasse and applicability of different adsorption models. Chem Engin J. 144, 188–196.

18. Duranoglu D., Trochimczuk A.W., Beker U., 2010. A comparison study of peach stone and acrylonitrile-divinylbenzene copolymer based activated carbons as Chromium(VI) sorbents. Chem Engin J. 165, 56–63.

19. Giri A.K., Patel R., Mandal S., 2012. Removal of Cr(VI) from aqueous solution by ichhornia crassipes root biomass-derived activated carbon. Chem Engin J. 185–186, 71–81.

20. Yang J., Yu M., Chen, W., 2015. Adsorption of hexavalent chromium from aqueous solution by activated carbon prepared from Longan seed: Kinetics, equilibrium and thermodynamics. J Ind Engin Chem. 21, 414–422.

21. Nemr A.E., Khaled A., Abdelwahab O., 2008. Treatment of wastewater containing toxic chromium using new activated carbon developed from date palm seed. J Hazard Mat. 152, 263–275.

22. Ben-Amor R., Aguayo E., de Miguel-Gómez M.D., 2015. The competitive advantage of the Tunisian palm date sector in the Mediterranean region, Span. J Agricultural Res. 2, e0101.

23. Al Farsi M.A., Lee C.Y., 2008. Nutritional and functional properties of dates: a review. Critical Rev in Food Sci Nutrition. 48, 877-887.

24. Al Farsi M., Al asalvar C., Al Abid M., Al Shoaily K., Al Amry M., Al Rawahy F., 2007. Compositional and functional characteristics of dates, syrups, and their by-products. Food Chem. 104, 943-947.

25. Langmuir I., 1916. The constitution and fundamental properties of solids and liquids. J Am Chem Soc. 38, 2221–2295.

26. Rao R.A., Rehman F., 2010. Adsorption Studies on Fruits of Gular (Ficus glomerata): Removal of Cr (VI) from Synthetic wastewater. J Hazard Mat 181, 405-412.

27. Freundlich H.M.F., 1906. Uber die adsoption in losungen, Zeitschrift fur physikslische Chemie. 385, 470-57.

28. Raji C., Anirudhan T.S., 1998. Batch Cr(VI) removal by polyacrylamide grafted sawdust: kinetics and thermodynamics, Water Res. 32(12), 3772–3780.

29. Mor S., Ravindra K., Bishnoi N.R., 2007. Adsorption of chromium from aqueous solution by activated alumina and activated charcoal, Biroresour. Technol. 98, 954–957.

30. Selvi K., Pattabhi S., Kadirvelu K., 2001. Removal of Cr(VI) from aqueous solution by adsorption onto activated carbon, Bioresour. Technol. 80, 87-89.

31. El Nemr A., Khaled A., Abdelwahab O., El-Sikaily A., 2008. Materials Treatment of wastewater containing toxic chromium using new activated carbon developed from date palm seed. J Hazard Mat. 152, 263–275.

32. Labied R., Benturki O., Ya A., Hamitouche E., Donnot A., 2018. Adsorption of hexavalent chromium by activated carbon obtained from a waste lignocellulosic material (*Ziziphus jujuba* cores): Kinetic, equilibrium, and thermodynamic study. Adsorp Sci Tech. 36, 1066–1099.

33. Liu W., Zhang J., Zhang C., 2010. Adsorptive removal of Cr (VI) by Fe-modified activated carbon prepared from Trapa natans husk, Chem. Eng. J. 162, 677–684.

34. Crini G., Peindy H.N., Gimbert F., Robert C., 2007. Removal of C. I. Basic Green 4 (Malachite Green) from aqueous solutions by adsorption using cyclodextrin-based adsorbent: kinetic and equilibrium studies. Sep Purif Technol. 53, 97–110.

35. Deveci H., Kar Y., 2013. Adsorption of hexavalent chromium from aqueous solutions by bio-chars obtained during biomass pyrolysis. J Indust Engin Chem. 19, 190–196.

36. Attia A.A., Khedr S.A., Elkholy S.A., 2010. Adsorption of chromium ion (VI) by acid activated. Carbon. 27(1), 183 – 193.

37. Enniya I., Jourani A., Rghioui L., 2018. Adsorption of hexavalent chromium in aqueous solution on activated carbon prepared from apple peels. Sustain. Chem Pharm. 7, 9-16.

38. Rai M.K., Shahi G., Meena V., Meena R., Chakraborty S., Singh R.S., Rai B.N., 2016. Removal of hexavalent chromium Cr (VI) using activated carbon prepared from mango kernel activated with H_3PO_4, M. K. Resource-Efficient Technol. 2, S63–S70.

39. Tran H.N., You S.J., Chao H.P., 2016. Thermodynamic parameters of cadmium adsorption onto orange peel calculated from various methods: A comparison study. J Environ Chem Eng. 4, 2671–2682.

40. Aregawi B.H., Mengist A.A., 2013. Removal of Ni(II) from aqueous solution using leaf, bark and seed of Moringa stenopetala adsorbents. Bull Chem Soc Ethiop. 27, 35–47.