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Date palm fiber as a potential low-cost adsorbent to uptake chromium (VI) from industrial wastewater

M.W. Rahman[a,*], M.Y. Ali[a], I. Saha[a], M. Al Raihan[a], M. Moniruzzaman[b], M.J. Alam[a], A. Deb[a], M.M.R. Khan[c]

[a]*Department of Chemical Engineering, Jessore University of Science and Technology, Jessore- 7408, Bangladesh, Tel. +88042162020, Fax +88042161199, email: w.rahman@just.edu.bd, wasikurjstu@gmail.com (M.W. Rahman), yousuf.ali.jstu@gmail.com (M.Y. Ali), indrajitche.jstu@gmail.com (I. Saha), raihan.jstu@gmail.com (M. Al Raihan), a jahangirche@gmail.com (M.J. Alam), njan_cep@yahoo.com (A. Deb)*

[b]*Designated Reference Institute for Chemical Measurements, Bangladesh Council of Scientific and Industrial Research, Dhaka- 1205, Bangladesh, email: monirbd79@yahoo.com (M. Moniruzzaman),*

[c]*Faculty of Chemical and Natural Resources Engineering, Universiti Malaysia Pahang, 26300 Gambang, Kuantan, Malaysia, email: mrkhancep@yahoo.com (M.M.R. Khan)*

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ABSTRACT

Date palm fiber (DPF) was demonstrated in the present issue as a potential low cost adsorbent for the removal of hexavalent chromium [Cr(VI)] from aqueous solution. A series of batch tests were conducted and the influence of initial metal ion concentration, contact time, pH of the solution and adsorbent dosage was investigated. The adsorbent was characterized by Fourier Transformed Infrared (FTIR) spectroscopy, scanning electron microscopy (SEM) and Brunauer–Emmett–Teller (BET) to confirm the surface properties of the DPF adsorbent. The adsorption process was found to be strongly pH dependent. The adsorption isotherm data were fitted with Langmuir equation and the adsorption process was found to be followed pseudo–second–order rate kinetics. Chromium showed peculiar activities in aqueous solution due to its transition properties and the mechanism of Cr(VI) adsorption onto the DPF solid surface exhibited physisorption due to intermolecular bonding. Therefore, DPF can be employed as an efficient cost–effective adsorbent for the removal of Cr(VI) as a model component for heavy metals present in industrial wastewater.

Keywords: Adsorption; Low-cost adsorbent; Date palm fiber; Cr(VI); reaction kinetics; Adsorption isotherm

1. Introduction

Heavy metals have been acknowledged as potential health and environmentally hazardous materials worldwide. During the last few decades, pollution by toxic heavy metals has been drawn extensive attention as they are causing severe damages to human health, agriculture and ecosystem. Unlike to organic pollutants, they do not degrade biologically into harmless end products due to complex physico–chemical properties [1]. Hexavalent chromium, Cr(VI) is one of the most hazardous and carcinogenic heavy metals and it is on the top–priority list of toxic pollutants defined by the US Environmental Protection Agency (EPA). Chromium enters into the environment primarily through its widespread use in industries including leather tanning, metallurgy, electroplating, paint and pigment manufacturing, mining operations [2], battery industries and chromate preparation industries, etc. [3]. It has been estimated that in the chromium tanning process, the leather takes up only 60–80% of applied chromium and the rest is usually discharged into the sewage system without any further treatment and thus causing serious environmental impact [4]. Therefore, Bangladesh Government has taken an advanced step to shift tannery industry from huge populated city of Hazaribagh, Dhaka to sub–city Savar of the country.

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*Corresponding author.

Due to transition properties of chromium, industrial effluents may contain Cr(III) and Cr(VI) at concentrations ranging from tenths to hundreds of mg/l. It is of interested to note that these two forms of chromium exhibit different level of toxicities. Cr(III) is relatively insoluble at higher pH (>5) in aqueous systems and is a micronutrient for insulin; exhibits little or no toxicity [5]. The hexavalent form is 500 times more toxic than the trivalent one [6]. According to US EPA, the maximum tolerance limit of Cr(VI) in the effluent of industrial wastewater is 0.1 mg/l and for potable water its limit is 0.05 mg/l [3].

The existing treatment processes for chromate–containing wastewater involves a chemical reduction process, ion–exchange [7], membrane filtration, detoxification process using living cells such as *Bacillus sp*. [8], *Pseudomonas putida* [9], *Anabaena variabilis* [10], etc. However, there are many problems related to these separation techniques such as generation of secondary wastes due to the uses of chemical reagents, instability of ion exchange resin because of high oxidizing ability of Cr(VI), poor economic feasibility, cell death due to high toxicity of Cr(VI) and complexity in separation of the treated liquid [11]. In this respect, adsorption seems to be very meaningful alternative from an economic perspective due to its simplicity in operation and the availability of low cost, eco–benign adsorbent including plant leaves, barks, roots, fruit shells, agricultural wastes, etc. It is evident from the last two decades that many researchers studied the possibility of application of low–cost adsorbents derived from natural resources and agricultural wastes and found its effectiveness and economic feasibility [12].

Despite the scarcity of consistent cost information, the widespread uses of low–cost adsorbents in industries for wastewater treatment applications today are strongly recommended. Many agricultural products, like cocoa shell [13], rice husk [14], olive stone[15], hog palm peel [16], garlic peel [17], sawdust [18], banana peel [19], carica papaya seed [20], Anabaena and Vetiveria [21], exhausted coffee [22], water hyacinth [23], tea dust [24], nypa fruticans [25] and date leaves [26] were tested for removal of metals from effluents. Date palm wastes have been extensively investigated as adsorbents for the removal of various metal ions from water and wastewater. Al Shayeb et al. [27] studied the date palm as a bio-monitor of lead, zinc, copper, nickel, chromium and lithium. The results showed that Pb was mostly superficially attached with surface of leaflets, whereas, Cr was strongly bonded with the surface of leaflet. All other metals understudies are partly superficially attached and partly bonded with the leaflet surfaces. Al–Khlaifat and Al–Khashman [28] carried out almost similar kind of study. The team of researchers used leaves of date palm to evaluate them as a bio-adsorbent for Fe, Pb, Zn, Ni, Cu and Cr metals contamination. The utilization of these raw plant materials as bio-sorbents has been limited due to the leaching of organic compounds such as cellulose, lignin, pectin and lignocellulose present into the solution. Further improvement has been achieved by introduction of nanomaterials and chemical modification of solid biomasses as a remedy to their physical, chemical and bio-sorption aspects [29,30].

Furthermore, literature discloses that surface modification of the adsorbents increased the removal efficiency of the system. Nevertheless, very less work has been carried out in this direction, especially, to understand the mechanism of adsorption. It is speculated that the possibility of the ion exchange mechanism plays an important role to uptake pollutants. Mechanistic studies need to be performed in detail to propose a correct binding mechanism of aquatic pollutants with low–cost adsorbents [31]. The potentiality of low–cost adsorbents under pollutants of transition properties needs to be assessed. This would make a significant impact on the practical application of low–cost adsorbents to the industrial system. There is a scarcity of available data for the competitive adsorption of pollutants. Therefore, more investigations need to be conducted in this trend.

In the present work, naturally available low–cost adsorbents such as locally available date palm fiber are used as adsorbent for Cr(VI) removal from aqueous solution. The influence of experimental parameters, such as contact time, initial pH, initial concentration of Cr(VI) ions, was investigated. The results of the experiments were analyzed using Langmuir adsorption isotherms. The kinetic model of the process was applied to establish the extent of the adsorption of Cr(VI) ions onto DPF and the mechanism of the system was studied.

2. Material and methods

2.1. Adsorbent preparation

Naturally available date palm fiber, used in the present work, was collected from the local area, Jessore in Bangladesh. DPF was washed with water for several times to remove mud, dirt, etc., followed by drying under sunshine and cutting into small pieces. After that the DPF was boiled in water for 30 min. Then DPF was soaked in 5% HCl for 20 min followed by washing with distilled water to remove remaining dirt and soluble impurities. The fiber was then dried in an oven at ~105°C for 2 h to exclude moisture from it. The dried fiber was ground into fine powder, subsequently sieved to obtain homogeneous particles and stored in an air tight bottle for further use.

2.2. Adsorbent characterization

Fourier transform infrared (FTIR) analysis was employed to determine the structural properties of DPF, using FTIR spectrometer (Spectrum 100, Perkin Elmer), where the spectra were recorded from 4000 to 500 cm^{-1}. Surface morphology was studied using Scanning Electron Microscope (SEM) (Zeiss Evo 50). Specific surface area based on N_2 physisorption was measured using Brunauer–Emmett–Teller (BET) (ASAP 2010, Micromeritics). The samples were degassed at 100°C for 2 h prior to the sorption measurements.

2.3. Adsorbate preparation

An aqueous solution of Cr(VI) was used as an adsorbate. $K_2Cr_2O_7$ (MW 294.185 g/mol) was dissolved in double distilled water to prepare a standard stock solution of Cr(VI). In order to determine the removal of the heavy metal during adsorption, it was further diluted to desired concentrations of 25, 50, 75, 100, 125, 150, 175, 200, 300, 400 and 500 ppm. pH of the solutions was analyzed over the pH range from 1 to 7. The absorbances of solutions were measured by a UV spectrophotometer (SHIMADZU Co., Japan) at a fixed wavelength of 352 nm. All the chemicals used through the whole experiment were analytical standard grade.

2.4. Batch adsorption study

Batch adsorption was studied to investigate the influence of various parameters on adsorption. Typically 1000 ml of stock solution with different initial concentration (100–500 ppm) was taken in a 250 ml Erlenmeyer flask. The pH of each sample was maintained at a constant value for a certain batch. Appropriate amount of adsorbent was added to each flask and was kept in a shaker (211 osc/min) until equilibrium was attained. The equilibrium time was taken as the time when the concentration of Cr(VI) becomes constant. After that the samples were centrifuged and analyzed to determine the percentage removal of Cr(VI) for each case of variable dosages.

2.5. Adsorption isotherm study

For isotherm studies, a series of 250 ml Erlenmeyer flasks were filled with 100 ml of adsorbate solution of varying concentrations 25, 50, 75, 100, 125, 150, 175 and 200 ppm and a desired pH was maintained for each sample. A known amount of adsorbent (0.5 g) was added into each flask and shaken continuously at a constant oscillation of 211 osc/min until the equilibrium was attained. After that, the samples of various concentrations were filtered and analyzed. Each experiment was repeated under identical conditions and the average values were taken. To estimate the percentage removal of chromium from aqueous solution, Eq. (1) was used:

$$\%\ \text{Removal of Cr}\left(\text{VI}\right) = \frac{C_o - C_t}{C_o} \times 100\% \tag{1}$$

where C_o is the initial concentration (mg/l) and C_t is the concentration at time t. The amount of adsorption at equilibrium, q_e (mg/g), was calculated by the following equation:

$$q_e = \frac{(C_o - C_e)V}{m} \tag{2}$$

where C_o and C_e are the liquid–phase concentrations (mg/l) of Cr(VI) at initial and at equilibrium, respectively. V is the volume (l) of the solution and m is the mass (g) of dry adsorbent used.

2.6. Adsorption kinetics

The experiment was carried out by contacting 100 ml Cr(VI) solution of 100 ppm with 0.5 g of powdered DPF in 250 ml stopper conical flasks. The samples were then shaken at a constant speed of 211 osc/min for 4 h. Samples were then withdrawn at different time intervals. The collected samples were then centrifuged and the concentration in the supernatant solution was analyzed. The amount of adsorption was calculated according to the Eq. (2) considering q_e as q_t and C_e as C_t at time t. To investigate the mechanism of sorption, both pseudo first and second–order kinetics were studied.

The linear form of pseudo first–order model can be expressed as Eq. (3):

$$\ln\left(q_e - q_t\right) = \ln q_e - k_1 t \tag{3}$$

where k_1 is the pseudo first–order rate constant (min^{-1}), q_e and q_t (mg/g) are the adsorption capacities at equilibrium and at time t (min), respectively.

The adsorption kinetics may be described by the pseudo second–order model [30] that is shown in Eq. (4)

$$\frac{dq}{dt} = k_2\left(q_e - q\right)^2 \tag{4}$$

where k_2 is the rate constant of pseudo second–order sorption (g/(g min). The integrated linearized form of the above equation becomes as follows:

$$\frac{t}{q} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{5}$$

The amount of adsorption (q_e) and the rate constant (k_2) can be determined from the plot of t/q against t.

3. Results and discussion

3.1. Adsorbent characterization

3.1.1. SEM and BET analysis

SEM micrograph of DPF with 500 times magnifications is shown in Fig. 1. The result revealed that DPF consisted of fibers with significant pore and uneven surface structure. This surface characteristic will substantiate the higher adsorption capacity.

The specific surface area of DPF has been observed by BET method and the results are inserted in Table 1. The

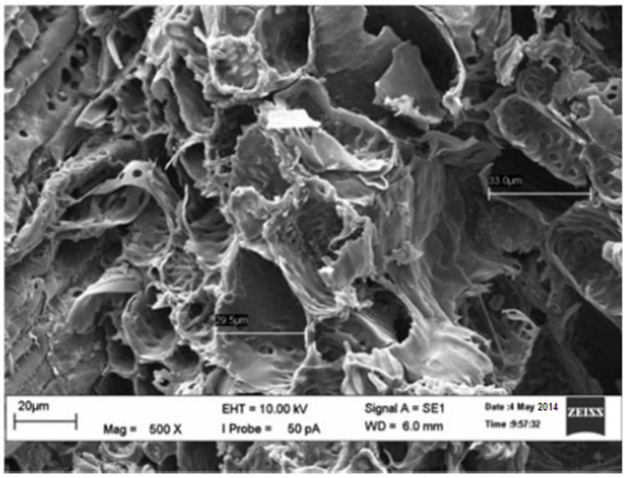

Fig. 1. SEM micrograph of DPF at 500× magnification.

Table 1
Surface properties of DPF obtained from BET experiment and compared with carbonaceous samples

Sample name	BET surface area (m^2/g)	Average pore diameter (nm)	Pore volume (cm^3/g)	Reference
Date palm fiber	128	10.25	0.69	Present study
Tea dust	59.9	5.33	0.031	[24]
Orange peel	6.88	2.48	0.016	[32]
Wood saw dust	159.48	2.36	0.102	[33]
Activated carbon	1688	2.5	1.04	[34]
Graphene oxide	32	17.3	0.11	[34]
Carbon nanotube	177	12.1	0.54	[34]

average pore diameter and surface area of DPF obtained from BET is 10.25 nm and 128 m^2/g, respectively. In addition, the surface properties of DPF such as BET surface area, pore diameter, and pore volume were compared with other carbonaceous samples. From the data presented in Table 1, it is very clear that while DPF does not have a very high surface area (128 m^2/g) as compared to that of the more expensive alternatives of activated carbon (AC) and carbon nanotubes (CNT) or even wood sawdust (WS); nevertheless, it shows reasonably higher properties than that of the more expensive graphene oxide (GO) and some other natural adsorbents. Furthermore, DPF is still a better alternative in comparison to sawdust as well as carbonaceous adsorbents due to its worldwide availability, in contrast to the very location–based availability and rather costly.

3.1.2. FTIR analysis for adsorption mechanism

The surface chemistry of the adsorbent and its effect on the adsorption process is generally investigated by Fourier transform infrared spectroscopy (FTIR). The FTIR spectra of DPF before and after the adsorption of Cr(VI) are shown in Fig. 2. The infrared spectrum exhibits a broad peak at 3412.08 cm^{-1} related to the O–H stretching vibrations of cellulose, pectin, hemicellulose and lignin components. Free hydroxyl groups and bonded OH bands of carboxyl groups were observed as the OH stretching vibrations occurred within a broad range of frequencies [35]. The peaks at 1760 and 1620 cm^{-1} may be due to asymmetric and symmetric stretching vibrations of the presence of (N–H) amide group. Peaks between 1111.00 and 1039.63 cm^{-1} may be due to stretching vibration of C–OH of alcohols and carboxylic acids [36]. Due to the presence of such functional groups, DPF shows acidic nature. At lower pH, the functionality of these groups is not changed but at higher pH, these groups begin to neutralize changing their activity and binding properties [37].

Comparing the spectra before and after sorption of Cr(VI), differences in the position of the absorbance peaks appeared. The asymmetrical stretching vibration at 3236.55 cm^{-1} after the bio–sorption of Cr(VI) was significantly distorted suggesting that chemical interactions occurred between the metal ions and the hydroxyl groups on the bio–sorbent surface. Slight shifting was observed on the C–O band (1109.07 to 1039.63 cm^{-1}) and on the amine (N–H) band (3527.80 to 3442.06 cm^{-1}). Peak at 1744 cm^{-1} shifted to 1640 cm^{-1} as the OH was involved in binding of Cr(VI) [38].

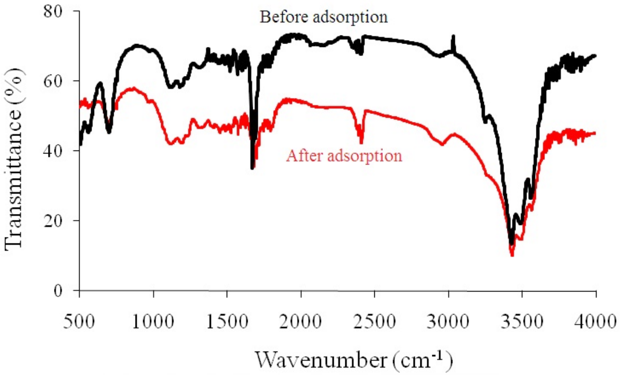

Fig. 2. FTIR spectra of DPF before and after adsorption of Cr(VI).

Metal ions form complexes with surface functional groups of the DPF such as cellulosic–OH and lignin–OH through ion exchange reactions as shown in Fig. 3.

3.2. Batch adsorption study

3.2.1.Effect of initial pH

The effect of pH on Cr(VI) adsorption has been reported from 1 to 7 in Fig. 4. As seen from the figure, the maximum metal adsorption capacity (19.55 mg/g adsorbent) was observed at pH 2.0 and a gradual decrease in adsorption takes place with the increase in pH. Only 47.9% Cr(VI) adsorption took place at pH 7. It can be explained as Cr(VI) exists in different forms such as $Cr_2O_7^{2-}$, $HCrO_4^-$, $Cr_3O_{10}^{2-}$, $Cr_4O_{13}^{2-}$ in aqueous solution and the stability of these forms is dependent on the pH of the system [39]. Cr(VI) exists mainly as $HCrO_4^-$ in aqueous solution at pH 2.0 and electrostatic interaction occurs between the protonated sorbent surface and $HCrO_4^-$ ions resulting in high chromium adsorption [40–43]. Since the DPF was positively charged at lower pH, the protonated amine groups ($-NH_3^+$) would adsorb anionic $HCrO_4^-$ and $Cr_2O_7^{2-}$ via electrostatic attraction. In the FTIR spectra of the DPF after chromate adsorption, the peaks at 1760 and 1620 cm^{-1} and a broadened peak shifted from 3527.80 to 3442.06 cm^{-1} verified the involvement of amine groups (N–H) in chromate adsorption [40].

$$-NH_3^+ + HCrO_4^- \rightarrow -NH_3^+ \cdots HCrO_4^-$$

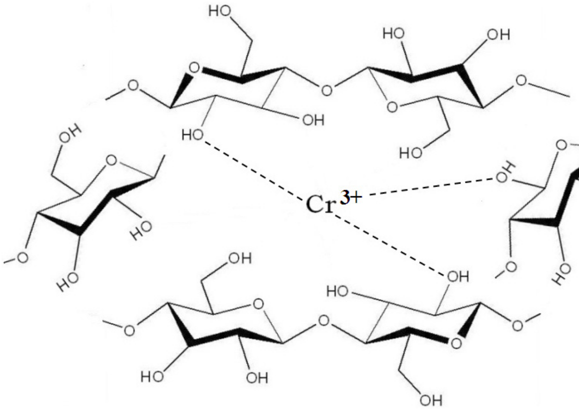

Fig. 3. Mechanism of Cr(VI) adsorption onto DPF surface.

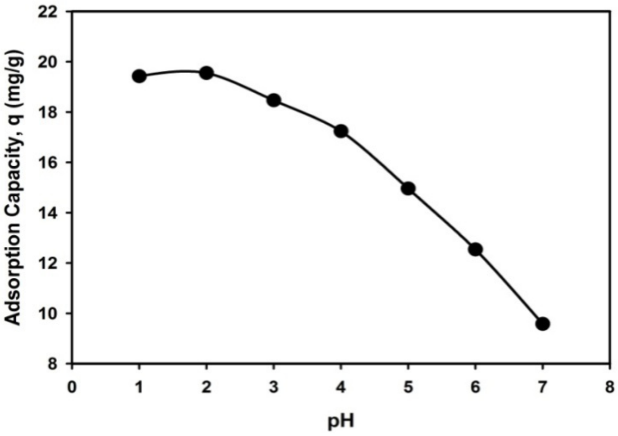

Fig. 4. Effect of pH on the adsorption of Cr(VI) on DPF.

Increase in pH facilitates the conversion of $HCrO_4^-$ to other forms, CrO_4^{2-} and $Cr_2O_7^{2-}$. At higher pH, the decreased adsorption capacity may be explained by the dual competition of both the anions (CrO_4^{2-} and OH^-) to be adsorbed on the surface of the adsorbent of which OH^- prevails [44]. It is clear that adsorption is highly pH dependent and works at highly acidic media.

3.2.2. Effect of adsorbent dosage

The effect of chromium removal at pH 2 with varying amounts of adsorbent dosages for the Chromium concentration of 100 ppm is depicted in Fig. 5. The separation of Cr(VI) is somehow proportional to adsorbent dosages. It was found that the removal of Cr(VI) increases from 56.18 to 97.76% with the increase of adsorbent doses from 1 to 5 g/l. With further increase in doses (5–9 g/l), separation of chromium increased (97.76–98.75%), which eventually being constant. The increase in the amount of metal removal with adsorbent dosages is due to greater availability of adsorbent surface area [45] and hence more active sites resulting from overlapping or aggregation of adsorption sites. However, the adsorption capacity of Cr(VI) showed a reverse trend to the percentage adsorption of metal ions. With increasing adsorbent dosage from 1.0 to 9 g l^{-1}, the adsorption of Cr(VI) ion per unit weight of adsorbent decreased from 56.18 to 8.26 mg/g.

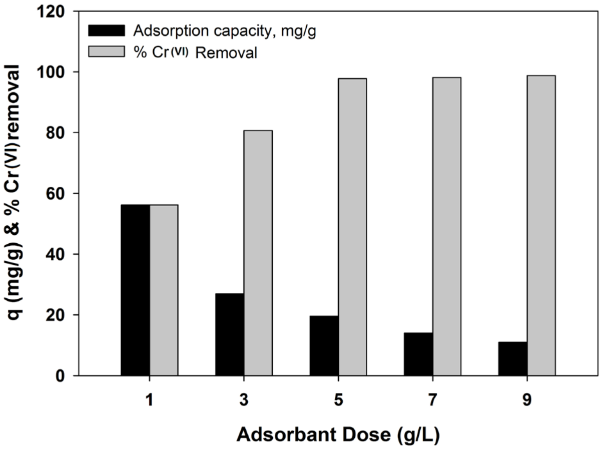

Fig. 5. Effect of adsorbent dosage on Cr(VI) adsorption.

3.2.3. Effect of initial Cr(VI) concentration

From Fig. 6 it is seen that, when the initial Cr(VI) ion concentration increased from 100 to 500 ppm, Cr(VI) adsorption decreased from 98.44% to 57.26% and the uptake capacity of DPF increased from 9.84 to 57.26 mg/g after a sorption time of 240 min. The increase in uptake capacity of DPF with the increase of Cr(VI) ion concentration is due to the higher availability of Cr(VI) ions in solution for adsorption. Moreover, higher initial Cr(VI) concentration increased driving force to overcome all mass transfer resistances of metal ions between the aqueous and solid phases resulting higher probability of collision between Cr(VI) ions and sorbents. This also results in higher metal uptake [38]. The decrease in percentage removal can be explained by the fact that all the adsorbents have a limited number of active sites, which would have become saturated above a certain concentration.

3.3. Adsorption isotherm study

Fig. 7 shows Langmuir adsorption isotherm plot regarding the effect of equilibrium concentration of DPF on Cr(VI) uptake. The performance of adsorbents is usually determined by their uptake capacity. Adsorbents can be compared based on their respective maximum uptake values, q_m, which can be calculated by fitting the Langmuir isotherm model to the actual experimental data. This approach is feasible if q_m reaches a plateau. A high affinity between the adsorbent and adsorbate reflected in good uptake values at low equilibrium concentrations, C_e is desirable. This is characterized by a steep rise of the isotherm curve close to its origin. An adsorbent is better at lower concentrations might be inferior to higher ones and vice versa.

The isotherm data were calculated from the least square method and the values of the parameters of the Langmuir model from Fig. 7 and the corresponding correlation coefficients (R^2) are listed in Table 2. The maximum sorption capacity of powdered DPF was found to be 62.5 mg/g at pH 2. In general, a good adsorbent being one with a high q_m, a steep initial adsorption isotherm slope and low Langmuir constants signifies a strong affinity between DPF and Cr(VI). Thus Langmuir equation nicely simulates the sorption equilibrium data.

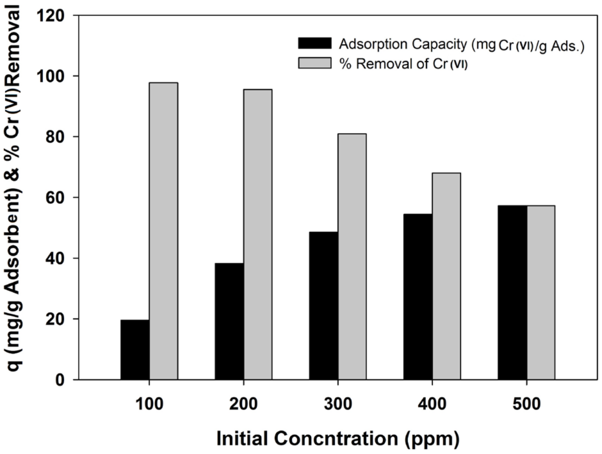

Fig. 6. Effect of initial concentrations of Cr(VI) adsorption on DPF.

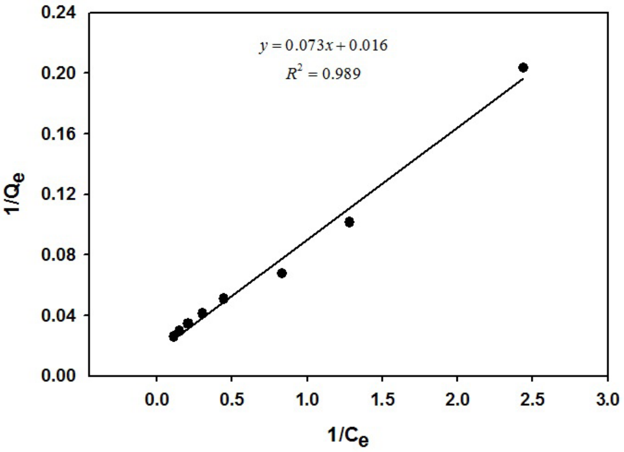

Fig. 7. Langmuir isotherm plot of Cr(VI) adsorption onto DPF.

The essential features of Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor or equilibrium parameter, K_R, which is used to predict whether an adsorption system is favorable or unfavorable. The separation factor is defined by the following relationship:

$$K_R = \frac{1}{1 + K_L C_0} \tag{6}$$

where K_R is a dimensionless separation factor, C_0 is the initial concentration (mg/l), and K_L is the Langmuir constant (l/mg). The parameter K_R indicates the shape of the isotherm accordingly: $K_R > 1$ (unfavorable), $K_R = 1$ (linear), $0 < K_R < 1$ (favorable) and $K_R = 0$ (irreversible). The values of K_R for initial adsorbate concentrations from 25 to 200 ppm were found to be from 0.15 to 0.02. The K_R values indicate that adsorption of Cr(VI) onto powdered DPF is favorable.

3.4. Adsorption kinetics

To express the mechanism of solute adsorption onto an adsorbent, in general, pseudo–first–order and pseudo–second–order kinetic models are used. The plot of $\ln(q_e - q_t)$ vs. t gives a straight line which represents the pseudo–first–order kinetics for the removal of Cr(VI) (Fig. 8). The regression correlation coefficient is found to be low ($R^2 = 0.957$), which seems to be unsatisfactory and shows the inapplicability of pseudo–first–order kinetic model for the removal of Cr(VI) using date palm fiber. Pseudo–second–order kinetics was also studied and the model showed better fitting ($R^2 = 0.995$) (Fig. 9). Similar phenomenon has been observed in the removal of methylene blue dye by sawdust and bamboo–based activated carbon adsorbents. The plot of (t/q_t) vs. t gives a straight line which represents the pseudo–second–order kinetics for the removal of Cr(VI) (Fig. 9). The regression correlation coefficient was found to be very close to 1, which seems to be very satisfactory and shows the applicability of pseudo–second–order kinetic model for the removal of Cr(VI) using date palm fiber. The equilibrium adsorption capacity is found as $q_e = 21.74$mg/g and the corresponding rate constant is $k_2 = 0.002$g/(g·min).

Table 2
Maximum adsorption capacity of various commercial and low cost adsorbents

Adsorbent	Maximum adsorbent capacity, q_m (mg g^{-1})	Optimum pH	References
Date palm fiber	62.5	2.0	Present work
Activated neem leaves	62.97	2.0	[46]
Activated carbon	57.7	–	[47]
Bentonite clay	49.75	3.0	[48]
Coconut husk fiber	29	2.05	[49]
Tea factory waste	27.24	2.0	[50]
Leaf mould	25.9	2.5	[51]
Pine needles	21.50	2.0	[52]

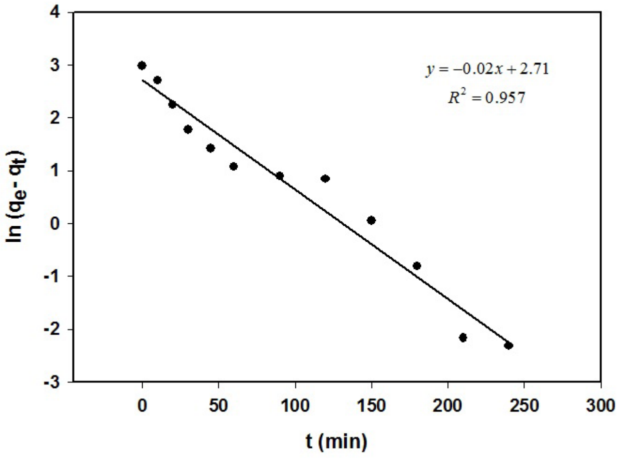

Fig. 8. Pseudo–first–order kinetics of Cr^{6+} sorption on DPF.

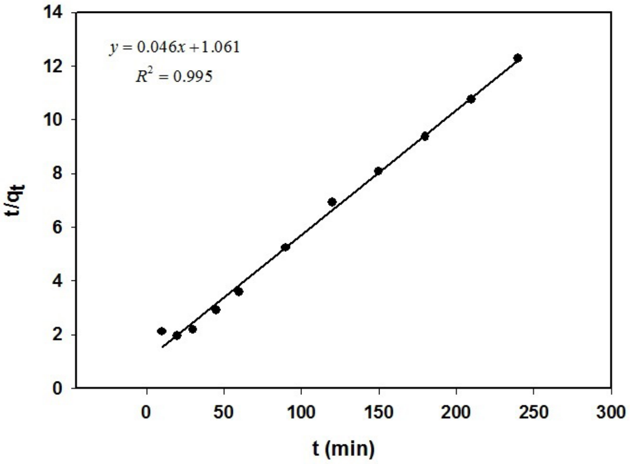

Fig. 9. Pseudo–second–order kinetics of Cr^{6+} sorption on DPF.

4. Mechanism of adsorption

To study the mechanism of the solute adsorption onto the solid surface is crucial for the certain removal of contaminants from aqueous solution. The surface chemistry of the adsorbent and its effect on the adsorption process is usually investigated owing to interpret the solute adsorption. The adsorption mechanism involves oppositely charged ionic interactions, e.g., dipole–dipole, dipole–induced dipole and induced dipole–induced dipole, hydrogen bonding, chemical bonding and ion exchange [53].

The raw date palm (RDP) consists of three main components such as cellulose (40–50%), hemicelluloses (20–35%) and lignin 15–35%, excepting some other minor constituents of protein, oil, etc. [54]. Both cellulose and hemicelluloses have average elemental compositions of 44.4 wt.% C, 49.4 wt.% O, and 6.2 wt.% H which are present in the cellulosic materials as hydroxyl, ether, and carbonyl, whereas, lignin is a complex, systematically polymerized, highly aromatic substance (C 62 wt% and O 32 wt%), and acts as a cementing matrix that holds within cellulose and hemicellulose units [55]. Parameters like pHzpc (pH at zero point charge), surface functional groups and pore size play very important roles in determining the adsorption mechanisms.

The RDP is acidic in nature due to the presence of various functional groups. Metal ions are possibly adsorbed by the date palm fiber by means of three processes of complexation through ion exchange reactions, adsorption mainly physisorption and hydrolysis results in product precipitation. The functionality of these groups is not changed at lower pH. However, at higher pH, these groups begin to neutralize by altering their activity and binding properties.

Fig. 3 represents the adsorption mechanism of Cr(VI) onto the DPF surface. Not much written in the literature about the adsorption mechanism of heavy metals, particularly chromium uptake from industrial wastewater. Hexavalent Cr shows peculiar activities in aqueous solution due to its transition properties. El Nemr et al. [56] prepared a new activated carbon from date palm seed for the removal of toxic Cr(VI) from different kinds of aqueous solution. A strong dependence of the adsorption capacity on pH was reported that the percentage removal of chromium (VI) increased as the pH value decreased and the optimum pH value was 1.0; very close to our results. A summary of adsorption capacities of date palm–based adsorbents for different metal ions has been presented in Table 2.

Al–Ghouti et al. [37] investigated the adsorption mechanism of removing heavy metal ions from aqueous solution using date pits as adsorbent. The isotherms exhibited the Freundlich behavior, which indicates a heterogeneous surface binding. The authors found that Cu^{2+} and Cd^{2+} form complexes with RDP surface followed by precipitation. The stability of the complexes is determined largely by the basicity of the donor groups; the greater the basicity, the higher the stability of the complex [57]. Moreover, the fixation depends on the chemical nature of metal ions, surface chemistry and affinity to the ligand. The fixation capacities of Cu^{2+} is higher than that of Cd^{2+} due to its strong affinity to hydroxyl groups that functions onto the substrate. Hence, two possible binding mechanisms are reported such as intramolecular and intermolecular complexation are predominant for Cu^{2+} and Cd^{2+} adsorption, respectively (Fig. 10). Besides, the adsorption of Pb^{2+} and Cd^{2+} ions onto date pits based activated carbon has been studied by El–Hendawy [58]. Lead is removed in somewhat higher amounts than cadmium due to its lower solubility and lower pH for complexation or deposition, that promotes its removal in comparison to Cd^{2+}.

A comparative study of copper and zinc ion adsorption onto CO_2–activated and non–activated date pits were reported by Banat et al. [59]. Raw date pits showed higher Zn^{2+} and Cu^{2+} ion uptake than activated date pits carbon. This behavior can be explained based on the surface active functional groups that were responsible for binding with Zn^{2+} and Cu^{2+} destroyed due to heat treatment during activation. The removal of Cu^{2+} ions by activated date pits carbon as well as raw date pits were higher than that of Zn^{2+} ions. This behavior may be attributed to the fact that the Cu^{2+} ions have smaller ionic radius (87 pm) than that of Zn^{2+} ions (88 pm) so that Cu^{2+} ions will be capable of greater accessibility to the surface of certain pores than Zn^{2+} ions. The ionic radius of Cr^{6+} (58 pm) is much lower than the divalent cations having excellent surface adhesion properties [60]. In fact, chromium is a reducing element like

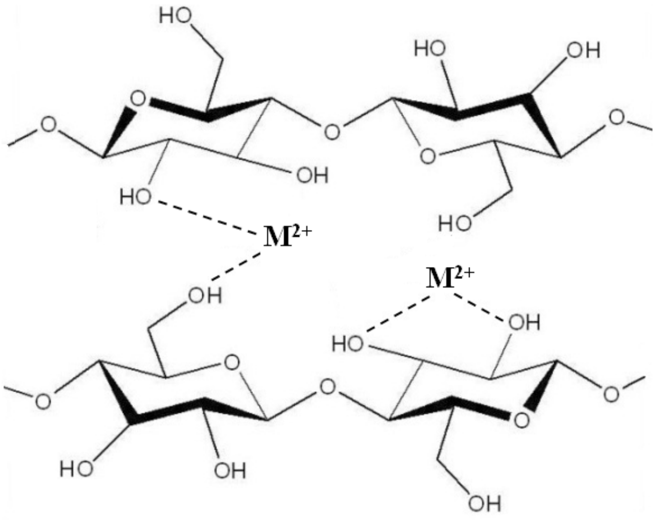

Fig. 10. Mechanism of divalent metals (M) adsorption onto DPF surface.

metals (Cr^{3+} cation in nature), having the possibility to form intermolecular bonding with surface functional groups of DPF (physisorption) as shown in Fig. 3. On the contrary, various anionic forms of Cr(VI) in aqueous solution may retain on the solid surface by inter– and intramolecular bonding. However, the existence of Cr^{6+} in aqueous solution is hardly possible due to the effect of steric hindrance; can be explained by the surface chemistry viewpoint. Therefore, to uptake Cr(VI) from industrial wastewater is a complex phenomenon.

Yao et al. [40] studied the adsorption mechanisms of Cr(VI) on the aminated wheat straw and reported the possibility of reduction of Cr(VI) into Cr(III) in dissolved organic matters (DOM)-rich environment and at low pH [61,62]. The reduced Cr(III) on the aminated surfaces may be released into solution or adsorbed on the adsorbent. Since some adsorbed Cr(VI) would be reduced to Cr(III) and released into the wastewater, the theoretical adsorbed amounts of Cr(VI) were higher than the actual measured values, and the difference was the amount of reduced Cr(III) released into the wastewater [40]. In fact, hexavalent chromium recovery is the key issue rather trivalent element due to strong toxicity of the previous one. Similar phenomenon is also applicable to the present system due to identical surface properties of the adsorbent and chemical features of the chromium adsorbate present in industrial wastewater.

In addition, the thermodynamic and kinetic properties of the process were also reported in the literature point out that a physical interaction between the sorbate and the sorbent solid was predominated [53]. The thermodynamic parameters of the copper ions uptake onto the solid sorbents indicated that the process was endothermic and proceeds spontaneously from the date stones. However, the thermodynamic studies of the adsorption of copper on palm tree waste indicated that the process was exothermic and proceeds spontaneously.

Most of the functional groups involved in the binding process are found in cell walls. Plant cell walls are generally considered as structures made by cellulose molecules, organized in microfibrils and surrounded by hemicellulosic materials, lignin and pectin along with small amounts of protein [37,63,64]. In fact, the adsorptive capacity is not determined solely by the surface area of the adsorbent but also by the pore–size distribution and the surface chemistry of the adsorbent.

5. Conclusion

Date palm fiber is found to be a better adsorbent for the removal of Cr(VI) as compared to some other low cost and commercially available adsorbents. The specific surface area of DPF was observed by BET method and found to be 128 m^2/g. Fourier Transform Infrared (FTIR) study of the adsorbent was carried out and found that different functional groups, such as amine, amide, alcohol, alkanes, carboxyl and hydroxyl are responsible for the chemical adsorption of Cr(VI) from aqueous solutions. The maximum percentage removal of Cr(VI) was obtained at pH = 2. The dominant form of Cr(VI) is $HCrO_4^-$ and the surface of adsorbent is charged positively at lower pH. The adsorption capacity increased rapidly with increasing initial concentration up to a certain level and then became saturated. The percentage removal of Cr(VI) increased up to 98.75% with increasing adsorbent doses at a certain Cr(VI) ion concentration. The equilibrium adsorption data were satisfactorily fitted with Langmuir isotherm and confirmed the monolayer adsorption of Cr(VI) onto the adsorbents. The maximum adsorption capacity of DPF was found as 62.5 mg/g. Pseudo–second–order kinetic model better explains the adsorption kinetics and the model was employed to determine various essential sorption parameter as well.

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