Activated carbon from date seeds for chromium removal in aqueous solution

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ABSTRACT

In this current work, activated carbon from date seeds (ACDS) was prepared through single step chemical activation using phosphoric acid. ACDS was characterized by scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FTIR), Thermogravimetric studies (TGA/DTA), surface chemistry and specific area analysis. Performance assessment of the ACDS was carried out through adsorption of chromium (VI) from its aqueous solution. Effect of adsorption parameters such as contact time (1–120 min), pH (2–8), operating temperature (10–50°C), adsorbent dosage (0.01–0.2 g/50 mL) and initial chromium concentration (5–50 mg/L) on Cr(VI) removal by ACDS was studied in detail. Maximum Cr(VI) adsorption of 42.57 mg/g was obtained for a contact time of 60 min and pH of 2 at 30°C using adsorbent dose of 0.1 g/50 mL for an initial feed concentration of 50 mg/L. The Cr(VI) adsorption efficiency of the ACDS was better as compared against commercial activated carbon. Experimental equilibrium data fitted well with Langmuir isotherm (R^2 = 0.9958) and kinetics studies predicted the pseudo-second order for Cr(VI) adsorption on ACDS. Re-usability studies showed that the ACDS could be used for a maximum of 3 times with a slight reduction in the Cr(VI) removal efficiency (< 10%). Results indicated the promising use of date seed biomass as a cheap and efficient starting material to prepare activated carbon for Cr(VI) removal from chromium polluted wastewater.

Keywords: Activated carbon; Date seeds; Chromium; Adsorption; Chemical activation

1. Introduction

Separation of toxic metal ions from wastewater streams is a highly imperative and widely studied research field [1]. Chromium ion is one such toxic contaminant present in industrial waste waters, usually in hexavalent and trivalent forms [2]. Industrial waste waters discharged by electroplating, tanning, textile, paint industries etc. contain a high level of chromium which needs effective separation [3]. The hexavalent form of chromium (Cr(VI)) is highly dangerous due to its adverse effects to living forms, including the carcinogenic effects [4]. Prolonged exposure to Cr(VI) causes digestive tract cancer and permanent skin damage in humans. Short time contact effects of Cr(VI) include nausea, vomiting, diarrhea, epigastric pain and hemorrhage [5]. Hence removal of Cr(VI) species from the wastewater streams to a safe discharge level is a very essential step in the industrial effluent treatment process.

Various chemical and physical processes such as chemical precipitation, electrochemical precipitation, ion exchange, adsorption, electro-dialysis and membrane technology are commercially available for the separation of Cr(VI) ions from the wastewater streams [6–10]. Use of excessive chemicals, generation of toxic sludge, need of additional separation steps and high cost are the major disadvantages associated with these processes. However,

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adsorption is still one of the preferred processes due to its economic feasibility and technical ease [11]. Adsorption is a promising technique for processing of aqueous streams with low contaminant concentration and meeting rigid level of treatment [12]. Activated carbon used as a predominat adsorbent in the adsorption process is a carbonaceous material with high porosity, large specific surface area and better mechanical strength [13]. Removal of various toxic pollutants including metals, dyes, gases etc. by activated carbon have made the activated carbon based adsorption system very attractive, especially for chromium removal application [14,15].

High cost and less re-usability of commercial activated carbon has led to development of waste biomass derived activated carbon, having better adsorption capacities [16]. This biomass mainly consists of agricultural waste having a rich content of cellulose, lignin and protein components [17]. Various agricultural biomass such as apricot kernel [18], bagasse [19], rice husk [20], mahogany fruit shells [21], eucalyptus sawdust [22], luffa sponge [23] etc. have been studied for activated carbon synthesis and their potential application for chromium removal. Activation of carbon derived from the biomass could be obtained by either physical or chemical means. Physical activation is a two-step process – (i) carbonization step which produces non-porous char and (ii) activation step using carbon dioxide (CO_2) or steam, to increase the porosity and surface area [24]. Chemical activation involves simultaneous carbonization and activation using chemical reagents such as sodium hydroxide (NaOH), potassium hydroxide (KOH), phosphoric acid (H_3PO_4), sulphuric acid (H_2SO_4), zinc chloride ($ZnCl_2$) etc. as the activating agents [25].

Dates seeds are suitable starting materials for production of activated carbon due to their excellent natural structure, better lignocellulosic composition and low ash content [26]. However, limited literature and research works have been carried out so for with the date seeds for activated carbon synthesis [27]. Highly porous activated carbon derived through pyrolysis and physical activation using steam has been developed from date seeds [28]. Physiochemical activated carbon derived from date seeds using CO_2 and KOH as activating mediums was studied for bentazon and carbofuran removal [29]. Hydrothermal carbonized and NaOH activated carbon derived from date seed was employed for methylene blue dye separation studies [30]. Date seeds activated carbon using $ZnCl_2$ was used to remove metallic salts and reduce BOD for textile and tannery effluents [31].

In this study, chemically activated carbon using H_3PO_4 was prepared from date seeds using one pot approach. The obtained activated carbon was characterized for its structure, thermal behavior, porosity factors and functional groups. The activated carbon was used to study its hexavalent chromium adsorption capacity from aqueous solution in batch mode. Different adsorption parameters such as contact time, pH, operational temperature, adsorbent dosage and initial feed concentration were studied to understand their effects on Cr(VI) adsorption to the surface of the date seed activated carbon (ACDS). Langmuir and Freundlich sorption isotherms were tested for equilibrium binding of Cr(VI) ions to the active sites of ACDS. Analysis on the adsorption kinetics of Cr(VI) on the ACDS surface was studied using pseudo-first and pseudo-second order kinetic models. Re-usability of the ACDS for Cr(VI) removal was also studied through adsorption-desorption regeneration studies. The obtained experimental observations and results are discussed.

2. Materials and methods

2.1. Materials

Date fruits (Kimia variety) were purchased from the local market and date seeds were obtained from it. These seeds were thoroughly washed in distilled water for 3 times and sun dried thoroughly. Subsequently, the seeds were powdered in a high speed rotary mill and sieved through mesh no. 100. The collected date seed powder was stored in an air tight container for further use. All the chemicals and solutions used in the study were of analytic grade, procured from Merck, India. Fresh distilled water was used for all wash purposes and solution preparation.

2.2. Preparation of activated carbon:

The sieved date seed powder was washed thoroughly with water and dried at 120°C for 8 h. The dried date seed powder was impregnated with concentrated phosphoric acid (85% H_3PO_4) for a weight (seed powder) by volume (acid) ratio of 1:2.5. After 12 h of impregnation, the filtered date seed powder was subjected to carbonization in a muffle furnace maintained under continuous nitrogen flow. The carbonization was carried out at 550°C for 120 min. The cooled carbon sample was removed from the furnace and washed repeatedly with distilled water till the discharge water showed neutral pH. Date seed activated carbon (ACDS) was then dried at 120°C for 4 h and preserved at room temperature in air-tight bottles.

2.3. Characterization of activated carbon

Functional group analysis on the ACDS surface was carried out through Fourier transform infrared (FTIR) studies using IR spectrophotometer (IR Affinity-1, Shimazdu, Japan) with KBr pellet over the range to 4000–400 cm⁻¹. FTIR analysis was performed at a resolution of 1 cm⁻¹ with an average of 32 scans at every level. Structural morphology of the activated carbon was investigated through scanning electron microscopy (SEM) (Evo-18, Carl Zeiss, USA) to compare the ACDS surfaces before and after chromium adsorption. The samples were dried using filter paper, snapped in liquid nitrogen and sputtered with gold prior to SEM studies. The quantity of various surface functional groups on the ACDS was estimated through Boehm's method using the standard reagents [32]. Porous characteristics of the ACDS sample was analyzed in an automatic adsorption unit (Autosorb-1, Quantachrome, USA) through nitrogen gas adsorption isotherms. Brunauer-Emmett-Teller (BET) method was applied for specific surface area (S_{BET}) determination. Total pore volume was estimated by the volume of nitrogen gas adsorbed to the ACDS surface per unit mass of the sample taken. Thermal characteristics of the raw seed powder and fresh ACDS were analyzed through TGA/DTA techniques in a Thermo-gravimetric analyzer (STA 449 F3, NETZSCH,

USA). The analysis was performed with a uniform heating rate of 10 K/min up to 900°C in nitrogen filled atmosphere.

2.4. Batch adsorption studies

A stock solution with a concentration of 1000 mg/L of Cr(VI) was prepared by dissolving required amount of $K_2Cr_2O_7$ in distilled water. Various sample feed solutions required for the Cr(VI) adsorption studies were prepared by diluting the stock solution. The pH of the feed solutions for adsorption studies was adjusted by HCl (0.1 mol/L) or NaOH (0.1 mol/L) buffer solutions. Adsorption studies of the Cr(VI) ions on the ACDS were carried out through batch mode in Erlenmeyer flasks. The feed solution was introduced into the flasks containing a definite amount of the ACDS adsorbate, at a specified initial concentration and operating temperature. Following parameters were studied in the mentioned ranges to understand their effects towards Cr(VI) adsorption on the ACDS surface: contact time (1–120 min), pH (2–8), operating temperature (10–50°C), adsorbent dosage (0.01–0.2 g/50 mL) and feed solution concentration (5–50 mg/L). All experiments were carried out under thorough mixing using a magnetic stirrer at an agitation speed of 300 rpm. Experiments were repeated out for three times to ensure their repeatability and the average values are reported.

Samples of the treated solution were extracted at different time periods and centrifuged at 1000 rpm for five minutes. The supernatant Cr(VI) concentration was estimated through UV-Vis-NIR spectrophotometer (Jasco V-670, Japan) at 550 nm after complexing the solution using 1,5–diphenylcarbazide reagent [33]. The percentage removal of Cr(VI) (%R) was calculated using Eq. (1) [34].

$$\%R = \frac{C_i - C_e}{C_i} \times 100 \tag{1}$$

where C_i (mg/L) is the initial concentration of Cr(VI) and C_e (mg/L) is the Cr(VI) concentration at equilibrium.

The Cr(VI) adsorption capacity after time t (min) of adsorption for the ACDS (q_t) was calculated using Eq. (2) [35].

$$q_t = \frac{(C_i - C_t) \times V}{m} \tag{2}$$

where C_t (mg/L) is the Cr(VI) concentration at time t, V (L) is the volume of Cr(VI) solution and m (g) is the mass of the ACDS adsorbent used. The equilibrium adsorption capacity of ACDS (q_e) can be calculated from Eq. (2) using C_e instead of C_t.

2.5. Re-usability studies

Re-usability of the spent ACDS is very important as it decides the economic success of the activated carbon and its adsorption application [36]. The batch mode of regeneration of the ACDS was carried out by using 0.01 M NaNO₃ solution as the regeneration medium [37]. Calculated amount of Cr(VI) adsorbed ACDS powder was added to 50 mL of NaNO₃ solution in Erlenmeyer flask and the solution mixture was mixed for 15 min at a constant speed of 300 rpm using magnetic stirrer. The regenerated ACDS absorbent

was then filtered, washed with distilled water, dried at 100°C and used for further Cr(VI) adsorption studies.

2.6. Adsorption theory

2.6.1. Equilibrium isotherm studies

Experimental equilibrium adsorption data was matched with two isotherm models, namely, Langmuir and Freundlich. According to Langmuir model, the adsorbate forms a mono layer on the adsorbate and there is no interaction between the adsorbed species [38]. The adsorbate possesses identical active sites and has a restricted adsorption capacity (q_{max}). The linear form of the Langmuir isotherm equation is presented in Eq. (3).

$$\frac{C_e}{q_e} = \frac{1}{q_{max} \times K_L} + \frac{C_e}{q_{max}} \tag{3}$$

where K_L (L/mg) is Langmuir isotherm constant and q_{max} (mg/g) is the mono layer maximum adsorption capacity. A dimensionless constant known as separation factor (R_L) explicates the favor of adsorption if $0 < R_L < 1$ and is given by Eq. (4) [39].

$$R_L = \frac{1}{1 + K_L C_i} \tag{4}$$

Freundlich isotherm assumes multi-layer adsorption on the adsorbate surface and existence of interactions between the adsorbed species [40]. Freundlich isotherm in the linear form is expressed as shown in Eq. (5).

$$\ln(q_e) = \ln(K_f) + \frac{1}{n} * \ln(C_e) \tag{5}$$

where K_f ($mg^{1-1/n}$ $L^{1/n}$ g^{-1}) is Freundlich isotherm constant and n is the adsorption intensity.

2.6.2. Kinetic studies

Adsorption kinetics studies of Cr(VI) on the ACDS powder were carried out by extraction of the solution samples at prescribed time intervals and estimating the amount of Cr(VI) in it (C_t). The experimental data were then correlated with the pseudo-first-order and pseudo-second-order kinetic models to understand the order of adsorption kinetics. The kinetic equation for the pseudo-first-order model for the solid/liquid sorption systems in the linear form is given by Eq. (6) [41].

$$\ln(q_e - q_t) = \ln(q_e) - k_1 * t \tag{6}$$

where k_1 is the pseudo-first-order rate constant (min⁻¹) and t is the contact time (min). The slope and intercept obtained from the linear plot of $\ln(q_e - q_t)$ vs. t, provides the values of k_1 and theoretical equilibrium adsorption capacity $q_{e,cal}$, respectively.

Eq. (7) represents the linearized form of pseudo-second-order kinetic model [42].

$$\frac{t}{q_t} = \frac{1}{k_2 \times q_e^2} + \frac{t}{q_e} \tag{7}$$

where k_2 is the pseudo-second order rate constant (mg/g min). The values of k_2 and $q_{e,cal}$ for the pseudo-second order model were obtained from the slope and intercept of linear plot between t/q_t and t.

3. Results and discussions

3.1. Adsorption capacity of Cr(VI) on various adsorbents

A comparison on the adsorption capacity of hexavalent chromium by various adsorbents prepared from the date seeds (as explained below) is presented in Table 1.

Adsorbent 1 – Raw seed powder

Adsorbent 2 – Dried seed powder at 100°C for 24 h ($DS_{100,24}$)

Adsorbent 3 – Phosphoric acid impregnated date seed activated carbon (ACDS)

Adsorbent 4 – Potassium hydroxide impregnated activated carbon (KOH-ACDS) which was synthesized by the same procedure of ACDS preparation except for the usage of potassium hydroxide as the activation agent instead of phosphoric acid

Adsorbent 5 – Commercial activated carbon (Commercial AC)

As shown in Table 1, ACDS resulted in the maximum adsorption capacity of 20.54 mg/g while raw date seed powder recorded the lowest adsorption capacity of 0.84 mg/g for Cr(VI) removal. ACDS produced two times better adsorption of Cr(VI) as compared with the commercial AC under similar adsorption conditions. Also, it was observed that the ACDS has adsorption ability of nearly three times greater as compared with the alkali based date seed activated carbon (KOH-ACDS). Hence the acid based activated carbon derived from dates was used for further studies to investigate the effect of adsorption parameters on Cr(VI) removal from its aqueous solution.

3.2. Characterization of ACDS adsorbent

The chemical and structural states of the ACDS before and after adsorption of hexavalent chromium were investigated by FTIR and SEM techniques. FTIR spectra of the ACDS sample before and after adsorption of Cr(VI) ions is shown in Fig. 1. These absorption spectra display the same shape with considerable amount of shifts in their peaks

due to Cr(VI) adsorption. The absorption peaks recorded at 2408, 2145 and 2062 cm^{-1} wave number for the ACDS sample before adsorption indicated the C≡C stretching. These peaks had a red shift to 2404, 2143 and 2059 cm^{-1} after chromium adsorption on ACDS sample. In similar way, the peak at 1576 cm^{-1} due to N–H bond of amines was shifted to 1569 cm^{-1} due to chromium adsorption [43]. The absorption peak at 1798 cm^{-1} due to C=O stretching had a reduced intensity after Cr(VI) adsorption, suggesting that there has been certain interaction between the chromium ions and oxygen atoms [44]. Similar trend of reduced intensity was observed for the absorption band at 1075 cm^{-1} due to C-O-C stretching vibrations. In addition, formation of new peak at 489 cm^{-1} can be assigned to the stretching vibration of Cr–O bond, indicating the adsorption of Cr(VI) to ACDS surface [45]. FTIR studies confirmed the successful adsorption of Cr(VI) ions on ACDS and the functional groups C≡C, N–H and C=O of ACDS were actively involved in the chromium adsorption.

Fig. 2 shows the SEM images of the ACDS sample before and after adsorption of Cr(VI) ions. The micro graphs of ACDS clearly illustrate the difference in the surface morphology of the ACDS pristine surface and their chromium loaded surface. The pure surface of ACDS exhibit significantly rough morphology with uniform pore distribution and high porosity. The roughness in the surface could be ascribed to the presence of various carbon based functional groups present in the ACDS. After adsorption of chromium, the surface morphology was changed to much less porous and decreased roughness with well interconnected fibrillary network. Specific surface area (S_{BET}), average pore radius (R_m) and total pore volume (V_p) for ACDS sample was determined through nitrogen adsorption-desorption techniques. The results, as presented in Table 2, clearly show the enhancement in porosity especially with the micro pore formation due to acid activation of ACDS, as compared to raw seed powder and KOH activated carbon. The ratio of micro porous to mesoporous volume for the fresh ACDS was around 50%. In addition to creation of new micro pores, phosphoric acid enlarged the existing micro pores to mesopores. ACDS was identified as mesoporous as
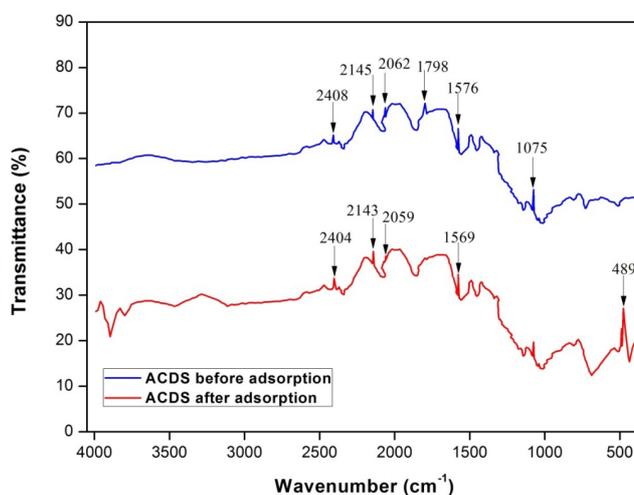
Table 1
Comparison of adsorption capacities of Cr(VI) on various prepared adsorbents for 50 mL feed with initial chromium concentration of 50 mg/L and adsorbent dosage of 0.05 g for 60 min at 30°C

Adsorbent	Cr(VI) adsorption capacity (mg/g)
Raw date seed powder	0.84
$DS_{100,24}$	4.26
KOH-ACDS	7.19
ACDS	20.54
Commercial AC	10.12

Fig. 1. FTIR Spectra of pure and Cr(VI) adsorbed ACDS surface.

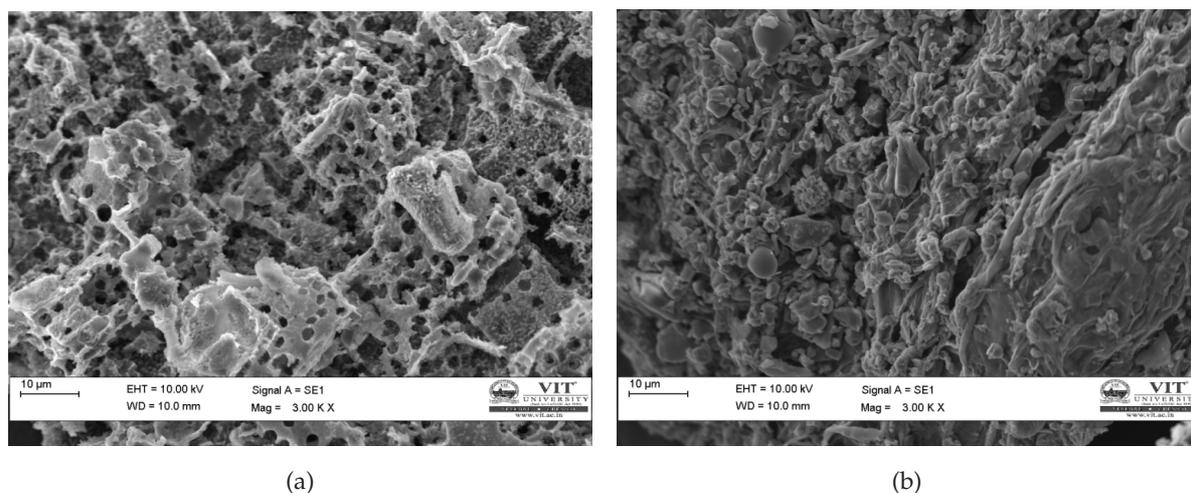(a)   (b)

Fig. 2. SEM images of ACDS (a) before adsorption and (b) after adsorption.

Table 2
Pore statistics for the pure and spent ACDS surface

Sample	BET specific surface area, S_{BET} (m²/g)	Average pore radius, R_m (nm)	Micro pore volume, V_{mic} (cm³/g)	Mesopore volume, V_{mes} (cm³/g)	Total pore volume, V_p (cm³/g)
Raw powder	0.147	3.32	0.12	0.42	0.54
KOH-ACDS	1.426	11.24	0.31	0.78	1.09
Fresh ACDS	5.725	20.46	3.75	3.92	7.67
Spent ACDS	0.026	1.89	0.04	0.28	0.32

the average pore radius was ≤ 25 nm and predominant pore volume (61%) was in the mesoporous region. BET studies on fresh and spent ACDS confirmed the successful adsorption of Cr(VI) ions on the adsorbent surface.

Boehm titration analysis for the concentration of different surface functional groups on the raw seed powder and ACDS were performed. Concentration ratio of total acidic to basic functional groups got increased from 0.574 of the raw seed powder to 0.844 for the ACDS. The acidic group analysis comprised of carboxylic, phenolic and lactonic functional groups. The specific concentration of various functional groups is given in Table S1. Increase in total acidic groups (especially the carboxylic acid group) with a reduction in total basic groups for ACDS is attributed to the phosphoric acid activation.

Effect of phosphoric acid impregnation on the thermal characteristics of the activated carbon was studied through TGA/DTA analysis and the results are presented in Fig. 3 and Fig. S1. The raw date seeds exhibited a predominant weight loss with a rapid rate between 200 and 400°C having a differential peak at 250°C (Fig.S1). A slow and decreasing weight loss rate was noticed from 400 to 900°C. TGA pattern of ACDS showed a gradual and steady weight loss upto 500°C with a broad weak peak around 350°C as shown in Fig. 3. A secondary higher weight loss was noticed from 500 to 750°C and further continued with a very slow rate upto 900°C. Through the temperature range of 400–900°C, ACDS recorded two differential peaks with maxima at 520°C and 695°C. From the results, it was understood that the phosphoric acid impregnation
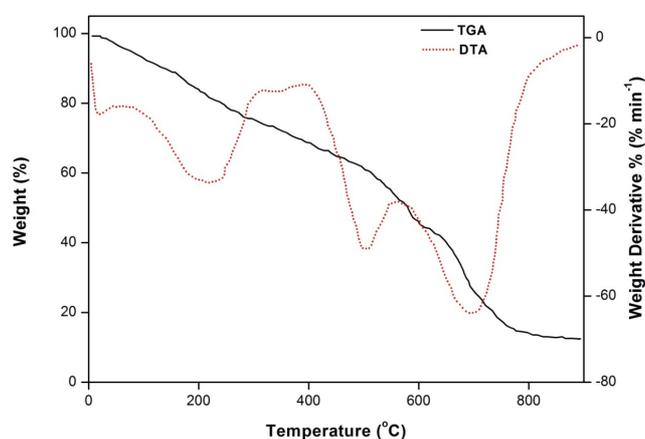

Fig. 3. TGA-DTG thermo gram of ACDS.

followed with thermal activation shifted the degradation of ACDS to higher temperatures. Also, the volatiles evolution was strongly retarded (at 600°C, only 50% of weight loss was noticed for ACDS whereas the raw seed got completely degraded) and the carbon yield was promoted in the range of 400–750°C. These thermal enhancements were due to the acid dissolution of certain functional components in the seed followed by their recombination at other active sites during thermal activation, giving rise to thermally resistant structures [46].

3.3. Adsorption effect due to adsorbent dosage

The effect of adsorbent dosage on Cr(VI) removal was studied by varying the ACDS dosage as 0.01, 0.05, 0.1 and 0.2 g/50 ml of the feed solution in the test flasks under prescribed conditions. The results are shown in Fig. 4. It was observed that increase in ACDS dosage resulted in increased Cr(VI) removal. This can be explained by the increase in availability of more active sites for Cr(VI) adsorption with the increase in ACDS dosage [20]. Similar results were reported by other related research works for chromium removal [5,34].

It was also observed that the Cr(VI) separation efficiency increased rapidly when the ACDS dosage was increased from 0.01 to 0.1 and reached a plateau nature for subsequent increase from 0.1 to 0.2. This indicated that 0.1 g of ACDS was an optimal dosage for effective Cr(VI) removal under prescribed experimental conditions.

3.4. Adsorption effect due to temperature

Adsorption studies were performed at five different temperatures of 10, 20, 30, 40 and 50°C under prescribed conditions. Effect of operating temperature on Cr(VI) adsorption to ACDS surface is presented in Fig. 5. From Fig. 5, it could be understood the adsorption capacity increased with increase in temperature until 30°C. For higher operating temperatures of 40°C and 50°C, there was slight decrease in adsorption capacity. Maximum adsorption capacity was obtained at 30°C (close to room temperature) indicating the adsorption process is spontaneous at room temperature. Decrease in Cr(VI) uptake capacity with raise in temperature above room level indicates that the adsorption is exothermic in nature [47]. Increase in temperature resulted in higher kinetic energy of $Cr_2O_7^{2-}$ anions than the binding energy between $Cr_2O_7^{2-}$ ions and active sites of ACDS. This caused a decrease in adsorption capacity and also explained that Cr(VI) binding to ACDS surface is more of physical in nature [48].

Adsorption thermodynamic parameters namely change in Gibbs free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) were obtained by expressions shown in Eqs. (8) and (9) [49].

$$\Delta G^o = -RT \ln\left(\frac{q_e}{C_e}\right) \tag{8}$$

$$\ln\left(\frac{q_e}{C_e}\right) = \frac{\Delta S^o}{R} - \frac{\Delta H^o}{RT} \tag{9}$$

ΔH° and ΔS° were evaluated using the slope and intercept obtained from a plot between $\ln(q_e/C_e)$ and $(1/T)$. The results for the thermodynamics parameters calculations are presented in Table S2 and Fig. S2. Negative values of ΔG° confirmed that the adsorption process is spontaneous and thermodynamically favorable for temperatures above room level. Decrease in negativity of ΔG° with rise in temperature above ambient level, showed the physical nature of the adsorption phenomenon. Negative value of ΔH° revealed that the adsorption of Cr(VI) on ACDS surface is exothermic in nature. The negative value of ΔS° highlighted the decreased randomness at the adsorbent–solution interface with possible interaction between the Cr(VI) ions and ACDS adsorption sites.

3.5. Adsorption effect due to pH

The pH of the feed aqueous solution of Cr(VI) was varied from 2 to 8 to study the impact of pH on Cr(VI) adsorption to ACDS. Fig. 6 explains the effect of pH on adsorption effect of Cr(VI) to ACDS. It was clearly seen that chromium adsorption increased with decrease in pH. A maximum value of 42.57 mg/g was obtained for Cr(VI) adsorption when the pH was maintained at a value of 2. Chromium exists in predominant forms of $HCrO_4^-$ followed with CrO_4^{2-} and $Cr_2O_7^{2-}$ ions in the pH range of 1–6 [50]. In the acidic environment, the ACDS surface was protonated with H^+ ions aiding the electrostatic attraction of Cr(VI) in the form of $HCrO_4^-$ ions to the charged ACDS surface. With increase in the pH, the $HCrO_4^-$ form of Cr(VI) diminished and CrO_4^{2-} and $Cr_2O_7^{2-}$ ions became abundant, requiring more active sites for adsorption. Also the degree of protonation of ACDS surface was weakened with increase in pH due to
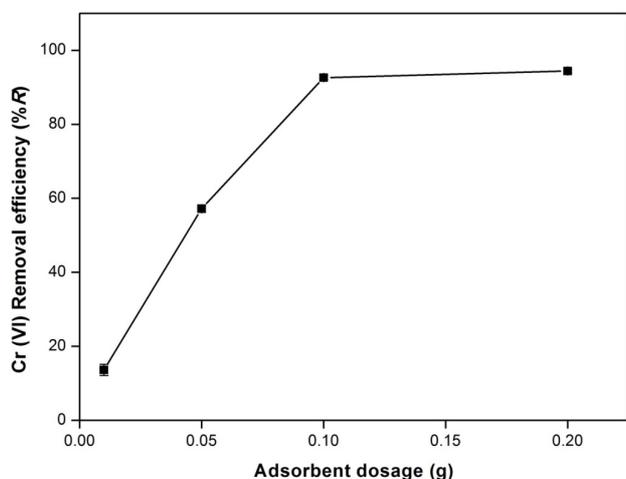

Fig. 4. Effect of ACDS dosage on Cr(VI) adsorption for pH = 2, Temperature = 30°C, Feed volume = 50 mL, Initial feed concentration = 50 mg/L and Time = 60 min.
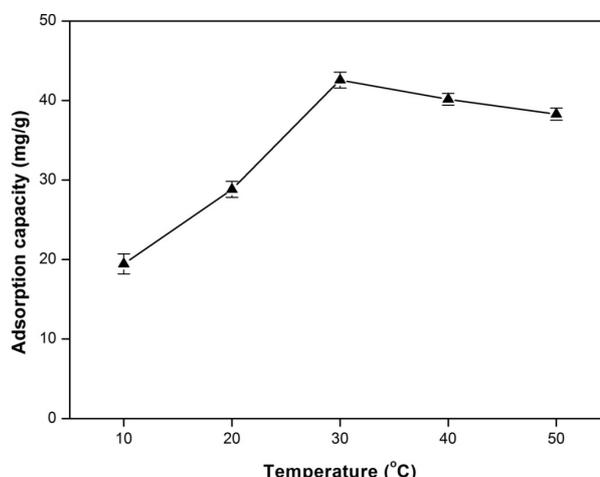

Fig. 5. Temperature effects on Cr(VI) adsorption to ACDS surface for pH = 2, Adsorbent dosage = 0.1 g/50 mL solution, Initial feed concentration = 50 mg/L and Time = 60 min.
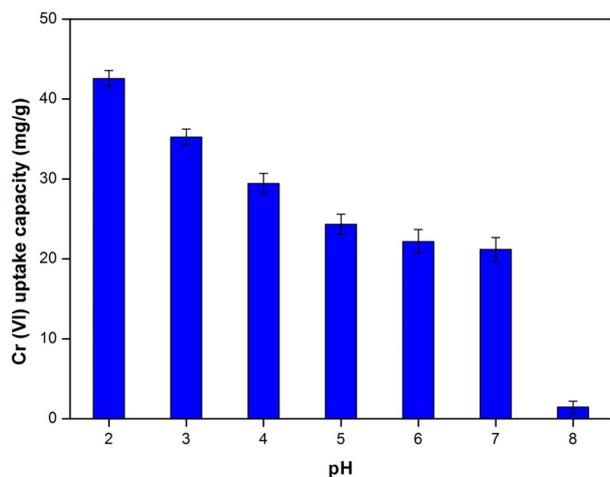
Fig. 6. pH studies on Cr(VI) adsorption to ACDS surface for Temperature = 30°C, Adsorbent dosage = 0.1 g/50 mL solution, Initial feed concentration = 50 mg/L and Time = 60 min.
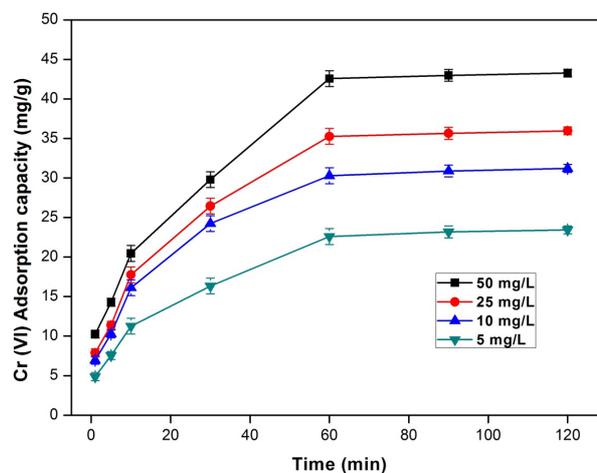

Fig. 7. Effect of Initial feed concentration and Time on Cr(VI) adsorption to ACDS surface for pH = 2, Temperature = 30°C and Adsorbent dosage = 0.1 g/50 mL solution.

low availability of H$^+$ ions. As a result, Cr(VI) adsorption ability got decreased with increase in the pH. A low value of Cr(VI) adsorption of 1.45 mg/g was observed for a basic pH of 8 indicating the suitability of Cr(VI) adsorption in acidic regime.

3.6. Adsorption effect due to initial Cr(VI) concentration and contact time

Feed solutions with varying Cr(VI) concentrations of 5, 10, 25 and 50 mg/L were used in the batch adsorption experiments to study the influence of initial concentration on the adsorption capacity. For a given feed concentration batch run, samples were pulled out at distinct time intervals to understand the impact of contact time on adsorption ability of Cr(VI) on ACDS. The results are illustrated in Fig. 7. From Fig. 7 it can be seen that the increase in initial concentration results in better uptake capacity of Cr(VI) on the surface of ACDS. High initial concentration of feed solution produced higher concentration gradient resulting in enhanced driving force for the adsorption process [29]. Similar trends of increase in Cr(VI) adsorption capacity with increase in initial concentration of feed have been reported by other researchers [3,23]. Effect of contact time on Cr(VI) adsorption on the ACDS was examined in the range of 1–120 min. As shown in Fig. 7, the Cr(VI) adsorption capacity had a rapid increase up to 60 min. Equilibrium was attained for Cr(VI) adsorption on the ACDS surface at 60 min for all feed concentrations and no appreciable increase in adsorption capacity was observed after 60 min of contact time. Hence the optimal time of adsorption was taken as 60 min for Cr(VI) adsorption on the ACDS surface.

3.7. Adsorption isotherm studies

Adsorption isotherm experiments were carried out at a pH of 2 and contact time of 60 min at 30°C for an adsorbent dose of 0.05 g/50 mL by varying the initial feed concentrations as 5, 10, 25 and 50 mg/L. To understand the interaction behaviour between the ACDS surface and the Cr(VI) molecules, equilibrium batch adsorption data was fitted with Langmuir and Freundlich isotherm models. Outcomes of the adsorption isotherm analysis are presented in Fig. 8, Fig. 9 and Table 3. Maximum adsorption capacity (q_{max}) using Langmuir model for Cr(VI) adsorption on ACDS was found to be 44.05 mg/g at 30°C. Values of the separation factor (R_L) was calculated in the range of 0.06–0.4 (<1) for Cr(VI) adsorption on ACDS surface representing favourable and spontaneous adsorption [51]. Parameters for Freundlich isotherm model is presented in Table 3. The isotherm constant K_F and the exponent $1/n$ were calculated as 16.42 mg$^{1-1/n}$ L$^{1/n}$/g and 0.2868. Upon comparison of the determination coefficient values (R^2) for both the isotherm fits, it can be concluded that Langmuir isotherm fitted the experimental data with good accuracy than the Freundlich model. Thus the adsorption of Cr(VI) on ACDS followed mono layer theory with the absence of interactions between the adsorbed Cr(VI) molecules.

3.8. Adsorption kinetic studies

Rate of adsorption is an important parameter for the design and estimation of adsorbent capacity for Cr(VI) sorption from its aqueous solutions. In order to envisage the adsorption mechanism of Cr(VI) ions on the ACDS, adsorption kinetic studies were carried out. The experimental data for the kinetic model analysis were obtained at pH of 2 and temperature of 30°C for an adsorbent dose of 0.1 g/50 mL with initial feed concentration of 50 mg/L in the time range of 1–120 min. The results obtained for the kinetic studies are presented in Fig. 10 and Table 4. To compare the experimental data with pseudo-first order kinetics and pseudo-second order kinetics, a plot of ln ($q_e - q_t$) vs time and a plot of (t/q_t) vs time was made. Values of the equilibrium adsorption capacity q_e calculated by experimental and theoretically approach are presented in Table 4. From the determination coefficient (R^2) related to the kinetic models, it can be observed that the pseudo-second-order kinetics is in good agreement with the
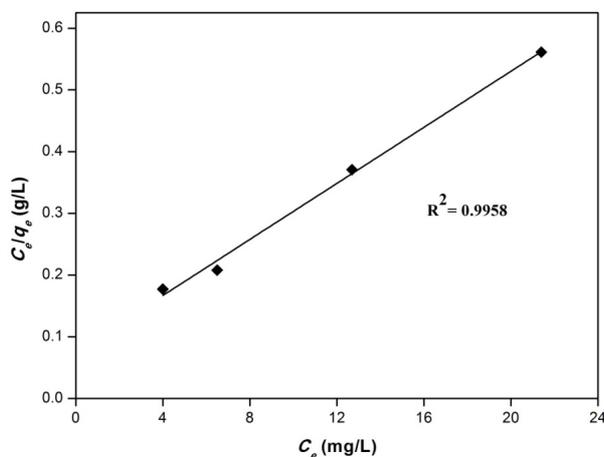
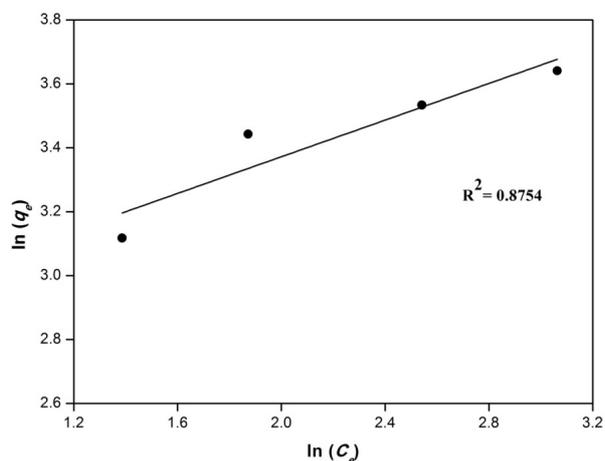Fig. 8. Langmuir isotherm plot for Cr(VI) adsorption on ACDS surface.

Fig. 9. Freundlich isotherm plot for Cr(VI) adsorption on ACDS surface.

Table 3
Adsorption isotherm parameters at 30°C

Langmuir isotherm	q_{max} (mg/g)	44.05
	K_L (L/mg)	0.299
	Determination coefficient (R^2)	0.9958
Freundlich isotherm	K_f mg$^{1-1/n}$·L$^{1/n}$/g	16.42
	$1/n$	0.2868
	Determination coefficient (R^2)	0.8754

experimental data. Also, the theoretically calculated equilibrium adsorption capacity $q_{e,cal}$ is found to be equal to experimentally value $q_{e,exp}$ for pseudo-second order model than the pseudo-first order kinetics.

3.9. Re-usability studies

Re-usability of the adsorbent is an economically desirable step for prolonged use of the adsorbent, decreasing
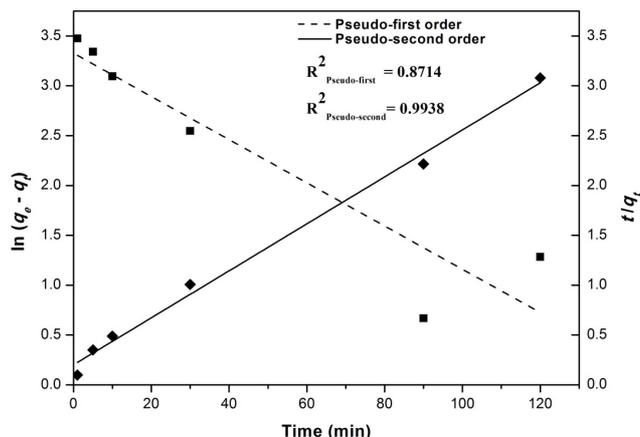

Fig. 10. Kinetic studies for Cr(VI) adsorption on ACDS surface for pH = 2, temperature = 30°C and adsorbent dosage = 0.1 g/50 mL solution and initial feed concentration = 50 mg/L.

Table 4
Parameters for adsorption kinetics

Experimental data	$q_{e,exp}$ (mg/g)	42.57
Pseudo-first-order kinetics	$q_{e,cal}$ (mg/g)	27.86
	Rate constant, k_1 (min^{-1})	0.0217
	Determination coefficient (R^2)	0.8714
Pseudo-second-order kinetics	$q_{e,exp}$ (mg/g)	42.37
	Rate constant, k_2 (g·mg^{-1}·min^{-1})	0.0028
	Determination coefficient (R^2)	0.9938

the operational cost of the separation process considerably. Spent ACDS was subjected to re-usability studies through batch experiments for 4 times. All experiments were carried out at the following conditions: pH of 2, temperature of 30°C, adsorbent dose of 0.1 g/50 mL, initial feed concentration of 50 mg/L and contact time of 60 min. The obtained Cr(VI) removal efficiency for each run is plotted in Fig. 11. It was seen that up to three regeneration cycles, Cr(VI) removal efficiency was almost constant with a marginal reduction of about 10% in the removal efficiency. Thus, the results showed that an efficient regeneration of ACDS adsorbent was achieved for a maximum of 3 cycles under prescribed conditions.

A comparison of hexavalent chromium adsorption ability of the ACDS with activated carbon derived from various other carbon precursors is shown in Table 5. The comparison clearly shows the high adsorption capacity of the synthesized ACDS for Cr(VI), indicating the potential use of ACDS to remove chromium ions from its aqueous solutions.

4. Conclusion

Phosphoric acid based activated carbon prepared from date seeds (ACDS) were applied for removal of hexavalent chromium from its aqueous solution. The results clearly showed that ACDS is as cheap, abundant, efficient and
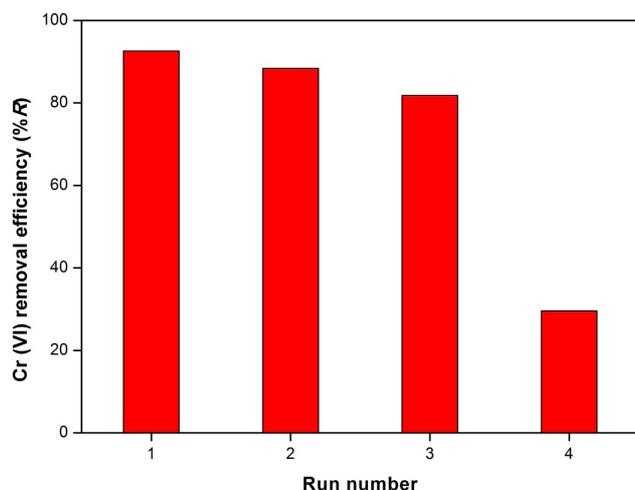
Fig. 11. Re-usability studies of ACDS for pH = 2, temperature = 30°C, adsorbent dosage = 0.1 g/50 mL solution, initial feed concentration = 50 mg/L and Time = 60 min.

Table 5
Comparison of Cr(VI) adsorption performance of various activated carbons

Biomass Precursor	Adsorption conditions				Q_{max} (mg/g)	Reference
	pH	T (°C)	Dosage (g/L)	C_i (mg/L)		
Date seed	2	30	2	50	42.57	This study
Bagasse fly ash	5	30	10	20	1.97	[19]
Eucalyptus sawdust	2	60	5	10	13.17	[22]
Luffa sponge	1	30	1.6	80	39.16	[23]
Bael fruit shell	2	40	3	8	43.54	[34]
Sugar cane bagasse	2	25	2.5	50	4.4	[50]
Maize corncobs	2	25	2.5	50	3	[50]
Jatropha oil cake	2	25	2.5	50	4.76	[50]
Fox nutshell	2	30	5	25	43.45	[52]
Chestnut shells	2	20	2	10–75	33	[53]

easy processed adsorbent for removing chromium (VI) from wastewater streams. ACDS recorded a Cr(VI) uptake capacity superior than commercial activated carbon. Effects of contact time, pH, operating temperature, adsorbent dosage and initial feed concentration on adsorption of Cr(VI) on ACDS surface were studied. It was observed that the adsorption capacity increased with increase in initial feed concentration and decreased with increase in pH. Contact time, temperature and adsorbent dosage were analysed for their optimum values of 60 min, 30°C and 2 g/L. Maximum Cr(VI) adsorption capacity was observed as 42.57 mg/g. Equilibrium studies indicated that the Langmuir model was more fitting than the Freundlich model. Theoretical adsorption capacity for the ACDS was calculated as 44.05 mg/g. Adsorption kinetics analysis confirmed that the Cr(VI) binding to ACDS surface followed pseudo-second order with a determination coefficient (R^2) of 0.9938. Re-usability studies proved the economic advantage of using the regenerated ACDS for a maximum of three times with a 10% decrease in Cr(VI) removal efficiency. Application of the ACDS for the removal of other metal pollutants from their aqueous streams could be carried out as a future study. Also a techno-economic study for the industrial application of the ACDS could also be performed as an extension of the current work. Thus the prepared activated carbon from date seeds seems to be a very promising adsorbent for hexavalent chromium removal from wastewater streams.

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Supplementary material

Table S1
Surface functional groups for the raw date seed powder and ACDS surfaces

Sample	Concentration of functional groups				
	Carboxyl (mmol/g)	Phenolic (mmol/g)	Lactone (mmol/g)	Total acidic (mmol/g)	Basic (mmol/g)
Raw seed powder	0.047	0.864	0.275	1.186	2.067
Fresh DSAC	0.557	0.785	0.207	1.549	1.836

Table S2
Thermodynamic parameters of Cr(VI) adsorption on ACDS

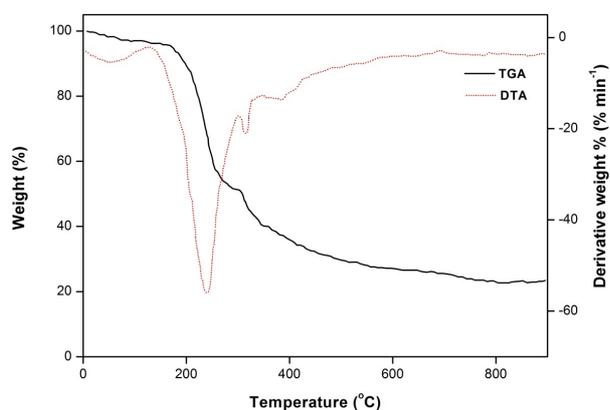| Temperature (K)	q_e (mg g^{-1})	$\Delta G°$ (KJ mol^{-1})	$\Delta H°$ (KJ mol^{-1})	$\Delta S°$ (KJ mol^{-1})
323	42.57	−6.439	−31.708	−0.078
333	40.15	−5.669		
343	38.29	−4.875		

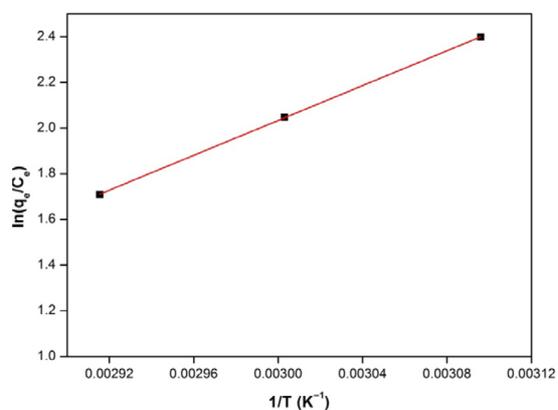Fig. S1. TGA-DTG thermogram of raw date seed powder.

Fig. S2 Thermodynamic studies for Cr(VI) adsorption on ACDS surface.