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Removal of chromium (VI) from aqueous solutions using surface modified composite nanofibers

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G R A P H I C A L A B S T R A C T

![Graphical Abstract](image_url)

A novel material composite nanofibers (PAN-CNT/TiO\textsubscript{2}-NH\textsubscript{2}) based on adsorption of Cr(VI) ions, was applied. Polyacrylonitrile (PAN) and carbon nanotube (CNTs)/titanium dioxide nanoparticles (TiO\textsubscript{2}) functionalized with amine groups (TiO\textsubscript{2}-NH\textsubscript{2}) composite nanofibers have been fabricated by electrospinning. The nanostructures and the formation process mechanism of the obtained PAN-CNT/TiO\textsubscript{2}-NH\textsubscript{2} composite nanofibers are investigated using FTIR, XRD, XPS, SEM, and TEM. The composite nanofibers were used as a novel adsorbent for removing toxic chromium Cr(VI) in aqueous solution. The kinetic study, adsorption isotherm, pH effect, initial concentration, and thermodynamic study were investigated in batch experiments. The composite nanofibers had a positive effect on the adsorption of Cr(VI) ions under neutral and acidic conditions, and the saturated adsorption reached the highest when pH was 2. The adsorption equilibrium reached within 30 and 180 min with an initial solution concentration increasing from 10 to 300 mg/L, and the process can be better described using nonlinear pseudo first than nonlinear pseudo second order model and Intra-particle diffusion. Isotherm data fitted well using linear and nonlinear Langmuir, Freundlich, Redlich-Peterson, and Temkin isotherm adsorption model. Thermodynamic study
1. Introduction

Chromium is a natural metal, commonly found in wastewaters, which is originated from several industrial processes such as electroplating industries, military purposes, textile dyeing, paint, leather tanneries, and pigment industries as critical industry materials [1,2]. Chromium possesses two oxidation states Cr(VI) and Cr(III). Cr(VI) is highly toxic, carcinogenic, mutagenic to most of the living organisms when its concentration level is higher than 0.05 ppm, and extremely mobile than Cr(III) [3–5]. Therefore, there is a great importance to remove Cr(VI) from aqueous solution, to prevent the deleterious impact of the Cr(VI) on the human health. Several methods, such as adsorption, reduction, solvent extraction, precipitation, reverse osmosis have been used for removal of Cr(VI) from industrially polluted wastewaters [6–12]. However, most of these techniques have several limitations and drawbacks, and they require high energy or massive use of reducing agents and they are not used widely [5,6]. In particular, adsorption is considered to be simple, economical, and remains one of the most attractive approaches for treating Cr(VI).

Several kinds of materials were used as an adsorbent for the removal of chromium, such as active carbon [13,14], metal oxide nanoparticles [15,16] and biomaterials [17,18]. Among the adsorbents available currently, TiO2 based adsorbents have been widely used for effective removal of chromium from the polluted water. They have great advantages showing higher removal capacities owing to their outstanding adsorption activities, due to its high adsorption capacities, nontoxic material, inert nature, and highly porous structure [19]. Moreover, the presence of high concentration of hydroxyl groups on the surface of TiO2 will interact and adsorb pollutant in water [20]. Surface modifications of CNTs have been applied recently to enhance the dispersion property and adsorption capacities of CNTs [21–26]. However, some of these adsorbents have some main drawbacks related to the complexity of the separation process of adsorbent from the solution after the adsorption stage, which will increase the operating cost. In order to avoid this problem, some researchers used nanofibers for the adsorption of several contaminants. PAN-CNT composite system was chosen as the template for loading TiO2–NH2 NPs due to that PAN possessed good electrospinnability, simultaneously, a large number of hydroxyl groups and amine groups existing on the surface of composite nanofiber as well as its non-toxic nature [27,28]. PAN fibers with amine groups were used for the removal of several metal ions [29]. In this regard, nanofibers with nanoparticles were investigated for removal Cr(VI) from aqueous solution [30–34].

In the present work, a novel PAN-CNT/TiO2–NH2 composite nanofibers was fabricated for removal of Cr(VI) from aqueous solutions and can be easily separated from the aqueous media. The adsorption kinetics, isotherms and thermodynamic were investigated by fitting the experimental data with different models. The possible adsorption mechanism was provided by testing the adsorption performance under different solution pH values, and initial concentration of the substrate. In addition, the PAN-CNT/TiO2–NH2 composite nanofibers were characterized by SEM, TEM, XRD, XPS and FTIR. We anticipated that this composite nanofiber showed promising potential for wastewater treatment.

2. Experimental

2.1. Materials

Multi-walled carbon nanotubes (MWNTs, purity 95 wt.%; diameter: 10–40 nm; length: about 20 μm), CNT synthesis procedure is described elsewhere [35,36]. Potassium dichromate (K2Cr2O7), Polyacrylonitrile, PAN (MW = 150,000); hydroxylamine hydrochloride (NH2OH·HCl), sodium carbonate (Na2CO3), N,N-dimethylformamide (DMF), sodium hydroxide (NaOH) and hydrochloric acid (HCl), titanium dioxide particulate powder (Degussa P-25), and 3-aminopropyltriethoxysilane (APTES), were purchased from Sigma Aldrich. All chemicals were used as received without any further purification.

2.2. Preparation of electrospun composites nanofibers

10 g DMF solution of PAN (9 wt.%) was mixed for 2 h. In parallel, 3 wt.% of functionalized CNTs were dissolved in DMF for 15 min and sonicated for 30 min. The mixture of PAN and CNTs was magnetically stirred for 30 min and then sonicated for 3 h. The above solution was loaded into a 5 ml syringe, with applied voltage of 25 kV and the tip-to-collector distance was 15 cm. The fabrication of PAN-CNT nanofibers functionalized with amino groups was described elsewhere [27], 8 g of NH3·OH·HCl and 6 g of Na2CO3 was dissolved in 100 ml distilled water and added to the nanofibers. The solution and the prepared PAN-CNT nanofibers were heated to 40 °C for 6 h. After that we remove the remaining salts by washing the nanofibers with distilled water and were dried in air. The surface functionalization of TiO2 NPs with the amino group was carried out according to a well-established procedure [37], 10 mL distilled water and 0.5 g of TiO2 was mixed and the value of pH was adjusted to 11 with sodium hydroxide, to facilitate the adsorption of the hydroxyl group. The hydroxyl group rich TiO2 NPs were washed twice with 20 mL of methanol to remove the excessive sodium hydroxide, and then dried in a vacuum oven at room temperature for use. Subsequent TiO2 NPs was dispersed in 100 mL of toluene via Ultrasonication for 30 min. Subsequently, 3 mL of silane was added to the solution. The suspension was further refluxed at 110 °C for 24 h leading to the NH2 functional group on the titania surface. The reaction product was centrifuged and washed three times with water, followed by methanol to remove the unreacted silane coupling agents, and then dried in a vacuum oven. The crosslinking of the amino functionalized composite nanofibers (PAN-CNT-NH2) to TiO2–NH2 via the amine side was carried out as follow: PAN-CNT-NH2 composite nanofibers were weighed and immersed in the crosslinking medium containing 2.5 wt.% Glutaraldehyde (GA), and kept shaking for 24 h at room temperature. After the activation reaction of the composite nanofibers was completed, the GA crosslinking medium was removed and then 2 ml of an aqueous dispersion of functionalized TiO2 was added to the nanofibers for 24 h. The crosslinked composite nanofibers were washed with ethanol followed by distilled water to remove the excess of non-crosslinked nanoparticles and then the composite nanofibers were dried in air at room temperature.
2.3. Characterization

The crystal phase of PAN-CNT/TiO₂-NH₂ was analyzed by a Bruker D8 Advance X-ray diffraction (XRD) with Cu Ka radiation ($\lambda = 0.15406$ nm) and the accelerating voltage and emission current were 40 kV and 40 mA, respectively. The morphology and microstructure of PAN-CNT/TiO₂-NH₂ was recorded by scanning electron microscopy (SEM, Gemini Zeiss-Ultra 55), and transmission electron microscope (TEM, JEOL-2100F). Fourier transform infrared (FTIR) spectroscopy were recorded on a Thermo Scientific Nicolet iS10 spectrometer in the range of 600–4000 cm⁻¹. The concentration of Cr(VI) was measured using an Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) (Thermo Fisher iCAP 6500). A ESCALAB 250Xi XPS (Thermo, U.S.) and UV–vis were used in the surface analysis of the resulting PAN-CNT/TiO₂-NH₂ composite nanofiber adsorbent before and after Cr(VI) adsorption.

2.4. Adsorption of Cr(VI)

The Adsorption of Cr(VI) in aqueous solution was carried out in a 100 mL quartz reactor containing 25 mg composite nanofibers and 50 mL 10 ppm Cr(VI). The pH values of Cr (VI) solution were measured using a pH-meter (WTW pH-330, Germany) and adjusted between 2 and 9 by the addition of HCl or NaOH solutions. Composite nanofibers were dispersed in Cr(VI) solution under shaking condition at room temperature, then 3 mL of the suspension was taken from the reactor at a scheduled interval. Isothermal studies at different temperatures (20°C, 40°C, and 60°C) were carried out by adding the composite nanofibers into 50 ml of Cr(VI) solution of varying concentrations from 10 to 300 ppm at pH 2. The concentration of chromium prior to and after adsorption were measured using UV–vis and ICP. The equilibrium adsorption capacity ($q_e$) was determined using Eq. (1), while % removal of Cr(VI) was calculated using Eq. (2).

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

$$\%\text{ Removal} = \left(\frac{C_0 - C_e}{C_0}\right) \times 100$$

where $C_0$ is the initial chromium concentration (mg/L) and $C_e$ is the chromium concentration in the aqueous solution at equilibrium (mg/L), $V$ is the total aqueous volume (L), and $m$ is the mass of the composite nanofibers (g). Thermodynamic parameters such as $\Delta H^\circ$, $\Delta S^\circ$, $\Delta G^\circ$ were also evaluated from equilibrium data.

3. Results and discussions

3.1. Characterization of PAN-CNT/TiO₂-NH₂ nanofiber

Fig. 1a and b represents SEM images of the PAN and PAN-CNT/TiO₂-NH₂ nanofiber, showing smooth surface of PAN nanofibers with fiber diameters ranged from approximately 120 nm. For PAN-CNT/TiO₂-NH₂ nanofiber, the diameters of the PAN nanofibers increased about 90 nm with rough surface compared to the PAN. Fig. 1c represents the TEM image of the prepared PAN-CNT/TiO₂-NH₂, indicate that the TiO₂ are dispersed and immobilized onto the PAN nanofibers and have a relatively dense and uniform distribution.

The crystal phase structure of the PAN-CNT/TiO₂-NH₂ nanofibers was characterized by XRD measurement as shown in Fig. 2a. The XRD patterns of the PAN-CNT/TiO₂-NH₂ nanofibers show a very strong anatase peak is observed at $2\theta$ of 25.41°, assigned to (101) plane. Other anatase peaks are observed at $2\theta$ of 37.96° (004), and 48.18° (200). The positions of all diffraction peaks correspond to anatase TiO₂ and they coincide well with the reported value [38]. However, a weak rutile peak is observed at $2\theta$ of 54.36°, and 62.92°, assigned to (211), and (002) plane. In addition, maximum diffraction peak is observed at $2\theta$ of 17.18° and 28.6° represented the crystallographic planes in PAN, while the other peak at $2\theta$ of 10.98° confirms the existence of a C(002) peak of CNTs. In addition, the FTIR spectrum of PAN nanofiber Fig. 2b exhibited the absorption peaks of a stretching vibration at 2240 cm⁻¹ (C≡N), 1732 cm⁻¹ (C=O), and 1455 cm⁻¹ (C–O), which
suggests that the PAN was a copolymer of acrylonitrile and methacrylate [29]. Also, the peaks at 1248 cm\(^{-1}\) and 1352 cm\(^{-1}\) are assigned to the aliphatic \(-\text{CH}--\) group vibrations of different modes in CH and CH\(_2\), respectively. The FTIR spectrum of PAN-CNT/TiO\(_2\)–NH\(_2\) nanofiber shows the absorption peak at 3170–3500 cm\(^{-1}\) and 1668 cm\(^{-1}\) corresponding to stretching vibrations of the –OH. It can be observed that there are broad peaks at 3345 and 1638 cm\(^{-1}\), which correspond to the surface adsorbed water and hydroxyl groups. The transmittance peak at 1620 and 1452 cm\(^{-1}\) were assigned to the (NH\(_2\)) group and the absorption bands at 1451, 1093, and 912 cm\(^{-1}\) were assigned to the C\(_\equiv\)H, C\(_\equiv\)C, and N\(_\equiv\)O, respectively [28]. The peak centered at \(-1002\) cm\(^{-1}\) due to characteristic O\(\equiv\)O stretching vibration. The sharp peak at 1455 cm\(^{-1}\) can be attributed to the lattice vibrations of TiO\(_2\). The absorption band at 1651 cm\(^{-1}\) was caused by a bending vibration of coordinated H\(_2\)O as well as Ti\(\equiv\)OH.

3.2. Effect of pH value on the adsorption performance

The pH value of the solution had significant influence on the adsorption of Cr(VI) for the composite nanofibers [32,39]. The influence of the pH value on the adsorption of Cr(VI) was studied in the range of 2–9 as shown in Fig. 3. The composite nanofibers exhibit much higher adsorption capacity under strong acidic condition rather than in neutral and alkaline conditions. This may be attributed that, the predominante ionic species of Cr(VI) was hydrogen chromate (HCrO\(_4\)) and dichromate (Cr\(_2\)O\(_7\)\(^{2-}\)) are negatively charged while the TiO\(_2\) is positively charged with the species TiOH\(^+\) under the pH value from 2 to 5 [40]. Thus, electrostatic attraction between anionic chromate species and the positively charged surface can lead to a strong adsorption of Cr(VI) at low pH [19]. On the other hand, when the pH was above 5, the amount of CrO\(_4\)\(^{2-}\) increased, while the TiO\(_2\) surface becomes gradually more negatively charged with the species TiO\(^{2-}\) which was hard to be adsorbed by the adsorbent. In addition, the electrostatic repulsion between the negatively charged surface and chromate species leads to inhibited adsorption of Cr(VI) [41]. On the other hand, the acidic medium facilitates the adsorption capacity of Cr(VI) because of the existence of abundant H\(^+\) that adsorbed onto the surface of TiO\(_2\), which have a large surface proton exchange capacity. The photogenerated electrons can be captured by the adsorbed H\(^+\) to form H\(_{\text{ads}}\), which is able to adsorbed Cr(VI).

3.3. Adsorption kinetics

Adsorption kinetics are one of the most important parameters for describing the adsorption efficiency. Kinetics adsorption is performed to evaluate the equilibrium time at the different concentra-
tion on the adsorption capacity of Cr(VI) as shown in Fig. 4. It demonstrated that the Cr(VI) adsorption capacity of PAN-CNT/TiO$_2$-NH$_2$ increases gradually with increasing the concentrations until an equilibrium was established. The removal of Cr(VI) occurred rapidly and reached adsorption equilibrium within 30 min for 10 ppm, while for 300 ppm take 3 h to reach adsorption equilibrium, and after that the adsorption of Cr(VI) becomes stagnant. It is further observed that the maximum adsorption capacity of Cr(VI) is 704 mg/g. This phenomenon may be due to the electrostatic interaction between the positive protonated amidine, amine groups and negative Cr(VI) ions beside the high density of active sites of PAN-CNT/TiO$_2$-NH$_2$ nanofiber [42]. Therefore, the adsorption process was very fast at short adsorption equilibrium time. Two kinetic models, nonlinear pseudo-first-order Eq. (3), and nonlinear pseudo-second-order Eq. (4), are utilized to fit the experimental data and evaluate the adsorption kinetic process [43–46].

\[
q_t = q_e(1 - e^{-k_1t})
\]  
\[
q_t = \frac{k_2q_m^2t}{1 + k_2q_m^2t}
\]

where \(q_e\) and \(q_t\) are the adsorption capacities of Cr(VI) (mg/g) at equilibrium time and at any instant of time \(t\) (min), respectively. Where \(k_1\) is the rate constant of nonlinear pseudo-first order adsorption (1/min), and \(k_2\) is the rate constant of nonlinear pseudo-second order \((g$/mg min\)) \(k_1\) and \(k_2\) are evaluated in the same concentration range, Madhumita et al. obtained 5.33 – 11.36 mg/g/min$^{1/2}$ using PPy-PANI nanofibers [50], Talreja et al. using Fe-PhB-A-CNF achieved 3.88 mg/g/min$^{1/2}$ [31].

### 3.4. Adsorption isotherm

Adsorption isotherms were investigated to exhibit the adsorption capacity of the composite nanofibers for the Cr(VI) removal. The effect of temperature on adsorption of Cr(VI) has been investigated at 20, 40 and 60 °C. The linear and nonlinear Langmuir, Freundlich, and Redlich-Peterson isotherms models are conventional models that were used to fit the experimental data [51–54]. The Langmuir model assumes that the adsorption of Cr(VI) occurs as a monolayer on a homogeneous adsorption surface and is expressed by the following equation,

\[
\frac{C_e}{q_e} = \frac{1}{q_mK_a} + \frac{C_e}{q_m}
\]

where \(C\) is the intercept related to the thickness of the boundary layer and \(K_a\) is the rate constant of intra-particle diffusion \((mg/g/min^{1/2})\), which can be fitted with the experimental data presented in the plot of \(q_e\) versus \(t^{1/2}\) depicted in Fig. 5. As can be seen from Fig. 5 and Table 2, the adsorption plots of Cr(VI) pass through the origin concluded that intra-particle diffusion was rate the controlling step [48]. The high value of \(K_a\) increases from 4.54 to 53.46 mg/g/min$^{1/2}$ with an increase in initial concentrations from 10 to 300 mg/L indicates that composite nanofibers exhibit fast removal rate of Cr(VI) from aqueous solutions [49]. In similar studies for the evaluation of \(K_a\) values in the same concentration range, Madhumita et al. obtained 5.33 – 11.36 mg/g/min$^{1/2}$ using PPy-PANI nanofibers [50], Talreja et al. using Fe-PhB-A-CNF achieved 3.88 mg/g/min$^{1/2}$ [31].

### Table 1

<table>
<thead>
<tr>
<th>(C_0) (mg/L)</th>
<th>(q_{e, exp}) (mg/g)</th>
<th>Nonlinear Pseudo-first-order model</th>
<th>Nonlinear Pseudo-second-order model</th>
<th>Intra-particle diffusion model</th>
</tr>
</thead>
</table>
|               |                       | \(k_1\) (1/min) | \(q_{e,cal}\) (mg/g) | \(R^2\) | \(k_1\) (1/min) | \(q_{e,cal}\) (mg/g) | \(R^2\) | \(K_a\) (mg/g/min$^{1/2}$) | \(C\) | \(R^2\) |}
| 10            | 24.9                  | 0.092              | 25.03                           | 0.998 | 0.0062         | 26.67                           | 0.959 | 4.54                           | 0.135 | 0.994 |}
| 20            | 49.85                 | 0.071              | 50.09                           | 0.998 | 0.0022         | 53.88                           | 0.958 | 7.94                           | 0.087 | 0.987 |}
| 30            | 74.75                 | 0.057              | 72.39                           | 0.995 | 0.0011         | 78.95                           | 0.981 | 9.81                           | 1.76  | 0.969 |}
| 50            | 124.625               | 0.0388             | 124.14                          | 0.996 | 3.83E-4        | 137.30                          | 0.973 | 16.28                          | -7.47 | 0.9888 |}
| 80            | 199.575               | 0.0338             | 193.85                          | 0.986 | 2.01E-4        | 217.47                          | 0.969 | 26.13                          | -20.55 | 0.951 |}
| 100           | 249.5                 | 0.0285             | 243.97                          | 0.998 | 1.28E-4        | 276.47                          | 0.974 | 30.13                          | -25.71 | 0.937 |}
| 200           | 490.75                | 0.0216             | 487.70                          | 0.983 | 4.72E-5        | 550.87                          | 0.962 | 35.45                          | -35.55 | 0.897 |}
| 300           | 704.125               | 0.0164             | 714.27                          | 0.987 | 1.95E-5        | 861.11                          | 0.969 | 53.46                          | -54.65 | 0.89 |}

Fig. 5. Intra-particle diffusion plot of Cr(VI) adsorption, pH 2, and T = 20 °C.
The Freundlich model is used to describe reversible adsorption and the adsorption onto a heterogeneous surface, which is expressed as follows:

$$\log q_e = \log K_f + \frac{1}{n} \log C_e$$  \hspace{1cm} (8)$$

$$q_e = K_f C_e^{1/n}$$  \hspace{1cm} (9)$$

The Redlich-Peterson isotherm contains three parameters, $K_R$, $a_R$, and $g$, incorporates the features of the Langmuir and the Freundlich isotherms [55]. It may be used to represent adsorption equilibrium over a wide concentration range of adsorbate. The exponent, $g$, lies between 0 and 1. When $g = 1$, the Redlich–Peterson equation becomes the Langmuir equation, and when $g = 0$, it becomes the Henry’s law. This isotherm is described as follows:

$$\ln \left( \frac{K_R C_e}{q_e} - 1 \right) = g \ln(C_e) + \ln(a_R)$$  \hspace{1cm} (10)$$

### Table 2

Langmuir, Freundlich, Redlich-Peterson and Temkin isotherm constants parameters for the adsorption of Cr(VI) onto the composite nanofibers.

<table>
<thead>
<tr>
<th>Model</th>
<th>Parameters</th>
<th>Linear Temperature (°C)</th>
<th>Nonlinear Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>20</td>
<td>40</td>
</tr>
<tr>
<td>Langmuir</td>
<td>$q_{max}$ (mg/g)</td>
<td>500</td>
<td>516</td>
</tr>
<tr>
<td></td>
<td>$K_L$ (L/mg)</td>
<td>0.002</td>
<td>0.002</td>
</tr>
<tr>
<td></td>
<td>$R^2$</td>
<td>0.861</td>
<td>0.913</td>
</tr>
<tr>
<td>Freundlich</td>
<td>$n$</td>
<td>3.77</td>
<td>4.32</td>
</tr>
<tr>
<td></td>
<td>$K_F$ (mg/g)</td>
<td>0.53</td>
<td>0.41</td>
</tr>
<tr>
<td></td>
<td>$R^2$</td>
<td>0.988</td>
<td>0.986</td>
</tr>
<tr>
<td>Redlich-Peterson</td>
<td>$g$</td>
<td>0.828</td>
<td>0.952</td>
</tr>
<tr>
<td></td>
<td>$K_R$ (L mg$^{-1/1}$)</td>
<td>86.52</td>
<td>296.33</td>
</tr>
<tr>
<td></td>
<td>$R^2$</td>
<td>0.980</td>
<td>0.984</td>
</tr>
<tr>
<td>Temkin</td>
<td>$A_T$ (L/g)</td>
<td>119.3</td>
<td>183.54</td>
</tr>
<tr>
<td></td>
<td>$b_T$ (kJ/mol)</td>
<td>47.78</td>
<td>33.53</td>
</tr>
<tr>
<td></td>
<td>$R^2$</td>
<td>0.632</td>
<td>0.581</td>
</tr>
</tbody>
</table>

**Fig. 6.** (a) Linear Langmuir isotherm model, (b) Freundlich isotherm model, (c) Redlich-Peterson isotherm model, and (d) Temkin isotherm model for adsorption of Cr(VI) using PAN-CNT/TiO$_2$-NH$_2$ nanofibers at different temperature (pH = 2).
Furthermore, Temkin isotherm model is used to evaluate the sorption potential of the sorbent for Cr(VI), and assumes that the fall in the heat of sorption is linear rather than logarithmic, as implied in the Freundlich equation [56]. The Temkin isotherm has generally been applied in the following form [57]:

\[ q_e = \frac{RT}{b_T} \ln(A_T C_e) \]  

(12)

where \( q_e \) is the amount adsorbed at equilibrium (mg/g), \( C_e \) is the equilibrium concentration of the solution (mg/L), \( q_m \) is the maximum adsorption capacity (mg/g), \( k_a \) is a Langmuir constant related to the affinity of the binding sites and energy of adsorption (L/g), \( k_F \) is a Freundlich constant (mg/g)(L/mg)^1/n, which related to the adsorption capacity, \( 1/n \) is the heterogeneity factor representing the deviation from linearity of adsorption and is also known as Freundlich coefficient, \( k_R \), \( q_0 \), and \( g \) (0 < g < 1), are three isotherm constants, \( A_T \) is the equilibrium binding constant corresponding to the maximum binding energy (L/g), \( b_T \) is the Temkin constant related to the heat of adsorption (kJ/mol), \( R \) is the universal gas constant (8.314 J/mol K), \( T \) is the absolute temperature (K). The values of the maximum loading capacity of Cr(VI) for linear and nonlinear Langmuir, Freundlich, Redlich-Peterson, and Temkin models can be are presented as shown in Figs. 6–8 and the obtained kinetic parameters are summarized in Table 2. The results indicate that the adsorption capacity increase as the temperature increases which confirms that the adsorption process is endothermic [50]. This may be due to an increase in thermal energy of the adsorbing species, which leads to higher adsorption capacity and faster adsorption rate. The very high values of correlation coefficients (R²) indicate that the Freundlich model fitted well the isotherm data better than the Langmuir, Redlich-Peterson and Temkin models and confirms the multilayer adsorption of Cr(VI) onto the composite surface.

3.5. Thermodynamic study

To evaluate the influence of temperature on the adsorption process of Cr(VI) onto the composite nanofibers, the thermodynamic parameters such as Gibbs free energy (\( \Delta G^0 \)), enthalpy (\( \Delta H^0 \)), and entropy (\( \Delta S^0 \)) are calculated using the following equations [58]:

\[ \ln K_d = \frac{\Delta S^0}{R} + \frac{-\Delta H^0}{RT} \]  

(13)

\[ K_d = \frac{(C_0 - C_e)V}{m C_e} \]  

(14)

\[ \Delta G^0 = \Delta H^0 - T \Delta S^0 \]  

(15)

where \( R \) is the universal gas constant (8.314 J/mol K), \( T \) is the absolute temperature (K), \( m \) is the adsorbent dose (g), and \( K_d \) is the thermodynamic equilibrium constant (L/mol). The values of \( \Delta H^0 \) and
nanofibers. In experimental results, the values in between 
/C0 
adsorption reaction is exothermic. This implies that the adsorption

process is energetically stable. The positive value of D S0 reflects the increased disorder and randomness of the Cr(VI) on the composite nanofibers at the solid/liquid solution interface during the adsorption process, and indicate the affinity of the adsorbent material toward Cr(VI) [61].

3.6. Adsorption mechanism

In order to confirm the adsorption mechanism, UV–vis and XPS were used, and the results are shown in Fig. 10. Fig. 10a shows that the maximum absorption wavelength of Cr(VI) is 351 nm with an absorbance of 0.94 before adsorption, and after adsorption the absorbance decreased, indicating complete removal of Cr(VI) ions. Further to confirm the reduction process involved in the removal of Cr(VI), the composite nanofibers after adsorption were analyzed with XPS. The XPS results in Fig. 10b shows that after the adsorption process, two energy bands at about 579.2 and 588.3 eV appeared, which correspond to the binding energies of Cr 2p3/2 and Cr 2p1/2 orbitals, respectively which are consistent with Cr (III) and Cr(VI) [62]. The existence of the Cr(VI) on the nanofibers is attributable to the anion exchange between doped Cl− in the adsorbent and Cr(VI) ions in the aqueous solution [63]. The presence of Cr(III) (binding energy of 577.1 and 586.5 eV) on the nanofibers surface suggests that some fraction of adsorbed Cr(VI) was reduced to Cr(III) by a reduction process [50]. This behavior attributable to the reduction of the Cr(VI) by the TiO2, which indicates that TiO2 has a strong reduction capability for Cr(VI) [28,64]. Overall, Cr(VI) is removed either by adsorbed on the surface of composite nanofibers or by being reduced into Cr(III), which is much less toxic. To sum up, the interaction of Cr with the composite nanofibers includes two process, adsorption (including both Cr(VI) and Cr(III) species) and reduction [65].

3.7. Effect of adsorbent dosage

The effect of the amount of sorbent dose as a function of time on the adsorption performance of Cr(VI) was studied by varying the amount of the TiO2 NPs ranging from 5 to 40 mg as shown in Fig. 11. The result indicated that the adsorption performance increases from 55.2% to 99.7% with an increase in adsorbent dose. This is attributed to the fact that as the mass of sorbent is increased, the total number of active sites on the sorbent surface also increases thereby resulting in an increase in a number of electrons which can be used for the removal of Cr(VI) [66]. With increasing the amount of TiO2 NPs dose above 30 mg on the surface of nanofibers, the dosage was aggregation. Therefore, reduces the penetration of light and the adsorption reaches a saturation level at high doses. This behavior can be attributed due to when the concentration of the sorbent exceeds an optimum value, the adsorption performance may decrease due to a decrease in the number of active sites on the TiO2 NPs surface available for Cr(VI) removal thereby resulting into a decrease in the performance of the adsorption [67].

3.8. Regeneration and reusability studies

Regeneration and reuse of the adsorbent material are an important factors in wastewater treatment processes for evaluating the cost effectiveness. The composite nanofibers were washed with 0.1 M NaOH to check the regeneration and reusability of PAN-CNT/TiO2-NH2 nanofiber for Cr(VI) removal. The Cr(VI) adsorption capacity still remained by 80% after 5 times usage. However, the removal percentage was declined gradually after five adsorption-desorption cycles, which may be attributed to the deformation of nanofibers in NaOH medium during regeneration. These results indicate that the PAN-CNT/TiO2–NH2 nanofiber could be regener-

Table 3
Thermodynamic parameters for Cr(VI) adsorbed by PAN-CNT/TiO2-NH2 composite nanofibers.

<table>
<thead>
<tr>
<th>T (K)</th>
<th>ΔC° (kJ/mol)</th>
<th>ΔS° (kJ/[K/mol])</th>
<th>ΔH° (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>293</td>
<td>−1301.89</td>
<td>3.026</td>
<td>−415.21</td>
</tr>
<tr>
<td>313</td>
<td>−1362.42</td>
<td></td>
<td></td>
</tr>
<tr>
<td>333</td>
<td>−1422.94</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Fig. 10. (a) UV–vis spectra, and (b) XPS of Cr(VI) solution before and after adsorption (Cr(VI) = 10 ppm, pH = 2, and T = 20 °C).

Fig. 11. Effect of TiO$_2$ NPs sorbent dose on the adsorption performance of Cr (VI) using PAN-CNT/TiO$_2$-NH$_2$ composite nanofibers. (Cr (VI) = 10 ppm, pH = 2, 40 min).

strates that PAN-CNT/TiO$_2$-NH$_2$ can be an effective adsorbent for toxic heavy metal removal.

References
