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Synthesis of eco-friendly Sp-EN-CPA adsorbent and its application for removal of Cr(VI) from aqueous solutions

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ABSTRACT

In this study, environmentally friendly Sp-EN-CPA was synthesized to effectively remove Cr(VI) ions from aqueous solutions and wastewater. The Sp (sporopollenin) was successfully modified with ethylenediamine (EN) compound. Finally, 1,8-bis(3-chloropropoxy) anthracene-9,10-dion (CPA) compound was immobilized on the modified sporopollenin (Sp-EN). The structural and chemical properties of the newly synthesized Sp-EN-CPA adsorbent were characterized by scanning electron microscopy and Fourier-transform infrared spectroscopy images. The impact of experimental parameters such as concentration, contact duration, and temperature, adsorbent amount, and pH on the removal of Cr(VI) ions in the wastewater and aqueous solution were researched. Some adsorption isotherms were used to interpret the formation of the reaction of Cr(VI) ions attachment to the adsorbent surface. The effective elimination (97%) of Cr(VI) ions using Sp-EN-CPA compound was performed at pH 2. The maximum amount of Sp-EN-CPA for the adsorption of Cr(VI) ions in the wastewater and aqueous solution was found to be 0.075 g. Adsorption remained stable after 150 min. The $\Delta H°$ values of Cr(VI) ions in aqueous solution and wastewater in the 25°C–50°C temperature range were found to be 18.82 and 26.18 kJ mol^{-1}, and $\Delta S°$ values were found to be 103.79 and 123.01 kJ mol^{-1}, respectively. The average adsorption energy for the Sp-EN-CPA adsorbent was found to be 26.73 kJ mol^{-1} for Cr(VI) ions in aqueous solution. Sp-EN-CPA exhibited an important achievement for the removal of Cr(VI) ions and can be suggested for the effectively elimination of Cr(VI) ions from the wastewaters.

Keywords: Sporopollenin; Cr(VI); Adsorption; Adsorption isotherms

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1. Introduction

World-wide water pollution has become a threat to the life of living things [1–3]. Heavy metals are the most lethal pollution because they are very toxic even in very small amounts [4–6]. For this reason, low-cost and highly efficient methods are needed to efficiently remove heavy metal ions from wastewater. Several separation and purification procedures have been developed, including ion exchange [7], electrodialysis, adsorption [8–11], ultrafiltration [12], chemical precipitation, reverse osmosis [13], photocatalyst [14], membrane, and phytoregulation etc. The adsorption and the photocatalytic reduction of organic pollutants and the sorption/reduction of heavy metal ions are generally considered as the main methods to decrease the concentration of pollutants in the natural environment [14,15]. It is vital to remove Cr(VI) ions from wastewater. Therefore, there are many studies and methods used in this field [16–18].

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Due to the high percentage of separation, simple use, and low cost, the adsorption method was selected as the most suitable process. Moreover, the technique of heavy metal removal by adsorption has advantages over other mechanical processes, it does not require external energy as a passive metabolic process [19,20]. Sporopollenin and silica based materials with many properties can be recommended for this purpose [21,22]. Also resins, activated carbon, clays, and biological materials [1] are used as adsorbent.

Chromium is one of the most dangerous heavy metal ions to the life of living things and has been identified as one of the top priority toxic pollutants by the US Environmental Protection Agency [23]. In aqueous environments, as a result of researches, chromium is mainly found in two forms, Cr(III) and Cr(VI) [24] Cr(III) is an important trace product in mammalian metabolism. However, Cr(III) metal ions in water can be adsorbed fairly easily on solids and can be found in sediments [25]. The Cr(VI), classified as heavy metal, is the most toxic and most mutagenic ion known in biological and environmental systems [26,27]. Cr(VI)-complexes are used in many industrial sectors such as metallurgy, chemistry, refractory materials and foundry industry, automotive, kitchen and bathroom metals [28–30]. The wastes containing Cr(VI) ions from these industrial sectors are discharged into water resources. Cr(VI) ions accumulating in the body at high doses causes various diseases such as Parkinson's disease, depression, speech disorders, high blood pressure, mood swings, memory loss, vascular occlusion, allergic reaction, Alzheimer's disease [31–33]. The World Health Organization (WHO) and US Environmental Protection Agency (USEPA) limitation of Cr(VI) ions in drinking water is 0.05 mg L^{-1} [34–38]. Therefore, it is very important to bring the amount of waste water containing Cr(VI) ions closer to these limit values. Sporopollenin is a natural biopolymer, whose chemical and molecular structures are, resistant to chemical substances, capable of high adsorption, suitable for modification of some groups, easy to obtain and cost-effective. The adsorbent synthesized in this study was used as the starting compound. Sporopollenin surface was modified with EN. The modified surface was immobilized with the compound CPA. The impact of experimental parameters such as pH, touch duration, adsorbent amount, concentration and temperature on the elimination of Cr(VI) ions were investigated. Isotherm and thermodynamics parameters related to the adsorption of Cr(VI) ions to Sp-EN-CPA adsorbent surface were investigated.

2. Materials and methods

2.1. Materials

Sporopollenin (particle size 20 μm) which is the starting material of the synthesized adsorbent was provided from Sigma-Aldrich product of Germany. Analytical grade dry toluene [39] (200 mL of toluene and 1.0 g of molecular sieves were added into a 250 mL flat bottom flask and it was kept closed for 24 h), methanol, ethanol (99%), sodium hydroxide, diethyl ether (99%), potassium dichromate, hydrochloric acid (37%), and ethylenediamine (EN) were procured from Merck in Germany. 1,8-bis(3-chloropropoxy) anthracene-9,10-dione (CPA) compound was used to immobilize the modified sporopollenin compound [40]. All chemicals used in the experimental studies were prepared with deionized water. Industrial wastewater sample (temperature: 318.15 K, pH = 2.0, concentration of sulfuric acid: 8.15 and 82.21 mg L^{-1} Cr(VI)) was obtained from chrome plating factory in Konya, Turkey.

2.2. Apparatus

The infrared spectra were measured in the 400–4,000 cm^{-1} range by a Perkin Elmer 100 Fourier-transform infrared spectrometer was produced in USA (KBr pellets, 21°C temperature, 39% moisture, 1 atm pressure). In addition, the morphology of Sp-EN-CPA was examined by scanning electron microscopy (SEM) (by applying 20 kV electron acceleration voltage). Cr(VI) ions quantities were measured by a UV-Vis. spectroscopy (Perkin Elmer, Lambda 25). pH values of Cr(VI) ions in aqueous solution and waste water were adjusted by adding NaOH and HCl and measured with a pH meter (Mettler Toledo Ion S220 digital). Thermostatic shaker, and ultrapure water device were also used in the experiments.

2.3. Synthesis of adsorbent (Sp-EN-CPA)

5 g of commercially available Sp was added to 150 mL of anhydrous toluene. 50 mL of ethylenediamine (1,2-diaminoethane) was added into the resulting mixture and stirred at reflux for 24 h [41]. The final product (Sp-EN) was filtered under vacuum for 1 h, washed 2 times with distilled water and 3 times with ethanol, then dried in a vacuum oven at 40°C for 4 h [42]. After drying was completed, Sp-EN was added to 1.5 g of CPA dissolved in 50 mL of ethanol. It was stirred under reflux for 12 h to form Sp-EN-CPA compound. The resulting product, Sp-EN-CPA adsorbent, was filtered on filter paper for 1 h and then washed with water and ethanol while filtering under vacuum. The adsorbent formed after washing was kept in a vacuum oven set at 60°C for adsorption studies [43]. The formation steps of the synthesis are shown in Fig.1.

2.4. Adsorption studies

Adsorption studies to be made with the obtained Sp-EN-CPA adsorbent were carried out using the well-known batch method, which is very common in the literature. To prepare the Cr(VI) ions stock solution used for adsorption experiments, 0.0294 g potassium dichromate ($K_2Cr_2O_7$) was taken and placed in a one liter flask. It was completed with pure water. The concentration of the obtained stock solution was 1×10^{-4} M. In pH and other parameter studies, the pH of the medium was adjusted with 0.1 M hydrochloric acid and sodium hydroxide solutions. Stock solution and wastewater experiments were carried out under the same conditions. To determine the parameters affecting the adsorption such as pH (2–7), concentration (8–40 mg L^{-1}), amount of Sp-EN-CPA adsorbent (0.010, 0.015, 0.025, 0.050, and 0.75 g), temperature (20°C–50°C), and time of interaction (30–180 min.) were performed with both wastewater and stock solution [44]. The concentration of Cr(VI) ions left in the solution without adsorption was measured by an ultraviolet visible

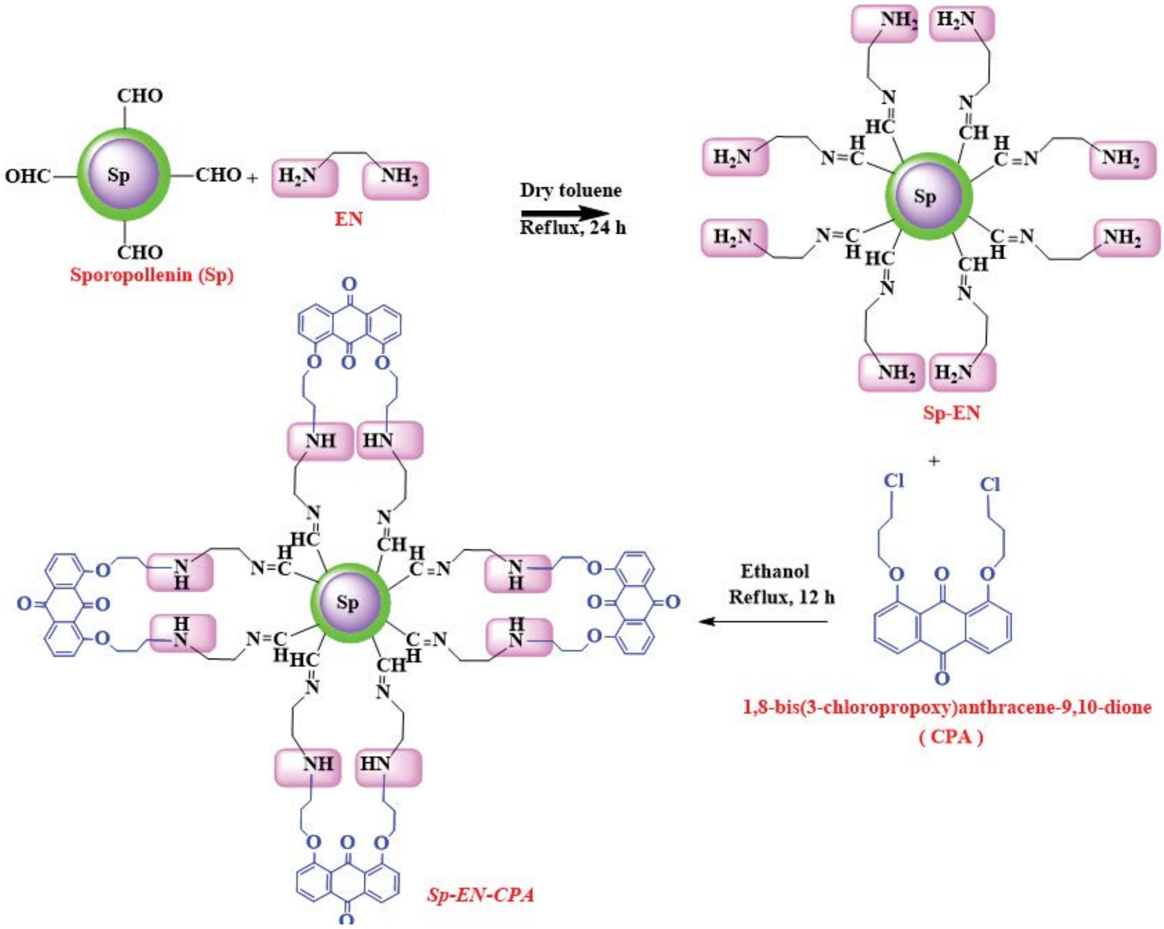

Fig. 1. The probable structures of Sp, Sp-EN and Sp-EN-CPA.

(UV-Vis) spectrophotometer. The most appropriate experiment conditions were determined by evaluating the data obtained from these experiments. The adsorption (%) was calculated according to Eq. (1):

$$\text{Adsorption\%} = \frac{\left(C_0 - C_e\right)}{C_0} \times 100 \tag{1}$$

where C_e: concentration of substance remaining from adsorption in solution (mg L^{-1}), and C_0: the solution initially concentration (mg L^{-1}). The adsorption coefficient (q_e in mg g^{-1}) is seen in Eq. (2) [45,46].

$$q_e = \frac{\left(C_0 - C_e\right)V}{W} \tag{2}$$

where C_e: concentration of substance remaining from adsorption in solution (mg L^{-1}), W: the dry weight (g) of adsorbent, V: the volume (L) of aqueous phase, and C_0: the solution initially concentration (mg L^{-1}) [47,48].

2.5. Environmental wastewater samples

Examples of chromium-containing wastewater was obtained from chrome plating factory in Konya, Turkey

3. Results and discussion

3.1. Characterization

3.1.1. Morphological and constructional studies

Adsorption is a surface event and the size of the adsorption is proportional to the specific surface area. Therefore, it is desirable that the adsorbent has a large surface area, pore volume, a specific pore distribution, and a particulate structure [49,50]. The pure Sp, Sp-EN and Sp-EN-CPA adsorbent surface was studied using SEM and in Fig. 2 SEM images are given. The SEM images of the pure Sp (Fig. 2a) show a much more uniform morphology than those of the Sp-EN (Fig. 2b) formed after the immobilization of the EN to the pure Sp surface. According to the modified sporopollenin (Sp-EN), the pore shapes and geometrical structures of the Sp-EN-CPA adsorbent deteriorate can be seen Fig. 2c. These images confirm that there is a modification of the EN on the Sp surface and the Sp-EN-CPA adsorbent is formed as a result of immobilization of the CPA compound to the surface of the Sp-EN solid support.

3.1.2. Fourier-transform infrared spectroscopy investigations

The Fourier-transform infrared (FTIR) spectra of Sp, Sp-EN and Sp-EN-CPA are shown in Fig.3. In the FTIR

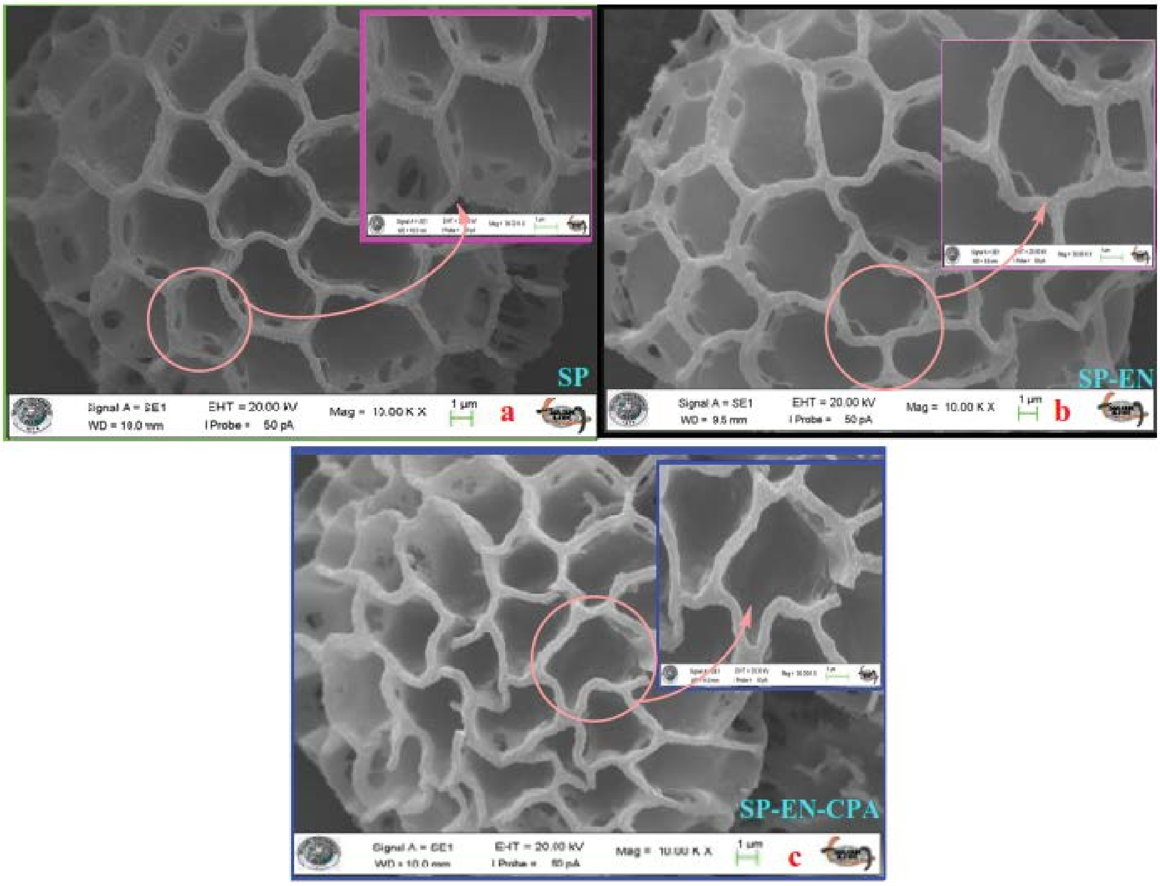

Fig. 2. SEM images of (a) pure Sp, (b) Sp-EN and (c) Sp-EN-CPA.

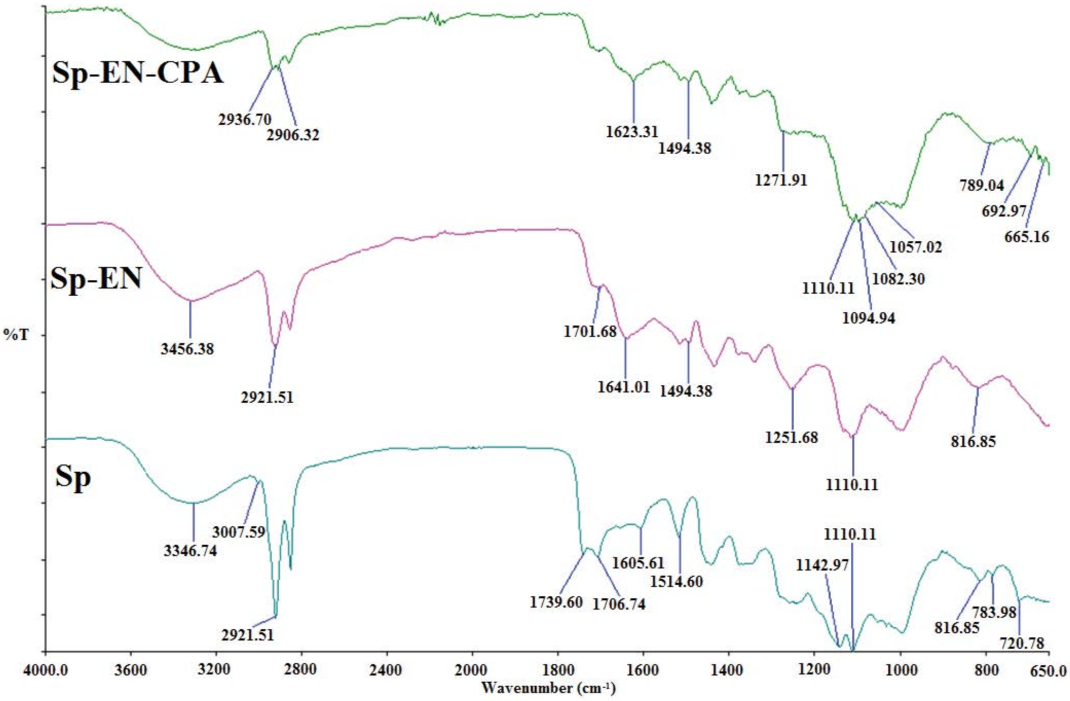

Fig. 3. FTIR spectra of activated pure Sp, Sp-EN and Sp-EN-CPA.

spectrum of Sp, the stress vibration frequency of the –OH group is 3,346 cm^{-1}, [51] Sp-EN-CPA adsorbent the stress vibration frequency of the aliphatic (–CH, –CH$_2$, –CH$_3$) group is between 2,850–2,921 cm^{-1} in the form of double bands [52], and the characteristic bands belonging to the carbonyl (C=O) group were observed as 1,739 cm^{-1} [8].

After the modification of EN on the surface of Sp, the stress vibration frequency of the –OH group in Sp shifted from 3,346 to 3,456 cm^{-1} in Sp-EN. Aliphatic –CH stress vibration frequencies in the structure of Sp-EN were observed between 2,861 and 2,921 cm^{-1}. The vibration frequency of –C=N in the structure of the newly synthesized Sp-EN compound was observed at 1,641cm^{-1}. In addition, the carbonyl peak observed at 1,739 cm^{-1} in Sp disappeared in Sp-EN compound.

The stress vibration frequency of the –OH group in Sp-EN shifted from 3,456 to 3,332 cm^{-1} in the Sp-EN-CPA. The –C–N vibration in the structure of Sp-EN-CPA was appeared at 1,271 cm^{-1}. –C=N vibration in Sp-EN structure shifted from 1,641 to 1,623 cm^{-1} in Sp-EN-CPA. Peaks observed in CPA and Sp-EN structures in the range of 2,936–2,840 cm^{-1} appear as three different peaks in the Sp-EN-CPA structure. This indicates the presence of different CH, CH$_2$ or CH$_3$ groups in the structure, which confirms that the CPA compound is immobilized to the Sp-EN surface.

3.2. Adsorption studies

3.2.1. Effect of pH on Cr(VI) removal.

pH is one of the most important parameters controlling adsorption efficiency (adsorption capacity). The adsorption efficiency of Cr(VI) ions can be affected by various charge density and Cr(VI) solution on the Sp-EN-CPA adsorbent surface. Therefore, various experiments have been carried out using the Batch method to find the capacity of the adsorbent with different amine groups to absorb Cr(VI) solutions at different pH (1–7) ranges. According to the results found from the experiments, the effect of pH on Cr(VI) adsorption is shown in Fig. 4a. As seen in Fig 4a, the removal efficiency of Cr(VI) in the wastewater and the aqueous solution on Sp-EN-CPA adsorbent surface is maximum at pH = 2.0 [53,54], then, at pH 3.0 to 4.0, decreases quite rapidly, while it decreases slightly between 5 and 6, and at pH 7.0 the adsorption is minimized, so that the adsorption capacity of Sp-EN-CPA adsorbent was 36.17 mg g^{-1} pH 2 that reduced to 8.94 at pH 7. The Cr(VI) is found in diverse ionic species such as $HCrO_4^-$, $Cr_2O_7^-$, and CrO_4^{2-}. Stability of these ions is depend on the total $Cr_2O_7^-$ concentration and pH of the solution. Thus, high adsorption efficiency or high adsorption capacity at low pH emerged [8].

In addition, while the Cr(VI) removal was 97% at pH 2, it decreased to 20% at pH 7 (Fig. 4). As the pH increases, the positive charges on the adsorbent surface decreases. Thus, electrostatic attraction occurs between the negative charges (NH_2^-, OH^-) and the positive charges of metal ions (Cr(VI) in the adsorbent and the adsorption efficiency increases [55].

3.2.2. Effect of contact time on Cr(VI) removal

To order to create a low cost and high yield wastewater treatment system, the balance period must be determined according to the maximum adsorption of Cr(VI) ions. Removal levels of Cr(VI) ions by the Sp-EN-CPA adsorbent increased fairly rapidly within the first 60 min (Fig. 4b) and achieved cleaning efficiencies over 32% for Cr(VI) ions in wastewater and 44% for Cr(VI) ions aqueous solution. Then, as seen in the graph, the Cr(VI) ions removal efficiency in both wastewater and aqueous solution gradually increases as time progresses and; then slows down after saturation occurs. As a result, both Sp-EN-CPA+Cr(VI) (%R ~ 97%) in aqueous solution and Sp-EN-CPA+Cr(VI) (%R ~ 50%) in wastewater reached saturation at around 150 min.

3.2.3. Effect of Sp-EN-CPA amount on Cr(VI) removal

The amount of Cr(wastewater) and Cr(VI) ions adsorbed on Sp-EN-CPA was calculated by using Eq. (1). Fig. 4c shows the graph of the Sp-EN-CPA amount against adsorption of Cr(wastewater) and Cr(VI) ions. With the increase in the amount of Sp-EN-CPA, the total amount of adsorbed Cr(VI) ions increases (Fig. 4c). The maximum amount of Sp-EN-CPA for the adsorption of Cr(VI) ions in the wastewater and aqueous solution was found to be 0.075 g. These results can be explained by the increased adsorption of Cr(VI) ions due to the increased active surface area of the Sp-EN-CPA adsorbent.

3.2.4. Effect of concentration on Cr(VI) removal

As shown in Fig. 4d, it shows that the adsorption of Cr(VI) ions in the wastewater and aqueous solution to the Sp-EN-CPA surface depends on the concentration of metal ion. As can be seen from the graph, with increasing the amount of metal ions in the solution, the amount of substance obtained on the Sp-EN-CPA surface has increased in parallel. This process continues until the system reaches equilibrium and until the surface area is full.

3.2.5. Effect of temperature on Cr(VI) removal

The results of the impact of temperature on the adsorption study are given in Fig. 4e. As seen in Fig. 4e, parallel to the increase in temperature, the amount of chromium adsorbed onto the Sp-EN-CPA surface appears to increase. According to structure of Sp-EN-CPA adsorbent, the thermodynamic parameters changed with increasing temperature.

3.3. Isotherm studies

Dubinin–Radushkevich, Temkin, Langmuir, and Freundlich isotherm parameters were calculated using data derived from the experimental results. The parameters Langmuir isotherm which express the balance dispersion between liquid and solid phases of metal ions, were calculated with the help of Eq. (3).

$$\frac{C_e}{q_e} = \frac{C_e}{q_0} + \frac{1}{bq_0} \tag{3}$$

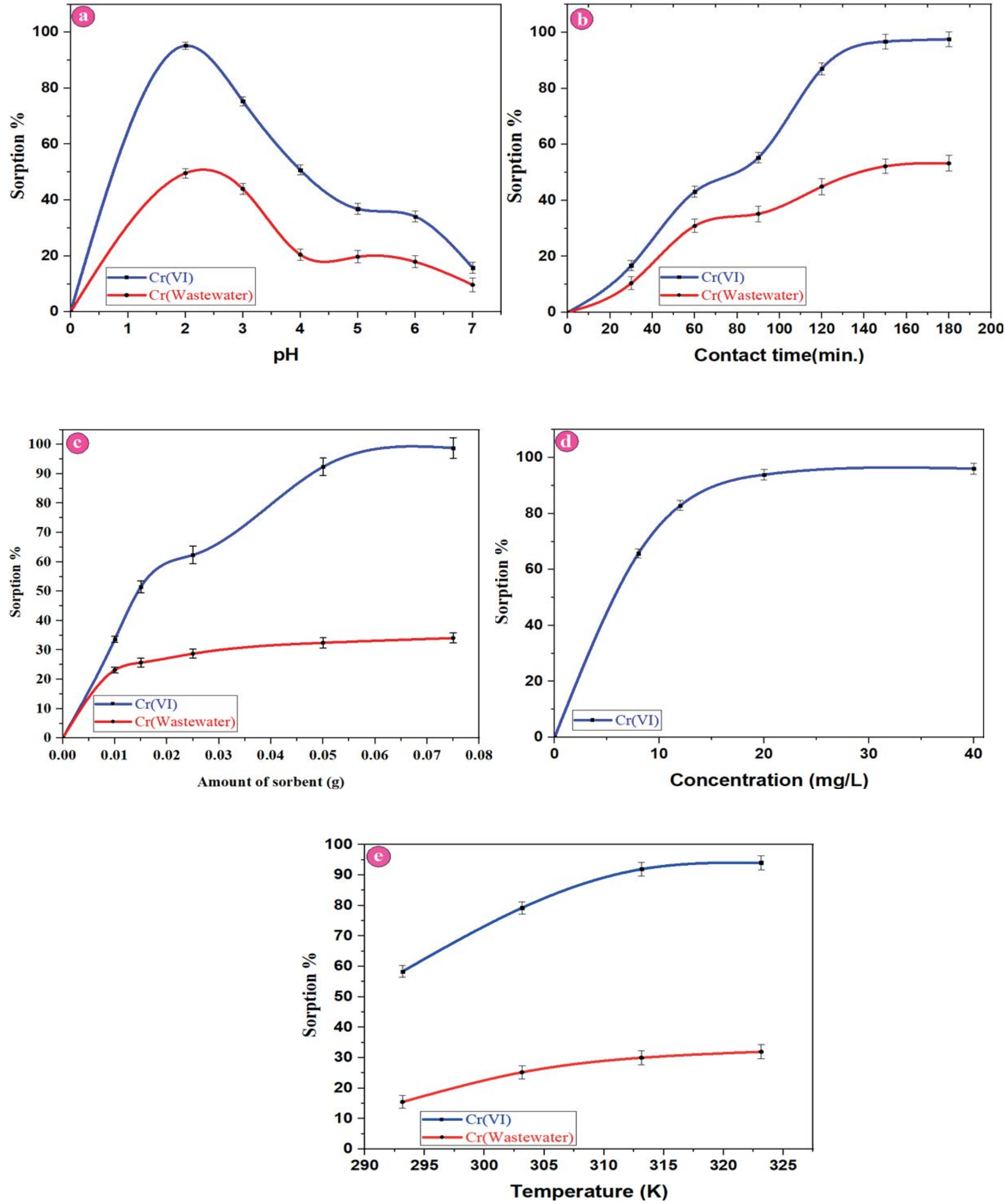

Fig. 4. The impact of pH on the adsorption of Cr(VI) ions in the wastewater and aqueous solution (a). The impact of the contact time on the adsorption of Cr(VI) ions in the wastewater and aqueous solution (b). The impact of the amount of Cr(VI) ions in the wastewater and aqueous solution (c). The adsorption impact dependence on concentration of Cr(VI) ions in aqueous solution (d). The impact of temperature on the adsorption of Cr(VI) ions in the wastewater and aqueous solution (e).

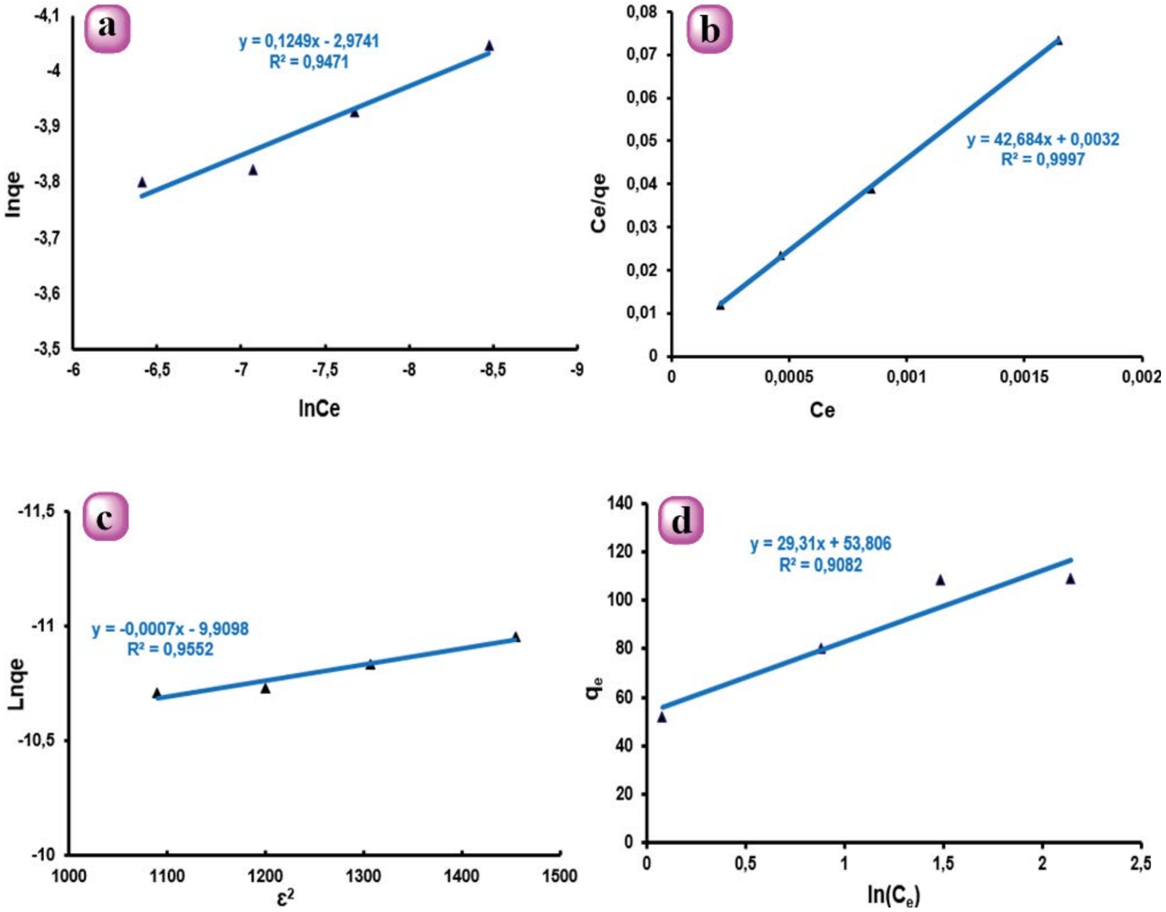

Fig. 5. Langmuir isotherm (a), Freundlich isotherm (b), Dubinin–Radushkevich isotherm (c) and Temkin isotherm (d).

where q_0 is maximum adsorption capacity (mmol g^{-1}), b is the Langmuir adsorption constant (mol L^{-1}), C_e is the equilibrium (remaining from adsorption) Cr(VI) ion concentration in Cr(VI) solution (mol L^{-1}), q_e is the amount of metal ions on the adsorbent surface (equilibrium adsorption capacity (mmol g^{-1}) [56, 57].

In the Langmuir isotherm graph (Fig. 5a), the slope of the line gives the value of $1/q_0b$ and the point where the line intersects the y-axis gives $1/q_0$ value. Freundlich isotherm was developed for the adsorption of heterogeneous surfaces [47]. It is shown in Eq. (4).

$$\ln q_e = \ln K_F + \frac{1}{n}\ln C_e \tag{4}$$

where K_F is the Freundlich constant [58]. q_e and C_e are explained in Langmuir isotherm equation.

According to Eq. (4), the graph of lnq_e vs. lnC_e gives a straight line, and the K_F value can be calculated from the intersection point of this straight line and the n value is the slope [47,59,60]. Sp-EN-CPA valuations of $1/n$ are <1, which indicates a high adsorption density [59]. K_F values show that the Sp-EN-CPA adsorbent in aqueous solution and wastewater has a very high adsorption capacity for Cr(VI) ions [61]. $n > 1$ values symbolize sufficient conditions for adsorption [62]. n and K_F values were calculated by the intercept and slope of the graph shown in Fig. 5b. The data obtained as a result of the calculations are shown in Table 1. Dubinin–Radushkevich isotherm was used to calculate the adsorption energy. The calculations were made with Eq. (5) [63].

$$\ln q_e = \ln q_m - k\varepsilon^2 \tag{5}$$

Table 1
Isotherms parameters for Cr(VI) ions by Sp-EN-CPA

Model	Constant	Value
Langmuir	q_0 (L mol^{-1})	0.023
	b (mol^2 (kJ^2)$^{-1}$)	14,067.96
	R^2	0.9471
Freundlich	$1/n$	0.1249
	K_F	0.050
	R^2	0.9997
Dubinin–Radushkevich	K (mol^2 K^{-1} J^{-1})	0.0007
	q_m (mol g^{-1})	0.048
	E (kJ mol^{-1})	26.73
Temkin	A	7.8325
	B (J mol^{-1})	0.3719
	R^2	0.9082

where ε is Polanyi potential, q_e is the amount of substance adsorbed onto the adsorbent surface (mol g^{-1}), k denotes the energy constant of adsorption (mol^2 (kJ^2)$^{-1}$), q_m is the adsorption capability (mol g^{-1}).

Therefore, by plotting lnq_e vs. ε^2, it is to create the value of q_m from the intercept and the value of k from the slope (Fig. 5c). The measured mean free energy factor (E) using Eq. (6) and Dubinin–Radushkevich isotherm data are shown in Table 1.

$$E = \left(2k\right)^{-1/2} \tag{6}$$

As a result of the experimental studies, the mean energy for Cr(VI) ions in aqueous solution was found to be 26.73 kJ mol^{-1} (Table 1). The adsorption of Cr(VI) ions in the aqueous solution to the surface of the Sp-EN-CPA adsorbent shows that it occurs by chemical adsorption. Average energy data confirm chemisorption [64].

Temkin isotherm has been researched to guess the influence of the adsorbent–adsorbate interaction on the adsorption mechanism and is defined by the regular distribution of binding energies [65, 66]. This model's principle notes that there is a linear association between adsorbent surface coverage and the molecules' adsorption heat, neglecting both very low and high concentrations [67]. The Temkin equation is given by Eq. (7):

$$q_e = \frac{RT}{b}\ln C_e + \frac{RT}{b}\ln \tag{7}$$

where T is temperature (Kelvin), A is Temkin isotherm constant (L g^{-1}), R is universal gas constant and B = (RT/b) is constant related to heat of sorption (J mol^{-1}) [66]. The Temkin linearity was obtained from plots of (lnC_e vs. q_e). Within the Eq. (7), the q_e vs. lnC_e the graph gives a straight line (Temkin linearity), and the A value can be determined from the intersection point of this straight line and the b value is the slope (Fig. 5d). The data obtained as a result of the calculations are shown in Table 1.

Table 1 shows the isotherm graphs of Temkin, Freundlich, Dubinin–Radushkevich and Langmuir plotted using the values calculated with the adsorption isotherm formulas and the adsorption parameters obtained from these graphs. As seen in Table 1, the isotherm with the highest R^2 (0.9997) value is the Freundlich isotherm. Therefore, the adsorption of Cr(VI) on Sp-EN-CPA can be explained by the Freundlich isotherm. Thus, the Freundlich isotherm model shows that the adsorption sites on Sp-EN-CPA have good affinity for Cr(VI) ions and adsorption takes place in multiple layers on the adsorbent surface.

3.4. Thermodynamic studies

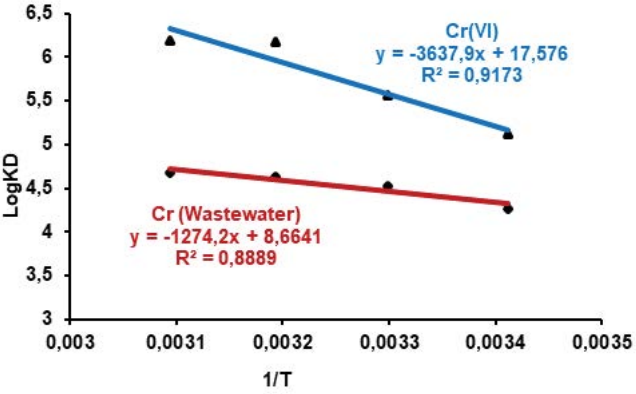

Fig. 6. Plots of 1/T vs. logK_D for Cr(wastewater) and Cr(VI) removal by Sp-EN-CPA.

The thermodynamic factors [68] such as enthalpy change ($\Delta H°$), free energy change ($\Delta G°$), and entropy change ($\Delta S°$) are crucial for explaining the adsorption event and should be considered to determine the spontaneity of a process. While the adsorption of Cr(VI) ions on modified sporopollenin (Sp-EN-CPA) was carried out, the effect of temperature (20°C–50°C) was investigated. Thermodynamic parameters were calculated from Eqs. (8)–(10).

$$K_D = \left(\frac{C_0 - C_e}{C_e}\right)\frac{V}{W} \tag{8}$$

$$\log K_D = \frac{\Delta S°}{2.303R} - \frac{\Delta H°}{2.303RT} \tag{9}$$

$$\Delta G° = \Delta H° - \Delta S° \tag{10}$$

where W is the adsorbent's dry weight (g), $\Delta G°$ is the change in Gibbs free energy (kJ mol^{-1}), the absolute temperature is T (K), R is the gas constant, V is the aqueous-phase volume (mL), K_D is the adsorption balance constant, $\Delta H°$ is the change in enthalpy (kJ mol^{-1}), and $\Delta S°$ is the change in entropy (J mol^{-1} K^{-1}) [64].

The $\Delta H°$ and $\Delta S°$ values for the adsorption of Cr(VI) ions on Sp-EN-CPA adsorbent surface were evaluated by the Van't Hoff plots: 1/T vs. logK_D. In addition, $\Delta G°$ values were calculated using Eq. (8). They are given in Table 2 [47, 69]. 1/T vs. the logarithmic distribution coefficient (K_D) graph has been drawn (Fig. 6).

Table 2
$\Delta H°$, $\Delta S°$, and $\Delta G°$ parameters for the adsorption of Cr(VI) in wastewater and aqueous solution for Sp-EN-CPA adsorbent

Metal	$\Delta H°$ (kJ mol^{-1})	$\Delta S°$ (JK^{-1} mol^{-1})	$-\Delta G°$ (kJ mol^{-1})			
			297	303	313	323
Cr(VI)	18.82	103.79	11.61	12.26	13.06	13.58
Cr(Wastewater)	26.18	123.01	9.88	10.27	11.41	11.91

Table 3
Adsorption capacity and adsorptive equilibrium time of different adsorbent materials for adsorption of Cr(VI) in aqueous solution and wastewater

Adsorbents	pH	Results	References
Sp-EN-CPA	2.0	Removal efficiency: 97%; q_m: 36.17 mg g^{-1}	This work
Sp Calix	1.5	q_m: 28.07 mg g^{-1}	[71]
Activated carbon	2.0	Removal efficiency: 93.48%	[72]
ZFC	2.0	Reduction efficiency: 84.7%	[54]
AMGO	2.0	q_m: 123.4 mg g^{-1}	[73]
MS-HMS-PL	4.0	q_m: 257.67 mg g^{-1}	[74]
Titania nanotubes	1.0–2.0	Removal efficiency: 98.5%	[75]
CH@*n*Fe^0	2.0–3.0	Removal efficiency: 90.91%	[76]
Chitosan nanoparticles	3.0	q_m: 55.80 mg g^{-1}	[77]
PANI/SiO_2 composite	2.0–4.0	q_m: 63.41 mg g^{-1}	[78]
GAFP aerogel	2.0	q_m: 170.64 mg g^{-1}	[79]
TiO_2	4.0	Removal efficiency: 79.0%	[80]
chitosan-g-PMMA/silica BNC	4.0	Removal efficiency: 98.00%	[81]
MI-Cl-KCC-1	3.0–4.0	q_m: 428 ± 8 mg g^{-1}	[82]
Fe_3O_4/SiO_2/CS-TETA	2.5	q_m: 254.6 mg g^{-1}	[83]

As shown in Table 2, $\Delta H°$ is positive. These positive results state that the adsorption is endothermic and negative values of $\Delta G°$ state that the adsorption reaction is spontaneous. Gibbs free energy ($\Delta G°$) values decreased with the increase in temperature. In other words, adsorption formation is inversely commensurate to temperature. The positive (+) value of entropy change ($\Delta S°$) expresses the increase in random adsorption in solid-solution interface. This also indicates that ion exchange reactions have been formed. The Cr(VI) ions coordinated with the water molecules in the solution, and water molecules were bound to the adsorbent by the formation of covalent bonds. Thanks to the released water molecules, the degree of randomness, the type of binding mechanism and the adsorption energy of the respective binding (physical and/or chemical) increases the magnitude of $\Delta H°$. The process is rapid and generally reversible owing to the small energy necessity in physical adsorption. The energy necessity for the hydrogen bond formation is 4–8 kJ mol^{-1} while the energy necessary for the London and Van der Waals interactions is 8–40 kJ mol^{-1}. Unlike, the enthalpy associated with chemical adsorption accepted as the transition limit between the physical and chemical adsorption processes was about 40 kJ mol^{-1} [70]. The $\Delta H°$ values of Cr(VI) heavy-metal ions in aqueous solution and wastewater in the 25°C–50°C temperature range were found to be 18.82 and 26.18 kJ mol^{-1}, respectively.

3.5. Comparison studies

The Sp-EN-CPA adsorbent that we have new synthesized was compared with sporopollenin supported and different adsorbent materials reported in the literature (Table 3). In the comparison process (Table 3), the pH and maximum adsorption capacity (removal efficiency) values of the Cr(VI) ions of different adsorbent supported materials were compared with the newly synthesized Sp-EN-CPA adsorbent. As can be seen in Table 3, it is seen that the adsorption capacity of Sp-EN-CPA adsorbent is quite good compared to other adsorbent materials. In other words, it can be said that the newly synthesized Sp-EN-CPA adsorbent adsorbs Cr(VI) ions very well. As for pH, the adsorption of the newly synthesized Sp-EN-CPA adsorbent with Cr(VI) ions takes place in an acidic environment (usually pH range: 2–4) and experimental studies are acidic, that is, pH: 2. As a result, the newly synthesized Sp-EN-CPA adsorbent has better adsorption performance of Cr(VI) ions compared to other adsorbents, and is also a great adsorbent that is safe, environmentally friendly, low cost and easy to prepare.

3.6. Mechanism

The pH of the aqueous solution influences Cr speciation (the formation of new and distinct species) and the dissociation of active functional groups (–OH, –COOH, –NH_2). Fore this reason, Cr adsorption is critically related to the solution pH. The presence of hydroxyl groups in the Sp-EN-CPA adsorbent was confirmed by FTIR [46]. In addition, there are C=O [8] and NH_2 groups in the structure of the adsorbent. At low pH, the functional groups in the surface of Sp-EN-CPA are protonated and restrict the approach of cationic species as the result of repulsive forces. Functional groups on the surface of Sp-EN-CPA are prototonated at low pH and the effect of repulsive forces restricts the approach of cationic species. As the pH increases, the degree of protonation decreases, and the functional groups become negatively charged (pH > pKa). The Cr(VI) is found in diverse ionic species such as $HCrO_4^-$, $Cr_2O_7^-$, and CrO_4^{2-}. Stability of these ions is depend on the total $Cr_2O_7^-$ concentration and pH of the solution [84]. These anionic species can be adsorbed to the protonated active sites of the Sp-EN-CPA adsorbent [85]. The following equilibria can be written for the Cr(VI) anions in aqueous solution [85];

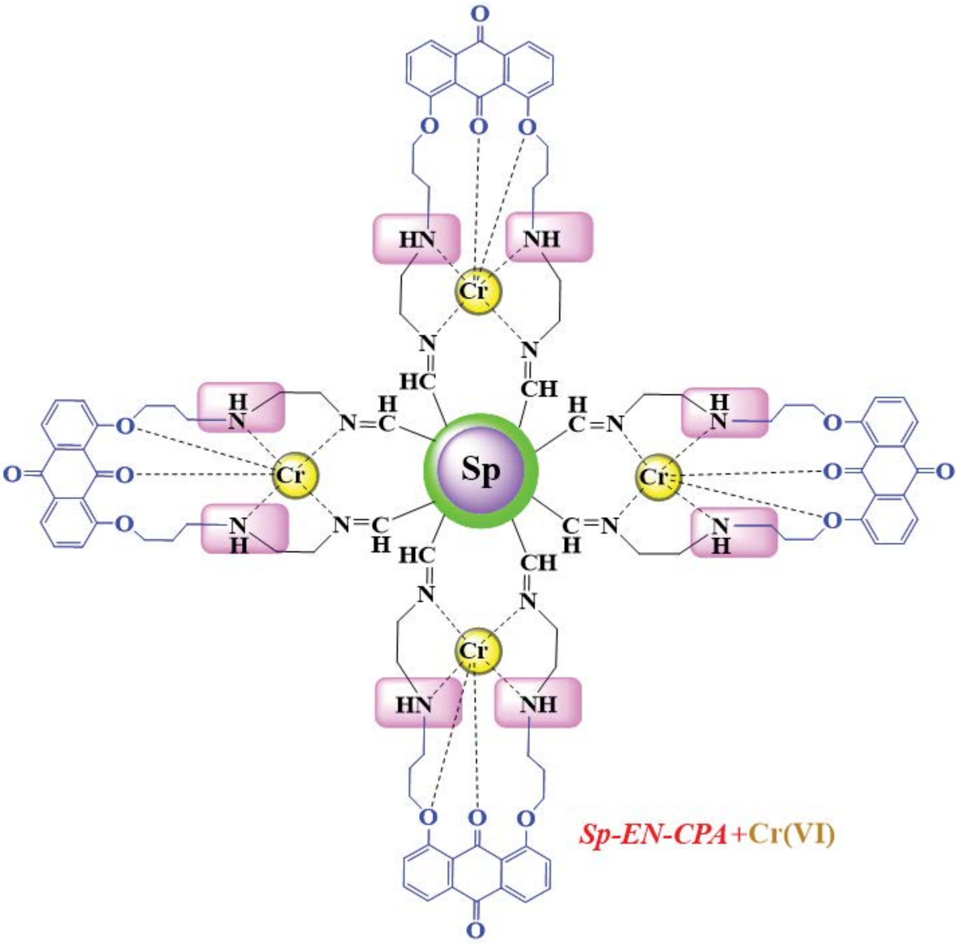

Fig. 7. Estimated structure of Sp-EN-CPA+Cr(VI).

$$H_2CrO_4 \leftrightarrow HCrO_4^- + H^+ \qquad k_1 = 1.21 \tag{11}$$

$$Cr_2O_7^{2-} + H_2O \leftrightarrow 2HCrO_4^- \qquad k_2 = 35.5 \tag{12}$$

$$HCrO_4^- \leftrightarrow CrO_4^{2-} + H^+ \qquad k_3 = 3 \times 10^{-7} \tag{13}$$

There is no significant adsorption for Cr(VI) at pH values above 6.0 due to the competition of CrO_4^-, $Cr_2O_7^{2-}$ and OH^- anions for the adsorption area.

The adsorption reaction of Cr(VI) ions on the adsorbent surface can be described as mechanism of an ion exchange. The chelating effect of the functional group of the organic compound CPA on Sp-EN-CPA is also thought to be involved in the adsorption system, and Cr(VI) heavy metal ions are thought to be attached. It can be said that Sp-EN-CPA surface (EN) donors nitrogens and CPA organic compound groups coordinate by chemisorption of heavy metal ions [86]. The appearance of the adsorption mechanism of Cr(VI) ions on the Sp-EN-CPA adsorbent surface can be predicted in Fig. 7.

4. Conclusion

The sporopollenin-ethylenediamine (Sp-EN) functionalized 1,8-bis(3-chloropropoxy) anthracene-9,10-dione (CPA) was successfully synthesized and each step was characterized by FTIR and SEM. It has been used as a promising Sp-EN-CPA adsorbent to remove Cr(VI) ions in wastewater and aqueous solutions. Adsorption experimental data fitted well with Freundlich isotherm. The effective elimination of Cr(VI) ions using Sp-EN-CPA adsorbent was performed at pH 2. The average adsorption energy for the Sp-EN-CPA adsorbent was found to be 26.73 kJ mol^{-1} for Cr(VI) ions in aqueous solution. These results demonstrate that the reaction on the adsorbent has formed chemically. Thermodynamic study parameters ($\Delta H°$ = + and $\Delta G°$ = –) showed that the adsorption reactions are endothermic and spontaneous process, respectively. The positive value ($\Delta S°$ = +) of the entropy change, one of the thermodynamic parameters, indicates that the adsorbate system becomes more random at the Sp-EN-CPA/Cr(VI) solution interfaces. Overall, it shows the conclusion that the proposed adsorption method is efficient and practical for the removal of Cr(VI) ions from wastewater and aqueous solutions, largely with the advantages of being practical, inexpensive and obtainable.

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