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Removal of Cr(III) from Water Solutions and Wastewater Using Immobilized Sporopollenin by 1,8-dihydroxyanthracene-9,10-dione

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Abstract
It is advantageous to use solid support adsorbents such as sporopollenin to remove heavy metals from aqueous solutions. In this paper, the compound of 3-chloropropyl)trimethoxysilane was first modified on the surface of a sporopollen, which showed great resistance to excellent mechanical properties and chemical and biological attack.Afterwards, 1,8-dihydroxyanthracene-9,10-dione (Danthron) compound was immobilized on the surface of the modified sporopolenin (Sp-CPTS) and a new adsorbent material SP-CPTS-Danthron was obtained. Our new adsorbent material (SP-CPTS-Danthron) was characterized by Fourier transform infrared spectroscopyandScanning Electron Microscopy. Various factors such as pH, temperature and initial concentration, contact time were investigated for sorption of Cr(III) metal ions inaqueous solution and wastewater to the surface of SP-CPTS-Danthron adsorbent. Freundlich, D-R (Dubinin-Radushkevich) and Langmuir adsorption isotherms calculatedfrom the experimental results.Dubinin-Radushkevich isotherm with high R^2 value revealed that Cr(III) adsorption in Sp-CPTS-Danthron adsorbent followed the mechanism of chemisorption. Experimental results of thermodynamic parameters such as enthalpy, entropy and free energy were investigated and the data obtained were used to explain the sorption mechanism.The results showed that this Sp-CPTS-Danthron adsorbent was successfully used to separate Cr(III)metal ions from aqueous solutions and wastewaters.

Keywords: Sporopollenin, Danthron, Thermodynamic, Adsorption isotherm,

INTRODUCTION

Chromium is a useful element for the industry, for example in leather tanning, wood processing, pigments, paints, textile dyes, inks, chemicals, catalysts and metal corrosion inhibitors as a component [1-2]. Chromium may occur in various oxidation states from 2+ to 6+, but only the 3+ and 6+ forms are stable in the environment [2-3-4]. The trivalent chromium is considered to be 500 to 1000 times less toxic than hexavalent chromium [5-6]. Cr(VI) metal ions are known as a highly potent oxidizing agent against plants and animals and are also known as a potential carcinogen[6-7]. The chromium (III) metal ionsare usually only toxic to plants at very high concentrations and are less toxic or non-toxic to animals [6]. While the presence of chromium (VI) metal ions in the environment comes mostly from industrial activities, Cr(III) metal ionsare naturally predominant in the environment, especially in acidic conditions [8]. Cr(III) metal ions can be considered as trace elements for the proper functioning of living organisms (mammals) e.g. for the maintenance “glucose tolerance factor “; It is thought that there is a cofactor for insulin action and that it plays a role in the peripheral reaction activity of this hormone [9]. Although Cr(VI) metal ions are more toxic [10], continued exposure to Cr(III) metal ions causes allergic reactions in the skin [11] and may cause serious structural defects in the membrane of human erythrocytes [12-13].

The main methods used in the treatment of wastewater containing Cr(III)metal ions include adsorption, ionic exchange, reverse osmosis, biosorption and reductive-chemical precipitation.In particular, adsorption can be used as a promising technology to process large volumes of dilute solutions [14]. The main advantages of the adsorption method are its efficacy, ease of use, a wide range of adsorbent materials and the possibility of regeneration in the removal of species in liquid solutions [14]. Depending on the material used as the adsorbent, the adsorption method can be a very common and low-cost technology for the treatment of industrial wastes [15].

In the present study, Sp-CPTS-Danthron adsorbent which is effective and inexpensive to remove Cr(III) metal ions from industrial wastes and aqueous solutions was prepared.Five different absorptions were performed to determine the adsorption ability of the adsorbent and then adsorption isotherms and thermodynamic calculations were made.

MATERIALS AND METHODS

The preparation of sporopolenin from Lycopodium Clavatum spores was done as indicated in the literature [16]. 10 g of Lycopodium Clavatum in 75 mL of acetone stirred under reflux for 4h [16-17]. The oil extracted spores were collected by filtration [16]. The obtained Lycopodium Clavatum was treated with 2.0 M of 100 mL potassium hydroxide for 24 hours with stirring at room temperature. The brown powder (sporopollenin) obtained was then washed with water (5x50 mL), ethanol and finally 50 mL of ether.

The modification of CPTS ((3-chloropropyl) trimethoxysilane) onto Lycopodium Clavatum sporopollenin was performed as follows: 15.0 g of sporopollenin and 100 mL of dry toluene were stirred and 9 mL of CPTS was added to the resulting suspension [18]. The suspension was then filtered and the obtained solid 3-chloropropyltrimethoxysilane-sporopollenin (Sp-CPTS) compound was kept in a vacuum oven set at 60 °C for 24 hours. 15.0 g of 3-chloropropyltrimethoxysilane-sporopollenine (Sp-CPTS) were added to 100 mL of dry (anhydrous) toluene and to which 10.0 g of 1,8-dihydroxyanthracene-9,10-dione (Danthron) were added. The mixture was then stirred under reflux for 15 hours. The possible structure of the resulting Sp-CPTS-Danthron compound is shown in Figure 1.

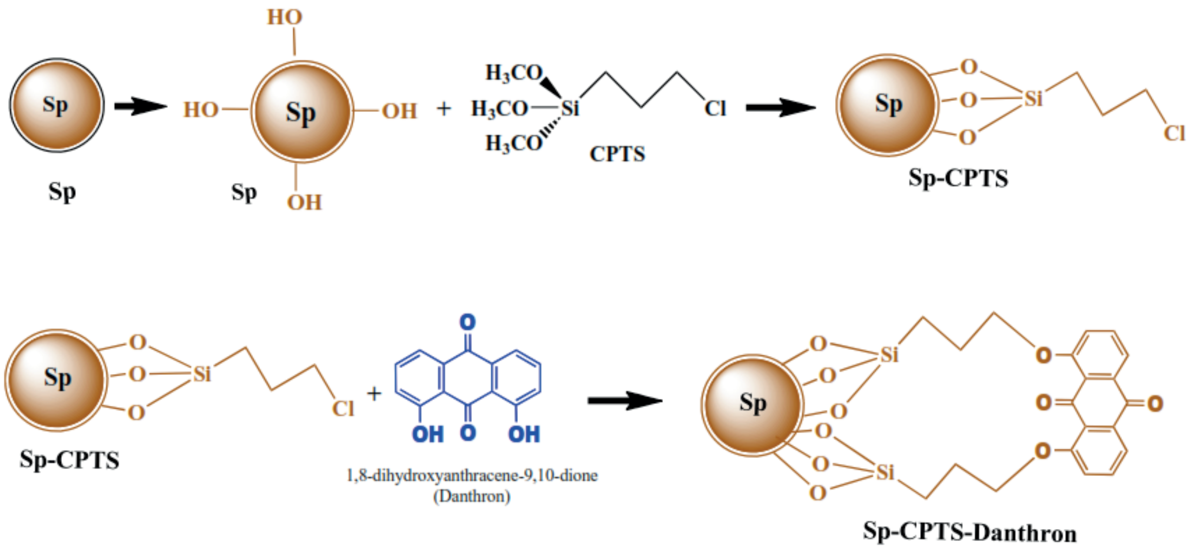


Figure 1. The possible structure of the resulting Sp-CPTS-Danthron compound

Preparation of Solutions Used in Adsorption Studies

Sodium hydroxide (NaOH) and hydrochloric acid (HCl) solutions of 0.1 M were used to adjust the pH of the solutions. Chromium (III) metal ion stock solutions were used with 1.0 x10^{-3} M chromium nitrate ($K(NO_3)_3$).

RESULT AND DISCUSSION

SEM Characterization of Sp-CPTS-Danthron Adsorbent

SEM images of the compounds of sporopollenin and modified sporopollenin (Sp-CPTS-Danthron) are shown in Figure 2.In the SEM images, the structure of the sporopollene was completely altered and distributed regularly to the surface of the super-macro-porous Danthron Sp of the sporopollenin modified with 1,8-dihydroxyanthracene-9,10-dione (Danthron).This change in the surface of sporopollenin shows us that different molecules are placed on the surface, that is, the surface is modified.

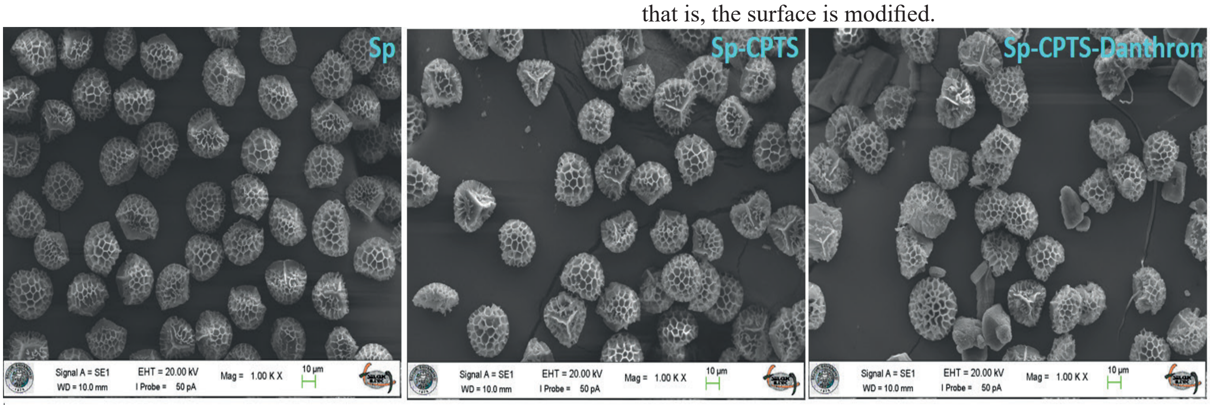


Figure 2.SEM Photo images ofsporopollenin (Sp), 3-chloropropyltrimethoxysilane-sporopollenin (Sp-CPTS) and Sp-CPTS-Danthron).

Characterization of Sp-CPTS-Danthron Adsorbent by FTIR Spectrophotometry

The FTIR spectra of the support substance sporopollenin (Sp), 3-chloropropyltrimethoxysilane-sporopollenin (Sp-CPTS) and the immobilized Sp-CPTS-Danthron compounds used in our study are demonstrated in Figure 3.

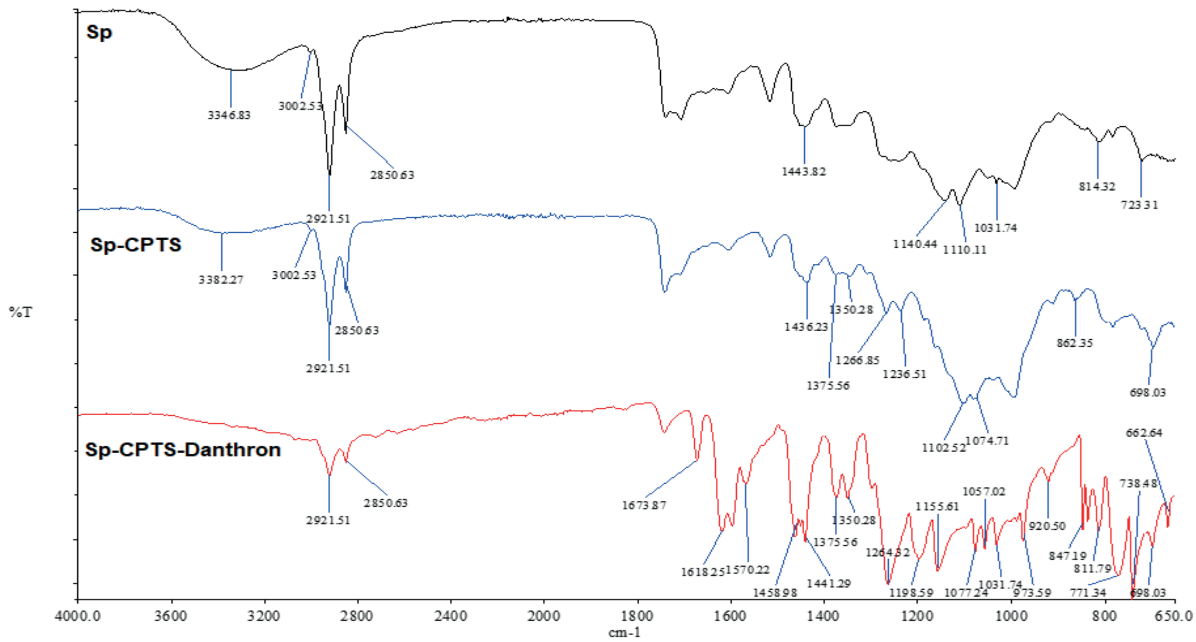


Figure 3. FTIR spectra of sporopollenin (Sp), 3-chloropropyltrimethoxysilane-sporopollenin (Sp-CPTS) and Sp-CPTS-Danthron

The FT-IR spectrum of sporopollenin (Sp) shows characteristic adsorption bands of broad banded hydroxyl groups (-OH) ranging from 3200 to 3400 cm^{-1} [19]. The peaks at 2921 and 2850 cm^{-1} are C-H symmetric and asymmetric stresses, respectively [20]. The first shows approximately 1600-1700 cm^{-1}, carbonyl (-C=O) stretching.The peak shown at 1443 cm^{-1} in Sp results from C=C tensile vibration of aromatic rings and is due to the C=O stretching vibration of a carboxylic group at 1723 cm^{-1} [21]. The frequency of the OH stretching vibration in 3-chloropropyltrimethoxysilane-sporopollenine (Sp-CPTS) was shifted from 3346 cm^{-1} (Sp) to 3382 cm^{-1} [18]. 3-chloropropyltrimethoxysilane-sporopollenine (Sp-CPTS) shows characteristic adsorption bands of the cyano group (C≡N) and siloxane (Si-O-Si) groups at 2248 and 1102 cm^{-1} stresses, respectively. The low density of the carboxylic group extending in the Sp-CPTS compared to the crude sporopollenin may be due to the modification process and this is due to the binding of CPTS to the hydroxyl and carboxylic group. For the SP-CPTS-Danthron, the appearance of a peak related to the siloxane stretching frequency Si-O-Si is observed at 1155 cm^{-1}. Further, the peaks at 1.057 and 920 cm^{-1} can be attributed to esteric groups obtained by the binding of Danthron (1,8-dihydroxyanthracene-9,10-dione) compoundto Sp-CPTS.

As a result, it confirms that the structure of the Danthron compound is immobilized to the surface of the modified sporopollenin.

Adsorption studies

Adsorption studies were carried out on five different parameters. These five different -parameters were studied and Figure 4 was obtained according to the data obtained [18-22-23-24].

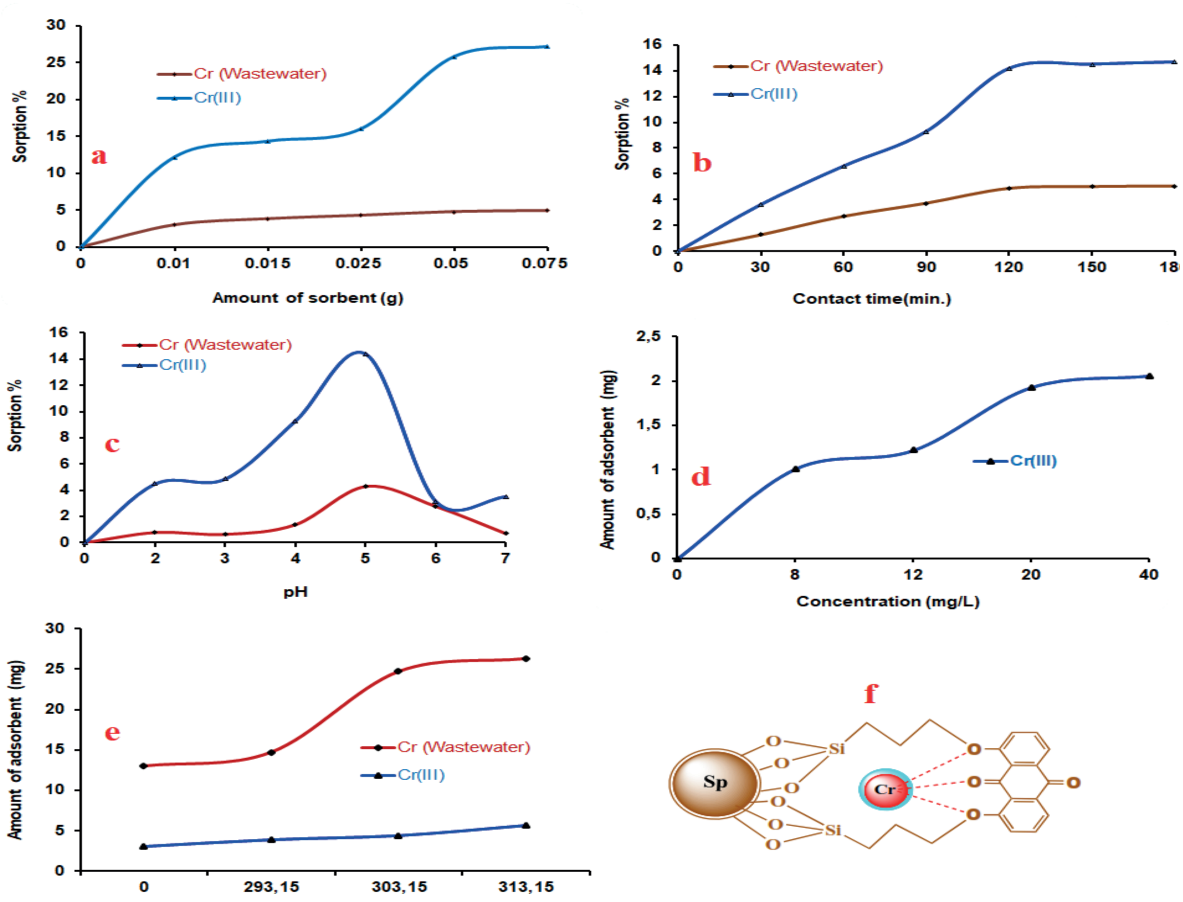


Figure 4. a) The effect of the amount of Sp-CPTS-Danthron adsorbent on the adsorption of Cr(III) and Cr(wastewater) metal ions. **b)** The effect of contact time on the adsorption of Cr(III) and Cr(wastewater) metal ions. **c)** The effect of pH on the adsorption of Cr(III) and Cr(wastewater) metal ions. **d)** Effect of concentration on the adsorption of Cr(III) metal ions.**e)**Effect of temperature on adsorption of Cr(III) and Cr(wastewater) metal ions. **f)** The estimated perspective of Sp-CPTS-Danthron-Cr(III) metal ions combination.

As seen in Figure 4.a, the amount of Sp-CPTS-Danthron adsorbent increases, while the sorption increases and after certain time it reaches a constant value. After this constant value, the amount of adsorbent Sp-CPTS-Danthron does not affect the chromium ion sorption even though is increased. The maximum sorption of chromium metal solutions (Cr (wastewater)) of 0.05 grams adsorbent is provided.

As shown in Figure 4.b, the amount of chrome metal ion in question is increased as the interaction time of Cr(III) and Cr(wastewater) metal ion solutions with the Sp-CPTS-Danthron adsorbent increases. It has been observed that the amount of chromium metal ion retained does not change, regardless of how much contact time is increased after the system has reached equilibrium. In the adsorption of chromium (III) in the two solutions of the Sp-CPTS-Danthron adsorbent, the system is observed to reach equilibrium in 150 minutes.

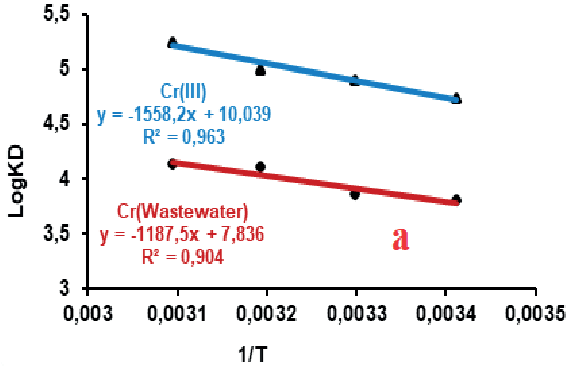
The amount of metal retention of the Sp-CPTS-Danthron adsorbent is significantly affected by the pH change of the medium as shown in Figure 4.c. For low pH of Cr(III) and Cr(wastewater) metal ions, adsorption of metal ions in adsorbents is very low.This is because as the pH decreases, the concentration of H_3O^+ in the medium increases and enters the competition with metal ions. As the pH increases for Cr(III) and Cr(wastewater) ions, adsorption occurs. At pH 5 for Cr(III)metal ions, the adsorption reached maximum.

Figure 4.d shows the effect of concentration against the adsorption of Cr(III) and Cr(wastewater) metal ions. As the metal retention capacity of the adsorbent is filled at a certain concentration, it is observed that the concentration increase does not affect the adhesion.The data obtained here is used to calculate the adsorption isotherms.

In the last parameter, it is aimed to investigate the effect of temperature on adsorption of Cr(III) and Cr(wastewater) metal ions as shown in Figure 4.e. As shown in Figure 4.e, adsorption of Cr(III) and Cr(wastewater) metal ions for the fixed adsorbent increased with temperature. It is observed that the sorption process for the Sp-CPTS-Danthron adsorbent is affected by an endothermic reaction.

Thermodynamic Properties of Adsorption

Thermodynamic parameters were determined by using data of the effect of different temperatures on the adsorption of Cr(III) and Cr(wastewater) metal ions. ΔH^0, ΔS^0 and ΔG^0 values were calculated by using the obtained data.Using these data, the distribution coefficient calculated for different temperatures is plotted graph against 1/T of the $\log_{KD}$ values and shown in Figure 5 [22-23-24].



Metal	ΔH^o ($kJmol^{-1}$)	ΔS^o ($JK^{-1}mol^{-1}$)	$-\Delta G^o$ ($kJmol^{-1}$)			
			297	303	313	323
Cr(III)	29.84	141.16	11.55	12.37	13.03	14.12
Cr(atık)	22.73	109.18	9.27	9.73	10.69	11.12

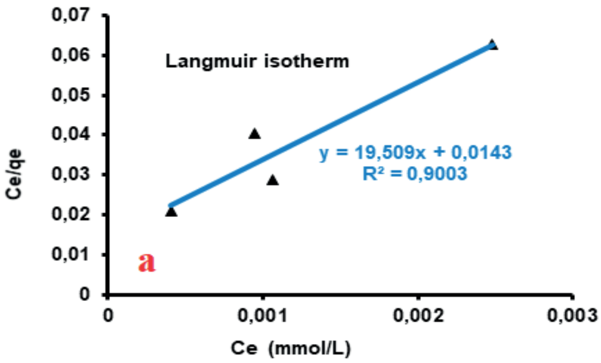
b

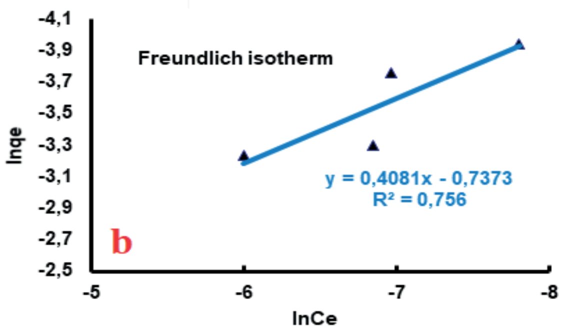
Figure 5. a) Plots of $\log_{KD}$ vs. 1/T for removal of Cr(III) in aqueous solution and wastewater by Sp-CPTS-Danthron **b)** Thermodynamic parameters for sorption of Cr(III) metal ions from wastewater solution and aqueous solution of Sp-CPTS-Danthron

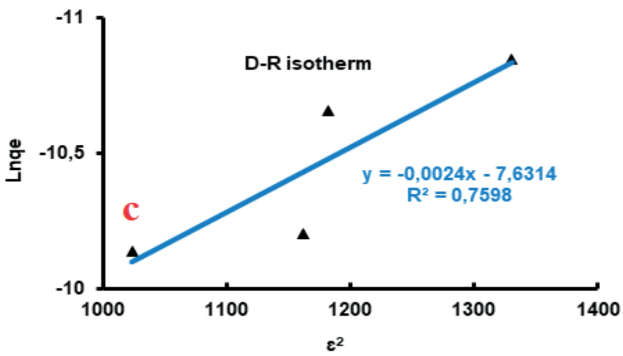
The values obtained for ΔH°, ΔS°and ΔG° has been calculated and is shown in Figure 5.b.The fact that the enthalpy change (ΔH) is positive indicates that the separation stages are endothermic processes.The positive values of ΔS° indicates that the balance of adsorption is an endothermic reaction.The negative values of ΔG° indicate that the adsorption process is spontaneous. With the increase of temperature, ΔG° has higher negative values and it shows that the adsorption process at the high temperatures is self-run. The positive entropy indicates the interest in the adsorbent of chromium ions.

Adsorption Isotherms

For the calculation of adsorption isotherms, the data of the effect of concentration on adsorption of Cr(III) metal ion in Figure 4.d was used [22-23-24]. The adsorption kinetics from D-R (Dubinin-Radushkevich), Langmuir and Freundlichadsorptionisotherm curves and data were obtained and experimental results were evaluated from the data. D-R (Dubinin-Radushkevich), Langmuir and Freundlich adsorption isotherms are given in Figure 6.







Freundlich isotherm			Langmuir isotherm	
Metal	1/n	K_F	Q_o(L/mol)	b(mol^2 $(KJ^2)^{-1}$)
Cr(III)	0.4081	0.457	0.051	1497.27
D-R isotherm				
k($mol^2K^{-1}J^{-1}$)		q_m(mol/g)		E ($kJmol^{-1}$)
0.0024		0.473		14.43

d

Figure 6. Graphs and constants of D-R (Dubinin-Radushkevich), Langmuir and Freundlich adsorption isotherms.

As a result, we can say that the adsorption of Cr(III) metal ions on the Sp-CPTS-Danthron adsorbent occurs as in monolayer. That is, adsorption of the adsorbent surface in specific homogeneous areas occurs, and each of these areas is occupied only by chromium (III) metal ion, more of these ions cannot be adsorbed [25]. To understand the nature of the interaction between the chromium metal ions and Sp-CPTS-Danthron adsorbent, the experimental equilibrium data were also fitted to the DR (Dubinin-Radushkevich) model (Figure 6.c). For chemical sorption, the E value should be greater than 8 kJ / mol [26]. As shown in Figure 6.d, the value of E was observed to be greater than 8 kJ / mol, indicating the chemical interaction as the mechanism of Cr(III) metal ion adsorption.

DISCUSSION

1,8-dihydroxyanthracene-9,10-dione (Danthron) functionalized with modified sporopollenin was successfully synthesized and characterized by FTIR and SEM spectra and then used as a promising novel adsorbent (Sp-CPTS-Danthron) for the removal of chromium (III) metal ions from wastewater solution and aqueous solution. The conclusionsdemonstrated that the maximum effect of Sp-CPTS-Danthron adsorbent on pH 5.0, adsorbent amount 0.05 g, contact time 150 minutes and temperature 303.15 K was found.According to the data obtained from thermodynamic parameters studies, Cr(III) metal ion sorption shows spontaneous in nature. In general, it can be concluded that the proposed adsorbent system is practical and efficient in removing heavy metals from the aqueous medium and has the advantages of being cheap and highly available.

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