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Equilibrium and thermodynamic study of cobalt adsorption on activated carbon derived from date seeds

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ABSTRACT

Preparation of activated carbon from date seeds and the possibility of using it as an adsorbent were evaluated. Pyrolysis of date seeds under nitrogen flow and activation with carbon dioxide was performed at three different temperatures (700, 800, and 900˚C). SEM micrographs of activated carbon produced at 900˚C indicate a rough structure on the surface with more mesopores than that produced at lower temperatures. In addition, EDS analysis showed that it has higher oxygen surface groups. However, the yield was 16.5% compared with 18.9% and 20.9% at 800, 700˚C, respectively. Batch adsorption of cobalt on S900 showed type III adsorption isotherm at three studied temperatures (25, 35, and 45˚C). This type of isotherm was explained using Freundlich's and BET models that showed very good agreement with the experimental data. The Gibbs free energy change was calculated as −4.154, −4.374, and −4.595 kJ/mol at 25, 35, and 45˚C, respectively. The adsorption of cobalt was found to be endothermic process ($\Delta H^\circ = 2.415$ kJ/mol) and entropy-driven rather than enthalpy-driven with $\Delta S^\circ = 0.022$ kJ/mol.K.

Keywords: Date seeds; Activation; Activated carbon; Cobalt; Adsorption

1. Introduction

Cobalt is essential for human well-being, since it is a component of vitamin B_{12} [1]. However, elevated concentrations of cobalt are harmful to human health, resulting in paralysis, diarrhea, lung irritations, and bone defects [2]. In addition, it has many toxic effects such as imparting neurotoxicological disorders, genotoxicity, carcinogenicity, cardiomyopathy, and bronchial asthma [3]. Cobalt is present in various industrial wastewaters including petrochemical, nuclear [4], mining, electronics, metallurgical, electroplating and paint industries [5]. Thus, elimination of cobalt from natural streams and industrial wastewaters is very important and has received much attention in recent years.

Different methods have been used to remove toxic cobalt from effluents and industrial wastewater before discharging into a natural water body, including coagulation and precipitation, ion exchange, membrane processes, electrolytic technologies, and adsorption. The selection of a treatment technology is based on cost and the concentration of waste. For example, conventional treatment technologies like precipitation and

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coagulation become less effective and more expensive when situations involving high volumes and low metal concentrations are encountered [6]. Among the known physico-chemical treatment methods, adsorption seems to be the most promising technique for the removal of metals from chemical process industries [7]. Hence, a large variety of materials was explored to remove cobalt from solutions such as: zeolites [8], vermiculite [9], sepiolite [10], kaolinite [11], and activated carbon [12]. The heavy metal adsorption mechanism from aqueous solutions on carbon materials is dependent on the surface chemistry of the activated carbon and the conditions of the experiment [13,14]. There are several suggested mechanisms which include: (i) ion exchange and/or formation of surface metal complexes, mainly operating on the acidic surface oxygen functionalities; (ii) adsorption on electron-rich regions within the graphene layers, acting as Lewis basic sites [14–18]; (iii) surface precipitation, which can occur under certain experimental conditions [19].

Activated carbons are widely used for water treatment, wastewater reclamation, gas purification, and as catalyst support [20]. However, the high cost of commercial activated carbon is inhibiting. Hence, it is desired to make use of the biomaterial wastes for the production of activated carbons in a cost-effective way. Activated carbon can be produced from any carbonaceous solid precursor that may be either natural or synthetic. A number of research work dealing with the applicability of activated carbon obtained from coconut shell, almond husk, olive cake, used tyres, sawdust, and jute fiber [21–26] have been investigated.

The process of converting such a waste material to activated carbon starts with pyrolysis, which is a thermal decomposition process of a material in an inert atmosphere at a temperature between 400 and 900˚C. The products of pyrolysis are gases, liquids (tars), and solids (chars). To improve the porosity of the char, chemical, or physical activation are the common methods. Physical activation—which follows the pyrolysis step—is done by steam or CO_2. In chemical activation, the organic precursor is impregnated by an activator such as $ZnCl_2$, H_2SO_4, KOH, H_3PO_4, etc. and then heated in an inert atmosphere.

Date stones can be considered as one of the best candidate among the agricultural wastes because they are cheap and quite abundant, especially in Mediterranean countries [27]. In Oman, there are 36,000 hectares planted with Palm trees which produce around 267 million kilogram of dates per year [28]. Carbohydrates are the major components of date seeds that are composed of 42% cellulose, 18% hemi cellulose, 25% sugar and other compounds, 11% lignin, and 4% ash. This lignocellulosic composition promotes the preparation of activated carbon from these precursors [20]. The main objective of this paper is to study the characteristics of activated carbon produced from Omani date seeds and test the adsorption capability of cobalt from aqueous solutions. The effect of pyrolysis temperature on the final product will be identified and the thermodynamics of adsorption isotherms will also be modeled.

2. Materials and methods

Date seeds were obtained locally from Nizwa region, Oman. The seeds were washed with distilled water and dried in a drier at 110˚C for 24 h. After drying, the seeds were crushed and grinded into powder form. Nitrogen (purity 99.995%) and carbon dioxide (purity 99.99%) were used for pyrolysis and activation of date seeds.

Production of AC was carried out in a stainless steel reactor, which is mounted vertically in a furnace as shown in Fig. 1. The reactor had an inside diameter of 30 mm, outside diameter of 40 mm, and a length of 30 mm. About 5.0 grams of date seeds was pyrolyzed by heating to 700˚C (S700), 800˚C (S800), and 900˚C (S900) at a rate of 5.5˚C/min for 2 h. During pyrolysis, nitrogen was allowed to flow through the reactor at a rate of 0.6 mL/min. Thereafter, the samples were activated by flowing 0.6 mL/min CO_2 through the bed at the same temperature for 1 h. After activation, all samples were cooled down to room temperature in an

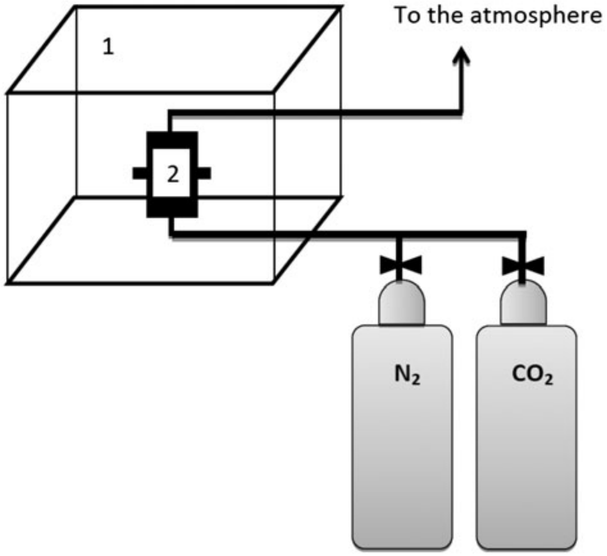

Fig. 1. Experimental setup; (1) muffle furnace and (2) stainless steel reactor.

inert atmosphere of nitrogen and then stored for characterization. The morphology of the AC was studied with scanning electron microscopy (JEOL, JSM-6060).

The prepared activated carbon samples were tested for their adsorptive capacity in removing cobalt from aqueous solution. Different concentrations were prepared by dissolving specific amount of $CoCl_2.6H_2O$ in 50 mL of distilled water. Then, 200 mg of the AC were added to the prepared solutions and put in an orbital shaker, which was kept at constant temperature (25, 35, 45˚C). After 24 h, the solutions were filtered, and the concentration was measured using SOLAAR Atomic Absorption (S4 AA, Thermo Electron Corp.) at wavelength of 228.8 nm. The amount of metal adsorbed per unit mass was calculated as follows:

$$q_e = \frac{(C_i - C_e)V}{m} \quad (1)$$

where C_i and C_e are the initial and equilibrium concentrations of cobalt solution (mg/L), q_e is the equilibrium amount adsorbed (mg/g), m is the mass of activated carbon, V is the volume of cobalt solution (L). The equilibrium data were analyzed using both Freundlich and BET isotherms.

Table 1
Yield and composition of activated carbon produced at different temperatures

T (˚C)	Yield (%)	Carbon content (%)	Oxygen content (%)
700	20.9	97.39	2.61
800	18.9	95.61	4.39
900	16.5	93.58	6.42

3. Results and discussion

The effect of activation temperature on yield of activated carbon is shown in Table 1. It can be seen that as the temperature increased from 700 to 900˚C, the yield decreased from 20.9 to 16.5%. This is due to increased losses of volatile organic compounds. At 900˚C, it is believed that a more stable carbon structure was formed and the rate of mass loss will be much smaller. In addition, pyrolysis and activation at higher temperatures is not industrially attractive.

Scanning electron microscopy is widely used to study the morphology of adsorbents. It is observed that the micrographs (Fig. 2) of activated carbon at S900 indicate a rough structure on the surface and the presence of many pores, which is favorable for adsorption. It also shows that the porosity increased with increasing temperature and the structure is mostly mesoporous.

Energy dispersive X-ray spectroscopy (EDS), Fig. 3, shows that the surface is mostly carbon with a very little amount of oxygen-containing surface groups as shown in Table 1.

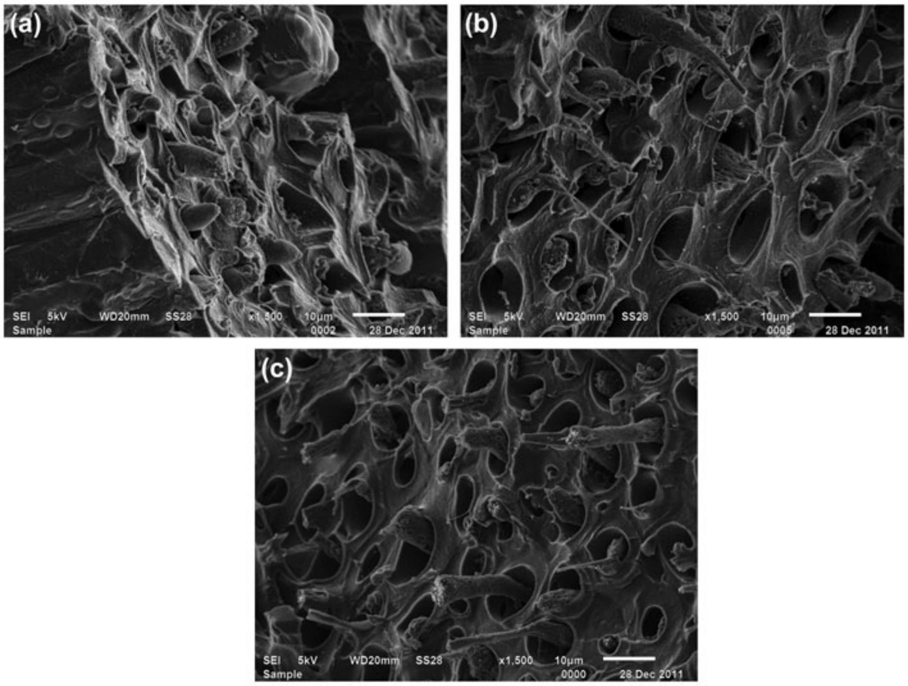

Fig. 2. SEM micrographs of activated carbon produced at (a) 700˚C, (b) 800˚C and (c) 900˚C.

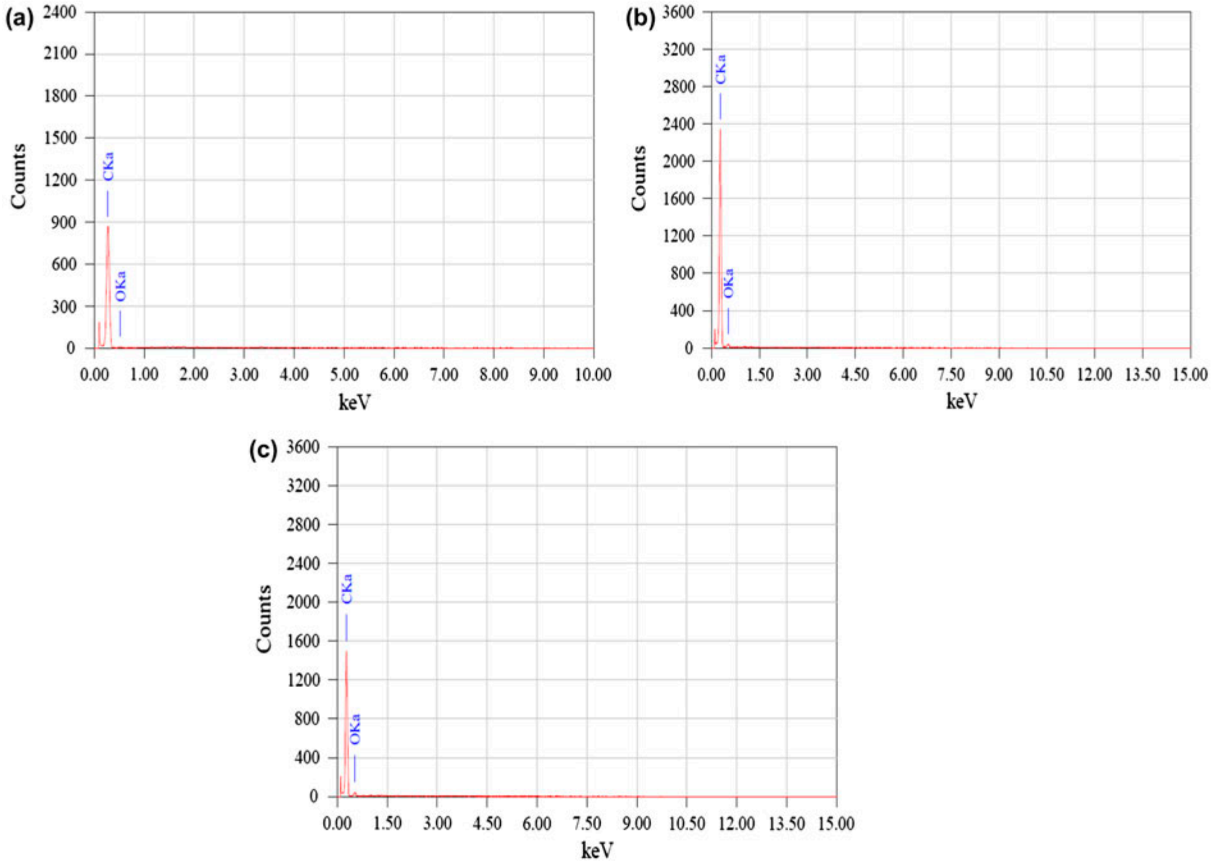

Fig. 3. EDS analysis of activated carbon produced at (a) 700˚C, (b) 800˚C and (c) 900˚C.

3.1. Adsorption equilibrium

Adsorption equilibrium is imperative information for correct analysis and design of adsorption separation processes. At equilibrium, a certain relationship prevails between liquid phase and solid phase concentrations of heavy metals. Several adsorption models originally used for gas phase adsorption are available to correlate adsorption equilibria of heavy metals.

Freundlich model [29] is used to describe nonlinear adsorption isotherms. This model proposes a monolayer sorption with a heterogeneous energetic distribution of active sites, accompanied by interactions between adsorbed molecules. The Freundlich model can be written as follows:

$$q_e = K_F C_e^{1/n} \tag{2}$$

and the linear form of this equation is:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \tag{3}$$

where q_e is the equilibrium metal ion concentration on the activated carbon, C_e is the equilibrium metal ion concentration in the solution, K_F is a constant relating the adsorption capacity, and $1/n$ is an empirical parameter relating the adsorption intensity, which varies with the heterogeneity of the activated carbon.

A widely used adsorption model describing type III adsorption isotherm is the BET adsorption isotherm. The BET adsorption isotherm model could be written as [30]:

$$q_e = \frac{q_s b_s C_e}{(1 - b_L C_e)(1 - b_L C_e + b_s C_e)} \tag{4}$$

where q_s (mg/g) is the monolayer saturation capacity, b_s (L/mg) and b_L (L/mg) is the equilibrium constant on the bare surface and on a layer of already adsorbed solute, respectively.

Fig. 4 shows the equilibrium adsorption isotherms of cobalt on activated carbon produced at 900˚C (S900). The isotherms were measured at three temperatures (25, 35, and 45˚C). The isotherms were identified as type III isotherms according to IUPAC classification of adsorption isotherms. This kind of isotherm is usually modeled using BET isotherm, Freundlich, or anti-Langmuir (Langmuir model with

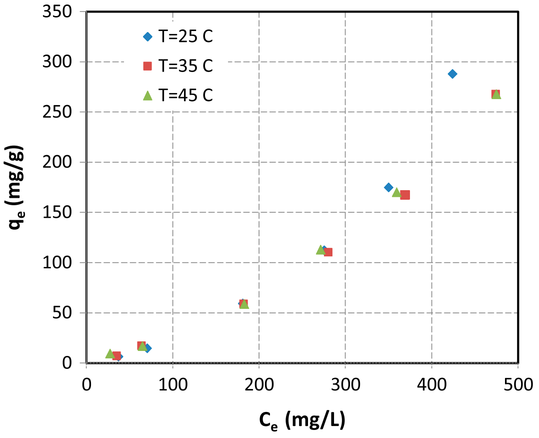

Fig. 4. Experimental adsorption isotherms of cobalt on activated carbon (S900).

negative constants) [31]. Freundlich's parameters can be obtained from Eq. (3) since a plot of $\ln q_e$ vs. $\ln C_e$ will result in a straight line with a slope of $1/n$ and an intercept of $\ln K_F$. However, linearizing Freundlich's isotherm will have two effects: distortion of relative weights of data points and distortion of error distribution [32]. To overcome this problem, the parameters can be calculated using non-linear regression method which uses the sum of relative squared errors (SRSE):

$$\mathrm{SRSE} = \sum_{i=1}^{N} \frac{(q_{e,i} - q_{p,i})^2}{q_{e,i}} \tag{5}$$

where $q_{e,i}$ is the experimental value of the amount adsorbed of point i, $q_{p,i}$ is the predicted value of the amount adsorbed of point i. The objective function was to minimize equation 5 by changing the model parameters. In this study, both linear and nonlinear regression methods were used for comparison.

Freundlich's parameters were calculated and presented in Table 2. It can be seen that the nonlinear regression gave a much better representation of the adsorption data according to the SRSE. It is also noted that values of $1/n$ is always greater than one. Values that exceed unity imply unfavorable adsorption while values close to zero imply heterogeneous adsorption [33].

BET parameters were calculated by minimizing equation 5 and presented in Table 3. If the solute–solute interactions are strong, the adsorption isotherm could become strictly convex downwards (type III), this takes place if $b_L \geqslant b_s/2$. If this condition does not hold, the BET turns to a type II adsorption isotherm [34]. The computed SRSE is clearly less than that of the Freundlich model at 35 and 45°C, while it is higher at 25°C. Keeping in mind that the BET model has three parameters (q_s, b_s, and b_l), while Freundlich model has two parameters (K_f, n), the SRSE is not the best method to compare between the two models. Akaike's Information Criterion (AIC) is a well-established statistical method that can be used to compare between models of different parameters. For a sample size, AIC is calculated for each model from the following equation [32]:

$$\mathrm{AIC} = N \ln\left(\frac{\mathrm{SSE}}{N}\right) + 2N_p + \frac{2N_P(N_P+1)}{N - N_P - 1} \tag{6}$$

where N is the number of data points, N_P is the number of parameters in the model, and SSE is the sum of squared error. The calculated AIC and SSE for the Freundlich and BET isotherms are shown in Table 4. Having a smaller AIC value suggests that the Freundlich isotherm is more likely to be a better fit at 25 and 45°C while the BET isotherm is better at 35°C.

3.2. Thermodynamics of adsorption

The thermodynamic parameters, such as the change in free energy ($\Delta G°$), enthalpy ($\Delta H°$), and entropy ($\Delta S°$), can be calculated from Eqs. (7) and (8) as:

$$\Delta G^\circ = -RT \ln K^\circ \tag{7}$$

$$\ln K^\circ = \Delta S^\circ/R - \Delta H^\circ/RT \tag{8}$$

Table 2
Freundlich's parameters calculated using linear and nonlinear regression

T (°C)	Non-linear			Linear		
	K_F $(mg/g)^{1-1/n}$	n	SRSE	K_F $(mg/g)^{1-1/n}$	n	SRSE
25	0.0185	0.6333	0.0000	0.0247	0.6591	2.1558
35	0.0323	0.6874	3.1899	0.0641	0.7497	4.9354
45	0.0396	0.7020	4.4383	0.1530	0.8453	12.1784

Table 3
BET parameters calculated using nonlinear regression

T (°C)	q_s (mg/g)	b_s (L/mg)	b_l (L/mg)	*SRSE*
25	490.05	5.07E−04	1.11E−03	7.8370
35	490.02	5.02E−04	9.51E−04	0.4870
45	490.04	5.53E−04	9.07E−04	1.4178

Table 4
The calculated SSE and AIC for Freundlich and BET models

T (°C)	Freundlich		BET	
	SSE	AIC	SSE	AIC
25	3E−04	−50.97	572.5	45.35
35	392.6	33.09	6.009	18.01
45	207.2	29.25	93.44	34.47

where K° is the equilibrium constant, R is the universal gas constant, and T is the absolute temperature (K). Since we are dealing with dilute solutions, the values of K° were determined from the intercepts by plotting $\ln q_e/C_e$ vs. q_e and extrapolating to zero at different temperatures [35]. Values of $\ln K^\circ$ were plotted against $1/T$ as shown in Fig. 5, and the thermodynamic parameters (ΔH° and ΔS°) were calculated from the slope and intercept, respectively.

Table 5 shows the equilibrium constant (K^o) at different temperatures as well as the calculated values of ΔH°, ΔS°, and ΔG°. These thermodynamic parameters were found to be close to what is available in the literature [10]. Positive values of ΔH° (2.415 kJ/mol) confirmed the endothermic nature of the adsorption process, which is also evidenced by the enhancement of cobalt adsorption at higher temperatures. It also suggests that this is a physisorption rather than chemisorptions since ΔH° is less than 40 kJ/mol. This endothermic nature of adsorption could result from intraparticle diffusion of cobalt into the pores since the rate of diffusion increases with temperature. However, the low value of ΔH° suggested that the electrostatic interaction between cobalt ions and the activated carbon surface was weak to a certain extent. Positive values of ΔS° (0.022 kJ/mol.K) imply that the adsorbed ions presented a certain amount of freedom in the solid/solution. It also implies that the adsorption process is entropy-driven rather than enthalpy-driven. A negative change in Gibbs standard free energy with temperature indicates that the adsorption reaction is a spontaneous and feasible process. The decrease in ΔG° with the increase in temperature demonstrates that the adsorption is more spontaneous at elevated temperatures.

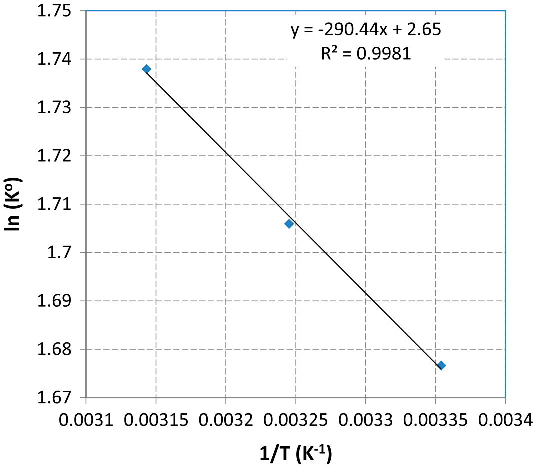

Fig. 5. A plot of ln(K°) vs. $1/T$ for the estimation of thermodynamic parameters.

Table 5
Thermodynamic parameters and equilibrium constants evaluated at different temperatures

T (°C)	K°	ΔH° (kJ/mol)	ΔS° (kJ/mol K)	ΔG° (kJ/mol)
25	5.348	2.415	0.022	−4.154
35	5.507			−4.374
45	5.686			−4.595

4. Conclusions

Activated carbon was successfully prepared from date seeds by pyrolysis under inert atmosphere and activation with carbon dioxide. Characteristics of the produced activated carbon and its adsorptive affinity of cobalt were investigated. The porosity of produced activated carbon favors higher activation temperatures, while the yield favors lower temperatures. Equilibrium data of batch adsorption experiments at different temperature followed type III adsorption isotherm which was well explained by Freundlich and BET models. Nonlinear regression was found to be a better method to calculate the model parameters. The thermodynamics of adsorption of cobalt on the prepared activated carbon showed that the process was spontaneous, endothermic, and entropy-driven under the studied conditions.

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