

Adsorption of Phenol from Aqueous Solution on Commercial Activated Carbon

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Abstract

Industrial effluents containing phenol are toxic to human health and aquatic organisms. Phenol cannot be effectively removed from water by conventional methods, making adsorption a promising alternative for this type of separation. This study aims to collect kinetic, isothermal and thermodynamic data, in addition to evaluating the removal of phenol from aqueous media through adsorption using commercial activated carbon Norit RB4. Therefore, adsorption equilibrium tests were carried out to obtain isotherms at 298.15, 313.15, and 328.15 K, resulting in maximum adsorption capacities of 151.34, 133.45, and 123.87 mg/g, respectively. When comparing the isotherms at 298.15, 313.15, and 328.15K, it was observed that the adsorbed amount decreased across the entire concentration range as the temperature increased. By applying the Langmuir isotherm model, standard enthalpy ($\Delta H^\circ = -11.07$ kJ/mol), standard entropy ($\Delta S^\circ = -0.02575$ kJ/mol.K), and standard Gibbs free energy ($\Delta G^\circ = -3.393, -3.006, \text{ and } -2.620$ kJ/mol at 298.15, 313.15, and 328.15K, respectively) values were calculated. The results indicate that the adsorption process is physical, since ΔH° is less than 20 kJ/mol, exothermic because $\Delta H^\circ < 0$, and spontaneous because $\Delta G^\circ < 0$. Therefore, commercial activated carbon Norit RB4 is effective in removing phenol from aqueous solutions due to its high adsorption capacity and the favorable thermodynamic properties observed.

Keywords: phenol; adsorption; Norit RB4; activated carbon; isotherm.

1. Introduction

Water is a finite natural resource and is considered the most important and fundamental means for maintaining life on Earth. Given the uncontrolled degradation that water has suffered in recent times, there are growing social and scientific concerns about its availability on the planet, despite its apparent abundance. Industrial activity, as a consequence of urban development, has intensified the generation of solid waste and liquid effluents, becoming the major cause of pollution in water bodies [1].

Among the various pollutants, phenolic compounds are widely used in industries across various sectors such as refineries, petrochemicals, pharmaceuticals, textiles, paints, polymers, and others. As a result, liquid effluents containing these compounds are often improperly disposed of in aquatic environments [2].

Phenol and its derivatives are contaminant compounds, many of which are carcinogenic. Even at low concentrations in water bodies, they pose a

significant obstacle to water reuse. These substances are soluble in water and organic solvents and exhibit high mobility, which facilitates their presence in springs, imparting an unpleasant smell and taste to the water. In addition to being easily absorbed through the respiratory tract, skin, and orally, phenolic compounds are highly toxic to humans and aquatic organisms, potentially causing health problems. Due to these risks, their concentrations in effluents are regulated by environmental agencies [1,2-3]. According to CONAMA Resolution 430/2011 [4], the maximum permissible levels of total phenols in wastewater are 0.5 mg/L. In Class 1 freshwater, these levels are limited to just 0.003 mg/L, as per CONAMA Resolution 357/2005 [5].

Given the limitations related to the disposal of phenol in surface waters and the inefficiency of conventional water treatment methods in removing this contaminant, alternative technologies can be employed for its removal. These methods include precipitation, coagulation, flocculation, biological treatment, oxyreduction, ion exchange, membrane separation, reverse osmosis, and adsorption [6-9].

In this context, adsorption on activated carbons emerges as an alternative and promising treatment for phenol removal from aqueous solutions, due to its low cost, easy implementation, and high efficiency [10]. As the effectiveness of this process is directly linked to the adsorption capacity of the adsorbent material, it is necessary to evaluate a range of adsorbent solids.

Therefore, this work aims to evaluate phenol adsorption on commercial activated carbon RB4 (Cabot Corporation, USA). To achieve this, the adsorption isotherm and thermodynamic parameters of phenol adsorption on activated carbon will be determined to assess the performance of Norit RB4 as a material for separating phenol from aqueous solutions.

2. Materials and methods

2.1. Materials

Commercial activated carbon Norit RB4 (Cabot Corporation, USA) was used in this study and was characterized by Siqueira [11], with a specific surface area of 907 m²/g, a specific total pore volume of 0.39 cm³/g, and a specific micropore volume of 0.37 cm³/g. The following materials were also used: 90% purity liquid phenol (Proquímicos Comércio e Indústria Ltda, Brazil), deionized water, an oven with air circulation and renewal (Tecnal, Brazil), PTFE syringe filter (0,45 µm), an analytical balance (PHD Equipamentos para Laboratórios, Brazil), an incubator shaker (Solab, Brazil); and a spectrophotometer (Gehaka, Brazil).

2.2. Adsorption isotherms at 298.15, 313.15, and 328.15 K

Commercial activated carbon Norit RB4 was first macerated and regenerated in a laboratory oven at 393.15 K for 12 hours. Afterward, the carbon was cooled to the target experimental temperatures (298.15, 313.15, and 328.15 K). For each of the 22 Erlenmeyer flasks (50 mL) used, 0.025 grams of Norit RB4 was weighed on an analytical scale. Separately, 0.5556 grams of 90% purity phenol was weighed, diluted in deionized water, and transferred to a 500 mL volumetric flask to prepare a 1000 ppm phenol solution. This solution was then diluted to obtain concentrations of 10, 20, 30, 40, 50, 75, 100, 200, 300, 400, and 500 ppm. After the dilutions, absorbance readings for each solution at different

concentrations were taken at 270 nm using a spectrophotometer to confirm the concentrations. Once confirmed, 25 mL of each solution was transferred to the Erlenmeyer flasks containing the activated carbon. The samples were prepared in duplicate and shaken at 160 rpm for 2 hours at the specified temperatures (298.15, 313.15, and 328.15 K) to achieve equilibrium. After 2 hours, aliquots were filtered through a 0.45 µm syringe filter to remove any residual activated carbon, and the filtrate was analyzed for absorbance to determine the final phenol concentration. The data were processed using Excel and OriginPro 8.5 to calculate the amount of phenol adsorbed, as determined by Equation 1, and to construct the adsorption isotherms. The Langmuir equation was then fitted to the experimental data to obtain the adsorption parameters. This procedure was applied to generated isotherms at 298.15, 313.15, and 328.15 K.

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

where q_e represents the amount of phenol adsorbed (mg/g), V is the volume of solution (L), C_o is the initial phenol concentration (mg/L), C_e is the equilibrium phenol concentration (mg/L), and m is the mass of activated carbon used (g).

2.3. Determination of adsorption isotherm and thermodynamic parameters

The parameters of the Langmuir model are obtained using Equation 2.

$$q_e = \frac{q_m k_L C_e}{1 + k_L C_e} \quad (2)$$

where q_m is the maximum monolayer adsorption capacity (mg/g), and k_L is the Langmuir constant (L/mg).

Thermodynamic parameters are determined through the van't Hoff equation, which relates the variation of the equilibrium constant to changes in temperature, enthalpy, and entropy, as shown in Equation 3.

$$\ln(K_e) = -\frac{\Delta H^\circ}{R} \frac{1}{T} + \frac{\Delta S^\circ}{R} \quad (3)$$

where K_e denotes the thermodynamic equilibrium constant, ΔH° is standard enthalpy (kJ/mol), ΔS° is

the standard entropy (kJ/mol.K), R is the ideal gas constant (8.314 J/mol.K), and T is the temperature (K). The procedure for determining the standard enthalpy variation can be found in the literature [12].

The standard Gibbs free energy (ΔG°) can be determined using Equation 4.

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (4)$$

where ΔG° is expressed in kJ/mol.

3. Results and discussion

3.1. Adsorption isotherms

Based on the experimental data, adsorption isotherms at 298.15, 313.15, and 328.15 K were plotted, and their behavior was analyzed, as shown in Fig. 1.

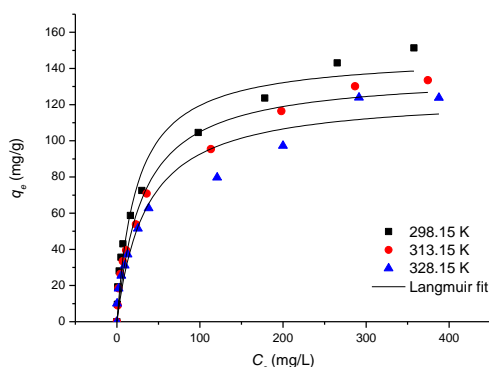


Fig. 1. Adsorption isotherms.

Fig. 1 illustrates that the amount adsorbed at equilibrium decreases as the temperature increases, with maximum adsorption capacities of 151.34, 133.45, and 123.87 mg/g at 298.15, 313.15, and 328.15 K, respectively. This trend suggests that the adsorption process is likely physical. Table 1 presents the phenol adsorption capacities on different types of activated carbon at 298.15 K, as reported in the literature. This comparison indicates that Norit RB4 has potential for phenol removal. By applying the Langmuir model, Equation 2, to each isotherm, the parameters q_m and k_L were determined and are shown in Table 2.

Table 1. Adsorption capacities of phenol on different activated carbons at 50 ppm and 298.15 K.

Sample	q_e (mg/g)	Reference
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Norit RB4	72	This work
Carbano 119	35	[1]
CAF	141	[13]
ESAC 1	45	[14]

Table 2. Langmuir parameters.

Isotherm (K)	q_e (mg/g)	k_L (L/mg)	R^2
298.15	147.68	0.04252	0.9618
313.15	137.23	0.03252	0.9761
328.15	125.36	0.02831	0.9482

3.2. Thermodynamics parameters

Using the data from Table 2, the values of K_e were determined. With these values, a plot of $\ln(K_e)$ versus $1/T$ was created, and the linearized data are presented in Fig. 2. From the equation shown in Fig. 2, along with Equation 3, the values for ΔH° and ΔS° were determined. The values of ΔG° were determined using Equation 4. The results are presented in Tables 3 and 4.

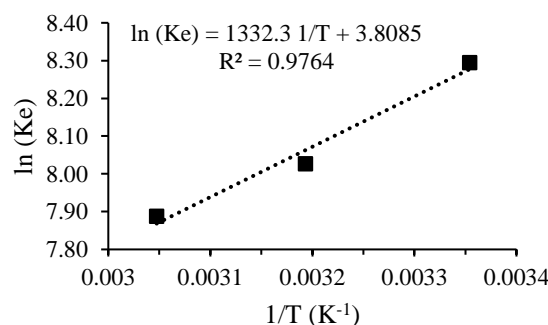


Fig. 2. Plot of $\ln(K_e)$ versus $1/T$.

Table 3. Fitted values presented in Fig. 2.

Isotherm (K)	$1/T$ (K ⁻¹)	K_e	$\ln(K_e)$
298.15	0.003354	4001.6	8.2945
313.15	0.003193	3060.5	8.0263
328.15	0.003047	2664.3	7.8878

Table 4. Thermodynamics parameters.

Temperature (K)	ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° (kJ/mol.K)
298.15 K	-20.517		
313.15 K	-20.992	-11.076	0.03166
328.15 K	-21.467		

As shown in Table 4, the values of ΔG° are negative, indicating that the adsorption process is exothermic. The value of ΔH° suggests that the adsorption is physical, as it occurs through van der

Waals forces. This is supported by the fact that ΔH° values lower than 20 kJ/mol typically indicate physical adsorption [12].

The values obtained are consistent with those found in literature for phenol adsorption on activated carbon, as shown in Table 5.

Table 5. Thermodynamics parameters

Sample	ΔH° (kJ/mol)	Reference
Carbano 119	-37.68	[1]
CAF	-17.50	[13]
ESAC 1	-22.23	[14]

4. Conclusions

Based on the adsorption isotherms experiments, it was observed that the amount of adsorbed phenol decreases as the temperature increases. The maximum adsorption capacities at 298.15, 313.15, and 328.15 K were 151.34, 133.45, and 123.87 mg/g, respectively, which is characteristic of physical adsorption. The calculated standard enthalpy ($\Delta H^\circ = -11.071$ kJ/mol) confirms that the adsorption is physical. The negative value of ΔH° also indicates that the process is exothermic. The standard Gibbs free energy values ($\Delta G^\circ = -3.3928$, -3.0064 , and -2.6201 kJ/mol at 298.15, 313.15, and 328.15 K, respectively) were all negative, indicating that the process of adsorption is spontaneous. Based on the experimental data and calculated parameters, it can be concluded that the commercial activated carbon Norit RB4 is effective for phenol removal in aqueous environments.

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