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Investigation of reduced graphene oxide derived from cotton waste as an adsorbent for phenol removal in aqueous solutions

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Abstract

The elimination of organic substances, such as phenol, in conventional and biological processes, has been a significant challenge for the petroleum industry. In this work, reduced graphene oxide obtained from cellulosic biomass (CB-rGO), specifically cotton waste, was employed as a phenol adsorbent in an aqueous solution simulating refinery effluent. The CB-rGO was characterized using XRD, Raman spectroscopy, and N_2 adsorption isotherms at 77 K for BET surface area determination. The effects of variables such as pH, contact time, temperature, CB-rGO mass, and adsorbate concentration on the adsorption process were thoroughly investigated. These parameters were evaluated across a range of adsorbate concentrations from 100-300 mg/L, pH from 2-10, adsorbent mass from 5-20 mg, contact time from 0-180 min, and temperature from 20-60 °C. The adsorption isotherm data were better described by the Toth equation compared to the Langmuir and Khan models, despite the small difference in R^2 values, with the *n* parameter of the Toth model suggesting a heterogeneous surface. The Elovich kinetic model was evaluated to describe the adsorption kinetics and assess its suitability for modeling the phenol adsorption process using CB-rGO. The average R^2 value of 0.992 for the Elovich model indicated an excellent fit to the experimental data, suggesting that the adsorption occurred on a heterogeneous surface, which is consistent with the nature of the CB-rGO material and aligns with what was observed from the adjustment of the Toth equation. The successful removal of phenol from synthetic effluents highlights the promising potential of this adsorbent, obtained from an industrial residue, as a more environmentally sustainable alternative to conventional materials used for phenol removal.

Keywords: Adsorption; phenol; reduced graphene oxide; cellulosic biomass; cotton waste

1. Introduction

Industrial effluents are a significant source of large quantities of organic and inorganic waste discharged into water bodies, posing a serious environmental risk to plants, humans, and animals [1]. Even at low concentrations, phenol is considered one of the most hazardous pollutants found in these effluents, due to its toxic and carcinogenic properties, as well as its solubility in water and various organic solvents [2]. Its presence not only poses risks to human health but also threatens vital organs such as intestine, lungs, liver, and brain [3].

In this context, various biological and physicochemical methods have been employed to eliminate phenol from effluents. Accordingly, a range of adsorbents, including activated carbon, minerals, and polymers, have been studied for phenol adsorption, with particular attention given to the development and use of novel adsorbents [4].

Based on this context, the objective of this study is to evaluate viability of cellulosic biomass reduced graphene oxide (CB-rGO), obtained from solid waste generated in the textile industry, for the removal of phenol from aqueous solutions. The characteristics of the phenol adsorption process using CB-rGO were analyzed under various parameters, such as initial concentration, solution pH, adsorbent mass, contact time, and temperature. The experimental adsorption isotherm data reported by Jesus et al. (2024) [5] were utilized to evaluate the applicability of various adsorption models, including the Elovich kinetic model, along with the Langmuir, Toth, and Khan isotherm models, offering insights into the mechanisms governing the interaction between phenol and CB-rGO.

2. Materials and methods

2.1. Materials

Waste from the cotton sanding process was collected and donated by Vicunha Têxtil S/A. The iron-base catalyst ferrocene ($FeC_{10}H_{10}$), CAS 102-54-5, with 98.5% purity (Merck, Germany) and phenol crystal P.A. – ACS (C_6H_6O), CAS 108-95-2, with 99% purity (Êxodo Científica, Brazil) were used in this study.

2.2. Synthesis and Characterization of CB-rGO

The CB-rGO was synthesized using a top-down method. In this process, 1 g of cotton fiber powder was placed in a ceramic crucible along with 0.1 g of the solid catalyst ferrocene ($FeC_{10}H_{10}$). After thorough mixing, the components were transferred to a muffle furnace and subjected to pyrolysis at 300 °C for 30 min. The resulting powder was then macerated until it reached a fine and dark consistency.

The CB-rGO synthesized from cotton waste was characterized using Raman spectroscopy, XRD, and N_2 adsorption isotherms at 77 K for BET surface area determination.

2.3. Adsorption Experiments and Isotherm Model Evaluation

Batch adsorption experiments were conducted using CB-rGO as an adsorbent to remove phenol from aqueous solutions. The experiments, carried out in 120 mL Erlenmeyer flasks with 50 mL of phenol solution, involved varying pH (2.0-10.0), initial phenol concentration (100-300 mg/L), adsorbent dosage (5-20 mg), temperature (20-60 °C), and contact time (0-180 min). After adsorption, the mixture was filtered, centrifuged, and analyzed using a UV-VIS spectrophotometer. Based on the determination of phenol concentrations at specific time points and at equilibrium, the amounts adsorbed at equilibrium (q_e), at time t (q_t), and the percentage of phenol removal (%R) were calculated. It is important to highlight that the experimental data from the procedure described above were previously published in Jesus et al. (2024) [5], and additional details regarding the adsorption isotherm determination can be found in the cited work.

Additionally, the Langmuir, Toth, and Khan adsorption isotherm models were evaluated.

3. Results and discussions

3.1. Characterization of CB-rGO

In the XRD diffraction analysis shown Fig.1a, a prominent diffraction peak at 2θ = 24° corresponds to the (002) plane of graphite and turbostratic structures, while the peak at 2θ = 36° is associated with the interplanar spacing of (100). The Raman spectrum in Fig.1b shows an I_D/I_G ratio of 0.66, indicating a low defect presence in the graphitic structure.

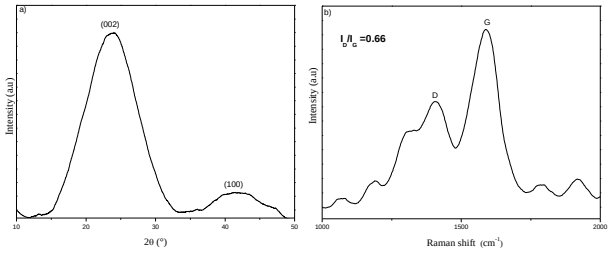

Fig. 1. (a) XRD pattern and (b) Raman spectrum of CB-rGO.

The analysis of the N_2 adsorption-desorption isotherms at 77 K revealed a type IV isotherm with H4-type hysteresis at P/P_0 ranging from 0.42 to 0.90, indicating the mesoporous nature of the material [6]. The specific surface area of CB-rGO is 208 m^2/g, the total pore volume is 0.12 cm^3/g, and the average pore diameter is 3.16 nm, indicated a mesoporous material based to the pore size [7].

3.2. Adsorption study

Fig. 2a confirms that as the pH of the solution increases, the best efficiency result was achieved at pH 8.0, which was maintained for further studies, resulting in a removal rate of 96%. Fig. 2b illustrates the influence of adsorbent mass on phenol removal. In this study, the maximum phenol removal rate of 96% was achieved using 10 mg of CB-rGO. Fig. 2c shows the effects of contact time between CB-rGO and phenol, which is also related to the initial concentration of the solution. The equilibrium in the adsorption process was reached at 120 min, with a 96% removal rate. Finally, Fig. 2d shows that the phenol removal percentage increases with rising temperature, ranging from 20 to 60 °C. Since this increase is subtle within the evaluated range, and considering the additional costs associated with operating at higher temperatures, it is likely more

advantageous to operate between 20 and 40 °C, balancing removal efficiency and energy costs.

Table 1 provides parameters for the Langmuir, Toth, and Khan adsorption models, fitted to the experimental isotherm data. Fig. 3a illustrates the adsorption isotherms and corresponding non-linear fits, all showing high accuracy with R^2 values close to 1. The table shows that the Toth model has the highest R^2, making it the adsorption isotherm model that best describes the studied system. It is also noted that the *n* parameter of the Toth equation presented values far from 1, suggesting that the surface of the CB-rGO sample is significantly heterogeneous.

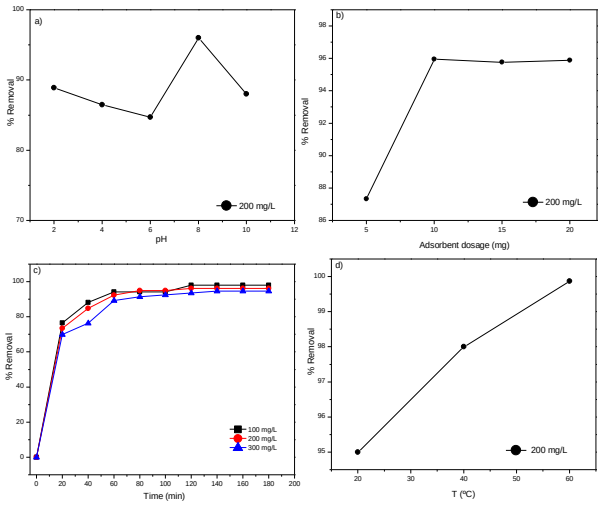

Fig. 2. Effects of (a) pH level, (b) adsorbent mass, (c) initial phenol concentration, and (d) temperature.

Table 1. Parameters for Langmuir, Toth, and Khan isothermal adsorption models.

Isotherm models	Parameters	Value (non-linear)
Langmuir	q_m (mg/g)	240.26
	K (L/mg)	0.103
	R^2	0.997
Toth	q_m (mg/g)	250.67
	K (L/mg)	10.77
	n (-)	0.26
	R^2	0.998
Khan	q_m (mg/g)	97.56
	K (L/mg)	0.443
	n (-)	0.39
	R^2	0.995

3.3. Adsorption kinetics

As presented in Table 2 and Fig. 3b, the Elovich kinetic model yielded an average R^2 value of 0.992, indicating excellent fit to experimental data. Furthermore, the adsorption capacity at equilibrium exhibited slight deviation from experimental results. These observations suggest the phenol adsorption process onto CB-rGO is accurately described by the Elovich model, reinforcing its suitability for modeling the kinetics of this system with high accuracy.

Table 2. Parameters for the Elovich kinetic model.

Conc. (mg/L)	q_{exp} (mg/g)	k_1 (min^{-1})	q_{cal} (mg/g)	R^2
100	336.4	0.042	344.78	0.990
200	531.4	0.025	525.62	0.991
300	650.1	0.017	685.55	0.994

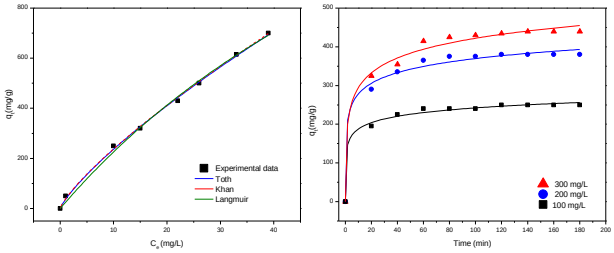

Fig. 3. (a) Adsorption isotherm plots with model fits and (b) adsorption kinetics plots.

3.4. Reuse study

Fig. 4 illustrates that by the fourth cycle, the removal rate undergoes a subtle deceleration, reaching 84% removal. The slight decrease in efficiency between the third and fourth cycles is minimal, highlighting CB-rGO synthesized from cellulosic biomass as an excellent candidate for repeated adsorption applications.

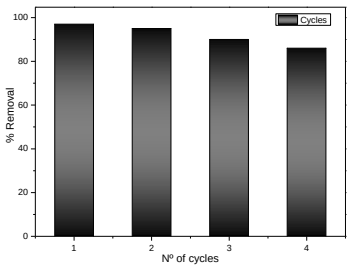

Fig. 4. Phenol removal efficiency (%) over multiple adsorption cycles using CB-rGO.

4. Conclusion

In this study, we report the synthesis, structural characterization, and application of CB-rGO as an efficient adsorbent for phenol removal. XRD and Raman analyses confirm the formation of rGO nanosheets. The Toth model provided the best fit, with the *n* parameter showing a value different from 1, suggesting a heterogeneous surface. This assumption is further supported by the Elovich kinetic model, which also demonstrated an excellent fit to the experimental data, indicating adsorption occurred on a heterogeneous surface, consistent with the nature of CB-rGO. Both models are in agreement, reinforcing the expected behavior of the system.

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