MACEIÓ - ALAGOAS
EBA 15
15° ENCONTRO BRASILEIRO SOBRE ADSORÇÃO
15th Brazilian Meeting about Adsorption

Study of Graphite Oxide Suspension as Adsorbent of Quinoline in the Aqueous Medium: Equilibrium, Regeneration and Phytotoxicity.

Gabriel Filipe Oliveira do Nascimento[a], Maurício Alves da Motta Sobrinho[a], Marta Maria Menezes Bezerra Duarte[a]

[a] *Universidade Federal de Pernambuco (UFPE), Av. Professor Moraes Rego 1235, Recife 50670-901, Brazil*

Abstract

Quinoline is a byproduct contaminant of the petroleum refineries, due to its toxicity to the environment, methods like adsorption are used to remove it from the aqueous medium. The aim of this work is to test graphite oxide (GO) suspension as an adsorbent for quinoline. Two GO samples were produced utilizing the Hummers method, after that preliminary tests were carried out to evaluate the viability of the adsorbents, then an adsorption equilibrium study was made utilizing the nonlinear isotherm models of Langmuir, Freundlich and Sips, regeneration tests were performed as well as phytotoxicity assays with cucumber seeds. The GO samples were capable of adsorbing more than 80% of quinoline solution with a q = 40 mg.g^{-1}. Langmuir and Sips isotherms were the best fit for the experimental data overlapping each other (R^2 = 0,995), with a q_{max} value of 74,8 mg.g^{-1}. The regeneration tests showed that it is possible to reutilize the material during multiple cycles, and the phytotoxicity essays showed an improvement in the seed's growth after the adsorption treatment. The GO in this work presented a good adsorption capacity when compared to other works presented in the literature, which indicates that the material is a good alternative as an adsorbent for quinoline in the aqueous medium.

Keywords: Quinoline; Graphite oxide; Equilibrium Study; Reutilization.

1. Introduction

Quinoline is a nitrogenous aromatic organic compound generated as a byproduct of the petroleum refineries processes, commonly present as a contaminant in the aqueous part of the industrial effluent. Due to its toxicity this substance needs to be removed from the aqueous medium, however conventional treatment methods present difficulties in removing quinoline from the effluent [1, 4, 5, 6].

Therefore, other treatment methods such as adsorption can be used to remove contaminants from the aqueous medium. When compared to other alternatives, adsorption has the advantage of being simple, efficient, versatile and applicable on industrial scale [2, 5].

Different materials can be utilized as adsorbents, and Graphite Oxide (GO) is one of them. It stands out due to its high surface area, oxygenated functional groups present on its surface such as hydroxyl (O-H), epoxy (C-O), and carbonyl (C=O), and physicochemical properties turning it an attractive material for removal of polar organic substances such as quinoline. GO can be synthesized utilizing the method proposed by Hummers and Offeman (1958), producing a suspension that can be utilized as adsorbent [3, 5].

The aim of this work is to utilize the GO suspension as an adsorbent for quinoline, studying the adsorption equilibrium with nonlinear isotherms models, regeneration of the material, and carry out phytotoxicity essays utilizing cucumber seeds as a bioindicator.

2. Materials and Methods

2.1 Preliminary tests

2 GO samples were produced using the Hummers method (GO 1 and GO 2). After that, preliminary tests were conducted in duplicate for each GO

sample utilizing 50 mL of quinoline solution (30 mg.L^{-1}) and 0,6 g.L^{-1} of GO, which were stirred in a shaker for 1 h (250 rpm, 298 K). The samples were microfiltered and quantified utilizing an UV-Vis spectrophotometer [4].

2.2 Adsorption equilibrium study

The adsorption equilibrium experiments were carried out in duplicate, where the initial concentration of quinoline varied from 5 to 50 mg.L^{-1}. Then 50 mL of the quinoline solutions were put in contact with 0,6 g.L^{-1} of adsorbent for 1 h (250 rpm, 298 K), subsequently filtered and quantified. The nonlinear equilibrium isotherm models of Langmuir, Freundlich and Sips were applied to the experimental data [5].

The nonlinear Langmuir equation is showed in Equation 1.

$$q = \frac{q_{max} K_L C_e}{1 + K_L C_e} \quad (1)$$

Where q is the adsorptive capacity of the material (mg.g^{-1}), K_L is the equilibrium adsorption constant of the Langmuir model (L.mg^{-1}) q_{max} is the maximum adsorptive capacity (mg.g^{-1}) and C_e is the concentration in the equilibrium.

The nonlinear Freundlich equation is demonstrated in Equation 2.

$$q_e = K_F C_e^{1/n} \quad (2)$$

Where K_F is the equilibrium adsorption constant of the Freundlich model (mg$^{(1-1/n)}$.g^{-1}.L$^{1/n}$), q_e is the adsorptive capacity at equilibrium (mg.g^{-1}) and *n* is a material heterogeneity constant of the Freundlich model.

The nonlinear Sips equation is described by Equation 3.

$$q_e = \frac{q_S.K_S.(C_e)^m}{1+K_S.(C_e)^m} \quad (3)$$

Where q_s is the maximum adsorptive capacity of the Sips model, K_S is the equilibrium adsorption constant of the Sips model (L.mg^{-1})^m and m is the heterogeneity constant of the Sips model material.

2.3 Regeneration tests

The adsorption tests were performed in duplicate, initially 0.6 g.L^{-1} of adsorbent was put in contact with 50 mL of an aqueous quinoline solution (30 mg.L^{-1}) under constant stirring (250 rpm at 298 K) for 1 h in a shaker. Then, the separation was conducted by centrifugation (8,000 rpm), and the supernatant underwent microfiltration before the final concentrations were measured using a UV-visible spectrophotometer. According to the literature [5], for desorption of quinoline, 25 mL of 0.3 mol.L^{-1} NaOH were used as eluent, which was added to each vial containing the adsorbent samples. The system remained under stirring at 250 rpm for 1 h at 298 K. Separation was performed by centrifugation (8,000 rpm), and the adsorbent samples were washed with distilled water until reaching pH 7. Then, the adsorbent samples were subjected to a new adsorption cycle. The adsorptive capacity of the material (q) was calculated for each cycle, for three adsorption-desorption cycles.

2.4 phytotoxicity essays

Phytotoxicity essays were performed using *Cucumis sativus L* (cucumber) seeds with a germination time of 4 to 8 days. The seeds were exposed to 4 mL of quinoline solution (30 mg.L^{-1}) before and after adsorptive treatment with GO for 1 h, 250 rpm, 298 K. Distilled water was used for the negative control and a solution of 0.02 g.L^{-1} of $Al_2(SO_4)_3$ in the same amount (4 mL) for the positive control, where the germination index (GI) should be greater than 90%. Five replicates were performed for the samples before and after adsorptive treatment and duplicates for the negative and positive controls. The relative growth index (RGI) and the germination index were calculated, according to Equations 4 and 5 respectively [7].

$$RGI = \frac{RLS}{RLC} \quad (4)$$

$$GI\ (\%) = \frac{RLS\ x\ GSS}{RLC\ x\ GSC} x100 \quad (5)$$

Where *RLS* is the radicle length of the sample (cm), *RLC* represents the radicle length of the negative control (cm), *GSS* corresponds to the number of germinated seeds in the sample and GSC is the number of germinated seeds in the negative control.

3. Results and Discussion

3.1 preliminary tests

The results of the preliminary tests are described in Table 1.

Table 1. Preliminary test results.

Samples	Removal (%)	q (mg.g^{-1})
GO 1	83,89%	39,27
GO 2	85,21%	40,03

According to Table 1 both GO samples demonstrated relatively high removal percentage and a good adsorption capacity when compared to other materials for quinoline adsorption [1, 2, 6]. The good results can be related the interaction between quinoline, which is a basic organic compound, and the oxygenated functional groups present on the adsorbent surface. Due to the similar results, by the end of this study GO 1 and 2 were mixed into one sample (GO) and used for the rest of the work.

2.2 Adsorption equilibrium study.

After the quinoline samples were measured in the UV-Vis spectrophotometer the experimental data were collected and the Langmuir, Freundlich and Sips models in their nonlinear form were applied, producing the graph shown in Figure 1.

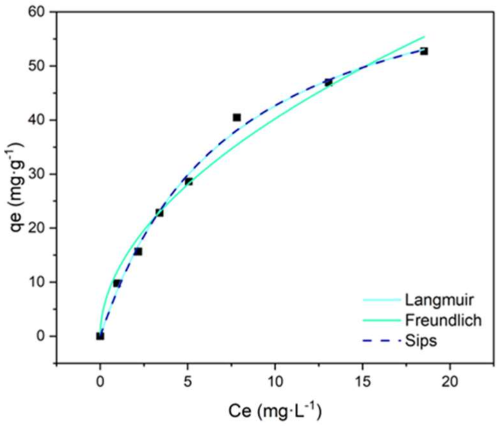

Figure 1. Equilibrium adsorption of quinoline and GO. (C_0 = 30 mg·g^{-1}, m/V = 0,6 g·L^{-1}, t = 1h, pH = 6,8, s. s. = 250 rpm, T = 298 K).

As can be seen in figure 1 Langmuir and Sips isotherms overlap each other, whereas the Freundlich isotherm is different from them. The parameters of the isotherms can be seen in table 2.

Langmuir and Sips isotherm models are the ones that fit better the experimental data (R^2 = 0,995), they have similar values (q_{max} and q_s, K_L and K_S), with the *m* value being exactly 1, with indicates the tendency of the Sips model to the Langmuir model.

The Freundlich model on the other hand presents n>1 which indicates the favorability of the adsorption but doesn't fit the experimental data better than the other models. The equilibrium study results show that the adsorption mechanism is better represented by the Sips model with the tendency to the Langmuir model, which indicates a monolayer model where the adsorption depends on the concentration of quinoline in the medium and the interaction between the molecules of adsorbent and adsorbate.

Table 2. Isotherm model parameters.

Models	Parameters	Values
Langmuir	q_{max} (mg·g^{-1})	74,8±3,4
	K_L (L·mg^{-1})	0,13±0,02
	R^2	0,995
	χ^2	1,878
Freundlich	K_F (mg$^{(1-1/n)}$·g^{-1}·L$^{1/n}$)	12,2±1,3
	n	1,9±0,2
	R^2	0,981
	χ^2	7,45
Sips	q_s (mg·g^{-1})	73,1±9,7
	K_S (L·mg^{-1})$^{m'}$	0,13±0,01
	m	1,0±0,1
	R^2	0,995
	χ^2	2,240

The results for GO in this study are better [1, 2, 6] or on par [5] with others presented in the literature.

2.3 Regeneration tests

The results of the regeneration test can be seen in Figure 2.

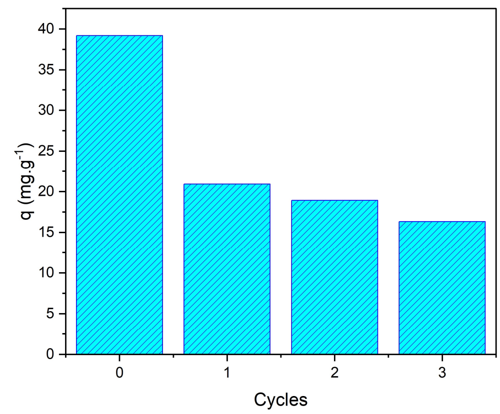

Figure 2. Regeneration tests of GO. (C_0 = 30 mg·g^{-1}, m/V = 0,6 g·L^{-1}, t = 1 h, pH = 6,8, s. s. = 250 rpm, T = 298 K)

Figure 2 demonstrates the difference between de adsorption capacity of the material in the different cycles, from the graph it can be inferred that the greatest loss in adsorption capacity is between the cycles 0 and 1, with the subsequent cycles having a steadier loss of the parameter. The cause of this is the loss of material during the first cycle which occurred due to equipment limitations, the centrifuge speed used in this work made so that the smallest adsorbent molecules could not be separated effectively, which in turn caused the loss of those adsorbent molecules that continued to be in the supernatant [5].

It is advised the usage of a more potent separation mechanism so that the material can be reutilized more efficiently. Nevertheless, the regeneration study demonstrated that the reutilization of the material is possible despite the loss in efficiency.

2.4 Phytotoxicity essays

The result of the phytotoxicity essays with cucumber seeds are shown in figure 3.

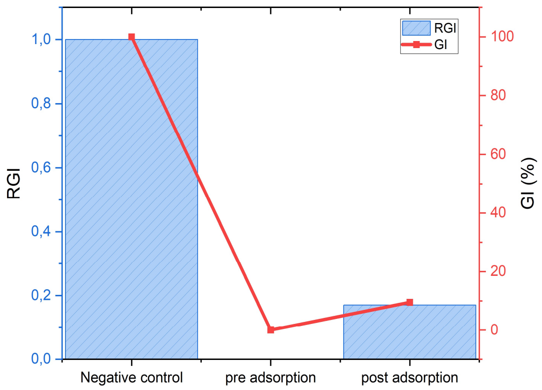

Figure 3. Results of the phytotoxicity essays using cucumber seeds.

As described in figure 3 the phytotoxicity results demonstrate that there is an improvement both in the RGI and the GI values when the post adsorption solution is compared with the pre adsorption solution of quinoline, which didn't have a single seed that grow. Even though the improvement shown is little (around 10 % for GI and around 17% for RGI) it is an indication that the adsorption process was beneficial to the studied seeds [5, 7].

4. Conclusion

The results of the preliminary tests demonstrated the adsorption capacity of the Graphite Oxide to remove quinoline from the aqueous medium, with a q value of approximately 40 $mg.g^{-1}$.

The equilibrium studies showed the similarities between the Langmuir and Sips models which better represented the experimental data with a q_{max} value of 74,8 $mg.g^{-1}$. The regeneration tests demonstrated that despite de loss of efficiency due to equipment limitations it is still possible to reutilize the material in the process. Phytotoxicity essays pointed out little improvement in the growth of the cucumber seeds used as a bioindicator.

When compared with literature results the GO synthesized in this study shows results better or on par with other materials, which indicates that it can be utilized as an alternative adsorbent for quinoline in the aqueous medium.

Acknowledgements

To UFPE, CNPQ, CAPES and PRH 30.1 for fomenting my research, to GPTA group, LIMA and LEAQ laboratories for the support and apparatus.

References

[1] Bian, Y.; Sun, H.; Luo, Y.; Gao, Q.; LI, G.; Wang, Y. Effect of inorganic salt ions on the adsorption of quinoline using coal powder. Water Science and Technology, (2018) 496-505.

[2] Feng, X., Ma, X., Li, N., Shang, C., Yang, X., Chen, X. D. Adsorption of quinoline from liquid hydrocarbons on graphite oxide and activated carbons. RSC Advances, (2015) 74684-74691.

[3] Hummers, W. S., Offeman, R. E. Preparation of graphitic oxide. Journal of the American Chemical Society, (1958) 1339.

[4] Kang, W., Cui, Y., Yang, Y., Zhao, Z., Wang, X., Liu, X. An acid induction strategy to construct an ultralight and durable amino-functionalized graphene oxide aerogel for enhanced quinoline pollutants extraction from coking wastewater. Chemical Engineering Journal, (2021) 128686.

[5] Santos, M. B. S.; Nascimento, B. F.; Ghislandi, M. G.; Araujo, C. M. B.; Motta Sobrinho, M. A. Production and characterization of graphene-based nanocomposites of different natures and their applications in aqueous quinoline adsorption: A comparative study. Case Studies in Chemical and Environmental Engineering, (2024) 100605.

[6] Wang, L.; Gao, Q.; Li, Z.; Wang, Y. Improved removal of quinoline from wastewater using coke powder with inorganic ions. Processes, (2020) 1-14.

[7] Young, B. J.; Riera, N. I.; Beily, M. E.; Bres, P. A.; Crespo, D. C.; Ronco, A. E. Toxicity of the effluent from an anaerobic bioreactor treating cereal residues on Lactuca sativa. Ecotoxicology and Environmental Safety, (2012) 182-186.