#### **RESEARCH ARTICLE**



### Application of graphene nanosheet oxide for atrazine adsorption in aqueous solution: synthesis, material characterization, and comprehension of the adsorption mechanism

Rodrigo de Souza Antônio<sup>1</sup> · Ana Carolina Sestito Guerra<sup>1</sup> · Murilo Barbosa de Andrade<sup>1</sup> · Letica Nishi<sup>1</sup> · Aline Takaoka Alves Baptista<sup>2</sup> · Rosângela Bergamasco<sup>1</sup> · Angélica Marquetotti Salcedo Vieira<sup>3</sup>

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#### Abstract

The present study aimed to investigate the application of graphene oxide (GO) as adsorbent material for the removal of atrazine (ATZ). The material produced was characterized to investigate the characteristics and applied as an adsorbent. The material obtained after the synthesis process presented oxygenated functional groups, which contributed to the development of a good adsorbent material. Studies were carried out to verify the influence of adsorbent material mass and initial pH of ATZ solution in adsorption capacity. Kinetic study determined that pseudo-second-order model best describes adsorbate-adsorbent interaction, with equilibrium time of 72 h. The effect of temperature on the material adsorption capacity was also studied. The Langmuir isotherm is the best fit to describe adsorption process GO-ATZ and maximum adsorption capacity obtained was 23.844  $\pm$  0.694 mg g<sup>-1</sup>, at 318 K. Variations in process energies were determined, being a spontaneous adsorption capacity was studied; the conclusion was that the presence of electrolytes affects the adsorption capacity of the material.

Keywords Herbicide · Emerging contaminant · Electrolytes · Removal · Graphene · Adsorption

### Introduction

In recent years, several studies have reported the presence of numerous chemical compounds harmful to the environment and human health in surface and groundwater, raising concerns about the hazardous effects of these contaminants (Mijangos et al. 2018; Pinasseau et al. 2019). These chemical compounds are denominated emerging contaminants (ECs). ECs are chemical compounds of various kinds and origins,

Responsible Editor: Tito Roberto Cadaval Jr.

- <sup>1</sup> Department of Chemical Engineering, State University of Maringá, 5790 - Colombo Avenue, Maringá, Parana 87020-900, Brazil
- <sup>2</sup> Federal Technological University of Paraná, 1233, Street Rosalina Maria Ferreira, Campo Mourão, Paraná, Paraná 87301-899, Brazil
- <sup>3</sup> Department of Food Engineering, State University of Maringá, 5790
   Colombo Avenue, Maringá, Parana 87020-900, Brazil

such as chemicals present in personal care products, pharmaceuticals, illicit drugs, various metabolites, and agrochemicals (herbicides, insecticides, and fungicides) (Pinasseau et al. 2019; Castiglioni et al. 2018; Mei et al. 2018).

Occurrence of ECs in water bodies is a global problem as they are aggravating the living conditions (Almeida et al. 2018; Munari et al. 2019). In addition, the ECs are still a problem in several parts of the world, such as Europe (Mijangos et al. 2018; Castiglioni et al. 2018), America (Griffero et al. 2019; Hansen et al. 2019; Sposito et al. 2018), Asia (Mei et al. 2018; Khalid et al. 2018), and Africa (Rimayi et al. 2018). Moreover, there are reports that ECs are capable of generating problems across geographical boundaries (Vystavna et al. 2018).

Due to associated risks for life and environment, herbicides are a class of ECs that are arousing alerts in the scientific community as for the presence in water bodies (Sposito et al. 2018; Sun et al. 2018). Among herbicides that are being found in surface waters, atrazine (ATZ) has been reckoned as a potential generator of environmental damage (Sposito et al. 2018; Araújo et al. 2018; Sai et al. 2018). Although this

Angélica Marquetotti Salcedo Vieira amsvieira@uem.br

herbicide is banned in European Union countries, atrazine is legalized in several countries around the world, being detected in rivers in countries like Brazil (Sposito et al. 2018) and the USA (Hansen et al. 2019) as well as in drinking water in Canada (Montiel-León et al. 2019).

Because of the presence of this herbicide in water bodies, some countries regulate the maximum tolerable limit of this and other herbicides in water for human consumption, among the standards that regulate the presence of atrazine in portable water are Council Directive 98/83/EC (EU), 0.1  $\mu$ g L<sup>-1</sup>; Ordinance No. 5 of 2017, Annex XX, of the Ministry of Health (Brazil), 2  $\mu$ g L<sup>-1</sup>; and Drinking Water Standards and Health Advisories (USA), 3  $\mu$ g L<sup>-1</sup> (Council Directive 1998; Brasil 2017; USA 2018).

Due to the concern with the presence of ATZ in water, a risk offered by this herbicide, several studies are being developed to solve this problem, such as oxidation process (Jing et al. 2018), biosorption (Cusioli et al. 2019), catalysts (Zhang et al. 2018), cavitation with hybrid treatment (Jawale et al. 2018), and application of chemical catalysts and graphene for degradation of atrazine (Wu et al. 2018).

The adsorption technique is being extensively studied to remove emerging contaminants, as it does not generate chemical reaction by-products, it is low cost, and it is easy to implement and operate (Souza et al. 2019). There are numerous adsorbent materials that are being applied to remove herbicides from water, such as bioadsorbents (Cusioli et al. 2019), clays (Souza et al. 2019), activated carbon (Herath et al. 2019), and biochar (Herath et al. 2019; Gámiz et al. 2019). There are countless adsorbent materials being studied to remove emerging contaminants, and graphene oxide (GO) has present a promising application for removal of dyes (Wei et al. 2018), pharmaceuticals (Hiew et al. 2019), and toxic metal (Wei et al. 2018; Wang et al. 2018). The application of GO as an adsorbent material has several advantages such as chemical stability, high surface area, and availability of chemical groups on its surface (de Mendonça et al. 2018; Verma et al. 2018).

Thus, considering the presence of emerging contaminants in water bodies, an ongoing global problem, and the presence of herbicide atrazine in water bodies, still a reality in countries like Brazil and the USA, the present work has the purpose of studying the application of GO as an adsorbent material for the removal of herbicide atrazine.

#### Materials and methods

#### Synthesis of graphene oxide

Graphene oxide was synthesized according to the Hummer's method (Hummers and Offeman 1958) and modified by Kovtyukhova (1999). This process consists of oxidation of

graphite using oxidizing reagents to transform graphite into graphene oxide.

#### Characterization of the adsorbent material

For the characterization of the synthesized adsorbent material, scanning electron microscopy coupled with energy-dispersive X-ray spectroscopy (SEM-EDX), in microscope (QUANTAFEI-250) and the sample coated with gold (Au), was used. Analyses of zeta potential ( $\zeta$ ) were also carried out at different pH levels with the objective of investigating charge variation present in double electrical layer of the material. The acidity or basicity was corrected with NaOH and HCl (Beckman Coulter Delsa Nano Zeta Submicron Size Analyzer<sup>TM</sup>) and the structure was checked with transmission electron microscopy (TEM) (JOEL JEM-1400). X-ray diffraction analysis was performed to investigate the crystalline structure of the material (Bruker-D8 Advance), and infrared spectroscopy (Vertex70v, Bruker) was performed in order to identify functional groups present in material structure and chemical iterations formed after adsorption process.

## Influence of solution pH and concentration on the adsorption capacity

The experiments were carried out in batches to investigate the influence of two factors: adsorbent concentration (mass of adsorbent/volume of ATZ solution) and initial pH of ATZ solution on adsorption capacity. The herbicide solution was prepared using distilled water and commercial atrazine supplied by Nortox S/A® (50% w/v). The studied factors were varied at three levels. The adsorbent mass was varied by 10 mg, 20 mg, and 30 mg for a solution volume of 20 mL. The solution pH was varied by  $5.0 \pm 0.2$ ,  $7.0 \pm 0.2$ , and  $9.0 \pm 0.2$ . The experiments were carried out in duplicates, with a time of 24 h, temperature of 298  $\pm$  1 K, initial concentration of atrazine solution of 10.0 mg  $L^{-1}$ , and orbital agitation of 100 rpm. After the established time, solutions were filtered using a qualitative cellulose acetate membrane with a 0.45-µm opening and permeate was read on a UV-vis spectrophotometer (Hach, DR 5000) at a wavelength of 222 nm. Adsorption capacity of the material was determined according to Eq. (1). Having determined the condition that provides the greatest adsorption capacity, kinetics and isotherm of adsorption process were performed:

$$q_i = \frac{(C_0 - C_i)V}{m_{\text{ads}}} \tag{1}$$

where  $q_i$  is the material adsorption capacity (mg g<sup>-1</sup>),  $C_0$  is the initial ATZ concentration (mg L<sup>-1</sup>),  $C_i$  is the remaining ATZ concentration at given time (*i*) (mg L<sup>-1</sup>),  $m_{ads}$  is the adsorbent mass (mg), and *V* is the solution volume (mL).

#### **Kinetic study**

In an established condition that provides the greatest adsorption capacity, the kinetic study was carried out. The experiment was performed in duplicate, at a constant temperature of  $298 \pm 1$  K, initial concentration of ATZ solution of 10.0 mg L<sup>-1</sup>, and GO-ATZ contact time varied from 0 to 120 h. Kinetic parameters studied were estimated according to pseudo-first-order (PFO) model (Lagergren 1898), Eq. (2):

$$q_{\rm t} = q_{\rm e} \left( 1 - e^{-k_1 t} \right) \tag{2}$$

where  $q_e$  is the material adsorption capacity at equilibrium (mg g<sup>-1</sup>), and  $k_1$  is the kinetic constant of adsorption process (h<sup>-1</sup>). Another kinetic model studied was the pseudo-second order (PSO) (Blanchard et al. 1984; Ho and McKay 1999), Eq. (3):

$$q_{\rm t} = \frac{q_{\rm e}^2 k_2 t}{1 + q_{\rm e} k_2} \tag{3}$$

where  $k_2$  is the kinetic constant of the adsorption process (g mg<sup>-1</sup>). Then, after determining equilibrium time, the experiment for adsorption isotherm was performed.

#### Isotherm of adsorption

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To investigate the influence of temperature on the material adsorption capacity, experiments were performed at varying initial concentration of ATZ solution from 2.0 to 30.0 mg L<sup>-1</sup>, being the experimental conditions of initial pH of solution and concentration of adsorbent whose adsorption capacity presented the greatest value. As a guarantee that the system would reach the adsorption equilibrium, the established contact time was twice the time necessary for the system to reach equilibrium. Thus, isotherms at temperatures of  $298 \pm 1$  K,  $308 \pm 1$  K, and  $318 \pm 1$  K were studied. Hence, to understand the influence of variation of concentration and temperature on adsorption capacity of the material, the Langmuir isotherm model was applied (Langmuir 1916), Eq. (4):

$$q_{\rm e} = \frac{q_{\rm max} K_{\rm L} C_{\rm e}}{1 + K_{\rm L} C_{\rm e}} \tag{4}$$

where  $q_{\text{max}}$  is the maximum adsorption capacity of the material at referred temperature (mg g<sup>-1</sup>),  $K_{\text{L}}$  is the adsorption constant of the model (L mg), and Ce is the concentration of equilibrium (mg L<sup>-1</sup>). Another model of isotherm studied was that of Freundlich (1906), Eq. (5):

$$q_{\rm e} = K_{\rm F} C_{\rm e}^{\overline{n}} \tag{5}$$

where  $K_{\rm F}$  is the constant of Freundlich isotherm (L g<sup>-1</sup>)<sup>1/n</sup> and n is a dimensionless parameter that represents adsorbate-adsorbent interaction force.

#### Adsorption thermodynamics

To determine variation of thermodynamic parameters of adsorption process with the influence of temperature, Gibbs free energy ( $\Delta G$ ), entropy ( $\Delta S$ ), and enthalpy ( $\Delta H$ ) variations were studied. The thermodynamic relation Eq. (6) and Von't Hoff equation Eq. (7) were used to determine these parameters (Zhu et al. 2017; Tran et al. 2020):

$$\Delta G = \Delta H - T \Delta S \tag{6}$$

where  $\Delta G$  is the change in Gibbs free energy (kJ mol<sup>-1</sup>),  $\Delta H$  the change in enthalpy (kJ mol<sup>-1</sup>), *T* the absolute temperature of the system (K), and  $\Delta S$  the entropy variation of the system (J mol<sup>-1</sup>K<sup>-1</sup>).

$$LnK_{e} = \frac{\Delta S}{R} - \frac{\Delta H}{RT}$$
(7)

where *R* is the thermodynamic constant (J mol<sup>-1</sup>K<sup>-1</sup>) and  $K_e$  the equilibrium constant of adsorption process determined according to the recommendations of Zhu et al. (2017).

# Influence of the presence of electrolytes on the adsorption capacity

In order to investigate the influence of the presence of ions on GO adsorption capacity, parameters such as concentration and the presence of different cations can influence on GO adsorption capacity. Thus, the influence of magnesium chloride (MgCl<sub>2</sub>), calcium chloride (CaCl<sub>2</sub>), and sodium chloride (NaCl) salts on adsorption capacity was studied, as already studied by Zhu et al. (2017) for adsorption of metformin. For this, the same molar ratios of 0.1 mol, 0.2 mol, and 0.3 mol of salts dissolved in ATZ solution were verified. The study was carried out in duplicate, with a contact time of 24 h, a temperature of 298  $\pm$  1 K, and initial concentration of ATZ solution of 10.0 mg L<sup>-1</sup>.

#### **Fitting data**

The models were adjusted according to the Levenberg-Marquardt algorithm, with 100 iteration points, maximum limit of 400 iterations and tolerance of  $10^{-9}$ . The criteria for determining the best fit were  $r_{adj}^2$  and  $\chi^2$ . The experimental data were plotted together with respective standard deviations.

#### **Results and discussion**

#### Characterization of the adsorbent material

Figure 1a and b referring to the EDX analysis allow for the identification of differences in elemental composition on the

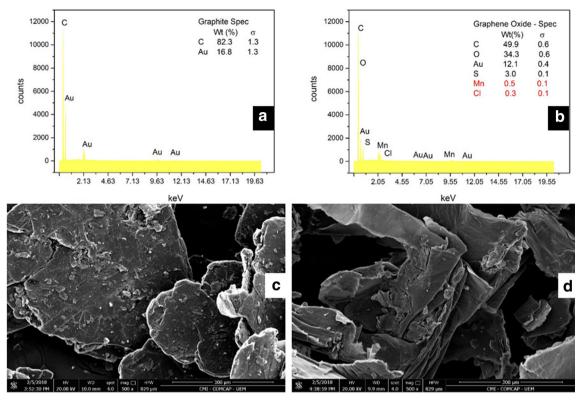


Fig. 1 EDX—graphite (a) and GO (b). SEM—× 500 magnification and 300-µm scale—graphite (c) and GO (d)

surface of graphite and graphene oxide. Graphite presents a predominantly carbon surface composition (Fig. 1a), while GO has a surface composed of chemical elements such as carbon, oxygen, sulfur, and a small amount of manganese, as shown in Fig. 1b. This finding allows us to have evidence of success of the synthesis process. When analyzing graphite surface morphology (Fig. 1c) and graphene oxide (Fig. 1d), using a scanning electron microscope, it is possible to verify differences on the surface structures of the materials.

From the XRD analysis of the materials (Fig. 2), it is possible to observe that the peak of greater intensity corresponding to graphite is obtained at  $2\Theta = 26.66^{\circ}$  (002), referring to the formation structure obtained by planes of carbon atoms. For the GO obtained from graphite, the highest intensity peak occurs at  $2\Theta = 10.39^{\circ}$  (001). This modification in structure is related to spacing of planes generated by insertions of oxygenated groups (Ain et al. 2018). In addition, it is possible to state that the observed change occurs due to the distance from the planes that constitute the crystalline structure of the material, since the graphite has a distance between planes equal to d = 3.38 Å, while GO is d = 8.64 Å generated by insertion of oxygenated groups, as estimated by Bragg's law (Guo et al. 2020; Kvick et al. 1999). The insertion of oxygenated groups between the GO layers after graphite oxidation can form mono-, bi-, or multilayer GO structures according to the degree of oxidation obtained during synthesis of the material, leading to separation of planes of graphite sheets and

promoting changes in the material structure (de Mendonça et al. 2018).

Transmittance electron microscopy (Fig. 3) shows GO planar character and consists of few layers, giving a translucent aspect to the material. Another analysis that reinforces success of the synthesis process of the adsorbent material is the potential zeta ( $\zeta$ ) of GO (Fig. 4). Negative character present in double electrical layer is predominant for the entire pH range studied. This characteristic is attributed to oxygenated groups

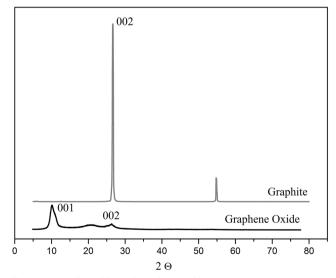
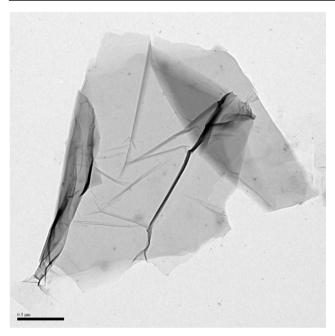


Fig. 2 XRD of graphite and graphene oxide



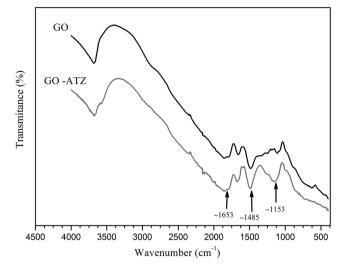


Fig. 5 IR spectrum of graphene oxide before and after adsorption process

Fig. 3 TEM graphene oxide in magnification  $\times$  25 and scale of 0.5  $\mu m$ 

present on the surface of the material and gives a greater or lesser negative character according to the degree of oxidation obtained in the synthesis of the material (Tan et al. 2017).

Functional groups present in GO can be identified with the analysis of IR spectroscopy (Fig. 5), being possible to verify the presence of carbon/oxygen bonds existing in the material, where ~  $3668 \text{ cm}^{-1}$  corresponds to –OH of water or hydroxyls present in the material structure. The valleys detected at ~  $1795 \text{ cm}^{-1}$ , ~  $1653 \text{ cm}^{-1}$ , ~  $1494 \text{ cm}^{-1}$ , and ~  $1107 \text{ cm}^{-1}$  correspond to the following functional groups present in GO structure: C=O corresponding to aldehyde or ketones, C=C referring to unsaturation present in carbon chain, O=CO characteristic of carboxylic groups, and C–O related to alcohol group, respectively. The last three chemical groups are being

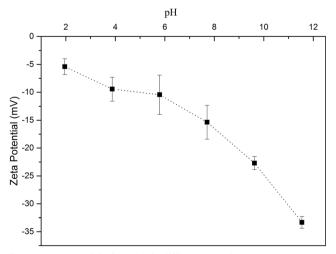


Fig. 4 Zeta potential of the GO in different pH values

identified as atrazine adsorption sites, as Fig. 6 suggests adsorption mechanism (Sheng et al. 2018; Lu et al. 2018).

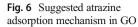
# Influence of solution pH and concentration on the adsorption capacity

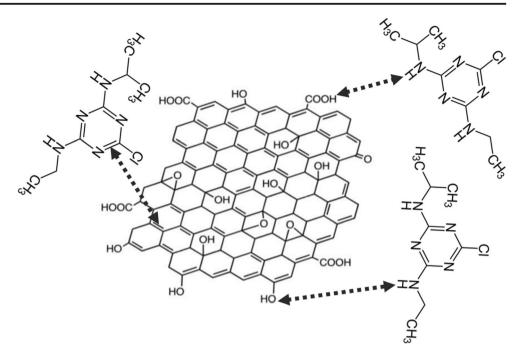
Results obtained for the determination of the best adsorption conditions allow for verification that in basic initial pH, there is a favoring increase of adsorption capacity (Fig. 7). The observed value of adsorption capacity went from  $q = (4.605 \pm 0.295) \text{ mg g}^{-1}$ , at pH 5, to  $q = (5.815 \pm 0.091) \text{ mg g}^{-1}$ , at pH 9. This increase can be explained by variation of charge present in the GO electric double layer in the studied pH range, as already justified by the potential zeta ( $\zeta$ ) analysis.

The influence of the material adsorbent mass in the adsorption process is greater as it increases, since the remaining ATZ concentration is lower due to more availability of active sites. However, with less mass, there is an increase in the adsorption capacity which can be attributed to the diffusion mechanism acting in a limited way in the adsorption process, since the time established for the experiment was fixed at 24 h. Influence of adsorbate-adsorbent contact time was studied in kinetic study. It was possible to determine that the best condition to carry out the experiment was at initial pH of ATZ solution equal to 9 and mass of GO equal to 10 mg.

#### **Kinetic study**

Analyzing the reduction of ATZ concentration over time (Fig. 8a), it is possible to verify that after 72 h, there is no variation of ATZ concentration in aqueous phase (dC/dt = 0), as verified with analysis of Fig. 8b, that is, the value of the concentration became constant according to the property of the infinitesimal calculus, being possible to affirm that the system

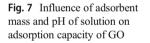


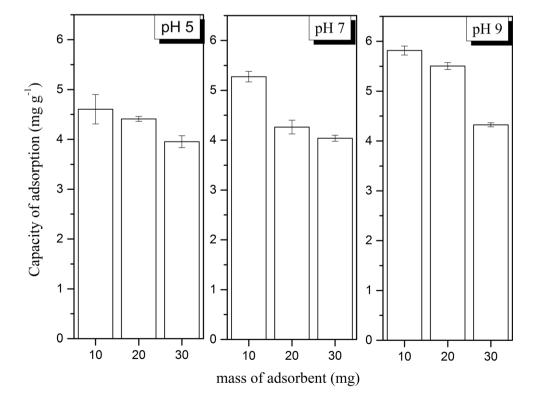


reaches chemical equilibrium. From the kinetic study (Fig. 8c), it was possible to verify that the model that best represents the phenomenon of adsorption studied is the PSO model, as shown in Table 1. The justification for the PSO model presenting a better fit to studied data set is attributed to the sharp slope present at the initial period of the kinetic study. This is explained by large availability of active sites at the beginning

of the adsorption process and it is reduced as ATZ is being adsorbed. Moreover, absence of adsorbate on the surface of the adsorbent material favors mass transfer mechanism, since the driving force responsible for mass transfer is the difference of concentration in the medium.

Figure 8d allows for the verification of the fidelity of the experimental data to the model that is best fitted according to





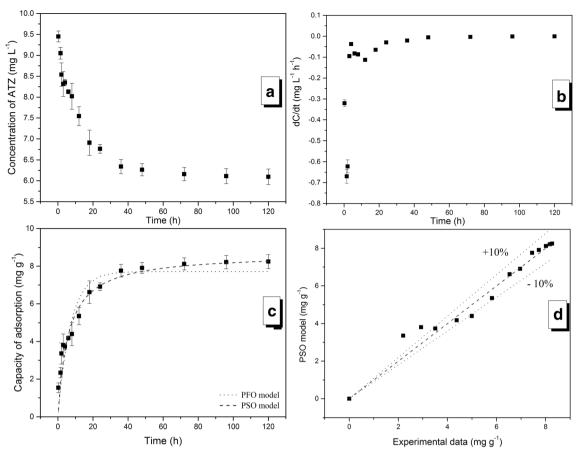


Fig. 8 Atrazine concentration reduction with time (a), ATZ concentration variation with time (b), adsorption capacity variation with time (c), and model validation (d). Experimental data (black square)

the adopted statistical criteria ( $r_{adj}^2$  and  $\chi^2$ ), enabling to determine if there was an error propagation during execution of experiments, as analyzed by the points on the graph bisector ( $y_{PSO model} = x_{Experimental data}$ ). Besides this criterion, adjustments of kinetic models were analyzed according to the statistic parameters  $r_{adj}^2$  and  $\chi^2$  (Table 1).

#### Isotherm of adsorption

Analyzing Fig. 9 and Table 2, it is possible to state that the model that best describes the adsorption phenomenon is the Langmuir isotherm model. Isotherm model proposed by

Table 1 Parameters of kinetic models studied in the present study

Model	Parameter	Value	$r_{\rm adj}^2$	$\chi^2$
PFO	$k_1 q_e$	$\begin{array}{c} 0.138 \pm 0.014 \\ 7.716 \pm 0.312 \end{array}$	0.911	5.799
PSO	$k_2$ $q_e$	$\begin{array}{c} 0.020 \pm 0.003 \\ 8.669 \pm 0.318 \end{array}$	0.952	3.159

Langmuir hypothesizes that adsorption sites of material have the same adsorption energy. Such hypothesis is possible to be applied because, as already analyzed in the IR spectrum (Fig. 5) and the mechanism suggested in Fig. 6, adsorption occurs through weak chemical interactions (Van der Waals force) and

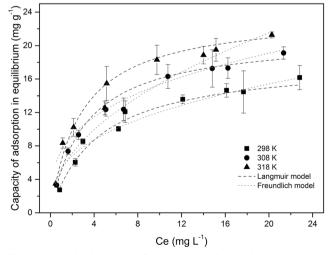


Fig. 9 Adsorption isotherms of atrazine in graphene oxide

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Langmuir model				
Temperature (K)	$q_{\max}(\text{mg g}^{-1})$	$K_{\rm L}({\rm L~mg})$	$r_{\rm adj}^2$	$\chi^2$
298	$18.233 \pm 1.363$	$0.228\pm0.037$	0.976	2.912
308	$21.114 \pm 0.656$	$0.317 \pm 0.022$	0.993	0.619
318	$23.844 \pm 0.694$	$0.356 \pm 0.022$	0.993	2.674
Freundlich model				
	$K_{ m F}$	n		
298	$5.326 \pm 0.124$	$0.355 \pm 0.009$	0.959	0.387
308	$7.402 \pm 0.172$	$0.316 \pm 0.009$	0.946	0.695
318	$5.106 \pm 0.226$	$0.480 \pm 0.018$	0.984	6.312

Table 2         Parameters of isotherm models studied in this s	study
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hydrogen bonds. Thus, it is possible to suggest that adsorption sites have very close adsorption energy, given hypothesis proposed by Langmuir.

In addition, analyzing Table 2, it is verified that adsorption process is favored with increase in temperature, indicating endothermic character. The maximum adsorption capacity ranges from 18.233  $\pm$  1.363 mg g  $^{-1}$  at 298 K to 23.844  $\pm$  $0.694 \text{ mg g}^{-1}$  at 318 K. In addition, a review in the literature showed that other authors studied different more adsorbent for removing atrazine from water, as shown in Table 3.

When buying with other works, it is possible to contact that there are different materials being developed and studied to be used as adsorbent materials, as shown in Table 3. However, a careful analysis should be made, since the Langmuir model was not always the one that best described the separation process observed by other authors. In addition, for comparison purposes, other factors should also be considered, such as adsorption conditions, physical and chemical phenomena involved, the yield of synthesis of the material, and physical characteristics of the material that may facilitate or hinder the separation process of the adsorbent material

#### Adsorption thermodynamics

Thermodynamic parameters obtained from Eq. (6) and Eq. (7) are shown in Table 4. It can be stated that increase in temperature makes adsorption process more spontaneous and increases, as already noted from Table 2, adsorption capacity. This increase is justified as variation in Gibbs free energy is greater as higher is the temperature  $(\Delta G^{318 \text{ K}} < \Delta G^{308 \text{ K}} < \Delta G^{298 \text{ K}} < 0).$ Furthermore, it was possible to quantify entropy variation, which represents the amount of energy irreversibly lost during adsorption process, being in the order of 108.415 J mol<sup>-1</sup>K<sup>-1</sup>. Enthalpy is the energy available through the adsorption system; the value of  $\Delta H$  found states that the adsorption process is endothermic, that is, the heat flow occurs from the environment to the adsorption system. The magnitude of variation of the enthalpy suggests that GO-ATZ has characteristically physical adsorption interactions with indications of the presence of stronger chemical bonds, such as hydrogen bonds, detected in the IR spectrum.

Absorbent		$q_{\text{max}} \text{ (mg g}^{-1} \text{) of the}$ Langmuir isotherm	References	
Magnetic multi-walled carbon nanotube		40.16	Tang et al. 2012	
Moringa oleifera Lam.		0.653	Coldebella et al. 2018	
Seed Shell Activated Carbon		3.235	Giwa et al. 2018	
Metal-organic framework	Type: ZIF-8 Type: UiO-66	6.78 2.57	Akpinar and Yazaydin 2018	
	Type: UiO-67	10.96		
Modified Moringa oleifera Lam. seed husks		4.297	Cusioli et al. 2019	
Graphene oxide impregnated with iron oxide		38.814	Andrade et al. 2019	
Graphene Oxide		18.233	This work	

Table 3 Maximum adsorption capacity obtained by the Langmuir isotherm at 298 K b different authors

Table 4 Thermodynamic parameters of adsorption process

Temperature (K)	$\Delta G \; (\text{kJ mol}^{-1})$	$\Delta H (\text{kJ mol}^{-1})$	$\Delta S (\text{J mol}^{-1}\text{K}^{-1})$
298 308 318	- 2.766 - 4.404 - 4.926	+ 29.480	+ 108.415

# Influence of the presence of electrolytes on the adsorption capacity

The influence of the presence of electrolytes in solution on adsorption capacity can be observed in Fig. 10. The presence of sodium chloride (NaCl), calcium chloride (CaCl<sub>2</sub>), and magnesium chloride (MgCl<sub>2</sub>) salts in the same molar ratio is unfavorable to the adsorption process, as there was a reduction in adsorption capacity when compared with solution without the presence of ions.

It is possible to verify that salts in which cations are bivalent (Ca<sup>2+</sup> and Mg<sup>2+</sup>); there is a greater reduction in adsorption capacity than salt whose cation is monovalent (Na<sup>+</sup>). The explanation is that the amount of dissociated ions in the system is different when comparing monovalent salt  $\left(YCl_{(s)} \rightarrow Y^+_{(aq)} + Cl^-_{(aq)}\right)$  with divalent salts  $\left(XCl_{2(s)} \rightarrow X^{2+}_{(aq)} + 2Cl^-_{(aq)}\right)$ . Furthermore, it was also possible to verify that adsorption capacity was reduced with increase in molarity of salts, and similar results were obtained by Tan et al. (2017) and Zhu et al. (2017).

### Conclusion

In this study, it is possible to conclude that graphene oxide (GO) can be used as an adsorbent material for removal of

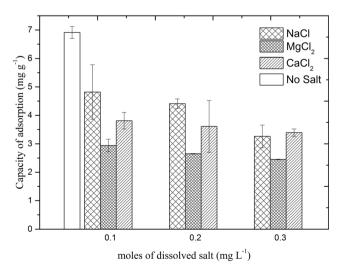


Fig. 10 Influence of the presence of salts on adsorption capacity of the material

atrazine herbicide. The chosen chemical synthesis process gives GO functional groups on its surface that is an excellent site for adsorption. Thus, adsorbent material chosen showed favorable characteristics for the adsorption of herbicide, as it was possible to verify with suggested adsorption mechanisms and maximum adsorption capacity determined. It was found that the most appropriate kinetic model to describe the process is the pseudo-second order. In addition, it is possible to affirm that there is an influence of temperature on adsorption capacity in equilibrium and that maximum adsorption capacity is favored with the increase of temperature. The maximum adsorption capacity varied from  $18.233 \pm 1.363 \text{ mg g}^{-1}$ at temperature of 298 K to 23.844  $\pm$  0.694 mg g<sup>-1</sup> at 318 K. Regarding adsorption thermodynamics, the process is considered thermodynamically favorable since variation in Gibbs free energy ( $\Delta G$ ) is negative. Heat exchanged during adsorption process is of an endothermic nature with an order of magnitude characteristic of physical adsorption promoted by  $\pi - \pi$  bonds together with hydrogen bonds. Finally, it was also possible to observe that the presence of electrolytes favors adsorption process as concentration of salts increases and according to characteristic of cation present in salt.

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