

## **Determination of immersion enthalpy of graphene oxide in aqueous solutions of emerging organic compounds with pharmaceutical activity.**

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### **Abstract**

The immersion enthalpy of a graphene oxide, GO, in aqueous solutions of phenol, salicylic acid, acetaminophen and methylparaben, which are emerging contaminants, is determined with the purpose of understanding the interaction process between the solid and the solution. The immersion of GO in water and benzene is also determined and from the results it is calculated that the adsorbent solid has a hydrophobic nature. The results are exothermic in nature with values for the change in the enthalpy of immersion,  $\Delta H_{imm}$ , in the aqueous solutions between -9.32 to -11.9 Jg<sup>-1</sup>.

Is calculated from the experimental results of  $\Delta H_{imm}$ , the change in the interaction enthalpy which leads to the fact that the different systems require energy to be able to carry out the displacement of the solvent in the adsorption process.

**Key words:** graphene oxide, emerging contaminants adsorption, immersion enthalpy, enthalpy contribution

### **Introduction**

Interest in the study of substances with biological activity present in water sources has increased in recent years because different countries on all continents reported the presence of such compounds in surface and groundwater. Water conservation is a global concern and is not limited only to developing countries since its use is increasing due to population growth and industrial processes that increasingly require its use and regeneration [1, 2]. Emerging contaminants (ECs) are compounds, organic or inorganic, that have been detected in the environment for a short time, approximately 20 years, although due to their continuous use they must have reached water sources for longer; however, due to the lack of sensitive analytical methods that could detect relatively low levels in the concentration of these compounds, they are only manifesting until now, and with their accumulation they can reach truly problematic concentrations for both humans and animals [3, 4]. Emerging contaminants are not commonly monitored in the environment, but can cause adverse environmental and human health effects even in small quantities, which is why they are also known as Contaminants of Emerging Concern [5].

Adsorption is a process that is applied with good results for the elimination of certain emerging contaminants (ECs) from water [6]. Adsorption occurs through mass transfer between two phases and for the particular case of the removal of ECs from water, said transfer occurs between a solid and the water that contains the contaminants. Adsorbents are used to adsorb certain contaminants using intermolecular forces. Adsorption involves  $\pi - \pi$  interactions, electrostatic attraction, van der Waals forces, and other hydrophobic interfaces. Physisorption, which is usually the process that occurs in most removal processes and chemisorption involves a chemical interaction between the adsorbate and the functionalities present on the surface of the adsorbent [7, 8]. Studies are found that demonstrate that adsorption on porous materials is an efficient technique for this purpose and for this reason adsorption studies of emerging contaminants on solid adsorbents are

recommended as an efficient solution. The study of adsorbate-adsorbent systems that include contaminants that put human health or the environment at risk is important due to the potential danger of such compounds [9].

An interesting material due to the interaction it can have with emerging contaminants and which is derived from carbon is graphene oxide (GO), which is a two-dimensional nanomaterial, with a thickness of a few nanometers and surface areas greater than those of graphene. The structure of graphene oxide is not completely defined, but it has two differentiable regions [10]. GO has a surface on which graphene sheets modified with oxygen-containing functional groups are found. GO has a greater surface area than graphene, is hydrophobic, easy to separate from water, and has chemical stability. The structure can be found in a single layer or in several layers. A structure with one layer is graphene oxide; two layers of graphene oxide are called two-layer GO [11].

The uses of graphene oxide (GO) extend to different fields, such as in the preparation of ultrafiltration membranes as a possible way to improve the filtration process. GO, being a nanoadsorbent obtained by incomplete oxidation of graphite. GO can interact with contaminants through hydrophobic, electrostatic, and  $\pi$ -stacking interactions, among others [12].

Immersion calorimetry is a technique used to determine the energy produced when a solid and a liquid are brought into contact. This energy is evaluated by calculating the thermodynamic property immersion enthalpy,  $\Delta H_{imm}$ , in order to establish the intensity of the interaction between the adsorbent solid, in the case of this study graphene oxide, and the solvents or solutions. Because it is not a conventional technique, it can show interesting and complementary results to those obtained from adsorption isotherms from the gas phase and liquid phase [13, 14, 15].

This work presents the determination of the immersion enthalpy of graphene oxide in benzene and water as polar and non-polar solvents respectively and in aqueous solutions of phenol, salicylic acid, acetaminophen and methylparaben, which are the emerging contaminants of this study, and which are organic compounds that have the phenol group as a common structure. Relationships are established between the structural characteristics of the emerging contaminating compounds and the intensity of the GO-solution interaction that allow us to know the affinity for the solid or the interference produced by the functional groups in the molecules. The change in the interaction enthalpy,  $\Delta H_{int}$ , between the solid and the organic compound is calculated to provide information about said interaction which takes place in the liquid phase.

## Materials and methods

GO graphene oxide used for the study of the change in immersion enthalpy.

The GO used in this study was prepared and characterized in a previous work in which the adsorption of metal ions from aqueous solution was performed [16]. Table 1 presents the physicochemical characteristics of GO, which are taken into account in the analysis of the results obtained for  $\Delta H_{imm}$ .

Table 1. Physicochemical characteristics of graphene oxide, GO [15,16]

$S_{BET}$ [ $m^2 g^{-1}$ ]	$V_{mic}$ [ $cm^3 g^{-1}$ ]	Total Acidity $\mu mol g^{-1}$	Total Basicity $\mu mol g^{-1}$	Hf
47.5	0.154	$3.564 \pm 0.007$	$1.639 \pm 0.006$	1.23

Determination of the adsorption capacity of GO for emerging contaminants.

$0.1 \pm 0.01$  g of graphene oxide, GO, is weighed in an amber glass container with a lid and 0.025 L of the solution is added with the emerging contaminant, EC, which is desired to be adsorbed with concentrations between 0.066 and 10.6  $mmol L^{-1}$ . The containers were stored for 120 hours at a temperature of  $293 \pm 1$  K and constant stirring (100 rpm). Once this time had ended, an aliquot of 0.001 L was taken, brought to an appropriate volume, and the concentration of the compound was determined by spectroscopy. UV-VIS (GENESYS 10S Vis spectrophotometer, Thermo Scientific™), the maximum wavelengths ( $\lambda_{max}$ ) for each compound and the

respective calibration curves were previously determined. The remaining concentration in each solution was obtained from the equation:

$$Q = \frac{(C_o - C_e)V}{m} \quad \text{Eq. 1}$$

Where  $C_o$  is the initial concentration,  $C_e$  is the final solute concentration after carrying out the adsorption,  $V$  is the volume of the solution containing the analyte and  $m$  is the mass of activated carbon.

Determination of immersion enthalpy of graphene oxide in aqueous solutions of emerging contaminants

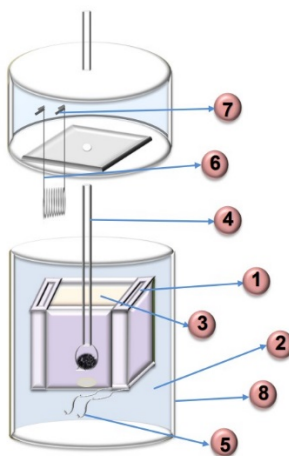


Fig 1. Scheme of the heat conduction microcalorimeter: 1. Sensors; 2. Heat reservoir; 3. Cell for immersion liquid; 4. Fragile spout glass vial; 5. Sensor output connection to the multimeter interface; 6. Resistance; 7. Output connection to power source; 8. Coverage to isolate the system [17, 18].

For the calorimetric characterization, a heat conduction microcalorimeter was used, shown in Fig 1 [18], which uses thermopiles as thermal sensors and a stainless-steel cell of 10 mL capacity. 100 mg of graphene oxide are weighed and placed in a glass vial. The electrical output potential of the thermopiles begins to be captured for approximately 40 minutes, the immersion of the sample is carried out, the recording of the electrical potential is continued, and the electrical calibration is carried out with an electrical resistance to determine the constant of the calorimeter [13, 17].

The determination of the enthalpy of immersion of graphene oxide is carried out in the solvent benzene and water of different chemical nature and in aqueous solutions of  $0.5 \text{ mmol}^{-1}$  of the compounds of phenol, salicylic acid, acetaminophen and methylparaben.

Determination of the hydrophobicity of GO by means of immersion calorimetry

The adsorption capacity of a porous solid is highly influenced by its surface chemistry, so its hydrophilic or hydrophobic nature is important because it allows determining the affinity that the porous solid may have with the adsorbate. To estimate the hydrophobic nature of GO, the hydrophobic factor ( $H_f$ ) is calculated, which is determined by dividing the value of the enthalpy of immersion of the solid in a liquid of a nonpolar nature (generally benzene), by the enthalpy of immersion of a liquid of nonpolar nature. polar (water) [19, 20, 21].

$$H_f = \frac{\Delta H_{imm} C_6H_6}{\Delta H_{imm} H_2O} \quad \text{Eq.2}$$

It is deduced that the immersion enthalpy is a thermodynamic parameter that not only allows determining the interactions that occur between the porous solid and the immersion liquid as a pure component or in binary mixtures, but also the calculation of the hydrophobic factor that is related to the surface chemistry of activated carbon and can account for the type of adsorbates with which it would generate greater affinity.

## Results and Discussion.

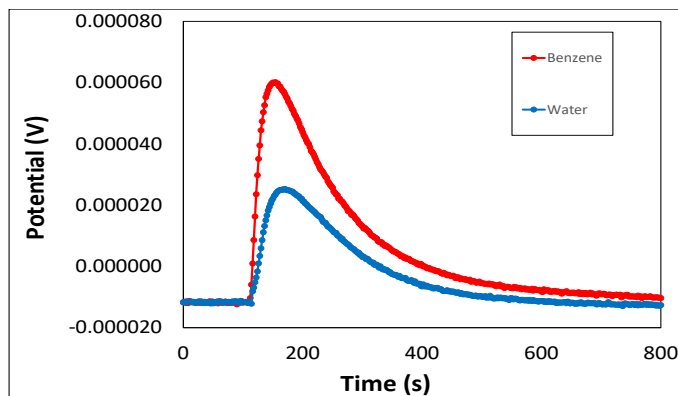


Fig 2. Electric potential versus time curves for GO immersion in benzene and water

Fig 2 shows the electrical potential curves as a function of time of the thermal effect that occurs when GO is brought into contact with benzene and water. The equipment used in this work corresponds to a heat conduction calorimeter [22]. For the determination, the two substances capable of reacting or interacting with each other have the same initial temperature, when they come into contact they react until reaching a final or equilibrium temperature between the system and the surroundings.

The area under the curve of the peak produced is proportional to the change in the enthalpy of immersion,  $\Delta H_{imm}$ , by a calibration factor specific to the calorimeter and which is determined by electrical calibration [23].

The values determined for the change in immersion enthalpy,  $\Delta H_{imm}$ , of GO in benzene and water are  $-40.2 \pm -0.76$  and  $-32.7 \pm -0.69 \text{ Jg}^{-1}$  respectively, which shows that the interaction between solid-liquid is exothermic in nature and that it is greater for immersion in benzene which indicates that GO has a greater affinity for the nonpolar solvent [24].

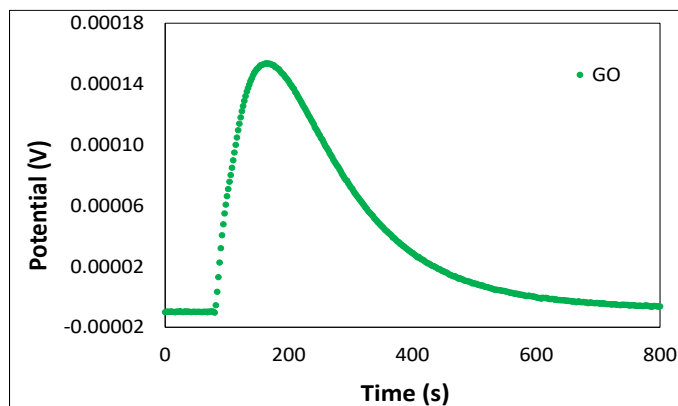


Fig 3. Electric potential curves as a function of time for the immersion of GO in the  $0.5 \text{ mmolL}^{-1}$  aqueous phenol solution.

Fig 3 shows the electric potential curve as a function of time for the immersion of GO in the aqueous phenol solution at  $0.5 \text{ mmolL}^{-1}$ . Once again, it can be seen that a peak occurs under the curve that is proportional to the energy produced in the immersion and that allows the change in the enthalpy of the process to be calculated. For the other ECs compounds, the behavior of the curves is similar, that is, the immersion process

of graphene oxide is exothermic in nature, considering that  $\Delta H_{imm}$  is obtained for a process that presents the contribution of several interactions. The immersion curves of graphene oxide in the aqueous solutions of salicylic acid, acetaminophen and methyl paraben have a shape similar to that shown in Figure 3 for immersion in the aqueous solution of phenol.

Table 2 presents the results obtained for the change in the immersion enthalpy,  $\Delta H_{imm}$ , of graphene oxide in the  $0.5 \text{ mmol L}^{-1}$  aqueous solutions of each emerging contaminant and the adsorbed amount,  $Q$ , of these by the solid. As can be seen in the results, and taking into account that  $\Delta H_{imm}$  is related to the solid-solution interaction in terms of the components of the system [25]. The higher values of  $\Delta H_{imm}$  are obtained for salicylic acid and for methyl paraben, indicating that the total energy that is released in the immersion process of graphene oxide is proportional to the interaction of the solvent and the compound with it and that the change in the enthalpy of immersion is the result of the sum of several interactions [26].

Table 2. Immersion enthalpy,  $\Delta H_{imm}$ , and adsorption capacity,  $Q$ , of graphene oxide

oxide graphene	Adsorbate	$\Delta H_{imm}$ ( $\text{J g}^{-1}$ )	$Q$ ( $\text{mmol g}^{-1}$ )
	Phenol	$-9.32 \pm 0.18$	2.58
	Salicylic acid	$-10.9 \pm 0.22$	1.37
	Acetaminophen	$-9.87 \pm 0.19$	1.21
	Methylparaben	$-11.9 \pm 0.24$	1.43

The ECs in this study are chemically speaking phenol and its derivatives, so their interactions with GO may have similarities in some aspects, among which are the interaction with a solid from a liquid phase, Awad et al. present the adsorption of organic compounds on graphitic materials showing the usefulness of GO as an adsorbent [27]. Regarding the root of the phenol group of the study compounds, it is observed that they increase their molecular mass from  $94 \text{ gmol}^{-1}$  for phenol to  $152 \text{ gmol}^{-1}$  for methyl paraben. Then additional interactions will occur due to the presence of a carboxylic acid group, in salicylic acid, an amide group, for acetaminophen, and an ester group, for methyl paraben [28]. The molar mass of the compounds reflects the change in the structure of the compounds, which is why Fig 4 is presented in which the molar mass of the ECs and the adsorption capacity of GO and the change in the immersion enthalpy of the same in aqueous solutions of organic compounds.

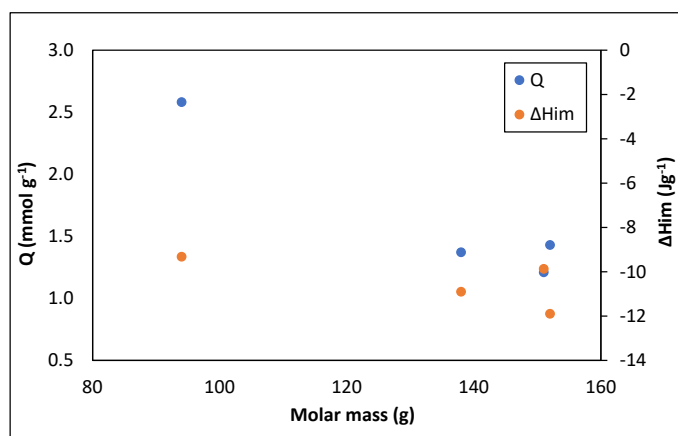


Fig 4. Relationship between the molar mass of the emerging contaminants, ECs, and the adsorption capacity of GO,  $Q$ , and the change in immersion enthalpy,  $\Delta H_{imm}$ .

The same trend is observed for the two parameters as a function of the molar mass, both the change in the immersion enthalpy and the amount of ECs adsorbed by the GO solid show a decrease in the y values for one of the compounds (acetaminophen) there is a deviation from the trend. Acetaminophen is composed of phenol and in the p position it has an acetamide as a functional group that shows as a result for  $\Delta H_{imm}$  a lower value than for the other two compounds with substituents to phenol and slightly higher than that of

the phenol that is taken as a molecule of starting in the series of compounds studied. Given its structure, GO shows a greater affinity for aromatic compounds due to the  $\pi$ - $\pi$  type interaction, which causes the functional group to establish the difference in the interaction of ECs with GO [29]. Also for the parameters analyzed, it must be taken into account that the adsorption process of aromatic compounds from the aqueous phase can involve two driving forces: one derived from the hydrophobicity of the solute that induces adsorption due to low adsorbate-solvent affinity and the specific affinity of the adsorbate on the surface, which contemplates adsorption by ionic interactions, by van der Waals forces and by chemical reactions [30].

In Fig 5, an interesting relationship is presented between the adsorbed amount of the ECs and the change in the immersion enthalpy  $\Delta H_{imm}$ , because it shows how the interaction is different for the phenol as the adsorbate with the base chemical structure.

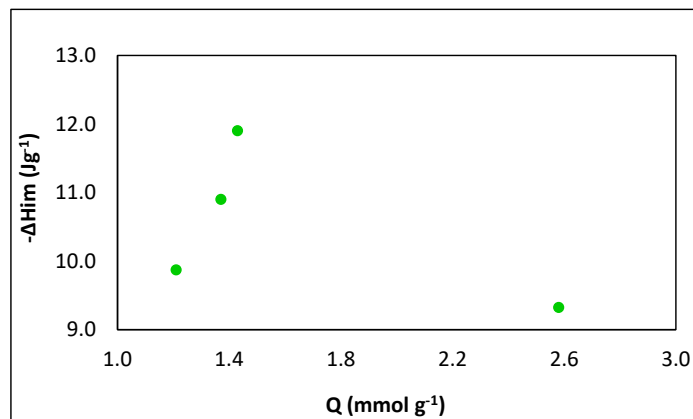


Fig 5. Relationship between the change in the immersion enthalpy,  $\Delta H_{imm}$  of GO in the aqueous solutions of the emerging contaminants, ECs, as a function of the adsorption capacity of GO, Q.

The adsorption capacity of a substance on an adsorbent solid is directly related to its immersion enthalpy in an aqueous solution [31]. For this reason, it is of interest to observe the relationship established between these two properties of the systems under study. It is observed that for compounds with a substituted phenolic ring, the trend is that when the adsorption capacity increases for the different compounds, the change in the enthalpy of immersion increases, but in the case of the phenol solution, the highest adsorption value is obtained and the lower value for  $\Delta H_{imm}$ , showing that the presence of substituents in the ring makes the interaction of the solution of these compounds with GO different from that between the phenol solution and GO.

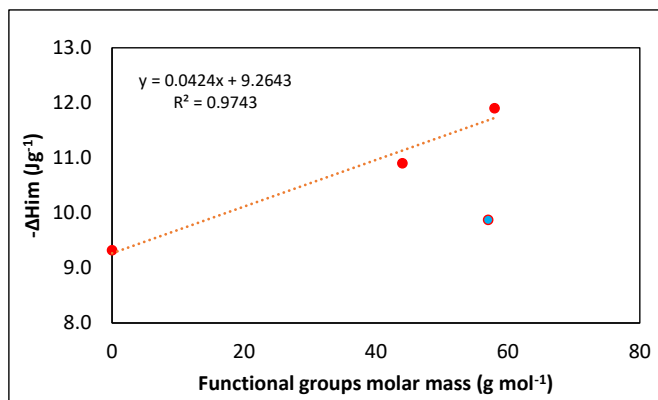


Fig 6. Change in the immersion enthalpy,  $\Delta H_{imm}$  of GO in the aqueous solutions of the emerging contaminants, ECs, as a function of the molar mass of the substituents.

As the set of ECs in this work has as its base structure that of phenol, it can be thought that there is a contribution from the substituent group (carboxylic acid, amide and ester) to the  $\Delta H_{imm}$ , therefore the ratio of  $-\Delta H_{imm}$  as a function of the molar mass of each substituent is represented in Fig 6.

An interesting result is observed, which is manifested for the aqueous solution of acetaminophen that moves away from the trend followed by the other three organic compounds including phenol. For a similar molecular weight between the substituent of methyl paraben and that of acetaminophen, it is found that the change in the immersion enthalpy for the latter is lower, which indicates that the interaction between the GO surface of the acetaminophen solution is lower and the difference is in the presence of a nitrogen atom in the structure, it must also be taken into account that the result obtained for  $\Delta H_{imm}$  is the sum of several thermal effects that occur between the solution (solute and solvent) and the surface of the solid [32, 33]. For the linear trend obtained for the other three compounds, a change per unit of molar mass of the substituent of  $0.0424 \text{ J g}^{-1}$  is calculated.

Assuming that the enthalpic contribution for the phenol group is maintained for the ECs of the study, the value of  $\Delta H_{imm}$  of GO in the aqueous solution of phenol can be subtracted from the values of the change in the immersion enthalpy of the other solutions and taking into account the recognition of the "additive-constitutive" character of thermodynamic properties, as established by Tanford in his work [34] in which he defines a substituent constant, has made it possible to properly study the contributions of the different constituent groups of the molecule to the property considered, in this case the enthalpy of immersion, as well as a better understanding of the solute and water interactions as a solvent on a porous solid such as GO. Fig 7 shows the relationship described.

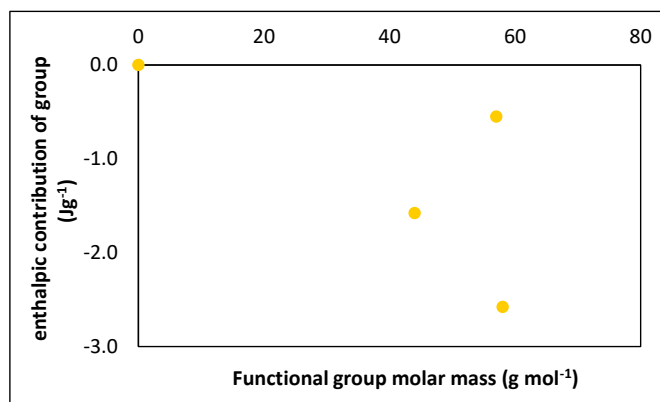


Fig 7. Enthalpic contribution of the phenol substituent group to  $\Delta H_{imm}$  as a function of the molar mass of this

The enthalpic contribution to  $\Delta H_{imm}$  for emerging contaminants is between  $-0.55$  to  $-2.58 \text{ Jg}^{-1}$ , this contribution is exothermic in nature and is lower for acetaminophen because, as already said, this compound has an amide group in its structure that establishes a minor interaction with the GO surface.

The correlation between the adsorption capacity and the formation of adsorbent-adsorbate interactions is difficult to analyze with the enthalpy of immersion,  $\Delta H_{imm}$ , because both the adsorbate and the solvent are interacting with the surface of the graphene oxide and an exchange occurs global energy in the system that involves specific and non-specific interactions and displacement of one substance by another on the surface of the adsorbent and all these processes produce a sum of energy transfer that is manifested in the immersion enthalpy [35]. However, by determining the enthalpy of immersion of the adsorbent (in this case GO) in the solvent (water) it is possible to calculate the enthalpy of interaction (adsorbate-adsorbent) from Hess's law. Equation 3 is the mathematical expression that allows calculating the interaction enthalpy ( $\Delta H_{int}$ ).

$$\Delta H_{int} = \Delta H_{imm_{solution-adsorbent}} - \Delta H_{imm_{solvent-adsorbent}} \quad \text{Eq. 3}$$

Once the change in the interaction enthalpy is calculated, it is possible to establish the relationship between the change in the interaction enthalpy,  $\Delta H_{int}$ , and the adsorbed amount of each ECs for the GO-aqueous solution system, which is shown in Fig 8

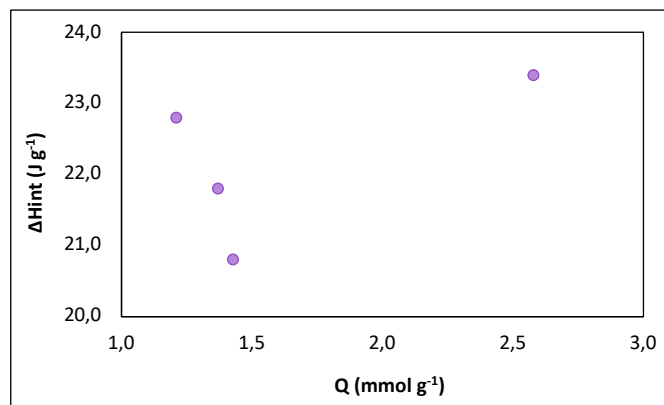


Fig 8. Relationship between  $\Delta H_{int}$  and GO adsorption capacity for ECs

The first observation made with respect to  $\Delta H_{int}$  is that for the four emerging contaminants, ECs, this change is endothermic in nature, which indicates that the different systems require energy to be able to carry out the displacement of the solvent from the surface of the oxide graphene taking into account that energy is needed to overcome the solvent-adsorbent attraction forces, which are surface interactions that are established because the solvent in the solution is found in greater quantity. Adsorption It is a process in which adsorbate-adsorbent interactions are formed to compensate for the surface energy of the adsorbent; however, the final state is not necessarily less energetic than the initial one because the adsorbates can adsorb (interact) with the surface of the solid due to low affinity with the solvent and not due to affinity with the surface. From this point of view, a positive interaction enthalpy value indicates that the adsorbate-adsorbent interactions have higher energy and are therefore more unstable than the interactions of the initial state, in which the graphene oxide surface is interacting with water.

It is also observed in Figure 8 that the ECs with substituents of the phenolic ring present a trend in which the  $\Delta H_{int}$  has lower values than that presented by the aqueous phenol solution and it is observed that this in turn presents the largest adsorbed amount, which which means that the substituents decrease the interaction with the graphene oxide surface; this result is similar to that obtained for the adsorption of phenol on activated carbon [36].

The relationship between the change in the interaction enthalpy,  $\Delta H_{int}$ , and the change in the immersion enthalpy,  $\Delta H_{imm}$ , reflects how these thermodynamic parameters adjust to the processes that occur on the surface of the adsorbent solid with water and each of the organic compounds referred to in this study. Fi 9 shows the relationship described above.

As can be seen, the trend of the relationship is linear and this is a result that can be expected given that between the two variables in Figure 9 there is an equal change when subtracting the effect of the solvent with the solid, however it shows that the behavior of The energy interaction with respect to the change in the immersion enthalpy (which is the experimental determination) for the four ECs is constant and therefore the linear trend.

It is also shown that for acetaminophen and methylparaben, which are the compounds with the largest substituents on the aromatic ring, interactions with the surface of graphene oxide represent an important component in the adsorption process because due to their molecular size they can present steric hindrance in the narrower porous structures, this leads to minimal changes in the surface chemistry of the adsorbent solid modifying the type of adsorbate-adsorbent interactions and the adsorption capacity.



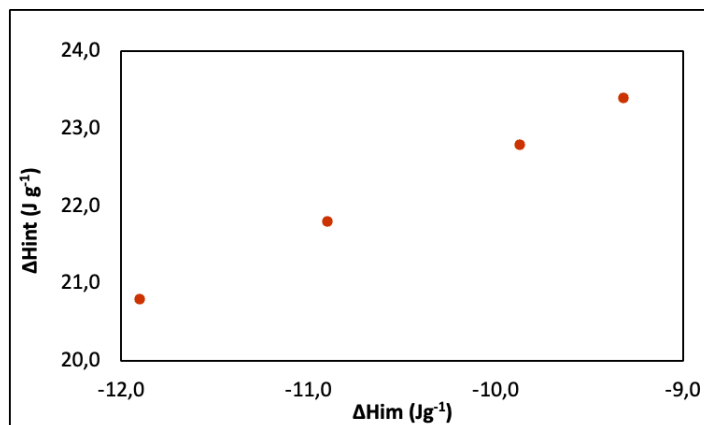


Fig 9. Relationship between  $\Delta H_{int}$  as a function of  $\Delta H_{imm}$

Additionally, it is observed that the two compounds with  $\Delta H_{int}$  with the lowest values are methyl paraben and salicylic acid with values of 20.8 and 21.8  $J g^{-1}$  respectively and for acetaminophen a higher value is presented, again showing a greater interaction that is due to the presence of the N atom in its structure and that is what marks a different behavior as shown in the other relationships.

#### Conclusions

The enthalpy of immersion of GO in solvents and aqueous solutions of emerging contaminants with pharmaceutical activity was determined, which allows the observation of the process and its thermodynamic characterization in terms of enthalpic interaction and adsorption equilibrium results.

The values for the change in immersion enthalpy,  $\Delta H_{imm}$ , were for the immersion of GO in aqueous solutions of phenol, salicylic acid, acetaminophen and methyl paraben of exothermic nature with values between -9.32 and -11.9  $J g^{-1}$ . The  $\Delta H_{imm}$  were also determined for the solvents water and benzene, which allowed the calculation of the hydrophobic factor for the solid adsorbent GO.

Different relationships are established between the change in the immersion enthalpy and the adsorption capacity of GO for the emerging compounds, their molecular weight, the molar mass of the substituents to the base compound, which is phenol, and in these a behavior is shown. different for acetaminophen, which in these cases deviates from the trend followed by the other three compounds and which is associated with the presence of nitrogen in this contaminating compound.

The enthalpic contribution to the change in the immersion enthalpy of each substituent of the phenolic ring is calculated and it is observed that for similar molar mass values such as that of the acetamide group and the methyl ester group, different values are obtained for said contribution of - 0.55 and - 2.58  $J g^{-1}$  respectively.

The change in the interaction enthalpy,  $\Delta H_{int}$ , of each ECs with the GO surface is calculated and the result is that they are endothermic in nature, which indicates that the different systems require energy to be able to carry out the interaction with the GO surface. solid adsorbent since these come from a solution in which the environment is dominated by water, which is the solvent.

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