

Adsorption of Three Chlorinated Herbicides on Two Activated Carbons: An Example of the Effect of Surface Charge, Pore Diameter and Molecular Size on the Adsorption Process

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Abstract – Two carbonaceous adsorbents CAT and CARBOPAL were tested for reducing the concentration of the three herbicides in water: 2,4-D (2,4-dichlorophenoxyacetic acid), TCP (2,4,6-trichlorophenol) and metolachlor. Textural and chemical characterization of the adsorbents include nitrogen isotherms, FTIR, titration and thermogravimetric analyses. Adsorption was studied in discontinuous adsorption experiments at different pH values. The experimental adsorption isotherms data were fitted to four theoretical models. Adsorbent characterization reveals that CAT has higher micropore area, lower pore diameter and lower acidity than CARBOPAL. The adsorption is a second-order process and the isotherms best fitted to Sips model. The efficiency of the process depends mainly on the charge of the adsorbate for TCP and 2,4-D, but it depends on the charge of the surface for metolachlor. Adsorption capacity is higher on CAT for 2,4-D and TCP (small molecules), and it is higher on CARBOPAL for metolachlor (large molecules). Theoretical calculations clearly support this assumption.

Key words: Adsorption, Activated carbon, Metolachlor, Trichlorophenol, 2,4-D

1. Introduction

The issue of mitigation of pollution caused by agrochemicals is one of the greatest problems facing science nowadays. Herbicides are applied in large quantities, leaking into the environment, and hence causing water, soil and air pollution. Therefore, it is necessary to find new materials for solving (or at least mitigating) this problem. The herbicides 2,4-D (2,4-dichlorophenoxyacetic acid), TCP (2,4,6-trichlorophenol) and metolachlor are three of the most widely used phytosanitary products in Argentina, and nowadays their pollutant effects are rising. The main features of the three herbicides are briefly commented below.

The herbicide 2,4-D (2,4-dichlorophenoxyacetic acid, Scheme 1) is a systemic herbicide, which kills selectively most broadleaf weeds by causing their uncontrolled growth, leaving most grasses such as lawn turf, cereals, and grass land unaffected. It is used in maize, corn and grazing land cultivation, and it has been used as defoliating agent and for the removal of water weeds as well. This herbicide kills plants by changing the way certain cells grow. 2,4-D is commercialized in several forms, including esters, salts, and acid form. The toxicity and

environmental impact of 2,4-D depend on the form. The International Agency for Research on Cancer (IARC) declared in 1987 that 2,4-D is a β -2 carcinogenic compound [1]. This herbicide has been recently classified as group D carcinogen by USEPA and is suspected to be endocrine disruptive [2]. It has been suggested that 2,4D increases the probability of immune deficiency disorders, reduces sperm immobility, and causes nervous, kidney and respiratory problems [3].

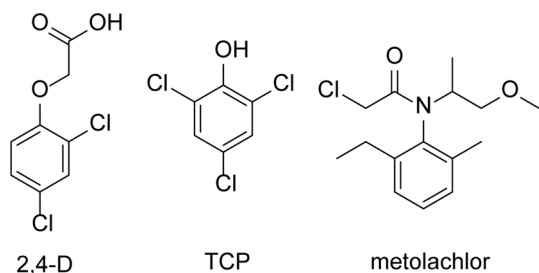
TCP (2,4,6-trichlorophenol, Scheme 1) is a highly chlorinated compound which has been commonly used as herbicide, pesticide, defoliant and wood preservative [4]. Wastewater from this pesticide is one of the most important sources of chlorophenol pollution [5]. TCP has been proven to cause many health disorders, including respiratory, cardiovascular, and gastrointestinal effects, as well as cancer [6-8]. There is also evidence of structural chromosomal aberrations in somatic and germ cells caused by TCP [6].

The herbicide metolachlor (2-chloro-N-(2-ethyl-6-methylphenyl)-N-(1-methoxypropan-2-yl) acetamide, Scheme 1) belongs to the chloroacetamide family and it is a selective pre-emergent herbicide. It has a stereocenter, being the S form the more effective, but it is often commercialized as a mixture of the two enantiomers. It is used for prevention of broad leaf weed and annual gramineae in a wide spectrum of crops, like soybean, cotton corn, and sunflower, among many others. It is slightly toxic (class 2) but it has been suggested that it could be carcinogenic agent [9]. Even not being long persistent in soil (mean life of 30-50 days) its solubility and persistence in

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Scheme 1. Molecular structures of the three herbicides.

water are relatively high ($530 \text{ mg}\cdot\text{L}^{-1}$, 90 days); it leaks into ground and superficial water currents [10].

Given the negative sanitary and environmental effects that these herbicides bring about, the search for new methods and materials for their mitigation is of utmost importance. In this sense, the methods that are nowadays being studied for reduction of water pollution caused by agrochemicals include: physical treatments (washing by surfactants, extraction), oxidative processes (ozonization, chlorination, Fenton and photo-Fenton processes), and biological degradation (aerobic and anaerobic) [11-14].

On the other hand, adsorption is coming up as one of the most promising, efficient and widely used methods for water remediation. Therefore, many materials have been tested for this purpose: siliceous materials, carbon, alumina, titanium dioxide and nanomaterials, among others [15-19].

Activated carbon is a very efficient adsorbent for a broad variety of pesticides due to its high superficial area and porosity, high thermal stability, good adsorption capacity, fast kinetic, and versatility for removal of both organic and inorganic pollutants dissolved in water [20-22]. Adsorption to solid phases is an easy and economical technique for removing substances from soils and aqueous media.

In this work, two commercial activated carbons were tested as adsorbents for reducing the concentration of the herbicides 2,4-D, TCP and metolachlor from aqueous solutions. This work also tempts to develop an approach on the effects of adsorbate and adsorbent charge, adsorbent pore diameter and herbicide molecular size by means of theoretical calculations.

2. Materials and Methods

2-1. Adsorbates

The herbicides 2,4-D, TCP and metolachlor were supplied by Sigma-Aldrich at purity analytical grade (99%), and they were used without further purification.

2-2. Adsorbents and adsorbent characterization

2-2-1. Textural characterization

Two commercial activated carbons were used, having different chemical and physical properties. Their commercial names are Hydrogen Sulfide CAT-Ox 4 mm pellet Activated Carbon (UMI2000)

and CARBOPALMB 4S (Donau). The adsorbents will be named as CAT and CARBOPAL, respectively, from now on. They were ground $500\text{-}355 \mu\text{m}$ and washed with boiling water in order to remove impurities and then dried in oven at $110 \text{ }^\circ\text{C}$ for 24 h. Both carbonaceous materials were characterized for studying their superficial and morphological properties.

The surface parameters of the adsorbents were estimated from the N_2 adsorption/desorption isotherms at $-195.8 \text{ }^\circ\text{C}$, using an automatic volumetric apparatus (ASAP 2020 from Micromeritics). The specific surface area (S_{BET}) was calculated by means of the BET method at P/P_0 0.21, while the total pore volume (V_{tot}) was obtained from the amount of adsorbed nitrogen at relatively pressure of $P/P_0 = 0.95$. The external surface area (S_{ext}), the micropore surface area (S_{mic}), and the micropore volume (V_{mic}), were calculated using the t-plot method. The mean pore diameter DP was estimated as $DP = 4 V_{\text{tot}}/S_{\text{BET}}$. The pore size distribution was also derived from the BET isotherm.

2-2-2. Chemical characterization

FT-IR spectra of the activated carbons were recorded with a Thermo Nicolet FT-IR spectrophotometer within a range of $400\text{-}4000 \text{ cm}^{-1}$ and using KBr as support.

The point of zero charge (pH_{PZC}) was determined using the mass titration method, according to ASTM D3838-05 (Standard Test Method for pH of Activated Carbon), measuring pH as a function of the mass concentration of the solid. Samples of the dried solids ranging from 0.1 to 1.0 g were placed in a flask. 40 mL of previously boiled distilled water was then added. The system was boiled, during 20 min approximately. After this time, the system was filtered and pH of the liquid was measured at $50 \pm 5 \text{ }^\circ\text{C}$. pH values were then plotted as a function of the mass percentage, and the pH_{PZC} was determined by extrapolation to zero mass percentage.

Boehm titration was also performed for determination of acidic and basic groups on the surface of the activated carbons. NaOH and NaHCO_3 were used as bases. It is assumed that NaOH neutralizes carboxylic acids, lactones, phenols, and carbonyls, while NaHCO_3 neutralizes only carboxyl groups. HCl was used for neutralization of basic groups. 0.1000 g of activated carbon was placed in a 100 mL Erlenmeyer flask, 100 mL of acidic or basic solutions was added (0.0500 M HCl, 0.0500 M NaOH or 0.0500 M NaHCO_3). The system was kept under constant stirring for 24 h and the mixture was then filtered. 25 mL of solution was titrated with 0.0500 M NaOH or 0.0500 M HCl using phenolphthalein or methyl orange as pH indicator. Blank experiments were performed for verifying the pH value of carbon dispersions in distilled water.

Scan electronic microscope (SEM) analyses were performed on a JEOL JSM 6400 microscope, equipped with a thermionic cathode electron gun, a tungsten filament and a 25 kV detector. Samples are placed on brass discs using graphite tape and ensuring that they have been adequately dewatered prior to analysis.

Thermogravimetric analyses (TG) were carried out under inert

conditions (nitrogen flow of 50 mL·min⁻¹), at heating rate of 10 °C min⁻¹ from room temperature to 1000 °C. TG analyses were performed with a Seiko Exstar 6000 TGA/DTA 6200 thermobalance.

2-3. Adsorption Experiments

2-3-1 Adsorption kinetics

Kinetic studies were carried out placing 0.0020 g of adsorbent into 50 mL of herbicide solution (50 mg·L⁻¹) in a bath at 293 K and 200 rpm. The adsorbent was allowed to settle at given times and 4.0 mL of solution was taken out by filtration through 22 µm nylon filters. The absorbance of each solution was obtained by means of a Metrolab 1700 UV spectrophotometer at 305, 311 and 266 nm for 2,4-D, TCP and metolachlor, respectively.

The amount of herbicide adsorbed q_t (mg·g⁻¹) at time t (min) was calculated as $q_t = (C_0 - C_t) \cdot V / W$, where C_0 and C_t (mg·L⁻¹) are the herbicide concentrations at the beginning of the experiment and after a time t ; W (g) is the mass of adsorbent and V (L) is the volume of the solution. A blank test was carried out for each experiment to verify that no adsorption occurred on the glass. Each kinetic experiment was performed in duplicate.

2-3-2. Adsorption isotherms

Discontinuous adsorption studies were performed by adding 0.0020 g of dry activated carbon into 20 mL of herbicide solutions with different initial concentrations (5-40 mg·L⁻¹). Distilled water was used as solvent and no buffer solutions were used to prevent possible precipitation or competition with the adsorbates. Ionic strength was kept constant by adding NaCl 0.01 M to all solutions. Temperature and stirring were controlled by a thermostat system. The herbicide concentration (before and after adsorption) was determined by UV spectrometry, as commented above.

The adsorption capacity q_e (mg·g⁻¹) was calculated as $q_e = (C_0 - C_e) \cdot V / W$, where C_0 and C_e (mg·L⁻¹) are the concentrations of herbicide before adsorption and when the system comes to equilibrium, respectively; V (L) is the volume of aqueous solution and W (g) is the mass of adsorbent. Each equilibrium adsorption experiment was performed in duplicate.

The experimental adsorption isotherms data were fitted to four theoretical adsorption models, shown in Equations 1-4 [23,24].

$$\text{Langmuir: } q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (1)$$

$$\text{Freundlich: } q_e = K_F C_e^{1/n_f} \quad (2)$$

$$\text{Sips: } q_e = \frac{q_m (K_S C_e)^{1/n}}{1 + (K_S C_e)^{1/n}} \quad (3)$$

$$\text{Tempkin: } q_e = \frac{RT}{b_T} \ln(A_T C_e) \quad (4)$$

where q_e is the adsorption capacity (in mg·g⁻¹), C_e is the herbicide equilibrium concentration (in mg·L⁻¹), q_m is the maximum monolayer capacity (in mg·g⁻¹), K_L is the Langmuir constant (in L·mg⁻¹), K_F is

the Freundlich constant (in mg·g⁻¹), n_f is the Freundlich exponent, K_S is the Sips constant (in L·mg⁻¹), n is the Sips exponent, A_T is the Tempkin isotherm constant (in L·mg⁻¹), b_T is the Tempkin constant related to the heat of sorption (in J·g·mg⁻¹·mol⁻¹).

2-3-3. pH effect

The acidity of each solution was adjusted to pH 4.0, 6.5 or 8.0 by adding aqueous HCl or NaOH 0.05M. The total volume was not modified significantly by this addition. The pH value of each solution was controlled before and after adsorption, checking that the value did not change in ± 0.1.

2-4. Computational calculations

To model the activated carbon structure, the structure of ideal graphite was considered to be closely approximated to the basic structural unit of active carbon [25,26]. The surface is composed of a layer of fuse hexagons where the carbon-carbon bond distance is 1.415 Å, indicating one-third double bond character. Three of the carbon's four electrons are engaged in forming localized regular covalent bonds with neighboring atoms, while the fourth one resonates between several valence-bond structures, giving each carbon-carbon bond a one-third double bond character. The arrangement of carbon atoms in the diffraction spectra indicates that this structural configuration is in fact predominant [26]. The carbon surface TCP and metolachlor molecules were previously modeled and the computational calculations were done using the Gaussian 09 program package [27]. The geometry optimization was performed with DFT-B3LYP method by using 6-311G ++(d,p) basis set.

3. Results and Discussion

3-1. Adsorbent characterization

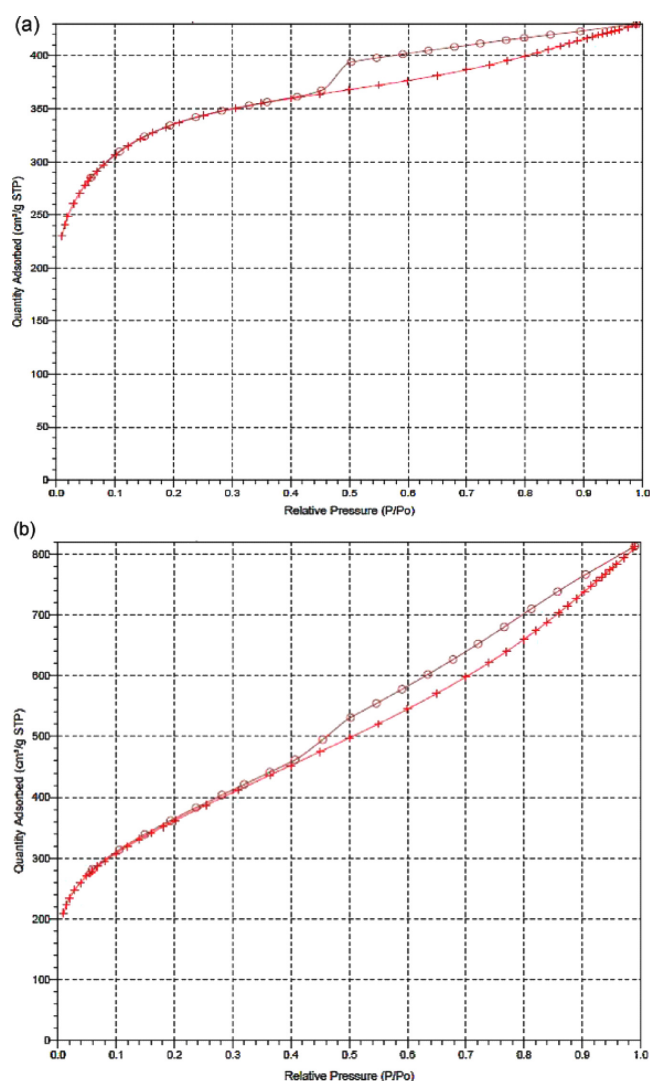
3-1-1. Textural characterization

Table 1 depicts surface area and pore diameter data for both activated carbons CAT and CARBOPAL. Specific surface and pore size were measured by N₂ adsorption isotherms (BET method). Results are shown in Figs. 1 and 2. The specific area and monolayer volume of CARBOPAL was found to be higher than that for CAT. The total pore volume was calculated from the amount of N₂ adsorbed at P/P₀ = 0.95, while the micropore volume was calculated by the Dubinin-Radushkevich method. The mesopore volume was obtained from the N₂ adsorption isotherm in the range of relative pressures P/P₀ from 0.40 to 0.95 assuming the molar volume of liquid nitrogen is 35 cm³mol⁻¹. In the case of the medium pore size, they can be obtained from the Barrett-Joyner-Halenda method (BJH). Note that the total specific area of CARBOPAL is greater than that of CAT, but the latter shows higher micropore specific area.

On the other hand, the pores of CARBOPAL are wider than those of CAT (compare the mean pore diameters: 3.9 nm vs 2.2 nm). This difference will mark a difference in adsorption between 2,4-D and TCP on one hand (whose molecules are small and flat)

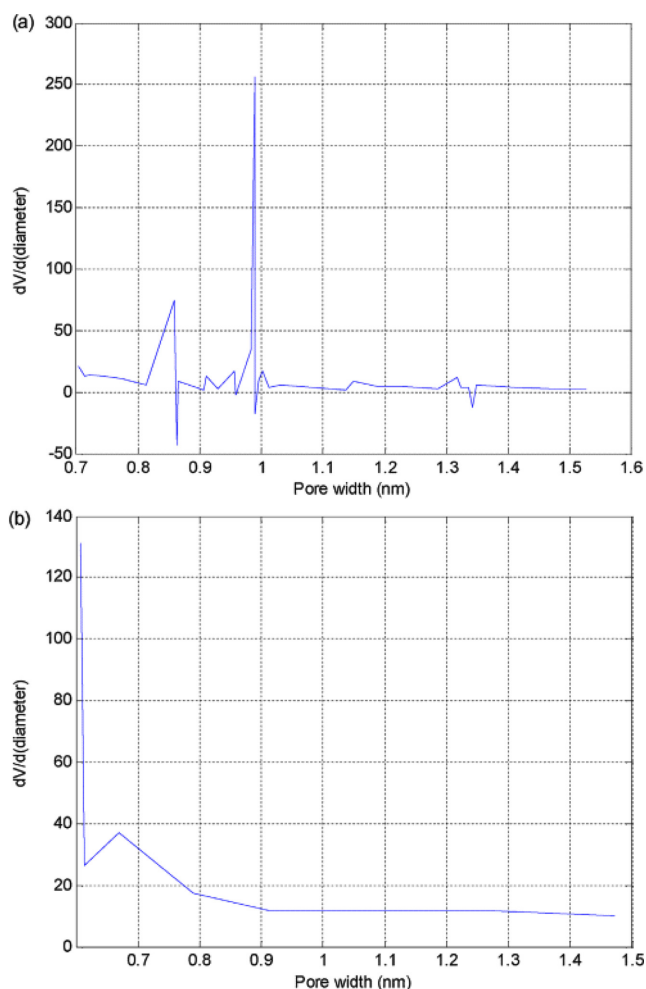
Table 1. Main textural and chemical properties of CAT and CARBOPAL surfaces

| | | CAT | CARBOPAL | |
|---------------------|--|---|----------|------|
| Textural properties | BET specific area ($\text{m}^2 \cdot \text{g}^{-1}$) | 983 | 1588 | |
| | Micropore area ($\text{m}^2 \cdot \text{g}^{-1}$) | 579 | 198 | |
| | Total pore volume ($\text{mL} \cdot \text{g}^{-1}$) | 0.66 | 1.25 | |
| | Micropore volume ($\text{mL} \cdot \text{g}^{-1}$) | 0.25 | 0.04 | |
| | Mesopore volume ($\text{mL} \cdot \text{g}^{-1}$) | 0.41 | 1.21 | |
| | Mean pore diameter (nm) | 2.23 | 3.89 | |
| Chemical properties | Boehm titration | Carboxylic groups ($\text{mmol} \cdot \text{g}^{-1}$) | 2.72 | 1.31 |
| | | Phenolic groups ($\text{mmol} \cdot \text{g}^{-1}$) | 7.78 | 7.92 |
| | | Basic groups ($\text{mmol} \cdot \text{g}^{-1}$) | 2.44 | 7.83 |
| | pH _{PZC} | 7.46 | 4.76 | |

**Fig. 1. N_2 adsorption isotherms for activated carbons CAT (a) and CARBOPAL (b).**

and metolachlor on the other hand (with larger are globular molecules).

The morphological characterization done by means of scanning electron microscopy (SEM) shows that that the structures of the solids are not uniform or ordered.

**Fig. 2. Pore size distribution for activated carbons CAT (a) and CARBOPAL (b).**

3-1-2 Chemical characterization

Boehm titration (results shown in Table 1) allows to quantify acidic and basic groups on the carbon surfaces. CAT adsorbent shows basic properties, while CARBOPAL surface is mainly acidic.

Point of zero charge values (pH_{PZC}) for the two carbons, shown in Table 1, suggest that the two adsorbents have different properties. CARBOPAL shows acidic behavior (its surface is neutral at pH 4.76, and negative over this value), while CAT is relatively neutral (its

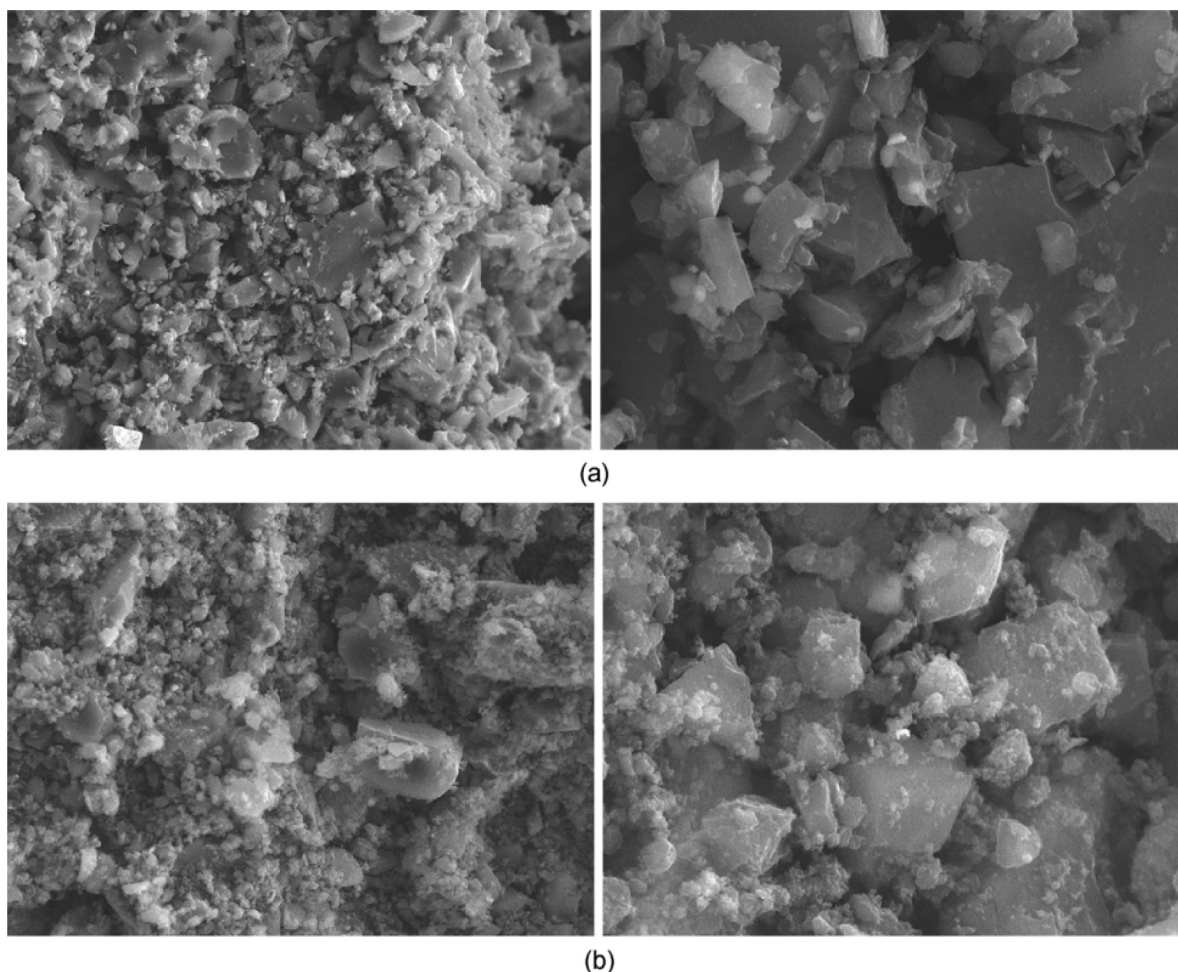


Fig. 3. SEM images for activated carbons CAT (a) and (b) CARBOPAL.

surface is neutral at pH 7.46, and negative over this value). This point is important since metolachlor is neutral (within the range of pH studied) but 2,4-D and TCP show acidic behavior (with pK_a 2.7 and 6.2), and this fact will affect the interaction between the adsorbates and surfaces depending on their charge.

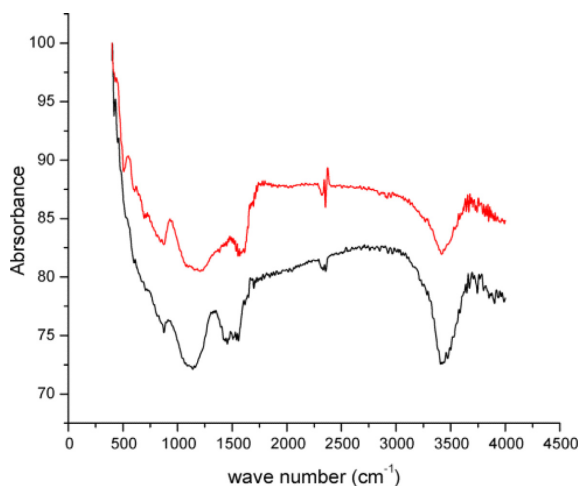


Fig. 4. FT-IR spectra of activated carbons CAT (black line) and CARBOPAL (red line).

Fig. 4 shows the FTIR spectra obtained for activated carbons CAT and CARBOPAL. Although the two spectra are similar due to the nature of the adsorbents, some differences are observed:

- A high intensity band is observed at $3400\text{--}3500\text{ cm}^{-1}$ in both cases that is assigned to hydroxyl groups and adsorbed water. Because this band is more intense in the CARBOPAL spectrum, it is possible to suppose that the concentration of OH groups in this activated carbon is higher.
- An intense peak is observed between 1000 and 1260 cm^{-1} in both spectra, indicative of C–O stretching of carboxylic acids, alcohols, and esters.
- The peaks at $1600\text{--}1610\text{ cm}^{-1}$ and the band observed at 1461 cm^{-1} in CARBOPAL spectrum are attributed to carboxyl groups. CARBOPAL has, therefore, a greater number of acidic functional groups, which explains the lower value of $pH_{PZC} = 4.76$, compared to CAT (7.46).
- Between 800 and 950 cm^{-1} , out-of-plane C–H bending signals of aromatic rings are observed in both spectrums.
- Peaks at $1582\text{--}1585\text{ cm}^{-1}$ (approximately) appear in both materials, and they indicate the C=O stretching of lactone and carbonyl groups.

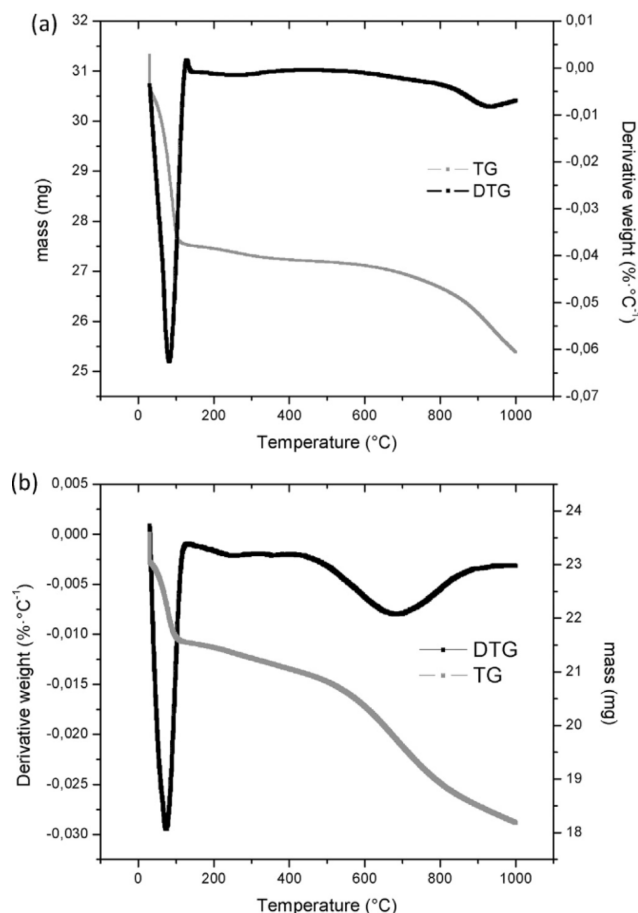


Fig. 5. TG and DTG spectra for activated carbons CAT (a) and CARBOPAL (b).

- The bands at $2850\text{--}2920\text{ cm}^{-1}$ (in both spectra) are characteristic of aliphatic groups.

Boehm titration and FTIR analysis show that the principal functional groups on the surfaces are phenolic > carboxylic > basic groups for CAT and phenolic > basic > carboxylic groups for CARBOPAL. Even when these results appear to contradict the pH_{PZC} values, it is important to note that not all the basic groups contribute to the global pH value (since they can be very weak).

Thermogravimetric analysis allows us to further characterize the surfaces. Results are shown in Fig. 5. The curves of the first derivatives (in black) show different depressions, which permit us to infer the functional groups present on each surface. In the case of CAT (Fig. 5a), the significant mass loss between 80 and 100 °C is due to dehydration of the material, and it characteristic of this type of solids. The very low mass losses below 900 °C suggests that CAT does not

present a great diversity of functional groups. A slight mass loss between 900 and 1000 °C can be due to the decomposition of quinones and carboxylic acids. In the case of CARBOPAL (Fig. 5b), an important mass loss is also observed between 80 and 100 °C (loss of water). There is also a deep depression due to CO_2 loss between 600 and 850 °C , suggesting the decomposition of carboxyl, anhydride and lactone groups. This is also in agreement with the pH_{PZC} values, where CARBOPAL presents a more acidic behavior than CAT.

3-2. Adsorption kinetics

Kinetic experiments were performed to find reliable times for equilibrium adsorption experiments. The adsorbed quantity was then registered at different times and then the experimental data were adjusted to three possible kinetic models: pseudo-first order, pseudo-second order and Elovich model. The linear formulae for these three models are shown in Eqs. 5, 6 and 7, respectively.

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (5)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (6)$$

$$q_t = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln t \quad (7)$$

where q_e and q_t are the adsorption capacities (in $\text{mg}\cdot\text{g}^{-1}$) in equilibrium and after a time t (in sec), respectively, k_1 (in sec^{-1}) is the first-order rate coefficient, k_2 (in $\text{g}\cdot\text{mg}^{-1}\cdot\text{sec}^{-1}$) is the second-order rate coefficient, and α and β (in $\text{mg}\cdot\text{g}^{-1}\cdot\text{sec}^{-1}$ and $\text{mg}\cdot\text{g}^{-1}$) are the Elovich rate coefficients.

In all cases, the experimental data fitted best to a pseudo-second order kinetic. The integrated equation of this model (Eq. 6) lets us obtain the kinetic parameters k_2 and q_e from the plot t/q_t vs t (Table 2). These two parameters allow the calculation of the time t needed for reaching a given adsorption capacity q_t . The time for completing 99% of the adsorption (t_{99} , in h) was calculated for each kinetic experiment and it falls (in all cases) between 1 and 23 h. Thus, a time of 24 h was defined for all the equilibrium experiments to ensure an accurate proximity to equilibrium.

This type of kinetic assumes that the adsorption capacity is proportional to the active number of active sites in the adsorbent. The adsorption process is very fast in the beginning and then it slows in a very significant way (data not shown) and, given the high mesoporosity of the materials, it can be suggested that adsorption takes place initially on the active sites of the mesopores, and that the adsorbate is then transported into the micropores, as it has been observed for similar materials in previous studies [28]. This fact

Table 2. Pseudo-second order kinetic parameters for adsorption of 2,4-D, TCP and metolachlor on CAT and CARBOPAL

| Kinetic parameter | CAT | | | CARBOPAL | | |
|--|-------------|---------------|----------------|-------------|-----------------|----------------|
| | 2,4-D | TCP | Metolachlor | 2,4-D | TCP | Metolachlor |
| q_e ($\text{mg}\cdot\text{g}^{-1}$) | 588 ± 7 | 714 ± 8 | 46.3 ± 0.6 | 417 ± 2 | 278 ± 2 | 17.3 ± 0.1 |
| $k_2 \cdot 10^3$ ($\text{g}\cdot\text{mg}^{-1}\cdot\text{h}^{-1}$) | 84 ± 2 | 5.9 ± 0.2 | 162 ± 6 | 138 ± 2 | 3.36 ± 0.06 | 840 ± 9 |
| R^2 | 0.9996 | 0.9994 | 0.9992 | 0.9999 | 0.9999 | 0.9992 |
| t_{99} (h) | 20.2 | 23.2 | 13.0 | 1.7 | 10.6 | 6.7 |

is in agreement with the higher micropore area observed in CAT (Table 1).

3-3. Adsorption isotherms

Fig. 6 shows the adsorption isotherms obtained for the herbicides 2,4-D, TCP and metolachlor at 25 °C, pH 6.5 and 0.01M ionic strength (NaCl) on the two activated carbons studied in this research.

The isotherms can be sorted following the classification proposed by Giles et al [29]. In these particular cases, the isotherms obtained for 2,4-D and metolachlor are L-type (more precisely: L2-type in the four cases, except in the case of 2,4-D on CAT, which is L3-type due to the second slope observed beyond the *plateau*); whereas, the two isotherms observed in the adsorption of TCP are S3-type on both adsorbents.

The isotherms were tested against four theoretical adsorption models: Langmuir, Freundlich, Sips and Temkin. In the case of adsorption of 2,4-D on CAT, only the first section of the isotherm (from zero to the *plateau*) was considered for the modeling. Tables 3 and 4 resume the results obtained for the adsorption of the herbicides on CAT and CARBOPAL, respectively. According to R^2 values, the Sips model is the best theoretical approach for describing adsorption

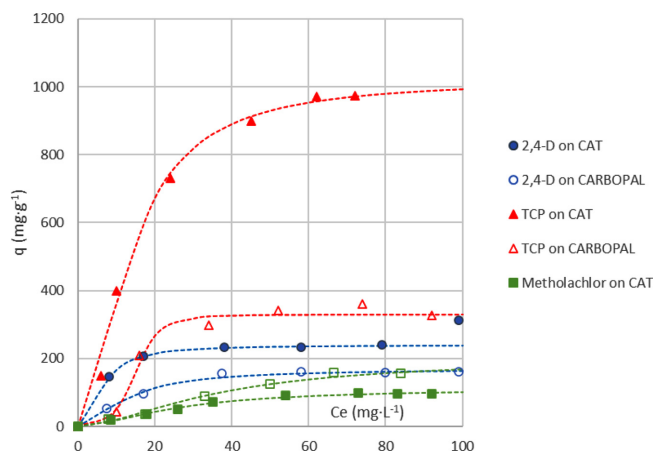


Fig. 6. Adsorption isotherms of 2,4-D, TCP and metolachlor on CAT and CARBOPAL at 25 °C. Theoretical Sips fittings are shown in dashed lines.

of the three herbicides on either of the two carbons. This model considers that there is heterogeneity in the system (which can be attributed to adsorbate and/or to the surface), and it therefore includes a parameter n , which can be considered as an expression of that heterogeneity [24]. In this case, given that the solids present no

Table 3. Isotherm modelling parameters for 2,4-D, TCP and metolachlor on CAT

| Model | Parameter | Herbicide | | |
|------------|--|--|---|--|
| | | 2,4-D | TCP | Metolachlor |
| Langmuir | q_m (mg·g ⁻¹) | 261 ± 7 | 13.10 ² ± 1.10 ² | 16.10 ¹ ± 2.10 ¹ |
| | K_L (L·mg ⁻¹) | 0.18 ± 0.03 | 0.04 ± 0.01 | 0.020 ± 0.005 |
| | R^2 | 0.9928 | 0.9764 | 0.9743 |
| Freundlich | K_F (mg·g ⁻¹) | 11.10 ¹ ± 2.10 ¹ | 12.10 ¹ ± 5.10 ¹ | 9 ± 3 |
| | nf | 5 ± 1 | 2.0 ± 0.4 | 1.8 ± 0.3 |
| | R^2 | 0.7795 | 0.8925 | 0.9113 |
| Sips | q_m (mg·g ⁻¹) | 240 ± 2 | 102.10 ¹ ± 4.10 ¹ | 112 ± 9 |
| | K_S (L·mg ⁻¹) | 0.155 ± 0.005 | 0.072 ± 0.005 | 0.038 ± 0.005 |
| | n | 0.53 ± 0.04 | 0.55 ± 0.06 | 0.6 ± 0.1 |
| | R^2 | 0.9994 | 0.9953 | 0.9847 |
| Temkin | b_T (J·g·mg ⁻¹ ·mol ⁻¹) | 49 ± 9 | 7.4 ± 0.5 | 69 ± 6 |
| | A_T (L·mg ⁻¹) | 3 ± 2 | 0.008 ± 0.002 | 0.004 ± 0.001 |
| | R^2 | 0.7736 | 0.9743 | 0.9551 |

Table 4 Isotherm modelling parameters for 2,4-D, TCP and metolachlor on CARBOPAL

| Model | Parameter | Herbicide | | |
|------------|--|--|--|--|
| | | 2,4-D | TCP | Metolachlor |
| Langmuir | q_m (mg·g ⁻¹) | 20.10 ¹ ± 1.10 ¹ | 48.10 ¹ ± 9.10 ¹ | 4.10 ² ± 1.10 ² |
| | K_L (L·mg ⁻¹) | 0.06 ± 0.01 | 0.04 ± 0.02 | 0.008 ± 0.004 |
| | R^2 | 0.9724 | 0.8913 | 0.9737 |
| Freundlich | K_F (mg·g ⁻¹) | 4.10 ¹ ± 1.10 ¹ | 5.10 ¹ ± 3.10 ¹ | 5 ± 3 |
| | nf | 2.9 ± 0.8 | 2.2 ± 0.8 | 1.3 ± 0.2 |
| | R^2 | 0.7985 | 0.6719 | 0.9402 |
| Sips | q_m (mg·g ⁻¹) | 170 ± 8 | 33.10 ¹ ± 1.10 ¹ | 20.10 ¹ ± 3.10 ¹ |
| | K_S (L·mg ⁻¹) | 0.077 ± 0.009 | 0.069 ± 0.004 | 0.027 ± 0.006 |
| | n | 0.6 ± 0.1 | 0.22 ± 0.05 | 0.6 ± 0.1 |
| | R^2 | 0.9864 | 0.9792 | 0.9847 |
| Temkin | b_T (J·g·mg ⁻¹ ·mol ⁻¹) | 56 ± 9 | 20 ± 4 | 38 ± 5 |
| | A_T (L·mg ⁻¹) | 0.3 ± 0.2 | 0.2 ± 0.1 | 0.010 ± 0.005 |
| | R^2 | 0.8877 | 0.8008 | 0.9315 |

Table 5. Maximum adsorption capacity q_m ($\text{mg}\cdot\text{g}^{-1}$) of the three herbicides at different pH values

| Adsorbent | 2,4-D | | | TCP | | | Metolachlor | | |
|-----------|--------|--------|--------|--------|---------|--------|-------------|--------|--------|
| | pH 4.0 | pH 6.5 | pH 8.0 | pH 4.0 | pH 6.5 | pH 8.0 | pH 4.0 | pH 6.5 | pH 8.0 |
| CAT | 391±9 | 240±2 | 159±3 | 962±42 | 1020±40 | 750±80 | 67±1 | 112±9 | 168±8 |
| CARBOPAL | 204±9 | 170±8 | 112±60 | 380±20 | 330±10 | 246±5 | 124±13 | 200±30 | 157±23 |

uniform or ordered structure (as shown in SEM images, Fig. 3), it is probable that the main source of heterogeneity comes from the variety of different adsorption energies in the active sites.

3-4. pH effect: adsorbate and adsorbent charge

The adsorption isotherms were registered at pH 4.0, 6.5 and 8.0. The theoretical model that best fitted the curves was the Sips equation in all cases, and the general shape of the isotherms did not change with the acidity of the solution. Table 5 shows the maximum capacity q_m of each adsorption system at the three pH values.

The adsorption capacity of both carbons towards 2,4-D and TCP clearly decreases as pH rises (in the case of TCP, this effect is observed at pH 8). This fact is in accordance with similar systems previously studied [30,31] and it can be explained regarding the charge of adsorbate and adsorbent in different media: as pH is increased, both the adsorbents and the adsorbates become more negative, and certain electrostatic repulsion appears, diminishing the interaction between them. In the case of TCP, the effect is observed at pH 8 due to a higher pK_a value when compared to 2,4-D (2.7 vs 6.2). The concentration of neutral molecules is always higher for TCP and its adsorption is therefore more effective.

The case of metolachlor appears more complex at first sight (Fig. 7), but the behavior of the adsorption system can be analyzed in the same terms. Metolachlor is neutral within all the pH range of study, but the two carbons are neutral only near the pH_{ZPC} ; therefore, the

intermolecular interaction (dispersion forces) is stronger near these pH values. That is why the adsorption is more effective when pH is near 8 in the case of CAT and near 6.5 in the case of CARBOPAL: at these pH values the charge of the adsorbent is minimum and the adsorption of metolachlor, which is neutral, is more effective.

3-5. Micropore diameter and molecular volume

The adsorption isotherms reveal an interesting fact: while the adsorption capacities of 2,4-D and TCP on the adsorbent CAT are greater than those on CARBOPAL, the opposite effect is observed in the case of metolachlor (see Table 5). This fact cannot be attributed to the acidity of the herbicides since this observation is independent of pH.

A plausible hypothesis would be the influence of molecular size of the three pesticides. TCP and 2,4-D are composed of relatively small flat molecules, while metolachlor molecules are bigger and more globular. The surfaces of the two adsorbents are different too: the micropore area represents 59% of the total area in CAT and only 12% in CARBOPAL. Moreover, the mean pore diameter in CAT is almost a half of that of CARBOPAL. Therefore, metolachlor would be more adsorbed on CARBOPAL because on CAT it would be very difficult to enter the smaller pores (which represent more than a half of the active sites).

Fig. 8 depicts the maximum adsorption capacity q_m (obtained from the fittings) for the herbicides studied in this work and three

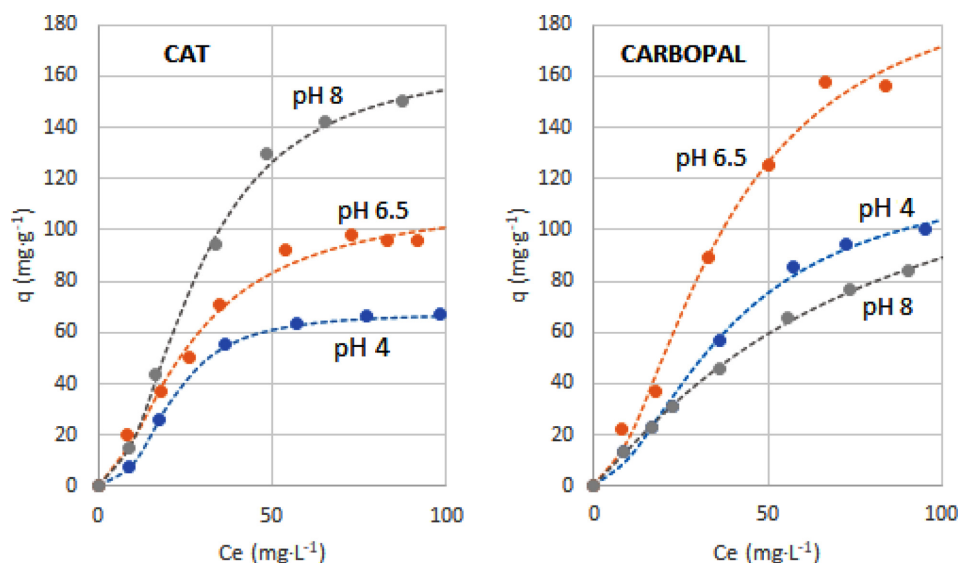


Fig. 7. Adsorption isotherms of metolachlor at different pH values on both adsorbents at 25 °C. Theoretical Sips fittings are shown in dashed lines.

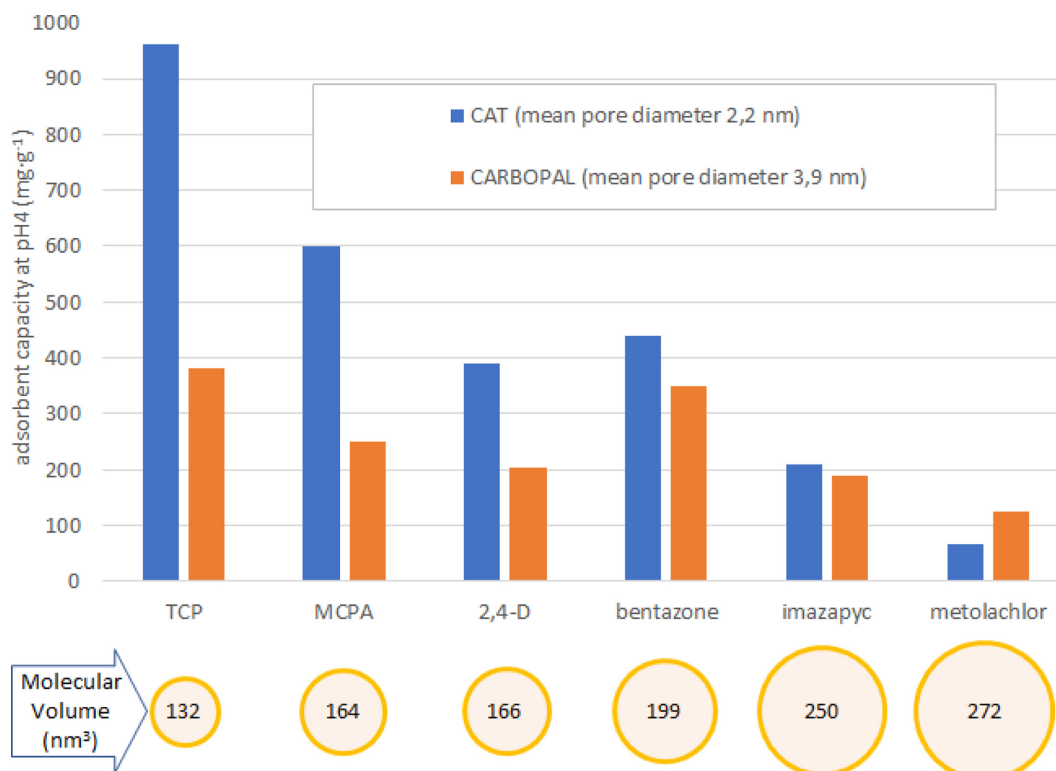


Fig. 8. Maximum adsorption capacity q_m ($\text{mg}\cdot\text{g}^{-1}$) for six different herbicides at pH 4 and 25 °C. Molecular volumes (nm^3) obtained by AM1 calculations.

others whose adsorption on CAT and CARBOPAL has been previously studied [18,22,32]. The six adsorbates are ordered by their molecular volume, which has been estimated by means of AM1 calculations for each herbicide [33].

As the molecular size of the herbicides increases, the adsorption on CAT is markedly reduced, which could be due to the difficulty of big molecules to enter the narrower pores of this adsorbent. This argument will be further supported by theoretical calculations commented in the next section.

3-6. Computational calculations

We studied the adsorption of TCP and metolachlor pesticides on activated carbon surface by means of molecular modelling. The most stable configurations are found upon full structural optimization (Fig. 9). The same analysis was previously done for 2,4-D [32].

Both molecules adsorb in a way that their benzene rings point toward the surface. The pesticides present similar stability on the carbon surface, the adsorption energy difference is 0.29 eV being TCP the most stable. Metolachlor has a bigger size than TCP and, in consequence, the TCP molecule presents lesser steric impediment for a better adsorption on the surface. The adsorption is weak, and a physical sorption is presented. Accordingly, no significant changes are observed in the geometry of the molecules during the interaction with the surface. The electron density from total SCF density (from electrostatic potential (EPS) map) for isolated TCP and metolachlor presents fewer reactive zone in the molecules (Fig. 9, right). To

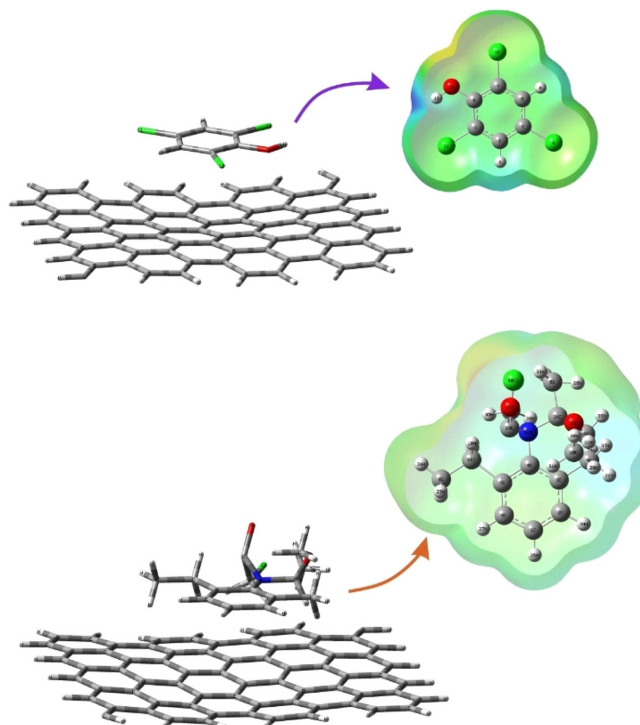


Fig. 9. Lateral view of TCP and metolachlor adsorbed on carbon surface (left). Total density of both pesticides.

correlate, charge changes to adsorption effectiveness, we performed charge analysis of both molecules. Tables 6 and 7 show the charge on

Table 6. Charges on metolachlor (MET) before and after adsorption on activated carbon surface

| Atoms | Isolated MET | MET on carbon |
|-------|--------------|---------------|
| C1 | -0.18907 | -0.18802 |
| C2 | -0.26011 | -0.26013 |
| C3 | -0.16020 | -0.16025 |
| C4 | 0.11896 | 0.11899 |
| C5 | -0.25983 | -0.25977 |
| C6 | -0.71162 | -0.71162 |
| C7 | 0.03179 | 0.03175 |
| C8 | -0.62895 | -0.62885 |
| C9 | -0.43369 | -0.43369 |
| C10 | -0.53374 | -0.53374 |
| C11 | -0.42074 | -0.42059 |
| C12 | -0.56081 | -0.56081 |
| C13 | 0.30575 | 0.30555 |
| C14 | 0.08324 | 0.08324 |
| C15 | -0.26948 | -0.26938 |
| O16 | -0.44773 | -0.44773 |
| O17 | -0.89141 | -0.89141 |
| H18 | 0.30405 | 0.30520 |
| H19 | 0.19167 | 0.19167 |
| H20 | 0.44544 | 0.44544 |
| H21 | 0.48085 | 0.48085 |
| H22 | 0.12542 | 0.12637 |
| H23 | 0.20750 | 0.20633 |
| H24 | 0.21357 | 0.21357 |
| H25 | 0.19260 | 0.19260 |
| H26 | 0.23158 | 0.23158 |
| H27 | 0.24196 | 0.24196 |
| H28 | 0.09466 | 0.09466 |
| H29 | 0.31992 | 0.31992 |
| H30 | 0.28974 | 0.28974 |
| H31 | 0.29439 | 0.29439 |
| H32 | 0.24502 | 0.24502 |
| H33 | 0.27660 | 0.27660 |
| H34 | 0.40843 | 0.409301 |
| H35 | 0.29917 | 0.29956 |
| H36 | 0.12252 | 0.12263 |
| H37 | -0.00177 | -0.00177 |
| H38 | -0.00895 | -0.00895 |
| H39 | 0.22762 | 0.22762 |
| C140 | 0.44097 | 0.44097 |
| N41 | -0.41533 | -0.41533 |

individual atoms of metolachlor and TCP molecules, respectively, before and after adsorption. In agreement, the electron distribution on TCP and metolachlor is partially modified after the interaction with the carbon surface. The electrons on benzene ring are mainly implied in the interactions with the carbon surface.

The interaction is produced between benzene ring and graphene through π - π interactions, and this is in agreement with the small changes observed in the atom charges confirming the physisorption (Table 6 and 7).

To study the adsorption of aromatic compounds, it is necessary to

Table 7. Charges on TCP before and after adsorption on activated carbon surface

| Atoms | Isolated TCP | TCP on carbon |
|-------|--------------|---------------|
| C1 | -0.06208 | -0.05340 |
| C2 | -0.21617 | -0.21936 |
| C3 | -0.10914 | -0.09734 |
| C4 | 0.36836 | 0.35231 |
| C5 | -0.21271 | -0.21725 |
| H6 | 0.26571 | 0.27154 |
| C7 | -0.08672 | -0.07954 |
| H8 | 0.26616 | 0.26785 |
| C19 | -0.00285 | -0.00152 |
| C10 | 0.01814 | 0.02417 |
| C11 | -0.01320 | -0.00696 |
| O12 | -0.73059 | -0.75271 |
| H13 | 0.51508 | 0.51324 |

consider the molecular dimension and orientation of the herbicides. The conformation in which the molecule is adsorbed is important to be considered since it could induce changes on the electronic behavior and consequently it will have influence in the π - π interactions responsible for the adsorption process. This is the case of TCP adsorption. On the other hand, the difference in the adsorption is mainly associated with the textural parameters, since the electrostatic interactions are practically discarded due to the non-polar character of metolachlor.

Some distances obtained from these calculations enlighten the assumptions made in the previous section. Considering the most stable adsorbent-adsorbate arrangements and van der Waals radii of the atoms, TCP, 2,4-D and metolachlor molecules would form layers on the surfaces having a height of approximately 5.0 Å, 5.2 Å and 7.5 Å, respectively. The thicker metolachlor layer explains why adsorption on CAT is more difficult (mean pore diameter 22 Å) than on CARBOPAL (mean pore diameter 39 Å), while adsorption of TCP and 2,4-D seems not to be affected by the pore size on these two adsorbates.

4. Conclusions

The adsorption of the herbicides 2,4-D, TCP and metolachlor has been studied on two activated carbons (CAT and CARBOPAL). Adsorbent characterization reveals important differences between them: 1) CAT has bigger micropore area and its micropores are narrower when compared to CARBOPAL, and 2) while CAT is not charged at neutral pH, CARBOPAL is positively charged in these conditions.

The adsorption kinetics could be adjusted as a second-order kinetic process in all cases with high confidence level ($R^2 > 0.999$), thus suggesting that adsorption takes place initially on the active sites of the mesopores, and that the adsorbate is then transported into the micropores.

All adsorption isotherms were tested against four theoretical models: Langmuir, Freundlich, Sips and Tempkin. The model that best

fitted the isotherms was Sips in all cases.

The pH of the solution strongly affects adsorption. In the case of the acidic herbicides (2,4-D and TCP), the efficiency of the process depends mainly on the charge of the adsorbate (within the studied pH range), being higher in acidic media, when there is more adsorbate in the neutral form. In the case of metolachlor (which is neutral), the adsorption capacity depends mainly on the charge of the surface (and that is why adsorption levels are higher for CAT at slightly basic pH and for CARBOPAL at acidic pH).

Adsorption also depends on the molecular size of the adsorbate: adsorption capacity of 2,4-D and TCP (small flat molecules) is higher on CAT and the adsorption capacity of metolachlor (bigger, more globular molecules) is higher on CARBOPAL. Theoretical calculations clearly support this assumption.

This work suggests that all these variables (acidity and molecular size of the adsorbate; surface charge and pore diameter and of the adsorbent) must be considered when searching activated carbon (and adsorbents in general) for removing pesticides from polluted water.

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