Removal of Plaguicides MCPA and Imazapic from Aqueous Solution Using Carbonaceous Materials

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Abstract— **Two different carbonous materials have been used in this study as adsorbents for the investigation of the adsorption kinetics and isotherms of two pesticides: (MCPA and Imazapic) from aqueous solution at various pH. Two simplified kinetic models, pseudo-first-order and pseudo-second-order, were used to predict the adsorption rate constants and activation energy. Both pesticides followed pseudo-second-order kinetics on both adsorbents. The adsorption capacity of activated carbon was found to be relatively higher in acidic rather than in basic solutions for both agrochemicals. The equilibrium data were analyzed by Langmuir, Freundlich, Temkin, Sips and Guggenheim–Anderson–de Boer (GAB) isotherms in order to define the best correlation model for each pesticide on both adsorbents. MCPA adapted to Langmuir model on CAT and CARBOPAL with a $R^2=0.997$ and 0.988, and Imazapic adapted to GAB model with $R^2=0.989$ and 0.933, respectively.**

Index Terms— **Pesticides, MCPA, Imazapic, Activated Carbon, Isotherm model**

I. INTRODUCTION

The rapid progresses of different industries and technologies have resulted in the production of a huge amount of wastewater that needs to be removed before being discharged into the environment. Inorganic and organic pollutants dissolved in aqueous solutions are hazardous because of their toxicity, even at low concentrations. Global increase of polluted waters seriously threatens human health and the environment.

Pesticides are one of many kinds of pollutants that affect environment and health of all living things. There are several procedures that were used for pesticide removal from water, such as photocatalytic degradation (Devipriya et al., 2005), combined photo-Fenton and biological oxidation (Ballesteros et al., 2008), and adsorption (Lai et al., 2013; Hammed et al., 2009). Adsorption on activated carbon is the most widespread technology used to deal with purification of water contaminated by pesticides and other kind of pollutants (Ho et al., 1998; Torrellas et al., 2015). The need for water quality is making this treatment successful. It is considered a refining treatment, and therefore the end of the most common treatment systems, specially after a biological treatment. Different materials (such as activated carbon, silica, titanium dioxide, alumina) and various nanomaterials (such as nanometal oxides, carbon nanotubes) are applied as adsorbent for removal of contaminants from aqueous solutions (Unob et al. 2007, Ren et al., 2011). Among the adsorbents available for removing herbicides from water, activated carbon is

preferred because of its high efficiency (Namasivayam et al., 2002; Salma et al., 2010). Charcoal is a meso-microporous adsorbent whose unique adsorption properties are the result of its large surface area and the wide range of surface functional groups, which influence its adsorption properties and reactivity. In this work, we have carried out studies in order to evaluate the adsorption of Imazapic and MCPA on two different types of carbon from aqueous solutions. In Argentina, Imazapic is preferably used on sugar cane in the northwestern regions (Tucumán, Jujuy, Salta) and Litoral zone. Most treatments performed with this pesticide in sugarcane generate dama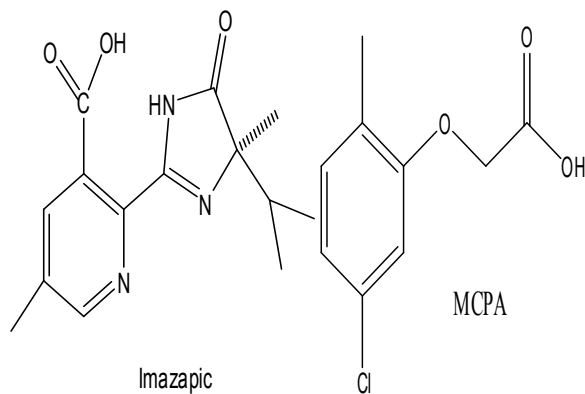ge at a greater or lesser extent. Imazapic (5-methyl-2-[4-methyl-5-oxo-4-(propan-2-yl)-4,5-dihydro-1 H-imidazol-2-yl] pyridine-3-carboxylic acid) is primarily used in commercial and non-selective weed control residential herbs. It can be transported rapidly across all regions of the plant, including the edible portions such as seeds, leaves, and fruits, and accumulates in tissues actively growing. Therefore, it is unsuitable for use on food crops. This imidazolinone inhibits the function of the enzyme acetolactate synthase (Paranjape et al., 2014), which is essential in the production of branched chain amino acids, disrupting protein synthesis which affects cell division and translocation of photosynthates in the growing point and eventually causes death. Azania et al. (2001) report that the phytotoxicity is greater over late pre-emergence applications. MCPA (4-chloro-2-methylphenoxyacetic acid) is a systemic post-used herbicide used for control of annual and perennial weeds in cereals, flax, peas, potatoes and forestry applications. MCPA is readily absorbed into most plants. It is a systemic hormonal action and selective herbicide for broadleaf weed control in cereals and other crops. It belongs to the group of hormone herbicides, so called because they affect the physiology of plants in the same way as natural auxins (indole acetic acid), but they are applied in exaggerated and uncontrolled ways, being effective in broadleaf weeds in certain crops. Due to its high selectivity, MCPA is ideal for application in crops such as oat, linseed, rice and wheat. Although insoluble in water, MCPA can have a high mobility in soil and it can negatively affect the growth of some crops, including onion, cabbage and lettuce. This herbicide is compatible with many other compounds and can be used in formulation with many other products, including bentazone and bromoxinyl, but is highly toxic to humans and nature (Environmental Protection Agency, 2004). In this work, we attempt to use two different activated carbons as low-cost adsorbent for the removal of pesticides from aqueous solutions. The use of these two particular materials as adsorbents for pollutants has not been reported in literature so far. So, they are novel substances with potential applications such as decontamination of surface and ground water.

II. MATERIALS AND METHODS

2.1 Adsorbates

MCPA was acquired in its commercial form under the name Glacoxan®. It was precipitated by adding concentrated HCl and purified by recristalization from H_2O. The mp was 137-138 °C. Technical grade Imazapic of 99.9% purity was supplied by Sigma-Aldrich and used as received. Fig. 1 shows chemical structure of both pesticides.

Fig.1: chemical structure of pesticides MCPA and Imazapic

Imazapic   MCPA

2.2 Adsorbents

Two types of commercial activated carbon were used, each one with different physical and chemical properties. Activated charcoal were Hydrogen Sulfide CAT-Ox 4 mm pellet Activated Carbon (UMI 2000) and CARBOPAL MB 4S (Donau). Adsorbents were ground and then calcined at 423 K in a stove for 24 h in order to eliminate adsorbed water. The two adsorbents will be named CAT and CARBOPAL from now on. These materials were analyzed considering their physical and chemical properties. Superficial areas and textural properties of carbons were determined using adsorption/desorption of N_2 at 77 K and analyzed by B.E.T equation. The porosity and pore size distribution could also be determined by using Barrett–Joyner–Halenda (BJH) method (Villarroel-Rocha et al., 2014). Surface chemical characterization of both adsorbents was performed with Boehm method, which is widely used for determination of acidic and basic surface groups of activated carbons (Boehm, 1994). Two bases were used for this purpose: NaOH and $NaHCO_3$. It is assumed that $NaHCO_3$ neutralizes only carboxyl groups while NaOH neutralizes carboxylic acids, phenols, lactones and carbonyls. HCl was used for neutralizing basic groups. 0.1000 g of carbon were placed in a 100 mL Erlenmeyer. 100 mL of 0.0563 M HCl solution were added. The system was kept under constant stirring for 24 h. After this time, the mixture was filtered and 20 mL of each solution were taken. They were titrated with 0.0539 M NaOH using phenolphthalein as pH indicator. For acidic groups, two measurements were made following the same procedure, using 0.0539M NaOH, and 0.0500 M $NaHCO_3$, and methyl orange as pH indicator. A blank experiment was also performed in order to verify the pH value of charcoal dispersion in distilled water.

Also, the pH of the point of zero charge, pH_{PZC}, was determined by drift method (Faria et al., 2004). pH_{PZC} is the pH at which the charge on the activated carbon surface is zero. Constant amounts of solids (0.1000 g) were weighted into closed 25 mL Erlenmeyers. 10.0 mL of 0.1000 M NaCl solution were added. pH adjustment was performed using 0.1000 M HCl and 0.1000 M NaOH solutions with pH values between (2 to 12). The initial pH of the solutions were measured with pHmeter Altronix-Mod EZDO-PC and noted as $pH_{initial}$. The system was magnetically stirred for 24 h. After this time, the dispersion was centrifuged and the pH_{final} of the solution was measured and plotted against $pH_{initial}$. pH_{PZC} of the activated carbon sample is the point when $pH_{initial} = pH_{final}$. Figure 2 is a hypothetical representation of the surface of activated carbon.
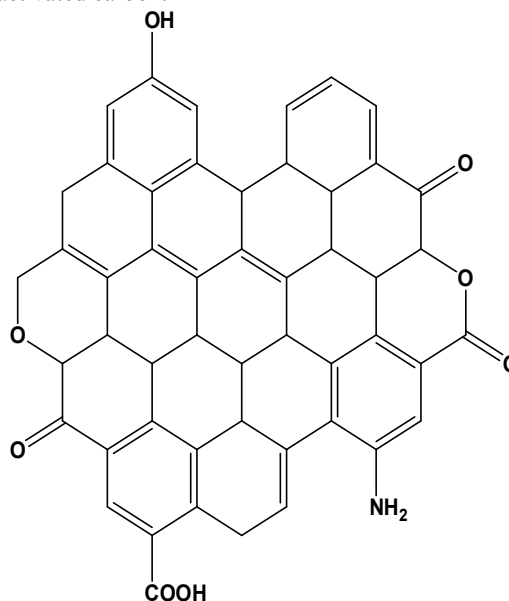

Fig.2. Chemical representation of activated charcoal.

2.3 Equilibrium studies

A classic batch contact experiment was performed for the equilibrium studies. The adsorption experiments of pesticides onto CAT and CARBOPAL were determined in a set of 50 mL Erlenmeyer flasks. 50 mL of aqueous solutions (containing NaCl 0.01 M as support electrolyte and fixed dosage of 2.00 ± 0.2 mg of adsorbents) bearing different initial pesticide concentrations (10-100 mg/L for MCPA and 10-50 mg/L for Imazapic) were used for each experiment. Distilled water was used to prepare all solutions and no buffers were used in order to avoid possible formation of precipitates or competition with the solute in adsorption equilibrium. Each flask was kept in an isothermal water-bath shaker with magnetic agitation speed of 100 rpm. The experiments were carried out for 24 h to ensure that the systems reach equilibrium. After this time, each sample was filtered using 22 μm nylon filters. The concentrations of MCPA and Imazapic in the solutions before and after adsorption were determined using a double beam UV–Vis spectrophotometer at 285 nm and 265 nm, respectively. It was then computed to pesticides concentration using standard calibration curve. The maximum capacity adsorption, q_e (mg/g), was calculated using Eq.1:

$$q_e = \frac{(C_0 - C_e)V}{m} \quad (1)$$

where C_o and C_e (mg/L) are the liquid-phase concentrations of pesticide at initial and at equilibrium, respectively. V (L) is the

volume of the solution and *m* (g) is the mass of dry adsorbent used. Each assay was performed in duplicate.

2.4 Sorption kinetics

For kinetic studies, 2.0 mg of adsorbent was contacted with 50 mL of 100 mg/L of MCPA and Imazapic solution using water bath shaker at 293 K. Magnetic agitation speed was kept constant at 100 rpm. At predetermined time intervals, the adsorbent was allowed to settle and 2 ml of solution were removed and filtered through 22 μm nylon filters, and their absorbance was measured by using UV spectrophotometer model METROLAB 1700 at 285 nm and 265 nm, respectively. The extracted volumes were returned to the initial solution in order to avoid changes in the solute-adsorbent ratio. A blank of each system was also performed in order to verify that no adsorption occurred at the surface of the glass material.

2.5 Effect of solution pH

The pH of a solution is recognized as a very influential parameter that governs the adsorption process and affects the surface charge of the adsorbent. The effect of solution pH on pesticides adsorption was investigated according to the following procedure. A mass of 0.002 g of dried activated carbon was added to a number of 50 ml Erlenmayers containing 50.0 ml of 25 mg/L pesticide solution. The pH of the pesticides solutions was adjusted over the range pH 3 to 11 using 0.1000 M NaOH solutions (prior to the addition of the adsorbent).

III. RESULTS AND DISCUSSION

3.1. Characterization of adsorbents

Table 1 summarizes pore diameter and surface area data for both CAT and CARBOPAL adsorbents. Specific surface and pore size were measured by B.E.T method of N_2 adsorption isotherm. It demonstrated that the two carbon are very different from each other. The method of Barrett, Joyner and Halenda (BJH) is a procedure for calculating pore size distributions from experimental isotherms using the Kelvin model of pore filling. This model assumes that the pores are slot type. It applies only to mesopore and small macropore size range. Fig. 3 and Fig. 4 show these results.
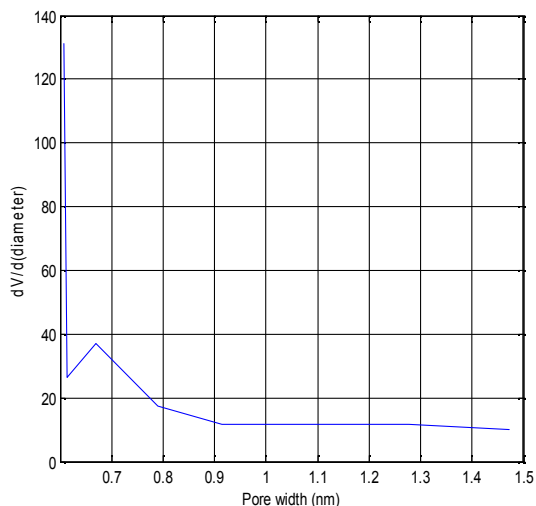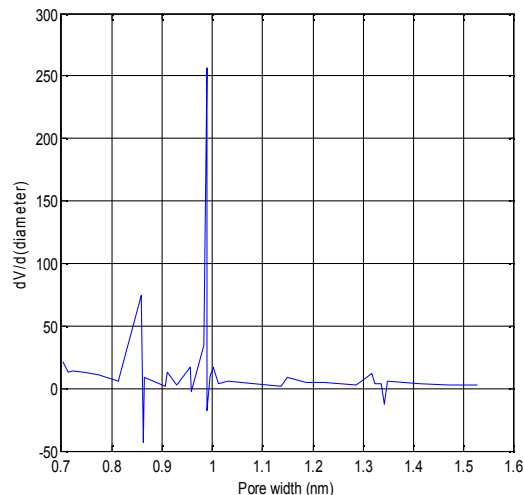

Fig.3. Pore size distribution of CARBOPA

Fig.4. Pore size distribution for CAT

Table 1. Physical properties of CAT and CARBOPAL

Properties	CAT	CARBOPAL
BET surface area (m^2/g)	983	1588
Average pore diameter (nm)	1	>0.8
Volume monolayer (mmol/g)	9.89	14.72

Fig.5 illustrates the plot obtained from the pH drift method. The pH_{PZC} value obtained for CAT was 7.46 and for CARBOPAL it was 4.78, indicating that the surface of the adsorbents have different chemical properties, causing differences in the adsorption processes. pH measurements of zero charge point (pH_{PZC}), and chemical properties are summarized in Table 2.
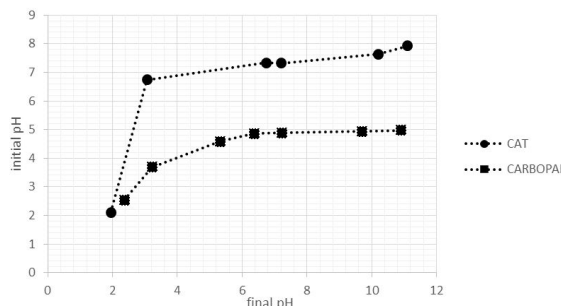

Fig.5. pH_{PZC} determination using pH drift method

Table 2. Adsorbents chemical properties

Adsorbents	pH point of zero charge	[Carboxyl group]	[Phenolic group]	[Basic group]
CAT	7.46	2.721 mmol/g	7.781 mmol/g	2.441 mmol/g
CARBOPAL	4.78	1.312 mmol/g	7.922 mmol/g	7.832 mmol/g

CAT adsorbent present basic properties, while CARBOPAL has a surface with acidic characteristic.

3.2. Adsorption kinetics models analysis

The adsorption kinetics of agrochemicals on both adsorbents was investigated by two models: the Lagergren pseudo-first-order model and pseudo-second-order model. Lagergren proposed a method for adsorption analysis (Tsenga et al., 2010) which is known as the pseudo-first-order kinetic equation expressed in Eq.2:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t \quad (2)$$

where q_e and q_t are the amounts adsorbed at equilibrium and at time t (mg/g), and k_1 is the of the pseudo-first-order rate constant adsorption (min^{-1}). The linear plot of $log\ (q_e-q_t)$ versus t gives a slope of k_1 and intercept of $log\ q_e$.

Pseudo-second-order kinetic model (Ho et al., 1999) can be represented by Eq.3:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (3)$$

where k_2 [g/(mg min)] is the pseudo-second-order adsorption rate constant (Azizian, 2004; Ho, 2006). The linear plot of t/q_t versus t gave $1/q_e$ as the slope and $1/(k_2 q_e^2)$ as the intercept. Tables 3-4 resumed the values obtained for kinetics studies on both adsorbents.

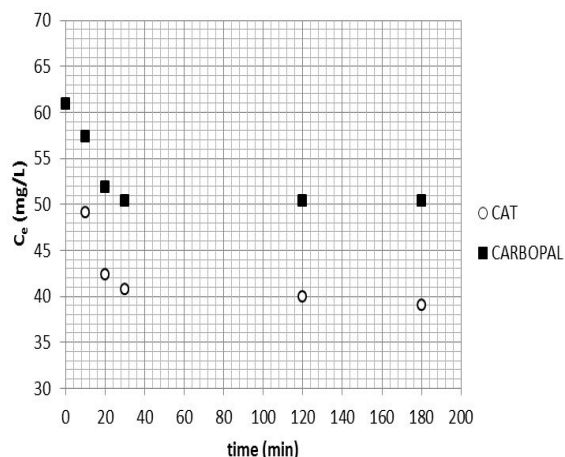Fig. 6. Adsorption kinetic of MCPA on CAT and CARBOPAL

Fig. 7. Adsorption kinetic of Imazapic on CAT and CARBOPAL

Table 3. Kinetic model parameters for adsorption of MCPA onto CAT and CARBOPAL

Kinetic model	CAT		CARBOPAL	
	Parameter	Value	Parameter	Value
Pseudo-first-order	k_1 (min^{-1}) R^2	0.0872 0.9395	k_1 (min^{-1}) R^2	0.3634 0.5902
Pseudo-second-order	k_2 (g/mg·min) R^2	0.00124 0.9997	k_2 (g/mg·min) R^2	0.0036 0.9996

Table 4. Kinetic model parameters for adsorption of Imazapic onto CAT and CARBOPAL

Kinetic model	CAT		CARBOPAL	
	Parameter	Value	Parameter	Value
Pseudo-first-order	k_1 (min^{-1}) R^2	0.0124 0.8403	k_1 (min^{-1}) R^2	0.0976 0.9010
Pseudo-second-order	k_2 (g/mg·min) R^2	3.086x 10^{-4} 0.9988	k_2 (g/mg·min) R^2	3.789x 10^{-4} 0.9899

This value confirms the pseudo-second order best describes the adsorption process for both pesticides on both adsorbents. This result is similar like other previous studies (Bakouri et al. 2009, Netpradit et al. 2004; Sadasivam et al. 2010; Senthilkumaar et al., 2010) on adsorption of pesticides, dyes and other pollutants.

3.3. Validity of kinetic model.

Two different kinetics models were employed to understand the adsorption process on both adsorbents (Dogan et al., 2003; Hameed et al., 2009). To compare fitting of the model, kinetic model was verified by the normalized standard deviation Δq (%), (Yang et al., 2005; Kumar et al., 2006) which is defined as Eq.6:

$$\Delta q(\%) = \sqrt{\frac{\left[\left(\frac{q_{exp} - q_{cal}}{q_{exp}}\right)\right]^2}{N}} \quad (6)$$

where q^{cal} and q^{exp} (mg/g) are the experimental and calculated adsorption capacity respectively, and N is the number of points. The lower the value of Δq the better the model fits. Table 5 summarizes these values.

Table 5. Normalized standard deviation (Δq) for kinetics models.

Kinetic model	Adsorbate: MCPA		Adsorbate: Imazapic	
	CARBOPAL	CAT	CAT	CARBOPAL
Pseudo-first-order	0.3151	0.2257	0.3217	0.3456
Pseudo-second-order	0.0100	0.0124	0.0079	0.0251

These values confirmed that pseudo-second-order is the best model to described kinetic adsorption of both pesticides on both adsorbents.

3.4 Effect of pH on MCPA and Imazapic adsorption
The effect of surface functionality on pesticide adsorption may be complicated by the charge characteristics of the carbon surface. A change in solution pH may also change the charge properties of ionizable pesticide molecules and, hence, their adsorption. With a pK_a of 3.85, MCPA is present in solution primarily in the molecular for at pH < 3.85, as an anionic species at pH > 3.85 because of the deprotonation of carboxylic acid group. Imazapic shows different ionic states, according to solution pH. Fig. 8-9 shows ionic states of the pesticides, and Fig. 10 shows the effect of pH on adsorption of both pesticides on both materials.
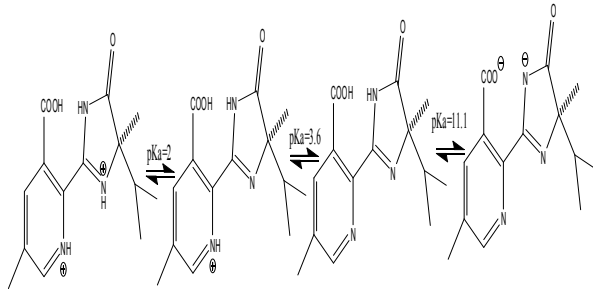

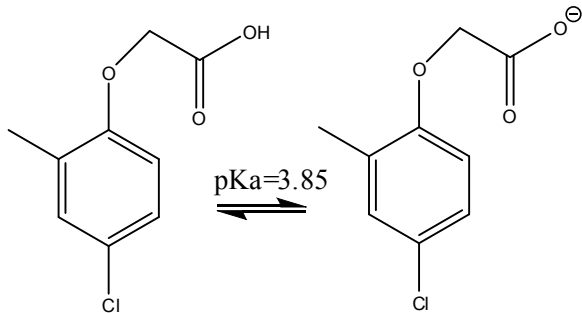Fig. 8. Imazapic ionization states: $pK_{a1} = 2$, $pK_{a2} = 3.6$ and $pK_{a3} = 11.1$
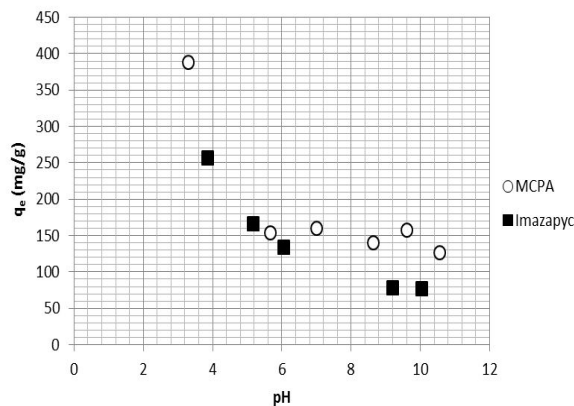

Fig. 9. MCPA ionization states: pKa = 3.85

Fig.10. Effect of pH on adsorption of MCPA and Imazapic on CAT (a) and CARBOPAL (b)

At pH < pH_{PZC}, the carbon surface has a net positive charge, whereas at pH > pH_{PZC}, the surface has a net negative charge. Electrostatic interaction must be taken into account to explain this phenomenon. (Newcombe et al., 1997). The adsorption of MCPA significantly decreased with increasing pH. This fact can be explained by the different species present at pH values and the effect produce on carbon surface because their pH_{PZC}. At pH=3.85, MCPA is in its neutral ionization state, while CAT and CARBOPAL are positively charged. In this case, adsorption is favorable. But, while pH increases, both pesticide and the two types of carbon generated negative charges, so that electrostatic repulsions are predominant, causing a decrease in adsorption capacity. Considering Imazapic, the conclusions are similar because generating negative charges by increasing the pH of the medium, adsorption decreases. The decrease in the adsorption capacity is in accordance with the general trend observed for many other pesticides and pollutants (Kumar Singh et al., 2013; Yang et al., 2004; Al-Degs et al., 2008)

3.5 Equilibrium modeling
Experimental data obtained was tested to describe the experimental results with common models: Langmuir, Freundlich, Temkin and Guggenheim–Anderson–de Boer and Dubinin-Raduskevich (Foo et al., 2010; Salman et al., 2010). The Langmuir isotherm sorption monolayer assumes a surface containing finite active sites. Once one of these sites is occupied by a molecule sorbate is not possible for it to interacts with other molecules sorbate. Langmuir isotherm has a hyperbolic dependence given by the Eq. 10

$$q_e = \frac{Q_m K_{eq} C_e}{1 + K_{eq} C_e} \quad (10)$$

where Q_m is the maximum adsorption layer per unit mass of sorbent, K_{eq} is the constant represents the equilibrium constant for sorption reaction. Langmuir model is derived from a number of assumptions:
All active sites have equal affinity for the sorbate
Sorption is limited to a monolayer
The number of sorbed species cannot exceed the number of active sites, this is the stoichiometry is 1: 1
The essential characteristics of the Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor R_L that is given by Eq. 11

$$R_L = \frac{1}{1 + K_L Q_m} \quad (11)$$

where Q_m is the highest initial concentration of adsorbate (mg/L), and K_L (L/mg) is Langmuir constant. The value of R_L

indicates the shape of the isotherm to be either unfavorable ($R_L>1$), linear ($R_L=1$), favorable ($0<R_L<1$), or irreversible ($R_L=0$). The R_L values between 0 and 1 indicate favorable adsorption.

Freundlich model assumes a heterogeneous adsorption, with adsorbents of active sites which exhibit affinity distribution sorbate. Higher affinity sites are the first to be occupied. The model can be expressed by Eq. 12

$$q_e = K_F C_e^{1/n_F} \quad (12)$$

where K_F denotes the quantity of adsorbate adsorbed onto the adsorbent for a unit equilibrium concentration and n_F indicates the heterogeneity of the system. In general, values for n_F in the range of 1–10 indicate that the adsorbate was favorably adsorbed onto the adsorbent; $n<1$ indicates that the adsorbate was inadequately adsorbed onto the adsorbent.

Guggenheim–Anderson–de Boer (GAB) model (1966) is frequently used in the fitting of experimental multilayer isotherms and is expressed mathematically as Eq. 13:

$$q_e = \frac{q_m K_1 C_e}{(1 - K_2 C_e)[1 - (K_1 - K_2)C_e]} \quad (13)$$

where q_m (mg/g) is the maximum adsorption capacity on the first monolayer, K_1 and K_2 (L/mg) are the equilibrium constants for the first and the second monolayer, respectively. In order to simplify the calculation of the equilibrium, the formation of only two monolayers has been supposed

The derivation of the Temkin isotherm assumes that the fall in the heat of sorption is linear rather than logarithmic, as implied in the Freundlich equation. The Temkin isotherm has generally been applied in the following form:

$$q_e = \frac{RT}{b_T} \ln A_T C_e \quad [14]$$

where b_T is a constant and A_T is a Temkin isotherm equilibrium binding constant (L/g).

Sips isotherm model is similar to the Langmuir isotherm, but has the additional parameter n; if this parameter is equal to unity, we recovered the Langmuir equation, applicable to surfaces ideals and homogeneous. That is, the parameter n can be identified as the degree of heterogeneity system. This heterogeneity can come from the adsorbate, the adsorbent or both of them. The model can be characterized by Eq. 15:

$$q_e = \frac{Q_m (K_{eq} C_e)^{1/n}}{1 + (K_{eq} C_e)^{1/n}} \quad [15]$$

Fig. 11 and Fig.12 show adsorption isotherm for MCPA and Imazapic on both adsorbents, respectively, and Table 6-7 resume the constant values for each adsorption model for MCPA and Imazapic.
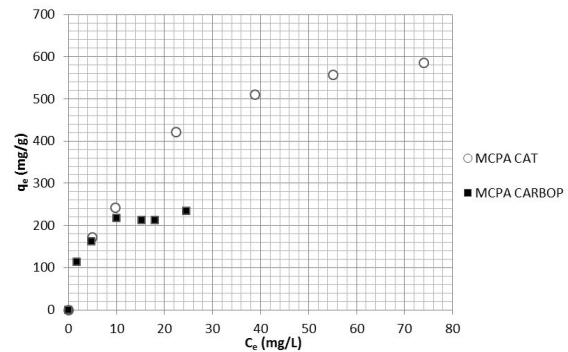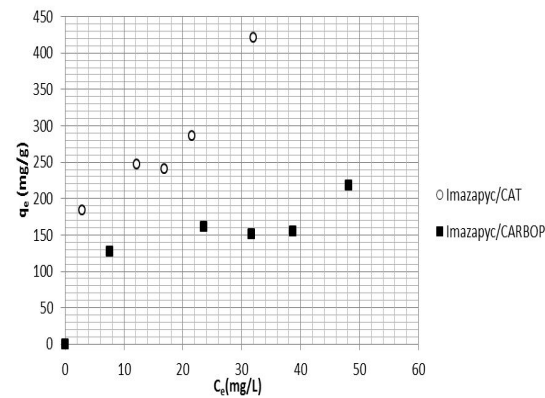

Fig.11. MCPA adsorption on CAT and CARBOPAL

Fig.12. Imazapic adsorption on CAT and CARBOPAL

Table 6. Adsorption modeling for MCPA.

Isotherm model	CAT		CARBOPAL	
	Parameter	Value	Parameter	Value
Langmuir	Q_m (mg/g) K_L (L/mg) R_L R^2	732.884 0.057 0.0233 0.9970	Q_m (mg/g) K_L (L/mg) R_L R^2	247.398 0.461 0.0087 0.9876
Freundlich	K_F (mg/g) n_F R^2	104.025 2.405 0.9756	K_F (mg/g) n_F R^2	108.98 4.0772 0.9756
Guggenheim–Anderson–de Boer	Q_m (mg/g) K_1 (L/mg) K_2 (L/mg) R^2	250.00 1.0862 1.0948 0.6569	Q_m (mg/g) K_1 (L/mg) K_2 (L/mg) R^2	149.9567 3.419 0.0159 0.8755

Temkin	b_T A_T R^2	15.215 0.542 0.9906	b_T A_T R^2	55.645 8.114 0.9841	
Sips	Q_m (mg/g) K_L (L/mg) n R^2	714.081 0.0606 0.9584 0.9960	Q_m (mg/g) K_L (L/mg) n R^2	260.618 0.4177 1.1681 0.9852	

Table 7. Adsorption modeling for Imazapic.

Isotherm model	CAT		CARBOPAL	
	Parameter	Value	Parameter	Value
Langmuir	Q_m (mg/g) K_L (L/mg) R_L R^2	409.315 0.1595 0.0151 0.8162	Q_m (mg/g) K_L (L/mg) R_L R^2	198.243 0.2027 0.0243 0.8875
Freundlich	K_F (mg/g) n_F R^2	93.746 2.525 0.9032	K_F (mg/g) n_F R^2	72.436 4.071 0.9131
Guggenheim–Anderson–de Boer	Q_m (mg/g) K_1 (L/mg) K_2 (L/mg) R^2	175.478 7.914 0.01819 0.9893	Q_m (mg/g) K_1 (L/mg) K_2 (L/mg) R^2	114.25 4.0298 0.00915 0.9328
Temkin	b_T A_T R^2	31.375 2.4594 0.8589	b_T A_T R^2	72.000 4.4086 0.9042
Sips	Q_m (mg/g) K_L (L/mg) n R^2	$2,997 \times 10^5$ $1,4442 \times 10^{-9}$ 2.522 0.871	Q_m (mg/g) K_L (L/mg) n R^2	$2,140 \times 10^5$ $1,042 \times 10^{-10}$ 4,041 0.8817

The results indicate that carbon with lower BET specific surface has a higher adsorption capacity for both pesticides. According to the values obtained from non-linear fits of the isotherms for each pesticide on carbonaceous materials, it is concluded that MCPA fits to Langmuir model on both CAT and CARBOPAL. Sips model confirms this conclusion, observing the values of R^2 and n. Therefore, the formation of a monolayer on the surface of both activated charcoals is expected through a process of chemisorption. While Imazapic adapts to multilayer model of Guggenheim–Anderson–de Boer on both materials and interactions on activated carbon are stronger than interactions between molecules adsorbed on the continuous layers, according to the values of K_1 and K_2.

The fraction of carbon surface that is occupied by each pesticide (θ) can be calculated from the amount of pesticide adsorbed and the surface area occupied by one pesticide molecule (σ) using the Eq. 16:

$$\theta = \frac{Q_{max} N \sigma \times 10^{-20}}{S_{BET}} \quad (16)$$

Where represents the fraction of the surface that is occupied by pesticide molecule saturation; Q_{max} (mol/g) is the amount of pesticide adsorbed at saturation, as obtained from the best correlated model; σ (Å^2/molecule) is the surface area occupied by one molecule; N is the Avogadro`s number (6.023×10^{23}); S_{BET} (m^2/g) is the specific surface area of the adsorbents. McClellan (1967) has proposed an empirical relationship (Eq. 17) that may be used for the estimation of σ of organic molecules adsorbed on activated carbon:

$$\sigma = 1.091 \times 10^{16} \left(\frac{MW}{\rho N} \right)^{2/3} \quad (17)$$

Where MW is the molar mass of the adsorbed molecule; ρ is the adsorbate density. Considering the formation of multilayers for adsorption of Imazapic, analysis is performed using the values of the first layer of pesticide. The corresponding values of σ and θ for each pesticide are given in Table 8.

Table 8. ρ, σ, and θ values for pesticides

Adsorbates	ρ (gr/cm^3)	σ (Å^2/molecule)	Adsorbents	θ
MCPA	1.56	38.933	CAT	0.9055
			CARBOPAL	0.5394
Imazapic	1.31	54.072	CAT	0.1956
			CARBOPAL	0.1157

The values of θ indicate that the formation of a complete molecular layer (θ=1) was not achieved for neither system. For MCPA molecules, a large fraction of the CAT surface is occupied by chemisorption processes according to Langmuir model.

Considering the formation of multilayers for adsorption on CARBOPAL, the analysis is performing using the values of the first layer of pesticide. The value of the constant K_1 is greater than K_2 (Table 9), which explains that the interactions between the agrochemical and the material is more intense than between molecules of the plaguicides.

Batch experiments of adsorption of two herbicides, MCPA and Imazapic, onto two types of carbonous materials named CAT and CARBOPAL, were performed under different solution conditions. Both materials appear to be very effective at removing these pollutants, but CAT seems to have a higher capacity. Both pesticides follow pseudo-second-order kinetic model on both materials. The adsorption capacity (q_e) of herbicides is significantly influenced by pH value. In the present study, both pesticides have a decrease on adsorption capacity on each carbon when basic conditions are used. At lower pH, for MCPA on CAT, q_e = 388.664 mg/g, and decreased with the increase in solution pH where q_e= 126.923 mg/g. Also, different models were analyzed to predict properties of each adsorption process. MCPA adapts to Langmuir theoretical model on both materials. Therefore, it is predicted a chemisorption process with the formation of a monolayer. On the other hand, Imazapic adapts to GAB model on CAT and CARBOPAL, with the formation of multilayer. Adsorption capacity is very high, so both materials can be used as an efficient and low cost-effective method to remove MCPA and Imazapic from water resources.

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