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## Study on the efficient removal of clopyralid from water using a resorcinol–formaldehyde carbon cryogel

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**Abstract:** A resorcinol–formaldehyde carbon cryogel was prepared, characterized and used for the removal of the commonly used herbicide clopyralid from aqueous solutions under varying experimental conditions. The carbon exhibited a relatively high specific surface area, significant mesoporosity and an amorphous structure. The following isotherm models were used to interpret the equilibrium data: the Langmuir, Freundlich, Temkin, Dubinin–Radushkevich, Jovanović, Hurkins–Jura and the Helsey Model. Several models fitted the data well although the calculated values for  $q_{\max}$  poorly correlated with the experimentally obtained data. The pseudo-first and pseudo-second-order kinetic models, the models of Elovich, Bangham and the intraparticle diffusion model were employed for fitting the kinetic data. The rate of the process was fast at the beginning, although the adsorption equilibrium was not attained before 24 h. The adsorption was found to be pH dependent and favored in acidic solutions.

**Keywords:** clopyralid; carbon cryogel; mesoporosity; adsorption mechanism.

### INTRODUCTION

Clopyralid (3,6-dichloro-2-pyridinecarboxylic acid) is an auxin-mimic type of herbicide from the chemical class of pyridine compounds that is used extensively to control broadleaf weeds, particularly those of the *Asteraceae*, *Fabaceae*, *Solanaceae*, *Polygonaceae*, and *Violaceae* families. Clopyralid kills the target weed by mimicking the plant growth hormone auxin (indole acetic acid), and when the dose is administered effectively it causes uncontrolled and disorganized growth of the plant, and its eventual death. Its low ability to bind with soils makes it both highly mobile and a long-term contamination threat to water resources.<sup>1</sup>

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The presence of clopyralid was reported in the surface drinking-water supplies of the Northern Great Plains.<sup>2</sup> A growing interest in the removal of clopyralid from water has evolved with its increasing usage in agriculture. Recently, several interesting studies reported the degradation of clopyralid by advanced oxidation processes, such as photocatalysis,<sup>3</sup> treatments with UV/H<sub>2</sub>O<sub>2</sub> or ozone<sup>4</sup> and electron beam treatment.<sup>5</sup> However, the removal of this undesirable pesticide from water by application of adsorption techniques has been scarcely examined.

Carbon cryogels (CC) are versatile carbon materials with a developed mesoporous structure. They are synthesized mostly by the sol-gel polycondensation process using, for instance, resorcinol and formaldehyde as precursors, followed by drying of the obtained hydrogels and their carbonization in an inert atmosphere.<sup>6,7</sup> Moderately high surface areas (500–1200 m<sup>2</sup> g<sup>-1</sup>) and large mesoporous volumes (>0.89 ml g<sup>-1</sup>)<sup>8</sup> are specific features of carbon cryogels, which are sufficient to meet application criteria in catalysis,<sup>9</sup> adsorption,<sup>10</sup> gas separations,<sup>11</sup> double layer capacitors,<sup>12</sup> column packings in HPLC,<sup>13</sup> *etc.*

Adsorption is recognized as an efficient and easy to operate technique that is used in the removal of a broad spectrum of chemical species from contaminated industrial and drinking water. Carbonaceous adsorbents, along with some modified clays and various biosorbents, are most frequently used for commercial purposes. Adsorption onto carbon cryogels has gained prominence for the removal of specific classes of compounds, including some inert and hardly binding pesticides that are resistant to photolysis and spontaneous biodegradation.

In the present paper, the batch adsorption properties for clopyralid removal from aqueous solutions using a synthesized resorcinol-formaldehyde (RF) carbon cryogel are presented and discussed. The experimental conditions were varied, *i.e.*, the initial pesticide concentration, the contact time and solution pH. The obtained data were linearly fitted to several adsorption models in order to establish the model that was the most appropriate to describe clopyralid adsorption.

## EXPERIMENTAL

### *Synthesis and characterization of the RF carbon cryogel*

The synthesis was based on the polycondensation of resorcinol with formaldehyde in the presence of sodium carbonate as a basic catalyst. The mole ratios of resorcinol to formaldehyde, resorcinol to water, and resorcinol to catalyst were 0.5, 20 and 100, respectively. The obtained homogenous white mixture was decanted into a glass tube of 10 mm inner diameter, sealed and aged for 2 days at 25 °C, 1 day at 50 °C and 4 days at 85 °C. The formation of the hydrogel is given in Fig. 1. Freeze-drying, according to the procedure of Tamon and coworkers, was used.<sup>14-16</sup> RF gel was immersed in a 10-times volume of *t*-butanol for more than one day to displace the liquid contained in the gels with *t*-butanol. Rinsing with *t*-butanol was repeated twice. The gel was freeze-dried using a Modulyo System (Edwards, England). Gel was frozen in a deep-freeze refrigerator at -30 °C for 24 h. After that, the gel was freeze-dried in the acrylic chambers of the freeze dryer with the shelves mounted directly on the top of the con-

denser of the freeze dryer. The pressure during these 24 h of freeze-drying was around 4 mbar. The obtained cryogel was further carbonized in a conventional furnace, in a protective flow of nitrogen at 800 °C. After pyrolysis, the furnace was cooled down to room temperature under a nitrogen atmosphere. The obtained black material was crushed to powder and kept in a closed PVC bottle.

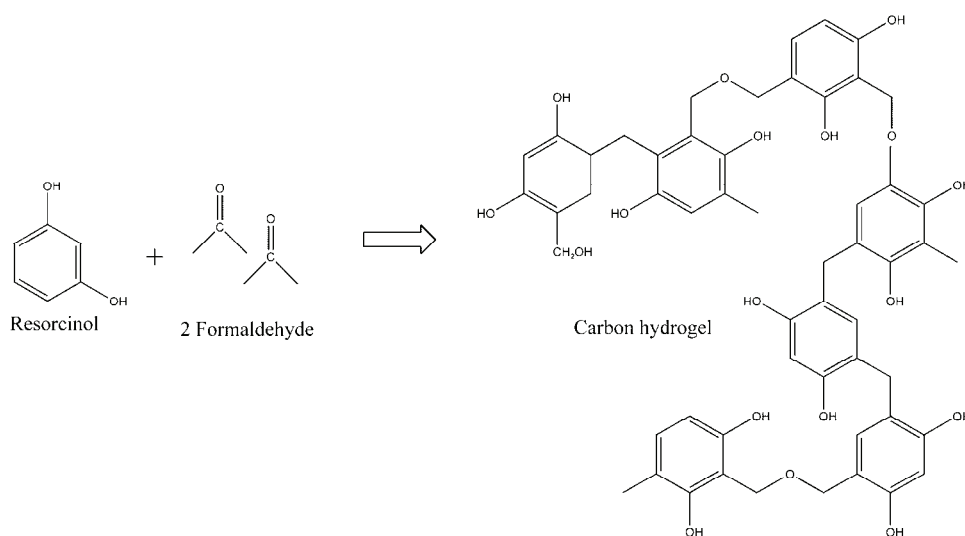


Fig. 1. Synthesis of the carbon cryogel.

The porous properties of the CC were examined by nitrogen adsorption/desorption isotherms obtained at  $-196\text{ }^{\circ}\text{C}$ , using the gravimetric McBain Method. From the isotherms, the specific surface area ( $S_{\text{BET}}$ ), the pore size distribution, the mesopore area including the external surface area ( $S_{\text{meso}}$ ), and the micropore volume ( $V_{\text{mic}}$ ) were calculated. The pore size distribution was estimated by application of the BJH Method to the desorption branch of the isotherms.<sup>17</sup> The mesopore surface and the micropore volume were estimated using the high resolution  $\alpha_s$ -plot method.<sup>18,19</sup> Micropore surface ( $S_{\text{mic}}$ ) was calculated by subtracting  $S_{\text{meso}}$  from  $S_{\text{BET}}$ .

The microstructure of the carbon sample was observed using a scanning electron microscope JEOL JSM 5800 LV (Japan). A representative image of micrometric structure of the CC is given in Fig. 2.

The  $\text{pH}_{\text{PZC}}$  of the cryogel suspension, corresponds to the pH value when the carbon surface has zero net charge, was determined using the pH drift method.<sup>20</sup>

#### Chemicals and solutions

Technical grade clopyralid (99.4 % purity) was purchased from Riedel-de-Haën, resorcinol (99 % purity) from Merck, methanol stabilized formaldehyde (36 % purity) from Fluka Chemie, *t*-butanol (*p.a.* quality) from Centrohem, and sodium carbonate (*p.a.* quality) was purchased from Merck. All the chemicals were used as received without further purification. Deionized water of  $18\text{ M}\Omega\text{ cm}^{-1}$  resistivity, obtained from a Milli-Q® Plus Total Water System (Millipore Corporation, Bedford, USA), was used to prepare all the solutions. The chemical structure of clopyralid, including its dimensions, is given in Fig. 3.

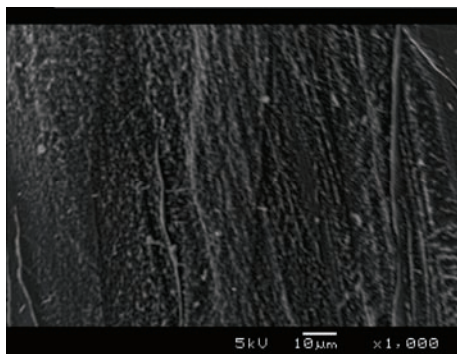


Fig. 2. SEM image of the obtained carbon cryogel.

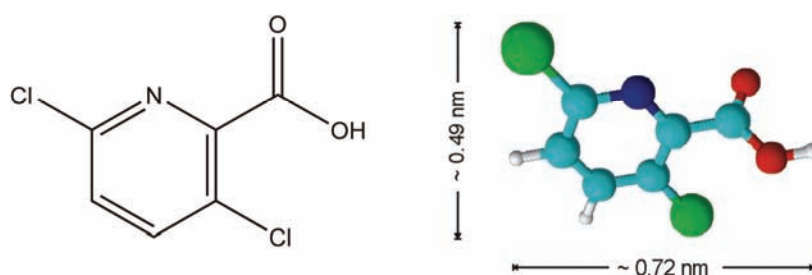


Fig. 3. Structural formula of clopyralid with dimensions.

#### *Clopyralid adsorption*

The kinetics of the adsorption were investigated by contacting 30 mg of carbon cryogel with 25 cm<sup>3</sup> of 100 mg dm<sup>-3</sup> clopyralid solution at 25 °C for different times up to 24 h. The native (unadjusted) pH of the pesticide suspensions were around 3 in all experiments. After contacting, the suspensions were filtered through Macherey-Nagel No. 5 filter paper. The residual concentration of the pesticide in the supernatant was estimated spectrophotometrically by monitoring the absorbance at 280 nm using a Lambda 40 UV/Vis spectrophotometer (Perkin-Elmer Instruments, USA). For the isotherm studies the experiments have been conducted in the same manner by contacting 20 mg of carbon cryogel with clopyralid solutions of different initial concentrations (30–100 mg dm<sup>-3</sup>) until the equilibrium was attained (24 h). The effect of pH on the adsorption was investigated by contacting 25 mg of carbon with 25 cm<sup>3</sup> of a 100 mg dm<sup>-3</sup> pesticide solution for 24 h at different initial pH values, from 2 to 12. The pH was measured using a Lutron YK-2001PH LT pH meter (Intelligent Meter, Taiwan). In all the cases, the adsorption capacity,  $q$  (mg g<sup>-1</sup>) was calculated using the equation:

$$q = \frac{(c_0 - c)V}{m} \quad (1)$$

where  $c_0$  (mg dm<sup>-3</sup>) is the initial clopyralid concentration,  $V$  (dm<sup>3</sup>) is the volume of the solution,  $m$  (g) is the mass of the adsorbent and  $c$  (mg dm<sup>-3</sup>) is the residual pesticide concentration at equilibrium or any time  $\tau$  (min), which then defines  $q_e$  or  $q_\tau$  (mg g<sup>-1</sup>), respectively.

## RESULTS AND DISCUSSION

*Porous properties of CC*

The results of the textural analysis of the CC surface are given in Table I. CC exhibited typical type-IV sorption–desorption curves showing a gentle but distinct hysteresis loop. This is characteristic for a material that contains a great deal of mesoporosity, and has a high energy of gas adsorption. The material often contains hysteresis attributed to its mesoporosity. In the present study, the obtained results for  $S_{\text{BET}}$  are typical and comparable to those reported for mesoporous carbons obtained by similar synthesis approaches.<sup>10</sup> Mesopores are acknowledged to possess an  $R_p$  of between 1 and 25 nm, while micropores have an  $r_p$  below 1 nm. The pore radius or half the distance across the pore is defined as  $r_p$ . Since the pore size distribution gave an  $r_p$  value of 2.1 nm, it could be concluded that the dominant number of pores in the CC were within the mesopore size range and this is exactly the reason for considering CCs as suitable mesoporous materials. The determined mesopore surface was  $285 \text{ m}^2 \text{ g}^{-1}$ , which is considered large for a carbon material.

TABLE I. Porous properties of the carbon cryogel

Property	Value
$S_{\text{BET}} / \text{m}^2 \text{ g}^{-1}$	517
$S_{\text{meso}} / \text{m}^2 \text{ g}^{-1}$	285
$S_{\text{micro}} / \text{m}^2 \text{ g}^{-1}$	232
$r_p / \text{nm}$	2.1
$V_{\text{micro}} / \text{m}^3 \text{ g}^{-1}$	0.11

*Scanning electron microscopy*

An SEM image of the CC sample is shown in Fig. 2. Magnifying the figure 1000 times was sufficient to observe the uniform and compact structure of the CC grain. An irregular surface texture could be noticed. In addition, a lamellar structure in the CC grain was assumed present. This would correspond to the parallel network of macropores that leads to pores of smaller dimensions.

*Isotherm modeling*

The Langmuir Model is defined as:

$$q_e = \frac{K_L c_e}{1 + \alpha_L c_e} \quad (2)$$

which, after linearization, gives:

$$\frac{c_e}{q_e} = \frac{1}{K_L} + \frac{\alpha_L}{K_L} c_e \quad (3)$$

where  $q_e$  ( $\text{mg g}^{-1}$ ) and  $c_e$  ( $\text{mg dm}^{-3}$ ) are the amount of adsorbate per unit mass of adsorbent and the concentration of unadsorbed adsorbate in solution at equilibrium, respectively.  $K_L$  ( $\text{dm}^3 \text{g}^{-1}$ ) represents the Langmuir equilibrium constant and  $K_L/\alpha_L$  gives the theoretical monolayer saturation capacity,  $q_0$ . A plot of  $c_e/q_e$  vs.  $c_e$  gives a straight line of slope  $\alpha_L/K_L$  and intercepts  $1/K_L$ . The essential features of the Langmuir isotherm can be expressed in terms of a dimensionless constant called the separation factor ( $R_L$ ) which is according to the following equation:

$$R_L = \frac{1}{1 + K_L c_0} \quad (4)$$

where  $c_0$  ( $\text{mg dm}^{-3}$ ) is the initial adsorbate concentration and  $\alpha_L$  ( $\text{dm}^3 \text{mg}^{-1}$ ) is the Langmuir constant related to the energy of the adsorption. The value of  $R_L$  indicates the shape of the isotherms and could be unfavorable ( $R_L > 1$ ), linear ( $R_L = 1$ ), favorable ( $0 < R_L < 1$ ) or irreversible ( $R_L = 0$ ).<sup>21</sup>

The Freundlich Model is used to describe adsorption onto heterogeneous surfaces where the adsorbate species are bound with different binding energies. It is represented by the equation:

$$q_e = K_F c_e^{1/n} \quad (5)$$

which, after linearization, becomes:

$$\log q_e = \log K_F + \frac{1}{n} \log c_e \quad (6)$$

The lower fractional value of  $1/n$  ( $0 < 1/n < 1$ ) indicates that some weak adsorptive forces are effective on the surface of the adsorbent.<sup>21</sup>

The Temkin Model is presented as:

$$q_e = \frac{RT}{b} \ln(K_T c_e) \quad (7)$$

After linearization, its form becomes:

$$q_e = \frac{RT}{b} \ln K_T + \frac{RT}{b} \ln c_e \quad (8)$$

where constant  $K_T$  ( $\text{dm}^3 \text{mg}^{-1}$ ) corresponds to the maximum binding energy, the constant  $B = RT/b$  represents the heat of adsorption, while  $1/b$  indicates the adsorption potential of the adsorbent. This model generally emphasizes that the adsorption process occurs through indirect adsorbate–adsorbate interactions.<sup>21</sup>

Dubinin–Radushkevich (D–R) isotherm postulates a fixed volume or “sorption space” close to the sorbent surface where sorption occurs. This very often-used model is based on the equation:

$$q_e = q_{\text{ads}} \exp(-k_{\text{ad}} \varepsilon^2) \quad (9)$$

It is applied in its linearized form as:

$$\ln c_{\text{ads}} = \ln q_{\text{ads}} - k_{\text{ads}} \varepsilon^2 \quad (10)$$

where  $\varepsilon$  is the Polanyi sorption potential ( $\varepsilon = RT \ln(1 + 1/c_e)$ ) equal to the energy required to pull a sorbed molecule from its sorption site to infinity.  $\beta$  ( $\text{mol}^2 \text{kJ}^{-2}$ ) is the activity coefficient related to the mean adsorption free energy  $E$  ( $\text{kJ mol}^{-1}$ ), which is defined as the free energy change required to transfer 1 mol of substance from solution to the solid surfaces.<sup>22</sup> This relation is given as:

$$E = \frac{1}{\sqrt{-2\beta}} \quad (11)$$

The value of  $E$  of the Dubinin–Radushkevich Equation ranges from 1 to 8  $\text{kJ mol}^{-1}$  for physical adsorption and from 8 to 16  $\text{kJ mol}^{-1}$  for chemical adsorption and ion exchange.

The Jovanović Model was developed to explain monolayer adsorption.<sup>23</sup> It is given as:

$$q_e = q_{\text{max}} (1 - \exp(-K_J c_e)) \quad (12)$$

and in linear form by:

$$\ln q_e = \ln q_{\text{max}} - K_J c_e \quad (13)$$

The Hurkins–Jura Model accounts for multilayer adsorption and can be explained by the existence of a heterogeneous pore distribution. It is given by:<sup>23</sup>

$$q_e = \left( \frac{A_H}{B_2 - \log c_e} \right)^{1/2} \quad (14)$$

and in linear form

$$\frac{1}{q_e^2} = \frac{B_2}{A_H} - \frac{1}{A_H} \log c_e \quad (15)$$

Fitting of the experimental data to the equation of the Hasley Model attests to the heteroporous nature of the adsorbent and multilayer adsorption.<sup>23</sup> This model is represented as:

$$q_e = \exp\left(\frac{\ln K_H + \ln c_e}{n}\right) \quad (16)$$

and in linear form:

$$\ln q_e = \frac{\ln K_H}{n} + \frac{1}{n} \ln c_e \quad (17)$$

The Temkin Model showed quite good fitting to the equilibrium data, indicating indirect interactions between the CC surface and the adsorbate. The

Langmuir Model, which is the most indicative proof of monolayer adsorption, also gave a high correlation coefficient. The determined separation factor  $R_L$  (0.44) indicates a favorable adsorption process (Table II).

TABLE II. Isotherm parameters for the adsorption of clopyralid onto the carbon cryogel

Parameter	Value	Parameter	Value
Langmuir		Jovanović	
$K_L / \text{L g}^{-1}$	0.013	$q_{\text{max}} / \text{mg g}^{-1}$	5.805
$q_{\text{max}} / \text{mg g}^{-1}$	32.2	$K_i$	0.014
$R_L$	0.44	$r^2$	0.895
$r^2$	0.971	Hurkins–Jura	
Freundlich		$A_H$	-34.542
$K_F / (\text{mg g}^{-1}) (\text{L mg}^{-1})^{1/n}$	0.975	$B_2$	-1.962
$n$	1.52	$r^2$	0.887
$r^2$	0.980	Halsey	
Temkin		$K_H$	0.914
$K_T / \text{L mg}^{-1}$	0.117	$n$	1.52
$B$	7.231	$r^2$	0.981
$r^2$	0.991		
Dubinin–Radushkevich			
$q_{\text{max}} / \text{mg g}^{-1}$	22.6		
$E / \text{kJ mol}^{-1}$	1.47		
$r^2$	0.991		

The value of adsorption free energy in the Dubinin–Radushkevich Model ranges from 1 to 8  $\text{kJ mol}^{-1}$  for physical adsorption and from 8 to 16  $\text{kJ mol}^{-1}$  for chemical adsorption and ion exchange.<sup>24</sup> Since in the present study, the calculated energy value was 1.47  $\text{kJ mol}^{-1}$ , physisorption interactions are probably most important for the binding of the adsorbate to the CC surface. In this context, van der Waals forces are the most probable. A molecule of clopyralid in acidic solutions, where the uptake is the most expressed, is rarely dissociated. In contact with the CC surface, polarization of the charge in the clopyralid molecule occurs and correlates the attraction to the active site on the CC surface, which is the most probable scenario for the binding and overall removal of this pesticide.

The Langmuir, D–R and Jovanović models indicate certain theoretical values of maximum adsorption capacities. In this work, large disagreement between the calculated and experimentally obtained values was registered. This refers to the inability of the models that were used to interpret the specific adsorption of clopyralid in an adequate manner under the applied conditions.

As can be seen from Fig. 4, an almost linear adsorption isotherm was present in the case of the studied adsorption. Such a shape indicates that the availability of sites remains constant at all the examined concentrations, without reaching a saturation level. This situation could arise when the solute has a higher affinity



for the substrate molecules than the solvent itself. With its molecular dimensions (Fig. 3), clopyralid could penetrate into the structure of the substrate in regions (narrow hydrophobic pores) that had not already been penetrated by the solvent; thus, the linear isotherm indicates that the solute penetrates into the regions that are inaccessible to the solvent.<sup>25</sup>

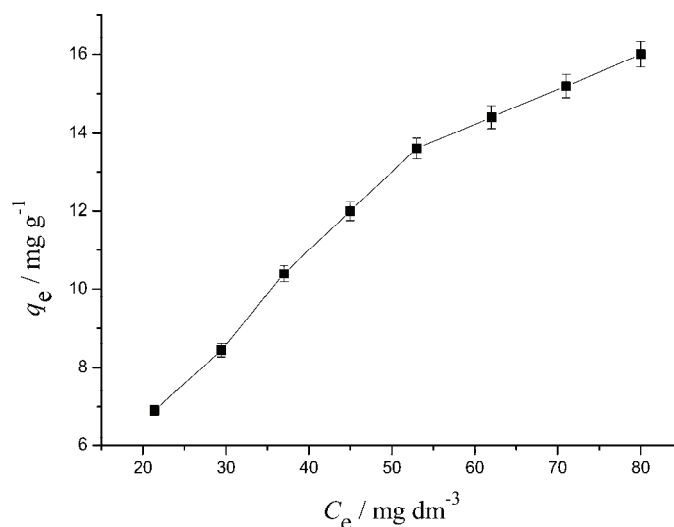


Fig. 4. Adsorption isotherm of clopyralid onto the carbon cryogel.

#### Adsorption kinetics

To evaluate the kinetic mechanism that controls an adsorption process, it is well-established that several theoretical models should be used. The applicability of the pseudo-first-order, the pseudo-second-order model, the Elovich Model, the Bangham Model and the intraparticle diffusion model were tested for the adsorption of clopyralid onto CC. The best-fit model was selected based on the values of the linear regression correlation coefficients,  $r^2$ .

A linear form of the pseudo-first-order model was defined by Lagergren as:

$$\ln(q_e - q_\tau) = \ln q_e - k_1 \tau \quad (18)$$

where  $k_1$  ( $\text{min}^{-1}$ ) is the rate constant of pseudo-first-order adsorption.<sup>26</sup> The slope of the linear plots of  $\ln(q_e - q_\tau)$  vs.  $\tau$  was used for the determination of  $q_e$  and  $k_1$ .

The Ho pseudo-second-order kinetics is represented in its linearized form as:

$$\frac{\tau}{q_\tau} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} \tau \quad (19)$$

This is an indicator of the chemisorption nature of the adsorption process. In Eq. (19),  $k_2$  ( $\text{g mg}^{-1} \text{ min}^{-1}$ ) is the equilibrium rate constant for pseudo-second order adsorption.<sup>27</sup>

The Elovich Model describes a number of reaction mechanisms, including bulk and surface diffusion and the activation and deactivation of catalytic surfaces.<sup>22</sup> It is represented as:

$$q_\tau = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln \tau \quad (20)$$

where  $\alpha$  ( $\text{mg g}^{-1} \text{ min}^{-1}$ ) and  $\beta$  ( $\text{g mg}^{-1}$ ) are adsorption constants and are determined from a plot  $q_\tau$  vs.  $\ln \tau$ .<sup>21</sup>

The applicability of the Bangham kinetic model was tested using the equation:

$$\log \log \left( \frac{c_0}{c_0 - q_\tau m} \right) = \log \left( \frac{k_0 m}{2.303V} \right) + \alpha \log \tau \quad (21)$$

where  $V$  the volume of solution ( $\text{cm}^3$ ),  $m$  is the adsorbent dose ( $\text{g dm}^{-3}$ ) and  $\alpha$  and  $k_0$  are constants. A plot of  $\log \log (c_0/(c_0 - q_\tau m))$  vs.  $\log \tau$  confirmed the applicability of the Bangham Equation and indicated that diffusion of clopyralid into the CC pores mainly controlled the adsorption process.<sup>28</sup>

The possibility of adsorptive diffusion in the volume of the particles of the adsorbent was explored using the intraparticle diffusion model, which is given as:

$$q_\tau = k_i \tau^{1/2} + C \quad (22)$$

where  $k_i$  ( $\text{g mg}^{-1} \text{ min}^{-1}$ ) is the intraparticle diffusion rate constant and  $C$  is a constant, which reflects the boundary effect.<sup>27</sup>

In the present study, several models fitted the experimental data well with quite high correlation coefficients (Table III). The theoretical maximum saturation capacity calculated under the pseudo-second-order model corresponded to the experimental values the best. Under all the other conditions, high disagreement was observed. The good fitting to the Bangham Model emphasized the importance of diffusion in the adsorption kinetics.

Considering the adsorption mechanism, it might be postulated that certain electrostatic attractions between the solute and the adsorbent occur. CC is considered as a complex carbonaceous matrix composed of regions of hydrophobic microcrystallites scattered in an irregular 3D structure. These are interconnected by various functional groups present at the edges of the graphene layers. Electron-rich regions located in the graphene layers could interact with the  $\pi$  electrons of the aromatic ring of pesticide. The two chlorine atoms in the clopyralid molecule act as electron-acceptor substituents and deplete the electron charge in the graphene rings, forming partially positive charges. Therefore, electrostatic inter-

actions between the partially negative benzene rings of clopyralid with the negative charge of the graphene layers are probable. The retained pesticide molecules are most likely adsorbed flat onto carbon surface or within its pores.

TABLE III. Comparison for kinetic parameters for adsorption of clopyralid onto the carbon cryogel

Parameter	Value
Pseudo-first-order	
$k_1 / \text{min}^{-1}$	0.186
$q_e / \text{mg g}^{-1}$	8.8
$r^2$	0.980
Pseudo-second-order	
$k_2 / \text{g mg}^{-1} \text{min}^{-1}$	0.061
$q_e / \text{mg g}^{-1}$	37.0
$r^2$	0.9997
Elovich	
$\alpha / \text{mg g}^{-1} \text{min}^{-1}$	102534.3
$\beta / \text{g mg}^{-1}$	0.376
$r^2$	0.975
Bangham	
$k_0$	35.914
$\alpha$	0.109
$r^2$	0.971
Intraparticle diffusion	
$k_i / \text{g mg}^{-1} \text{min}^{-1}$	2.222
$r^2$	0.842

### Effect of pH

The solution pH is an important factor that could affect the interactions of the adsorbent surface and the molecules of an adsorbate. The effect of the initial pH on the adsorption of clopyralid onto CC under the given experimental conditions is shown in Fig. 5. At first sight, the strong dependence of the adsorption on the solution pH is obvious. It is evident that at pH values under 6, the adsorption capacity is much higher. As for many carbon materials including CC, the existence of various organic functional groups on their surface has been established. Groups such as carboxylic, phenolic, lactonic, pyrrolic, hydrophilic, *etc.* play the main role in their surface reactivity. All those groups are deprotonated and negatively charged in strongly basic solutions. The  $\text{pH}_{\text{PZC}}$  of the carbon cryogel was determined earlier using the pH drift method and a value of 10.5 was found. This means that under this pH value, surface of this material is dominantly positively charged. This is in accordance with the rule: the more acidic the solution is, the more positive charges on the surface exist.

Acidic characteristics of clopyralid are defined by the acidity constant  $\text{p}K_a \approx 2.1$  at 25 °C. Having such acidic properties, the clopyralid molecule is

almost completely dissociated in water at pH values above 3, and so bears a negative charge.<sup>29</sup> Hence, certain electrostatic attractions between the positively charged CC surface and the negatively charged clopyralid molecule occur over a wide range of pH values, especially in acidic conditions. With increasing pH, the positive charge at the CC surface decreases, thereby reducing the uptake of clopyralid. Celis and coworkers also reported a higher uptake of clopyralid in acidic solutions under adsorption onto montmorillonite–chitosan bionanocomposites.<sup>30</sup>

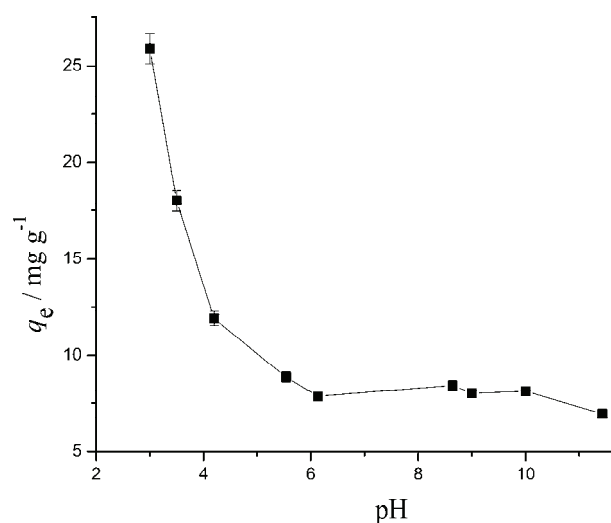


Fig. 5. Effect of pH on the adsorption of clopyralid onto the carbon cryogel.

#### CONCLUSIONS

A resorcinol–formaldehyde carbon cryogel that was synthesized in this study exhibited a pronounced adsorption affinity towards the commonly used pesticide clopyralid under batch adsorption conditions. Characterization of the synthesized carbon cryogel revealed it a porous carbon material with an amorphous structure, a considerably high specific surface area and developed mesoporosity, which is particularly important for the adsorption of pesticides. Although a set of seven isotherm models fitted the adsorption results well in most cases, the predicted values for the maximum adsorption capacities showed considerable disagreement with the experimental data. The maximum adsorption capacity, experimentally obtained from isotherm studies, was  $16 \text{ mg g}^{-1}$ . The adsorption process is considered slow since equilibrium was only fully attained after 24 h of contact. However, most of the uptake was related to the first few hours of the process. The effect of solution pH was noticeable and defined, the uptake being favored under acidic conditions. This was attributed to a probable electrostatic attractions between the positively charged cryogel surface and the dissociated clopyralid molecule. Another possibility of electrostatic interactions is based on the inter-

actions between a partial positive charge on the clopyralid molecule and a negative charge on the graphene layers of the CC.

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## ИЗВОД

## ЕФИКАСНО УКЛАЊАЊЕ КЛОПИРАЛИДА ИЗ ВОДЕ ПОМОЋУ РЕЗОРЦИНОЛ-ФОРМАЛДЕХИДНОГ УГЉЕНИЧНОГ КРИОГЕЛА

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Резорцинол-формалдехидни угљенични криогел је припремљен, окарактерисан и употребљен за уклањање често коришћеног пестицида под именом клопиралид из водених раствора при различитим експерименталним условима. Добијени угљенични материјал поседује релативно велику специфичну површину, аморфну структуру и има значајан удео мезопорозности. У раду је коришћен низ модела адсорпционих изотерми за интерпретацију равнотежног стања, и то: Ленгмиров, Фројндлихов, Тјомкинов, Дубинин–Радушкевичев, Јовановићев, Хуркинс–Јурин и Хелсијев модел. Иако је неколико модела показало добро поклапање са теоријским моделима уз високе корелационе коефицијенте, предвиђене вредности за  $q_e$  се слабо слажу са експериментално измереним вредностима. Кинетички модели псеудо-првог и псеудо-другог реда, Еловичев модел, Бангамов модел и модел унутарчестичне дифузије су коришћени за фитовање кинетике. Брзина процеса је на почетку велика, а до успостављања адсорпционе равнотеже долази после 24 h. Утврђено је да процес адсорпције зависи од и рН, као и да је фаворизован у киселој средини.

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