Effect of activated carbon surface chemistry on adsorption of phenoxy carboxylic acid herbicides from aqueous solutions

Krzysztof Kuśmierek⁎, Arkadiusz Białek⁎, Andrzej Świątkowski⁎

⁎Institute of Chemistry, Military University of Technology, 00-908 Warsaw, Poland, emails: krzysztof.kusmierek@wat.edu.pl (K. Kuśmierek), andrzej.swiatkowski@wat.edu.pl (A. Świątkowski)

⁎ŁUKASIEWICZ - Institute of Industrial Organic Chemistry, 02-236 Warszawa, Poland, email: arkadiusz_bialek@poczta.onet.pl (A. Białek)

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ABSTRACT

The adsorption of the phenoxy herbicides including 2-(4-chloro-2-methylphenoxy)acetic acid (MCPA), 2-(4-chloro-2-methylphenoxy)propanoic acid (MCPP), and 4-(4-chloro-2-methylphenoxy)butanoic acid (MCPB) on the activated carbons with different surface chemical properties was investigated. The activated carbon was demineralized (AC–NM) and modified by nitric acid oxidation to produce oxidized adsorbent (AC–OX) which possesses acidic surface. Basic activated carbon (AC–AM) was prepared by heat treatment in ammonia at 900°C. Adsorption of the herbicides was strongly pH dependent; no effect of ionic strength was observed. The adsorption kinetics was analyzed using pseudo-first-order and pseudo-second-order models, while the equilibrium data were examined using Langmuir and Freundlich isotherm equations. The obtained results showed that the pseudo-second-order kinetic and Langmuir isotherm models were that best fitted to the experimental data. The adsorption rate, as well as the adsorption efficiency of the herbicides on all of the adsorbents, increased in the order: MCPA < MCPP < MCPB. All of the adsorbates were preferably adsorbed on the basic activated carbon (AC–AM) although it had the lowest specific surface area, indicating that in the adsorption process the availability of the functional groups on the adsorbent surface was more important than the surface area.

Keywords: Adsorption; Activated carbon; Surface chemistry; MCPA; MCPP; MCPB

1. Introduction

Phenoxy herbicides 2-(4-chloro-2-methylphenoxy)acetic acid (MCPA), 2-(4-chloro-2-methylphenoxy)propanoic acid (MCPP or mecoprop), and 4-(4-chloro-2-methylphenoxy)butanoic acid (MCPB) are a very popular group of crop protection active substances, used worldwide in the control of broad-leaf weeds in cereals cultivation. MCPA and MCPP are especially popular in Poland where MCPA is produced for 60 y and MCPP for 30 y in the chemical plant in Nowa Sarzyna under the brand name “Chwastox” [1]. The herbicides are also very popular in other world countries especially Great Britain, Australia, and Russia. The basic common element in the MCPA, MCPP, and MCPB molecules structure is the 2-metyl-4-chlorophenoxo radical, which is introduced into molecules as 4-chloro-o-cresol (PCOC) in the production technology. Production is optimized for the maximum recovery of PCOC and herbicides. The methods of extraction and adsorption on activated carbon are used in production technologies.

MCPA, MCPP, and MCPB are biodegradable but the main metabolites, for example, PCOC might be environmentally hazardous. The main risk for the environment related to this group of herbicides is connected to the accidents in production plants, resulting in uncontrolled emission of herbicides to the environment or sewage treatment plants [2,3].
The problem of recovery of active substances traces from production wastes both in the economic (reduction of raw materials consumption) and environmental context is the most important issue in the production. One of the most commonly used methods of recovery of these substances from sewage streams, as well as their removal from ground and surface water, is adsorption on activated carbons [4].

The most frequently tested herbicides are MCPA and 2,4-dichlorophenoxyacetic acid (2,4-D). The adsorption of MCPA from aqueous solutions was studied on various synthesized [5] as well as commercially available activated carbons [6–15]. Adsorption of MCPP [14–16] and MCPB [15,16] was described in only a few papers.

The effectiveness of the adsorption process depends on the physical properties of the activated carbon used [4,5,13,17–19] but also to a large extent on the chemical properties of the adsorbent which determines the functional groups present on its surface [18,19]. To the best of our knowledge, no study has been reported on the effect of activated carbon surface chemistry on adsorption of phenoxy herbicides from aqueous solutions. Therefore, the main objective of this paper was to evaluate the adsorption of the MCPA, MCPP, and MCPA on the adsorbents with different surface chemical properties.

2. Experimental

2.1. Materials and methods

The phenoxy herbicides: MCPA (>98%), MCPB (>99%), and MCPP (99%) were received from Sigma-Aldrich (St. Louis, MO, USA). Their physico-chemical properties are listed in Table 1. All other chemicals used in this work were purchased from Avantor Performance Materials (Gliwice, Poland).

The R3-ex activated carbon was purchased from Norit (The Nederlands). The activated carbon was demineralized (AC–NM) and modified by oxidation with concentrated nitric acid (AC–OX) or by heat treatment in ammonia at 900°C as described elsewhere [20]. Prior to use, the carbon samples were crushed in a mortar, dried in an oven at 110°C to a constant weight and stored in a desiccator until use. The specific surface areas ($S_{BET}$), the total ($V_{total}$), and micropore ($V_{micro}$) volumes of the activated carbons were calculated from the N₂ adsorption–desorption isotherms obtained using Micromeritics ASAP 2010 (Norcross, GA, USA) volumetric adsorption analyzer. Surface acid/base properties of the activated carbons were determined by standard neutralization with 0.1 mol/L NaOH and HCl. The points of zero charge (pH$_{PZC}$) were determined by the drift method according to the procedure described elsewhere [21].

2.2. Adsorption experiments

Batch adsorption studies were conducted in a set of Erlenmeyer flasks containing 0.05 g of the adsorbent and 40 mL herbicide solutions with various initial concentrations. The flasks were agitated at 200 rpm at the temperature of 25°C. Equilibrium adsorption studies were conducted with different initial herbicide concentrations (from 0.1 to 0.5 mmol/L). Adsorption kinetics as well as the effects of solution pH and solution ionic strength were carried out for initial herbicide concentration of 0.5 mmol/L. The effect of pH on the adsorption was studied by varying the initial pH of the solutions from pH 2 to 10. In order to investigate the effect of a salt presence on the herbicides removal, the adsorbates were adsorbed from 0.01, 0.02, 0.05, and 0.1 mmol/L solutions of NaCl.

The herbicides adsorption at time $t$ ($q_t$, mmol/g) and at equilibrium ($q_e$, mmol/g) was calculated by the following Eqs. (1) and (2):

$$q_t = \frac{(C_0 - C_t) V}{m} \quad (1)$$

$$q_e = \frac{(C_e - C_0) V}{m} \quad (2)$$

where $C_0$ is the initial herbicide concentration (mmol/L), $C_t$ is the concentration at time $t$ (mmol/L), $C_e$ is the adsorbate

| Compound | Chemical structure | CAS number | Molecular weight | Solubility in water at 20°C (g/L) | logK$_{ow}$ | pK$_a$
|----------|--------------------|------------|-----------------|----------------------------------|------------|--------
| MCPA     | ![MCPA structure](image) | 94–74–6    | 200.6           | 0.820                            | 2.8        | 3.1
| MCPP     | ![MCPP structure](image) | 93–65–2    | 214.6           | 0.620                            | 3.1        | 3.2
| MCPB     | ![MCPB structure](image) | 94–81–5    | 228.7           | 0.044                            | 3.3        | 4.6
concentration at equilibrium (mmol/L), \( m \) is the mass of activated carbon used (g), and \( V \) is the volume of solution (L).

All the experiments were performed in duplicates and average values were used for further calculations. The maximum relative standard deviation observed was less than 5%.

The herbicides concentrations before and after adsorption were determined using UV-Vis spectrophotometer (Carry 3E, Varian, USA) at the wavelength of 278 nm. The calibration curves for all of the herbicides were linear in the studied ranges from 0.05 to 0.5 mmol/L. The equations for the regression line were: \( y = 1.436x + 0.084 \) for MCPA \( (R^2 = 0.998) \), \( y = 1.305x + 0.087 \) for MCPP \( (R^2 = 0.999) \), and \( y = 1.305x + 0.087 \) \( (R^2 = 0.998) \) for MCPB, respectively.

### 3. Results and discussion

#### 3.1. Adsorbents characterization

The specific surface areas \( (S_{BET}) \) and pore volumes calculated from the \( N_2 \) adsorption–desorption isotherms [20] are listed in Table 2. The micro- and total pore volumes were calculated as described elsewhere [18]. The specific surface area of the AC–NM activated carbon is high (1,390 m\(^2\)/g) and its modification decreased the specific surface areas of the carbon samples (about 7% and 15% for oxidized and ammonia-treated materials, respectively). The oxidation of activated carbons was largely studied in the past and the effect of various oxidizing agents on the specific surface areas of the carbon samples (about 7% and 15% for oxidized and ammonia-treated materials, respectively). The oxidation process led to an increase in specific surface area as a result of heat-treatment with gaseous ammonia.

Table 3 presents some chemical characteristics of the activated carbons. The oxidation process led to an increase in surface acidity via the insertion of oxygen groups such as carboxyl, lactone, carbonyl, and phenol. Heat treatment in ammonia at high temperatures caused the increase of amino groups on the activated carbon surface giving it more basic properties.

#### 3.2. Effects of solution chemistry on the adsorption

The solvent properties, including pH and salt presence, are important parameters in adsorption process due to the fact that the solution chemistry can modify the adsorbent–adsorbate interactions. The pH variation can promote changes in the adsorbent surface charges and influence in the protonation or dissociation of adsorbate molecules. The presence of inorganic salts in the solution (ionic strength) can modify the strength of the electrostatic interactions between adsorbent surface and adsorbate.

The influence of initial pH value on adsorption of the MCPA, MCPP, and MCPB on the activated carbons was studied in a wide range of 2–10, and the results are shown in Fig. 1.

Important parameters necessary to understand the effect of pH on adsorption are \( pH_{\text{pzc}} \) of an adsorbent and \( pK_a \) of an adsorbate. The \( pH_{\text{pzc}} \) is defined as the pH value where in the liquid surface charge of the adsorbent is equal to zero. At a pH lower than \( pH_{\text{pzc}} \), the adsorbent surface is positively charged, while at a pH greater than \( pH_{\text{pzc}} \), the surface has a net negative charge. The \( pH_{\text{pzc}} \) values of the AC–NM, AC–OX, and AC–AM activated carbons were found to be 6.1, 3.4, and 7.9, respectively. The ionization constant of the adsorbate \( (pK_a) \) determines the degree of ionization of the molecule at different solution pH. In general, at a pH greater than \( pH_{\text{pzc}} \), the adsorbate is positively charged, while at a pH lower than \( pH_{\text{pzc}} \), the adsorbate exists predominantly in anionic forms as negatively charged ions. As shown in Table 1, the \( pK_a \) values of the MCPA, MCPP, and MCPB are 3.1, 3.2, and 4.6, respectively.

Adsorption of all three herbicides on individual activated carbons was similar (Fig. 1). This is due to their similar physico-chemical properties. Adsorption of the herbicides on the AC–OX activated carbon decreases rapidly in the pH range 2–4 and further remains constant. The highest adsorption capacity \( (q) \) values were found at pH of 2 at which the neutral form of the herbicide is predominant and the surface charge of the AC–OX activated carbon is positive. This suggests that the non-dissociated forms of herbicides are preferred by the positively charged surface of the adsorbent.

### Table 2

Textural properties of the activated carbons

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>( S_{BET} ) (m(^2)/g)</th>
<th>( V_{mic} ) (cm(^3)/g)</th>
<th>( V_{t} ) (cm(^3)/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AC–NM</td>
<td>1,390</td>
<td>0.589</td>
<td>0.665</td>
</tr>
<tr>
<td>AC–OX</td>
<td>1,296</td>
<td>0.547</td>
<td>0.658</td>
</tr>
<tr>
<td>AC–AM</td>
<td>1,212</td>
<td>0.530</td>
<td>0.591</td>
</tr>
</tbody>
</table>

### Table 3

Chemical properties of the activated carbons

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>( pH_{\text{pzc}} )</th>
<th>NaOH up-take (mmol/g)</th>
<th>HCl up-take (mmol/g)</th>
<th>Chemical composition of surface* (% wt.)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>C</td>
</tr>
<tr>
<td>AC–NM</td>
<td>6.1</td>
<td>0.212</td>
<td>0.183</td>
<td>92.63</td>
</tr>
<tr>
<td>AC–OX</td>
<td>3.4</td>
<td>2.022</td>
<td>0.081</td>
<td>83.53</td>
</tr>
<tr>
<td>AC–AM</td>
<td>7.8</td>
<td>0.092</td>
<td>0.388</td>
<td>95.11</td>
</tr>
</tbody>
</table>

*Results from XPS [20].
The large reduction in the adsorption at higher pH (above the $\text{pH}_{\text{PZC}}$ of the AC–OX) can be attributed to the electrostatic repulsion between the negatively charged adsorbent surface and the dissociated herbicide molecules.

The adsorption mechanism of the herbicides on the non-modified activated carbon (AC–NM) was considered to be the same mechanism. However, the removal efficiency of the herbicides decreased relatively slowly at the pH range of 2–6; then the decreasing rate became faster (at the pH range from 6 to 10). This difference is due to the higher $\text{pH}_{\text{PZC}}$ value of the AC–NM activated carbon (6.1) compared to the AC–OX (3.4). Also, in this case, the lowest adsorption was observed at pH 10 as a result of repulsion between herbicide molecules and the negative surface of the adsorbent.

A different mechanism of adsorption was observed on the activated carbon modified by heat treatment in ammonia (AC–AM). The highest adsorption capacity values were found at the pH range from 3 to 7 when the surface charge of the adsorbent was positive and the herbicides were dissociated and existed in solution in anion forms. Under these conditions, the adsorption is promoted by attractive electrostatic interaction between the positively charged –NH$_3^+$ groups on the adsorbent surface and negatively charged carboxylic groups of the adsorbates (AC–NH$_3^+$······OOC–R). Similar interactions were observed for adsorption of 2,4-D herbicide on NH$_2$–functionalized SBA-15 mesoporous silica [28] as well as 2,4-D and MCPP on hexagonal mesoporous silica modified by 3-aminopropyltriethoxy groups [29]. The adsorption of the herbicides on the AC–AM activated carbon decreased significantly at pH values above 8 ($\text{pH}>\text{pH}_{\text{PZC}}$), due to the charge repulsion between negatively charged adsorbent surface and ionized carboxyl groups of the adsorbates.

The effect of solution ionic strength on the adsorption of the MCPA, MCPP, and MCPB on the activated carbons is presented in Fig. 2. Small changes observed in $q_e$ values (±5%) were caused by measurement errors rather than by changes in the ionic strength of the solution.

### 3.3. Adsorption kinetics

The plots of $q_t$ as a function of time are presented in Fig. 3. As can be seen, the contact time needed for the herbicides solutions to reach equilibrium is approximately 60–90 min. The adsorption kinetics of the MCPA, MCPP, and MCPB on the activated carbons was tested using the linearized pseudo-first-order Eq. (3) [30] and pseudo-second-order Eq. (4) [31] kinetic models:

\[
\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t
\]  
\[
\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t
\]

where $q_t$ is an amount of adsorption at time $t$ (mmol/g), $q_e$ is an equilibrium amount of adsorbate adsorbed per unit mass of activated carbon (mmol/g), $k_1$ and $k_2$ are the rate constants of pseudo-first-order (1/min) and pseudo-second-order adsorption (g/mmol min), respectively and $t$ is time (min).
Fig. 2. Effect of solution ionic strength on adsorption of MCPA, MCPP, and MCPB on the activated carbons.

Fig. 3. Adsorption kinetics of MCPA, MCPP, and MCPB on the activated carbons.
The assessment of the employed models for fitting the herbicides adsorption data was obtained by the analyses of both the correlation coefficients ($R^2$) and normalized standard deviation values ($\Delta q$). The values of the $\Delta q$ were estimated by the following Eq. (5):

$$
\Delta q = 100 \times \sqrt{\frac{\sum (q_{\text{EXP}} - q_{\text{CAL}})^2}{N - 1}}
$$

where $N$ is the number of data points, $q_{\text{EXP}}$ is the experimental value of $q_e$ and $q_{\text{CAL}}$ is the theoretical (calculated) $q_e$ obtained from Eqs. (3) ($q_{\text{CAL,1}}$) and (4) ($q_{\text{CAL,2}}$), respectively.

The kinetic model parameters are listed in Table 4. The $R^2$ values for the pseudo-second-order kinetic model are greater than 0.99 for adsorption of the herbicides on all of the activated carbons. In addition, the values of the calculated $\Delta q$ are lower than those obtained for the pseudo-first-order. Therefore, it can be concluded that the pseudo-second-order kinetic model provided a better correlation for the adsorption of the MCPA, MCPP, and MCPB on the activated carbons compared to the pseudo-first-order model. This fact suggests that the rate of the adsorption process was controlled by chemisorption. The results are in agreement with the other works on adsorption of MCPA on activated carbons [8,12]. The adsorption rate on all of the adsorbents increased in the order: MCPA < MCPP < MCPB, which was correlated with a respective increase in the molecular weight and log $K_{ow}$ as well as the decrease in the water solubility of the herbicides. A similar tendency was observed for the adsorption of phenol and its chlorinated derivatives [32,33]. All of the herbicides were adsorbed faster on the AC–OX than on the AC–NM and AC–AM activated carbon. The values of the $k_2$ for all of the herbicides followed the sequence: AC–AM < AC–NM < AC–OX. The adsorption rate increased with an increase in the percentage of mesopores in the total porous structure of the activated carbons (10.3%, 11.4%, and 16.9 % for AC–AM, AC–NM, and AC–OX, respectively).

3.4. Adsorption isotherms

The adsorption isotherms of the phenoxy herbicides from aqueous solutions on the activated carbons are presented in Fig. 4.

<table>
<thead>
<tr>
<th>Adsorbate</th>
<th>Parameter</th>
<th>AC–NM</th>
<th>AC–OX</th>
<th>AC–AM</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$q_{\text{EXP}}$ (mmol/g)</td>
<td>1.162</td>
<td>0.774</td>
<td>1.944</td>
</tr>
<tr>
<td></td>
<td>$k_1$ (1/min)</td>
<td>0.0384</td>
<td>0.0565</td>
<td>0.0405</td>
</tr>
<tr>
<td></td>
<td>$R^2$</td>
<td>0.971</td>
<td>0.966</td>
<td>0.968</td>
</tr>
<tr>
<td>MCPA</td>
<td>$q_{\text{CAL,1}}$ (mmol/g)</td>
<td>1.320</td>
<td>1.070</td>
<td>1.774</td>
</tr>
<tr>
<td></td>
<td>$\Delta q$ (%)</td>
<td>13.5</td>
<td>38.3</td>
<td>8.7</td>
</tr>
<tr>
<td></td>
<td>$k_2$ (g/mmol min)</td>
<td>0.0373</td>
<td>0.0458</td>
<td>0.0283</td>
</tr>
<tr>
<td></td>
<td>$R^2$</td>
<td>0.998</td>
<td>0.996</td>
<td>0.998</td>
</tr>
<tr>
<td></td>
<td>$q_{\text{CAL,2}}$ (mmol/g)</td>
<td>1.105</td>
<td>0.843</td>
<td>2.037</td>
</tr>
<tr>
<td></td>
<td>$\Delta q$ (%)</td>
<td>4.9</td>
<td>8.9</td>
<td>4.8</td>
</tr>
<tr>
<td></td>
<td>$q_{\text{EXP}}$ (mmol/g)</td>
<td>1.276</td>
<td>0.896</td>
<td>1.988</td>
</tr>
<tr>
<td></td>
<td>$k_1$ (1/min)</td>
<td>0.0506</td>
<td>0.0386</td>
<td>0.0414</td>
</tr>
<tr>
<td></td>
<td>$R^2$</td>
<td>0.875</td>
<td>0.972</td>
<td>0.951</td>
</tr>
<tr>
<td>MCPP</td>
<td>$q_{\text{CAL,1}}$ (mmol/g)</td>
<td>1.639</td>
<td>1.176</td>
<td>1.765</td>
</tr>
<tr>
<td></td>
<td>$\Delta q$ (%)</td>
<td>28.4</td>
<td>31.3</td>
<td>11.2</td>
</tr>
<tr>
<td></td>
<td>$k_2$ (g/mmol min)</td>
<td>0.0391</td>
<td>0.0529</td>
<td>0.0304</td>
</tr>
<tr>
<td></td>
<td>$R^2$</td>
<td>0.997</td>
<td>0.997</td>
<td>0.999</td>
</tr>
<tr>
<td></td>
<td>$q_{\text{CAL,2}}$ (mmol/g)</td>
<td>1.344</td>
<td>0.932</td>
<td>2.103</td>
</tr>
<tr>
<td></td>
<td>$\Delta q$ (%)</td>
<td>5.3</td>
<td>4.0</td>
<td>5.8</td>
</tr>
<tr>
<td></td>
<td>$q_{\text{EXP}}$ (mmol/g)</td>
<td>1.378</td>
<td>1.003</td>
<td>2.038</td>
</tr>
<tr>
<td></td>
<td>$k_1$ (1/min)</td>
<td>0.0350</td>
<td>0.0315</td>
<td>0.0429</td>
</tr>
<tr>
<td></td>
<td>$R^2$</td>
<td>0.961</td>
<td>0.981</td>
<td>0.968</td>
</tr>
<tr>
<td>MCPB</td>
<td>$q_{\text{CAL,1}}$ (mmol/g)</td>
<td>1.248</td>
<td>0.798</td>
<td>2.212</td>
</tr>
<tr>
<td></td>
<td>$\Delta q$ (%)</td>
<td>9.4</td>
<td>20.4</td>
<td>8.5</td>
</tr>
<tr>
<td></td>
<td>$k_2$ (g/mmol min)</td>
<td>0.0417</td>
<td>0.0581</td>
<td>0.0351</td>
</tr>
<tr>
<td></td>
<td>$R^2$</td>
<td>0.994</td>
<td>0.998</td>
<td>0.999</td>
</tr>
<tr>
<td></td>
<td>$q_{\text{CAL,2}}$ (mmol/g)</td>
<td>1.513</td>
<td>1.088</td>
<td>1.927</td>
</tr>
<tr>
<td></td>
<td>$\Delta q$ (%)</td>
<td>2.5</td>
<td>8.5</td>
<td>5.4</td>
</tr>
</tbody>
</table>
The experimental data were fitted with Langmuir [34] and Freundlich [35] isotherm models. The linear forms of the Langmuir and Freundlich isotherms can be represented by the following Eqs. (6) and (7):

\[
\frac{C_e}{q_e} = \frac{1}{q_m} + \frac{1}{q_m b} C_e \tag{6}
\]

\[
\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \tag{7}
\]

where \(q_m\) (mmol/g) and \(b\) (L/mmol) are the Langmuir parameters, while the \(K_F\) [(mmol/g) (L/mmol)\(^n\)] and \(n\) are the Freundlich isotherm constants. These adsorption isotherm parameters were calculated from the slope and intercept of the linear plots of \(C_e/q_e = f(C_e)\) and \(\ln q_e = f(\ln C_e)\) using the Eqs. (6) and (7), respectively. The results are given in Table 5.

The higher values of correlation coefficient (>0.99), as well as the lower values of \(\Delta q\), indicates the applicability of the Langmuir isotherm. This model assumes a monolayer coverage and uniform activity distribution on the adsorbent surface. The adsorption efficiency of the herbicides increased in the order: MCPA < MCPP < MCPB. This was coincident with an increase in their molecular weight and decrease solubility in the aqueous phase. Similar results were reported by Yang et al. [15] for adsorption of MCPA, MCPP, and MCPB on Filtrasorb 400 activated carbon. Hu et al. [16] also noticed better adsorption of MCPB on powdered activated carbon compared to MCPP.

Comparison of MCPA adsorption capacity on the activated carbons used in this paper with other activated carbons studied in other works is presented in Table 6. The \(q_m\) and \(K_F\) values for the herbicides obtained for all of the activated carbons increased in the order AC–OX < AC–NM < AC–AM. All of the adsorbates were preferably adsorbed on the activated carbon modified by heat treatment in NH_3, followed by the non-modified adsorbent and the worst on the oxidized activated carbon. The adsorption capacity of the AC–AM activated carbon was highest despite the lowest surface area, indicating that in the adsorption process the availability of the functional groups on the adsorbent surface was more important than the surface area. It is well-known from the literature review that the chemical properties of an adsorbent play an important role in the adsorption process. For example, adsorption of phenols increases on activated carbons with basic properties by the formation of hydrogen bonds, and decreases on activated carbons containing acidic surface oxygen groups. The decrease in adsorption with the increase in surface acidity is associated with formation of water clusters as a result of hydration of polar groups that can block active sites on the adsorbent surface and thereby reduce its availability for adsorbent molecules as well as with formation of polymorphic forms of the phenol as a result of its interaction with adsorbent surface groups [36].

Adsorption behavior of MCPA, MCPP, and MCPB is the same as phenols, thus the adsorption of the herbicides on the activated carbons follows a similar mechanism.

Fig. 4. Adsorption isotherms of MCPA, MCPP, and MCPB on the activated carbons.
### Table 5
Isotherm parameters of MCPA, MCPP, and MCPB adsorption on the activated carbons

<table>
<thead>
<tr>
<th>Adsorbate</th>
<th>Isotherm parameter</th>
<th>Activated carbon</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>AC–NM</td>
</tr>
<tr>
<td>MCPA</td>
<td>Langmuir</td>
<td></td>
</tr>
<tr>
<td></td>
<td>( q_m ) (mmol/g)</td>
<td>1.896</td>
</tr>
<tr>
<td></td>
<td>( b ) (L/mmol)</td>
<td>4.343</td>
</tr>
<tr>
<td></td>
<td>( R^2 )</td>
<td>0.992</td>
</tr>
<tr>
<td></td>
<td>( \Delta q ) (%)</td>
<td>1.899</td>
</tr>
<tr>
<td></td>
<td>Freundlich</td>
<td></td>
</tr>
<tr>
<td></td>
<td>( K_f ) [(mmol/g) (L/mmol)^{1/2}]</td>
<td>2.337</td>
</tr>
<tr>
<td></td>
<td>( n )</td>
<td>1.602</td>
</tr>
<tr>
<td></td>
<td>( R^2 )</td>
<td>0.977</td>
</tr>
<tr>
<td></td>
<td>( \Delta q ) (%)</td>
<td>4.418</td>
</tr>
<tr>
<td>MCPP</td>
<td>Langmuir</td>
<td></td>
</tr>
<tr>
<td></td>
<td>( q_m ) (mmol/g)</td>
<td>2.005</td>
</tr>
<tr>
<td></td>
<td>( b ) (L/mmol)</td>
<td>4.843</td>
</tr>
<tr>
<td></td>
<td>( R^2 )</td>
<td>0.999</td>
</tr>
<tr>
<td></td>
<td>( \Delta q ) (%)</td>
<td>2.132</td>
</tr>
<tr>
<td>MCPB</td>
<td>Langmuir</td>
<td></td>
</tr>
<tr>
<td></td>
<td>( q_m ) (mmol/g)</td>
<td>2.229</td>
</tr>
<tr>
<td></td>
<td>( b ) (L/mmol)</td>
<td>4.588</td>
</tr>
<tr>
<td></td>
<td>( R^2 )</td>
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</tr>
<tr>
<td></td>
<td>( \Delta q ) (%)</td>
<td>1.512</td>
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<td>Freundlich</td>
<td></td>
</tr>
<tr>
<td></td>
<td>( K_f ) [(mmol/g) (L/mmol)^{1/2}]</td>
<td>2.538</td>
</tr>
<tr>
<td></td>
<td>( n )</td>
<td>1.647</td>
</tr>
<tr>
<td></td>
<td>( R^2 )</td>
<td>0.985</td>
</tr>
<tr>
<td></td>
<td>( \Delta q ) (%)</td>
<td>3.597</td>
</tr>
</tbody>
</table>

### Table 6
Adsorption capacities of MCPA on various activated carbons

<table>
<thead>
<tr>
<th>Activated carbon</th>
<th>Adsorption capacity, ( q_m ) (mmol/g)</th>
<th>( S_{\text{BET}} ) (m²/g)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Commercial AC GAB</td>
<td>2.999</td>
<td>1,189</td>
<td>[11]</td>
</tr>
<tr>
<td>Flax derived AC</td>
<td>2.725</td>
<td>1,587</td>
<td>[5]</td>
</tr>
<tr>
<td>R3-ex AC–AM</td>
<td>2.703</td>
<td>1,210</td>
<td>This study</td>
</tr>
<tr>
<td>Commercial AC Ceca AC40</td>
<td>2.600</td>
<td>1,201</td>
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</tr>
<tr>
<td>Willow derived AC</td>
<td>2.413</td>
<td>1,280</td>
<td>[5]</td>
</tr>
<tr>
<td>Commercial AC CPB</td>
<td>1.999</td>
<td>1,288</td>
<td>[11]</td>
</tr>
<tr>
<td>Commercial AC F-400</td>
<td>1.934</td>
<td>800</td>
<td>[6]</td>
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<tr>
<td>R3-ex AC–NM</td>
<td>1.896</td>
<td>1,385</td>
<td>This study</td>
</tr>
<tr>
<td>Commercial Lewatit AF5</td>
<td>1.390</td>
<td>1,255</td>
<td>[13]</td>
</tr>
<tr>
<td>R3-ex AC–OX</td>
<td>1.376</td>
<td>1,295</td>
<td>This study</td>
</tr>
<tr>
<td>Commercial AC Organosorb-10</td>
<td>1.186</td>
<td>1,079</td>
<td>[13]</td>
</tr>
<tr>
<td>Commercial AC Desotec D43/1</td>
<td>1.150</td>
<td>1,053</td>
<td>[13]</td>
</tr>
<tr>
<td>Commercial AC F-300</td>
<td>0.852</td>
<td>963</td>
<td>[13]</td>
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<td>Commercial AC Norit 0.8</td>
<td>0.666</td>
<td>1,150</td>
<td>[12]</td>
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<tr>
<td>Commercial AC WG-12</td>
<td>0.597</td>
<td>948</td>
<td>[13]</td>
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<tr>
<td>Commercial AC Aquacarb 207C</td>
<td>0.586</td>
<td>1,100</td>
<td>[12]</td>
</tr>
</tbody>
</table>
4. Conclusions

In this paper, the effect of activated carbon surface chemistry on adsorption of phenoxy carboxylic acid herbicides, including MCPA, MCPP, and MCPB, from aqueous solutions was studied. The adsorption process was strongly pH dependent but no effect of ionic strength was observed. The adsorption data were found to follow pseudo-second-order kinetic and reached equilibrium within 60–90 min. The adsorption rate of the herbicides on all of the activated carbons increased in the order: MCPA < MCPP < MCPB. All of the herbicides were adsorbed faster on the AC–OX than on the AC–NM, and AC–AM activated carbon. Equilibrium adsorption data fit the Langmuir model more than the Freundlich. The adsorption efficiency of the herbicides followed the sequence: MCPA < MCPP < MCPB. The herbicides were preferably adsorbed on the activated carbon with basic surface (AC–AM, \( S_{BET} = 1,210 \text{ m}^2/\text{g} \)), followed by the non-modified adsorbent (AC–NM, \( S_{BET} = 1,385 \text{ m}^2/\text{g} \)), and the worst on the activated carbon with an acidic surface (AC–OX, \( S_{BET} = 1,295 \text{ m}^2/\text{g} \)), indicating that in the adsorption process the availability of the functional groups on the adsorbent surface was more important than the surface area.

References


