Adsorptive Characteristics of Ionogenic Aromatic Pesticides in Water on Powdered Activated Carbon

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(First received July 1997; accepted in revised form December 1997)

Abstract—The adsorptive characteristics of ionogenic pesticides on powdered activated carbon were described. The effects of pH on the adsorbatilities of MCPB (an acidic pesticide) and imazalil (a basic pesticide) onto powdered activated carbon (PAC) were evaluated by correlating 1-octanol-water partition coefficients (log $P_{ow}$) with the Freundlich adsorption constants over a pH range of 3 to 9. After being corrected with pH, the values of log $P_{ow}$ were found to be linearly related to the logarithm of $k$ (i.e. log $k$). For MCPB, log $k$ as well as log $P_{ow}$ decreased with the increase of pH in the range of pH > $pK_a$ and became constant in the range of pH < $pK_a$ and vise versa for imazalil. Adsorption of ionic species onto PAC became negligible at an ionic strength of $10^{-3}$ M when pH – $pK_a$ was lower than 4 for MCPB and pH – $pK_a$ higher than –4 for imazalil. Similar relationship between log $k$ and log $P_{ow}$ was obtained for other four acidic pesticides (bentazone, pentachlorophenol, denoseb and MCPP) and two neutral pesticides (imidacloprid and linuron), which suggested that the log $P_{ow}$ values mainly determined the adsorbabilities of these pesticides onto PAC. The calculation results showed that the activated carbon amount needed (ACAN) for lowering pesticide concentration from 500 to 50 mg/l was also linearly related to log $P_{ow}$, and the ACAN for bentazone (log $P_{ow}$, 0.11 at pH = 7) was 51.9 mg/l, while that for imazalil (log $P_{ow}$, 3.80 at pH = 8.0) was 3.1 mg/l.

Key words—activated carbon adsorption, 1-octanol-water partition coefficient, ionogenic aromatic pesticides, drinking water treatment, dissociation constant, pH

INTRODUCTION

The powdered activated carbon (PAC) adsorption process has been used as an effective method in temporal and emergent practice to remove residual pesticides and other hazardous chemicals in raw water during drinking water treatment. The residual pesticides in raw water can be divided into two categories: i.e. neutrals and ionogens and about 20% of the 400 pesticides commercially available in Japan are ionogenic pesticides. It was found that the PAC adsorbability of acidic pesticides, such as 2,4-dichlorophenoxyacetic acid (2,4-D), 2-methoxy-3,6-dichlorobenzoic acid (dicamba), and 3-amino-2,5-dichlorobenzoic-acid (amiben) significantly decreased upon increasing the pH of aqueous phase (Ward and Getzen, 1970). From the experimental results that the decline of PAC adsorbability of ionogenic organic compounds followed the dissociation curves, it was postulated that only the neutral species of the solutes were relevant for adsorption processes (Kipling, 1948). On the other hand, it was reported that the ion species of organic compounds were also adsorbed onto activated carbon (Snoeyink et al., 1969). In order to quantitatively describe the effects of pH on adsorption of acidic organic compounds, several models have been established by either using semiempirical binary Langmuir isotherm (Getzen and Ward, 1969; Muller et al., 1980) or Polanyi potential theory (Rosene and Manes, 1977). While these studies on pH effects have provided some valuable general insights into the adsorption of ionogenic organic compounds, more efforts are needed for establishing PAC dosage strategy in the routine operation of drinking water treatment plant.

It is well known that the adsorbatilities of organic compounds onto PAC are dependent mainly on their physico-chemical properties. For neutral organic compounds, many efforts have been made to quantitatively describe the adsorbatilities by using several physico-chemical parameters, including molecular weight, molecular refraction, and molar-attraction constant (Giusti et al., 1974; Abe

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These studies have been especially successful in evaluating the adsorbabilities of organic compounds with structural similarities. In order to quantitatively evaluate the adsorbabilities of neutral pesticides having no structural similarity, the logarithm of octanol–water partition coefficient (i.e., log $P_{ow}$), which is the ratio of a neutral compound in octanol and water phases, has been introduced into PAC adsorption processes (Hu et al., 1997). We had demonstrated that the log $P_{ow}$ values could be used to estimate the needed PAC dosage for the removal of most of pesticides tested. On the other hand, it has been shown that the concept of log $P_{ow}$ could be extended to weak organic acids and bases by correcting the effects of pH, or by correcting both the effects of pH and ionic strength when ionic strength effects became significant (Schellenberg et al., 1984; Westall et al., 1985; Jafvert et al., 1990; Escher and Schwarzenbach, 1996). The modified log $P_{ow}$ concept has been successfully applied to both quantitative structure–activity relationship studies (Scherrer and Howard, 1977) and adsorption of ionogenic compounds to soil (Linda et al., 1990) and wood pulp (Severtson and Banerjee, 1996). Therefore, it is possible that both the effects of pH on the adsorbabilities of ionogenic pesticides and the differences of adsorbabilities onto activated carbon including both ionogenic and neutral pesticides could be quantitatively evaluated by using the modified log $P_{ow}$ concept.

In this study, in order to develop a simplified method for determining PAC dosage in drinking water treatment, we focused on quantitative evaluation of the effects of pH on the adsorbabilities of ionogenic pesticides onto PAC in water by selecting an acidic pesticide (MCPB) and a basic one (imaza-lil) as model substances and correlating their equilibrium constants with the pH corrected log $P_{ow}$ at an ionic strength of $2 \sim 3 \times 10^{-3}$ M. The effectiveness of the model was verified on PAC treatment of other aromatic pesticides including other four acidic pesticides and two neutral ones.

### THEORETICAL BACKGROUND

#### Dependence of log $P_{ow}$ on $pK_a$ and pH for ionogenic pesticides

The $P_{ow}$ of an acidic pesticide can be expressed as follows:

$$P_{ow} = ([HA]_w + [A^-]_w)/([HA]_o + [A^-]_o)$$

$$= ([HA]_o/[HA]_w + [A^-]_w + [A^-]_o)/([HA]_o + [A^-]_o) + [A^-]_w$$

(1)

where the subscripts o and w refer to octanol and water phases, respectively, and $[HA]$, $[A^-]$ are the concentrations of the neutral and ionic species of the pesticide, respectively. Assuming activity coefficients to be near unity, the fractions of neutral and ionic species can also be described by equations (2) and (3), respectively.

$$[HA]_o/[HA]_w + [A^-]_w = 1/(1 + 10^{pH-pK_a})$$

(2)

$$[A^-]_o/[HA]_w + [A^-]_w = 1 - 1/(1 + 10^{pH-pK_a})$$

(3)

where $pK_a$ is the logarithmic value of dissociation constant. From equations (1)–(3), $P_{ow}$ can be expressed as equation (4).

$$P_{ow} = P_{ow0}/(1 + 10^{pH-pK_a})$$

$$+ P_{ow}(1 - 1/(1 + 10^{pH-pK_a}))$$

(4)

where $P_{ow0}$ (i.e., $[HA]_o/[HA]_o$) and $P_{ow}$ (i.e., $[A^-]_o/\[A^-]_w$) represent the $P_{ow}$ values of an ionogenic pesticide in neutral and ionic species, respectively.

### Table 1. Conditions in each isotherm test

<table>
<thead>
<tr>
<th>Pesticides</th>
<th>pH</th>
<th>Conditions</th>
<th>pH</th>
<th>Activated carbon dosage (mg/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MCPP</td>
<td>8.7 ± 0.2</td>
<td>10.0</td>
<td>15.0</td>
<td>20.0</td>
</tr>
<tr>
<td></td>
<td>7.9 ± 0.1</td>
<td>10.0</td>
<td>15.0</td>
<td>20.0</td>
</tr>
<tr>
<td></td>
<td>7.0</td>
<td>2.0</td>
<td>5.0</td>
<td>10.0</td>
</tr>
<tr>
<td></td>
<td>6.0</td>
<td>1.0</td>
<td>2.0</td>
<td>5.0</td>
</tr>
<tr>
<td></td>
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<td>1.0</td>
<td>2.0</td>
<td>4.0</td>
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<td>2.0</td>
<td>4.0</td>
</tr>
<tr>
<td></td>
<td>3.0</td>
<td>1.0</td>
<td>2.0</td>
<td>5.0</td>
</tr>
<tr>
<td>Imazalil</td>
<td>8.6 ± 0.2</td>
<td>1.5</td>
<td>2.0</td>
<td>2.5</td>
</tr>
<tr>
<td></td>
<td>7.9 ± 0.1</td>
<td>0.5</td>
<td>1.0</td>
<td>1.5</td>
</tr>
<tr>
<td></td>
<td>6.9</td>
<td>1.0</td>
<td>2.0</td>
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<td></td>
<td>3.0</td>
<td>1.0</td>
<td>2.0</td>
<td>3.0</td>
</tr>
<tr>
<td>Betazone</td>
<td>7.0</td>
<td>5.0</td>
<td>10.0</td>
<td>15.0</td>
</tr>
<tr>
<td>MCPP</td>
<td>7.0</td>
<td>2.0</td>
<td>5.0</td>
<td>10.0</td>
</tr>
<tr>
<td>Dinoseb</td>
<td>7.0</td>
<td>2.0</td>
<td>4.0</td>
<td>6.0</td>
</tr>
<tr>
<td>PCP</td>
<td>7.0</td>
<td>2.0</td>
<td>4.0</td>
<td>6.0</td>
</tr>
<tr>
<td>Imidacloprid</td>
<td>7.0</td>
<td>1.0</td>
<td>2.0</td>
<td>4.0</td>
</tr>
<tr>
<td>Linuron</td>
<td>7.0</td>
<td>0.5</td>
<td>1.0</td>
<td>2.0</td>
</tr>
</tbody>
</table>
Table 2. HPLC conditions for determining residual concentration of pesticides in treated water

<table>
<thead>
<tr>
<th>Pesticides</th>
<th>Wave length (nm)</th>
<th>CH₃CN/buffer*</th>
<th>RT (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MCPB</td>
<td>230.4</td>
<td>60:40</td>
<td>8.0</td>
</tr>
<tr>
<td>Imidacloprid</td>
<td>255.4</td>
<td>60:40</td>
<td>4.84</td>
</tr>
<tr>
<td>PCP</td>
<td>220.4</td>
<td>60:40</td>
<td>4.62</td>
</tr>
<tr>
<td>Dinoseb</td>
<td>240.4</td>
<td>60:40</td>
<td>3.19</td>
</tr>
<tr>
<td>Imazalil</td>
<td>270.4</td>
<td>60:40</td>
<td>3.30</td>
</tr>
<tr>
<td>Bentazone</td>
<td>228.4</td>
<td>60:40</td>
<td>4.84</td>
</tr>
<tr>
<td>Linuron</td>
<td>215.4</td>
<td>60:40</td>
<td>4.62</td>
</tr>
</tbody>
</table>

*0.025 M KH₂PO₄ + H₃PO₄, pH = 3.2.

has been reported that the distribution of PCP, an acidic pesticide, in ionogenic species between octanol and water was highly dependent on the ionic strength of aqueous solution, and the distribution of ionogenic species was very limited at a lower ionic strength (Westall et al., 1985). In this case, the distribution of ionogenic species can be neglected and \( P_{ow} \) can be omitted as follows:

\[
P_{ow} = P_{ow}/(1 + 10^{(\text{pH} - pK_a)})
\]  

For a basic compound, equation (5) can be rewritten as equation (6) under the conditions of lower ionic strength.

\[
P_{ow} = P_{ow}/(1 + 10^{-(\text{pH} - pK_b)})
\]

**EXPERIMENTAL SECTION**

**Reagents and chemicals**

A single batch of commercial charcoal-based activated carbon (powder, 300 mesh size) was obtained from Wako Co. (Japan). The BET surface area was approximately 1340 m²/g. The carbon was washed with distilled water and subsequently drying in oven at 115°C for 3 h before use. Five acidic, one basic and two neutral pesticides were selected in this study and they were from Riedel-de Haen (Seelze, Germany). The compounds, and their common names as pesticides [in parentheses] were as follows: 3-isopropyl-1H-1,3-benzothiadiazin-4(3H)-one 2,2-dioxide [bentazone], 4-(4-chloro-o-tolyloxy) butyric acid [MCPB], (RS)-2-(4-chloro-o-tolyloxy) propionic acid [MCPP], pentachlorophenol [PCP], 2-sec-butyl-4,6-dinitrophenol [dinitrochlorophene] [2], (+)-allyl 1-(2,4-dichlorophenyl)-2-imidazol-1-ylethyl ether [imidacloprid], 1-(6-chloro-3-pyridylmethyl)-N-nitroimidazolidin-2-ylidenemine [imazalil], 3-(3,4-dichlorophenyl)-1-methoxy-1-methylurea [linuron]. 1000 mg/l individual standard solutions were prepared by dissolving 20 mg of each pesticide in 20 ml methanol, respectively. For \( P_{ow} \) determination, 10 mg/l individual methanol solution was prepared by dissolving the 1000 mg/l standard solutions into methanol.

For determining the \( P_{ow} \) value of imidacloprid, five organic compounds were used as standard materials: acetone (~0.24), nitroethane (0.18), thiazole (0.44), benzylalcohol (1.10), and benzoaldehyde (1.480). These organics were purchased from Wako Co. (Japan), 10 mg/l individual standard solution was prepared by diluting the 1000 mg/l methanol stock solution into methanol.

**Determination of \( P_{ow} \)**

The log \( P_{ow} \) value of linuron and log \( P_{ow} \) values of the ionogenic pesticides in neutral species were determined at a methanol-water ratio of 60:40 (v/v) by interpolating the log-log plot between column hold-up corrected retention time RT and \( P_{ow} \) of standards as described in our previous paper (Hu et al., 1997). In order to determine the \( P_{ow} \) values of the ionogenic pesticides, the pH of aqueous phase of HPLC was adjusted to 2 for acidic pesticides or 8.5 for imidazalil by adding an appropriate amount of HCl or NaOH to 0.01 M orthophosphoric acid solution. In order to determine the log \( P_{ow} \) value of imidacloprid with a high precision, five standards with log \( P_{ow} \) values lower than those used in our previous paper was selected, and the ratio of methanol-water was set at 20:80 (v/v). The log \( P_{ow} \) of imidacloprid was determined based on the correlation equation between log \( P_{ow} \) values of the five standards and their log RT values, i.e. \( \log P_{ow} = 1.12 \log \text{RT} - 0.134 \) (\( r^2 = 0.99 \)).

**Isotherm test**

Activated carbon adsorption experiment was carried out in 300 ml flasks by agitating with a stirrer for 24 h in a thermostated room at 25 ± 1°C. The experimental pH values shown in Table 1 were adjusted by adding an appropriate amount of NaOH to 0.001 M orthophosphoric acid solution. The ionic strength was maintained at 0.002–0.003 M by adding an appropriated amount of NaCl to the above solution. In all experiments, the initial concentration of single-solute solution was 500 mg/l. The activated carbon dosages are shown in Table 1. After activated carbon was introduced, the flask was capped with a stopper, leaving a minimum headspace to avoid pH change due to the loss or uptake of CO₂. The residual concentrations of pesticides were determined by HPLC method (HiP1090) directly under the conditions shown in Table 2 after activated carbon was separated from samples through a disposable PTFE syringe filter (pore size 0.5 μm, 4 mm I.D., Millipore, Japan). Liquid chromatography was carried out at a flow rate of 1 ml/min on a Showdex DE-613 column (6.0 mm I.D., 150 mm length) at column temperature of 40°C. The injection volume was 100 μl.

**RESULTS AND DISCUSSION**

**Determination of \( P_{ow} \)**

The log \( P_{ow} \) or log \( P_{ow} \) values of the objective pesticides determined by the HPLC method are shown in Table 3 as well as other properties of the pesticides. Because the experimental ionic strength was set at 2 × 3 × 10⁻⁵ M, it was possible to calculate the log \( P_{ow} \) values at a given pH from the log \( P_{ow} \) values following equations (5) and (6). The calculated log \( P_{ow} \) values at the experimental pH were shown in Table 4. The dependency of the pH corrected log \( P_{ow} \) values of MCPB and imazalil on
pH–pKₐ is shown in Fig. 1. It was found that the log Pₐw of MCPB decreased linearly with the increase of pH within the range of pH < pKₐ, and it became almost constant at pH > pKₐ. For basic compound, imazalil, the opposite tendency was observed.

**Effects of pH on adsorbabilities of acidic pesticides**

MCPB was used as a model substance of acidic pesticides for evaluating the effects of pH on the adsorbabilities of ionogenic pesticides. The Freundlich isotherm is empirically expressed as follows:

\[ q = kC^{1/n} \]  

(7)

where \( q \) is the adsorbed amount per unit weight of adsorbent, \( C \) is the equilibrium concentration, \( k \) and \( n \) are the experimental parameters.

Table 4. Results of regression analysis using Freundlich equation

<table>
<thead>
<tr>
<th>Pesticides</th>
<th>pH</th>
<th>log Pₐw ¹</th>
<th>kᵇ</th>
<th>n</th>
<th>ACAN (mg/l)</th>
<th>( r^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>MCPB</td>
<td>8.7</td>
<td>-0.58</td>
<td>99.3</td>
<td>3.6</td>
<td>30.3</td>
<td>0.98</td>
</tr>
<tr>
<td></td>
<td>7.9</td>
<td>0.22</td>
<td>144.2</td>
<td>3.1</td>
<td>22.1</td>
<td>0.99</td>
</tr>
<tr>
<td></td>
<td>7.0</td>
<td>1.12</td>
<td>234.9</td>
<td>3.8</td>
<td>12.5</td>
<td>0.99</td>
</tr>
<tr>
<td></td>
<td>6.0</td>
<td>2.09</td>
<td>310.5</td>
<td>4.5</td>
<td>8.9</td>
<td>0.95</td>
</tr>
<tr>
<td></td>
<td>5.0</td>
<td>2.87</td>
<td>486.0</td>
<td>3.4</td>
<td>6.3</td>
<td>0.97</td>
</tr>
<tr>
<td></td>
<td>4.0</td>
<td>3.22</td>
<td>532.0</td>
<td>4.1</td>
<td>5.6</td>
<td>0.97</td>
</tr>
<tr>
<td></td>
<td>3.0</td>
<td>3.27</td>
<td>523.1</td>
<td>8.0</td>
<td>4.5</td>
<td>1.00</td>
</tr>
<tr>
<td>Imazalil</td>
<td>8.6</td>
<td>3.82</td>
<td>602.6</td>
<td>4.8</td>
<td>3.6</td>
<td>0.97</td>
</tr>
<tr>
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<td>3.1</td>
<td>0.96</td>
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<td>6.9</td>
<td>3.66</td>
<td>676.1</td>
<td>3.6</td>
<td>3.7</td>
<td>0.97</td>
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<tr>
<td></td>
<td>5.9</td>
<td>3.12</td>
<td>562.3</td>
<td>4.2</td>
<td>4.1</td>
<td>0.93</td>
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<td></td>
<td>4.9</td>
<td>2.21</td>
<td>380.2</td>
<td>5.0</td>
<td>5.8</td>
<td>0.99</td>
</tr>
<tr>
<td></td>
<td>3.9</td>
<td>1.22</td>
<td>218.8</td>
<td>5.0</td>
<td>9.9</td>
<td>0.97</td>
</tr>
<tr>
<td></td>
<td>3.0</td>
<td>0.32</td>
<td>154.9</td>
<td>5.0</td>
<td>14.2</td>
<td>0.86</td>
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<tr>
<td>Bentazone</td>
<td>7.0</td>
<td>-1.75</td>
<td>41.7</td>
<td>10.0</td>
<td>51.9</td>
<td>0.93</td>
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<tr>
<td>MCPB</td>
<td>7.0</td>
<td>-0.86</td>
<td>60.3</td>
<td>10.0</td>
<td>40.4</td>
<td>0.99</td>
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<tr>
<td>Dinoseb</td>
<td>7.0</td>
<td>1.26</td>
<td>218.8</td>
<td>3.8</td>
<td>12.9</td>
<td>0.86</td>
</tr>
<tr>
<td>PCP</td>
<td>7.0</td>
<td>1.88</td>
<td>309.0</td>
<td>3.2</td>
<td>9.3</td>
<td>0.99</td>
</tr>
<tr>
<td>Imidacloprid</td>
<td>7.0</td>
<td>1.33</td>
<td>288.4</td>
<td>2.9</td>
<td>10.6</td>
<td>0.97</td>
</tr>
<tr>
<td>Linuron</td>
<td>7.0</td>
<td>2.99</td>
<td>537.0</td>
<td>3.8</td>
<td>5.2</td>
<td>0.91</td>
</tr>
</tbody>
</table>

¹ log Pₐw values of acidic pesticides at given pH were calculated by eq. (5) or (6).
² k unit: \( \mu \text{mol}^{-1/\l} \cdot \lg^{-1/\l} \cdot \text{g}^{-1} \).

and \( n \) are the experimental parameters. Figure 2 shows the effects of pH on the Freundlich adsorption isotherm of MCPB. In this study, molar concentration was used for the plots. The results of regression analysis using Freundlich equation are presented in Table 4. It was found that the amounts of MCPB adsorbed onto PAC decreased with the increase of pH, which agreed with other studies (Ward and Getzen, 1970).

Figure 3(a) shows the effects of pH on \( k \). It was found that the logarithm of \( k \) (i.e. \( \log k \)) decreased almost linearly with the increase of pH within the range of pH < pKₐ, and became almost constant at pH > pKₐ. From the similarity of the behaviors of \( \log k \) and \( \log Pₐw \), a regression analysis on \( \log k \) and \( (1 + 10^{\text{pH-}pKₐ}) \) was carried out and equation (8) was obtained.

\[ \log k = -0.188 \log(1 + 10^{\text{pH-}pKₐ}) + 2.74 \quad (r^2 = 0.99) \]  

(8)

From equations (6) and (8), and by substituting the measured \( Pₐw \) value, a relation between \( \log k \) and

![Fig. 1. Dependence of log Pₐw on (pH–pKₐ).](image1)

Fig. 1. Effects of pH on the Freundlich adsorption isotherm of MCPB. Ionic strength is 0.002 ~ 0.003 M.
log $P_{ow}$ was obtained as shown in equation (9).

$$
\log k = 0.188 \log P_{ow} + 2.12 \quad (r^2 = 0.99)
$$

(9)

When log $P_{ow}$ increased from ~0.58 at pH 8.7 to 3.28 at pH 3.0, log $k$ increased linearly from 2.00 to 2.72. On the other hand, another parameter, $n$, was found to be relatively irrelevant with log $P_{ow}$ as shown in Fig. 3(b). Except one point, the values of $n$ were found to be almost around 3.3.

From the adsorption isotherms obtained, the activated carbon amount needed (ACAN) for lowering pesticide concentration from 500 to 50 mg/l was calculated and listed in Table 4. Figure 3(c) shows the correlation between ACAN and pH–p$K_a$. From Fig. 3(a–c), it was found that the relationship between ACAN and pH–p$K_a$ was similar with that between $k$ and pH–p$K_a$, and that $n$ had little effects on ACAN. The ACAN increased from 4.5 mg/l at pH 3.0 to 30.3 mg/l at pH 8.7. That is, an increase from 3.0 to 8.7 in pH resulted in an increase of ACAN of ca. 6.7 times for MCPB. The effects of pH on ACAN could be quantitatively represented as follows:

$$
\log ACAN = 0.203 \log(1 + 10^{\text{pH–p}K_a}) + 0.700
$$

$$
= -0.203 \log P_{ow} + 1.37 \quad (r^2 = 0.99),
$$

(10)

which suggests that the adsorbability of MCPB at a given pH was dependent on the pH corrected log $P_{ow}$.

From the above results, it could be postulated that the ionic species of MCPB was almost not adsorbed onto activated carbon under the experimental conditions used in this study; i.e. at ionic strength of $2 \times 10^{-3} M$ and pH range of 3.0 ~ 8.7 (i.e. pH–p$K_a$ ~ 4). It turned out that MCPB was still able to be adsorbed onto activated carbon.

Fig. 3. Effects of pH on $k$ (a), $n$ (b) and ACAN (c) of MCPB. ACAN is the activated carbon amounts needed for lowering concentration from 500 to 50 mg/l; ionic strength is 0.002 ~ 0.003 M.

Fig. 4. Effects of pH on the adsorption isotherm of imazalil. Ionic strength is 0.002 ~ 0.003 M.
carbon at pH–pK_a > 2, even though more than 99% of MCPB in the aqueous phase was supposed to be ionized under the conditions. This phenomenon was supposed to be attributed to a dynamic adsorption equilibrium as follows:

\[ \text{PAC} \rightleftharpoons \text{HA} \rightleftharpoons \text{H}^+ + \text{A}^- \]

In fact, the dissociated and undissociated species of MCPB were co-existed under any conditions although their ratio varied largely with the pH and ionic strength of the aqueous phase. When PAC was added into the aqueous phase at a given pH, a part of the undissociated species would be adsorbed onto activated carbon, which would break the old dissociation equilibrium. The dissociation equilibrium then shifted toward the direction to form undissociated species until a new equilibrium which included the adsorption equilibrium and the dissociation one, was established. Thus, the co-existing ionic species enhanced the adsorption of MCPB by supplementing the undissociated species through dissociation equilibrium shift, which was consistent with the synergistic-adsorption effects as exemplified in other studies (Getzen and Ward, 1969; Ward and Getzen, 1970).

Effects of pH on the adsorbatibilies of basic pesticides

Imazalil was used as a model pesticide to investigate the effects of pH on the adsorbatibilities of basic pesticides. Figure 4 shows the adsorption isotherms of imazalil at different pH values, and the values of \( k, n \), and ACAN were listed in Table 4. Figure 5(a–c) shows the respective relationship of \( k, n \), and ACAN with pH–pK_a. It was found that \( k \) and ACAN of imazalil were also dependent on pH–pK_a.

Fig. 5. Effects of pH on \( k \) (a), \( n \) (b) and ACAN (c) of imazalil. ACAN is the activated carbon amounts needed for lowering concentration from 500 to 50 µl/g; ionic strength is 0.002 M.

Fig. 6. Adsorption isotherms of 4 acidic and 2 neutral pesticides. Ionic strength is 0.002 ~ 0.003 M; pH = 7.
and log $P_{ow}$, and the correlation equations (11) and (12) were accordingly obtained. The values of $n$ were in the range 3.6–5.0 and relatively irrelevant with the log $P_{ow}$ values. By comparison of equation (11) with equation (9), it was found that the two equations were almost the same. That is, $k$ of the pesticides could be estimated from equation (9) no matter the objective pesticides were acidic or basic. On the other hand, equation (12) was essentially same with equation (10) although the two regression equations were slightly different. The slight differences of the two regression equations could be covered by replacing ACAN per morals adsorbed with ACAN.

$$
\log k = -0.187 \log(1 + 10^{P_{ow} - \text{pH}}) + 2.85 \\
= 0.187 \log P_{ow} + 2.13 \quad (r^2 = 0.99) \quad (11)
$$

$$
\log \text{ACAN} = -0.178 \log(1 + 10^{P_{ow} - \text{pH}}) + 0.516 \\
= -0.178 \log P_{ow} + 1.20 \quad (r^2 = 0.99) \quad (12)
$$

From equations (11) and (12), it was clear that in contrast to the behavior of MCPB, the adsorbability of imazalil increased with increasing pH. When log $P_{ow}$ decreased from 3.82 at pH 8.6 to 0.32 at pH 3.0, $k$ decreased from 620.6 to 154.9 while ACAN increased from 3.6 to 14.2 mg/l.

The above results indicated that the effects of pH on the adsorbabilities of ionogenic pesticides, including acidic and basic ones, could be evaluated by the pH corrected log $P_{ow}$. At a given pH and ionic strength as low as $2 \sim 3 \times 10^{-3}$ M, ACAN could be estimated through equation (10) or equation (12) no matter the objective pesticides were acidic or basic.

### Adsorptive behavior of other 4 acidic and two neutral pesticides

To investigate if the above results were widely applicable, Freundlich adsorption isotherms of four other acidic pesticides (PCP, denoseb, MCPP, and bentazone) and two neutral pesticides (imidacloprid and linuron) were also determined. Freundlich adsorption isotherms of the above pesticides were obtained at 25 ± 1°C and pH 7.0 (Fig. 6), and $k$, $n$, and ACAN were listed in Table 4. The results indicated that the adsorbability of each pesticide was significantly different even at the same pH.

In this study, Freundlich adsorption isotherms of five acidic pesticides (MCPB, PCP, denoseb, MCPP and bentazone), one basic one (imazalil), and two neutral (imidacloprid and linuron) were obtained. In order to evaluate the relationship between the adsorbabilities of the objective pesticides and log $P_{ow}$, $k$, $n$ and ACAN were respectively plotted with log $P_{ow}$ in Fig. 7. It was found that even for different pesticides, log $k$ and the logarithm of ACAN were almost linearly related with the pH corrected log $P_{ow}$ as shown in equations (13) and (14), while $n$ was relatively irrelevant with log $P_{ow}$. This suggests that log $P_{ow}$ is the dominant factor affecting the seven pesticides used in this study.

$$
\log k = 0.210 \log P_{ow} + 2.08 \quad (r^2 = 0.97) \quad (13)
$$

$$
\log \text{ACAN} = -0.213 \log P_{ow} + 1.34 \quad (r^2 = 0.97) \quad (14)
$$

### CONCLUSIONS

In this paper, a fundamental study was carried out to develop a simplified method for estimating PAC dosage in drinking water treatment to remove ionogenic aromatic pesticides in water. The results indicated that the pH correcting log $P_{ow}$ not only determined the adsorptions of one ionogenic pesticide at different pH but also accounted for the adsorption of these structurally diverse aromatic pesticides. The competitive effects of natural organic matter on the adsorbabilities of these ionogenic aromatic pesticides will be studied and reported in due course.
Acknowledgements—This work was partly granted by the Governmental Research Fund (Environmental Agency). J.-Y. Hu thanks the Japan Science and Technology Corporation, for researching in the National Institute of Public Health.

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