Investigation of adsorption kinetics and isotherms of imidacloprid as a pollutant from aqueous solution by adsorption onto industrial granular activated carbon

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Abstract

Adsorption of pesticide imidacloprid as an insecticide from aqueous solution onto granular activated carbon (GAC) under different conditions was studied. Kinetics of adsorption was followed by an on-line spectrophotometric analysis system, which consists of UV-spectrophotometer, a designed adsorption cell, peristaltic pump and special glassy reactor. The obtained data were treated according to three various rate models. In all experiments, adsorption process was studied at 25°C and pH value about 7. Our results showed on the basis of $P$, in higher concentration of imidacloprid ($C_0 \geq 25$ ppm) and lower amount of GAC ($GAC \leq 2$ g) the second order model was the most suitable. Isotherm data were treated according to Langmuir and Freundlich models. The adsorption data at 25°C were found to fit almost equally well to Langmuir and Freundlich models, but according to complementary criteria, the Freundlich is preferred.

Key words: Adsorption, on-line analysis system, imidacloprid, kinetics, isotherm, water treatment.

Introduction

Pollution of surface and ground waters causes risk to environment and human health because of the potential health hazards of their contents of inorganic and organic compounds. Also the contamination of these waters by pesticides is an important problem that the scientists are dealing with over the years. Although much benefit is obtained from use of pesticides, they have some undesirable side effects, such as toxicity, carcinogenity and mutagenity. Imidacloprid is an insecticide used to control sucking insects, including rice, leaf and plant hoppers, aphids and whitefly. It is also effective against soil insects, termites and some species of biting insects, such as rice water weevil and Colorado beetle. It is used as seed dressing, soil treatment and foliar treatment in different crops, e.g., rice, cotton, cereals, maize, sugar beet, potatoes, vegetables, citrus fruit, pome fruit and stone fruit. Imidacloprid that may pollute water due to its extensive application in agriculture as insecticide has some undesirable side effects, such as toxicity ($LD_{50}$ for rat is 450 mg/kg), too.

Many of studies toward the solution of this problem involve determination of adsorption behavior of pesticides on various adsorbents such as bentonite, kerolite and zeolite. Activated carbon materials have a special place among the adsorbents, as for a long time they are known to be capable of adsorbing various organic compounds and in recent years the number of studies on adsorption of pesticides on carbon materials from aqueous solution has increased. Yang et al. studied the phenoxyacid herbicide adsorption on granular activated carbon. Martin-Gullon and Font compared the activated carbon fiber and granular activated carbon for their effectiveness in removal of pesticides from aqueous solution by adsorption. Ayaranci and Hoda studied adsorption of some pesticides such as metribzin and atrazine on activated carbon-cloth. Most of the adsorption studies from aqueous solutions involve the measurement of concentration of the adsorbate as function of time, amount of adsorbent and temperature. Therefore, a suitable, practical, fast responding and preferably non-destructive in situ method should follow the concentrations of adsorbate. In this respect, optical absorbance measurements provide a convenient way for molecule absorbing in UV-VIS region. In situ measurements also allow the study of kinetics of the adsorption process.

The purpose of the present work was to study the kinetics of adsorption and isotherms of imidacloprid (Table 1) onto industrial granular activated carbon (GAC) by adsorption using an on-line spectrophotometric analysis system. This method was selected to follow the adsorption since the imidacloprid is capable of absorbing UV light, but the main reason for selection of the imidacloprid was its high solubility in water which can cause toxicity problems in the environment.

Table 1. Chemical structure, molecular weight, WHO class and solubility in water of imidacloprid.

<table>
<thead>
<tr>
<th>Pesticide</th>
<th>Molecular weight (g mol$^{-1}$)</th>
<th>WHO Class</th>
<th>Solubility (mg l$^{-1}$) in water</th>
</tr>
</thead>
<tbody>
<tr>
<td>Imidacloprid</td>
<td>255.7</td>
<td>(II)</td>
<td>610</td>
</tr>
</tbody>
</table>
Material and Methods

The industrial granular activated carbon (GAC) used in the present work was obtained from typical market, and its properties such as the point of zero charge (PZC) and iodine number were determined in our laboratory as 3 and 1330.24 mg g⁻¹, respectively. This GAC is cylindrical and its average diameter and length are 4 and 7 mm, respectively. The pesticide imidacloprid (purity 95%) was obtained from Chem-service (USA). Deionized water was used in adsorption experiments.

On-line spectrophotometric analysis system: The schematic presentation of on-line spectrophotometric analysis system, which consists of UV-spectrophotometer, a designed absorption cell, peristaltic pump, water reservoir with temperature controller and special glassy reactor, is shown in Fig. 1. The UV-VIS spectrophotometer (Perkin-Elmer 550 SE, Germany) was used for optical absorbance measurements. A special cell was designed to carry out the absorption measurements. The glassy reactor contains a tube as inlet of argon (Ar) gas which mixes the contents of reactor and eliminates dissolved CO₂ and air. The other tube allows circulating the turning solution. One thermometer has been attached to watch temperature of solution, and one hatch is as gas outlet.

Optical absorbance measurements: The sliding door of the sample compartment of the spectrophotometer was left open and covered with black plastic. Because of being a little distance between reactor and absorbance measuring cell, delay time was calculated that had constant value equal to 0.5 min (the pumping speed should be constant). At first, the reactor was loaded by pesticide solution. After degassing the solution by Ar flow to remove all air in the solution, GAC added to solution and the solution was pumped to the absorbance measuring cell and its absorbance was recorded. Delay time was calculated that had constant value equal to 0.5 min (the pumping speed should be constant). At first, the reactor was loaded by pesticide solution. After degassing the solution by Ar flow to remove all air in the solution, GAC added to solution and the solution was pumped to the absorbance measuring cell and its absorbance was recorded and then it was returned to the reactor.

Whole optical absorption spectrum of imidacloprid was recorded and it was seen that λ max of imidacloprid is nearly 270 nm (Fig. 2). Absorbance data in λ max were recorded in certain time intervals over a period of 90 min.

Absorbance data were converted into concentrations using calibration line. Adsorption study was repeated on duplicate. The absorbance values were reproducible (with σ² = 0.002).

Determination of adsorption isotherms: The adsorption isotherms of pesticide on GAC was determined on the basis of batch analysis. Different amounts of GAC were allowed to equilibrate with constant initial concentrations of imidacloprid solution (C₀=100 ppm). Because of enough confidence of approach to equilibrium, these solutions were allowed to stay 1 week in experimental condition and then the equilibrium concentration of imidacloprid solutions was measured spectrophotometrically. The amount of imidacloprid adsorbed per mass unit of GAC in equilibrium condition, qₑ, was calculated by Eq. 1,

\[ qₑ = \frac{V}{m} (C₀ - Cₑ) \]

where \( V \) is the volume of imidacloprid solution in l, \( C₀ \) and \( Cₑ \) are the initial and equilibrium concentrations, respectively, of the imidaclopride solutions in mg l⁻¹ and \( m \) is the mass of the GAC in g. Eq. 1 gives \( qₑ \) in mg pesticide adsorbed per g GAC.

Results and Discussion

The maximum absorbance wavelength (λ max) of imidacloprid at different pH values is nearly 270 nm (Fig. 2). Absorbance versus concentration data for imidacloprid was treated by linear regression analysis with \( R² = 0.999 \).

In all experiments, adsorption process was studied at 25°C and pH value about 7. Adsorption of the pesticide at different initial concentration (\( C₀ = 30, 25, 20 \) and 15 ppm) and amounts of GAC (\( m = 10, 5, 2 \) and 1 g) were monitored spectrophotometrically by the procedure described above. Absorbance data of imidacloprid were obtained in one-minute intervals from 0 to 25 min, five-minute intervals from 25 to 60 min and ten-minute intervals from 60 to 90 min during the adsorption process, then absorbance data were converted into concentration data using the corresponding calibration plots. The concentrations were plotted as a function of time. They are shown in Figs 3 and 4. Initial concentration in all experiments was adjusted to be the same (25 ppm) in order to compare the adsorption behavior easily.

Adsorption of imidacloprid at different initial concentrations (\( C₀ \)): The initial concentrations of imidacloprid were 30, 25, 20 and 15 ppm, respectively, and the weights of GAC were kept the same in all adsorption experiments. The changes in imidacloprid removal...
Adsorption of imidacloprid at different amount of GAC (m): In order to make a comparative study for adsorption of imidacloprid, the initial concentration of imidacloprid was kept the same (C₀ = 25 ppm). The changes in imidacloprid concentration with time during the adsorption process at each GAC amount, are shown in Fig. 4 in order: k (m = 10 g) > k (m = 5 g) > k (m = 2 g) > k (m = 1 g). Naturally, with increasing amount of adsorbent surface, extent of adsorption will be larger.

Kinetics of adsorption: Some probable kinetic models were applied to fit them to experimental data. These models included intraparticle diffusion 13, which can be formulated as:

\[ q_t = k_1 t^{1/2} \]  

(2)

with time during the adsorption on the GAC for each initial concentration are shown in Fig. 3. A clear distinction can be seen at later stage as \( k (C_0 = 30 \text{ ppm}) > k (C_0 = 25 \text{ ppm}) > k (C_0 = 20 \text{ ppm}) > k (C_0 = 15 \text{ ppm}) \). The differences in the extent of adsorption at 90 min are clear.

Adsorption isotherms of imidacloprid: In order to assess the potential adsorption capacity of the GAC toward the imidacloprid, its adsorption isotherms at 25ºC were derived on the basis of batch analysis as described. The isotherm data were treated according to the well known Langmuir and Freundlich isotherm models. The Langmuir model assumes uniform energy sites on the surface. The linearized Langmuir isotherm equation can be written as follows:

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

(7)

where \( q_e \) is the amount of adsorbate adsorbed at any time, \( C_e \) is initial concentration of adsorbate, \( C \) is the concentration of adsorbate at any time, \( t \) is time and \( k_1, k_2 \) and \( k_i \) are rate constants for diffusion, the first order and the second order models, respectively. \( q_e \) is obtained from \( C_e \) and \( C \) values by the following equation:

\[ q_e = \frac{(C_0 - C)V}{m} \]  

(5)

where \( V \) (l) is the volume of adsorbate solution and \( m \) (g) is the mass of the GAC.

The applicability of the three models was studied by drawing linear plot of \( q_e \) versus \( t^{1/2} \) for intraparticle diffusion, \( lnC \) versus \( t \) for first order and \( 1/C \) versus \( t \) for second order models. The rate constant of \( k_1, k_2 \) and \( k_i \) obtained from the slopes of corresponding linear plots are given in Tables 2 and 3 at different initial concentration and masses of GAC respectively, with correlation coefficients, \( r \). When the correlation coefficients of the three models are compared for each initial concentration and amount of GAC, it can be seen that all of them are greater than 0.92. So, it is very difficult to prefer a certain kinetic model to fit the adsorption data, but in different \( m \) (m=2 g), intraparticle diffusion model does not seem to be successfully applicable for the present adsorption data because of its low correlation coefficient \((r<0.8)\) in these conditions. A better criteria is to introduce a parameter known as normalized percent deviation 14, the lowest average absolute percent deviation (%D) 15 or in some literature percent relative deviation modulus, \( P \), given by the following equation:

\[ P = \frac{100}{N} \sum \frac{|y_{\text{exp}} - y_{\text{pred}}|}{y_{\text{exp}}} \]  

(6)

where \( y_{\text{exp}} \) is the experimental y at any x, \( y_{\text{pred}} \) is the corresponding predicted y according to the equation under study with best fitted parameters, \( N \) is the number of observations. It is clear that the lower the \( P \) value, the better is the fit 13. The \( P \) values calculated for the fit of kinetics data of imidacloprid to three kinetic models are given in Table 2 and 3. The fit accepted to be good when \( P \) is below 5. On the basis of \( P \) in higher concentration of imidacloprid \((C_0=25 \text{ ppm})\) and lower amount of GAC \((\text{GAC} \leq 2 \text{ g})\) the second order model was the most suitable.

Ad sorption isotherms of imidacloprid: In order to assess the potential adsorption capacity of the GAC toward the imidacloprid, the first order model which can be formulated as:

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where $q_e$ (mg g$^{-1}$) is the amount of solute adsorbed per unit mass of adsorbent in equilibrium condition, $C_e$ (mg l$^{-1}$) the equilibrium concentration of solute, $q_m$ (mg g$^{-1}$) the amount of solute adsorbed per unit mass of adsorbent required for complete monolayer coverage of surface, $b$ (l mg$^{-1}$) a constant related to the heat of adsorption. When $C_e/q_e$ is plotted against $C_e$ and the data are regressed linearly, $q_m$ and $b$ constants are calculated from the slope and the intercept.

On the other hand the Freundlich isotherm equation in linearized form can be given as follows:

$$\ln q_e = \ln K + \frac{1}{n} \ln C_e$$

where $q_e$ and $C_e$ have the same definitions as in Langmuir equation. Freundlich constant, $K$, related to the adsorption capacity of the GAC and $1/n$ is another constant related to the surface heterogeneity. When $\ln q_e$ is plotted against $\ln C_e$ and the data are treated by linear regression analysis, $1/n$ and $K$ constant are determined from the slope and the intercept. The value of $1/n$ is known as the heterogeneity factor and ranges between 0 and 1, the more heterogeneous the surface, the closer $1/n$ value is to 0.

The parameters of Langmuir and Freundlich equations for the adsorption of imidacloprid on GAC are given in Table 3. In Fig. 5 calculated results of two isotherm models are compared with experimental data, and it is seen that predicted results by Freundlich equation are a little better fitted to experimental data.

The fit accepted to be good when $P$ is below 5. The fit of experimental data to Freundlich equation seems to be excellent for imadacloprid because $P$ value is much below 5. In general one can say that Freundlich equation is fitted to experimental data better than Langmuir equation.

The dimensionless constant known as separation factor ($R_L$) was calculated from the following equation using Langmuir $b$ parameter

$$R_L = \frac{1}{1 + bC_0}$$

where $b$ (l mg$^{-1}$) is the Langmuir constant and $C_0$ (mg l$^{-1}$) the initial concentration. Isotherm is considered to be unfavorable, linear, favorable or irreversible depending on the value of $R_L$. $R_L$ was calculated and was 0.258. Since the obtained value $R_L$ is in the range of zero and one, the adsorption is favorable.

**Conclusions**

It was found that imadacloprid as a pollutant of environment could be removed from aqueous solution better in higher initial concentration of imadacloprid and higher amount of absorbent by adsorption onto the GAC. The adsorption processes were found to be favorable for imadacloprid.

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**Table 2.** Rate constants, correlation coefficients and $P$ from treatment of adsorption data according to the three kinetic models in different masses of GAC.

<table>
<thead>
<tr>
<th>Amount of GAC (g)</th>
<th>First order</th>
<th>Second order</th>
<th>Intraparticle diffusion</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_1$</td>
<td>$r$</td>
<td>$P$</td>
<td>$k_1$</td>
</tr>
<tr>
<td>$m=10$</td>
<td>0.0506</td>
<td>0.93</td>
<td>&gt;&gt;5</td>
</tr>
<tr>
<td>$m=5$</td>
<td>0.0336</td>
<td>0.90</td>
<td>&gt;&gt;5</td>
</tr>
<tr>
<td>$m=2$</td>
<td>0.0159</td>
<td>0.98</td>
<td>6.19</td>
</tr>
<tr>
<td>$m=1$</td>
<td>0.0101</td>
<td>0.998</td>
<td>1.16</td>
</tr>
</tbody>
</table>

$[k_1]=\min^{-1}$, $[k_2]=\min^{-1}$ and $[k_i]=\text{mg g}^{-1}\min^{-1/2}$

**Table 3.** Rate constants, correlation coefficients and $P$ from treatment of imadacloprid adsorption data according to the three kinetic models in different initial concentrations of imadacloprid.

<table>
<thead>
<tr>
<th>Initial concentration</th>
<th>First order</th>
<th>Second order</th>
<th>Intraparticle diffusion</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_1$</td>
<td>$r$</td>
<td>$P$</td>
<td>$k_1$</td>
</tr>
<tr>
<td>$C_0= 30$ ppm</td>
<td>0.0204</td>
<td>0.98</td>
<td>7.46</td>
</tr>
<tr>
<td>$C_0=25$ ppm</td>
<td>0.0159</td>
<td>0.98</td>
<td>6.19</td>
</tr>
<tr>
<td>$C_0=20$ ppm</td>
<td>0.0112</td>
<td>0.93</td>
<td>7.67</td>
</tr>
<tr>
<td>$C_0=15$ ppm</td>
<td>0.0111</td>
<td>0.95</td>
<td>6.1</td>
</tr>
</tbody>
</table>

$[k_1]=\min^{-1}$, $[k_2]=\min^{-1}$ and $[k_i]=\text{mg g}^{-1}\min^{-1/2}$

**Figure 5.** The fit of experimental adsorption data to Langmuir and Freundlich models for imadacloprid.
to follow the first order or second order kinetics over a period of 90 min. On the basis of $P$, at the higher concentration of imidacloprid ($C_0 \geq 25$ ppm) and the lower amount of GAC ($GAC \leq 2$ g) the second order model was the most suitable. Also the adsorption data at $25^\circC$ were found to fit almost equally well to Langmuir and Freundlich models, but according to complementary criteria, the Freundlich is preferred.

Acknowledgements
The authors would like to express their gratitude to the University of Tabriz, Iran for their financial support and assistance.

References