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# Study of imidaclopride removal from aqueous solution by adsorption onto granular activated carbon using an on-line spectrophotometric analysis system

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**Abstract**

The removal of imidaclopride as a pesticide by granular activated carbon (GAC) and its adsorption kinetics were studied at different pH values and temperatures. In all experiments, the amount of GAC and initial concentration of imidaclopride were 2 g and 25 ppm, respectively. The adsorption process was followed by an on-line spectrophotometric analysis system, which consisted of UV-spectrophotometer, a designed absorption cell, peristaltic pump and special glassy reactor. The effect of pH and temperature on adsorption was studied over 90 min adsorption periods. The obtained data were treated according to various kinetic models. The results showed that second order model was the most suitable one on the overall. The our results also showed that the adsorption rate constants for first order, second order and intraparticle diffusion models followed decreasing order: pH = 7 > 4 > 10 > 1, $T$ = 25 > 35 > 45 > 55 °C.


*Keywords:* Adsorption; Imidaclopride; On-line spectrophotometric analysis system; Removal; Water treatment

## 1. Introduction

The contamination of surface and ground water by pesticides is an important problem that the scientists are dealing with over the years. Pesticides are group of inorganic and organic compounds that may pollute water due to their extensive application in agriculture as rodenticides, insecticides, larvacides, miticides, mollucides, synergists, fumigants, fungicides, plant growth regulators and sterilants. Although much benefit is obtained from their uses, they have some undesirable side effects such as toxicity, carcinogenity and mutagenity [1,2]. Imidaclopride as an insecticide uses to control of sucking insects, including rice, leaf and plant hoppers, aphids and whitefly. It also effective against soil insects, termites and some species of biting insects, such as rice water weevil and Colorado beetle. It uses as a seed dressing, as soil treatment and as foliar treatment in different crops, e.g. rice, cotton, cereals, maize, sugar beet, potatoes, vegetables, citrus fruit, pome fruit and stone fruit. Imidaclopride has some undesirable side effects such as toxicity ($LD_{50}$ for rats is 450 mg/kg) [3]. Many of studies toward the solution of mentioned problem involve determination of adsorption behavior of pesticides on various adsorbents such as kerolite, Al-pillared clay, Fe–Al pillared clays, bentonite, soil, zeolite and cross-linked chitoson fibers [4–12]. 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. The number of studies on adsorption of pesticides on carbon materials from aqueous solution has increased in recent years. Pelaekani and Snoeyink [13] reported the adsorption of atrazine on activated carbon fibers, Yang et al. [14] studied the phenoxy-acid herbicide adsorption on granular activated carbon (GAC), Ayranci and Hoda [15] studied adsorption of some pesticides such as metribzin and atrazin on activated carbon-cloth. Martin-Gullon and Font [16] compared the activated carbon fiber and granular activated carbon for their effectiveness in removal of pesticides from aqueous solution by adsorption. More attractive carbon materials are now available with large specific areas on the order of 2000–2500 $m^2\,g^{-1}$ [15]. In industry water and waste water treatment processes GAC is preferred to powder activated

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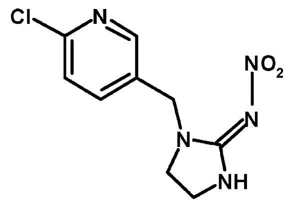
Table 1
Properties of imidaclopride

| Pesticide | Imidaclopride |
|---|---|
| Structure |  |
| WHO class | (II) |
| Molecular weight (g/mol) | 255.7 |
| Solubility (mg/l) in water | 610 |
| $\lambda_{max}$ (nm) | 270 |

carbon (PAC) because of its recoverability, therefore we studied on adsorption behavior of imidaclopride as a pesticide on industrial granular activated carbon, which is founded in plenty in market.

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 the concentration of adsorbate should be followed by a suitable, practical, fast responding and preferably non-destructive in situ method. In situ measurements also allow the study of kinetics of the adsorption process [15].

The purpose of the present work is to study the adsorption behavior of imidaclopride (Table 1) on industrial GAC under different conditions by an on-line spectrophotometric analysis system, which consisted of UV-spectrophotometer, a designed absorption cell, peristaltic pump and special glassy reactor. This method was selected to follow the adsorption since the imidaclopride is capable of absorbing UV light. Other main reason for selection of the imidaclopride is its high solubility in water, which can cause toxicity problems in the environment.

## 2. Experimental

### 2.1. Materials and methods

The industrial granular activated carbon used in the present work was obtained from typical market and its properties such as the point of zero charge (PZC) [17] and iodine number are determined in our laboratory [18] 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 imidaclopride (purity = 95%) was obtained from Chem-service (USA). Deionized water was used in adsorption experiments.

### 2.2. On-line spectrophotometric analysis system

On-line spectrophotometric analysis system, which consisted of UV-spectrophotometer, a designed absorption cell, peristaltic pump, water reservoir with temperature controller and special glassy reactor, was shown in Fig. 1. A Perkin-Elmer UV–Vis spectrophotometer (Perkin-Elmer 550 SE, Germany) was used for optical absorbance measurements.

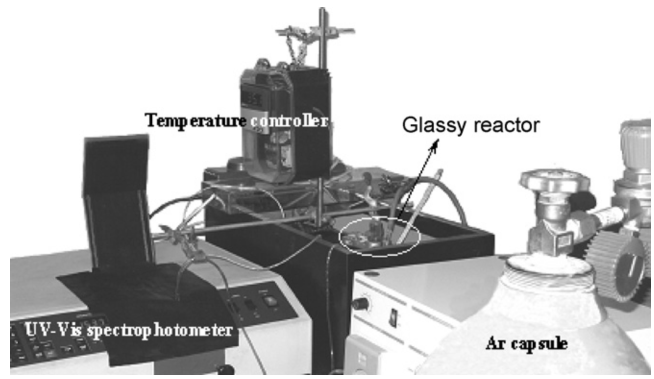



Fig. 1. On-line spectrophotometric analysis system.

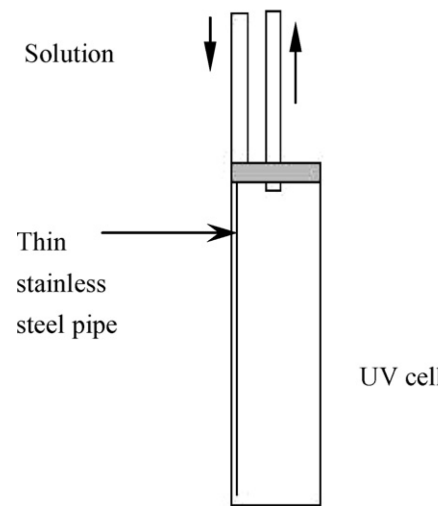



Fig. 2. Schematic of absorption cell.

#### 2.2.1. Absorption cell

A special cell was designed to carry out the adsorption measurements, which is shown in Fig. 2.

#### 2.2.2. Glassy reactor

The glassy reactor (Fig. 3) contains a tube as inlet of Argon gas, which mixes the contents of reactor and eliminates dissolved $CO_2$ and air [19]. 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, too.

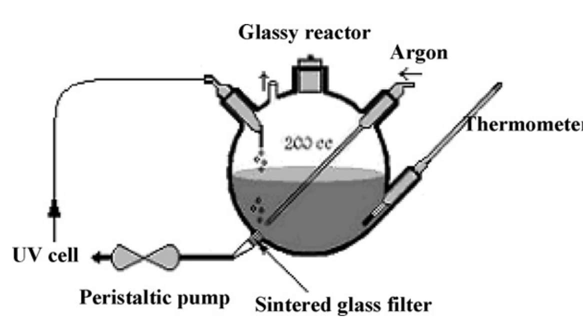



Fig. 3. Schematic of the special glassy reactor.

### 2.3. Optical absorbance measurements

In order to make a comparative study for the adsorption of imidaclopride at different pH values (1, 4, 7 and 10) and different temperatures (25, 35, 45 and 55 °C), the initial concentration of imidaclopride ($C_0 = 25$ ppm) and the weight of GAC ($m = 2.000$ g) were kept the same in all adsorption experiments. 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). In some experiments, the weight of GAC was kept as constant as possible (about $2 \pm 0.001$ g).

At first the reactor was loaded by pesticide solution. In order to avoid possible adsorption of $CO_2$ that might have been dissolved in water [15], the solution was degassed by Argon flow to remove all $CO_2$ in the solution. Then GAC added to the solution and solution was pumped to the absorbance measuring cell and its absorbance was recorded and then, it was flowed back to the reactor.

Whole optical absorption spectrum of imidaclopride was recorded and it was seen that $\lambda_{max}$ of imidaclopride is nearly 270 nm (Fig. 4). Absorbance data in $\lambda_{max}$ 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 $\sigma^2 = 0.002$).

## 3. Results and discussion

### 3.1. Optical absorption characteristics and calibration data for imidaclopride

It could be seen in Fig. 4 that maximum absorbance wavelength ($\lambda_{max}$) of imidaclopride at different pH values is nearly 270 nm. Absorbance versus concentration data for imidaclopride was treated by linear regression analysis with $R^2 = 0.999$.

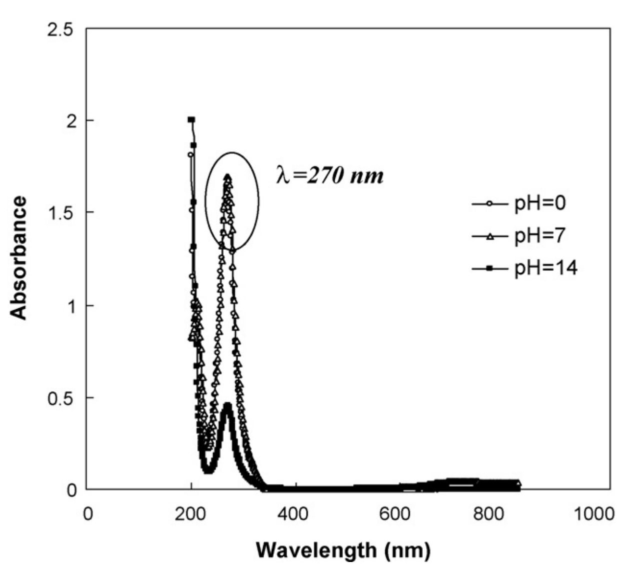



Fig. 4. Maximum absorbance wavelength of imidaclopride in different pH values.

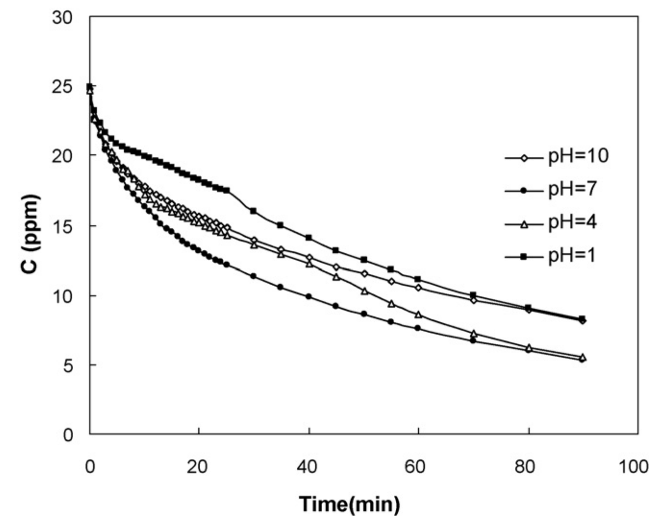



Fig. 5. Effect of pH in removal of imidaclopride.

### 3.2. Adsorption behavior of imidaclopride

#### 3.2.1. Adsorption behavior of imidaclopride at different pH values

In order to make a comparative study for the adsorption of imidaclopride at different pH values, the initial concentration of imidaclopride ($C_0 = 25$ ppm) and the weight of GAC ($m = 2.000$ g) were kept the same in all adsorption experiments. The changes in imidaclopride removal with time during the adsorption on the GAC for each pH value are shown in Fig. 5. The adsorption seems to start with the same rate in different pH values. However, a clear distinction can be seen at later stage as pH $7 > 4 > 10 > 1$. The differences in the extent of adsorption of imidaclopride at difference pH at 90 min were small but significant. The reason of these observations may be attributed to the varying of surface charge of GAC with pH. When $pH_{pzc}$ (3) > pH of solution, GAC surface possesses a positive charge and vice versa [20]. Since imidaclopride in acidic and basic pH hydrolyses [3], we cannot predict the individual behavior of imidaclopride in these conditions, but it is clear that with decreasing of negative charge of GAC surface, the adsorption of imidaclopride onto GAC reduces.

#### 3.2.2. Adsorption behavior of imidaclopride at different temperatures

In order to make a comparative study for adsorption of imidaclopride in different temperatures, the initial concentration of imidaclopride and the weight of GAC used were kept almost the same, too. The changes in imidaclopride concentration with time during the adsorption process at each temperature are shown in Fig. 6 in order: $T = 25 > 35 > 45 > 55$ °C. The differences in the removal efficiency of pesticide were small. These small differences should originate from the effect of energy of reaction. Namasivayam and Kavitha studied removal of Congo Red from water by adsorption onto activated carbon. They evaluated the

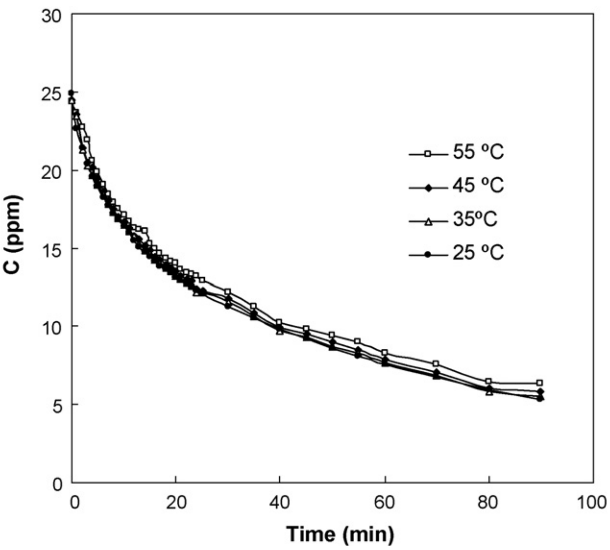



Fig. 6. Effect of temperature in removal of imidaclopride.

first order rate constants of adsorption for different temperatures [21]. A similar trend has been observed for the adsorption of pesticides on porous polymeric adsorbents. The temperature dependence of adsorption was investigated for the tested herbicides on the porous polymeric adsorbents at pH 3–6.5. The effect of temperature on the adsorption isotherms, in most cases, is that by increasing temperature, adsorption decreases. Particularly, this temperature effect is observed in the adsorption of trifluralin and prometryn [22].

### 3.3. Kinetics of adsorption

Adsorption of the pesticide in different pH values ($T = 25\,°C$) and temperatures (pH 7) on GAC was monitored spectrophotometrically by the procedure described above. Absorbance data of imidaclopride were obtained in one-minute intervals from 0 to 25 min, 5-min intervals from 25 to 60 min and 10-min intervals from 60 to 90 min during the adsorption process and were converted into concentration data using the corresponding calibration plots. Then, the concentrations were plotted as a function of time. They are shown in Figs. 5 and 6. Initial concentration in all experiments was adjusted to be the same (25 ppm) in order to compare their adsorption behaviors easily. Some probable kinetic models were applied to fit them to experimental data. These models include intraparticle diffusion [19], which can be formulated as

$$q_t = k_i t^{1/2} \tag{1}$$

first order which can be formulated as

$$\ln C - \ln C_0 = k_1 t \tag{2}$$

and second order model which can be formulated as

$$\left(\frac{1}{C} - \frac{1}{C_0}\right) = -k_2 t \tag{3}$$

where $q_t$ is the amount of adsorbate adsorbed at any time, $C_0$ the initial concentration of adsorbate, $C$ the concentration of adsorbate at any time, $t$ the time and $k_i$, $k_1$ and $k_2$ are the rate constants for diffusion, first order and second order models, respectively. $q_t$ is obtained from $C_0$ and $C$ values by the following equation:

$$q_t = \frac{(C_0 - C)V}{m} \tag{4}$$

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 $q_t$ versus $t^{1/2}$ for intraparticle diffusion, ln $C$ versus $t$ for first order and $1/C$ versus $t$ for second order models. The rate constant of $k_i$, $k_1$ and $k_2$ obtained from the slopes of corresponding linear plots are given in Tables 2 and 3 at different pH values and temperatures with correlation coefficients, $r$. When the correlation coefficients of the three models are compared for each pH and temperature, it can be seen that all of them are greater than 0.97. So, it is very difficult to prefer a certain kinetic model to fit the adsorption data. A better criteria is to introduce a parameter known as normalized percent deviation [23], the lowest average absolute percent deviation (%$D$) [24] or in some literature percent relative deviation modulus, $P$ [25,26], given by the following equation:

$$P = \frac{100}{N} \sum \frac{|C_{t,\mathrm{expt}} - C_{t,\mathrm{pred}}|}{C_{t,\mathrm{expt}}} \tag{5}$$

where $C_{t,\mathrm{expt}}$ is the experimental concentration at any time, $C_{t,\mathrm{pred}}$ the corresponding predicted concentration according to the equation under study with best fitted parameters, and $N$ is the number of observations. It is clear that the lower the $P$ value, the better is the fit [19]. The $P$ values calculated for the fit of kinetics data of imidaclopride to three kinetics models are given in Tables 2 and 3. The fit accepted to be good when $P$ is below 5.

Table 2
Rate constants and correlation coefficients from treatment of adsorption data according to the three kinetic models for different pH values

| pH values | Kinetic model | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | First order | | | Second order | | | Intraparticle diffusion | | |
| | $k_1$ | $r$ | $P$ | $k_2$ | $P$ | $r$ | $k_i$ | $r$ | $P$ |
| 10 | 0.011 | 0.9768 | 30.57 | 210.59 | 1.92 | 0.9965 | 0.0843 | 0.9943 | 4.34 |
| 7 | 0.0159 | 0.9763 | 6.19 | 386.62 | 2.28 | 0.9973 | 0.1035 | 0.9860 | 7.91 |
| 4 | 0.0149 | 0.9907 | 38.07 | 343.63 | 5.86 | 0.9794 | 0.0987 | 0.9966 | 4.22 |
| 1 | 0.0116 | 0.9961 | 29.13 | 212.61 | 3.57 | 0.9919 | 0.0888 | 0.9907 | 8.76 |

$[k_1] = \mathrm{min}^{-1}$; $[k_2] = \mathrm{min\,M}^{-1}$; $[k_i] = \mathrm{mg\,g}^{-1}\,\mathrm{min}^{-1/2}$.

Table 3
Rate constants, correlation coefficients ($r$) and $P$ from treatment of adsorption data according to the three kinetic models for different temperatures

| Temperature, $T$ (°C) | Kinetic model | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | First order | | | Second order | | | Intraparticle diffusion | | |
| | $k_1$ | $r$ | $P$ | $k_2$ | $r$ | $P$ | $k_i$ | $r$ | $P$ |
| 55 | 0.0148 | 0.9727 | 6.26 | 329.32 | 0.9968 | 2.40 | 0.1035 | 0.9851 | 15.99 |
| 45 | 0.0154 | 0.9746 | 6.25 | 360.31 | 0.9971 | 2.34 | 0.1031 | 0.9855 | 13.42 |
| 35 | 0.0157 | 0.9760 | 6.14 | 377.13 | 0.9973 | 2.22 | 0.1032 | 0.9858 | 11.99 |
| 25 | 0.0159 | 0.9763 | 6.19 | 386.62 | 0.9973 | 2.28 | 0.1035 | 0.9860 | 7.91 |

$[k_1] = \text{min}^{-1}$; $[k_2] = \text{min M}^{-2}$; $[k_i] = \text{mg g}^{-1}\text{ min}^{-1/2}$.

On the whole the fit of experimental data to second order seems to be excellent for imidaclopride because $P$ value is below 5. In general one can say that second order is fitted to experimental data better than first and intraparticle diffusion models.

## 4. Conclusion

The adsorption of imidaclopride onto GAC could be followed by an on-line spectrophotometric analysis system. It was found that imidaclopride could be removed significantly from aqueous solution by adsorption onto the GAC in experimental conditions. The results showed that second order model was the most suitable one on the overall. The our results also showed that the adsorption rate constants for first order, second order and intraparticle diffusion models followed decreasing order: pH = 7 > 4 > 10 > 1, $T$ = 25 > 35 > 45 > 55 °C.

## Acknowledgement

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