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Modeling of the adsorption of metribuzin pesticide onto electro-activated granular carbon

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ABSTRACT

The main purpose of the present study is to investigate the mechanism which governs the adsorption of the pesticide onto electro-granular activated carbon (GAC). The operating conditions assessed are: electrical potential, electro-activation time, the initial metribuzin—electro-activated GAC concentration ratio ($R = C_p/C_{\text{GAC}}$). In the first step, it has been confirmed using an experimental design that the C/C_0 ratio is much more affected by the electrochemical potential application than by R ratio. The mathematical model indicates that the electrochemical potential has a significant effect during the metribuzin adsorption during the first half an hour on GAC and thereby demonstrates the electroactivation beneficial effect. In the second step, a mass transfer model has been applied in order to evaluate the effect of the electro-activation of GAC on the kinetic constant. Indeed, the results showed that the electro-activation accelerates the process with kinetic constants 2–3 times higher than those obtained without the electro-activation of GAC.

Keywords: Granular activated carbon; Electro-activation; Pesticide; Metribuzin; Adsorption; Water treatment

1. Introduction

An increasing concern about the pollution of superficial waters by pesticides has been observed during the last decade, which has led to renewed interest from industrial operators in existing processes in order to be able to promote their affordable use in the face of increasingly severe environmental standards [1–6]. These processes are based on conventional techniques of oxidation, photolysis, chemical hydrolysis, adsorption, and microbial degradation [7–12]. Recently, a technique was developed for the activation of granular activated carbon (GAC) based on the electrochemical method [13]. It was applied to a column of GAC, in which the adsorption of the pesticide metribuzin was investigated under process-affecting variables, namely, the electrochemical potential, the initial metribuzin to GAC concentration ratio, and the ionic strength of the adsorbed solution, which was varied by adding solutions of NaCl, KCl, and Na_2SO_4. The results obtained for a solution with an initial metribuzin to GAC concentration ratio of

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30 mg g^{-1}, an electrical potential of −200 mV/CSE, and an NaCl solution of 2 g dm^{-3} showed a significant increase in the adsorption capacity of metribuzin of 38% (27 mg g^{-1}) compared with that obtained without the electro-activation of GAC.

The main purpose of the present study is to assess the improvement of the performance of the electro-activated GAC as adsorbent of pesticide. To achieve this target, two approaches were applied to determine the process capacity and the mechanism which governs the adsorption of the pesticide onto electro-activated GAC. The first approach consists of the utilization of an experimental design to optimize the experiments organization in order to minimize their number and increase their reliability.

In the second approach, two adsorption kinetic models were used in order to determine the mechanism which governs the adsorption of the pesticide onto electro-activated GAC. The first one, a simple external resistance model is based on film resistance. The second model is based on the diffusion phenomena [14].

The experimental design is an efficient statistical technique for the optimization of multiple variables in order to predict the best performance conditions with a minimum number of experiments. These designs are used to find improved or optimal process settings, troubleshoot process problems and weak points and make a product or process more robust against external and noncontrollable influences [14–16].

Using response surface methodology (RSM) for conventional method is advantageous, because there is a variation of only one parameter at a time, keeping the other parameters constant and thus, the cumulative effect of all the affecting parameters at a time cannot be studied [17]. However, in RSM, the interactions of two or more variables can be studied simultaneously. Ibrahim and Elkhidir [18] have discussed in detail the efficiency of RSM over other statistical optimization techniques. RSM approach has been used by many researchers to optimize the effects of process parameters for enhanced production and yields of many target products used for commercial and industrial application [19–22].

The main aim of the experimental design in this work is the achievement of key experiments whose results help developing a mathematical model describing faithfully the studied process. The design conception is based on a rigorous pre-selection of parameters and their variation ranges in order to systematically study the individual effects and the interactions of these parameters on the response function considered. The previous results suggest that the C_p/C_{p0} ratio is much more affected by the electrochemical potential application than by the ratio $R = C_{p0}/C_{\mathrm{CAG}}$. To test this hypothesis and taking account of the 2^k full factorial matrices properties, the construction of such an experience matrix satisfies our objective. Matrix 2^2 where the response is the C_p/C_{p0} ratio evolution vs. time for metribuzin adsorption onto electro-activated GAC was established. The advantage of this approach is, on one hand, that once the kinetic curves are plotted, 2^3 matrices can be built for any adsorption time within the considered time domain, and by simple results operation without resorting to the experience. On the other hand, it achieves the effect kinetics, while a conventional matrix 2^3 gives an effect value [23].

The parameters and intervals considered for modeling the adsorption onto GAC, by reduced variables X_1 and X_2 lower and higher levels of the electrochemical potential and the R ratio, respectively, are summarized in Table 1.

In this modeling attempt, and to simplify the procedure, the electrochemical potential as a higher value was set at −200 mV/ECS. The parameters variations areas used were set to increase the probability of including the optimal values to obtain the highest capacity adsorption.

The obtained mathematical model is a polynomial function that connects the response function (response variable) to the chosen parameters, in the case of two variables or parameters. It takes the following form:

$$Y = a_0 + a_1X_1 + a_2X_2 + a_{12}X_1X_2 \tag{1}$$

Several mathematical models describing the adsorption process are reported in the literature. Some authors used a simple first- or second-order kinetic model to simulate adsorption of heavy metals on porous solids, supposing that the process kinetic is controlled only by the adsorption step [24,25]. Various diffusion models have been used to simulate adsorption on porous solids, considering that the process limiting step is diffusion [26–32]. In a study on the bioaccumulation of chromium,an empirical equation with two time constants was proposed. The two time constants correspond to two kinetic steps; first, a rapid step followed by a slower second step [33].

According to the mechanism reported in the literature [26–28], a model was developed considering the various steps and their contributions to the global kinetic of the process.

Sorption kinetic is mainly controlled by various steps including diffusion process. Three steps can be enumerated as follows:

- Step 1: Metal ion transfer from the boundary film bordering the particle surface which constitutes the film mass transfer resistance. A good

Table 1
Parameters and levels

Parameters	Electrochemical potential E (mV/SCE)	$R = \frac{C_{\text{pesticide}}}{C_{GAC}}$	
		Domain 1	Domain 2
Variables	X_1	X_2	X_2
Low level (−1)	−200	16.6	25
High level (+1)	0	33	50

agitation or turbulent flow may reduce considerably the film thickness and its resistance become negligible.

- Step 2: Metal ion transfer from the surface to the intra-particle active sites. This step is controlled by diffusion;
- Step 3: Uptake of metal ion on the active sites via complexation, sorption, and intra-particle precipitation phenomena, which is generally a rapid no-limiting step.

The transfer of a solute from a solution to a porous solid is in accordance with the mechanism described above, and it is the slowest step that controls the process rate. Kinetic models, based on the sorption capacity, assume that the adsorption sites are easily accessible and do not involve the diffusional properties. However, diffusion models consider that interparticle diffusion is the mass transfer-limiting step.

In the case of particles with a spherical geometry, the diffusion equation for a constant diffusivity takes the form:

$$\frac{\partial C_S}{\partial t} = D\left(\frac{\partial^2 C_S}{\partial r^2} + \frac{2}{r}\frac{\partial C_S}{\partial r}\right) \tag{2}$$

For $u = r.\ C_S$, Eq. (2) becomes:

$$\frac{\partial u}{\partial t} = D\frac{\partial^2 u}{\partial r^2} \tag{3}$$

(1) The solid particles are assimilated to spheres of characteristic radius R.
(2) The density of the solid remains constant during the entire diffusion.
(3) The temperature remains constant.
(4) The agitation makes that the mass transfer resistance in liquid phase is neglected (The liquid flow rate or agitation should be fixed so that its influence on the kinetic curves is negligible).
(5) The distribution of solute in solution is considered as uniform (due to agitation in turbulent flow).
(6) At the interface, the thermodynamic equilibrium is instantaneously reached.
(7) Taking into account the symmetry problem, the solute concentration depends only on the spatial variable (r) and time (t).
(8) The diffusion coefficient is assumed constant throughout the diffusion process.

Eq. (2) can be solved by integration with the appropriate initial and boundary conditions [34,35]. For simple geometrical cases such as slab, cylinder, or sphere, the solution is as follows:

$$\frac{q_t}{q_e} = A(1 - e^{-kt}) \tag{4}$$

where k is a kinetic constant including the effective diffusion coefficient (mn^{-1}).

Eq. (4) obtained is identical to equations developed in other studies considering that the adsorption capacity obeys to a first-order velocity law. In this case, the constant k in Eq. (4) is replaced by k_1, the latter represents the first-order adsorption velocity constant (min^{-1}) [24,25]. So, in this form, Eq. (4) can describe both diffusional and sorptionnel phenomena.

2. Experimental

2.1. Material

The GAC, NFEN12915 (OTV©, France), with a surface area of 1,183 $\text{m}^2\ \text{g}^{-1}$, was prepared for each experiment by soaking it overnight in distilled water. The main characteristics of the CAG are presented in Table 2. The metribuzin solution was prepared synthetically by mixing the required amount of metribuzin (Bayer©, Germany) in a solution of distilled water. The metribuzin concentration of the solutions studied was in the range of 50–300 mg L^{-1}. The values used in our study were similar to those measured in

Table 2
Chemical physical characteristics of the granular electro-activated carbon

Parameter	Average value
Total ash (%)	3.59
Moisture (%)	9.6
Porosity	0.4
Density (g cm^{-3})	1.54
Iodine ASTM (mg g^{-1})	952.5
pH at 20°C	5.7
Specific surface area—BET (m^2 g^{-1})	1,045

discharges from metribuzin manufacturers. The metribuzin concentration in the contaminated water solution was determined with a spectrophotometer (SHIMADZU, 1240CE) at a wave length of $\lambda = 293$ nm. The peroxide solution used was 50% in mass. The advantage of working with this high concentration is that it adds very little volume (in the order of a microliter) to the reactor containing the metribuzin solution. The peroxide concentration employed varied between 5×10^{-4} and 0.1 M. The effect of supporting electrolyte (*S*) on metribuzin removal was studied using NaCl with a concentration in the range of 0.01–1 g L^{-1}.

2.2. Methods

2.2.1. Electro-activation operation

The electro-activation experiments were conducted using an electrochemical cell (Fig. 1). This apparatus was equipped with two stainless steel electrodes that formed the working and auxiliary electrodes, which were introduced into a Polyvinyl chloride column (internal diameter: 0.02 m and length: 0.2 m) to produce an electrical field in the GAC bed. The column was initially filled with wet GAC, and then deionized water was added until a homogeneous contact with the salt bridge was assured. The electrochemical potential was then maintained at a constant level for the selected activation time by means of a Tacussel PRT20-2X potentiostat. The applied electrochemical potential was measured by means of saturated calomel electrodes, PHYWE 07-13300. The metribuzin adsorption capacity of the electro-activated GAC was then tested in a batch mode.

2.2.2. Determination of the adsorption capacity of the adsorbent

The kinetic curves were obtained by following the evolution of residual pesticide concentration (C_p) at regular time intervals. The adsorption capacity (X) was calculated by Eq. (5), expressed as follows:

$$X = \frac{Cp_0 - C_e}{C_{\mathrm{GAC}}} \tag{5}$$

The metribuzin concentration was determined by UV-spectroscopy using a UV–vis mini 1240CE apparatus (SCHIMADZU, Japan) at a wavelength of 293 nm.

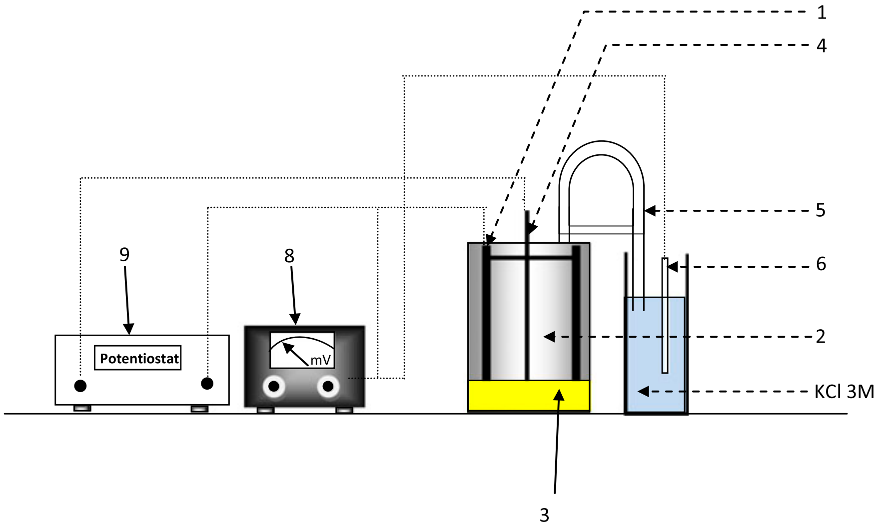

Fig. 1. Electro-activation apparatus.
Notes: 1—Auxiliary electrode, 2—Granular activated carbon, 3—Wool barrier, 4—Working electrode, 5—Salt bridge, 6—Reference electrode, 7—Saturated KCl solution (3 M), 8—Millivoltmeter, and 9—Potentiostat.

Table 3
Coefficients values for domain 1

t	a_0	a_1	a_2	a_{12}
5	0.43	0.14	−0.005	−0.015
10	0.3375	0.1175	0.0025	−0.0075
15	0.27	0.085	−0.015	−0.02
20	0.2425	0.0825	0.0075	0.0075
25	0.2025	0.0575	−0.0025	0.0025
30	0.1925	0.0775	0.0075	0.0025
35	0.165	0.055	0.015	0.015
40	0.155	0.065	0.02	0.01
45	0.1475	0.0425	0.0025	0.0075
50	0.135	0.045	0.005	0.015
55	0.1225	0.0475	0.0075	0.0125
60	0.1225	0.0425	0.0025	0.0125

Table 4
The coefficients values for domain 2

t	a_0	a_1	a_2	a_{12}
5	0.5325	0.0825	0.0225	0.0325
10	0.445	0.075	0.03	1.388E-17
15	0.4025	0.0525	0.0325	0.0125
20	0.365	0.055	0.05	0
30	0.2925	0.0325	0.0225	0.0025
35	0.255	0.03	0.04	0.005
40	0.2375	0.0275	0.0375	−0.0025
45	0.2175	0.0275	0.0325	−0.0075
50	0.2	0.015	0.04	−0.005
60	0.1675	0.0225	0.0275	−0.0075

3. Results and discussion

A full 2^2 factorial design of experiments was used to obtain the best conditions for metribuzin adsorption onto electro-activated GAC from water solution. The two factors considered were electrochemical potential, and the R ratio ($C_{\text{pesticide}}/C_{\text{CAG}}$). Two levels for each factor were used; electrochemical potential (−200 and 0 mV/SCE), and electro-activated GAC concentration ratio (16.6 mg g^{-1}). The factorial experimental design, which involves changing all the variables from one experiment to the next, was chosen in order to estimate the influence of the different variables. Factorial designs are widely used to investigate the effects of

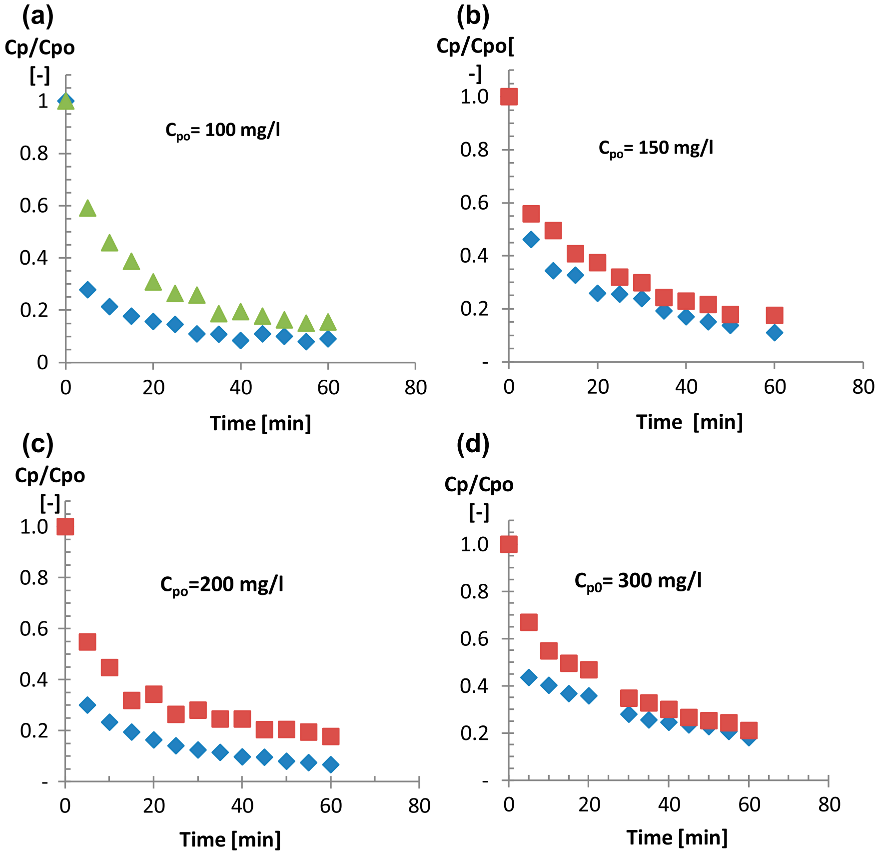

Fig. 2. Effect of GAC electroactivation on adsorption kinetics at various metribuzin concentrations, $E = -200$ mV/SCE, TA = 60 min, $C_A = 6{,}000$ g m^{-3}, ■ without electro-activation, ♦ with electro-activation (a) $R = 16{,}6$ mg g^{-1} (b) $R = 25$ mg g^{-1} (c) $R = 33$ mg g^{-1} and (d) $R = 50$ mg g^{-1}.

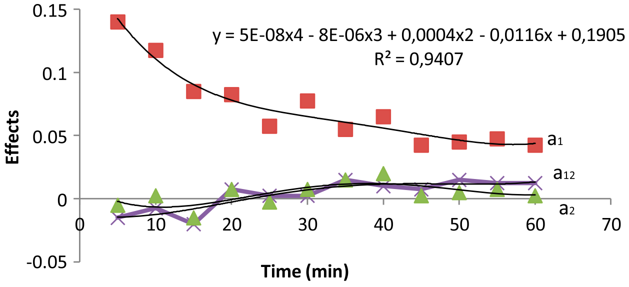

Fig. 3. The mathematical model kinetic coefficients in the domain 1 case.

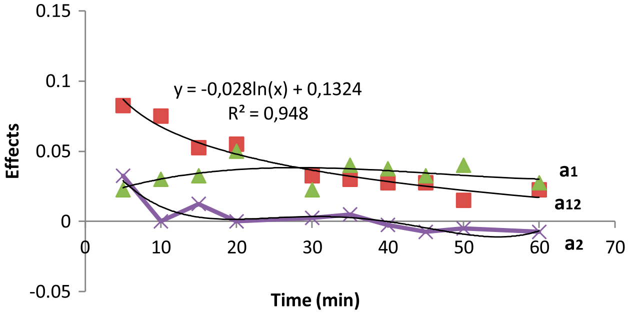

Fig. 4. The mathematical model kinetic coefficients in the domain 2 case.

experimental factors and the interactions between those factors, that is, how the effect of one factor varies with the level of the other factors in a response. The advantages of factorial experiments include relatively low cost, a reduced number of experiments, and increased possibilities to evaluate interactions among the variables.

The use of a 2^2 full factorial design and the determination of the a_o, a_1, a_2, and a_{12} for each domain are summarized in Tables 3 and 4. The obtained results allowed determining the individuals and combined effects evolution according to time, which are presented in Figs. 2–4. A significant effect was observed for the X_1 parameter (the electrochemical potential) and it is increased during the first half an hour adsorption more in the first domain than in the second. For the X_2 parameter (the R ratio) the effect is negligible compared with the electrochemical potential as shown in Figs. 3 and 4.

The a_{12} coefficient describing the combined effect of both studied parameters X_1 and X_2 is practically equal to zero during the adsorption kinetics in both domains 1 and 2.

As expected, the results showed that the best metribuzin adsorption capacity onto CAG is obtained during the first 30 min with an electrochemical potential of −200 mV/SCE and a ratio $R = 16.6$ mg g^{-1}.

In order to assess the electro-activation contribution on the metribuzin retention kinetics in general and in particular on the diffusional and kinetic parameters, the developed model was applied to the different obtained kinetics in this study. The simulation kinetic curves obtained for different experimental conditions are shown in Figs. 5–8. These curves showed that the experimental results and those simulated by the adopted model match. The model parameter values achieved by Eq. (4) and the correlation coefficients linearization for different experimental conditions are summarized in Table 5.

Table 5 shows a comparison between the model parameters obtained in the kinetic studies carried out with and without electro-activation of carbon granules and, for different ratios R.

These results showed that the pre-exponential factor A is practically not affected by the electro-activation, because this parameter values obtained in both cases (with and without electro-activation) are very similar.

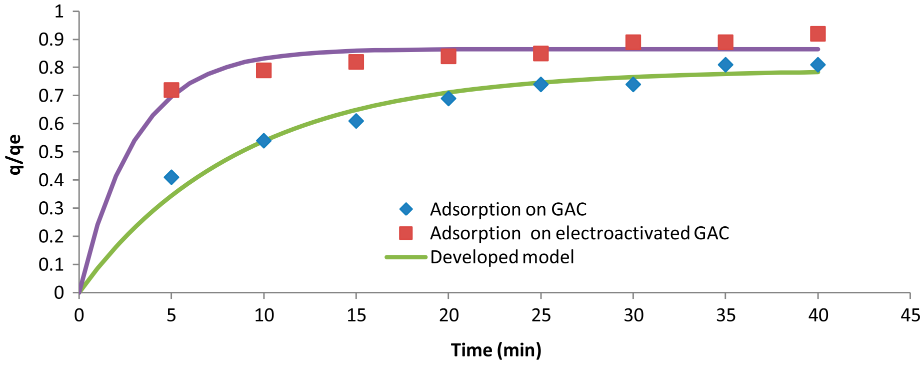

Fig. 5. Simulation of metribuzin adsorption kinetic by the developed model. $R = 16.6$ mg g^{-1} GAC, TA = 60 min, and $E = -200$ mV/SCE.

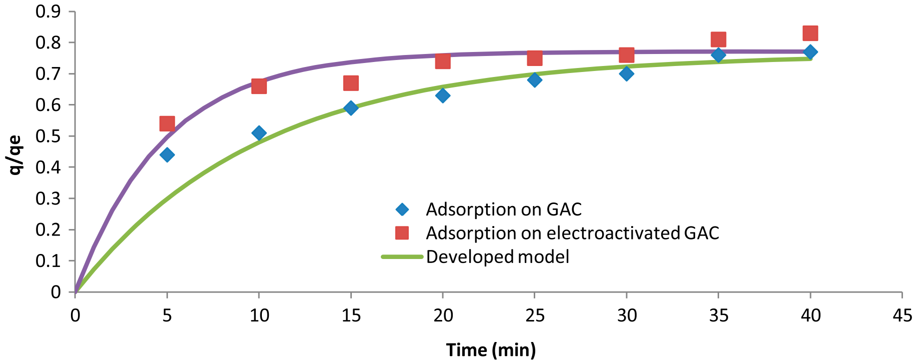

Fig. 6. Simulation of metribuzin adsorption kinetic by the developed model. $R = 25$ mg g^{-1} GAC, TA = 60 min, and $E = -200$ mV/SCE.

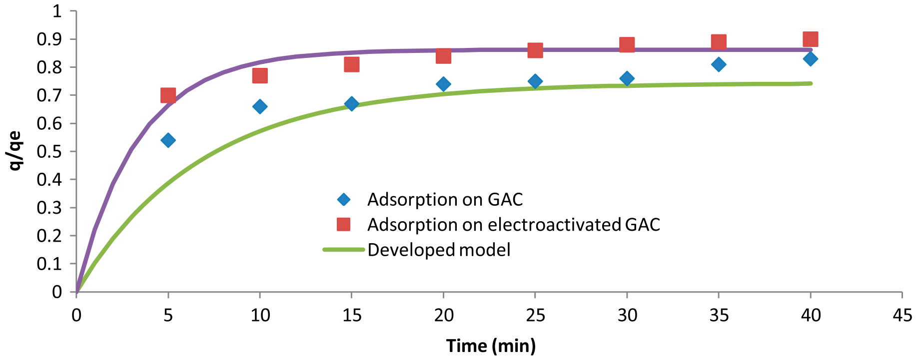

Fig. 7. Simulation of metribuzin adsorption kinetic by the developed model. $R = 33$ mg g^{-1} GAC, TA = 60 min, and $E = -200$ mV/SCE.

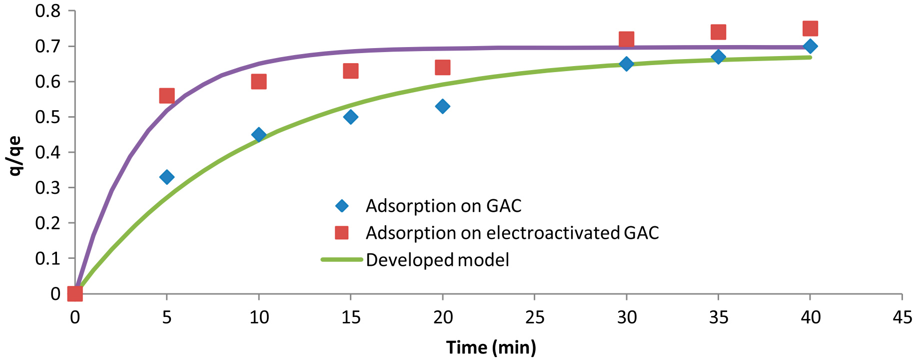

Fig. 8. Simulation of metribuzin adsorption kinetic by the developed model. $R = 50$ mg g^{-1} GAC, TA = 60 min, and $E = -200$ mV/SCE.

However, the comparison of the kinetic constants values shows that the electro-activation can either double or triple the constant k with an average of 2.4.

As in the case where the process is controlled by diffusion and for certain experimental conditions the kinetic constant is proportional to the apparent diffusion coefficient, the diffusivity in the electro-activated carbon granules is at less twice higher than those obtained in nonelectro-activated carbon granules. This result showed that the carbon granules electroactivation has accelerated the pesticide retention process. The process acceleration and the kinetic

Table 5
Model parameters

Potential (mV/SCE)	−200				0			
R (mg g^{-1})	16.6	25	33	50	16.6	25	33	50
A	0.865	0.771	0.862	0.696	0.792	0.761	0.743	0.680
k (min^{-1})	0.326	0.207	0.295	0.271	0.114	0.010	0.147	0.102
R^2	0.982	0.969	0.984	0.954	0.982	0.981	0.983	0.970

constant value increase clearly reinforce the experiments factorial planning results and explain the cause of the favorable effect of activated carbon granules electro-activation on the metribuzin retention.

4. Conclusion

In the light of the results and discussion, It was confirmed by the utilization of an experimental design that the C/C_0 ratio is much more affected by the electrochemical potential application than by the ratio $R = C_{\text{pesticide}}/C_{\text{CAG}}$. It was also proved that the electrochemical potential has a significant effect during the metribuzin adsorption in the first half an hour on CAG and thereby demonstrated the electroactivation beneficial effect.

The first-order model gave a good agreement between experimental data and model results with a correlation factor higher than 0.95. This modeling showed that electro-activation led to a significant increase in the kinetic constants and accelerates the adsorption process. This result is in agreement with those obtained during the experiments factorial planning and can provide some answers to the reasons of the favorable effect of activated carbon granules electroactivation on the metribuzin retention.

Nomenclature and units

C_{p0}	initial concentration of metribuzin, gm^{-3}
C_{GAC}	GAC concentration, gm^{-3}
C_e	metribuzin residual concentration at equilibrium, gm^{-3}
C_p	residual concentration of metribuzin, gm^{-3}
E	electrochemical potential, volt
R	C_{p0}/C_{CAG}
q	amount of solute adsorbed at time t, mg g^{-1}
q_e	amount of solute adsorbed at equilibrium, mg g^{-1}
R^2	correlation coefficient

Abbreviations

GAC	granular activated carbon
GC	granular carbon
SCE	saturated calomel electrode
X	adsorption capacity of the adsorbent, g pesticide/g GAC

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