Simulated kinetic modeling of the aldicarb pollutant with catalytic degradation removal from water and soil resources

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Abstract

Aldicarb is a relatively stable environmental pollutant that finds its way into natural resources via agricultural pesticides. In this study, modeling and simulation of the aldicarb diffusion and decomposition process were carried out in water and soil resources. Different kinetic models, such as the first-order, second-order, and the Power-law model with two orders of 0.5 and 1.5 were initially considered to predict aldicarb degradation in sterile and non-sterile soils. The aforementioned models were defined and executed in the reaction engineering module of the COMSOL MULTIPHYSICS software (version 4.2). The experimental data available in the literature were utilized to evaluate and validate the presented models. The predictions of second-order and Power-law (with order of 0.5) decomposition models had a further accordance regarding experimental data in sterile and non-sterile soils, respectively. In the following, simulations were run at various initial concentrations of contaminant using the best kinetic models to specify the effect of pollutant concentration on the removal process. Then, the diffusion trend and degradation of aldicarb were investigated in groundwater aquifers. For this purpose, a combination of the reaction engineering model (based on the 0.5-order power-law model) and components mass transfer model in dilute environments was utilized in the structure of COMSOL MULTIPHYSICS. According to the results, it was found that only the top 25% of the aquifer layers are contaminated with aldicarb.

Keywords: Aldicarb, Aldicarb sulfoxide, Kinetic modeling, Diffusion and transfer modeling, Simulation

1. Introduction

Pesticides, fungicides, and herbicides usage in agriculture are significant contributors to contaminate soil and water resources. The majority of these chemicals contain harmful compounds that do not decompose naturally or degrade slowly [1]. Aldicarb was introduced as an oxime carbamate pesticide by Union Carbide Company (USA) in 1962. Carbamate pesticides are very significant in pest controlling, and they are being utilized more and more instead of organophosphate and organochlorine pesticides. The active component in aldicarb is Tamik which is very toxic. The possible lethal dosage for a human is less than 5 mg/l (less than 7 drops) for a person weighing 150 pounds. This pesticide is highly toxic through both oral and dermal routes. Nevertheless, the report on the chemicals evaluated for their carcinogenic potential showed that there was no evidence of carcinogenicity to humans through aldicarb. Aldicarb is combustible, and the fumes and gases produced by its combustion are poisonous and irritating. Weakness, blurred vision, headache, nausea, sweating, and tremors are all the symptoms of high aldicarb exposure [1,2]. Aldicarb comes in the form of white crystals with a sulfur-like odor, and it is sold in granular form. Aldicarb's physical and molecular characteristics are shown in Table 1. This pesticide is frequently used to protect a variety of crops world wide, such as onion, potato, walnut, cotton, tobacco, sugar beet and sugarcane. The use of aldicarb for whitefly control is widespread [2,3]. The chemical structure of aldicarb is shown in Fig.1.

Table 1. Chemical and physical properties of aldicarb

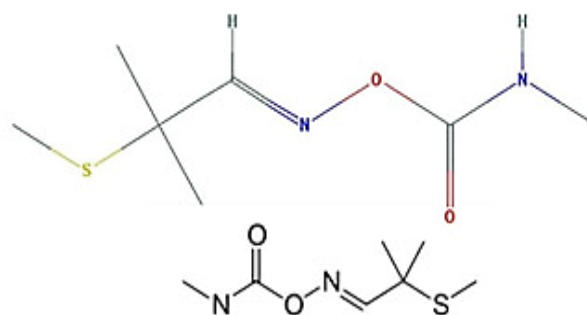| Property	Value
Molecular weight	190.26 gr/mol
Chemical formula	$C_7H_{14}N_2O_2S$
Melting point	100 ºC
Solubility in water	0.6 gr per 100 ml at 25 °C

Fig.1. Aldicarb structure.

The most important and efficient techniques of aldicarb elimination and decomposition from natural resources are oxidation to aldicarb sulfoxide (using oxidants such as

ozone, hydrogen peroxide, mono-chloramine and permanganate), bio-absorption (absorption through the planting of sorbent plants), and bio-degradation (degradation through bacterial and fungal species) [4,5]. The application of each of these methods depends on the depth of aldicarb penetration into water and soil resources. For instance, the decomposition of aldicarb occurs mostly through biology and microbial activity in surface waters and soils, whereas it proceeds more chemically (oxidatively) in groundwater aquifers and subsoil [6].Various studies have been conducted to investigate the removal of aldicarb from contaminated environments, some of the most important of which are listed below.

Sun et al. [7] conducted experiments to investigate the degradation of aldicarb in sterile, non-sterile and plant-grown soils, and the ability of different plant species to accumulate the pesticide. They reported that the half-life ($t_{1/2}$) of aldicarb in sterile soil was more than four times that of non-sterile soil. This fact indicated that microorganisms played an important part in the degradation of aldicarb in soil. According to the results of their research, aldicarb disappears faster in the soil with the presence of plants, and the half-life of the pesticide in the soils grown with corn, mung bean and cowpea are less than two days.

Lawrence et al. [8] investigated the decomposition of aldicarb, and the metabolites aldicarb sulfoxide and aldicarb sulfone in cotton farm soils previously exposed to aldicarb. They observed the loss of efficacy in two (Limestone county soli (LM) and Washington county soil (MS)) of the three (The Colbert county soil (CL)) field soils as measured by *R. reniformis* population development and a lack of cotton yield response. In their study, two soils were compared for the first test: one where aldicarb was effective (CL) and the second where aldicarb had lost its effectiveness (LM). They cited that the total degradation of aldicarb and its metabolites happened within 12 days in the LM soil, and aldicarb sulfoxide and aldicarb sulfone were both present in the CL soil at the end of the experiment at 42 days after aldicarb application. In their second test, three soils were considered: autoclaved, non-autoclaved and treated with aldicarb, or not treated with aldicarb. They reported that autoclaving the LM and MS soils increased the persistence of the aldicarb metabolites as compared to the same soils not autoclaved, and the rate of decomposition was not changed when the CL natural soil was autoclaved.

Xu et al. [9] studied the effect of surfactants on desorption of aldicarb from spiked soil. They tested anionic (sodium dodecyl benzene sulphonate, SDBS), cationic (hexadecyl trimethyl ammonium bromide, HTAB), and nonionic (octyl polyethylene glycol phenyl ether, OP) surfactants to determine optimal desorption conditions, including desorption time, mixing speed and surfactant concentrations. According to their results, the optimal operating conditions were achieved at 2 h, 150 rpm, and

surfactants concentrations were 1000, 100, and 200 mg l^{-1} for SDBS, OP, and HTAB, respectively. Also, in this study, the desorption efficiency of mixture of different kinds of surfactants was evaluated for aldicarb-spiked soil. They concluded that anionic–nonionic surfactant mixtures provided the best desorption efficiency up to 77%, while the anionic–cationic surfactant mixture had a poor desorption efficiency similar to water. This fact suggests that mixture of anionic–nonionic surfactants were highly promising on remediation of aldicarb-contaminated soil.

Osborn et al. [10] evaluated the degradation potential of the carbamoyloxime nematicides aldicarb and oxamyl and the organophosphate fosthiazate in 35 UK agricultural soils. They stated that high organic matter content and low pH have inhibitory effect on aldicarb degradation rate. The potential for increased degradation of aldireb and oxamyl was observed in 9 out of 15 and 9 out of 10 soils, respectively, that were previously treated with these active materials. Based on their results, degradation of fostiazates happened at a much slower rate, with no evidence of increased degradation. Therefore, Fosthiazate may be a useful alternative in cases where the efficacy of aldicarb and oxamyl has been reduced as a result of increased degradation.

Ding et al. [11] investigated the decomposition of aldicarb using liquid chromatography spectroscopy. They applied aldicarb to farmed cabbages and monitored its quantities on a regular basis. According to their findings, the half-life of aldicarb decomposition is 29.1 days.

As it is clear from the literature review, most of the work done in this field has been performed experimentally, which requires a lot of time and money. Therefore, it is necessary to provide theoretical studies to cover these weaknesses. For this reason, modeling of the diffusion and decomposition processes of aldicarb in polluted resources was done in this research in order to evaluate the elimination trend of this pollutant in the environment. In this regard, various degradation kinetics and diffusion models were defined and implemented in COMSOL MULTIPHYSICS software (version 4.2). Simulations were run at different times and initial concentrations of the contaminant.

2. Process modeling and simulation

Today, modeling plays a major role in accelerating and improving engineering activities such as design and construction, scale-up and process optimization [12]. In this paper, modeling and simulation of aldicarb penetration and degradation process was conducted in soil and water resources. In this regard, diffusion models and aldicarb decomposition kinetics were defined and implemented in the environment of COMSOL MULTIPHYSICS software. COMSOL MULTIPHYSICS is a computational fluid dynamics software based on chemical engineering topics such as mass transfer and chemical reactions. This software can simultaneously combine and model different physics

such as mass transfer, heat transfer, fluid mechanics, chemical reactions, etc. In this study, decomposition kinetics, which are type of ordinary differential equations, were established in the "*reaction engineering*" module and solved by fourth-order Runge-Kutta method and the mass transfer diffusion models, which are type of partial differential equations, were set up in the "*diluted species*" module and solved by finite element method.

2.1. Kinetic Modeling

In the environment, aldicarb undergoes oxidation and converts into aldicarb sulfoxide [13]:

$C_7H_{14}N_2O_2S$ (Aldicarb) $+ \frac{1}{2}O_2 \rightarrow C_7H_{14}N_2O_3S$ (Aldicarb sulfoxide)
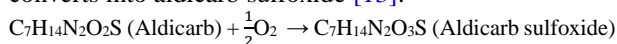
Various kinetic models including first and second-order models and Power-law model (with two orders of 0.5 and 1.5) were considered to predict the decomposition and elimination of aldicarb in the soil and water resources. The mentioned kinetics are given in Table 2.

Table 2. Applied decomposition kinetics

Kinetic model	Definition
First-order	$\dfrac{dc}{dt} = -kc$
Second-order	$\dfrac{dc}{dt} = -kc^2$
Power-law	$\dfrac{dc}{dt} = -kc^{\alpha}$

In Table 2, "*c*"denotes the aldicarb concentration, "*t*" is the time, and "*k*" is the reaction rate constant. It should be noted that the power-law kinetic expresses a deviation from the first and second-order kinetics. The value of α usually varies between zero and two. In this case, values of 0.5 and 1.5 were considered for α. The cited models in Table 2 were defined in the "*reaction engineering*" module along with study type of "*Time Dependent*" in the environment of COMSOL MULTIPHYSICS software.

2.2. Transport modeling

An adequate mass transfer model should be applied to evaluate the diffusion of aldicarb in natural resources, specifically water. Since the concentration of aldicarb in water resources is low, the mass transfer used in this study is applicable to dilute solutions. The mass transfer model applied in current study is as follows:

$$\frac{\partial c_i}{\partial t} + \nabla \left(-D_i \nabla c_i \right) + u \nabla c_i = R_i \qquad (1)$$

The left hand-side terms are describing the accumulation, molecular diffusion, and convection transfer of aldicarb, respectively. The right hand-side term refers to aldicarb consumption in the environment. The flow was considered as laminar, due to the low transfer rate. In laminar flow, the majority of the mechanism of aldicarb transfer happens through molecular diffusion. Therefore, the convection transfer term was eliminated to simplify the suggested model. The governing equation is then translated into the following:

$$\frac{\partial c_i}{\partial t} + \nabla \left(-D_i \nabla c_i \right) = R_i \qquad (2)$$

The law of momentum conservation was used to calculate the rate of velocity. The mass transfer module, called "*diluted species*", in combination with the "*reaction engineering*" module (described in section 2.1), was used to model the mass transfer and diffusion of aldicarb in groundwater aquifers in the environment of COMSOL MULTIPHYSICS. The following equation was used to compute the diffusion coefficient (D_i) of aldicarb and aldicarb sulfoxide in water:

$$D_i = \frac{(117.3 \times 10^{-18})(\phi MW)^{0.5}T}{\mu v_i^{0.5}} \qquad (3)$$

Where Φ is the association factor for solvent, MW is the molecular mass of water (solvent), T is the temperature, μ is the viscosity of water (solvent), and v_i is the pollutant molar volume.

2.3. Process simulation

In order to validate the kinetic models, the experimental results of Sun et al. [7] were used. Therefore, the initial concentration of aldicarb was considered in accordance with the mentioned research (10.79 mol/m^3). Sun et al. [7] evaluated the elimination of aldicarb at a constant temperature of 25˚C. Accordingly, the simulations were done at this temperature. In the "*species*" section of the "*reaction engineering*" module, the properties of aldicarb and aldicarb sulfoxide such as molecular weight (190.26, 206.26 gr/mol), density (1195, 1217 kg/m^3), and initial concentration (10.97, 0 mol/m^3) were given, respectively. It should be noted that the non-linear regression was applied using the "*nlinfit*" function in the environment of MATLAB software (version 2018a) to calculate the values of the reaction rate constant (k) in the kinetic models. These values are shown in Table 3 for various soils.

Table 3. The values of reaction rate constant used in the simulations

Type of soil	k value (1/s)
Sterile soil	0.09
Non-sterile soil	0.158

Table 4 provides the numerical values used to compute the diffusion coefficients of aldicarb and aldicarb sulfoxide in water for mass transfer model.

Table 4. The parameters used in calculating the diffusion coefficient of aldicarb and aldicarb sulfoxide in water

Parameter	Value	Unit
Φ	2.26	-
MW	18.02	kg/kgmol
μ	0.001	kg/m.s
v_A	0.229	m^3/kmol
v_{AO}	0.234	m^3/kmol

v_A is the molar volume of aldicarb and v_{AO} is the molar volume of aldicarb sulfoxide.

The values of diffusion coefficient calculated by Equation (3) for aldicarb and aldicarb sulfoxide are given in Table 5.

Table 5. The diffusion coefficient of aldicarb (D_A) and aldicarb sulfoxide (D_{AO}) in water

Diffusion coefficient	Value (m²/s)
D_A	5.41×10^{-10}
D_{AO}	5.33×10^{-10}

3. Results and Discussion

In Figs. 2 and 3 the predictions of the kinetic models used in this research are given along with the experimental data of Sun et al. [7] for the degradation of aldicarb in sterile and non-sterile soils.

As can be seen in Fig. 2, the trend of aldicarb decomposition in sterile soil accelerates more in the first four days, and more than 70% of aldicarb is degraded. In the following days, the rate of decomposition proceeds at a gentle slope. According to Fig. 3, the trend of aldicarb decomposition in non-sterile soil is different from sterile soil. Although in the first few days, the degradation of aldicarb in non-sterile soil is carried out slightly faster, but in general, this trend decreases with an almost uniform intensity during 16 days.

For a more accurate comparison, the sum of squared error (SSE) of each of the mentioned models is calculated and reported in Table 6 for sterile and non-sterile soils. According to Table 6, among the applied models, the second-order kinetic model and the 0.5-order power-law kinetic model have higher accuracy in predicting the decomposition process of aldicarb into aldicarb sulfoxide in sterile and non-sterile soils respectively.

Table 6. SSE of different kinetic models for aldicarb decomposition into aldicarb sulfide in sterile and non-sterile soils

Kinetic model	SSE (sterile soil)	SSE (non-sterile soil)
First-order	101.745	92.482
Second-order	**1.031**	184.694
Power-law (α=0.5)	187.046	**1.918**
Power-law (α=1.5)	22.911	148.054

In the following, the effect of initial concentration of aldicarb on its decomposition rate in sterile and non-sterile soils was investigated based on the best decomposition kinetics (second-order and Power-law with order of 0.5). In Fig. 4, the trend of aldicarb decomposition at different initial concentrations (2, 5 and
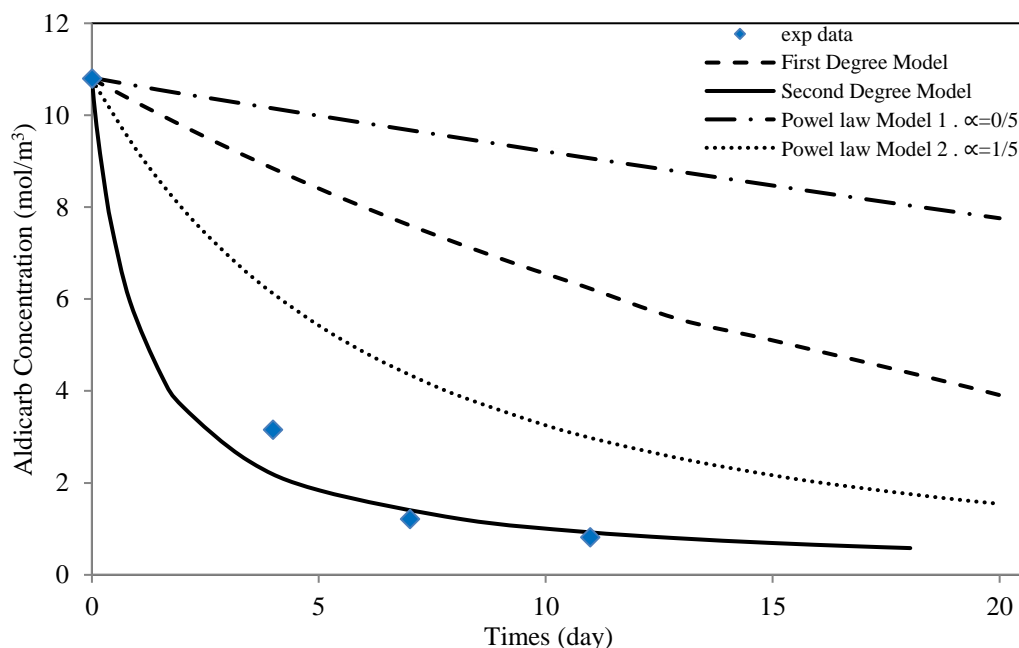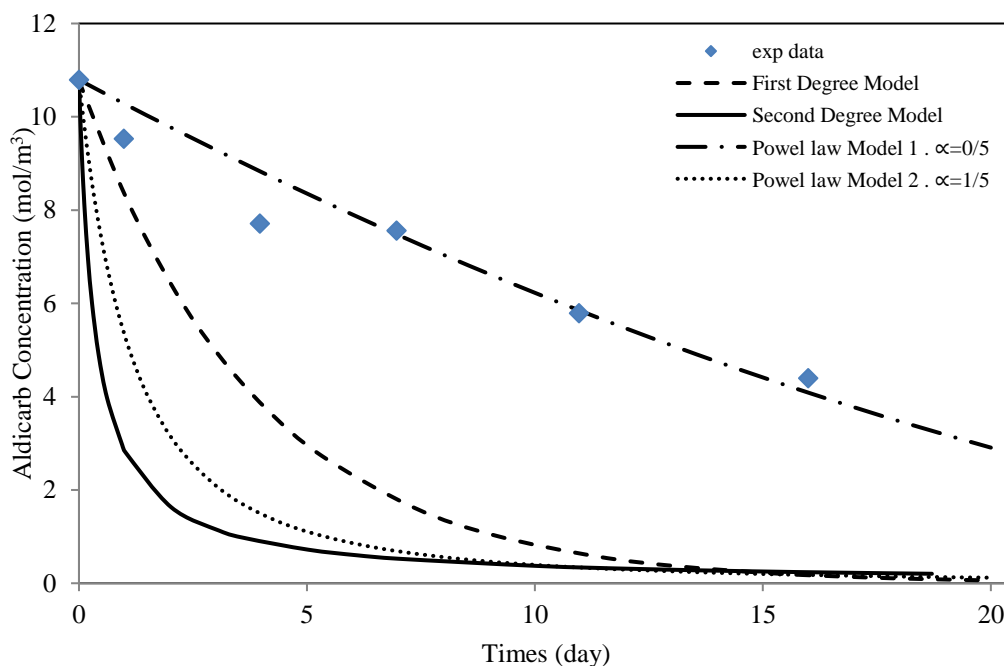

Fig. 2. The predictions of different kinetic models for aldicarb decomposition into aldicarb sulfoxide along with experimental data of Sun et al. [7] in sterile soil.

As can be seen from Fig. 4, the higher the initial concentration of aldicarb, the faster its decomposition rate will be at the beginning of the process. In this regard, in the initial concentrations of 2, 5, and 15 mol/m³, a decrease of approximately 200, 500, and 1700 percent occurs in the concentration of aldicarb, respectively.

Fig. 3. The predictions of different kinetic models for aldicarb decomposition into aldicarb sulfoxide along with experimental data of Sun et al. [7] in non-sterile soil.

In Fig. 5, the trend of aldicarb decomposition at different initial concentrations (2, 7 and 15 mol/m³) was shown in non-sterile soil. As it is clear from Fig. 5, in contrast to sterile soils, here the aldicarb concentration decreases with an almost uniform slope from the beginning to the end.
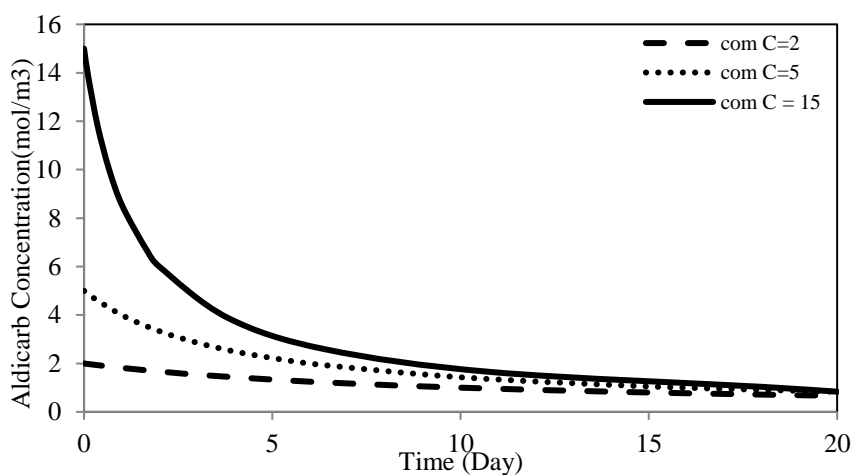

Fig. 4. The effect of initial concentration of aldicarb on its decomposition rate in sterile soil.

In the following, the trend of aldicarb removal was evaluated in water resources. Fig. 6 depicts the predictions of the mass transfer model combined with the removal kinetic model of Power-law with order of 0.5 (the most accurate degradation kinetic in non-strile environments) in a two-dimensional schematic for the diffusion and degradation of aldicarb to aldicarb sulfoxide in an aquifer with hypothetical dimensions. As shown in Fig. 6, the process of diffusion and decomposition of aldicarb in the aquifer is carried out almost uniformly from the point of its release. Due to the conversion and decomposition of aldicarb into aldicarb sulfoxide, no trace of aldicarb can be seen in the lower layers of the aquifer. Only the upper 25% of the aquifer layers are contaminated with pollutants.
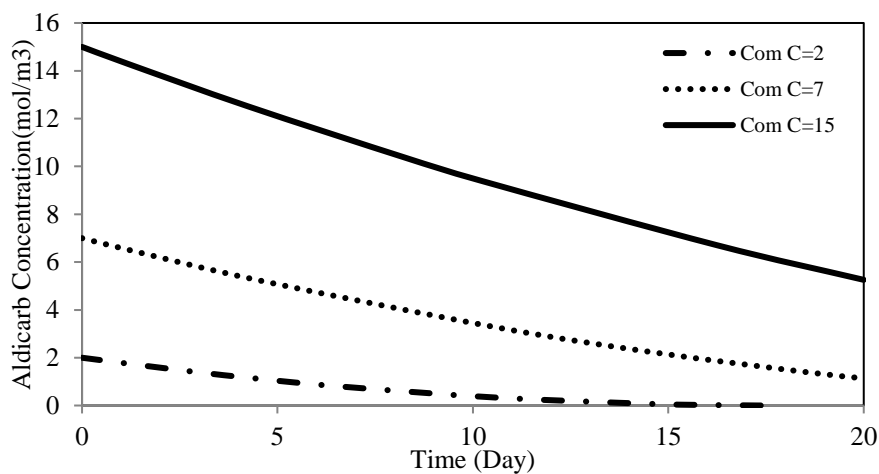
Fig. 5. The effect of initial concentration of aldicarb on its decomposition rate in non-sterile soil.

The current work can serve as a good starting point for practical and industrial research projects on aldicarb elimination from various environments. It is worth mentioning that other factors affecting the removal of aldicarb, including temperature, pH of the environment, humidity, and their magnitudes, will be investigated in the subsequent studies.
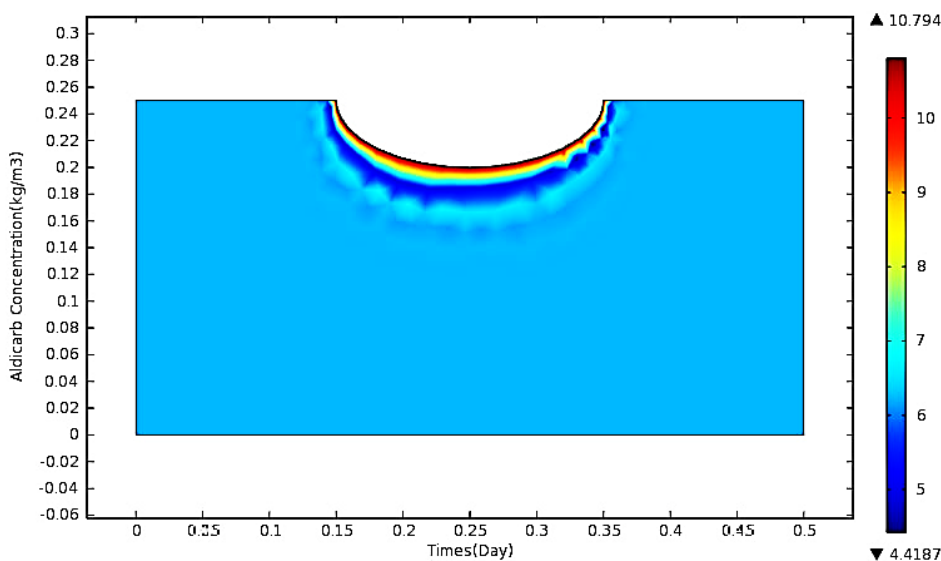

Fig. 6. The predictions of mass transfer model for the diffusion and decomposition of aldicarb in aquifer.

4. Conclusion

Process modeling and simulation can be a suitable solution for establishing correct practical and experimental strategies. In this research, the process of diffusion and decomposition of aldicarb pollutant (used in agricultural pesticides) in soil and water sources was modeled and simulated. In this regard, among the different kinetic models used to investigate the process of aldicarb decomposition, the second-order kinetic model for sterile soil and the 0.5-order Power-law kinetic model for non-sterile soil had the best performance and the lowest error value compared to the experimental data. In sterile soil, the higher the initial concentration of aldicarb, the faster its decomposition rate will be at the beginning of the process, while in non-sterile soil, the aldicarb concentration will decrease with an almost uniform slope from the beginning to the end. On the other hand, the used mass transfer model showed uniform diffusion and dispersion of aldicarb only in the upper 25% of the aquifer layers.

The findings of this study provide a general approach to select the optimum kinetics of aldicarb diffusion and removal, which can be utilized in practical and experimental researches.

List of symbols

c: Aldicarb concentration (mol/m^3)
D: Diffusion coefficient (m^2/s)
k: Reaction rate constant (1/s)

MW: Molecular weight (kg/kmol)
t: Time (day)
T: Temperature (K)
R: Reaction rate (mol/m^3.s)
u: Velocity (m/s)
μ: Viscosity solution (kg/m.s)
ϕ: Association factor for solvent (dimensionless)
υ: Molar volume of pollutant (m^3/kmol)
α: Order of Power-law model (dimensionless)

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