Application of the differential neural network observer to the kinetic parameters identification of the anthracene degradation in contaminated model soil

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Abstract

In this work a new technique dealing with differential neural network observer (DNNO), which is related with differential neural networks (DNN) approach, is applied to estimate the anthracene dynamics decomposition and to identify the kinetic parameters in a contaminated model soil treatment by simple ozonation. To obtain the experimental data set, the model soil (sand) is combined with an initial anthracene concentration of 3.24 mg/g and treated by ozone (with the ozone initial concentration 16 mg/L) during 90 min in a reactor by the "fluid bed" principle. The anthracene degradation degree was controlled by UV–vis spectrophotometry and HPLC techniques. Based on the HPLC data, the obtained results confirm that anthracene may be decomposed completely in the solid phase by simple ozonation during 20 min and by-products of ozonation are started to be destroyed after 30 min of treatment. In the ozonation process the ozone concentration in the gas phase at the reactor outlet is registered by an ozone detector. The variation of this parameter is used to obtain the summary characteristic curve of the anthracene ozonation (ozonogram). Then, using the experimental decomposition dynamics of anthracene and the ozonogram, the proposed DNNO is trained to reconstruct the anthracene decomposition and to estimate the anthracene ozonation constant using the DNN technique and a modified Least Square method.
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1. Introduction

1.1. Removal of polynuclear aromatic hydrocarbons from contaminated soil

Polynuclear aromatic hydrocarbons (PAHs) are considered to be hazardous pollutants and are listed as priority pollutants by the U.S. EPA. Most of PAHs are known as toxic compounds to living organisms [1]. PAHs have been found in air, soil and water environments and they are classified as pollutants associated with mutagenic and carcinogenic activities [2,3]. PAHs are formed in the pyrolysis of petroleum products at high temperatures (about 700 °C) as well as in acetylene synthesis from natural gas, refinery operations, etc. [4]. The presence of PAHs has been detected in marine, surface and groundwater with the concentration reaching up to 1.5 µg/L [5]. It is very important to emphasize that the PAHs concentration in sediments of river found near 5 mg/g [6,7], and in contaminated soil near railway around 1–4 mg/kg [8] forming an important domain of environment [9]. Up to now, the most common method for remediation of contaminated sites is excavation followed by land filling or incineration. However, the excavation followed by landfilling cannot destroy contaminants; even more, incineration can cause secondary pollution of groundwater and air. These methods are now less environmentally sufficient and expensive. Actually, biodegradation and advanced oxidation processes (AOPs) or their combinations are also available to treat contaminated soils. Nevertheless, PAHs are considered to be quite resistant to degradation by microorganisms: as a matter of fact, the effectiveness of the PAHs biodegradation depends on many factors such as the biodegradability of contaminant, its concentration, toxicity, etc. A lot of investigation has reported the information on the efficiency degree of the PAH biodegradation in soil [10] and on

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the combination of the preoxidation treatment with bioremediation [11–16]. The application of ozonation and other AOP for the contaminated soil treatment has demonstrated to be one of the environmentally adequate methods [17–21].

In this research, the degradation of anthracene in the solid phase by simple ozonation is studied. Anthracene is always combined with other PAHs. That is why it has been selected as a model compound for the preparation of the contaminated model soil, which was treated by means of ozone during 90 min. The degradation degree of anthracene was controlled by UV–vis spectrophotometry and HPLC techniques. To realize the kinetics study of the anthracene decomposition in the solid phase, it seems to be welcomed to have a mathematical model of this process. However, the known mathematical models describing the ozone interaction with pollutants in a solid phase are very complex [24]. It is well known that a real soil could present mixed composition with nonhomogeneity distribution and nonhomogeneity shape for each soil particles. Some efforts in studying the main characteristics of the ozone transport in a porous media have been realized in [22,23]. The crucial point of the majority of modern publications still remains the validation of the suggested mathematical models describing the ozone transport phenomena into the porous media and the contaminants degradation dynamics. Some attempts to describe the ozone mass transfer in gas–solid system as in a model soil with the phenanthrene presence have been made in [24]. Nevertheless, all these studies have the following disadvantages: the description of the process in partial differential equations that requires a complex numerical integration method application for the solution and the realization of noneasy experimental repeatability conditions required for the calculation of the factors involved into the model description (this period is usually referred to as "calibration" of the model [24]).

The approach employed in the present study consists in the implementation of the differential neural networks (DNN) method [25] to avoid all the uncertainties involved in the mathematical model description. It provides a good enough state estimation (in our case, the contaminant concentrations) without either preliminary parameter identification or any mathematical model structure knowledge: only the exact number of states and the observable components is required. Following to [26,27], for the estimation of the current concentration of anthracene during the ozonation reaction, the differential neural network observer (DNNO) is suggested to be applied. Using the obtained neuro-observer output estimates, the modified version of the least square (LS) algorithm is applied to estimate the unknown chemical reaction constant. As it is shown below, the suggested approach demonstrates a good correspondence between the experimental anthracene decomposition and the estimates obtained by DNNO application.

2. DNN approach

2.1. Overview of state observers and DNNO technique

The current state vector of a system specifies its behavior (or dynamics). Particularly, for some process, the exact knowl-

edge of each state component permits to a designer to propose different control schemes to obtain the desired optimal regime. However, in practice, the frequent situation takes place when only an input and output of a system are available and the rest of the internal state components cannot be measured on-line because of the absence (or a high cost) of the corresponding sensible devices. In this case, some sort of the state estimator is required. Its designing is based on the available information (input and output signals only) [28]. In the engineering community such type of devices is called S*tate Observers* and is commonly referred to as *software sensors* [29]. The most of known state observers are designed based on a complete knowledge of the system structure (mathematical model): for example, the interval observers [29], and the moving horizon observers [30] the so-called, set membership observers [31], etc. All of them are widely implemented for state estimation of chemical and biotechnological systems. But, if the mathematical model of a considered process is incomplete, partially known or even completely unknown, it is possible to use the advantages of the learning capacity of the artificial neural networks (ANN) [32] involving them into the observer structure [25]. In our case, we consider the special type of neural networks known as DNN, which provides an effective instrument to attack wide problems such as identification, state estimation, trajectories tracking, etc. [27,28,33] without the complete knowledge of the corresponding mathematical model. The DNN application permits to avoid many problems related to global extreme search (which are common when the usual static neural networks are used) converting the learning process into an adequate feedback design [27,32]. The DNN demonstrate good identification properties in the presence of some uncertainties or external disturbances, which usually accompany real processes.

To implement the DNNO to the estimation of anthracene decomposition in solid phase we have used the following next steps [25].

2.1.1. DNNO training

It consists in the adjustment of free parameters in DNNO structure (see the next section) according to some valid data source that, in turn, can be realized by two different methods: the *first* one consists in the usage of an experimental value set measured directly from a real process that requires the measurement of all state components (at least once during the training phase); if this is not feasible, the *second* option using some simplified mathematical model of the process may be employed. It is worth to notice that any information on the model structure is recommended to be taken into account to design the corresponding DNNO. In fact, a mathematical model is only consider as an artificial data source to describe a training process. In this study, a simplified mathematical ozonation model is considered for the DNNO training.

2.1.2. State-reconstruction

During this step, based on on-line experimental data monitoring (the variation of the ozone concentration in the gas phase at the reactor output), we reconstruct the nonmeasurable com-
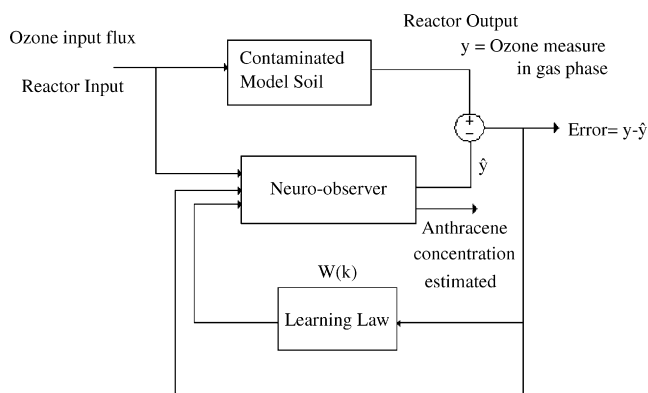
Fig. 1. Scheme of the implementation of DNNO for the estimation of the anthracene decomposition.

ponents (anthracene decomposition in the model soil), using the *trained* DNNO.

2.1.3. Validation

During this final step, we compare the estimated results with experimental data obtained by UV–vis and HPLC techniques.

2.2. Scheme of the DNNO implementation

The detail description of the DNNO structure can be found in [25]. Here, only the general scheme of the state identification is presented. It is based on the ozone concentration measurement in the gas phase at the reactor outlet. This technique for the system ozone–water estimation and kinetics parameters identification of the mixtures of phenols has been suggested in [26]. The same approach for the system ozone–soil is investigated in this study. The block-diagram of the DNNO implementation for the identification of the decomposition dynamics of anthracene is presented in Fig. 1.

The DNNO is governed by the differential Eq. (1):

$$\frac{d\hat{x}}{dt} = A\hat{x}_t + W_1\sigma(V_1\hat{x}_t) + W_2\varphi(V_2\hat{x}_t)\gamma(u_t)$$
$$+ K(y_t - \hat{y}_t) \quad \hat{y}_t = C\hat{x}_t \tag{1}$$

Here, $\hat{x}_t$ is the states vector of DNNO representing the estimations of each variables of the process: x_1, ozone concentration at output; x_2, ozone in solid phase; x_3, ozone reacting with contaminants and x_4, contaminant concentration, u_t is the gas input flow. We consider y_t as the ozone concentration at output. This is the unique variable available (measurable) on line. The constant matrix A (usually having stable eigen-values) as well as the gain constant matrix K, are selected during training process. The maps $\sigma(\cdot)$, $\varphi(\cdot)$ are standard sigmoid functions, C is the state-output transition matrix (it allow us to select an specific state or linear combination as the measurable output), W_i ($i = 1, 2$), V_i ($i = 1, 2$) are neural networks weights adjusted by the learning law, which general description can be found in [25,27].

2.3. DNNO training using the simplified ozonation model

Ozone is capable to oxidize a variety of organic materials in liquid, solid and gas phases. The oxidation by ozone involves the phenomenon of the ozone mass transfer with simultaneous chemical reaction in surface of the soil. It is important to notice that the DNNO does not use any information on the real process model, however, a simplified mathematical model of ozonation in the solid phase is proposed in this study, for being used in the DNNO training phase. This model is covered by the following ordinary differential equation (ODE) set:

$$\frac{dC_t^{\text{out}}}{dt} = V_{\text{gas}}^{-1}\left[W_{\text{gas},t}C_t^{\text{in}} - W_{\text{gas}}C_t^{\text{out}} \right.$$
$$\left. - \left(\frac{dQ_t^{\text{react\_abs}}}{dt}\right) - \left(\frac{dQ_t^{\text{free\_abs}}}{dt}\right) \right] \tag{2}$$

$$\frac{dQ_t^{\text{free\_abs}}}{dt} = K_t^{\text{abs}}[Q_{\text{max}}^{\text{free\_abs}} - Q_t^{\text{free\_abs}}] \tag{3}$$

$$\frac{dQ_t^{\text{react\_abs}}}{dt} = \sum_{i=1}^{n} k_i c_t^i Q_t^{\text{react\_abs}} \tag{4}$$

$$\frac{dc_t^i}{dt} = -k_i c_t^i \left(\frac{Q_t^{\text{react\_abs}}}{G}\right) \tag{5}$$

where C_t^{in} C_t^{out}, are the ozone concentration in the gas phase at the input and output of reactor, respectively (mole L^{-1}); W_{gas} is the gas flow (L s^{-1}); V_{gas} is the volume of the gas phase in the reactor (L), $Q_{\text{max}}^{\text{free\_abs}}$ is the maximum amount of ozone that can be absorbed by the soil without contaminant at experimental conditions (mole); $Q_t^{\text{free\_abs}}$ is the current amount of absorbed ozone in solid phase (mole). $Q_t^{\text{react\_abs}}$ is the current amount of ozone in solid phase consuming in reaction with contaminant (mole); c_t^i is the current contaminant concentration for the ith contaminant (mg$_{\text{con}}$/g$_s$), k_i is the ozonation constant for "i" contaminant (g$_s$/mg$_{\text{con}}$ s); K_t^{abs} is an empiric parameter (soil geometric, soil composition, etc) called "absorption parameter" and is calculated experimentally (s^{-1}); G is the solid phase mass (g).

It is worth notice that this model does not involve the ozone autodecomposition, since it is not observed during ozonation in solid phase.

This mode of training is insensitive to the selection of a concrete mathematical model, or, in another words, it is *robust* with respect to differential equations, which generate the training data. Only these data themselves, but not the method of their generation, turns out to be essential during this first stage. That means that the training is invariant with respect to a model generating the data sequences.

The stationary matrices A and K of the differential Eq. (1) are tuned by a simple "try-to-test" technique, in order to guarantee a small enough state estimation error between DNNO and the process represented by the simple model (2)–(5). The weights W_i and V_i are quickly adjusted on-line by the special differential learning law [25,27].

3. Methods

3.1. Preparation of the model contaminated soil

The soil (sand) with distilled water (during 0.5 h) and with ethanol (0.5 h) preliminary was washed under the continuous mixing. However, the washing degree was controlled by the UV-spectrum variation of the filtrated water and ethanol. 40 g of dry model soil (sand) was spiked with anthracene by adding 40 mL of anthracene–ethanol solution with a concentration of 52.6 mg/L, and then the ethanol was evaporated at 60 °C. The anthracene distribution and its concentration in the sand surface were controlled by the UV-spectrum variation of the anthracene extracted in ethanol from the soil by the Soxhlet apparatus during 15 min (1 g of soil in 20 mL of ethanol). The model soil (sand) has the initial anthracene concentration 3.24 mg/g.

3.2. Soil ozonation procedure

The ozonation of the contaminated soil was carried out in the reactor by the "fluid bed" principle (40 g) during the different treatment times 2, 5, 10, 15, 20, 30,60 and 90 min, using an ozone generator "AZCO" with the initial ozone concentration 16 mg/L, with the gas flow of 0.5 mL/min. The measurement of ozone in gas phase in the outlet of the reactor was done with an ozone analyzer BMT 930, connected with a PC. The ozone analyzer provides the ozone detection in the gas phase for the ozone monitoring to measure the ozonation degree. In Fig. 2 the schematic diagram of the ozonation is shown that includes: the oxygen tank, the ozone generator, the microreactor, the bypass system with electrovalves, the ozone analyzer connected with the data acquisition system and PC.

To measure the anthracene stripping degree the blank test of the contaminated soil with oxygen flow only without the ozone presence during 25 min was considered. The anthracene stripping degree by the comparison of the UV-spectrum of its extracts in ethanol was determined.
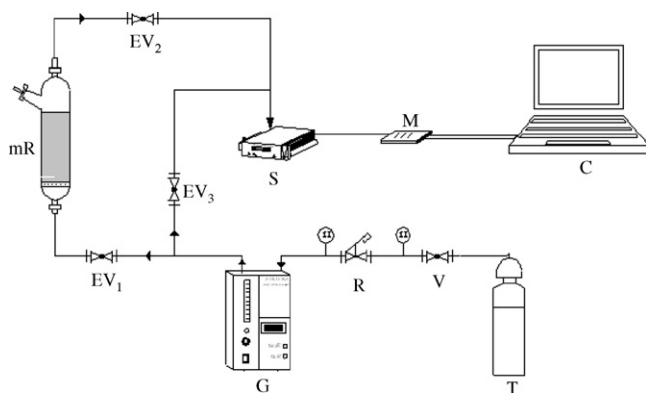

Fig. 2. Schematic diagram of the ozonation apparatus: (mR) microreactor, (T) oxygen tank, (V) valve, (R) manifold, (G)ozone generator, (EV1, EV2, EV3) bypass system with electrovalves, (S) ozone analyzer, (M) data acquisition system, (C) PC.

3.3. Analytical methods

To analyze the anthracene decomposition by UV-spectrophotometry, all soil samples in ethanol were extracted. Then, all extracts were analyzed by absorbency UV–vis variation at 190–340 nm on a spectrophotometer (Perkin–Elmer - Lambda 2B) to obtain the summary information on the anthracene decomposition dynamics in soil (sand). The control of PAHs decomposition as well as the intermediates and final products identification has been realized by the HPLC analysis. It was made by the liquid chromatography Perkin–Elmer series 200 coupled with a automatic UV–VIS detector accompanied by the chromatographic column Nova Pack C-18, 250 × 4.6 mm with mobile phases of water: acetonitrile: phosphoric acid mixture (70:29.9:0.1) for the initial aromatics decomposition observation and of water: acetonitrile mixture (53:47) for the simple by-products identification with the flow 1.0 mL/min. The injected sample volume is 20 μL.

4. Results and discussion

4.1. Results of the DNNO training

Using the ozonation mathematical model and applying the DNNO, we can obtain the anthracene decomposition dynamics in model soil, based only of the monitoring data C_t^{gas}. Fig. 3(a)–(d) depicts the modeled and identified trajectories for the ozone concentration at the output of reactor (C_{gas} and $\hat{C}_{gas}$) (a), for the absorbed ozone (b), for the reacting ozone (c). The evolution in time of the estimated $\hat{c}_1$ and the modeled dynamics c_1 for the anthracene concentration are given in Fig. 3(d). The DNNO parameters are showed in Table 1.

4.2. Dynamics of the anthracene decomposition (experimental data)

Ozonation of the model contaminated soil (sand) in the heterogeneous two phase's system (ozone–soil) was carried out. The anthracene stripping degree is not observed. The obtained results confirm that anthracene may be completely decomposed by the simple ozonation in the solid phase based on the HPLC data of the anthracene extracts in ethanol (see Fig. 4). As it is seen from this data, the anthracene decomposition was carried out during 20 min of ozonation. After 15 min of ozonation the by-products formation also is observed. In Fig. 4 is represented also the by-products summery concentration variation during ozonation. From this data we can see that these compounds are

Table 1
DNNO matrices values

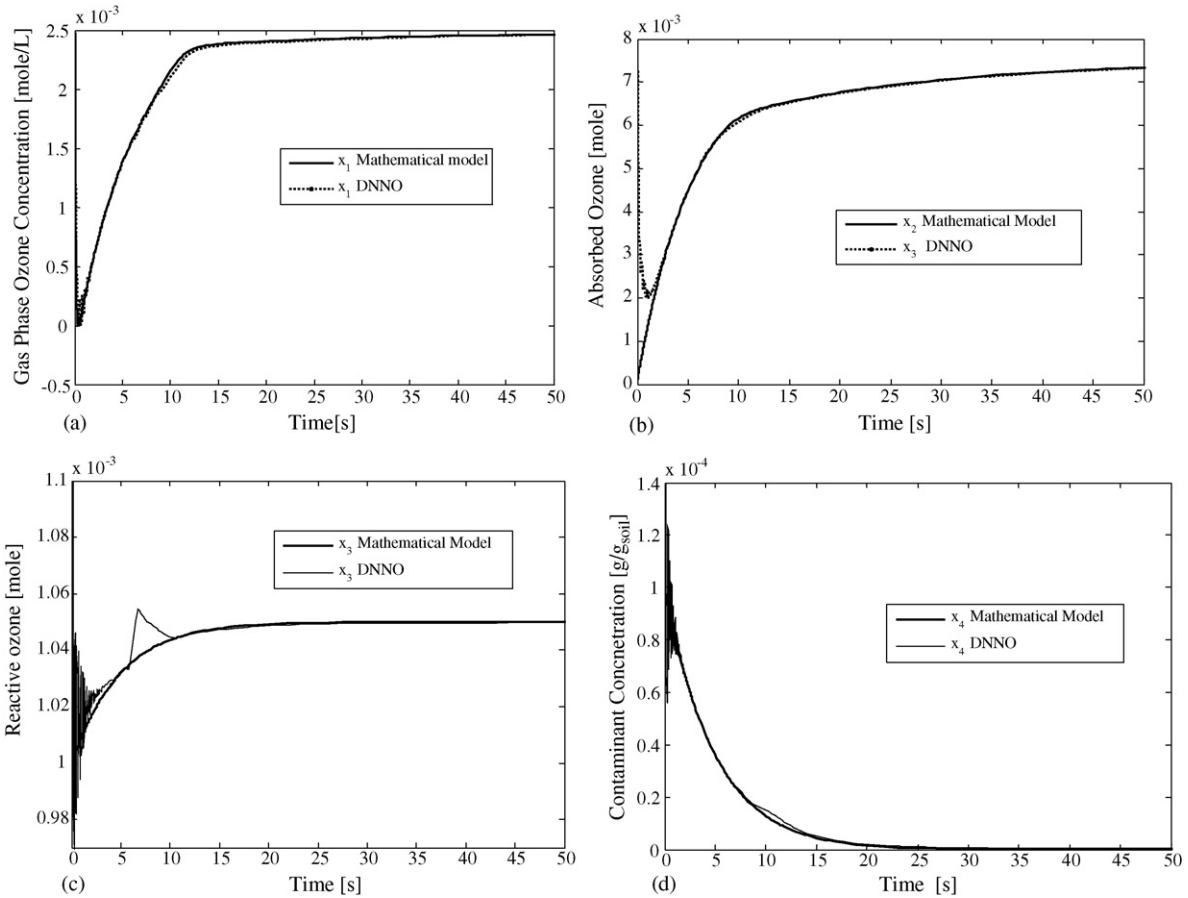| A				K
−2.6	0	0	0	0.001
0	−1.64	0	0	0.001
0	0	−1.4	0	0.1
0	0	0	−1.2	−0.01

Fig. 3. Modeled and estimated trajectories for: the ozone concentration at the reactor output (a), the absorbed ozone (b), the reacting ozone (c), and the anthracene decomposition (d).

accumulated from 15 to 30 min of ozonation, and are started to be destroyed after 30 min.

The phtalic acid formation during ozonation is also observed. This compound is interpreted as a final product of ozonation. If taken into account that the initial anthracene concentration is high (3.24 mg/g) and the initial ozone concentration is compar-

Fig. 4. Anthracene and by-products decomposition in ozonation (HPLC data at $\lambda = 251$ nm).

atively less (16 mg/L), the contaminant decomposition degree may be treated at the adequate time by the increasing of the initial ozone concentration.

4.3. Anthracene decomposition dynamics estimation using DNNO

Fig. 5 depicts the ozone concentration at the reactor outlet (ozonogram) for three cases: when the reactor is completely empty, when the reactor contains the model soil (sand) and when the reactor is fulfilled with the contaminated model soil. Notice that the upper area, bounded by each one of the ozonograms, corresponds in the first case to the ozone quantity fulfilling the reactor. In the second case, this area corresponds to ozone absorbed by the soil, and, in the third case (which involves two previous cases), it corresponds to the ozone quantity reacting with the anthracene and its by-products. In the first two cases, the ozone output concentration attains the input concentration in a short time. Meanwhile, in the third case, the existence of anthracene and its by-products provokes an ozone consumption, that is why the current ozone concentration do not return back at all to the input (initial) value, that can be seen in Fig. 5(b).

Employing the monitored ozone concentration variation in the gas phase in the reactor outlet (Fig. 5 ozonogram (3)) and the trained DNNO, we can estimate the dynamics decomposition of
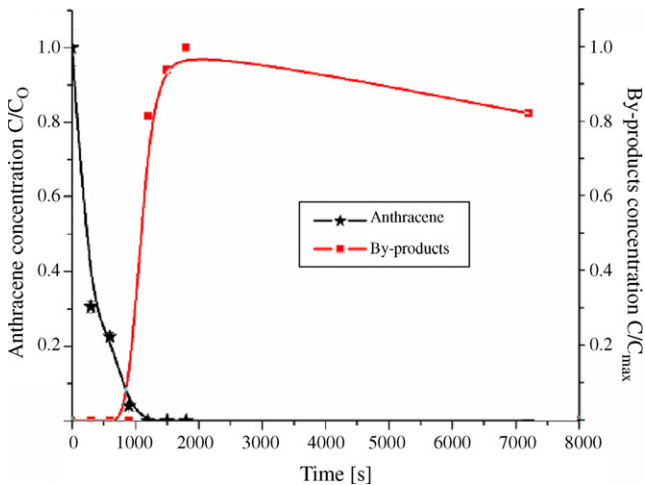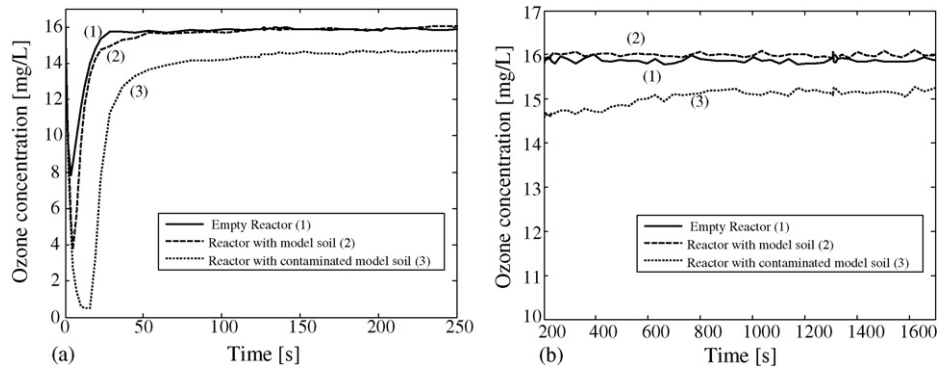
Fig. 5. Ozonograms of: (1) Empty reactor (blank test), (2) model soil and (3) contaminated model soil. (a) 0 to 250 s and (b) 250 to 1700 s.
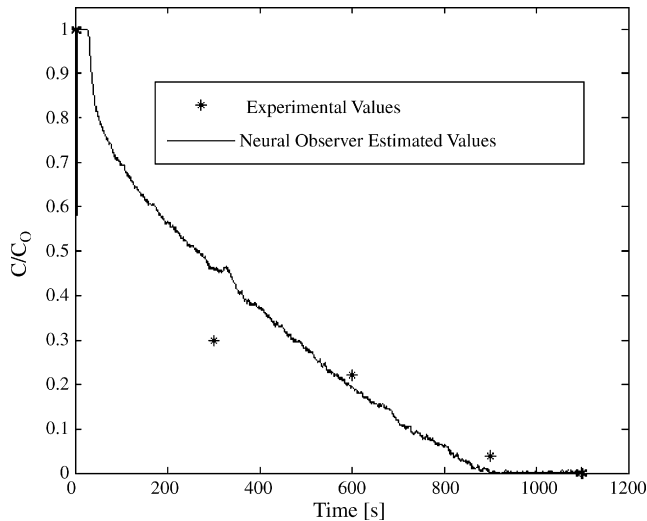

Fig. 6. Removal of anthracene in ozonation (✳ HPLC data at $\lambda = 251$ nm) and DNNO estimation.

anthracene and make the comparison with the experimental data obtained by HPLC technique (see Fig. 4). This provides the good correspondence between the experimental data and the estimated ones by DNNO (see Fig. 6) with the average estimation error of -0.02 ± 0.0795.

Comparing the anthracene decomposition and the corresponded ozonogram (Fig. 7), one can detect two different parts
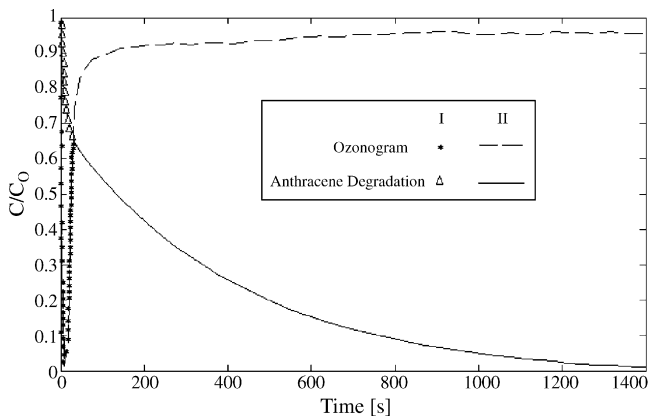

Fig. 7. Ozonogram and anthracene degradation.

in the ozonogram and in decomposition curve of anthracene. The part I corresponds to the kinetic regime of anthracene ozonation, and the part II corresponds to the diffusion regime of the reaction ozone with anthracene. Based on these data, we may conclude that the anthracene ozonation in solid phase is carrying out in two regimes: kinetic and diffusion.

4.4. Estimation of reaction rate constant

Considering the kinetic regime (the part I) of anthracene ozonation and the results, obtained in Section 3.3, it follows that DNNO can be used to estimate the ozonation kinetic parameters. The rate constant is an important parameter for the reaction mechanism interpretation. In this case, a mathematical model is not available that provokes notable difficulties in the kinetic parameter identification. In addition, the ozone mass transfer in solid phase includes the inter particles and intra particle diffusion with simultaneous chemical reaction that makes the modeling task difficult. To overcome this problem, the technique based on DNN may be used to obtain the model free representation of the ozonation dynamics as it was mentioned before. Observe that $\hat{c}_t$, $\hat{Q}_t$ as well as $d\hat{c}_t/dt$ are available. Under these conditions it is possible to define the LS estimates of $k_i(t)$ as the solution of the following optimization problem:

$$k_{i,t}^* = arg\min_{k_t} \int_0^t \left(\left(\frac{dc_t^i}{dt} \right) + k_i c_t^i \left(\frac{Q_t^{\text{react\_abs}}}{G} \right) \right)^2 d\tau \qquad (6)$$

The solution is as follows:

$$k_{i,t}^* = -G \left[\frac{\int_0^t (c_\tau^i Q_\tau^{\text{react\_abs}} (dc_t^i/dt)) d\tau}{\int_0^t (c_\tau^i Q_\tau^{\text{react\_abs}})^2 d\tau} \right] \qquad (7)$$

The estimation of the rate constant has an excellent correspondence with the experimental dynamics (see Fig. 6). The numerical value of the estimate of the ozonation rate constant is equal to 6.1×10^4 g_s/mg_{con} s, where g_s is the mass of the soil, mg_{con} is mass of the contaminant, s are seconds. This value corresponds to the part I of ozonogram in the Fig. 7, where kinetic regime occurs.

5. Conclusions

The obtained results confirm that the anthracene decomposition in the solid phase (in the model contaminated soil) proceeds with the simple ozonation completely based on the HPLC data during 20 min. The subproducts are started to be destroyed after 30 min of ozonation. The DNNO approach is shown to be able to guarantee a good anthracene dynamics decomposition estimation. The dynamics behavior predicted by DNNO shows a good enough correspondence to experimental data with the average estimation error of -0.02 ± 0.0795. The estimated ozonation rate constant, obtained by this method, exactly corresponds to the experimental dynamics decomposition of anthracene. The dynamic neuro observer can be incorporated into a real-time control system to optimize the decomposition dynamics without the application of any monitoring apparatus for on-line contaminants concentration control. The unique monitoring, demanded for the realization of this method, is the ozone concentration variation in the gas phase in the reactor output.

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