Treatment of simulated industrial wastewater by photo-Fenton process: Part II. The development of mechanistic model

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ABSTRACT

The aim of the study was to develop the mechanistic model describing the behavior of photo-Fenton process treating the simulated industrial wastewater containing oxalates and formates. In Part I of the study, the optimal conditions for each of applied photo-Fenton processes ($UV-C/Fe/H_2O_2$ and $UV-A/Fe/H_2O_2$) were determined and used in this study for model development and verification. The mechanistic model simulates the influence of various factors: the type of UV irradiation, the changes in concentrations of pollutants, catalysts and oxidant, on photo-Fenton process performance. pH dependent equilibrium of ferrous, ferric, oxalate and formate species was simulated as well. The model was tested to evaluate its accuracy in predicting the system behavior at different pollutant concentrations. Good agreement of the data predicted by model and the empirically obtained values was confirmed by calculated standard deviation for each experimentally monitored parameter. The developed mechanistic model describing the behavior of photo-Fenton process treating simulated wastewater can be characterized as interpretable, transparent, flexible and accurate. The comparison of electrical energy costs for each of the studied processes was performed. The obtained results indicate that the process using UV-C source is more efficient and cheaper. However, the simulation of process effectiveness using the solar UV-A irradiation recorded at annual basis for the location of proposed wastewater treatment plant speaks in the favor of solar $UV-A/Fe/H_2O_2$ process application instead of artificial UV irradiation.

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1. Introduction

Petrochemical wastewaters, containing the variety of aromatic and aliphatic pollutants, which are often toxic and present in high concentration, represent a serious threat to surrounding ecosystems [1,2]. Thus, efficient treatment of such wastewater prior to discharge into the natural water bodies is highly demanded. Advanced oxidation processes (AOPs), have been shown as an appropriate treatment tool for industrial wastewaters [3–5].

In Part I of the study [6] the photo-Fenton process was successfully applied for the treatment of simulated industrial wastewater upon pretreatment by the dark-Fenton process, and the optimal process parameters were determined using design of experiments (DOE) approach. The applied statistical modeling in Part I of the study [6], i.e. response surface modeling (RSM) within DOE, provided success in predicting the chosen system response in dependence of process parameters. Such techniques do not include

chemical phenomena underlying the system behavior. Hence, mechanistic models predicting the overall system performance seem to be a better option, especially for industrial applications [7]. In the case of AOPs, this is particularly challenging due to the complex reaction mechanism influenced by the type of applied energy (e.g. chemical, radiation or mechanical) for OH radicals' generation and present pollutants. Hence, such processes encompass several reactions characteristic for a type of applied AOP and typical reactions describing the inorganic radical mechanism in water matrix [7–13]. In the mechanistic model describing the behavior of photo-Fenton process, the specific reactions involving the generation of main radical species should be included. Due to the fact that the formation of ferric organic and inorganic complexes strongly influences the overall process performance, their equilibrium should also be included in model formulation [13–16]. In photo-Fenton processes formed complexes restraining Fenton catalytic cycle in the dark can be degraded. In such manner the Fe^{3+} ions can participate in the Fenton catalytic cycle thus allowing further degradation of present organic pollutants [14]. Besides recovering ferric ions from their complexes and simultaneously generating reactive radical species (e.g. oxalate radicals, Eq. (1)), the UV irradiation provide further benefits to the overall treatment efficiency: additional OH

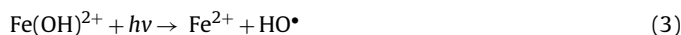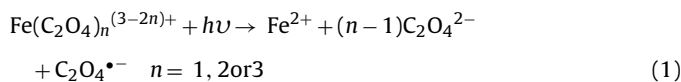* Corresponding author. Tel.: +385 1 4597 160; fax: +385 1 4597 143.
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Table 1
Compositions of simulated industrial wastewater.

	SIM1	SIM2	SIM3
γ(NaOx) (mg L^{-1})	120	240	60
γ(NaFor) (mg L^{-1})	90	180	45
[Ox] (mM)	1.36	2.72	0.68
[For] (mM)	2.00	4.00	1.00
[Ox]/[For]	0.68	0.68	0.68
TOC (mg C L^{-1})	57.18	114.28	28.31

radical generation through the photolysis of H_2O_2 and ferric hydro-complexes, Eqs. (2) and (3), respectively [15–17]:

$$Fe(C_2O_4)_n^{(3-2n)+} + h\upsilon \rightarrow Fe^{2+} + (n-1)C_2O_4^{2-}$$
$$+ C_2O_4^{\bullet-} \quad n = 1, 2 \text{ or } 3 \tag{1}$$

$$H_2O_2 + h\nu \rightarrow 2OH^\bullet \tag{2}$$

$$Fe(OH)^{2+} + h\nu \rightarrow Fe^{2+} + HO^\bullet \tag{3}$$

The study was focused on the investigation of the photo-Fenton process for the treatment of simulated industrial wastewater from 1,2-DCA/VCM plant (DINA Petrokemija Ltd., Omisalj, Croatia), upon pretreatment by dark-Fenton process. In Part I of the study [6], the optimal conditions for each of the applied photo-Fenton processes were determined using design of experiment approach (for UV-C/Fe/H$_2$O$_2$: initial pH 3.9, [Fe^{2+}] = 5.01 mM, [Fe^{3+}] = 8.0 mM and [H$_2$O$_2$] = 30 mM; and for UV-A/Fe/H$_2$O$_2$ initial pH 1.9, [Fe^{2+}] = 8.39 mM, [Fe^{3+}] = 8.0 mM and [H$_2$O$_2$] = 30 mM). In this part of the study a mechanistic model describing the behavior of applied processes is developed. In order to evaluate the potential of studied processes for the practical application, the cost estimation was performed. On the basis of acquired global radiation data, a solar UV-A irradiation was calculated. The approximated values of photonic fluxes of solar UV-A irradiation were included in the developed mechanistic model and the prediction of simulated wastewater was compared by those obtained/predicted using artificial UV-C and UV-A irradiation.

2. Experimental

2.1. Chemicals

Oxalic acid (OxAc), +99%; formic acid (ForAc), GC grade; ortho-phosphoric acid (*o*-H$_3$PO$_4$), $w \approx 85\%$; sodium oxalate (NaOx), p.a.; sodium formate (NaFor), p.a.; ferrous sulphate, (FeSO$_4 \times$ 7H$_2$O), p.a.; ferric sulphate (Fe$_2$(SO$_4$)$_3 \times$ XH$_2$O), p.a.; hydrogen peroxide (H$_2$O$_2$), w = 30%; sodium hydroxide (NaOH), p.a.; and sulphuric acid (H$_2$SO$_4$), >96%, were purchased by Sigma Aldrich, USA and Kemika, Croatia. All experiments were performed with deionized water with conductivity less than 1 μS cm^{-1}.

2.2. Experimental procedure

The experiments were performed in the glass water-jacketed batch reactor following the procedure described in detail in Part I of the study [6] at determined optimal conditions: initial pH 3.9, [Fe^{2+}] = 5.01 mM (along with [Fe^{3+}] = 8.0 mM) and [H$_2$O$_2$] = 30 mM for UV-C/Fe/H$_2$O$_2$ process; and pH 1.9, [Fe^{2+}] = 8.39 mM (along with [Fe^{3+}] = 8.0 mM) and [H$_2$O$_2$] = 30 mM for UV-A/Fe/H$_2$O$_2$ process. It can be seen that the optimal conditions determined for each performed photo-Fenton process (UV-C/Fe/H$_2$O$_2$ and UV-A/Fe/H$_2$O$_2$) differed regarding the type of UV irradiation, which is explained in detail in Part I of the study [6]. Photo-Fenton processes were applied for the treatment of simulated industrial wastewater (SIM) with various organic loads (Table 1). SIM1 consists of NaOx and

NaFor as model pollutants and corresponds to the composition of wastewater obtained upon pretreatment by dark-Fenton process studied in the previous study [5]. The duration of each experiment was 120 min; samples were taken periodically from the reactor and thereafter immediately analyzed. All experiments were performed in triplicates and averages were reported, with the reproducibility >95%.

2.3. Analysis

The measurement of total organic content during experiments was performed using Total Organic Carbon analyzer, TOC-V$_{CPN}$, Shimadzu, Japan. The decomposition of oxalates and formates was monitored by HPLC, Shimadzu, Japan, equipped with diode-array UV detector, SPD-M10A$_{VP}$, Shimadzu, Japan, and SUPELCOGEL-H column, USA, 9 μm, 25.0 cm $\times$ 4.6 mm. 1% *o*-H$_3$PO$_4$ was used as a mobile phase operated with isocratic method at 0.2 mL min^{-1}. Handylab pH/LF portable pH-meter, Schott Instruments GmbH, Mainz, Germany, was used for pH measurements. The concentration of hydrogen peroxide during the treatment of simulated industrial wastewater was monitored using modified iodometric titration method [18]. Concentrations of iron ions were determined by colorimetric methods using UV/VIS spectrophotometer, Lambda EZ 201, Perkin Elmer, USA. Ferrous ions were identified by the reaction of Fe^{2+} with 1,10-phenanthroline giving orange-red colored complex (λ_{max} = 510 nm), while ferric ions were determined by the reaction of Fe^{3+} with thiocyanate forming under acidic conditions a red colored complex (λ_{max} = 480 nm) [18].

3. Model formulation

The mechanistic model (MM) predicting the performance of photo-Fenton process for the treatment of SIM originated from 1,2-DCA/VCM plant (DINA Petrokemija Ltd., Omisalj, Croatia) upon pretreatment by dark-Fenton process [5] was developed. MM comprises 50 reactions, which are presented in Table 2, involving 25 chemical species (ions, atoms, radicals, molecules).

The reactions correspond to reactions of inorganic species typical for H$_2$O$_2$/OH radical based systems (1–12), reactions involving iron species typical to occur in photo-Fenton type processes (13–20), reactions typical for ferri-oxalate systems (21–30, 39–41), equilibrium reactions of ferri-oxalate, ferrous-oxalate, ferri-formate and ferri-hydroxyde species (31–38) and reactions and equilibriums of organic species typical for oxalate/formate containing systems (42–50) (Table 2). The reactions' rate constants (k) and quantum yields (Φ) are mostly taken from the literature [8–13,17,19–30], while equilibrium constants (K) were calculated using Visual MINTEQ 2.61 software, USEPA, and compared by those available in the literature [9,25]. It should be noted that, in cases where a range of values for reaction rate constants depending on the specific process conditions are reported (#2, 6, 14, 15, 16, 18, Table 2), the values adopted in our previous study were used [13].

The general mass balance for a well-mixed, constant volume and constant temperature batch reactor is given by:

$$\frac{dc_i}{dt} = -r_i \tag{4}$$

where c_i is concentration of specie i in the bulk and r_i is a bulk phase rate of specie i (i.e. sum of rates of reactions including the degradation or the formation of specie i, $r_i = \sum_{m=1}^{n} r_m$) [31]. Treatment of SIM by photo-Fenton process was simulated by *Mathematica 6.0* (Wolfram Research, Champaign, IL) using GEAR method which finds the numerical solution to the set of ordinary differential equations.