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The use of D-optimal design to model the effects of process parameters on mineralization and discoloration kinetics of Fenton-type oxidation

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ABSTRACT

The aim of this experimental investigation was to study kinetics of Fenton and modified Fenton oxidation applied to miscellaneous dye solutions. Several bench scale laboratory tests for the treatment of colored wastewaters containing model pollutant compounds, reactive azo dyes C.I. Reactive Violet 2 (RV2) and C.I. Reactive Yellow 3 (RY3) were performed. In order to examine the effects of initial Fe^{2+} concentration, oxidant/catalyst molar ratio and oxidant type on TOC reduction and color removal, the following reactants were used: classic Fenton's reagent (Fe^{2+}/H_2O_2) and modified Fenton's reagent, where potassium peroxodisulfate, alone and in combination with hydrogen peroxide, was selected as oxidant. Response surface methodology (RSM), particularly D-optimal design, was used for the purpose.

This research contributed in several ways: (i) evaluation of more effective Fenton oxidant on pollutant content reduction, in terms of TOC and color removal, (ii) assessment of the optimal reactant doses, (iii) describing the RV2 kinetic behavior in applied systems and (iv) determining the apparent rate constants. Mineralization was described by pseudo-first-order kinetics with observed rate constant $k_m = 0.0133\ \mathrm{min}^{-1}$. A kinetic model describing discoloration was composed of two first-order in-series reactions with discoloration rates; $k_1 = 0.9447\ \mathrm{min}^{-1}$ and $k_2 = 0.0236\ \mathrm{min}^{-1}$, at optimal operating conditions and with the highest initial organic load.

1. Introduction

Wastewaters originated from dye manufacturing and textile industries or by those related to dye consumption are usually loaded with significant quantities of dyes, causing the coloration of waste streams visible even in concentrations such as $1\ \mathrm{mg\,L}^{-1}$. Hence, a small amount of such effluents discharged into water bodies might significantly change the color of rivers or lakes inhibiting the transmission of natural light and consequently present a hazard to aquatic ecosystems together with the increase of loading of organic content [1–3]. Among all dyes produced today a group of reactive dyes participates with a large portion and becomes the most remarkable due to specific characteristics of linkage between colorant and natural fibers. It is estimated that 15% of the world's dye production end up in the environment during the manufacturing and application processes [1]. Furthermore, many synthetic organic dyes and their metabolites are toxic, carcinogenic and mutagenic and pose a potential health hazard to humankind [4]. Due to this fact and rapid development and implementation of more and more stringent environmental regulations [5], convenient methods for the treatment of different types of colored wastewater have been a subject of a strong interest in recent years [3,6,7]. Generally, methods for the colored wastewater treatment can be grouped as biological, physical and chemical methods [8]. Biological methods have been widely used for the treatment of municipal and industrial wastewater. Despite of the lot of advantages, due to the complex aromatic structure and stability of reactive dyes, conventional biological treatment methods are ineffective for the structure degradation. Physical methods of wastewater treatment (adsorption, flocculation/coagulation, membrane processes, and ion exchange) [9–13], generally present transfer of pollution from one phase to the other, often expensive and not enough eco-efficient. Formation of secondary waste disposal and adsorbents regeneration additionally decreases economical efficiency of these processes. The alternative to the conventional colored wastewater treatment processes presents advanced oxidation processes (AOPs) that can be applied individually or as a part of integral treatment process [14]. The advantage of these processes in comparison with conventional wastewater treatment methods is the possibility of complete degradation of organic load towards water, carbon dioxide, nitrates, sulfates and chlorides. Advanced oxidation processes include formation of highly reactive species (radicals) under the chemical, electrical or radioactive energy and react non-selectively with per-

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sistent organic compounds transferring them into by-products which are not always harmless but can be degraded much more easily [2,10]. These species have high redox potential and one of the most important is hydroxyl radical (2.8 V). It can attack and destruct organic compounds towards water and carbon dioxide, i.e. mineralize it completely [15,16]. Depending on the hydroxyl radical generation, different types of AOPs are known, such as Fenton and Fenton "like" processes, UV photolysis, UV peroxone process, TiO_2 photo-catalysis, high voltage electrical discharge, radiolysis, γ-radiation. Fenton process is based on oxidation with Fenton reagent which presents an oxidative mixture of hydrogen peroxide and ferrous ions (Fe^{2+}) as catalyst. The efficiency of Fenton process depends on: concentration of ferrous (Fe^{2+}) and hydrogen peroxide Eq. (1), their molar ratio, pH of the system and temperature [3,8]

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO^- + HO^\bullet \quad (1)$$

Peroxodisulfate is the most recent form of oxidant agent being used for environmental applications in the field of water and soil remediation. Sodium peroxodisulfate ($Na_2S_2O_8$) is the most commonly used form of peroxodisulfate salt, as the low solubility of potassium peroxodisulfate ($K_2S_2O_8$) limits its application as remediation agent [17,18]. Peroxodisulfate salts dissociate in water to peroxodisulfate anions ($S_2O_8{}^{2-}$), which, although strong oxidants (standard redox potential about 2.0 V), are kinetically slow in destroying the majority of the organic pollutants. Like in the case of modified Fenton's reagent, the addition of transition metal ions (e.g. ferrous ion) could activate the peroxodisulfate anion ($S_2O_8{}^{2-}$) to produce a powerful oxidant known as the sulfate free radical ($SO_4{}^{\bullet-}$), Eq. (2). Sulfate free radicals have a standard redox potential of 2.6 V and may be able to oxidize many organic pollutants [19]. In the presence of hydroxyl radicals, peroxodisulfate free radicals could be generated [20,21], Eq. (3):

$$S_2O_8{}^{2-} + Fe^{2+} \rightarrow 2SO_4{}^{\bullet-} + Fe^{3+} \quad (2)$$

$$S_2O_8{}^{2-} + {}^\bullet OH \rightarrow S_2O_8{}^{\bullet-} + OH^- \quad (3)$$

The experience in scientific research of application of peroxodisulfate as modified Fenton's reagent for dye wastewater treatment is currently very limited.

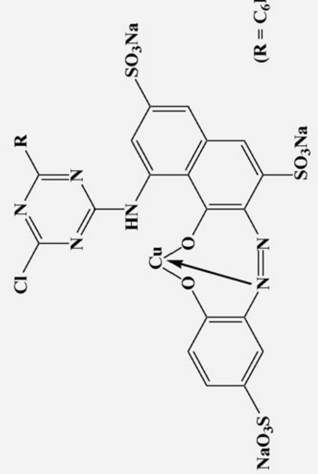
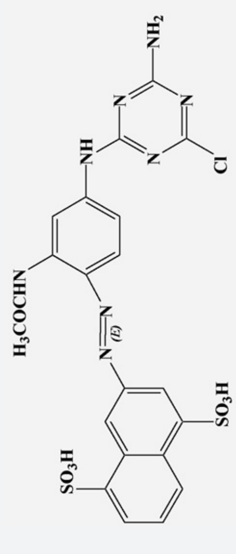
In the context of developing the mathematical models that describes the effects of process parameters on process performance and chemical kinetics, experimental designs are often common practice. Response surface methodology (RSM) is important branch of experimental design. It is a critical technology in developing new processes and optimizing their performance. It is often an important concurrent engineering tool in process development because the objectives of process performance improvement can often be accomplished directly using RSM [22,23]. RSM design is a helpful tool for quantification of the relationships between one or more measured responses and the vital input factors. Regarding the general model structure of a response surface, Eq. (4):

$$Y = bX + \varepsilon \quad (4)$$

where Y, X, b, and ε are the matrices of response, coefficients to be estimated, independent variable levels, and errors, respectively; an optimal experimental plan can be computed by using the methodology of optimal experimental design for parameter estimation [24]. D-optimal criterion, one of the several "alphabetic" optimalities [22], was developed to select design points in a way that minimizes the variance associated with the estimates of specified model coefficients [25]. D-optimal design assumes a wide choice of "candidate" points and an adequate coverage of design space.

The scope of this study was to evaluate the application of Fenton-type processes (Fe^{2+}/H_2O_2, $Fe^{2+}/H_2O_2 + K_2S_2O_8$ and $Fe^{2+}/K_2S_2O_8$) for the treatment of colored wastewaters containing model pollutant compounds, reactive azo dyes C.I. Reactive

Table 1
Structure and absorptivities of selected reactive dyes at studied wavelengths.

Dye		C.I. Reactive Violet 2 (RV2)	C.I. Reactive Yellow 3 (RY3)
Structure		 ($R = C_6H_5O, NH_2$)	
Molar extinction coefficient, $cm^{-1} L\,mol^{-1}$	385 nm	120	13,000
	550 nm	16,000	0