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Research article

Modelling and experimental checking of the influence of substrate concentration on the first order kinetic constant in photo-processes

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ABSTRACT

Most photoprocesses follow a pseudo first order kinetic law and, commonly, the kinetic parameter depends on the initial concentration of the substrate. In this work, a kinetic model, which explains this dependence on the substrate concentration and on the other operational variables, has been developed. In the model, mass transfer of substrate from the bulk solution to the wall of the photoreactor was assumed as the step determining the rate of the process. To check the model, methylene blue (MB) has been used as model substrate and photodegradation experiments have been carried out in an exciplex KrCl flow-through photoreactor, It was observed that the methylene blue conversion improved with a decrease in its initial concentration, in good agreement with the model. Also, by fitting the experimental data to the model, high correlation coefficients and a high degree of agreement between experimental and calculated conversion was obtained, which validates the model.

1. Introduction

In most of the photodegradation processes the progress curves can be successfully fitted to a pseudo first order kinetics and, commonly, the first order kinetic parameter is not constant and shows a dependence on the initial concentration of substrate, which is not the expected behaviour for a true first order kinetics. In this work, a kinetic model, which explains this dependence on the substrate concentration and the influence of other operational variables, has been developed. To check the model, methylene blue (MB) has been used as model substrate and experiments have been carried out in an exciplex KrCl flow-through photoreactor, both in the presence of H_2O_2 and Fenton reagent.

Methylene blue (MB) has been chosen as model substrate in this work because this cationic dye has not only been used in the textile industry, but also in numerous therapeutic applications, from microbiology to psychiatry (Bruchey and González-Lima, 2008; Gonzalez-Lima and Bruchey, 2004; Poteet et al., 2012; Wainwright and Crossley, 2002).

Nowadays, more than 10,000 different types of dyes and commercial pigments are available (Tan et al., 2007) and more than 700,000 tons are produced worldwide (Fassold et al., 1999; Kannan and Meenakshisundaram, 2002). Industrial dyes are known to be among the main water contaminants due to the strong colour of their wastewater, which, once discharged in the receiving water bodies, diminishes water oxygenation capacity and blocks light absorption, avoiding plants photosynthesis and damaging biological activity (Eyvaz et al., 2009; Pearcea et al., 2003). The main risk for human health derived from dyes is the fact that most of them are formed from aromatic amines, which after the metabolic oxidation of dyes can lead to reaction products that covalently bond with the DNA nucleic acids (Gerulis, 1985). As a result, many dyes are carcinogenic, teratogenic or mutagenic to both aquatic and human life (Adam et al., 2013).

Moreover, as the required characteristics for industrial dyes are resistance to light, temperature, wash and microbial attack, these substances are highly recalcitrant, which, in addition to their complex structure, makes their treatment more complicated, especially when using conventional biological treatments (Frijters et al., 2006; Seshadri et al., 1994). Enzymatic treatments have shown better results, although their high cost remains as the main disadvantage (Ferreira-Leitão et al., 2003; Ferreira-Leitão et al.,

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2007). Adsorption has proven to be a simple physical method successfully used to remove methylene blue, among other dyes (Shi et al., 2013; Suteu and Malutan, 2013).

Among the chemical methods used to degrade dyes and other organic pollutants, Advanced Oxidation Processes (AOPs) have been able to achieve complete mineralization of the most recalcitrant contaminants due to their high oxidant power (Benitez et al., 2000; Lachheb et al., 2002). The main characteristic of these systems is the generation of very reactive and oxidizing free radicals, especially hydroxyl radicals produced by combining ozone, hydrogen peroxide, UV radiation and Fenton reagent (Ledakowicz et al., 2001; Liu et al., 2013; Pera-Titus et al., 2004).

Photodegradation techniques are a significant part of the AOPs and, recently, excimer lamps or excilamps have been developed, as new UV sources based on transitions of exciplex (rare gas halides) or excimer molecules (rare gas or halogen dimmers). They have important advantages such as the emission in a narrow-band UV radiation, nearly monochromatic and matching the dissociation energies of the main organic compounds bonds, the absence of toxic mercury and long lifetime, among others (Lomaev et al., 2006; Sosnin et al., 2006).

Excilamps have been successfully used in the removal of different organic pollutants, mainly phenolic compounds (Gómez et al., 2010a, 2010b; Matafonova et al., 2008; Tchaikovskaya et al., 2012), although recently some preliminary studies on their application for the removal of dyes have been performed. In this way, degradation of methyl green and congo red was tested in discontinuous reactors using KrCl, XeBr and Cl_2 excilamps (Gómez et al., 2011; Murcia et al., 2011), obtaining the best results with the KrCl excilamp for both dyes. In addition, a pseudo first order kinetic model was proposed and validated, but some of the results obtained in the fitting of the model to the experimental data, such as the presence of a residual concentration of substrate in the kinetic law, initially justified by the shielding effect, and the dependence of the pseudo-first order kinetic parameter on the initial concentration, were not well supported by the model. Several authors have also proposed a pseudo-first order kinetic for the photodegradation of methylene blue (Banat et al., 2005; Zhang et al., 2013). However, the influence of the dye initial concentration remains unclear and does not agree with the mentioned kinetic.

In the present work, and based on the good results previously obtained with the KrCl excilamp, the same excimer molecules have been used but with a different reactor configuration: a flow-through photoreactor, previously tested for 4-chlorophenol degradation (Gomez et al., 2012), which allows the treatment of higher sample volumes as a first step towards continuous processes. Also, a new and more detailed kinetic model has been developed. The model assumes mass transfer of methylene blue from the bulk solution to the wall of the photoreactor as the step determining the rate of the photodegradation process, which explains the existence of a limit concentration of MB not degraded after long time of phototreatment. Also, a density of the radiation intensity per mass unit is defined in the model, which explains the dependence of the kinetic parameter on initial substrate concentration. Methylene blue has been selected as a model dye both to study the experimental conditions leading to efficient degradation and to check the proposed kinetic model.

2. Materials and methods

2.1. Reagents and materials

The main chemicals and reagents, methylene blue (95%) and hydrogen peroxide (35%), were obtained from Sigma–Aldrich. $FeSO_4$ was purchased from Probus. Other chemicals were of analytical grade and were used without further purification.

All experiments have been carried out using a KrCl photoreactor, purchased from the Institute of High Current Electronics of Tomsk (Russia). The lamp has a wavelength of maximum emission at 222 nm and an average radiation intensity of 2.38 mW cm^{-2}, as previously described (Batalova et al., 2003; Gomez et al., 2012).

An ultraviolet/visible Shimadzu spectrophotometer, model UV-160, was used to measure the decreasing of methylene blue concentration along time. In addition, COD was also analyzed with specific equipment consisting of reactor and photometer, model HI 938800 and model 83,099, respectively, from HANNA Instruments.

2.2. Experimental and analytical methods

Methylene blue was pumped from a stirred feed tank to the photoreactor and the effluent was continuously recycled to the tank, so that the system acts as a discontinuous batch reactor (flow-through reactor). In the UV/H_2O_2 and photo-Fenton assays hydrogen peroxide and $FeSO_4$ were added to the feed tank together with the dye at the required initial concentration.

All the experiments were done at room temperature (23–25 °C), with an operational time of 120 min (except for the last experimental series, of 60 min). Samples were taken at different reaction times (0, 2.5, 5, 10, 20, 40, 60, 90 and 120 min) from the feed tank. Fig. 1 shows a scheme of the system, including the main components and the nomenclature used in the present work. Duplicate experiments were carried out and average values were obtained. Standard deviation calculated for the whole set of data was 1.95%.

The following operational variables were studied: H_2O_2:MB mass ratio; flow rate (with the variation of the rotational speed of the pump, flow rate (ml/min) = 2.3039 × rotational speed (rpm), R^2 = 0.9975); initial MB concentration; sample volume and Fe^{2+} concentration.

Samples were analyzed by spectrophotometry at the wavelength of maximum absorption of the dye, 660 nm. The corresponding calibration curve was done, being the obtained equation: [MB] (mg/l) = Absorbance/0.1996 (R^2 = 0.9917). Additionally, COD determination was done for several assays corresponding to the first experimental series.

3. Kinetic model

In the development of a kinetic model for the photodegradation process, the configuration of the reaction system shown in Fig. 1 as well as the following experimental behaviour observed in the photodegradation of the substrate type used, MB, have been taken into account:

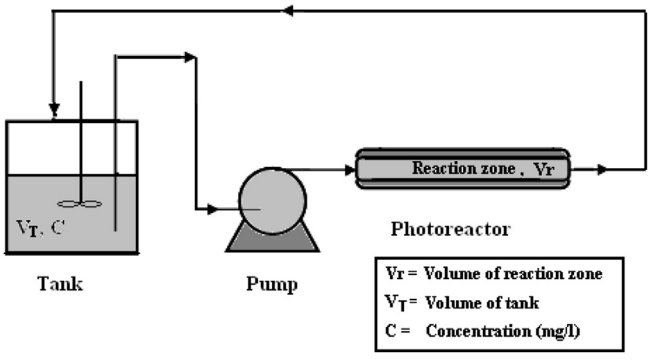

Fig. 1. Scheme of the experimental reaction system.