

Detoxification of diluted azo-dyes at biocompatible pH with the oxone/ Co^{2+} reagent in dark and light processes

Yu Zhiyong^{a,b}, Liubov Kiwi-Minsker^a, Albert Renken^a, John Kiwi^{a,*}

^a *Laboratory of Chemical Reaction Engineering, Swiss Federal Institute of Technology (EPFL), Lausanne 1015, Switzerland*

^b *Department of Chemistry, Renmin University of China, Beijing 100872, China*

Received 5 January 2006; received in revised form 14 February 2006; accepted 15 February 2006

Available online 27 March 2006

Abstract

Accelerated bleaching and photobleaching of diluted solutions of Methyl Orange and other dyes occur only when Co^{2+} -ions are present in solution mediating oxone ($2\text{KHSO}_5 \cdot \text{KHSO}_4 \cdot \text{K}_2\text{SO}_4$) decomposition. The bleaching of Methyl Orange, Orange II and Methylene Blue dyes in dilute solutions (0.01 mM) proceeds within a few minutes and occurs at biocompatible pH leading to a decrease in the toxicity of the initial solution under simulated daylight radiation. A reduction in the toxicity of 35% was observed at biocompatible pH-values when a solution Orange II (0.01 mM) was irradiated in the presence of oxone (0.06 mM)/ Co^{2+} (0.004 mM). Only traces of Co^{2+} were necessary to accelerate the decomposition of the dyes in the presence of oxone in the dark and even more under daylight irradiation. The photobleaching proceeds with a photonic efficiency of ~ 0.24 . The solution parameters were optimized for the photobleaching of azo-dyes by the oxone/ Co^{2+} reagent. H_2O_2 generation was observed to be possible only as long as Orange II was present in the solution. The decomposition kinetics of H_2O_2 was followed under solar radiation. The dye decomposition was also investigated as a function of the applied light intensity. No saturation effects were observed when simulated solar light with 90% AM1 was applied. The photobleaching reaction proceeded with acceptable kinetics with light intensities 5–10 times lower than AM1. This makes the photocatalytic treatment suitable under diffuse daylight.

© 2006 Elsevier B.V. All rights reserved.

Keywords: Bleaching; Photobleaching; Azo dye; Methylene Blue; Oxone; Co^{2+} ; Toxicity reduction; Photocatalysis

1. Introduction

Dyes and organic compounds decomposition in waste water effluents by Advanced Oxidation Technologies has become an important subject of research during the last decade [1]. This subject has actively been the focus of research out of many laboratories and practical solutions for industrial processes able to sustain long-term efficient operation have to be found [2].

The objective of this study is to explore, optimize, and test the experimental parameters for the oxone/ Co^{2+} reagent that allows the degradation of commercial textile dyes at a low concentration. By this approach, no costly pH adjustment is needed before or after the photocatalytic pre-treatment. The detoxification introduced by the dyes and the catalytic reagent will be assessed by a routine method used in toxicological studies. Recently, light enhanced homogeneous Fenton systems have

been widely reported. But either initial acidification of polluted wastewaters and post-neutralization of the iron species precipitation was necessary in Fenton systems. This is costly in terms of time, chemical reagents and labor.

The catalytic decomposition of oxone by Mn^{2+} and Cu^{2+} -ions [3] and also in the presence of Co^{2+} -ions have been known for some time [4–6]. The present investigation addresses the kinetics of the photobleaching of azo dyes diluted solution. The observed kinetics was drastically accelerated when Co^{2+} -ions mediate the photocatalysis under daylight irradiation. In the presence of Co^{2+} -ions, oxone has been reported [5–7,9] to generate a variety of highly oxidative sulphate radicals in aqueous solution.

Oxone is an oxidant used in organic synthesis, analytical chemistry, catalysis and degradation of organic pollutants [3–9]. The redox potential of the radical generated by oxone [5,10,11], $\text{HSO}_5^- \rightarrow \text{HO}^\bullet + \text{SO}_4^{\bullet-}$, $E^0 = 1.82 \text{ eV}$ is higher than the potential of the radicals generated by H_2O_2 ($\text{H}_2\text{O}_2 \rightarrow 2\text{HO}^\bullet$, $E^0 = 1.76 \text{ eV}$) when used as the oxidant in dark or in the light activated decomposition of dyes and organic compounds.

* Corresponding author. Tel.: +41 21 801 7536; fax: +41 21 693 3190.
E-mail address: john.kiwi@epfl.ch (J. Kiwi).

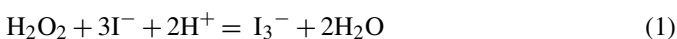
2. Experimental

2.1. Materials

Methyl Orange, Orange II, Methylene Blue, oxone (2KHSO₅·KHSO₄·K₂SO₄), CoSO₄·7H₂O, NaOH and KI were Fluka products and used as received. Solutions were prepared by dissolving in Milli-Q water.

2.2. Bleaching reactions and analytical methods

Solutions were prepared by mixing appropriate concentration of the appropriate dye, Co²⁺, and oxone in this sequential order. The dye bleaching reactions were followed by measuring the optical density at the peak of Methyl Orange, Orange II and Methylene Blue absorption bands at λ = 465, 486 and 665 nm, respectively in a Hewlett-Packard 38620N diode array spectrophotometer. The pH-values were measured by pH meter Copenhagen 701. H₂O₂ concentration was measured using the colorimetric method developed by Hochanadel [13,14]. The iodide-ion was oxidized in neutral or slightly acidic solution and the absorption of I₃⁻ was measured at λ = 354 nm. The iodide reagent was prepared immediately before using by mixing equal volumes of two solutions containing: (a) 66 g KI, 2 g NaOH and 0.4 g (NH₄)₆Mo₇O₂₄·4H₂O/l with (b) 20 g KHC₈H₄O₄/l. A measured volume of the sample was diluted to a specified volume with distilled water and the reagent used. The optical densities for sample and blank were measured following the I₃⁻ absorption peak with ε = 26,000 M⁻¹ cm⁻¹ (354 nm). The iodide reacts in a 3:1 ratio with H₂O₂ according to the relation



The Merckoquant (Merck AG) test for quantitative determination of peroxides was used as a second method to confirm the results obtained by the iodometric test.

2.3. Irradiation procedures

The photochemical reactor consisted of 80 ml cylindrical Pyrex flask each containing 60 ml of solution. Irradiation of the cylindrical reactor were carried out in the cavity of a Suntest solar simulator (Hanau, Germany) air cooled at 45 °C. The Suntest lamp emitted 5–6% of the photons between 290 and 400 nm. The profile of the photons emitted between 400 and 800 nm followed the solar spectrum with a light intensity at 70 mW/cm² corresponding to 70% of AM1 full solar light intensity. The radiant flux was monitored by an ISI Corporation power meter of Yellow Springs, Co., USA.

2.4. Toxicity determination via the *Vibrio fischeri* bio-assay

The effect of Orange II and the intermediates produced in the solution during the photocatalytic pre-treatment on the luminescence of the bacterium *Vibrio fischeri* (Microtox test) was carried according to AFNOR NFT 90-320 (Fluorescence Test in Bacteria, German Din-Norms 38412 (L 34) 1991). Essentially, this test measures the luminescence inhibition of *Vibrio fischeri*.

The concentration that inhibits 50% of the bacterial luminescence is expressed as CE₅₀ and this value is converted in (units of toxicity) by the expression UT₅₀ = 100/CE₅₀. These toxicity units are dimensionless and always take into consideration the value of the control sample. The control sample was the growth medium of *Vibrio fischeri*. During the pre-treatment of the dye Orange II, the residual H₂O₂ produced in solution was eliminated by the addition of peroxidase. The initial pH for the five samples pre-treated at different times for the toxicology determination was adjusted to 6.5 by a solution of NaOH (0.1 M) before the carrying out the Microtox test. The measurements were carried out in a salt solution (2% NaCl) since the bacteria used is of marine origin.

3. Results and discussion

3.1. Effect of Co²⁺ and oxone concentration on the bleaching and photobleaching of Methyl Orange

Fig. 1A shows the bleaching (dark process) of diluted Methyl Orange (0.01 mM) in the presence of oxone (0.06 mM) as a function of the increasing concentration of Co²⁺-ion. The bleaching increases with the concentration of Co²⁺-ion added up to trace (f) for the highest Co²⁺ concentration added in solution. The control experiment in Fig. 1A (trace a) indicates that no Methyl Orange bleaching takes place in the absence of oxone. Fig. 1A also shows that the bleaching of Methyl Orange dye in the presence of Co²⁺ was accelerated in relation to the bleaching observed when oxone was added in the absence of the Co²⁺ (Fig. 1A, trace b), the oxone decomposition becomes faster due to the added Co²⁺-ions as recently reported [7–9]. In the case of relatively concentrated solutions of dyes and oxone [9], the solutions contained about 20 times higher concentrations of azo dye and about 100 times higher concentration of oxone in relation to Co²⁺-ion concentration. The initial pH dropped from pH 5.9 to about 2 upon oxone addition. In the present study by using much lower concentrations of Methyl Orange and oxone (Fig. 1A), the pH of the solution did not change with respect to the initial pH of 4.3 after the bleaching process (Fig. 1A, traces b–f). This makes possible to carry out the azo dye bleaching using the oxone/Co²⁺ reagent at biocompatible pH values as it will be shown in later sections of this study. Doubling the concentration of oxone (0.06 mM) did not accelerate of the photobleaching kinetics of Methyl Orange.

Fig. 1B shows the bleaching of Methyl Orange under the same experimental conditions as used in Fig. 1A, but at an initial pH of 10.5. This pH was observed to remain constant during the bleaching process. The bleaching kinetics and efficiency was observed to be lower than the one observed in Fig. 1A, but Methyl Orange bleaching increased as a higher concentration of Co²⁺-ions were added to the solution.

Fig. 1C shows the photobleaching (Suntest light, 70 mW/cm²) of diluted of Methyl Orange (0.01 mM) in the presence of oxone (0.06 mM) as a function of increasing concentration of Co²⁺-ion. The results show that the photobleaching kinetics is considerably enhanced with respect to the bleaching kinetics reported in Fig. 1a. Nevertheless the TOC

Download English Version:

<https://daneshyari.com/en/article/68977>

Download Persian Version:

<https://daneshyari.com/article/68977>

[Daneshyari.com](https://daneshyari.com)