Chemical Engineering Journal 255 (2014) 553–567

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

# Ozone oxidation kinetics of Reactive Blue 19 anthraquinone dye in a tubular *in situ* ozone generator and reactor: Modeling and sensitivity analyses

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## HIGHLIGHTS

- Modeling of ozone absorption and reaction in an *in situ* ozone generator and reactor.
- Reaction kinetics and stoichiometry of primary and secondary product formation represented well.
- Second order reaction rate constants are invariant with initial dye concentration.
- Absorption and reaction model predict extents of reaction in the liquid film and the bulk liquid.

## ARTICLE INFO

*Article history:*
Received 27 January 2014
Received in revised form 8 June 2014
Accepted 16 June 2014
Available online 27 June 2014

*Keywords:*
Ozonation
*In situ* reactor
Absorption and reaction
Dye

## ABSTRACT

The absorption of ozone and reaction with a high molecular weight anthraquinone dye was studied in a tubular *in situ* ozone generator and reactor. In this reactor, ozone is generated around the periphery of the porous tubular reactor by corona discharge, and the generated ozone migrates through the pores and reacts with the contaminated fluid flowing in the tubular electrode. Dye oxidation was modeled to account for dye decolorization reaction with molecular ozone in the hydrodynamic film and bulk liquid. A parallel second order reaction stoichiometry was used to represent reaction of ozone with the dye to form primary and secondary products. The model developed represents physical phenomena well, as indicated by the good match between model predictions and experimental data. The reaction rate constants estimated from the model are invariant with initial dye concentration. Moreover, the model can predict the extent of reaction in the film and the bulk liquid based on input parameters.



## 1. Introduction

There has been a rapid growth in industrial production worldwide in recent years and concomitant increase in generation of waste streams that is impacting the environment and human health. The appearance of recalcitrant compounds that are toxic, mutagenic, carcinogenic or endocrine disrupting in water supplies has created a need for improvements in existing technologies, and the development of new technologies to contain this problem. Many dyes, pharmaceutical products, drugs, hormones and synthetic organic chemicals are not captured by current waste treatment processes and are discharged to receiving waters. Compounds such as 17β-estradiol, estrone, bisphenol A, and metabolites of alkyl phenol polyethoxylates are present in ng/L to μg/L concentrations in receiving waters and disrupt endocrine functions of aquatic organisms [1,2]. As a result, there is increased impetus to improve existing technologies, and to develop new technologies that provide effective treatment of wastewaters at affordable costs. New oxidation techniques using ozone, supercritical water, UV photons, ultrasound irradiation, electron beam irradiation, and non-thermal plasmas are being developed or improved upon to address this problem [3]. Among these oxidation techniques, ozone has been gaining popularity as an oxidant by itself or in combination with hydrogen peroxide or UV to produce hydroxyl radicals for oxidation of recalcitrant organics and the disinfection of water supplies. The oxidation potential of ozone is 1.5 times that of chlorine, and it does not generate chlorinated disinfection byproducts that are carcinogenic. Hence, the potential for use of ozone oxidation technology is high due to its high technical feasibility. However, the widespread use of ozone in water and wastewater treatment

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http://dx.doi.org/10.1016/j.cej.2014.06.071
1385-8947/

**Nomenclature**

| | |
|---|---|
| $a$ | specific interfacial area ($m^2/m^3$) |
| $C$ | concentration of substances in liquid (mg/L) |
| $D$ | diffusivity in the liquid ($m^2/s$) |
| $E_{inst}$ | instantaneous enhancement factor |
| $E$ | enhancement factor |
| $G$ | concentration of ozone in gas phase (mg $L^{-1}$) |
| $Ha$ | Hatta number |
| k | reaction rate constant |
| $k_d$ | ozone decomposition rate constant in liquid phase ($L^{m-1}$ $mg^{1-m}$ $s^{-1}$) |
| $k_1$ | reaction rate constant for reaction of ozone with dye (L/mg s) |
| $k_2$ | reaction rate constant for reaction of ozone with byproducts (L/mg s) |
| $K_La$ | overall mass transfer coefficient ($s^{-1}$) |
| $k_L$ | liquid film mass transfer coefficient (m/s) |
| $m$ | reaction order for ozone decomposition in liquid phase |
| $n$ | number of reactors in reactors in series model in *in situ* reactor |
| $q_i$ | feed gas flow rate to *i*th reactor in *in situ* reactor model (L/s) |
| $Q$ | volumetric flow rate (L/s) |
| $r$ | rate of absorption (mg/L s) |
| $V$ | volume (L) |
| $x$ | distance in the liquid from the gas–liquid interface (m) |
| $z_1$ | stoichiometric factor for dye and ozone reaction |
| $z_2$ | stoichiometric factor for dye and byproducts |
| $z_3$ | stoichiometric factor for byproducts and ozone reaction |
| $z_4$ | stoichiometric factor for product formation from byproducts |

*Greek letters*

| | |
|---|---|
| $\varepsilon$ | holdup (dimensionless) |
| $\alpha$ | partition coefficient for ozone (dimensionless) |

*Subscripts*

| | |
|---|---|
| *A* | ozone |
| *abs* | absorption |
| *B* | dye |
| *b* | bulk |
| *exp* | experiment |
| *g* | gas |
| *hs* | headspace |
| *i* | reactors in the ozonation model for *in situ* reactor |
| *in* | ozone generation into the reactor |
| *l* | liquid |
| *mod* | model |
| *o* | off-gas |
| *P1* | primary products of ozonation |
| *P2* | secondary products of ozonation |
| *R* | reactor |
| *U* | recirculation unit |
| *ss* | steady state |

*Superscripts*

| | |
|---|---|
| $*$ | equilibrium ozone concentration in liquid |

applications is limited at present due to the relatively high cost of ozonation. This is in part due to mass transfer limitations stemming from the low solubility of ozone, and improper choice of contactors without consideration of the operative reaction regime.

Ozone is typically produced in bulk through high voltage electrical discharge across a thin gap of dry air or oxygen. Conventional ozonators are typically of bubble column design, and the generated ozone is transported through ozone resistant pipes and bubbled into the bulk liquid. If deep tanks are not used, there will be substantial loss of ozone to the gas phase, and this ozone must be destroyed before the exhaust gas can be vented. The electrical corona discharge process can generate in addition to ozone, other short-lived species such as OH radical, $OH^+$ ion, atomic hydrogen, electrons, and oxygen atomic radicals [3–5]. The generation of these species depends upon the reactor configuration and the voltage used. These reactive species can enhance oxidation rates if they can react with contaminants in the fluid before decay. Several different designs have been reported in the literature attempting to generate ozone *in situ* to utilize the reactive species to enhance oxidation rates [4–6]. These are studies mainly aimed at evaluating the effectiveness of the active species formed near the corona in the oxidation of organic compounds. It may be noted that the ozonator design and gas flow pattern affects the transfer and availability of these species for reaction with organics. So an efficient reactor design must provide a high mass transfer rate of ozone from gas to liquid phase, immediate reaction of any short-lived species on generation, and feasibility for practical application in water and wastewater treatment with reduced cost. These aspects were considered in this research to develop an *in situ* ozone reactor system.

The *in situ* reactor design developed in this research utilizes a porous ceramic tubular electrode around the periphery of which ozone is generated by corona discharge. The generated ozone and reactive species migrate through the pores of the electrode and react with the contaminants in the fluid flowing inside the tubular electrode. Panda and Mathews [7] have reported on the enhanced mass transfer obtained using this system. The voltage used in this study is not sufficiently high to generate significant quantities of reactive species. The goal of this paper is to examine the kinetics of oxidation of a high molecular weight organic compound (Reactive Blue 19 dye) using the porous electrode ozonator, and to present modeling and sensitivity analysis data pertaining to absorption and reaction in the *in situ* porous electrode ozonator.

## 2. Materials and methods

### 2.1. Materials

Ultra high purity oxygen (minimum purity of 99.994%, OX UHP 300+) was obtained from Airgas Inc., (Radner, PA), for use in the production of ozone. Reactive Blue 19 (RB-19) dye (Remazol Brilliant Blue R) was obtained from Sigma–Aldrich Company (St. Louis, MO), and used without purification. The dye solution was prepared in distilled water and the pH was adjusted to 2 using sulfuric acid. A schematic of the *in situ* ozone generator–reactor system is shown in Fig. 1. Ozone is generated around the periphery of the electrode by high voltage discharge, and the ozone and reactive species diffuse immediately and react with the contaminants flowing inside the porous electrode. Fabrication details of the laboratory unit have been reported elsewhere [7]. The electrical circuitry was designed