

Catalytic ozonation with non-polar bonded alumina phases for treatment of aqueous dye solutions in a semi-batch reactor

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Abstract

Semi-batch experiments were conducted to investigate the effects of catalyst type, pH, initial dye concentration and production rate of ozone on the catalytic ozonation of the dyes, namely Acid Red-151 (AR-151) and Remazol Brilliant Blue R (RBBR). The used catalysts were alumina, 25% (w/w) perfluorooctyl alumina (PFOA), 50% (w/w) PFOA and 100% (w/w) PFOA. The results showed that the overall percent dye removal after 30 min of the reaction was not affected significantly by the catalyst type. However, highest COD reduction was achieved by ozonation with alumina for AR-151, and 100% PFOA for RBBR at pH 13. The behavior of COD reduction with the increasing amount of perfluorooctanoic (PFO) acid amount can be explained by the enhancement of catalytic activity of PFOA with alkyl chains. For both of the dyes, the highest dye and COD removals were reached at pH 13. The overall dye reduction after 30 min of ozonation was almost independent of the initial dye concentration at relatively low values while at the higher concentrations, it changed with the initial dye concentration for both of the dyes. Similarly, COD reduction changed on a limited scale with the increasing initial dye concentration from 100 mg/L to 200 mg/L; however, an increase of initial dye concentration to 400 mg/L decreased the COD reduction significantly. All the studied production rates of ozone were sufficient to provide almost 100% dye removal in 30 min, whereas the COD removal percentage was increased gradually by the increasing ozone input to the reactor. The reaction kinetics for the ozonation of each dye with and without catalyst was investigated and discussed in the paper.

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1. Introduction

In water treatment, ozonation is a widely used method to remove organics from wastewaters (WWs), especially the colored substances. Textile WWs containing a high concentration of dyes can be efficiently treated by ozone giving 90% or higher color removals. However, chemical oxygen demand (COD) removal cannot be achieved at high levels, it is limited to around 50% [1–3]. The reason of low COD removal is due to the incomplete mineralization of organics to carbon dioxide and water by sole ozonation, since some of the ozonation by-products show resistance to further oxidation.

In the recent years, new advanced oxidation techniques have been searched to overcome the limitations of sole ozonation and to use ozone more effectively. Among them, catalytic ozonation has become a promising method. Many studies have been made for the catalytic ozonation of organics in a homogeneous

or heterogeneous phase with several different catalysts [4–10]. In the literature, alumina was shown to be an effective catalyst and support in the removal of organics by ozonation. Catalytic ozonation using metal ions (Fe_2O_3 , TiO_2) impregnated on alumina (Al_2O_3) provided higher removals of both target organic and also DOC–TOC than those achieved by sole ozonation. Cooper and Burch [7] found oxalic acid degradation to be 85%, 88%, 87% in catalytic ozonation with Al_2O_3 , $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$, $\text{TiO}_2/\text{Al}_2\text{O}_3$, respectively. At the same conditions, the target acid removal was only 15% by ozone alone. Similarly, Ernst et al. [6] investigated the catalyst effect on the ozonation of oxalic, succinic and salicylic acids by using Al_2O_3 . In non-buffered conditions, the initial DOC was reduced by 90% in catalytic ozonation compared to 20% in ozonation alone.

Efficient two-phase ozonation has been provided by the immobilization of perfluorinated hydrocarbons on the surface of alumina so as to avoid the dissolution of perfluorinated molecules into the aqueous phase [11]. This innovative method involves the liquid–liquid extraction of organic substances from the aqueous phase into the organic phase and subsequent oxidation by molecular ozone dissolved in the organic phase

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Nomenclature

A_{BET}	BET area of the catalyst in Table 1 (m^2/g)
AR-151	Acid Red-151
$C_{\text{d,i}}$	initial dye concentration (mg/L)
$C_{\text{O}_3,\text{s}}$	equilibrium O_3 concentration in solution (mg/L)
COD	chemical oxygen demand (mg/L)
D_{pore}	pore diameter of the catalyst in Table 1 (\AA)
DOC	dissolved organic carbon (mg/L)
m_{cat}	Catalyst dose (g)
m_{PFOA}	PFOA dose (g)
PFO acid	perfluorooctanoic acid
PFOA	perfluorooctyl alumina
pH_{PZC}	the pH of “point of zero charge” of the catalyst
PR_{O_3}	production rate of ozone (g/h)
PZC	point of zero charge
Q_{G}	gas volumetric flow rate (L/h)
RBBR	Remazol Brilliant Blue R
S_{BET}	catalyst surface area (m^2/g)
t	time (min)
T	temperature ($^{\circ}\text{C}$)
TOC	total organic carbon (mg/L)
V_{T}	total pore volume in Table 1 (cm^3/g)

Greek letter

ρ_{p}	particle density (kg/m^3)
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(non-polar perfluorinated hydrocarbon solvent saturated with ozone) [11]. It was found that ozone solubility in fluorinated hydrocarbon solvents was 10 times higher than that in water. Non-polar perfluorinated alkyl chains on the alumina surface were very active towards ozone and organics. Accordingly, ozone and organic matter reacted on the surface of hydrocarbon fixed alumina. The most preferred perfluorinated hydrocarbons were perfluorooctanoic (PFO) and perfluorooctadecanoic (PFOD) acids; especially the prepared perfluorooctyl alumina (PFOA) using PFO acid was observed to increase the stability of ozone in perfluorinated solvent [4].

Kasprzyk-Hordern et al. [4,12] used PFOA in the ozonation of humic acid and natural organic matter (NOM). They found that ozonation with PFOA was more effective than ozonation alone for both of the organics. Also, TOC analysis showed that degradation of NOM in aqueous phase was mainly due to PFOA/ O_3 system. The same researchers in another study [5] conducted ozonation for the removal of several ethers with PFOA. They observed no improvement of ether removal with alumina. In the case of PFOA, it was shown that the catalytic activity of PFOA depended on the alkyl chains on the alumina. The presence of more PFO acid on the surface created longer alkyl chains making PFOA more active. The hydrophobicity of the surface enhanced the adsorption capacity of PFOA.

The cost effectiveness of two-phase catalytic ozonation (PFOA/ O_3 system) can be emphasized with the high adsorption capacity of bare alumina toward anionic perfluorinated surfactants from water [13]; thus, the bare alumina usage in the

removal of perfluorinated surfactants from water can be considered as profitable because of the further possible application of the formed perfluorinated alumina as a catalyst in the ozonation process. Also FT-IR studies proved that ozone did not deactivate the catalyst [4]. Therefore, the aim of this study is to investigate the two-phase catalytic ozonation process using alumina and different types of PFOA as the catalysts in the degradation of Acid Red-151 and Remazol Brilliant Blue R, by determining dye and COD removals and the reaction kinetics at different operating conditions, the experimental parameters being pH, initial dye concentration ($C_{\text{d,i}}$), and production rate of ozone (PR_{O_3}).

2. Experimental

2.1. Materials

Acid Red-151 (AR-151) and Remazol Brilliant Blue R (RBBR) are the dyes used in the sole ozonation and catalytic ozonation experiments. AR-151 was purchased from Aldrich Chemical Company (Milwaukee, USA), whereas Acros Organics (New Jersey, USA) was the supplier of the RBBR. The structures of the dyes are shown in Fig. 1. AR-151 is an azo dye containing two azo groups with a maximum wavelength of 512 nm. RBBR has no azo group but one hydrocarbonated sulphonate group. It is an anthraquinone dye with a maximum wavelength of 591 nm. All other chemicals used were reagent grade and were supplied by Aldrich Chemical Company or Acros Organics.

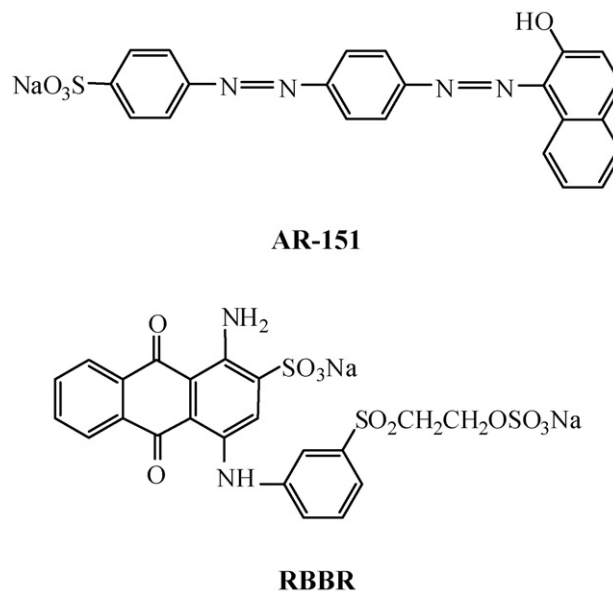


Fig. 1. The structures of the dyes used in the experiments.

2.2. Preparation and characterization of the catalysts

For the experiments, alumina particles (Damla Kimya Ltd., Ankara) were used as a catalyst and also as a support for PFO acid. The screen analysis of these particles composed of active γ -alumina was carried out, thus the appropriate sized particles of

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