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Catalytic ozonation of an industrial textile wastewater in a heterogeneous continuous reactor

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ABSTRACT

Textile wastewaters (WWs) are highly colored and non-biodegradable having variable compositions of colored dyes, surfactants and toxic chemicals. Discharge of these WWs to the environment is very detrimental for ecosystems, therefore new methods have been investigated in order to meet the quality criteria of water and the discharge standards of the partly treated WWs. Recently, catalytic ozonation being one of the advanced oxidation processes (AOPs), is considered as an effective method that can be used in the treatment of industrial WWs. In this study, catalytic ozonation of industrial textile WW obtained from AKSA Textile Plant in Yalova/Turkey has been examined in a three phase reactor where the solid catalyst phase was fluidized at different experimental conditions. The effects of inlet chemical oxygen demand (COD) value, pH, different catalyst types [perfluorooctylalumina (PFOA) and alumina] and gas to liquid flow rate ratios (Q_G/Q_L) have been determined. Pseudo-first order degradation rate constants for the dyes in the real industrial textile WW were determined in terms of COD, by taking samples at different heights along the reactor during an experimental run at steady state. Moreover, "absorbance vs. concentration" calibration correlations were developed to estimate the concentrations of colored dyes in the sample. This provided the opportunity to measure the dye concentrations and estimate the percent removals of each dye in the samples, separately. Besides COD removals, also total organic carbon (TOC) removals and ozone consumptions were measured and discussed by comparing the results obtained in both sole and catalytic ozonation experiments.

Introduction

The textile WW resulting from different production steps in a textile plant, has different dye types and concentrations and includes harmful compounds that prevent or reduce the rate of self-purification processes in the environment. The industrial textile WW has a relatively low ratio between biological oxygen demand (BOD) and chemical oxygen demand (COD) which shows that the conventional biological treatment methods are not effective enough [1]. This high non-biodegradability of industrial textile WWs leads researchers to investigate other alternative methods such as adsorption, membrane processes, and chemical oxidation including ozonation, other advanced oxidation processes or chlorination [1,2].

Ozone as one of the most promising chemical oxidant is used for color removal from dyed WWs. During ozonation of a wastewater, ozone firstly attacks unsaturated bonds of chromophores providing the rapid removal of color [3]. Ozone can degrade complex organic molecules to smaller ones such as organic acids, aldehydes and ketones. This provides color removal; however, sole ozonation is not enough for complete removal of by-products. The difficulty of removing recalcitrant by-products, low ozone solubility and stability in water and high cost of ozone production bring the need for advanced oxidation processes (AOPs). Thus, higher TOC and COD reductions are possible due to the mineralization of by-products to water and CO_2. Some important AOPs can be listed as the use of ozone together with some chemicals or combination with UV radiation and some chemicals [O_3/H_2O_2, $O_3/H_2O_2/Fe^{2+}$ (Fenton's reagent), O_3/UV, H_2O_2/UV, O_3/H_2O_2/UV] and catalytic ozonation [4]. One of the main purposes of the AOPs is the generation of hydroxyl radicals ($HO^{\bullet}$) which are more powerful and active than ozone. In this case, ozone can decompose into these species which provide higher oxidation potential for organic pollutants and their by-products. Although generation of powerful oxidants seems to be the solution to by-products removals from WWs, non-selective $HO^{\bullet}$ can be scavenged by other species that can be present in WWs and this may decrease the selectivity of the oxidation reaction against the target organic pollutants [3,4]. New studies are needed on ozonation systems to

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Nomenclature

AOP	Advanced oxidation processes
BB 41	Basic Blue 41
BOD	Biological oxygen demand (mg O_2/L)
BR 18.1	Basic Red 18.1
BY 28	Basic Yellow 28
$C_{d,in}$	Inlet concentration of dye (mg/L)
C_d	Dye concentration at any height (mg/L)
$C_{O3,in}$	Inlet concentration of ozone (mmol/L gas)
$Cons_{O3}$	Ozone consumption per liter of liquid (mmol/L liq.)
COD	Chemical oxygen demand (mg O_2/L)
COD	Chemical oxygen demand at any height (mg O_2/L)
COD_{in}	Inlet chemical oxygen demand (mg O_2/L)
DL	Axial dispersion coefficient for liquid phase, m^2/s
H_E	Expanded bed height (cm)
H_S	Static bed height (cm)
WW	Wastewater
k	Overall reaction kinetic constant in terms of COD removal (1/(mM min))
k'	Pseudo first order reaction rate constant in terms of COD removal (1/min)
k_1	Overall reaction kinetic constant (1/(mM min))
k'_1	Pseudo first order reaction rate constant (1/min)
k_La	Volumetric mass transfer coefficient in liquid film (1/s)
PFOA	Perfluorooctylalumina
Q_G	Gas flow rate (L/h)
Q_L	Liquid flow rate (L/h)
TOC	Total organic carbon (mg C/L)
TSS	Total suspended solids (mg/L)
WW	Wastewater

Greek Letters

τ	Residence time (min)
λ_{max}	Maximum absorbance wavelength (nm)

enhance the ozone solubility and stability in the reaction media. Catalytic ozonation on metals and metal oxides which is generally known as one of the AOP methods is usually based on ozone decomposition and radical formation. On the other hand, solid–liquid ozonation systems carried out in the presence of non-polar heterogeneous catalysts, such as perfluorinated alumina bonded phases involve the liquid–liquid extraction of organic substances from the aqueous phase into the organic phase and subsequent oxidation by molecular ozone dissolved in this organic phase (non-polar perfluorinated hydrocarbon solvent saturated with ozone) [5–7].

Although ozonation or catalytic ozonation has been widely used in the degradation of many organic/toxic pollutants as a single or as a mixture of pollutants mostly in batch, semi-batch and fixed-bed reactors [8], the studies in continuous flow reactors or in fluidized beds are limited. Wijannarong et al. [8] studied the ozonation of a wastewater containing reactive dyes in a batch reactor. Decolorization experiments showed that the color of wastewater was reduced when the reaction time increased. At reaction times 5 and 120 min, decolorization efficiencies were 32.83% and 56.82%, respectively. Abdul Aziz et al. [9] reported that there was a continuous need to develop alternative treatment methods to replace conventional processes for textile wastewaters. They compared the performance of different oxidizing agents and concluded that ozone, sulphate radicals, and permanganate could be employed as alternatives for textile wastewater treatment, but selection of the oxidizing agents should be based on economic optimization and the characterization of wastewater to be treated. Gupta et al. [10] conducted a review study from 1988 to 2015 to present the different diversified attempts, such as photodecolorization, combination of coagulation with catalytic oxidation, adsorption, photocatalysis etc., used for decolorization and degradation of a mixture of dyes, where the problem of dye removal becomes more difficult for effluents containing a dye matrix. As it can be seen from the critical review [10], there is a need for application of heterogeneous catalytic oxidation of industrial textile WWs in continuous flow reactors with different catalysts. Traditional water treatment facilities operate mostly based on biochemical treatment methods. This study presents a treatment method based on chemical treatment conducted in a fluidized bed with a novel catalyst. Fluidized bed reactors are not common equipments in water treatment plants although research on water treatment with fluidized bed reactors were carried out by researchers around the world. It is also worth to note that there are only a few studies in the literature related with dyed wastewater treatment using fluidized bed reactors [10,24,26]. Therefore to fill this gap in the literature, the treatment of real dyehouse effluents (from AKSA Textile Plant, Yalova/Turkey) in a continuous laboratory system at different operating conditions was considered to be worthwhile to investigate. The effects of inlet COD value, pH, different catalyst types (PFOA and alumina) and gas to liquid flow rate ratios (Q_G/Q_L) were determined. Dye removal kinetics in terms of COD removal was also studied. After estimating absorbance–concentration calibration correlations for the dye species present in the real industrial textile WW with an unknown composition, the amount of each dye in the samples and the individual dye removals could be estimated.

Experimental

Materials

Real industrial textile wastewater

The industrial textile wastewater was provided from AKSA Acrylic Plant which is established in Yalova/Turkey. AKSA now possesses the world's largest acrylic fiber production capacity. Characterization of the WW for its properties, namely COD, TOC and TSS amounts, color (how highly colored) and pH, was done. Also metal analysis was done in order to determine which metals were in the WW solution. Depending on the information obtained from AKSA Acrylic Plant, the WW sample contained three different cationic dyes which were blue, red and yellow in color, but their concentrations in the WW were not provided by the Company. The compositions of these dyes in their individually prepared solutions were [11]: (i) blue dye: CI Basic Blue 41 (BB 41), 40–50% with acetic acid 25–35%, (ii) yellow dye: CI Basic Yellow 28 (BY 28), 35–45% with acetic acid 20–30%, (iii) red dye: CI Basic Red 18.1 (BR 18.1), 35–45%, with acetic acid 20–24%, and caprolactam 3–7% [11].

For the simulation of this real WW, these three dyes (BB 41, BY 28 and BR 18.1) were obtained in the powder form from AKSA Acrylic Plant. These dyes are all in the cationic class with characteristic properties shown in Table 1.

Preparation of the catalysts

For the catalytic ozonation experiments, alumina particles supplied from Damla Kimya Ltd. (http://www.damlakimya.com) in Ankara/Turkey were used as a catalyst and also as a support for perfluorooctanoic (PFO) acid. The appropriately sized active γ-alumina particles between 2.4 and 3.3 mm were selected by the screen analysis. The perfluorooctylalumina (PFOA) catalyst was prepared by the impregnation of PFO acid (Aldrich Chemical Company, Milwaukee, USA) on selected sized alumina particles.

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