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Application of a planar falling film reactor for decomposition and mineralization of methylene blue in the aqueous media via ozonation, Fenton, photocatalysis and non-thermal plasma: A comparative study

Kosar Hikmat Hama Aziz[a,b,*], *Ali Mahyar*[a], *Hans Miessner*[a], *Siegfried Mueller*[a], *Dieter Kalass*[a], *Detlev Moeller*[a], *Ibrahim Khorshid*[b], *Muhammad Amin M. Rashid*[b]

[a] *Laboratory of Atmospheric Chemistry and Air Quality, Brandenburg University of Technology (BTU Cottbus-Senftenberg), Volmerstrasse 13, D-12489 Berlin, Germany*

[b] *Department of Chemistry, College of Science, University of Sulaimani, Qlyasan Street, Kurdistan Region, Iraq*

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ABSTRACT

The efficiencies of ozonation and different advanced oxidation processes (AOPs) including photocatalytic ozonation, Fenton, photo-Fenton, photocatalytic oxidation, UVA/TiO_2/H_2O_2, and non-thermal plasma generated by a dielectric barrier discharge (DBD) were compared in terms of the energy yield (G50) for decolorization of MB and total organic carbon (TOC) removal using a planar falling film reactor. Fenton oxidation and ozonation were found to be the most efficient methods for the decolorization of MB, although these techniques attained rather low mineralization. A combination treatment of the ozonation with the photocatalysis demonstrates a synergistic effect on the mineralization efficiency. The photocatalytic oxidation and UVA/TiO_2/H_2O_2 provide only a moderate MB decolorization. The degradation efficiency of the DBD plasma is significantly dependent on the composition of gas atmosphere. The addition of Fe^{2+} to the solution in the DBD plasma under argon atmosphere improves the degradation efficiency due to the occurrence of Fenton reaction. The energy yield for 50% conversion of MB is calculated between 0.13 and 20.5 g/kWh, and the maximum and minimum values were obtained by the ozonation and photocatalytic oxidation, respectively. Ozonation with the highest energy yield provided a moderate mineralization by only 19%, while the DBD plasma obtained the highest TOC removal by 88%.

1. Introduction

During the past decades, global concerns about discharging wastewaters from textile industries which usually contain a large amount of various dyes has been intensified (Khan and Malik, 2014). Dyes and pigments are widely used in various industries such as textile, leather, ceramic, cosmetic and food processing. Therefore, a significant amount of unfixed dyes are released into the environment as wastewater during synthesis and industrial processing, resulting in a trace amount of dispersed dyes that have been detected in rivers and sediments which can affect the aquatic life, minimizing the sunlight penetration into the stream and reducing photosynthetic process (Vacchi et al., 2016).

* *Corresponding author at*: Department of Chemistry, College of Science, University of Sulaimani, Qlyasan Street, Kurdistan Region, Iraq.
E-mail address: kosar.hamaaziz@univsul.edu.iq (K.H. Hama Aziz).

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Table 1 – Various AOPs reported for MB degradation.

Type of oxidation process	Conditions	Reference
Ozonation	Continuous reactor system.	Wu and Upreti (2015)
	Batch bubble column.	Turhan et al. (2012)
Fenton	Photo-Fenton and sono-photo-Fenton were compared.	Vaishnave et al. (2011)
	Under the exposure to UV or vacuum-UV in a micro photo-reactor.	Li et al. (2016)
	CdS/multi-walled carbon nanotube-TiO_2 under the visible light.	Kim and Kan (2015)
Photocatalysis	TiO_2/UV-based photocatalysis.	Houas et al. (2001)
	UVA/TiO_2 nanoparticle in a self-made photocatalytic reactor.	Dariani et al. (2016)
	Synthesized copper, zinc, tin, and sulfide nanoparticles under the visible light.	Phaltane et al. (2017)
	Photocatalysis using ZnO:Eu nanoparticles.	Trandafilović et al. (2017)
Non-thermal plasma	Liquid film over the inner electrode using DBD in cylindrical reactor.	Magureanu et al. (2008)
	Pulsed corona discharge in a multi wire plate geometry.	Magureanu et al. (2013)
	DBD plasma jet in air, nitrogen and argon gas atmospheres.	Chandana et al. (2015)
	Coaxial DC corona discharge in air, N_2, He and CO_2.	Liu et al. (2015)
	Double-chamber DBD reactor in air and oxygen carrier gases.	Wang et al. (2017)
	Microwave plasma jet at atmospheric pressure in argon.	García et al. (2017)

The majority of these dyes are chemically stable, less adapted to the biological treatment and are toxic to the environment due to their resistance to the aerobic degradation and formation of carcinogenic aromatic amines during the anaerobic degradation (Badr et al., 2008; Jiang et al., 2013). Therefore, decomposition and removal of these pollutants from wastewater is a necessary step before being discharged into the aquatic ecosystem.

Various treatment techniques including physical, biological, chemical and electrochemical methods as well as a combination of these techniques for removing organic dyes from wastewater have been reported and reviewed in the literature (Brillas and Martínez-Huitle, 2015; Dos Santos et al., 2007; Forgacs et al., 2004).

Biological treatment is commonly used for the removal of organic pollutants from textile wastewater. These methods are environmentally friendly, produce less sludge, and are relatively inexpensive (Kornaros and Lyberatos, 2006; Solís et al., 2012). However, application of these techniques may be limited by their needs for a large land area, very slow treatment process and the presence of recalcitrant toxic organic dyes. Physicochemical methods such as adsorption by activated carbon (Singh et al., 2003) and nanostructured porous metal-organic framework materials (Ayati et al., 2016), as well as various chemical methods such as ozonation (Tehrani-Bagha et al., 2010), UV assisted advanced oxidation (Grčić et al., 2014) and dielectric discharge in a falling liquid film (Dojčinović et al., 2011) are also widely used techniques for the removal of organic dyes from aqueous solution. Physiochemical techniques are able to remove organic pollutants from water and wastewater. However, these techniques are not effective methods for the decomposition of pollutants and therefore, a large amount of untreated sludge is produced. Hence, these treatment techniques only transfer pollutants from the aqueous phase to the solid adsorbent that cannot avoid the risk of contaminating the environment. Consequently, additional treatments such as filtration, reactivation of adsorbents, and decomposition of pollutants are required. Chemical oxidation processes such as ozonation are effective for the decolorization of organic dyes. However, the use of such oxidant is limited due to the formation of possibly toxic non-degradable by-products. Therefore, beside the decolorization of polluted water, it is important to mineralize by-products which can be generated during the treatment process, as some of those by-products might be more toxic and carcinogenic than the initial pollutant (Sweeney et al., 1994). Hence, it is necessary that the maximum degree of mineralization of wastewater to be achieved prior to being discharged into the aquatic ecosystem.

In order to overcome these limitations in one hand, and the need for environmentally friendly methods that would not produce residual toxic by-products on the other hand, advanced oxidation processes (AOPs) have been widely considered. AOPs are recognized as a powerful and effective methods for the degradation and mineralization of a wide range of recalcitrant organic contaminants in wastewater which cannot be eliminated by conventional treatment techniques. These methods involve the in-situ generation of active, unstable and non-selective oxidizing species like hydroxyl radicals ($^{\bullet}OH$) that can oxidize most of the persisted organic contaminants in polluted water (Andreozzi et al., 1999; Deng and Zhao, 2015; Oturan and Aaron, 2014).

Methylene blue (MB) is one of the most commonly colored compounds used during the dyeing process of cotton, wood and silk (El-Ashtoukhy and Fouad, 2015). Removing methylene blue from aqueous solution by ozonation and various AOPs was intensively investigated in the literature (Table 1).

Most studies have been focused on the application of one AOP using specific experimental setup and operational conditions; thus, the attained results of different studies may not be comparable. Therefore, the present study aims to compare the energy yields (at 50% decolorization) and efficiencies of the examined methods for total organic carbon (TOC) removal (degree of mineralization) from the aqueous solution of MB. To this end, different treatment methods for the degradation of MB as a model pollutant including ozonation (O_3), photocatalytic ozonation (UVA/TiO_2/O_3), photocatalytic oxidation (UVA/TiO_2/O_2), Fenton (H_2O_2/Fe^{2+}), photocatalytic-Fenton (UVA/TiO_2/H_2O_2/Fe^{2+}), hydrogen peroxide combined with photocatalysis (UVA/TiO_2/H_2O_2), and non-thermal plasma generated by the dielectric barrier discharge (DBD) under different gas atmospheres were investigated using a planar falling film reactor with a common design. The comparison also includes the efficiency of each tested method for destruction of acetate, oxalate and sulfate anionic by-products that are produced during the decomposition of MB.

2. Experimental

2.1. Materials

All the chemicals used for the analysis were analytical grade and utilized without further purification, as follows: methylene blue (C.I. 52015, Merck), oxalic acid (99.5%, Merck), sodium thiosulfate (>99%, Fluka), potassium nitrate (99%, Merck), iron(II) sulfate heptahydrate (≥90%, Sigma-Aldrich), ammonium sulfate (99.5%, Merck), sodium carbonate and bicarbonate (0.1 M, Fluka, for ion chromatography), potassium titanium oxide oxalate (≥99%, Sigma-Aldrich), hydrogen peroxide solution (30% GR, Merck), sulfuric acid (95–97%, Merck).

2.2. Falling film reactor and equipment

The planar falling film reactor with an approximately 10 L volume (66 × 29 × 5 cm) which is used in this work is shown in Fig. 1. The design of the reactors is based on our previous works (Aziz et al., 2017; Mahyar et al., 2017). The reactor consists of two Pilkington Activ^{TM} glass (PAG) sheets, each with the sur-