Water Research 98 (2016) 39–46

Contents lists available at ScienceDirect

Water Research

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

Efficiency comparison of ozonation, photolysis, photocatalysis and photoelectrocatalysis methods in real textile wastewater decolorization

Juliano Carvalho Cardoso*, Guilherme Garcia Bessegato, Maria Valnice Boldrin Zanoni

Department of Analytical Chemistry, Institute of Chemistry, Universidade Estadual Paulista "Júlio de Mesquita Filho" – UNESP, Av. Prof. Francisco Degni, 55, 14800-060, Araraquara, SP, Brazil

ARTICLE INFO

Article history:
Received 6 January 2016
Received in revised form
28 March 2016
Accepted 3 April 2016
Available online 5 April 2016

Keywords:
Annular bubble reactor
Photoelectrocatalysis
Ozonation
TiO_2 nanotube arrays
Textile effluent
Decolorization

ABSTRACT

Treatment of real effluents from industries using AOPs stands to be an imperative task of crucial importance yet quite huge a challenge largely given the nature of complexity of these wastewaters. The present work sought to develop a versatile system aimed at the treatment of real wastewater using a bubbling annular reactor, which enables us to test the efficiency of photolysis; photocatalysis, photoelectrocatalysis and direct ozonation using oxygen or ozone as gas flow. A TiO_2 nanotubes electrode was used as photocatalyst in photocatalytic and photoelectrocatalytic measurements with and without coupling with ozonation under pH 3.0 and pH 8.0 leading to 50% of color removal after 60 min reaction. However, the results indicated 90% of color removal upon the bubbling of ozone after 15 min of treatment. A synergistic effect was observed in all experiments using the AOPs in the presence of ozone under both pH values. Interestingly though, 85% of decolorization was obtained through direct ozonation without any change in the effluent following 10 min of treatment. The results were discussed in terms of electric energy per order and were compared to those reported previously. For real textile wastewater, ozonation appears to be a promising candidate for full-scale effluent decolorization.

1. Introduction

The last decades have witnessed a dramatic surge in interest in water and wastewater treatment as a way to protect the environment and human health. Nonetheless, in the last few years, huge attention has been given to the development, extension and advancement of new approaches, ideas or designs focusing on the efficiency enhancement of well-known technologies or reducing costs/other disadvantages by merging them with cheaper, sustainable and more environmentally friendly methods. The advanced oxidation processes (AOPs) being considered here are among the recent developments regarding water treatment with a wide range of application (Glaze et al., 1987).

One of the greatest challenges of this century lies in efficiency improvement of the treatment of dye wastewater from textile and dyestuff industries. About 200 L of water are used to produce 1 kg of textile (Ghaly et al., 2014), resulting in a high amount of high colored and often harmful waste (Alves de Lima et al., 2007). It is estimated that 280,000 t of textile dyes are discharged in such industrial effluents annually worldwide (Jin et al., 2007), with complex aromatic molecular structures which are very stable and highly difficult to biodegrade (Azbar et al., 2004; Saratale et al., 2011). In addition, other organic and inorganic chemical reagents are found to be used in the textile sector, with both direct and indirect toxic effects on humans (Bakshi and Sharma, 2003; Moawad et al., 2003; Sponza, n.d.). Consequently, methods that can be used for the treatment of these effluents have by and large drawn great interest due to strict environmental legislation and high cost of water. Although several methods have been proposed for color removal, it is noteworthy that most of them have presented some underlying disadvantages (Banat et al., 1996; Gogate and Pandit, 2004; Malpass et al., 2007; Robinson et al., 2001).

Physical methods which are known to be the most widely used tend to, nonetheless, result in the formation of solid waste that requires further treatment, examples of which include membrane filtration, coagulation/flocculation, precipitation, flotation and adsorption (Gogate and Pandit, 2004). Biological processes include aerobic, anaerobic, and combinations of the two that can be subdivided into suspended and attached growth systems (Banat et al.,

* Corresponding author.
E-mail address: jcarvalho82@gmail.com (J.C. Cardoso).

http://dx.doi.org/10.1016/j.watres.2016.04.004
0043-1354/

1996; Gogate and Pandit, 2004). These processes are generally slower, requiring large storage areas and usually exhibit low efficiencies when it comes to color removal (Malpass et al., 2007; Robinson et al., 2001). Chemical processes are generally simpler in application and most of them rely on the formation of an oxidizing agent such as H_2O_2, ·OH or O_3 (Gogate and Pandit, 2004).

It is undoubtedly fair to give the due merits to the meaningful contributions brought to the fore by a number of researchers through their studies vis-à-vis the combinations of ozone, oxygen, hydrogen peroxide, a wide range of homogenous and heterogeneous catalysts as well as (photo)catalysts in light/dark conditions for the oxidation of textile effluents (Azbar et al., 2004; Cardoso et al., 2015; Garcia et al., 2007; Gimeno et al., 2007; Gomes de Moraes et al., 2000; Poyatos et al., 2009; Santiago-Morales et al., 2012). These methodologies have been used for the treatment of contaminated water and wastewater to evaluate their capability in the decomposition of pollutants and to assess the treatment efficiencies of these combinations.

Ozone is a powerful oxidizing agent ($E^0 = 2.07$ V) with some applications in drinking water, swimming pools, industrial waters containing phenols and cyanides, among others (Hoigne, 1998). However, as ozone reacts selectively and slowly with organic compounds, it is sometimes combined with catalysts that can convert it into secondary oxidants, mainly to hydroxyl radicals known to be the most important and most reactive oxidants which are unselective by nature and capable of reacting with all types of solutes that can be subjected to oxidization (Hoigne, 1998). One of these combinations employs photoactivated semiconductors such as TiO_2, resulting in a new advanced oxidation method called photocatalytic ozonation (Agustina et al., 2005). In this process, besides the generation of ·OH radicals by the TiO_2 and the direct attack of ozone, the contaminant can be degraded by ·OH radicals produced in a sequence of reactions when O_3 captures an electron of TiO_2 conduction band. This process also minimizes the recombination of electron/hole pairs, improving the generation of hydroxyl radicals by oxidation through the holes at TiO_2 valence band. This combination (allied to the resulting synergistic effects) is seen as a promising technique for the decomposition of refractory microorganisms and organic compounds in water. Recently, it has been noted that the combination of photoelectrocatalysis and ozone could significantly enhance the efficiency observed in the photocatalytic ozonation once photoelectrocatalysis is said to be capable of improving charge separation of TiO_2 electron/hole pairs which consequently leads to more ·OH radicals (Bessegato et al., 2016).

The objective of this work is thus to design a versatile bubbling annular reactor operating with oxygen or ozone gases and a TiO_2 nanotubes electrode as catalyst aiming at promoting the total decolorization of real wastewater from textile industries. The assessment of its efficiency was made comparing the following methods: photolysis, photocatalysis and photoelectrocatalysis with oxygen and ozone bubbling, as well as direct ozonation. The extent of the apparent color removal was evaluated by Platinum Cobalt (Pt/Co) scale color measurements (also referred to as the Hazen scale or APHA color). The electric energy per order (E_{EO}) was calculated for the different processes in order to compare and evaluate the color removal efficiency. Lastly, the extent of color removal and E_{EO} are compared with the reported levels presented in the literature.

2. Experimental

2.1. Preparation of TiO_2 NTs

The TiO_2 nanotubes arrays were produced by electrochemical anodization in an electrolyte composed of glycerol (90%)/water (10%) in the presence of 0.25% NH_4F (Cardoso et al., 2010). Titanium pipes of 6 cm of diameter and 100 cm of length were firstly polished on different sandpapers and washed in isopropanol, acetone and deionized water for 10 times in each solvent, respectively. In sequence, this Ti pipe was inserted inside a PVC pipe of 10 cm of diameter and 110 cm of length and connected to a power supply as anode. In the center, a DSA electrode® (De Nora company) of 3 cm of width and 100 cm of length was positioned and connected as cathode. The system was filled up with the electrolyte and the anodization process was conducted for 50 h at 30 V using a Minipa MPL-1303 power supply. After this step, the sample was then washed in distilled water, dried in N_2 gas and annealed at 450 °C for 1 h under atmospheric condition.

2.2. Annular bubble reactor

A versatile reactor was developed for real wastewater treatment using a glass vessel connected to a PVC pipe of varying lengths allowing the increasing of the effluent volume. A pipe with 145 cm length and 10.2 cm of diameter was then used to treat 12 L of effluents for direct ozonation and 8.5 L for treatment under irradiation as a result of the volume occupied by the glass tube using 100 W UV-B lamp Lightech (315 nm and 0.128 mW cm^{-2}) inserted in the center of the reactor.

Four techniques were used to evaluate the performance of the reactor during the treatment among them including direct ozonation; photolysis; photocatalysis and photoelectrocatalysis, and their representative schemes have been depicted in Fig. 1. Gas diffusers were positioned at the bottom of the glass base to generate small bubbles. Four gas diffusers were as such necessary to obtain a complete mix and homogeneity besides the improvement of mass transport and the hydrodynamics of the reactor.

2.3. Ozone and oxygen gases

Ozone and oxygen were the gases tested in these experiments. Oxygen was supplied from a cylinder containing dry oxygen (99.9% purity). Ozone was generated by a corona discharge O3R model ID-05 (Brazil) ozone generator from dry oxygen used as the feed gas. The ozone input rate varying between 1.11 and 2.91 g h^{-1} was delivered at a gas flow rate of 1–4 L min^{-1}. The residual ozone in the water was measured by the Indigo method (Bader and Hoigné, 1981) and excess ozone was destroyed chemically after treatment.

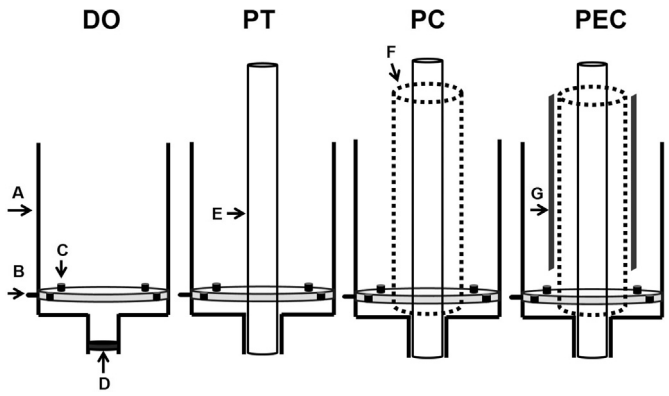

Fig. 1. Scheme of the reactor developed for the treatment of wastewater using DO, PT, PC and PEC processes, where: A: reactor glass wall; B: gas inlet; C: sintered glass diffusers for injecting O_2/O_3; D: rubber tip; E: glass tube to accommodate the UV-B 100 W lamp; F: cylindrical TiO_2 nanotubes electrode (photoanode); G: DSA used as cathode.