Chemical Engineering Journal 229 (2013) 9–19

Contents lists available at SciVerse ScienceDirect

Chemical Engineering Journal

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

Degradation of various textile dyes as wastewater pollutants under dielectric barrier discharge plasma treatment

Martynas Tichonovas [a,b], Edvinas Krugly [a], Viktoras Racys [a], Rainer Hippler [b], Violeta Kauneliene [a], Inga Stasiulaitiene [a], Dainius Martuzevicius [a,*]

[a] Department of Environmental Engineering, Kaunas University of Technology, Radvilenu pl. 19, LT-50254 Kaunas, Lithuania
[b] Institute of Physics, University of Greifswald, Felix-Hausdorff-Str. 6, 17489 Greifswald, Germany

HIGHLIGHTS

- Wastewater polluted with textile dyes was treated under DBD plasma.
- A large variety of dyes were decomposed in a pilot reactor.
- The process proved to be efficient for degradation of most dyes.
- The by-products were investigated by FTIR and toxicity analyses.
- The by-products of degradation revealed a complete loss of toxicity.

ARTICLE INFO

Article history:
Received 18 March 2013
Received in revised form 21 May 2013
Accepted 27 May 2013
Available online 6 June 2013

Keywords:
Water pollution
Wastewater treatment
Advanced oxidation
Dielectric barrier discharge
Plasma
Textile dyes

ABSTRACT

Textile dyes represent some of the most complicated environmental pollutants due to their variety and complex structure. Plasma oxidation methods have emerged as viable techniques for effective decomposition of these pollutants. We examined the degradation of a wide variety (13 overall) of industrial textile dyes in a pilot dielectric barrier discharge (DBD) semi-continuously operated plasma reactor. Plasma was generated in a quartz tube with central liquid-filled electrode immersed in wastewater; ambient air was used as a feeding gas for the reactor. The performance of the reactor was evaluated based on the production of ozone (gas and liquid phase). The kinetics and by-products of the oxidation process were determined by UV/VIS spectrophotometry, FTIR analysis and toxicity tests. The yield of ozone production ranged between 0.19 mg/s and 0.46 mg/s by varying the discharge power between 3 and 33 W. The demand of energy to decompose separate dyes ranged from 18.7 to 866 kJ/g. 10 of 13 dyes were decomposed up to 95% during 300 s of reactor operation. The FTIR analysis revealed that degradation by-products consisted mostly of carboxylic acids, nitrates, amides and amines. The treatment process was found to decrease the toxicity of the wastewater to near-zero values. Low energy consumption and short decolorization time suggested that DBD plasma method may be competitive technology for primary decomposition of hardly degradable textile dyes in wastewater.

1. Introduction

Various organic synthetic dyes are used as coloring material in textile industry. Approximately 1 million tons of these dyes are produced annually [1]. Many other chemicals are utilized in the textile dying process, including acids, alkalis, surface active substances, and salts. Processes in textile production including dyeing, washing, etc. produce large quantities of wastewater polluted with various chemicals. Synthetic dyes are the substances of the highest concern, being relatively stable compounds and difficult to degrade in wastewater treatment plants based on physical, chemical or/and biological treatment. Various systems of advanced oxidation were employed for the decomposition of organic dyes, including ozone (O_3) at pH > 8.5; O_3 and hydrogen peroxide ($O_3 + H_2O_2$); O_3 and catalyst; Fenton system ($H_2O_2 + Fe^{2+}$); O_3 and UV; H_2O_2 and UV; O_3, H_2O_2 and UV; photo-Fenton system; and photocatalytic oxidation (TiO_2 + UV) [2]. These methods are mostly based on the formation of HO^* radical and its destructive behavior on organic matter.

Recently, the applications of plasma-based oxidation methods on the degradation of pollutants have been increasingly explored due to their complexity, versatility and high oxidant capacity. Many plasma generation methods have been applied, such as electrohydraulic discharge, corona discharge, dielectric barrier discharge (DBD), microwave discharge, radio-frequency and others. DBD technology is one of the most promising, because it allows

* Corresponding author. Tel.: +370 613 25111; fax: +370 37 300152.
E-mail address: daimart@ktu.lt (D. Martuzevicius).

1385-8947/$ - see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.cej.2013.05.095

for various reactor configurations, such as axial with metal–glass/quartz electrodes [3–6], axial with glass electrodes [7], and DBD-falling liquid [8,9]. Low temperature, atmospheric pressure plasma is very stable and relatively easy to operate. This method, depending on conditions, can produce large amounts of ozone and UV radiation. HO* radical is produced directly inside the plasma and during dissolution of O_3 in water. Reactions of ozone and radicals with organic matter have been discussed extensively [10]. Moreover, this method does not require additional chemicals and does not produce dangerous chloro-organic by-products [11,12] compared to e.g. chlorination. It has been reported that the products of dye degradation by ozonation revealed low to zero toxicity [9] or at least lower than the original compound [13].

Attempts to decompose synthetic dyes by DBD and ozonation based methods have emerged during the last decade and provided promising results. Mok et al. [3] researched the decomposition of azo dye Orange II (Acid Orange 7), Dojcinovic et al. [9] worked with four azo dyes: Reactive Black 5, Reactive Blue 52, Reactive Yellow 125 and Reactive Green 15. Gomes et al. [14] reported a successful degradation of azo dye Acid Orange 7 and antraquinone dye Acid Green 27 under ozonation. Most researchers limit their studies to only one or a few dyes in their experiments. There are very few studies addressing possible development of prototypes or industrial-scale devices for a larger variety of textile dyes.

The aim of this study was to research the decomposition of 13 dyes in synthetic wastewater under DBD plasma treatment, with the evaluation of decomposition efficiency, reaction products and their toxicity, as well as energy consumption in the reactor. We present results from a complex study on the application of the degradation of several groups of dyes under DBD plasma treatment in a prototype reactor. The results provide a background for the further application of this technique to the industrial-scale device.

2. Materials and methods

2.1. Model wastewater

The dyes were obtained from a textile-producing company, following their suggestions on the most frequently utilized in production process and occurring in wastewater. Four groups of dyes with industrial names Astrazon (cationic type, DyStar Colours Deutschland GmbH, Germany), Realan (reactive type, DyStar Colours Deutschland GmbH, Germany), Lanaset (acid type, Huntsman Textile Effects GmbH, Germany), Optilan (metal complex type, Riddhi Siddhi Trading CO., India) were tested. These dyes were grouped based on their chemical classification to azo, anthraquinone and mixed dyes (Table 1). Each of these groups consisted of several dyes, making a total of 13 tested samples. It must be noted that the remaining composition of industrial dyes (apart from color-producing compounds) was not known, since this information is not distributed publically by dye-producing companies.

The model wastewater was prepared by dissolving 20 mg/L of each dye in tap water. The tap water in Lithuania is of the underground origin and has the following characteristics: pH value about 7–8, conductivity 486–540 μS, permanganate index 3.0–4.0 mgO_2/L. Such quantity was selected based on the monitoring results of industrial wastewater (15–20 mg/L) of a textile company using thermal coloring technology. 100 mg/L concentrations were used for FTIR measurements.

2.2. Experimental setup

A pilot DBD plasma semi-continuously operated reactor was developed. Such pilot reactor allowed for simulating the conditions similar to those possibly occurring in the up-scaled industrial device. The reactor was hand-manufactured from glass and quartz (Simax, Kavalierglass Co. Ltd., Praha, Czech Republic) at a glass-blowing workshop of Kaunas University of Technology. The reactor volume was 2 L, with 1 L utilized as a working volume during experiments. The principal layout of this setup is presented in Fig. 1.

DBD plasma was generated in the 4 mm air gap between the walls of two quartz and glass cylinders (1). The first cylinder was a high voltage central glass electrode (5) of 10 mm diameter, filled with NaCl solution (concentration 100 g/L). The other cylinder was a UV-transparent quartz tube of 16 mm inner diameter which was surrounded by the model wastewater. A grounded copper rod (6) was immersed into wastewater. Wastewater acted as a cooling medium for the DBD reactor. Reaction vessel (2) was fabricated of a glass tube, measuring 80 mm in inner diameter and 600 mm in height with the wall thickness 2 mm. DBD plasma was generated using an AC high voltage power supply (peak-to-peak voltage from 30 kV to 50 kV) (11). Power supply consisted of a transformer and its driver. The AC frequency was set to 8000 Hz as a resonant frequency for the high voltage transformer.

The air supply pump (3) was used to supply air into the reactor at the flow rate of 14.5 L/min. Such flow rate was determined by preliminary tests as optimal one for assuring sufficient cooling of electrodes and producing high quality plasma. Higher flow rates increased bubbling of the wastewater and the size of bubbles, reducing solubility of gases. The air flowed into the gap between electrodes; plasma (ozone and highly reactive species) was generated in the DBD discharge zone. O_3 and other highly reactive species enriched in air were dispersed into the model wastewater water by five 10 × 30 mm ceramic diffusers (9). Outlet gasses were directed to the exhaust (8). The discharge also produced UV radiation, able to reach the wastewater through the quartz cylinder walls. Liquid dosing pump (DME2, Grundfos Holding A/S, France) (4) was used for the accurate dosage of dye solution. The samples were taken using 10 and 50 mL syringes (7). The treatment of wastewater was carried out for 10 min. During that time, the solution of most dyes became completely decolorized.

An oscilloscope (Rigol DS1052E, Rigol Tehnologies, Inc., PRC) (10) was connected to the system trough a 1:1000 voltage divider for the measurements of electrical parameters. Discharge power in the DBD reactor was measured using the Lissajous figure method [15,16]. For this purpose a 27 nF capacitor was connected in series to the reactor.

2.3. Determination of process parameters

2.3.1. Production of ozone

Ozone concentrations in the reactor outlet gasses were measured by iodometric method [17]. A portion of the reactor outlet gases (1 L/min) were directed to two subsequent bubbling flasks filled with buffered 10% KI solution. Gas samples were taken for 6 min. It must be noted, that iodometric method is not selective for O_3 only, and may be affected by other oxidants, such as nitrogen oxides. It has been shown that non-thermal plasma may produce substantial quantities of nitrogen oxides [18]. At the same time, the study by Simek et al. [18] suggested that in similar setups production of N_yO_x may be insignificant at low energy densities.

Dissolved ozone concentration was determined by the indigo decolorization method [19]. Samples were taken directly from reactor vessel with a 50 mL syringe filled with 20 mL of indigo reagent solution, after 1 min of DBD operation. The resulting solution was transferred into a 5 cm quartz cell. The absorbance was measured using UV/VIS spectrophotometer (Genesys™ 8, Thermo Scientific Inc., UK) at a 600 nm wavelength.

In general, ozone production in DBD reactor (M_{O3}) can be calculated using the following mass balance equation: