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FULL LENGTH ARTICLE

Testing the advanced oxidation processes on the degradation of Direct Blue 86 dye in wastewater

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KEYWORDS

Ozone; Ultraviolet; Direct Blue 86; Advanced oxidation; Dye degradation **Abstract** This work tests the viability of applying ozone (O_3) and O_3 combined with ultraviolet (UV) to degrade the content of synthetic wastewater containing Direct Blue 86 (DB-86) dye. The tested parameters, which included pH, initial concentration of DB-86 dye and time of reaction, were tested in a batch reactor to achieve optimum operating circumstances. The results obtained in this study showed that pH and initial concentration of DB-86 dye controlled the efficiency of the decolorization process. The maximum decolorization was obtained at pH 11. More than 98% of color removal was reported after 35 min of O_3 treatment (for 100 ppm dye concentration). Kinetic analyses showed that color removal of DB-86 dye followed first-order kinetics. The rate of color removal was primarily relative to the initial DB-86 dye concentration. The effect of seawater on the efficiency of the process was studied. Gas Chromatography Mass Spectrum analysis of treated synthetic DB-86 dye solution was performed at the end of the pre-treatment time to study the final degradation products of DB-86 dye. The obtained results revealed that ozonation processes had reduced the zooplankton toxicity belonging to the raw solution and had improved the biodegradability of the DB-86 dye wastewater.

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Introduction

The textile industry is considered one of the biggest industries in Egypt according to the number of labor, the export prices and the local production cost. This industry has been reported as a significant provider of environmental pollution in streams, particularly in wet processes where harmful chemicals are used. The Egyptian textile industry consists of 31 public sector firms and about 3000 private sectors and joint venture facilities (Sultan, 2002; EPAP/EEAA, 2003).

The occurrence of organic contaminant compounds such as most of dyes, DDT, HCHs, other pesticides, PCBs, PAHs, surfactants and aromatic amines etc. in the hydrosphere, is of particular worry for the freshwater, coastal and marine environments because of their non-biodegradability and possible carcinogenic nature (El Nemr, 2007, 2007; Bulut and Aydin, 2006; El Nemr et al., 2007, 2009, 2010, 2014, 2015; Khaled et al., 2009; Amini et al., 2011). The main concern with color is its esthetic character at the point of release in respect to the brightness of the receiving waters (El Nemr, 2012a,b).

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Direct dye is still the most widely applied in the dying and printing processes of the textile industry. Manly the factories of the dying printing process-textile belong to the homemade textile products (small factory group). Great volumes of synthetic dyes are used by numerous industries including textile dyeing (60%), paper (10%) and plastic matter (10%) (El Nemr, 2012a,b; Guivarch et al., 2003).

The existence of very small quantities of dyes in water (less than 1 ppm for some dyes) is highly noticeable and unwanted (Robinson et al., 2001). Due to their high solubility, synthetic dyes are common water contaminants that are also poisonous and carcinogenic; this poses a severe threat to the aquatic living organisms (El Nemr, 2012a,b). Wastewater comprised of dyes are hard to treat, since the dyes are recalcitrant organic molecules that are resistant to aerobic digestion and are stable to light, heat and oxidizing agents (Sun and Yang, 2003).

Glaze et al. (1987) defined AOPs as treatment processes of wastewater at room temperature and pressure which involve the formation of hydroxyl radicals ('OH) radicals in an amount sufficient for wastewater purification. Hydroxyl radicals ('OH) have the highest oxidation potential (E^0 : 2.8 eV) following the fluorine radicals (E^0 : 3.06 eV), which are toxic and cannot be used for wastewater treatment. These explanations reveal that the formation of OH radical using AOPs, has drawn the attention of most researchers and technology developers (Azbar et al., 2005). Direct molecular and indirect radical type chain reactions are the two different methods of the reaction of ozone with pollutants (Arslan and Balcioglu, 2000). The simplified reaction mechanism of the ozone is given below in Eq. (1).

$$3O_3 + H_2O \rightarrow 2 \cdot OH + 4O_2 \tag{1}$$

The photolysis of ozone in water, in the presence of 200-280 nm UV radiation, can lead to the formation of hydrogen peroxide. Hydroxyl radicals can be created in this way as given below in Eqs. (2)-(4).

$$O_3 + hv + H_2O \rightarrow H_2O_2 + O_2 \tag{2}$$

$$H_2O_2 + hv \to 2^{\circ}OH \tag{3}$$

$$2O_3 + H_2O_2 \rightarrow 2 \cdot OH + 3O_2 \tag{4}$$

Due to the fact that the O_3/UV process does not have the same limits as the H_2O_2/UV process, low pressure mercury vapor UV lamps are the most widely used sources of UV irradiation in this process. The efficiency of the AOPs are affected by many variable parameters including temperature, pH, UV intensity, lamp spectral characteristics, scavengers, turbidity and type of pollutants (Azbar et al., 2005). The goal of this work is to investigate the application of O_3 and UV/ O_3 processes in the degradation of the Direct Blue 86 dye. The effects of dye concentration, initial pH as well as the effect of seawater on the efficiency of the process were studied. The toxicity of the treated wastewater to zooplankton was also investigated.

Materials and methods

Chemical, materials, instruments and removal methods

Direct Blue 86 (DB-86) dye was obtained from ISMA dye company in Kafer Eldawar, Egypt, 75% of the dye's content

was used without further purification. The chemical structure of DB-86 dye is shown in Fig. 1. A stock of 1000 mg/l of DB-86 dye was prepared using double distilled water. Other working aqueous solutions that used (100, 200, 300, 400 and 500 mg/l) of DB-86 dye were obtained from the stock solution by dilution in double distilled water to the required concentration. Throughout this work, dye concentrations were determined in aqueous solutions via comparison with standard solutions in the visible range of the spectrum using UV–VIS spectrophotometer (Analyticjena Spekol 1300 UV–VIS Spectrophotometer, Model No 45600-02, Cole Parmer Instrument Co., USA). The maximum wavelength λ_{max} for the DB-86 dye was determined at 594 nm (http://www.worlddyevariety.com/direct-dyes/direct-blue-86.html). The color removal rate of DB-86 dye was determined by Eq. (5).

Color removal efficiency
$$\% = \frac{A_0 - A_t}{A_0} \times 100$$
 (5)

where A_0 and A_t are the initial and the measured absorbance of the samples at different time intervals.

Ozonation was handled in a 200 ml cylindrical glass reactor as shown in Fig. 2. All links from the ozonator to the reaction vessels were made of Teflon tubes. Because of low reactor capacity, 200 ml of freshly prepared dye was employed for every run time. Ozone generator, Model: N 1668A power: 18 W, Vol AC 220V/50HZ, was used to produce ozone with a flow of 500 mg of O₃/h. The ozone that left the reactor was caught into two-sequential bubblers filled with (KI) (2%) solution. Other tests were also performed using the AOPs (O₃/UV). Therefore, Horizontal Clean Bench/Laminar Floe Cabinet (Bw-LFH1300) with UV low pressure mercury lamp 254 nm power 30 W was used.

The chemical oxygen demand was determined according to the procedure stated in (APHA, 2005). The COD was calculated for both untreated and treated DB-86 dye at a concentration of 500 mg/l.

The influence of the pH was studied by adjusting the reaction's mixture to a different initial pH (3–11) value using 1 M H_2SO_4 or 1 M NaOH before starting ozonation or UV enhanced O_3 processes. The pH measurements were carried out using JENCO Electronics, LTD pH meter (Model: 6173, Serial No: JC 05345).

The extraction of the intermediates in addition to the end byproducts in the advanced oxidation treated wastewater sam-

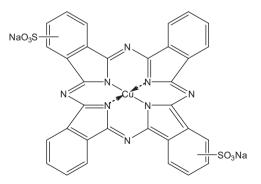


Figure 1 Chemical structure of DB-86 dye (MF: $C_{32}H_{14}CuN_8$ -Na₂O₆S₂) (MW: 780.17). Soluble in water of the lake blue solution, the solubility of 40 g/l (60 °C), 80 g/l (97 °C). The strong sulfuric acid for yellow green, diluted into a green light blue, green and blue light precipitation, $\lambda_{max} = 594$ nm; C.I.18820.

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