Research Article

Application of Ozonation and UV assisted Ozonation for Decolorization of Direct Yellow 50 in Sea water

Mohamed A Hassaan[1]*, Ahmed El Nemr[1], Fedekar F Madkour[2]

[1]Marine Environment Division, National Institute of Oceanography and Fisheries, KayetBey, El-Anfoushy, Alexandria, Egypt
[2]Marine Science Department, Faculty of Science - Port Said University, Port Said, Egypt

Abstract This paper examined the possibility of applying ozone (O_3) and O_3 combined with ultraviolet (UV) to degrade the content of seawater containing Direct Yellow 50 dye. The Experimental parameters such as initial dye concentration and time of reaction were assessed in a batch reactor to achieve the optimum operating circumstances. The Results of this study showed that more than 88% color removal was obtained after 35 min of O_3 treatment (for 100 ppm dye concentration) and also partially removal of COD. These results also indicated that the application of O_3 is more effective than UV assisted Ozonation to reduce the reaction time. Also, Gas Chromatography Mass Spectrum analysis of treated synthetic dye solution was performed at the end of the pre-treatment time to the final degradation products of Direct Yellow 50 dye and showed no toxic compounds.
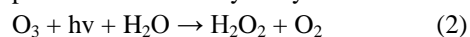
1. Introduction

The existence of organic impurities such as dyes, surfactants, pesticides, etc. in the hydrosphere is of particular concern for the fresh water and marine environments because of their non-biodegradability and possible carcinogenic nature of most of these complexes [1-12].
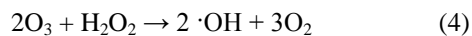
The textile industry is considered one of the basic industries in Egypt with respect to the number of labor, the exports cost, and the local production cost. This industry has been revealed as an important supplier for the environmental pollution, and the streams, mainly the wet processes where risky chemicals are used. The Egyptian textile industry consist of 31 public sector companies and about 3000 private sector and joint venture facilities, [13,14].

Direct dye is still the most extensively used in dying printing process of the textile industry. Most of the printing process-textile plants belong to the small factory group (home-made textile products). Great volumes of synthetic dyes are used by numerous industries including textile dyeing (60%), plastic matter (10%) and paper (10%), [15-19]. Ozone reacts with wastewater compounds in two different techniques namely direct molecular and indirect radical type chain reactions [20-22]. Simplified reaction mechanisms of ozone at alkaline pH are given in below;

$$3O_3 + H_2O \rightarrow 2 \cdot OH + 4 O_2 \qquad (1)$$
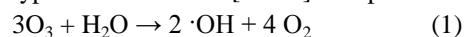
Photolysis of ozone in water in the existence of UV radiation in the range of 200-280 nm can lead to hydrogen peroxide creation. Hydroxyl radicals can be produced by this as given equations below:

$$O_3 + hv + H_2O \rightarrow H_2O_2 + O_2 \qquad (2)$$
$$H_2O_2 + hv \rightarrow 2 \cdot OH \qquad (3)$$

$2O_3 + H_2O_2 \rightarrow 2 \cdot OH + 3O_2$ (4)

Due to O_3/UV process does not have same limits of H_2O_2/UV process, Low pressure mercury vapor UV lamps are the most widely sources of UV irradiation used for this process. Many factors such as pH, temperature, scavengers in the influent, turbidity, UV intensity, lamp spectral characteristics and pollutant type(s) affect the efficiency of the system [21,23].

The goal of this work is to study the application of O_3 and UV/O_3 processes for degradation of the Direct Yellow50 dye. The effect of initial dye concentration was also studied.

2. Materials and Methods

The sea water sample was collected during summer season, in front of QayetBey Castle at Alexandria, Egypt (31°12'49.3"N 29°53'03.2"E). Some physical and chemical parameters were measured as shown in Table 1.

Table 1: Physical and chemical parameters of collected seawater

Temp.	27.5°C
pH	7.75
EC	60.9 ms/cm
TSM	0.0152 mg/l
DO	1.14 mg/l
Salinity	38.7ppt

Direct Yellow 50(DY-50) was purchased from ISMA dye company KaferEldawar, Egypt and was used without further purification. DY-50chemical structure is shown in (Fig. 1).A standard solution of 1000 mg/L of DY-50was prepared using Seawater. The working aqueous solutions (100, 200, 300, 400 and 500 mg/L) of DY-50 were prepared from the standard solution by dilution. The samples with 2 mL volume were withdrawn periodically from the reactor in order to monitor the change in the parameters like color. The experiment was run at the same conditions stated at Table 1, to stimulate the discharge of industrial dye wastewaters in coastal areas.

During this work, dye concentrations in aqueous solution were measured by Comparison with standard solutions in the visible range of the spectrum. UV-VIS spectrophotometer (AnalyticjenaSpekol 1300 UV VIS Spectrophotometer (Model No 45600-02, Cole Parmer Instrument Co., USA) was employed for absorbance measurements The maximum wavelength λ_{max} for the DY-50 was determined at 390 nm.

The Color removal rate of DY-50 was determined as:-

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

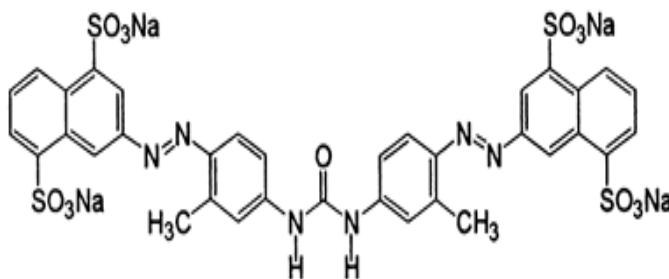Where A_0 and A_t are the initial and the measured absorbance of the samples at different time intervals.

Figure 1: Chemical structure of DY-50 (Molecular Formula: C35H24N6Na4O13S4) (Molecular Weight: 956.82)

DY-50 is soluble in water for golden brown, solubility of 60 g/L (60 ^{0}C), 80 g/L (97 ^{0}C), slightly soluble in ethanol, insoluble in other organic solvents. The strong sulfuric acid for quality in red, dilute for green light blue after blue precipitation; in nitric acid solution for purple. λ_{max} = 390 nm; C.I. 29025.

Ozonation was handled in a 200 ml cylindrical glass reactor (Fig. 2).Ozone generator was connected with reaction vessels with Teflon tubes. Due to small reactor volume, a fresh dye sample of 200 ml was used for each run. Ozone generator (Model N 1668A, power 18W, volume AC 220V/50HZ) was used to produce ozone with a flow rate of

500 mg O_3/h. The ozone leaving the reactor was trapped into two-sequential bubblers containing potassium iodine (KI) (2%) aqueous solution.

Also, Other tests were performed using the AOPs (O_3/UV) therefore Horizontal Clean Bench/Laminar Floe Cabinet (Bw-LFH1300) with UV low pressure mercury lamp (254 nm) and 30W power was used. The pH measurements were carried out using JENCO Electronics, LTD pH meter (Model 6173, Serial No JC 05345).

The chemical oxygen demand was determined according to the procedure stated in APHA procedures,[24].The COD was calculated for both untreated and treated DY-50 at concentration 500 mg/l using synthetic double distilled wastewater sample.

The identification of the intermediates in addition to the end by-products in the advanced oxidation treated wastewater samples was done using Agilent Technologies 7890A GC instrument equipped with a HP5 column (30 m × 0.25 mm i.d., 0.25_μm film thickness) corresponding to the USEPA procedures, using benzene for the extraction [25]. The temperature of the injector was 280°C (splitless). Other Chromatographic conditions included an initial oven temperature of 80°C, with a 63 min isotherm and a program rate of 8°C min^{-1} and a final oven temperature of 300°C. The gas carrier was He, with a column flow of 1.5 ml min^{-1}. An identification of GC separated compounds was carried out with a 5975C MS Detector [25].The identification of the intermediates was done using treated synthetic double distilled wastewater samples.
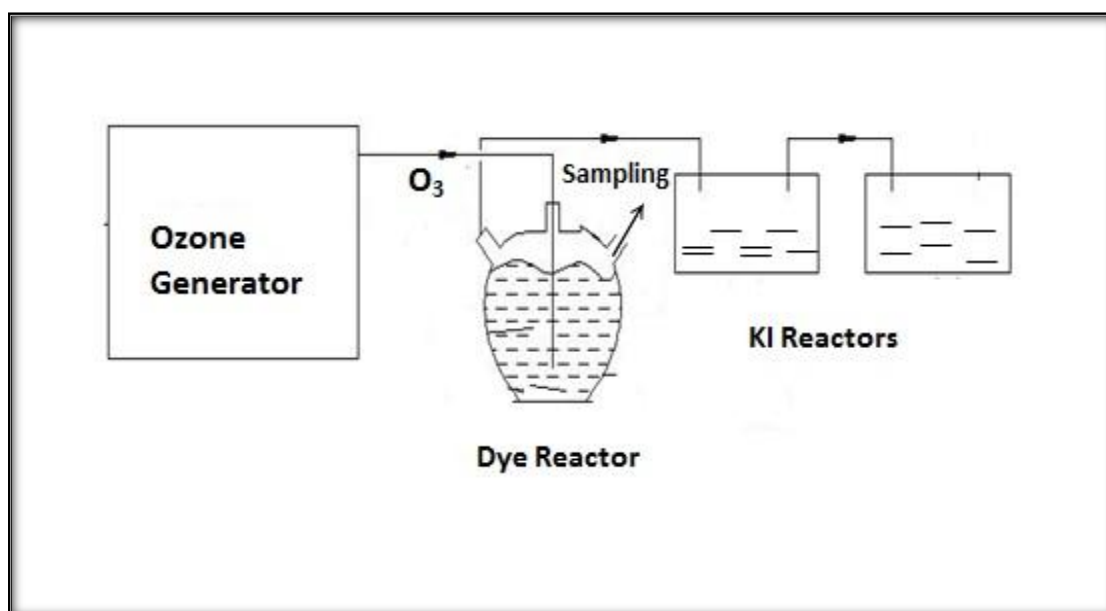

Figure 2: Design of the ozonation experiment

3. Results and Discussion
3.1. Effect of initial dye concentration
It is essential from applied point of view to study how the initial dye concentration affect color removal efficiency. Therefore the effect of initial DY-50 (with different concentrations of 100 to 500 mg/L) on color removal was investigated. The effect of DY-50 initial concentrations on decolorization efficiency is shown in figures 3 and 4.

Figure 3 shows the color removal efficiency of DY-50 in various initial concentration values. The color removal efficiency for initial concentration values of 100, 200, 300, 400 and 500 mg/L in first 35 min were 88.4 %, 92%, 89.1 %, 87.6% and 79.8%respectively for O_3 only. Although the removal efficiency for 200 mg/L concentration was higher than 100 mg/L concentration at the first 35 minutes but it take about 85 minutes more to reach the complete colour removal.
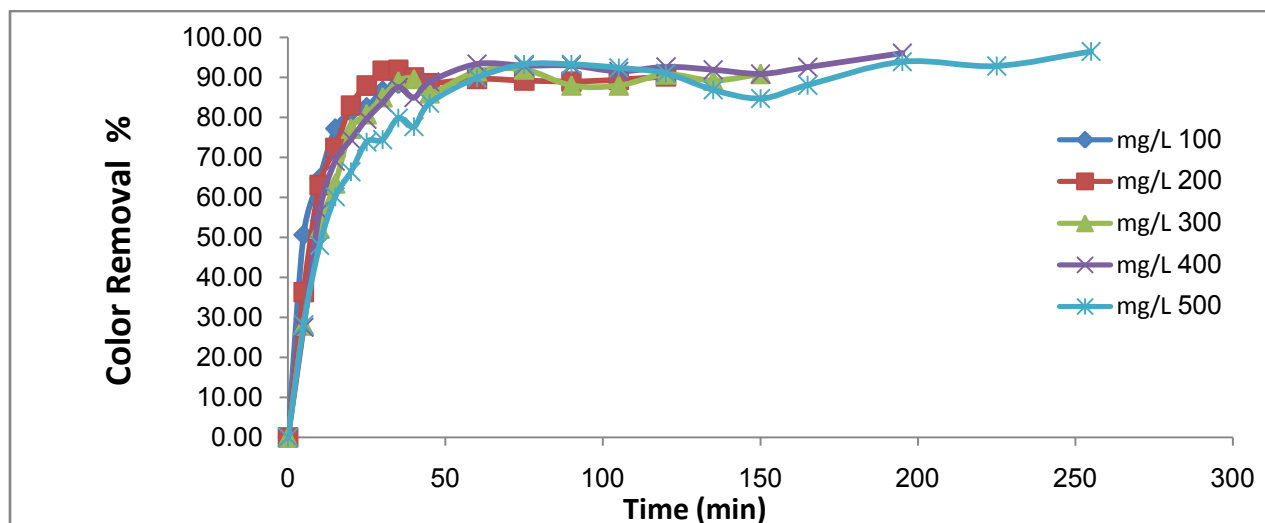
Figure 3: effect of Ozone one Different DY-50 concentrations (100, 200, 300, 400 and 500 mg/L) versus time. ([O3] = 500 mg/h, treated volume = 200ml, initial solution pH 7.75).
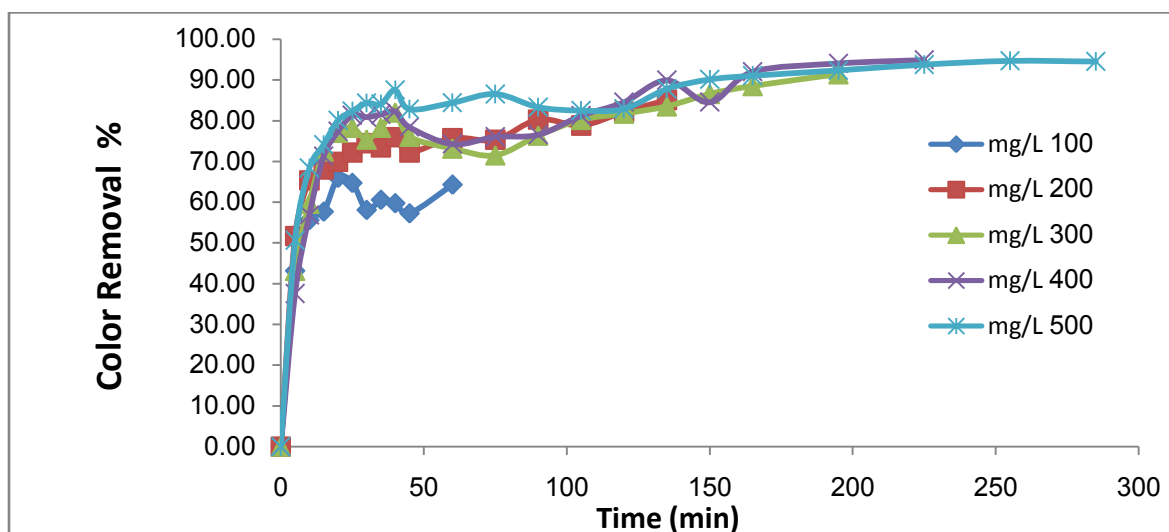

Figure 4: Effect UV assisted Ozone on Different DY-50 concentrations (100, 200, 300, 400 and 500 mg/L) versus time. Ozonation ([O3] = 500 mg/h, treated volume = 200ml, initial solution pH 7.75).

Figure 4 shows the colour removal effeminacy for initial concentration values of 100, 200, 300, 400 and 500 mg/L in first 35 min were 60.6 %, 73.5%, 78.3%, 81.5% and 84.1% respectively for UV assisted O_3 treatment. Moreover, it was noticed that after 165 minutes from ozonation process the higher concentration of dyes (300,400 and 500ppm) were precipitated.

Also, it is worth to mentioning from figures 3 and 4 by increasing the dye concentration, the decolorization rate decreased and the complete removal of color is attained more slowly.

From Figures3 and 4 it is clearly shown that the ozone was more effective than UV assisted O_3 for the all concentrations (100, 200, 300, 400 and 500 mg/L), this phenomenon can be explained by considering the scavenging effect of Cl on Hydroxyl radicals (˙OH). It is worth noting that Cl⁻ to consume (˙OH) and O_3 via serial groups of chemical reaction as mentioned by Muthukumar and Selvakumar [26].

Also another important reason is the pH of the reaction which is the seawater pH 7.75 which is not high enough to stimulate the decomposition of O_3 and produce hydroxyl radical. It is also known that Ozone stability is affected by

the presence of salts, pH and Temperature. Mallevialle [27] reported that if alkaline salts are present, the solubility of Ozone is reduced, while neutral salts may increase its solubility.

It is also could be the appropriate pH control might be required after the major oxidation mechanisms are determined. And in this study where the experiment is running under slightly alkaline pH which is not higher enough to make Hydroxyl radicals dominates the oxidation process.

Muthukumar and SelvaKumar [26] reported the impact of the salts presence in solution affects the time necessary for complete dcolor removal. The higher the salt content (38.7 ppt), the longer the time required for complete color removal. This is could be an alter different reaction pathway depending on UV assisted O_3 reaction that leads to more resistant intermediate products to further oxidation, This is may be due to the higher the salt content, the longer the time required for complete decolorization, these results in agreement with Khadhraoui et al 2009 [28].

3.2. Identification of the Intermediates byproducts of DY-50 during the AOP

The identification and/or ecotoxicological assessment of the intermediates and ozonation final products have to be done to prevent problems with successive biological treatment [29-31]. As stated before [32-34], a lot of earlier data show that the intermediates and end products of ozonation rely on the dye parent compounds chemical structure, in addition to the ozonation conditions.
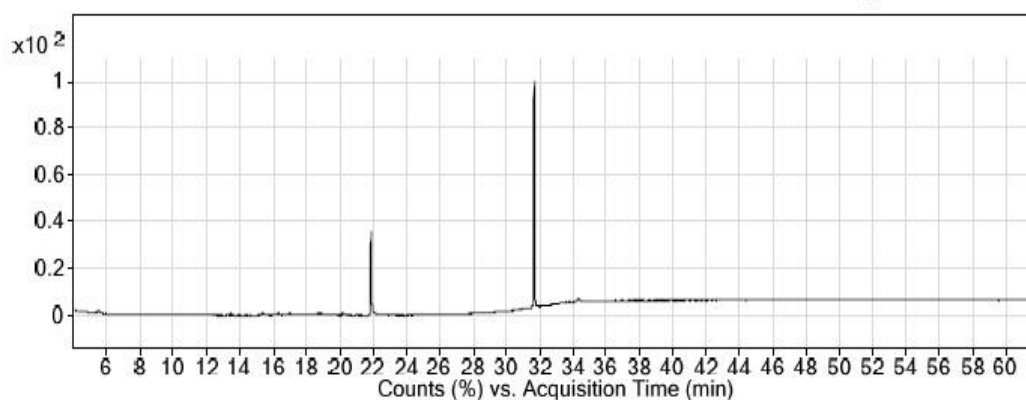

Figure 5: GC chromatograms of the UV assisted ozonation for synthetic wastewater of DY-50

Figure 5 show the GC-MS chromatograms of ozonated textile wastewater. From Fig. 5, it is obvious that AOPs lowered considerably the substances of the organic textile wastewater extracts. A preliminary analysis of the ozonated synthetic wastewater samples showed absorption peak with a retention time of 21.88 min, which was identified as being (Diethyl Phthalate). On the other hand, presence of Bis(2-ethylhexyl) phthalate(retention time 31.67min) (Fig. 5). Somensi et al. [35] stated that certain aromatic compounds can react quit slowly during ozonation process and will need much times of treatment to oxidized. We can notice that most of the Fragmentation of DY-50 dye degradation (phenol or other aromatic amine) almost disappear and the concentration of the alkene and phethlate compounds appeared is very low (ng/l). It is also say that it is well-defined that ozonation reduced notably the contents of the organic synthetic wastewater extracts.

3.3. COD removal

Chemical oxygen demand (COD) test is commonly used to indirectly measure the amount of organic compounds in the water. After complete color removal about 60% of the initial COD was eliminated for 500 ppm (Eq. 6). Likewise with what was reported by [36] the ozonation of dyes is commonly produce a little organic molecular fragments, (e.g. ketones, epoxides, aldehydes, etc.), that may lead to a remaining COD. Such COD developing from those few new produced compounds that can be later reduced by biological treatment methods as defined by [37].

$$COD \ removal \ rate \ \% = \frac{COD_i - COD_t}{COD_i} \times 100 \qquad\qquad (6)$$

COD_i =102 mg/l and COD_t = 41 mg/l

Conclusion

The aim of this study is to investigate the efficiency of using ozone and the combination of Ozone and UV to decolorize an aqueous solution of DY-50. Regarding to the results obtained, the following conclusions can be drawn: Ozone treatment proves to be very effective for complete removal of color and only partial reduction of COD. Color removal efficiency was higher in case of ozone alone as compared to UV and O_3 combination and may be related to the slightly alkaline pH and which is not higher enough to make Hydroxyl radicals dominates the oxidation process and also the scavenging effect of Cl on Hydroxyl radicals ($^\cdot$OH).

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