



OZONATION AND BIOLOGICAL TREATMENT OF AZO-VIOLET DYE: A GREEN APPROACH

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ABSTRACT

Azodyes have been largely used in textile industry for dyeing cellulose and cotton fibers. Waste water from dye industrial effluent is complex synthetic organic compounds that should be treated properly to reduce toxicity, color and COD. In this paper, ozonation and biodegradability have been studied for azoviolet. The influence of pH, Ozone dose and activated sludge used for biological treatment have been studied for color removal and complete oxidation of azodye. The ozonation constitutes AOP'S for itself, decomposition of Ozone generates hydroxyl free radical. Hence, hydroxyl free radical and Ozone both directly react with dissolved azodyes. The combination of both pathways for elimination of compounds depends on the nature of azodyes, pH of medium and of the Ozone dose. The biological treatment is an effective natural process for the waste water. The suitable microorganisms are used to convert the colloidal and dissolved carbonaceous organic matter into various gases.

Keywords: Azo-violet, COD, AOP method, Hydroxyl radical

Introduction

One of the main problems in the treatment of textile dyeing waste water and dye manufacture wastewater is the removal of dye color [1]. In the late 1950s, the trickling filter and activated sludge processes were shown to be capable of removing between 84 to 93% of the color in textile effluents [2]. Bacterial decolorization and degradation of azo dyes under certain environmental conditions can be applied to wide range of such dyes[3]. However, the color of waste-water from today's new dyes is much more difficult to treat by physical techniques such as adsorption and chemical coagulation to achieve complete decolorization, especially for highly soluble dyes. Apart from the physical methods of decolorization, chemical oxidation using oxidants such as ozone, chlorine or hypochlorite, hydrogen peroxide, potassium permanganate can be used to destroy the dye to a colorless solution, the breakdown products can be removed by conventional biological treatment processes. Bacterial decolorization and degradation of azo dyes under certain environmental conditions has gained momentum as a method of treatment, as these are inexpensive, eco-friendly and can be applied to wide range of such dyes[4]. During photocatalytic degradation of azo dye, the disappearance proceeds through both oxidation and reduction [5]

Ozone generally produces nontoxic breakdown-products [6] which are finally converted to CO₂ and H₂O if the conditions are drastic enough, and excess ozone decomposes after a few minutes to oxygen without harmful residue, as opposed to other inorganic oxidants.

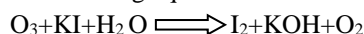
In an earlier study [7], The removal of azoviolet dye by ozonation was carried out. The results proved that textile dyeing wastewater treatment by ozone is a promising technique. The aim of the present work is to study the factors affecting the rate of decolorization of a synthetic waste solution containing a water-soluble azoviolet by ozone

gas. The study was conducted using a batch bubble column to take an advantage of the intensive back-mixing that prevails in bubble columns.

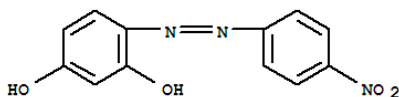
Materials and methods

The experimental set-up in Fig.1 consists of an oxygen-fed ozonizer Glass bubble column reactor and four washing bottles. Ozone was generated using a laboratory Ozonizer (Eltech).

The reactor had a glass column of 5-cm diameter and 35-cm height with sintered glass at the bottom through which O₃ was introduced to the solution. The reactor was followed by four washing bottles, each of them containing 250 ml of acidified 2% KI solution for determining unreacted ozone. Before each run the bubble-column reactor was filled with 500 cm³ of the dye solution. In the ozonizer where ozone formation takes place, the outlet stream from the ozonizer containing O₃ was allowed to pass through tygon tubing connected to the bottom of the bubble column. The gas flow rate was controlled by a needle valve and was measured by air flowmeters. The temperature was fixed at 200C during all the experiments. The un-reacted ozone was taken out of the bubble column reactor through the tygon tubing and bubbled into the 2% KI solution contained in the washing bottles where the potassium iodide solution reacted with the excess ozone according to the following equation:



The resulting iodine was titrated using standard sodium thiosulphate in the presence of starch as the indicator. The values of unreacted and reacted ozone were determined, accordingly [8]. The dye concentration time date during decolorization was detected using spectrophotometry. The dye used in the present work was water-soluble azoviolet having the following structure. The λ max value has been observed at 535nm.



AZOVIOLET

Results and discussion

Fig. 2 shows the change of dye concentration with time during ozonation at different initial dye concentration. The rate of dye removal is high at the beginning and then decreases with time.

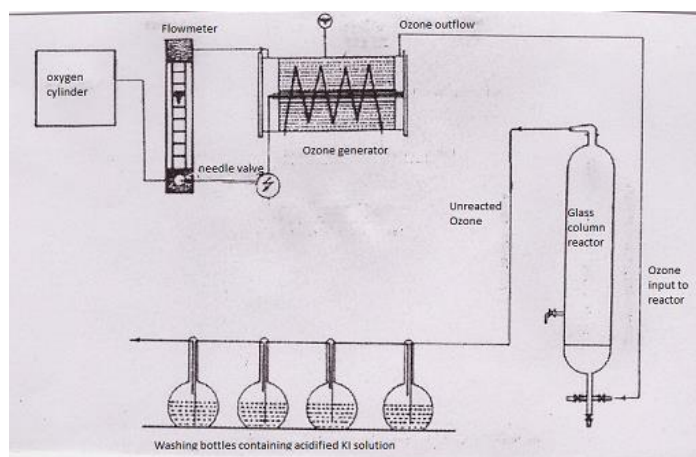


Fig. 1 Experimental set-up

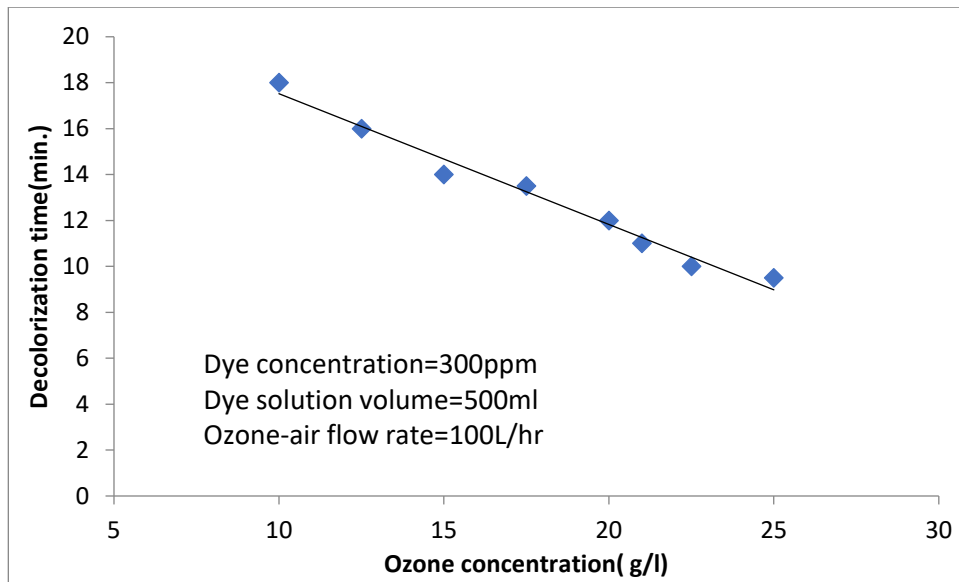


Fig.2 The change of dye concentration with time during ozonation

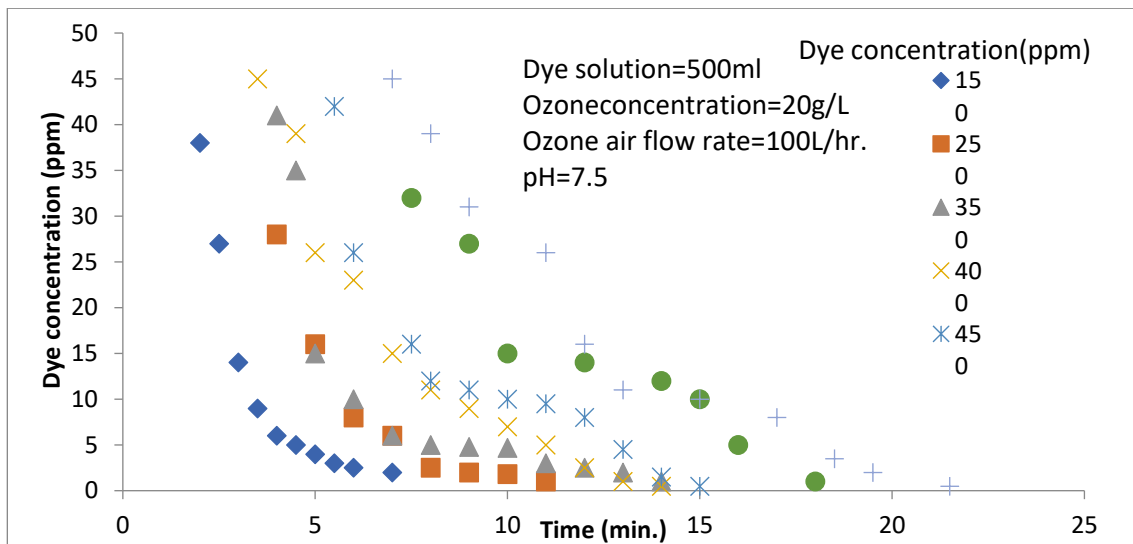


Fig.3 Concentration time for different azoviolet concentration treated with ozone at different times.

Fig.3 & 4 show the effect of initial azoviolet dye concentrations (150 to 600 ppm) on the time required for the decolorization process. The decolorization time increases with increasing initial dye concentration in the waste. The data fit equation where t_D is the dye decolorization time (min.), m is a constant, and c the initial dye concentration (ppm).

$$t_D = mc$$

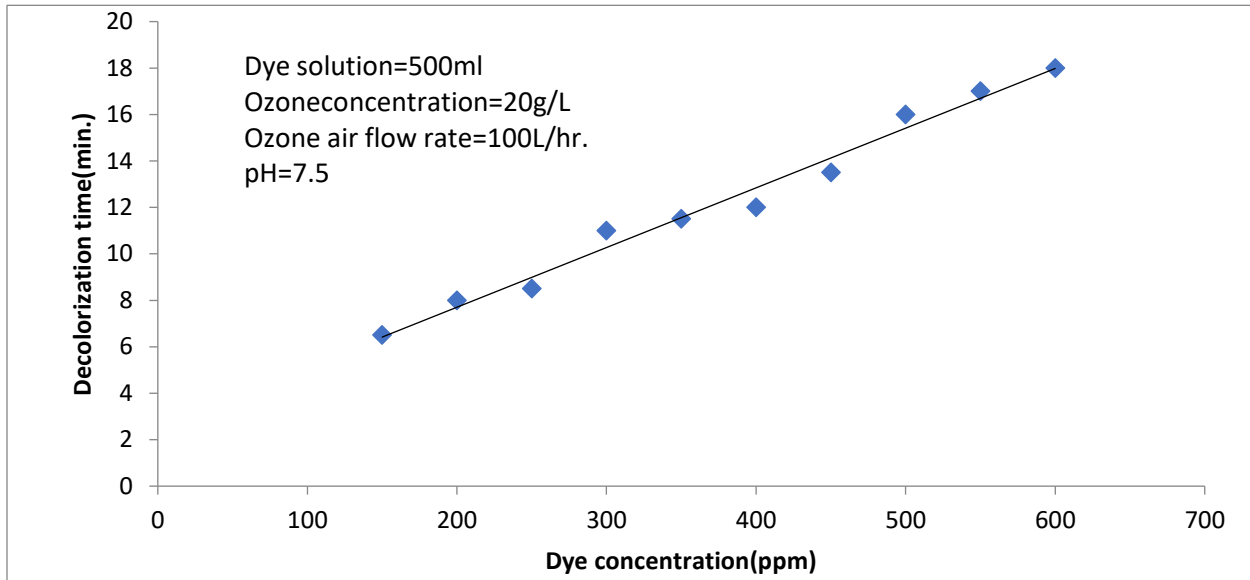


Fig.4. Effect of initial dye concentration on the decolorization time of azoviolet treated with Ozone.

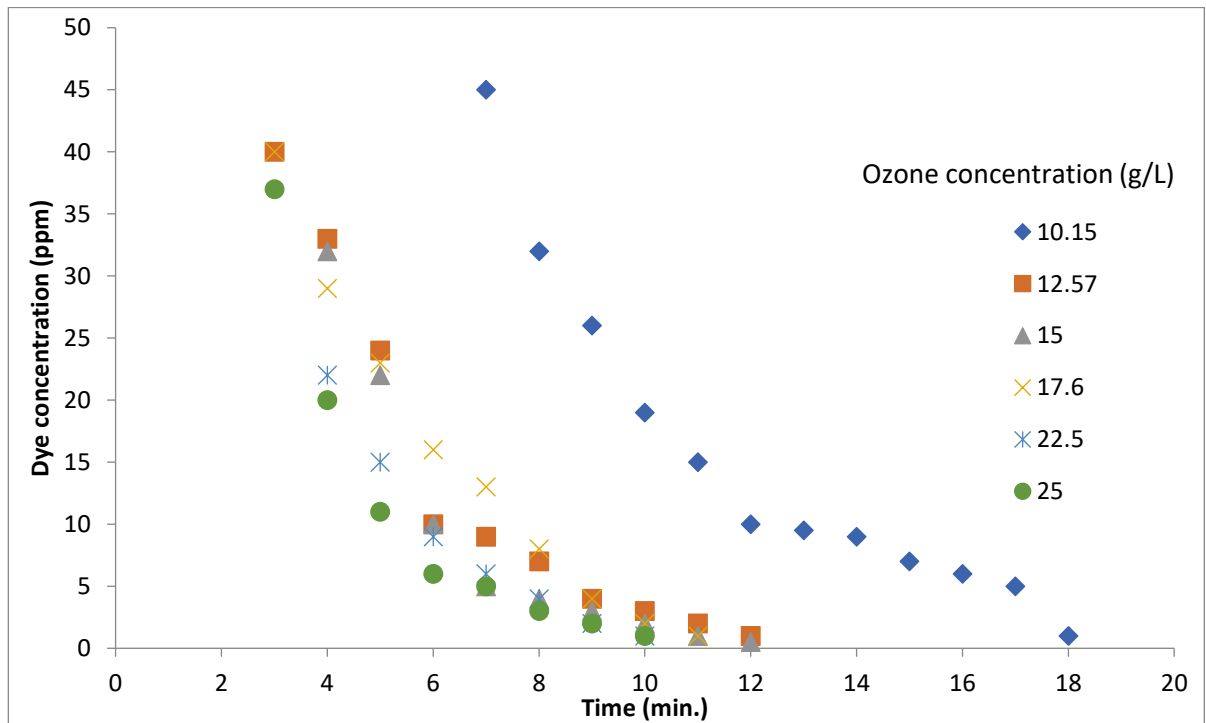


Fig.5. Concentration time data for azo-violet dye treatment.

Fig.5 shows the decrease of the dye concentration with time at different ozone concentrations. The rate of dye removal increases with increasing ozone concentration.

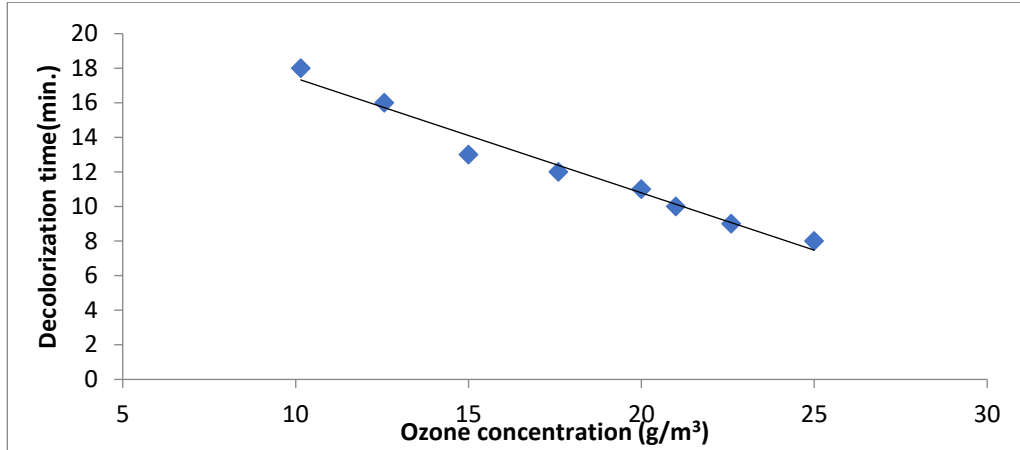


Fig.6. Effect of Ozone concentration on dye decolorization time.

Fig.6 shows the effect of ozone concentration on the decolorization time; it is obvious that the decolorization time decreases linearly with an increasing ozone concentration. For instance, increasing ozone concentration from 10.15g/m³ to 25.14g/m³ in the gas phase reduces the decolorization of 300 ppm (initial dye concentration) was reduced by about 54.3%. This result is consistent with the theories of mass transfer [9]. The driving force for the transfer of ozone to the dye solution increases with a consequent increase in ozone concentration in the solution and rate of dye oxidation. Figs. 7 and 8 shows the effect of ozone flow rate on the decolorization time. The decolorization time decreases with increasing gas flow rate until it reaches a minimum and then increases with a further increase in the gas flow rate. The initial decrease in decolorization time with increasing gas flow rate (V_g) is attributed to the enhancement of the rate of mass transfer [10] of ozone bubbles to the liquid phase.

$$E \propto (v_g)^n$$

Where n ranges from 0.7 to 1.2 in the bubbly regime which prevails at a relatively low gas flow rate from the gas bubbles to the solution. The increase in the decolorization time with gas flow rate after reaching a minimum value may be attributed to the transfer of the bubbly regime to the heterogeneous regime where large bubbles start to form. As a result of frequent bubble collision and coalescence [11]. The formation of the large size bubbles reduces the gas-liquid interfacial area considerably, with a consequent reduction in the rate of ozone transfer from the gas phase to the liquid phase. As a result, the ozone concentration in the solution decreases, with a consequent decrease in the rate of dye oxidation. The above Analysis assumption is justified by the low solubility of O₃ in aqueous solutions [12].

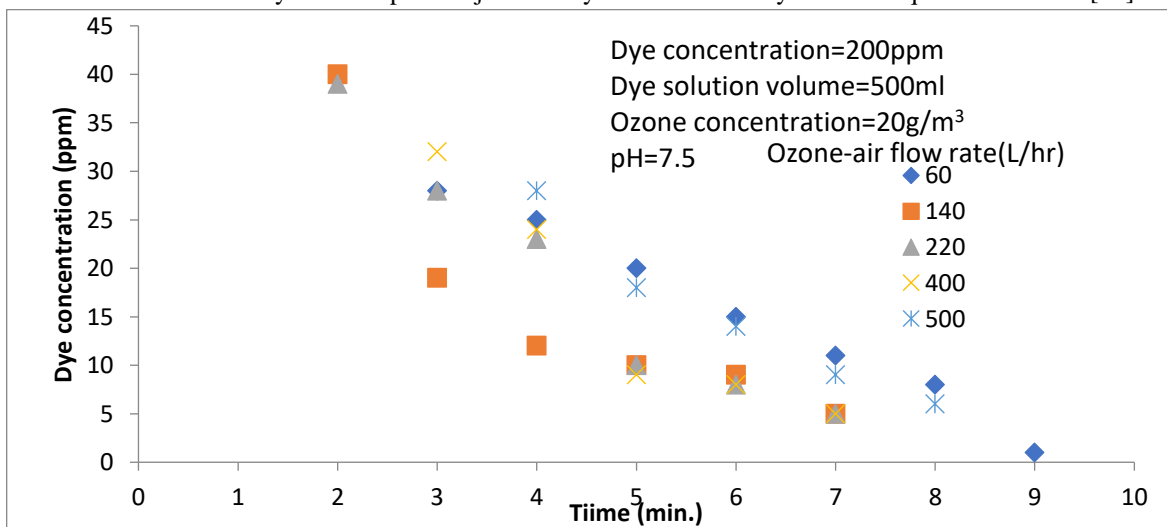


Fig.7. Concentration time data for different ozone-air flow rates.

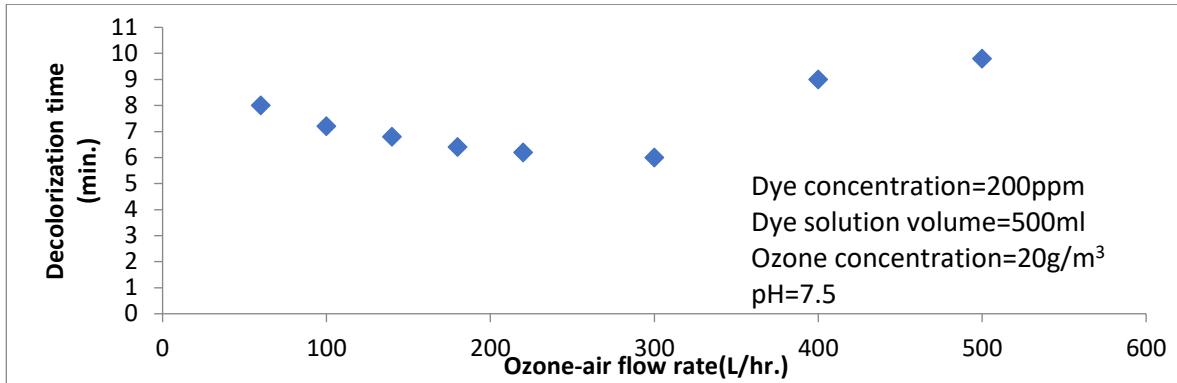


Fig.8. Effect of ozone-air flow rate on decolorization time.

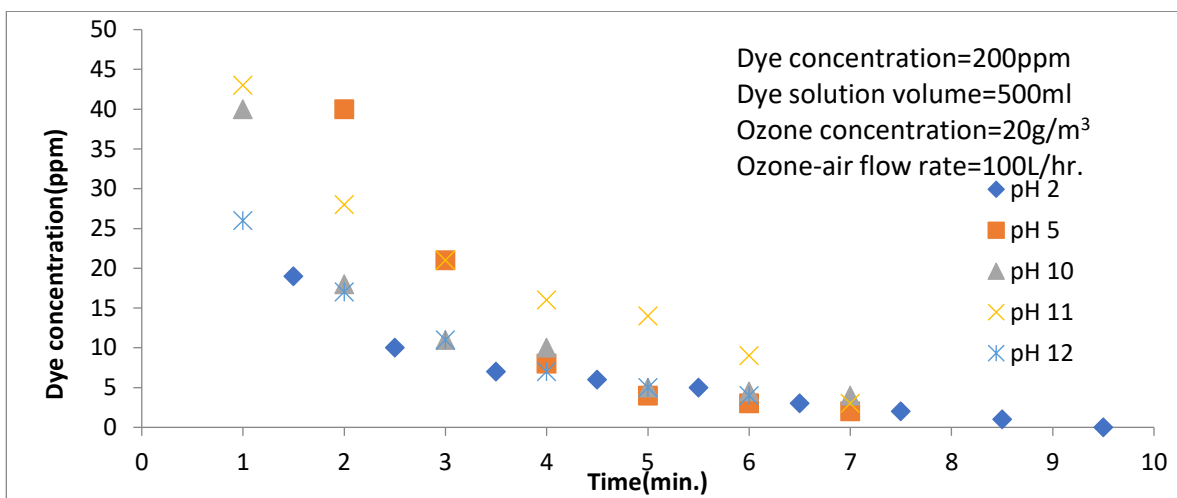


Fig.9. Dye concentration versus time at different solution pH.

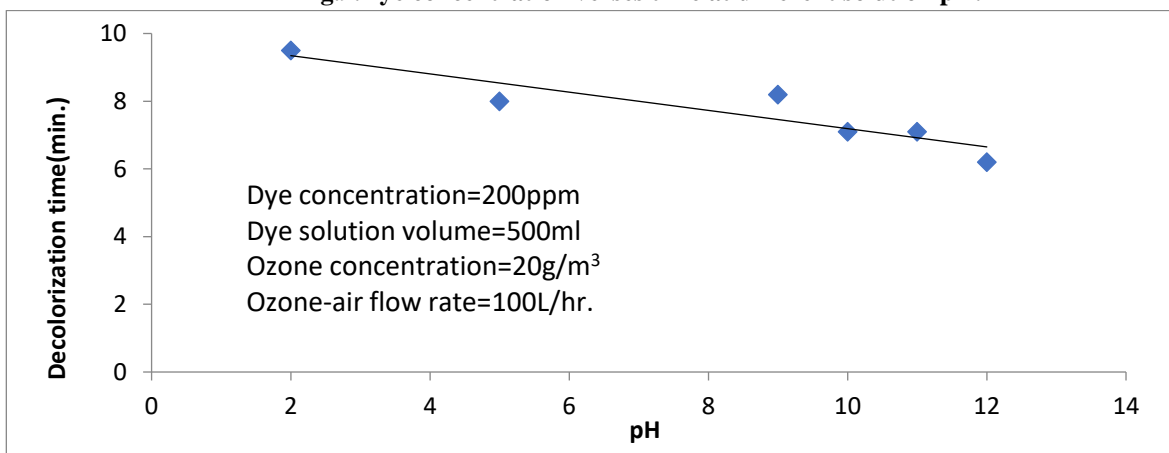


Fig.10. Effect of initial solution pH on decolorization time.

Figs.9 and 10 shows the effect of different initial dye solution pH on the dye decolorization efficiency and dye decolorization time. It is seen that the decolorization time decreases with increasing initial solution pH. According to Elovitz et al. [10], the pH affects the ozonation process by affecting the rate of ozone decomposition and ozonation kinetics. The rate of ozone decomposition is favored by the formation of hydroxyl at higher pH values. This explains



the reduction in the dye decolorization time by about 32% when the pH value changed from 2 to 12. Finally, the decolorization breakdown products were subjected to toxicity and a biodegradability test. An algae toxicity test was carried on the decolorization (ozonation) breakdown products of the azo-violet to determine the presence of toxic breakdown products which might adversely affect subsequent biological treatment. It was found that the oxidation products are nontoxic to algae and have a high tendency for biodegradation.

Conclusions

The decolorization of azo-violet by ozone in a batch bubble column reactor was found to be an efficient technique for textile dyeing wastewater treatment. Dye concentration, ozone concentration, ozone flow rate and pH were found to have a considerable effect on the rate of dye oxidation by ozone. Toxicity tests performed on the dye decolorization breakdown products revealed that these breakdown products are nontoxic, i.e., the waste solution is amenable to further treatment by biological techniques in order to reduce the BOD of the solution.

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