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OZONE TREATMENT OF TEXTILE WASTEWATER RELEVANT TO TOXIC EFFECT ELIMINATION IN MARINE ENVIRONMENT

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ABSTRACT

Ozone is a powerful oxidizing agent. The reaction of ozone with organic compounds in aqueous media has achieved a variety of treatment goals. The advantage of ozonation over the other oxidants is that the degradable products of ozonation are generally non-toxic, its final products are CO_2 and H_2O, and also the residual O_3 in the system changes in few minutes to O_2 .Convential treatment of textile wastewater includes various combinations of biological (activated sludge), physical and chemical processes. The dyestuffs existed in these wastewater are highly structured organic molecules which are hardly break down biologically. Decolorization of two types of dyes, Direct Pink 3B and Reactive Violet SH-2R, by ozonation in aqueous medium was studied in presence of some effective variables.These variables were: the rate of ozone generation, ozone dose, current, pH and the initial concentration of the wastewater. The total quantity of ozone generated is determined from the calibration curve of the ozoniser performance, while the unused ozone is determined from the titration of iodine liberated; the difference being the amount of ozone actually used in the reaction. It was found that 98% decolorization occur in few minutes. Data on time of ozonation, temperature and other chemical variables were discussed. This research proved its success as a method for treatment of wide concentration range from the dye wastewater (100-1000 ppm), so it overcomes the problems of textile wastewater treatment.

1- INTRODUCTION

Water pollution occurs due to the presence of dissolved inorganic and organic materials such as proteins, fats, carbohydrates and other substances found in the industrial waters as well as physical factors such as turbidity, color, and temperature of the effluent, etc. Wastewater treatment techniques are classified into 3 classes namely physical, chemical and biological treatment. This classification is based on the type of pollutant to be removed. Strong color is the most visual characteristic of textile wastewater. Decolorization has become an integral part of the textile wastewater treatment process. Although some dyestuffs can be partially removed by an aerobic biological method. Decolorization by organic decoloring agents is a common practice in the textile industry. Ozonation represents perhaps the latest method that has ever been attempted for treating the textile wastewater. Ozone is a powerful oxidizing agent. The reactions of ozone with organic compounds in aqueous media have been under investigation by different authors. These reactions are complex with many intermediates (Imamura *et al*., 1982, Rizzuti *et al*., 1976, Snider and Porter 1974)

Bromide can be found in natural waters from a few micrograms to several thousands of micrograms per liter (Myllykangas *et al*., 2005). Ozoneation of bromide-containing

waters has been found to result in the formation of bromate (Myllykagas, *et al*., 2003).

Chemical oxidation is frequently another tool in wastewater treatment; chemical oxidants in wide use today are chloride, ozone and hydrogen peroxide. However, the use of chloride for such application has come under intense scrutiny because, ozone, on the other hand, with only a short half life is found to be effective in many applications for color removal, and in oxidation of many complex inorganic. Oxidation with chlorine and chlorine dioxide can lead to satisfactory color abatement, but ozone remains the most efficient oxidizer, for highly colored water removal will usually be performed by combining several types of treatment.

The purposes of ozonation include the following:

1-Oxidation of inorganic pollutants, e.g. iron and manganese,

2-Oxidation of organic micro-pollutants (taste, odor compounds, phenolic pollutants and pesticides),

3- Oxidation of organic macro-pollutants (bleaching of colour and increasing the biodegradability of organics)

4-Disinfection and algae control

5- Improvement of coagulation.

Decolourisation of wastewater by ozone can be carried out successfully and could be quantitavely predicted. The presence of some inert inorganic salt such as zinc sulphate catalyses decreasing both amount of ozone reacted and time of decolorisation (Abdo and Al-Hadad 1988, Abdo *et al*., 1988). For highly colored water, color removal will usually be performed by combining several types of treatment (Constantine 1982, Klimkine *et al*., 1987, Meyers 1977). A number of authors (Gould 1985, Gould *et al*., 1984, Greaves *et al*., 1988) have suggested an ozonation stage before slow sand filtration. The results obtained using this type of treatment is interesting not only from the point of view of color but, also in relation to TOC removal. Other authors have tested ozonation followed by diatomaceous earth filtration and have achieved satisfactory results (Bryani and Yopijakij 1977, Gehm 1953).

The use of advanced oxidation processes (AOPs), including ozone (Helble *et al*., 1999, Kallas and Munter 1994, Oeller *et al*., 1997), ozone + hydrogen peroxide (Aydin *et al*., 2002, Gulyas *et al*., 1995, Sevimli and Kinaci 2002, Haapea *et al*., 2002, Glaze *et al*., 1987), have been successfully applied for the removal of refractory organics and color from wastewater effluents due to the high oxidation power of the OH radical (Mehmet, Sevimli, 2005). The use of ozone as a chemical oxidant has been suggested in the recent literature as a potential alternative for decolorization purposes (Chu, W. and Ma, C.W. 2000, Hao *et al*., 2000). The efficiency of color removal by ozone is accelerated by hydrogen peroxide (Perkowski *et al*., 2000).

2. MATERIAL AND METHODS

The experimental set up is shown in Fig (1). It is consisted of an ozone generator, a reactor and washing bottles. The ozone generator is cooled with water, and is supplied by a constant flow rate of oxygen or dry air, which is led through a flow meter that indicates the rate of gas flow; it can be adjusted with a needle valve. If the rate of gas flow is increased, the amount of ozone liberated is increased, but its concentration is decreased, and vice versa. The azonated oxygen stream passes traveled through Tygon tubing into a reactor stirred with magnetic stirrer. The reactor holds the dye solution ubder investigation, and ozonated gas stream is dispersed into the solution to a very small bubles by means of a sintered glass dispersion stone. The unreacted ozone passes out of the reaction vessel through Tygon tubing through two washing bottles contained a known volume of an acidified 2% KI solution. Finally the excess gas is vented to a hood (it contains no ozone). The potassium iodide solution reacts with the excess ozone according to the equation:

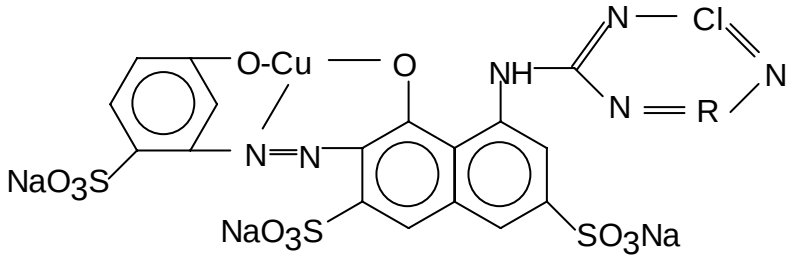
$O_3 + 2KI + H_2O \longrightarrow I_2 + 2KOH + O_2$ **(1)**

The resulted iodine is then titrated using standard sodium thiosulfate with starch as indicator.

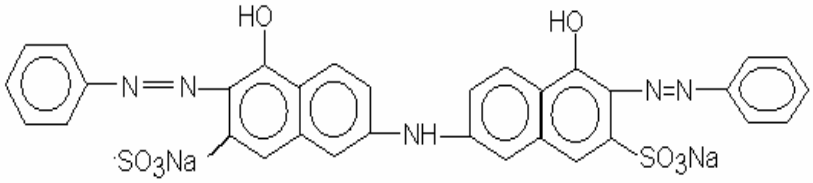
$I_2 + 2S_2O^{-2}_3 \longrightarrow 2I^- + S_4O_6^{-2}$ **(2)**

A standard calibration curve for the ozone generated at different oxygen flow rate and different periods of time, without any solution in the reactor is established. From this calibration curve, the ozone input to the reactor could be determined. The unreacted ozone is calculated from the titration .The reacted ozone at any specified conditions can be easily calculated by material balance.

The two dyestuffs used are products of Dyestuffs and Chemical Company; (ESMA Dye of Egypt). Both of them are water soluble. The chemical structures of the two dyes are:



Reactive Violet SH- 2R (CI Reactive Violet 2)



Direct pink 3B (CI Direct Red 31)

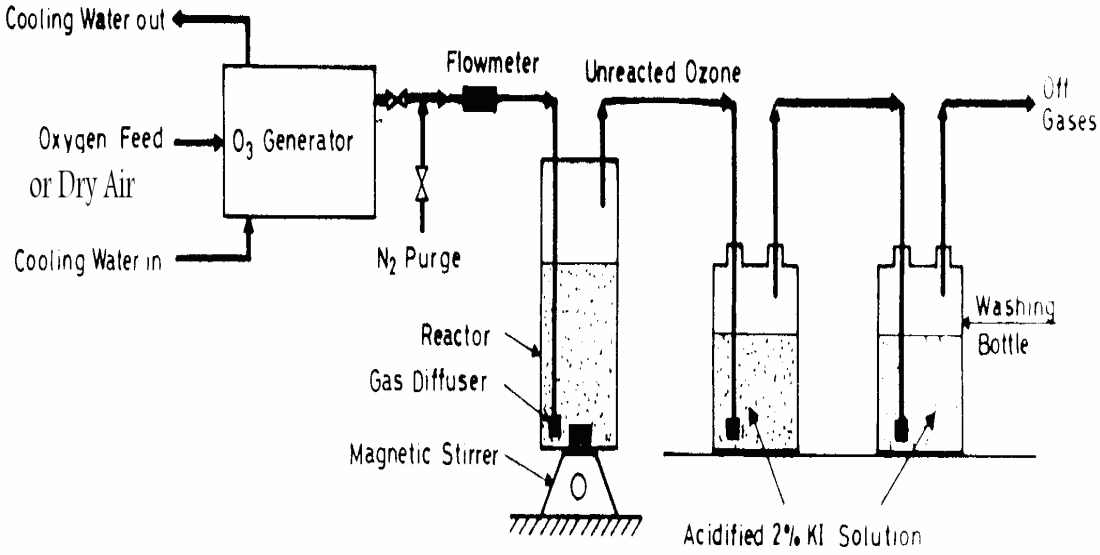


Fig. (1): Schematric Representation of the Ozonation set-up.

For each dye the wave length of the maximum absorbance (λ_{max}) and the calibration curves at λ_{max} of the dye were determined. The absorbance curve was carried out at different concentrations (5-40 mg/L)

For each dye the following variables were studied: Concentrations of the dye, pH value of the dye solution, the current and the air-ozone flow rate.

The temperature was kept constant 25 C° and the dye solution volume was 700 mL.

The ozoniser apparatus is laboratory organizer type: 301.7. A product of Erwin sander is supplied with compressed air from air dryer the dried air is subjected to the effect of high voltage for the ozone generation, water is used as cooling medium in the ozoniser.

Specifications:

Operation gas: oxygen, or dry air

Capacity: 5-10 g ozone/h

Concentration: 20 g ozone /m^3,

Maximum concentration: 40-90 g/m^3

The quantity of ozone generated is determined by calibration of the performance of the apparatus. It depends on: Flow rate, current and time. It is to be noted that potassium iodide solution should be kept neutral (using a buffer mixture), otherwise oxygen, whether unconverted to ozone or resulting from ozone consumption according to equation 1, reacts with HI as follows:

$$O_2 + 4\,HI \longrightarrow 2\,H_2O + 2\,I_2 \qquad (3)$$

And a false indication of the quantity of ozone generated is obtained.

3. RESULTS AND DISCUSSION

Fig. (2) shows the absorbance of 40 mg/L of both Reactive Violet and Direct Pink at wave length range from 400 to 620 nm. It is found that the maximum absorbance (λ_{max}) of the Reactive Violet dye is 550 nm, while it is 520 nm for the Direct Pink dye.

On the other hand when the absorbances of both dyes were plotted against different concentrations Fig (3), straight curves were obtained which means linear relationships between absorbance and concentration.

Figs. 4, 5, 12, 13 illustrated the effect of initial dye concentration on the amount of ozone reacted and time of decolorization of Direct Pink and Reactive Violet dyes. It was found that the amount of ozone needed ranged from 2000 to less than 5000 mg when the initial dye concentration ranged between 40 to 200 mg/L and when concentration of the dye increases, the time required for decolorization increases too for both dyes.Colour was removed by 20-60% during the ozonation step,then following activated carbon filtration, most of the remaining colour was removed, resulting in an overall removal of 90-95%. Many studies show that for water with a colour between 20 and 50 Hazen units, the application of 1mgO_3/L will lead to a colour abatement of about 10 Hazen units (Britton and Mc Fadzean 1984, Flogstad and Odegaard 1985, Thureson 1962, Wallentin and Nyberg 1962).

Plots of the effect of dye concentration against the time of decolorization at different pH values for both dyes are shown in figures 6, 7, 14, 15. It was found that the type of dye was the considerable factor, for Reactive dye the lower pH was much better,i.e. acidic medium (3-5) where the amount of reacted ozone and time of ozonation are lower than in the alkaline medium (Fig.14, 15). While in case of Direct Pink the suitable pH was found to be in alkaline medium (7-10).The effect of pH on the ozonation seems minor or at least, is for less important that it is for chlorine. The change in ozonation efficiency with variation in pH seen to be due to changes in the ozone decomposition rate. The ozone dose required to meet the treatment objectives is usually the most – important input to the design of the ozone generation and contacting system.

Figures 8, 9, 16, 17 show the effect of current values on the time of ozonation and on the reacted ozone dozes at different dye concentrations of both dyes. As the current increases, the time of decolorization and amount of ozone decreases sharply for each dye.It is estimated that 50% of the time of decolorization and 50% of the amount of ozone were achieved when the current increases from 0.2 to 0.6 ampere.

For the ozone -air flow rate in case of direct dye and Reactive dye, it was found that as the rate increases both the amount of reacted ozone and time of ozonation decreases slightly (Figures 10, 11, 18, 19). The effect of ozone-air flow rate effect is less important than the effect of other factors for the decolorization of both dyes. The ozonation rate is generally increased with increasing temperature. (Kyoung *et al*., 2005, Sylivia *et al*., 2000).

The temperature was kept constant at 20°C in this study but when the temperature increases, the ozone is less soluble and less stable in water, the increase of ozonation temperature from 0 to 30°C will enhance the ozonation rate and this enhancement will exceed all the other effects of ozone instability and lower solubility.It is generally accepted that increasing temperature by 10°C increases the reaction rate by a factor of 2 or 3. (Faroq *et al*., 1991), but the ozone reaction rate increases.

Fig. (20) shows the calibration curves for performance at different currents and flow rate 60L/hr.While Fig. (21) shows the performance-diagram laboratory of ozonizer 301.7 Dry-Air used in the present study.

The present study indicated that adjusting some controlling factors such as pH, current, dye air flow rate and temperature will be of economic value in the ozonation of wastewater.

According to different authors (Kishikowa *et al*. 1973, Watts, C.D. 1985), ozone doses of 1-3 mgO_3/mg C lead to almost complete colour removal. Using ozone dose 8-13 mg/L followed by filtration on activated carbon.

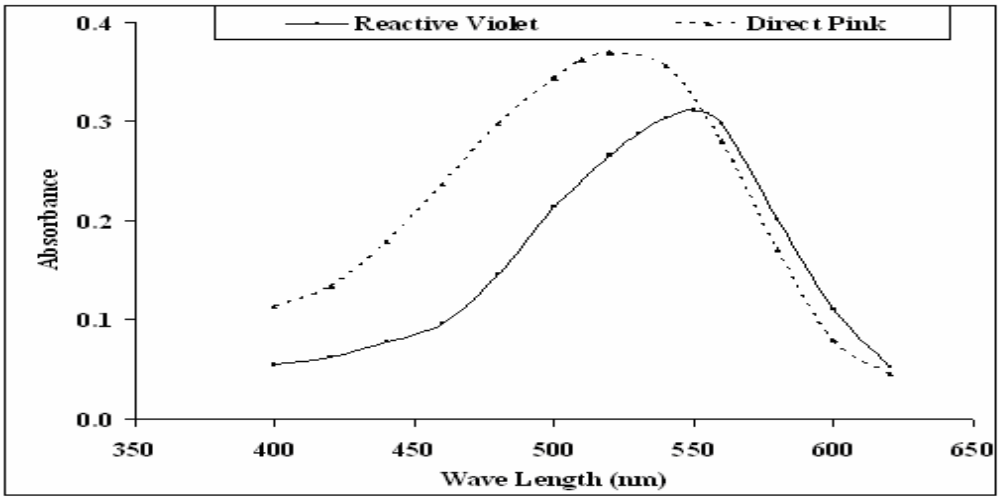


Figure (2): Absorpance curves for Reactive Violet and Direct Pink at 40mg/L

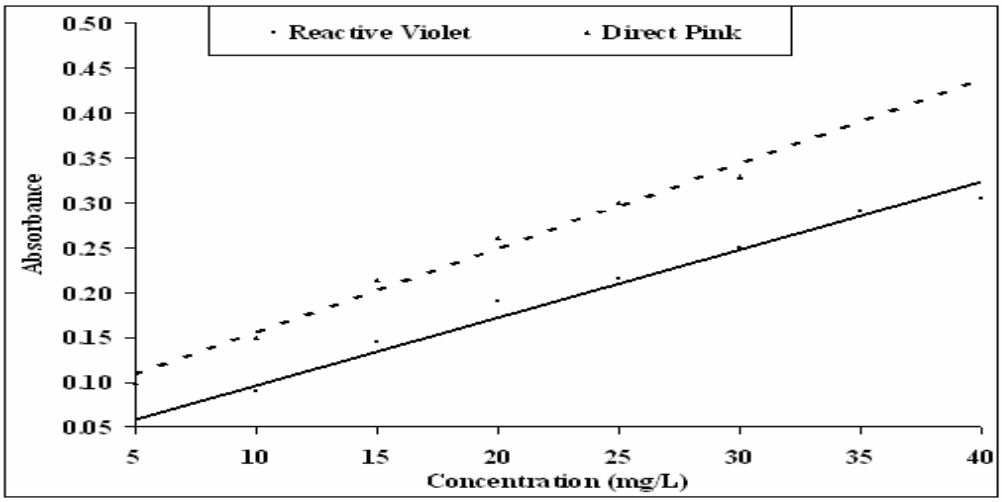


Figure (3): Calebration curves for Reactive Violet and Direct Pink at their λ_{max}

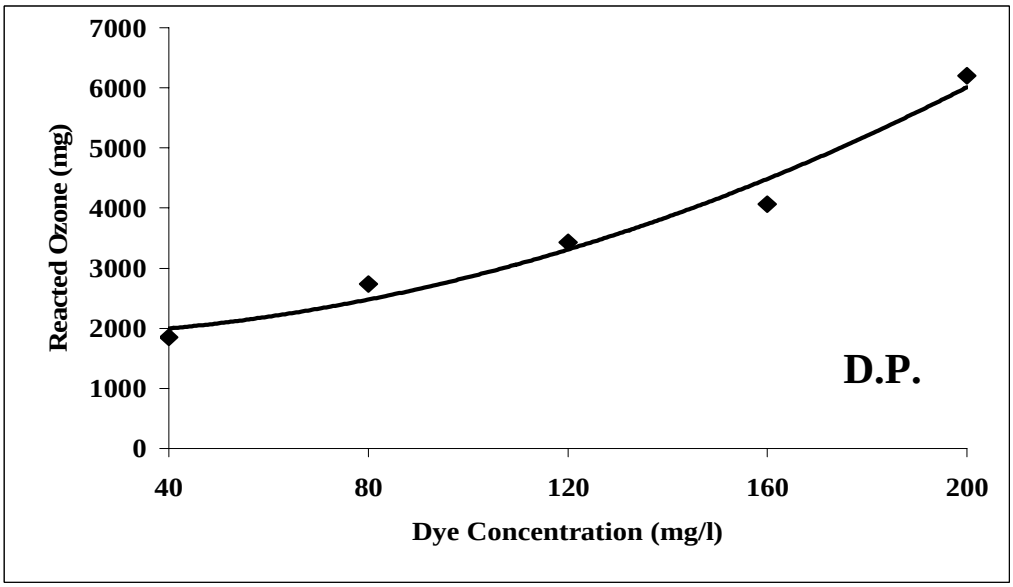


Figure (4): The effect of the initial dye concentration on the amount of Ozone Reacted

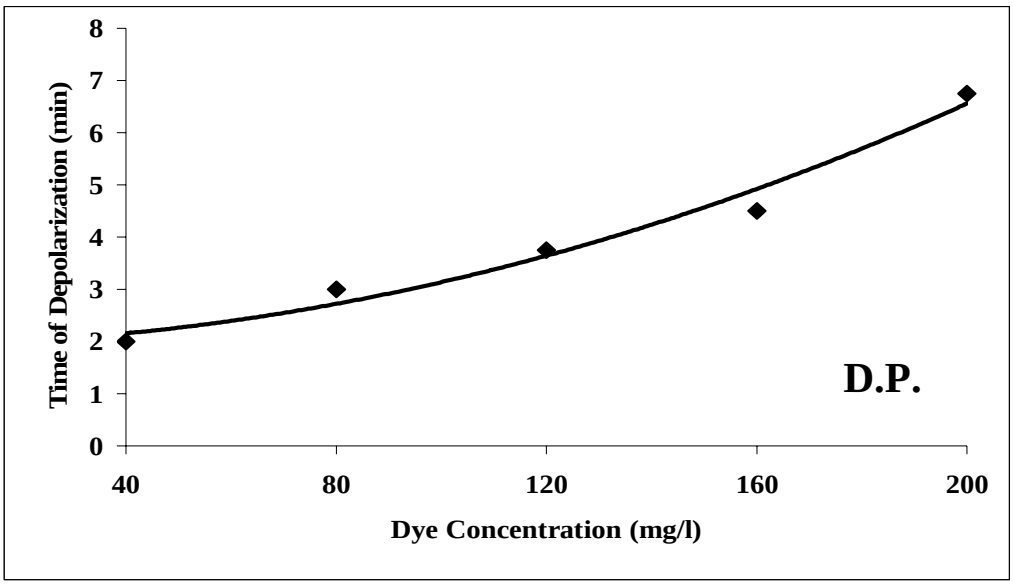


Figure (5): The effect of the initial Dye Concentration on time of decolarization

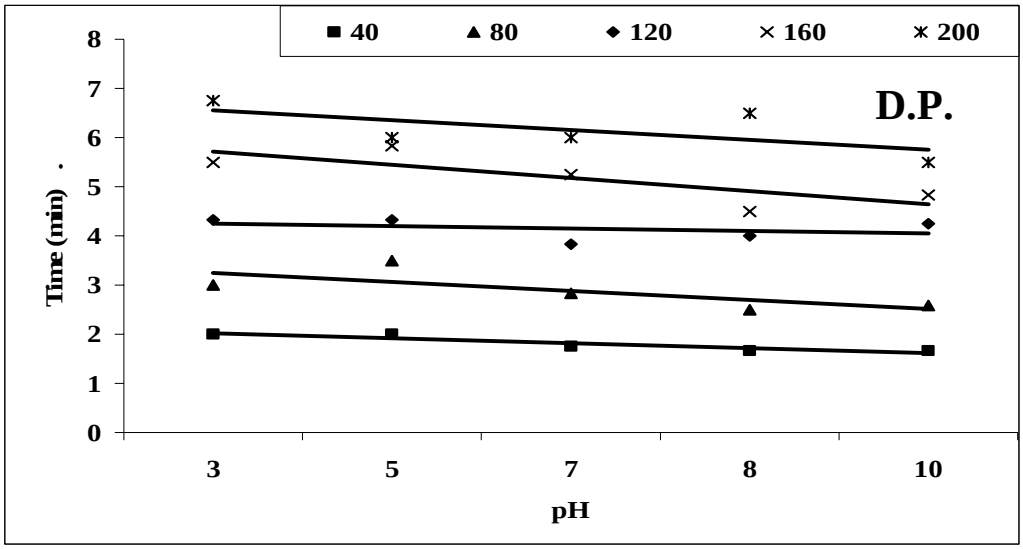


Figure (6): The effect of the Dye Concentration on the time at different pH values

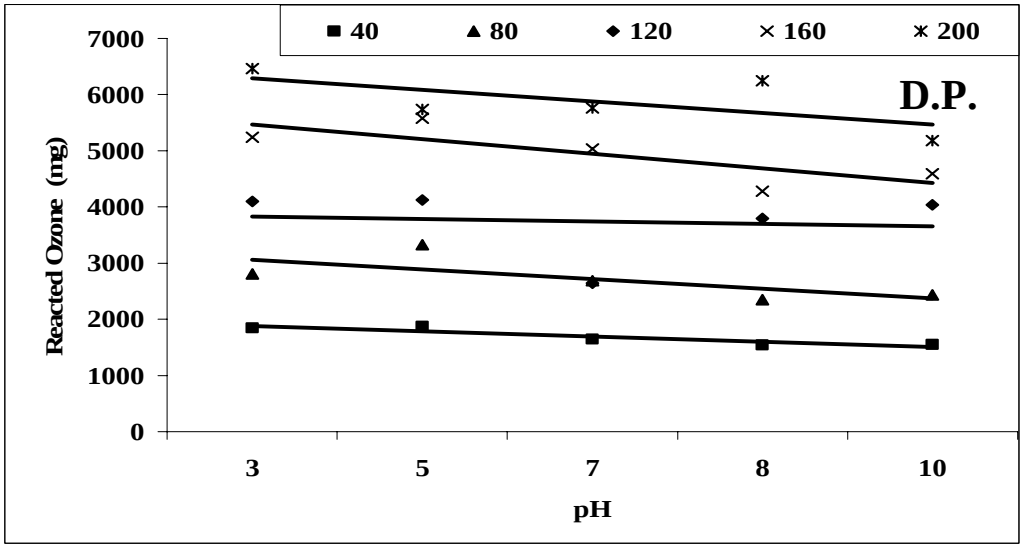


Figure (7): The effect of the Dye Concentration on the reacted Ozone at different pH values

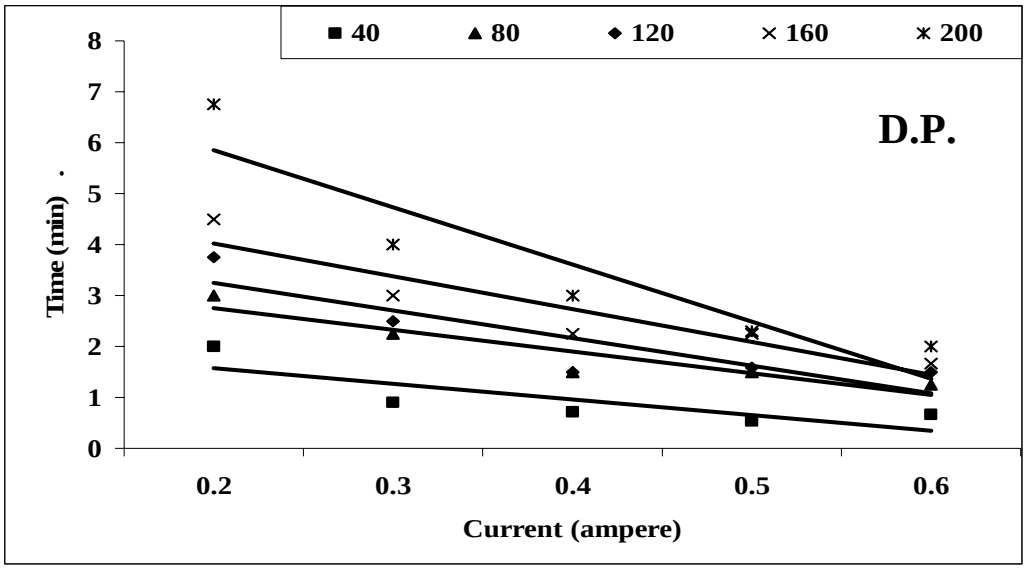


Figure (8): The effect of the different current values on the time of ozonatian at different Dye Concentrations

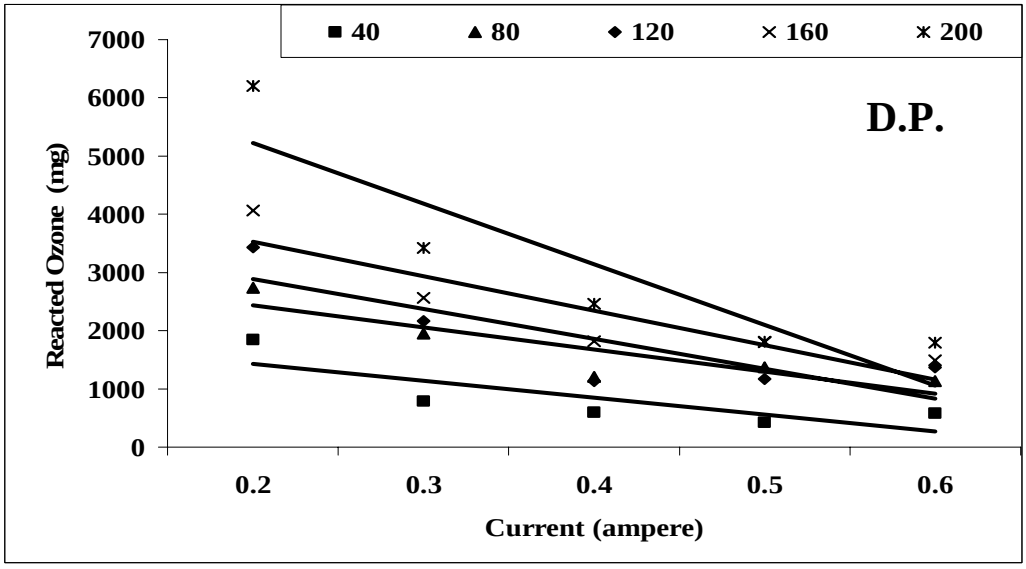


Figure (9): The effect of different current values on the reacted Ozone at different Dye Concentration

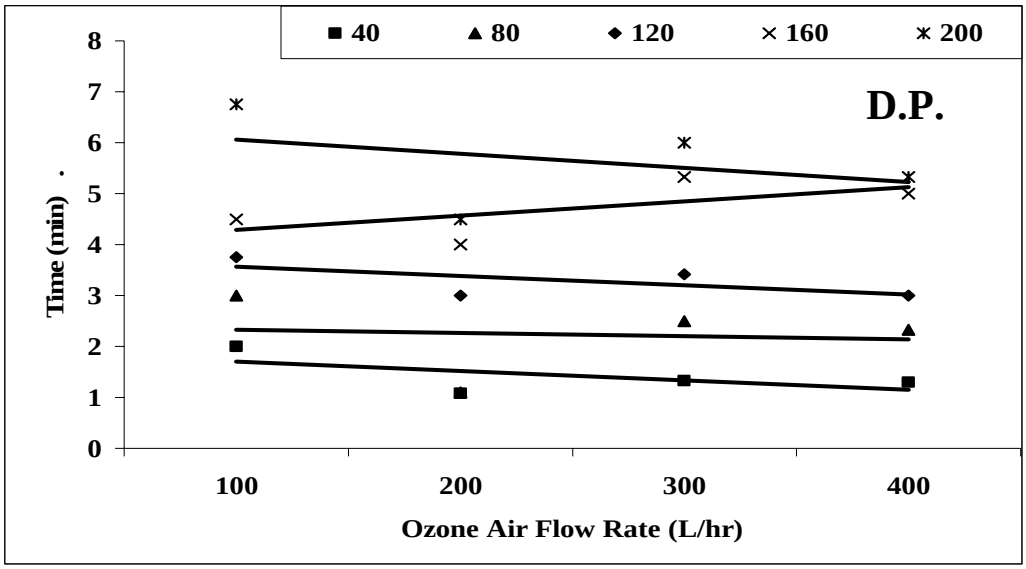


Figure (10): The effect of Ozone-Air Flow Rate on the Decolarization time at different Dye Concentrations

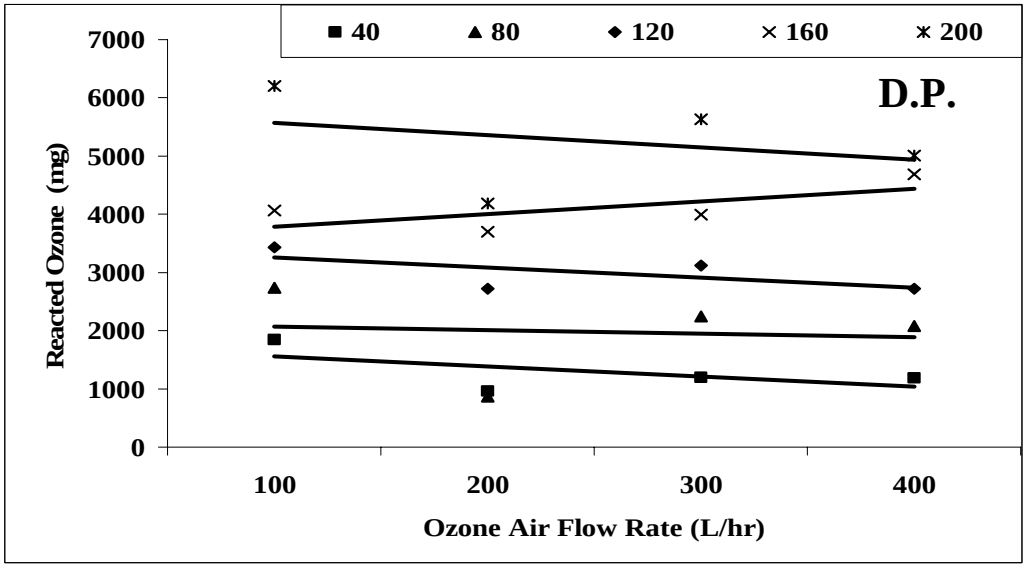


Figure (11): The effect of Ozone-Air Flow Rate on the amount reacted Ozone at different Dye Concentrations

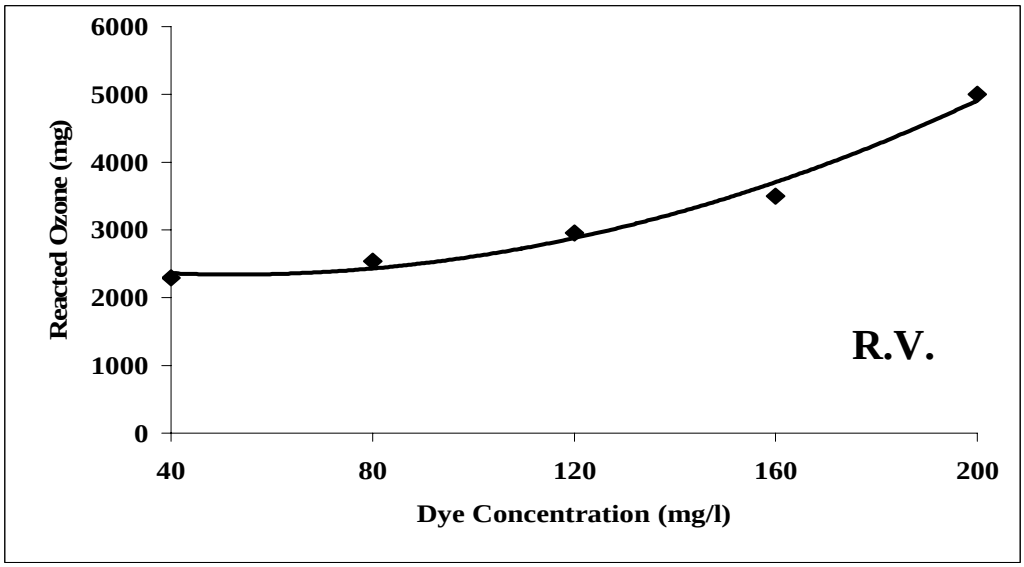


Figure (12): The effect of the initial dye concentration on the amount of Ozone Reacted

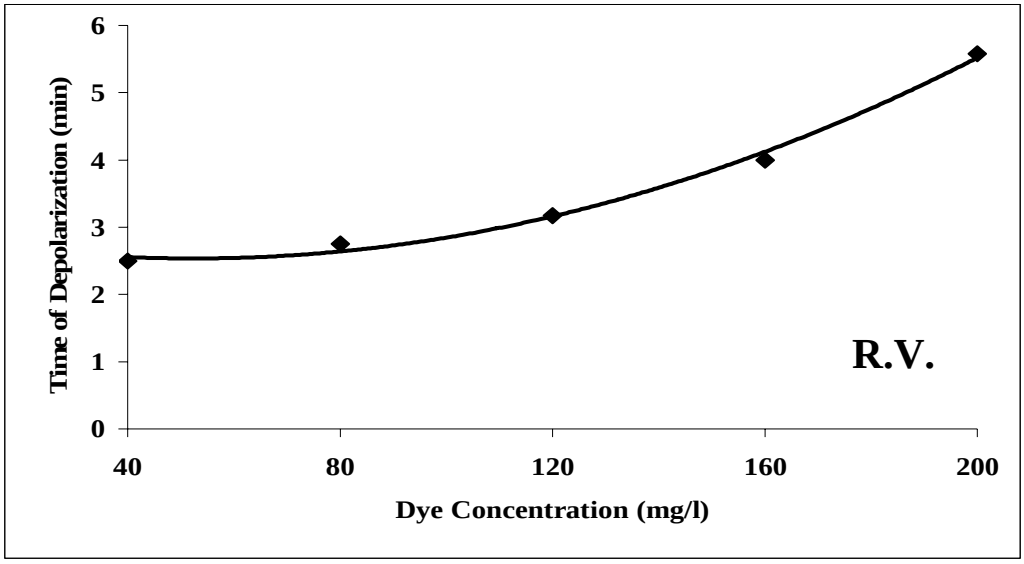


Figure (13): The effect of the initial Dye Concentration on time of Decolarization

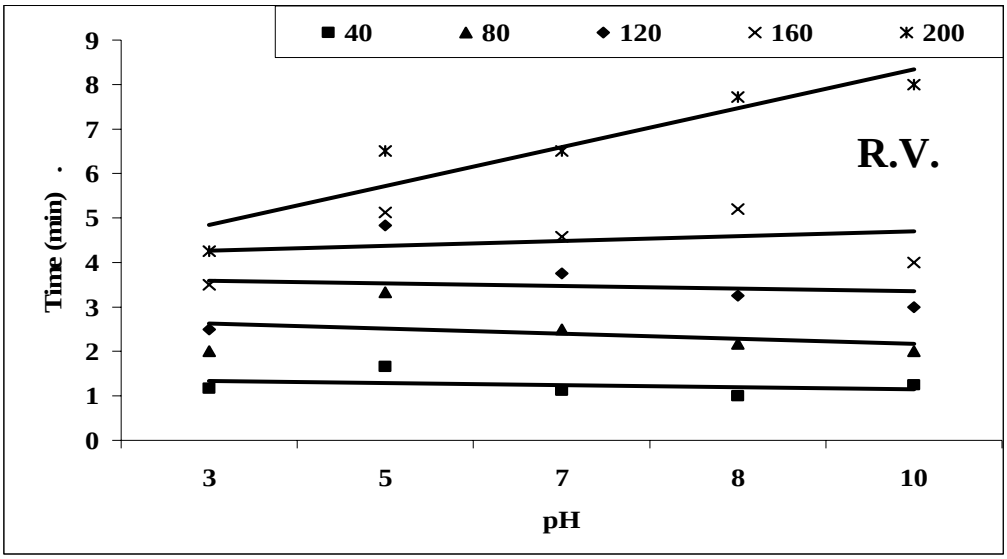


Figure (14): The effect of the Dye Concentration on the time at different pH values

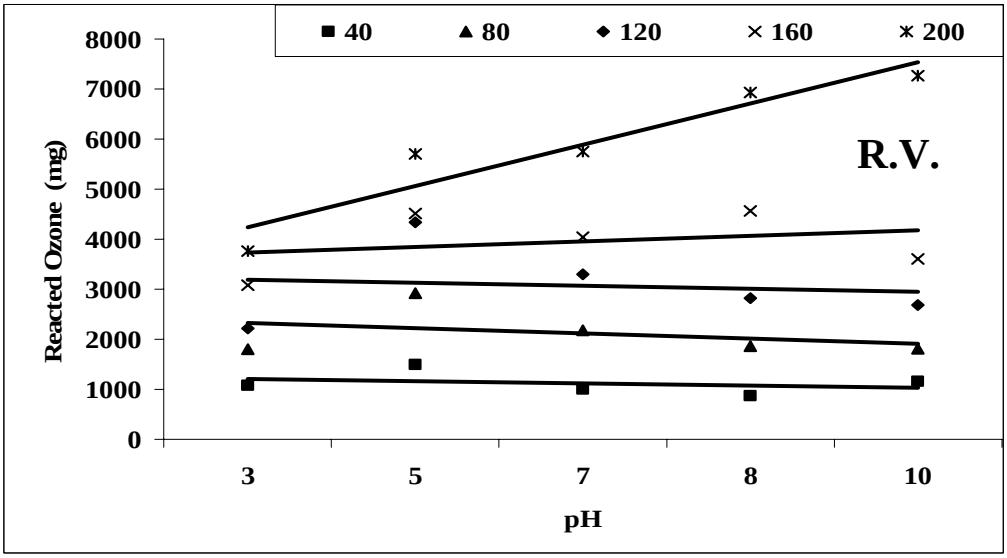


Figure (15): The effect of the Dye Concentration on the reacted Ozone at different pH values

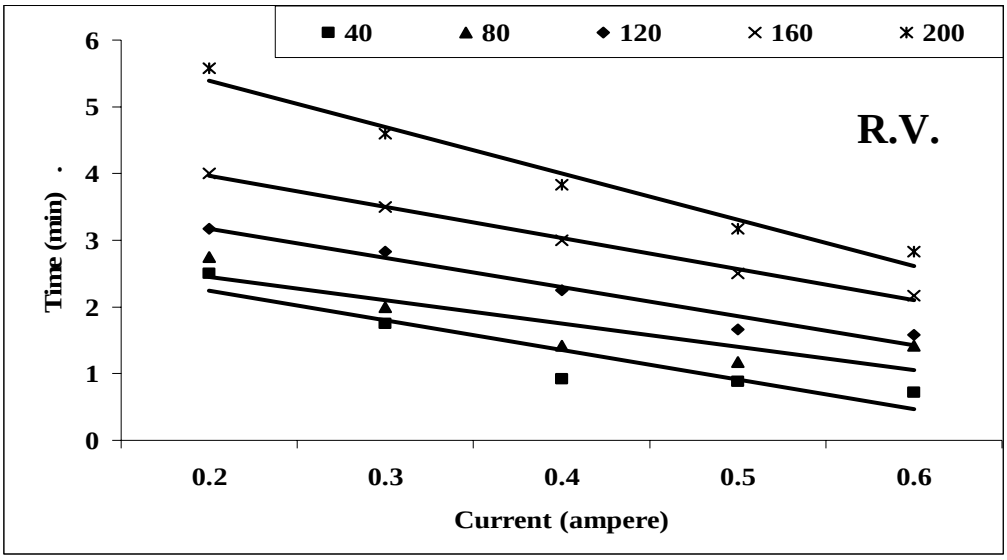


Figure (16): The effect of the different current values on the time of ozonatian at different Dye Concentrations

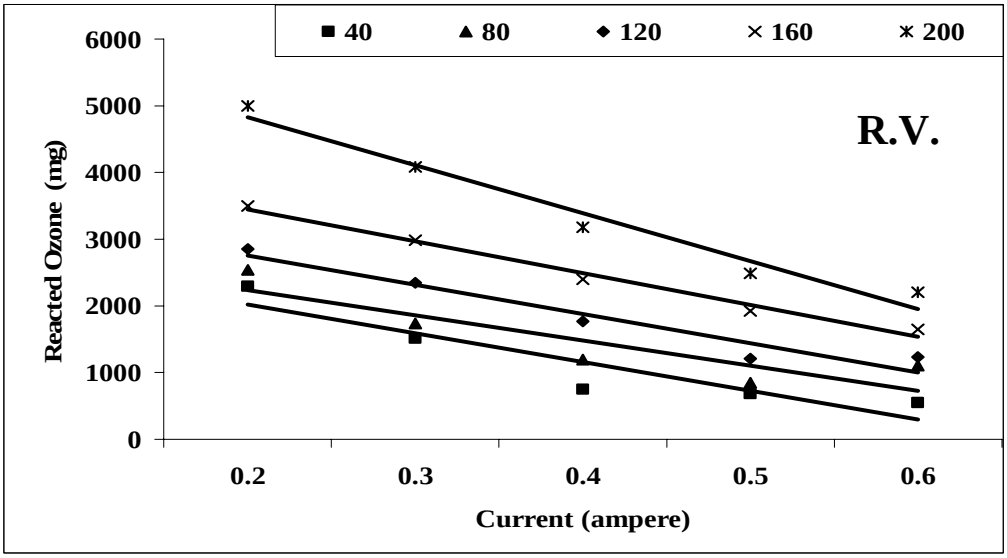


Figure (17): The effect of different current values on the reacted Ozone at different Dye Concentration

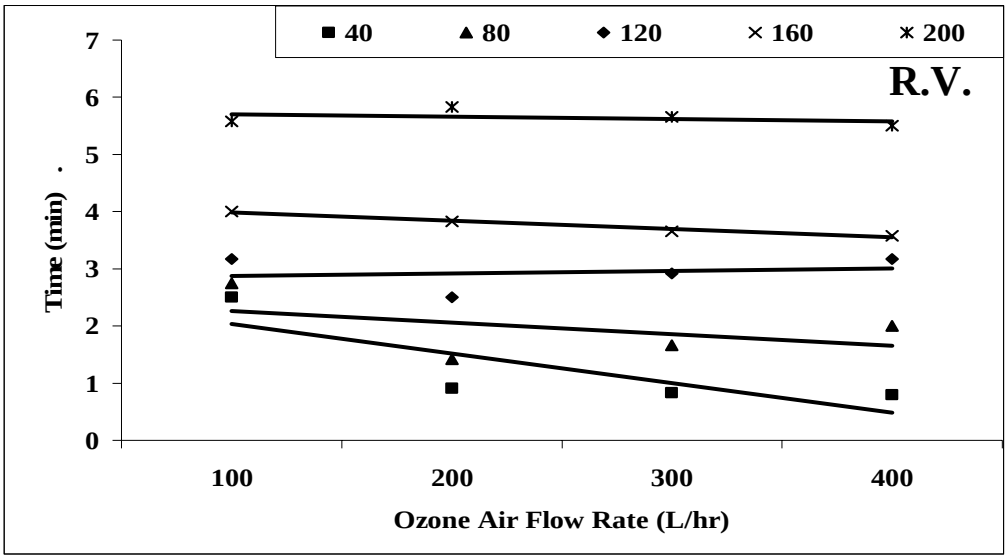


Figure (18): The effect of Ozone-Air Flow Rate on the Decolarization time at different Dye Concentrations

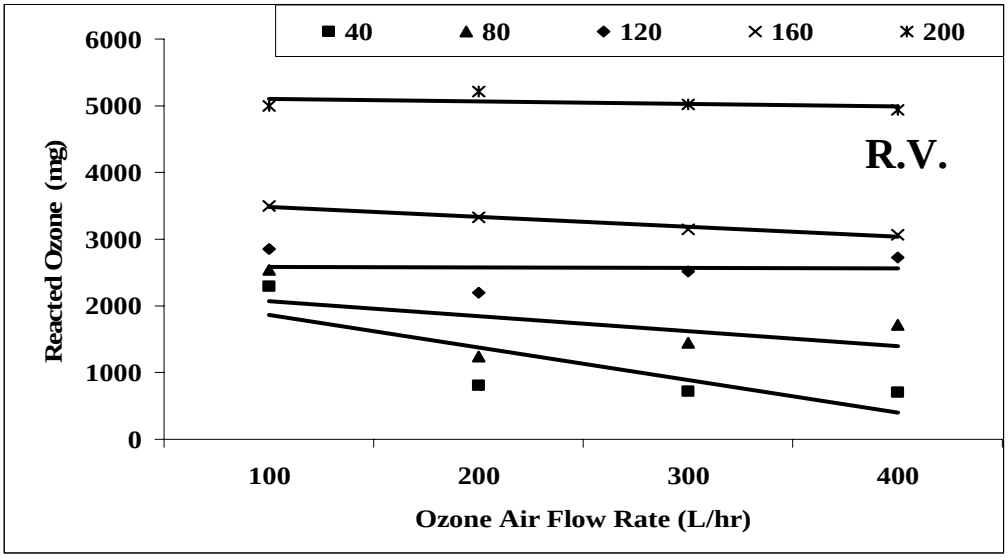
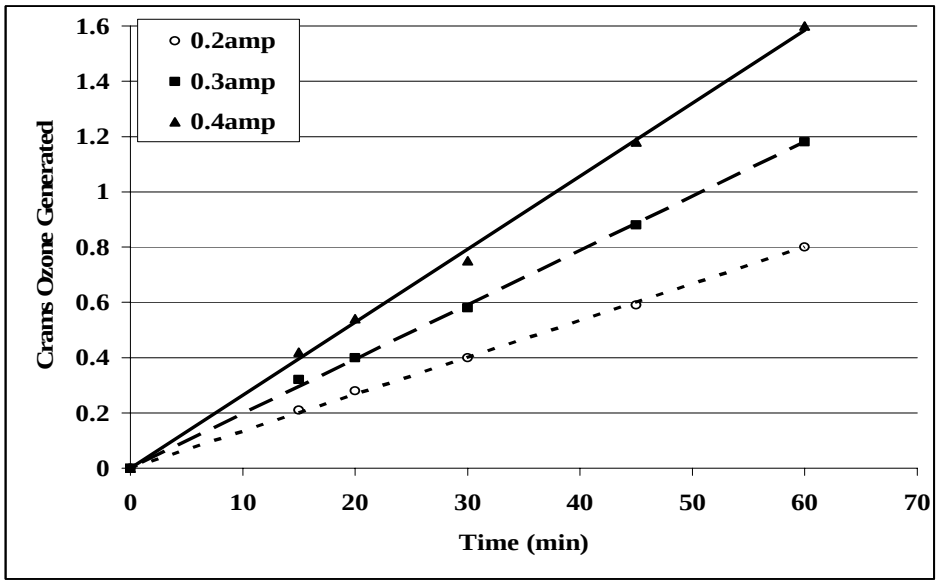
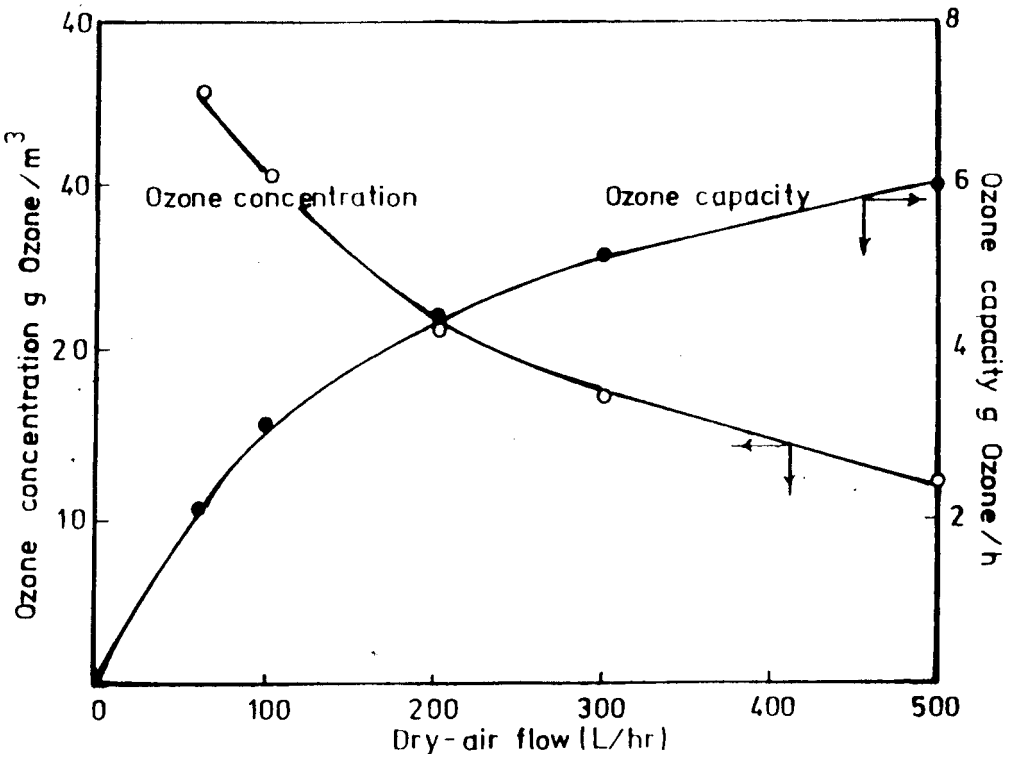


Figure (19): The effect of Ozone-Air Flow Rate on the amount reacted Ozone at different Dye Concentrations



Calibration curvies for ozoniser performance at different currents and flow rate 60l/hr



4. CONCLUSION

From the obtained data in the present study, it can be concluded that, the ozonation process is a very effective process for the decolorization of textile wastewater,as we can reach 98% decolorization in few minutes. Adjusting some controlling factors will give high result of decolorization.

It is recommended that, there is a direct need to enhance the ozonation process as a very effective method for wastewater treatment to modify the allowable limits for discharging wastewaters to the marine environment.

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