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DISCOLORATION OF REACTIVE DYES IN WASTEWATERS BY OZONATION

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Dedicated to the memory of Krassimir Genov PhD (1974-2011)

Abstract

Three different reactive dyes - Reactive Blue 19, Reactive Orange 16 and Reactive Red 180 were dissolved in water separately in concentration 0.04g/l as model pollutants for contaminated wastewaters from textile industry. Every wastewater sample was treated by ozone with concentration 2000 ppm for 30 minutes at ambient temperature and the effect of discoloration was traced after 5, 10, 20 and 30 minutes. The highest degree of discoloration was obtained for Reactive Blue 19 model water pollutant dye where 98% discoloration was reached after 5 minutes ozonation and 99% after 30 minutes treatment, while the lowest discoloration was observed for Reactive Orange 16 – 84% after 30 minutes treatment. The discoloration degree for the three sample solutions in the whole time interval was as follows: Reactive Blue 19 > Reactive Red 180 > Reactive Orange 16. In summary it can be concluded than application of ozone treatment for wastewaters, containing different reactive dyes is very effective and practically applicable.

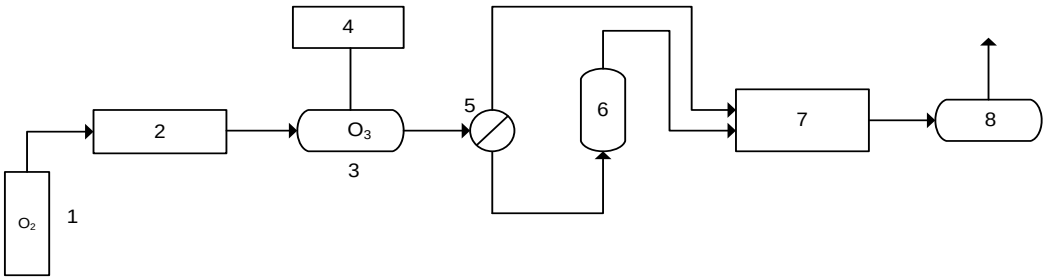
Key words: *ozonation, purification, wastewaters, azo dyes, antraquinone dyes, reactive dyes*

1. INTRODUCTION

The extensive use of different dyes in textile, pharmaceutical and food industries leads to sizeable contamination of natural waters. The azo dyes are the most commonly used textile dyes worldwide, accounting for more than a half of all commercial dyes (Turhan 2013). There are about 3000 different kinds of azo dyes with wide variety of colors and shades and easy for industrial use. Azo dyes are often with high water solubility and therefore their removal from wastewaters is difficult (Chen 2003). The dyes containing antraquinone chromophore group are with high chemical and biological resistance to degradation by conventional procedures (Andrade 2007). Many of the dyes are suspected to be carcinogenic and mutagenic (Peralta-Zamora 2009), toxic and poisonous (Knapp 1995, Daneshvar 2006). There are different methods of dye removal, including sedimentation, filtration, chemical treatment, oxidation, electrochemical methodology, Advanced Oxidation Processes (AOPs), biological, adsorption and ion exchange, and different combinations among them (Gupta 2009). One of the most effective methods with considerable application potential is the oxidation with ozone**.** Ozonation can break down double bonds of dye chromophors and other functional groups leading to partial discoloration (Basiri Parsa 2012). Chen (2009) used the ozone for reduction of color content in wastewater with content of Blue-19 and Orange-13, investigating the influence of ozone dosage and pH of the contaminated water. Fanchiang (2009) conducted effective degradation of Reactive Blue 19 in aqueous solution by ozonation.

2. MATERIALS AND METHODS

The process of discoloration has been monitored by UV-Vis absorbance spectrophotometer BOECO S26 in the wavelength range from 200 to 800 nm. The degree of discoloration is expressed as functional dependence versus time $-\ln (C/Co) = f(t)$ (where C_0 is initial concentration of the dye, C is the dye concentration after discoloration for selected time interval at λmax at 592 nm (maximal absorbance specific for Reactive Blue 19), λmax = 540 nm (maximal absorbance specific for Reactive Red 180) and λ = 494 nm (maximal absorbance specific for Reactive Orange 16). For conduction of ozonation of the wastewaters was used catalytic installation represented in Scheme 1. A series of small quantities (30ml) from the base sample are discoloured and the amount of ozone which is used with concentrations in the stream – 2000 ppm was investigated at 6 L/h flow rate.



Scheme 1. Catalytic installation used for ozonation:

1-oxygen, 2-flow control, 3-ozonator, 4-power supply, 5-three-way valve, 6-bubling reactor,

7-ozone analyzer, 8-residual ozone destroyer.

The chemical structures of the investigated reactive dyes in model solutions are presented in Figs 1÷3. C.I. Reactive Blue 19 has anthraquinone molecular structure, while C.I. Reactive Red 180 and C.I. Reactive Orange 16 have single azo structure.

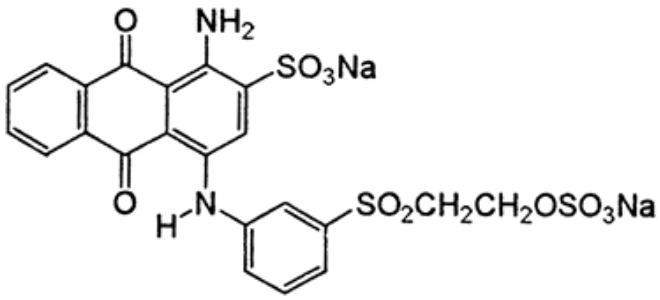


Fig.1. The chemical structure of textile coloring dye Reactive Blue 19.

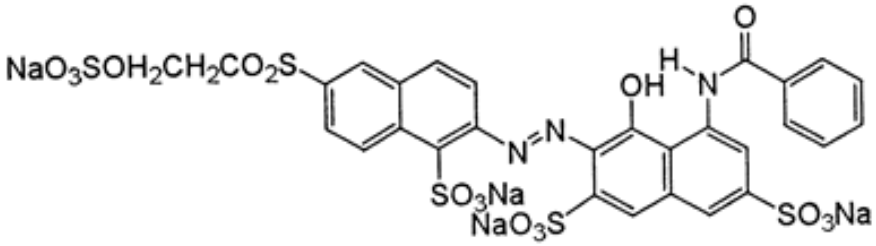


Fig. 2. The chemical structure of textile coloring dye Reactive Red 180.

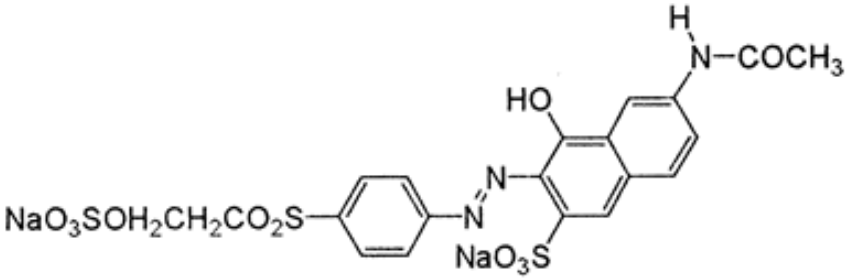


Fig. 3. The chemical structure of textile coloring dye Reactive Orange 16.

3. RESULTS AND DISCUSSION

The degrees of discolorarion of the dyes in model solutions after ozonation treatment for 30 minutes are shown in Figure 4. It can be seen for all of the dye-contaminated wastewaters that ozone treatment method leads to high extent of discoloration. The RB 19 polutant solution exhibits higher discoloration than those of the RO 16 and RR 180 solutions after ozonation.

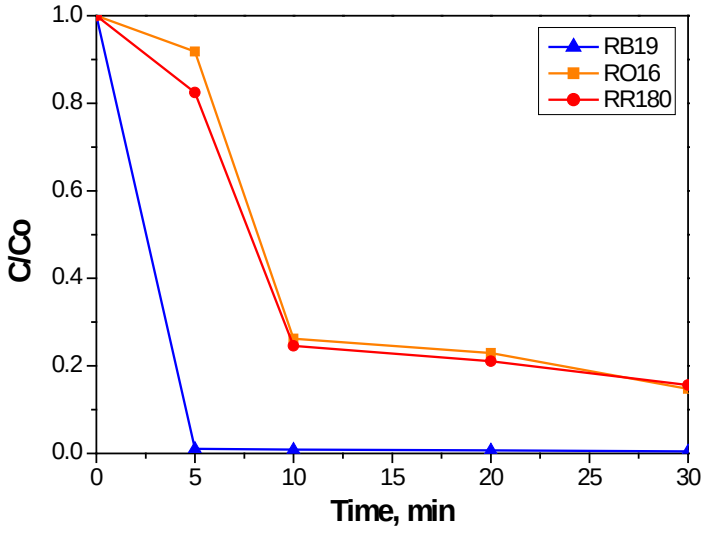


Fig. 4. Discoloration degree of the dyes (at concentration 0.04g/l), based on changes in the intensity of the absorbance peak with the course of time.

The degree of dye degradation has been calculated and it is represented in Figure 5. The degradation of Reactive Blue 19 model pollutant at room temperature is more than 98% after 5 minutes ozonation, while the other two model pollutants - Reactive Orange 16 and Reactive Red 180 reached around 74 and 75 % degradation respectively after 10 minutes ozonation. After 30 minutes treatment of the model wastewaters the degradation degree of RB 19 is higher than 99%, while the one for RR 180 is 85% and color removal for RO 16 is more than 84%. It should be noted that ozonation was exclusively effective for discoloration of antraquinone dye Reactive Blue 19, compared to the observed discoloration for azo dyes Reactive Orange 16 and Reactive Red 180, both with lower and similar discoloration degree, which leads to conclusion, that ozone treatment easily decompose antraquinone chromophore group. However, the color removal of dyes with azo bonds is also significant which means that ozonation is sufficiently effective method for treatment of mixture of different dyes.

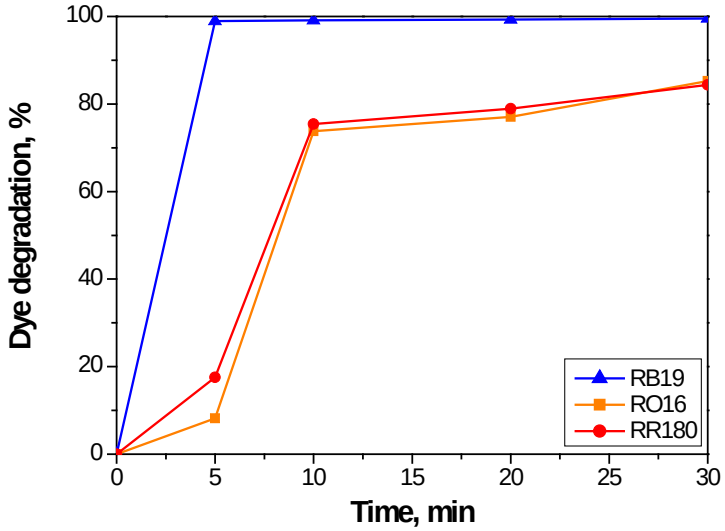


Fig.5. Degree of dye degradation as a function of the time of the dyes - Reactive Blue 19, Reactive Orange 16 and Reactive Red 180.

Degradation rate constants for the three investigated dyes Reactive Blue 19, Reactive Red 180 and Reactive Orange 16 are presented in Figures 6, 7 and 8.

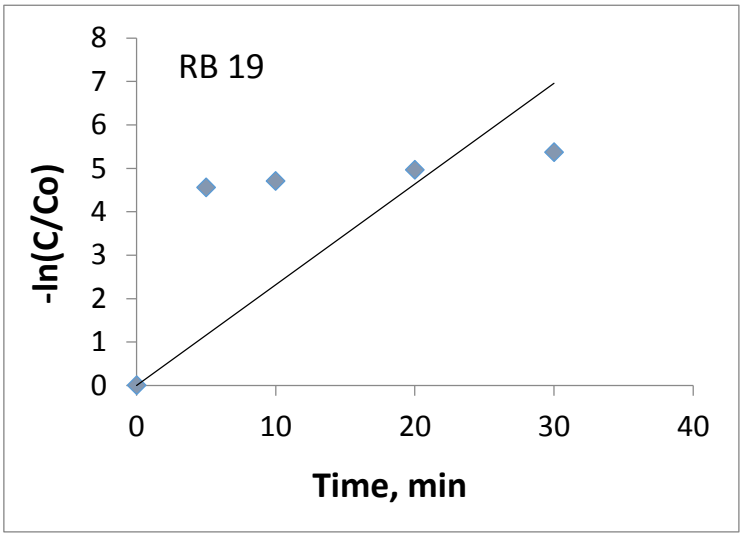


Fig. 6. Reaction course as a function of the time of discoloration –ln (C/C_0) of Reactive Blue 19 (RB 19); where C_0 is initial concentration of the dye, C is the dye concentration after discoloration.

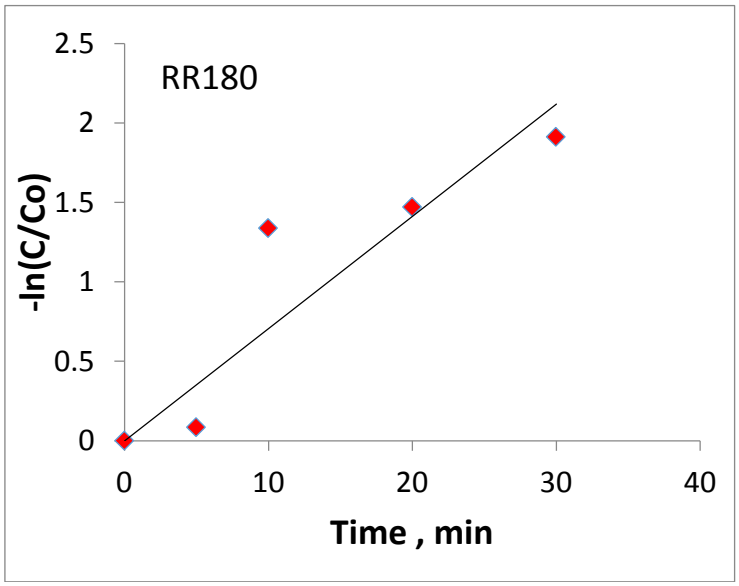


Fig.7. Reaction course as a function of the time of discoloration –ln (C/C_0) of Reactive Red 180 (RR 180); where C_0 is initial concentration of the dye, C is the dye concentration after discoloration.

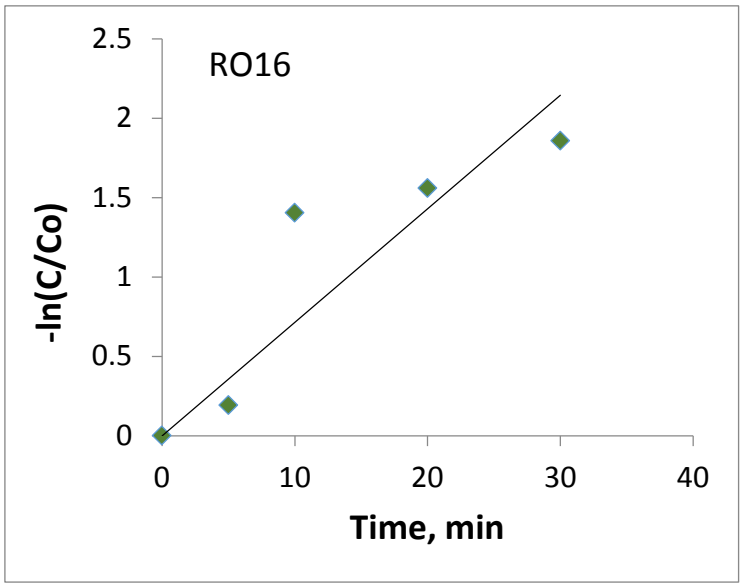


Fig. 8. Reaction course as a function of the time of discoloration –ln (C/C_0) of Reactive Orange 16 (RO16); where C_0 is initial concentration of the dye, C is the dye concentration after discoloration.

Degradation rate constants were calculated using the equation $-\ln(C/C_0) = K_t$ on the basis of the slope of linear dependence and the values are presented in Table 1. The units of the initial and momentous concentrations (mol/L) in the nominator and denominator are cancelled in the left logarithmic part of the equation and for this reason the unit for the rate constant becomes (min^{-1}). As it is seen from these values the performance of the RB 19 is outstanding.

Table 1. Rate constant evaluation.

Dye	Abbreviation	Degradation rate constant, min^{-1}
Reactive Blue 19	(RB19)	$23x10^{-2}$
Reactive Orange 16	(RO16)	$7.06\ x10^{-2}$
Reactive Red 180	(RR180)	$7.15\ x10^{-2}$

4. CONCLUSION

The ozonation for treatment of contaminated model wastewaters samples with three different reactive dyes proved as one of the most efficient methods for decomposition of pollutants and discoloration of wastewaters. Highest effectiveness is observed for decomposition of antraquinone dyes (Reactive Blue 19), where there is more than 98% dye degradation after 5 minutes treatment and practically full discoloration after 30 minutes ozonation. Significant dye degradation is achieved for azo dyes Reactive Red 180 and Reactive Orange 16, where more than 84% of color removal is observed after 30 min. ozonation. The obtained data from recent investigation clearly indicates the possibility for universal practical application of ozonation for treatment of different kinds of dyes with different chromophore groups and its high efficiency.

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