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Application of oxidation process with the use of H_2O_2 and NaClO to dyes aqueous solutions

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Hydrogen peroxide and sodium hypochlorite were applied to discoloration of dyes Reactive Orange 20 and Reactive Blue 13 in water solution concentration 100 mg L-1.
Influence of ferrous ions concentration ranging from 0 to 30 mg L-1, different doses of oxidants at varied pH and at ambient temperature was investigated. Both dyes were oxidized by hydrogen peroxide at pH below 4 at 5 mg L-1 Fe2+ ions as catalyst. Oxidation by sodium hypochlorite of Reactive Orange 20 was effective at pH below 4 with the presence of 5 mg L-1 of ferrous ions. Reactive Blue 13 was sufficiently discolored by sodium hypochlorite both at values of pH below 4 and at pH 8. High removal of color (95–100 %) was obtained for dyes used.

Keywords: discoloration, dyes, hydrogen peroxide, sodium hypochlorite

1. INTRODUCTION

Colored wastewaters from dye syntheses works and textile dye exhausted baths are very resistant to biological treatment [1]. Specific color of wastewater is particularly difficult to remove by biochemical oxidation due to high persistence of organic dyes for biodegradation. Large number of papers, to be dealt with oxidation of organic substances in aqueous systems by chemical oxidative agents, discuss the problem of color removal [2,3]. Chemical oxidation of dyes belongs to the group of methods available for color removal from dyes containing wastewaters [4].

In that paper there are presented the results of examination of discoloration efficiency of two organic dyes Reactive Orange 20 and Reactive Blue 13 in water solutions with concentration of 100 mg L^{-1}. Hydrogen peroxide and sodium hypochlorite were used in the presence of Fe^{2+} as a catalyst in the so--called Fenton process [5]. Fenton reaction denotes high efficiency of oxidation due to hydroxyl radicals generated as a result of decomposition of oxidative agent molecules by ferrous ions at low pH of the reaction environment:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO^{\cdot} + OH^-$$

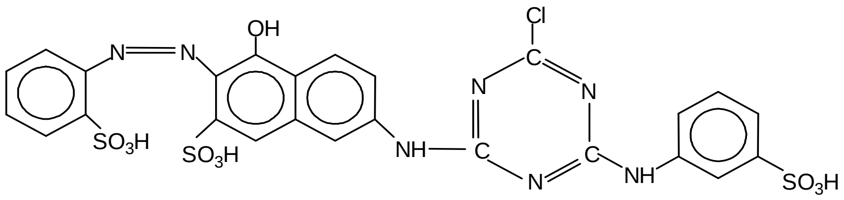
$$Fe^{2+} + HOCl \rightarrow Fe^{3+} + HO^{\cdot} + Cl^-$$

Hydroxyl radicals are very strong oxidants because their redox potential has one of the highest observed values of 2.8 V. These radicals are non-selective oxidants and react vigorously with many organics, thus can be trapped by some substances. It is known that Fenton process is highly dependent on reaction parameters such as pH, temperature, time and dose of reagents. Range of reaction conditions ought to be investigated using optimum amount of substrates. For instance at higher doses of oxidative agents or catalysts their amounts decrease and as a result smaller yields are obtained. It is a reason why optimum parameters of Fenton reaction should be found in laboratories. The aim of the herewith paper was to present the application of hydrogen peroxide and sodium hypochlorite for discoloration of model water solution dyes.

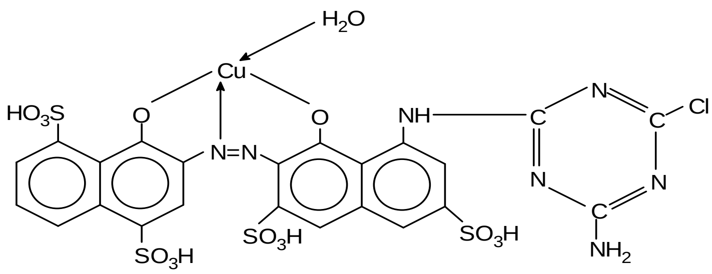
2. EXPERIMENTAL

The investigations with hydrogen peroxide and sodium hypochlorite were carried out in the batch reactors. Concentration of 100 mg L^{-1} commercial form of dyes in demineralized water was applied. Varied doses of oxidative agent and $FeCl_2$ were added to the reactor, which contained dye solution and then pH was adjusted by means of H_2SO_4 and NaOH solutions. Time of reaction was set for two hours at ambient temperature for all trials. Absorbances were measured before A_0 and after oxidation A_t with the use of Shimadzu UV-VIS spectrophotometer at specific wavelength for Reactive Orange 20 and Reactive Blue 13 at 480 nm and 580 nm, respectively. From measured absorbance values percentage of color removal was calculated according to formula $(A_0 - A_t)/A_0 x100\%$. The percentage of dye discoloration was plotted as a function of reaction time – t. Molecule formula of dyes is presented below:

Reactive Orange 20



Reactive Blue 13



3. RESULTS AND DISCUSSION

Oxidation by hydrogen peroxide. The optimal reaction conditions were investigated during the first series of experiments. At first pH of reaction habitat ranged from 2 to 5 at 0.34 and 0.68 mg doses of H_2O_2 per 1 mg of dyes. It was found that pH of reaction environment cannot be higher than 4 and optimal value of pH was in the range from 2.5 to 3.5 for both dyes used.

Effect of ferrous ion catalyst was investigated with concentration range from 0 to 30 mg L^{-1} Fe^{2+}. The results are presented in Figure 1.

One can see from Figure 1 that addition of ferrous ions to the both examined dye solutions increased color removal. Optimum catalyst concentration was stated at 5 mg L^{-1} Fe^{2+}. It was also visible that at higher doses of hydrogen peroxide from 0.34 to 0.68 mg per 1 mg of dye increased considerably color removal.

Effect of different doses of hydrogen peroxide was investigated at pH 2.5 and 5 mg L^{-1} Fe^{2+}. The results are shown in Figure 2. One can see from Figure 2 that percentage of color removal was higher for Reactive Blue 13 than for Reactive Orange 20 at the same doses in the range from 0.07 to 0.34 mg H_2O_2 per 1 mg of dye. At maximum used doses of 0.7 mg of hydrogen peroxide, the obtained color removal was much higher than 95 % for both examined dyes.

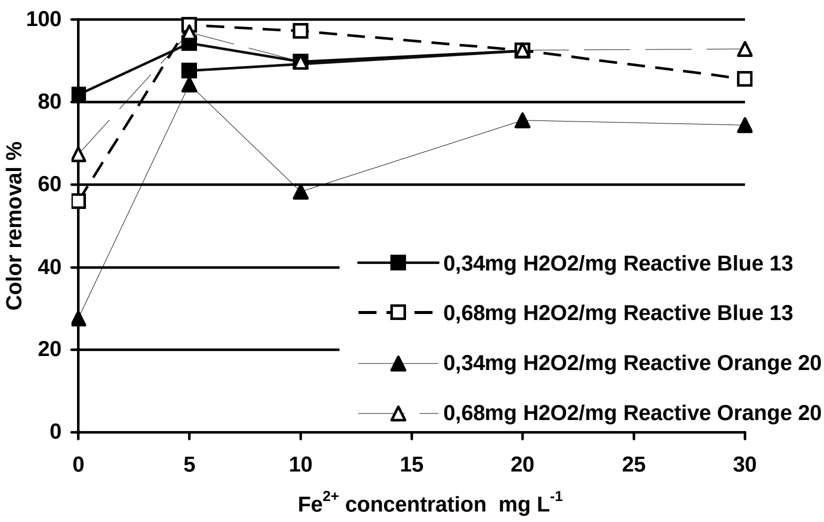


Fig. 1. Effect of ferrous ion catalyst on color removal by hydrogen peroxide at pH 2.5

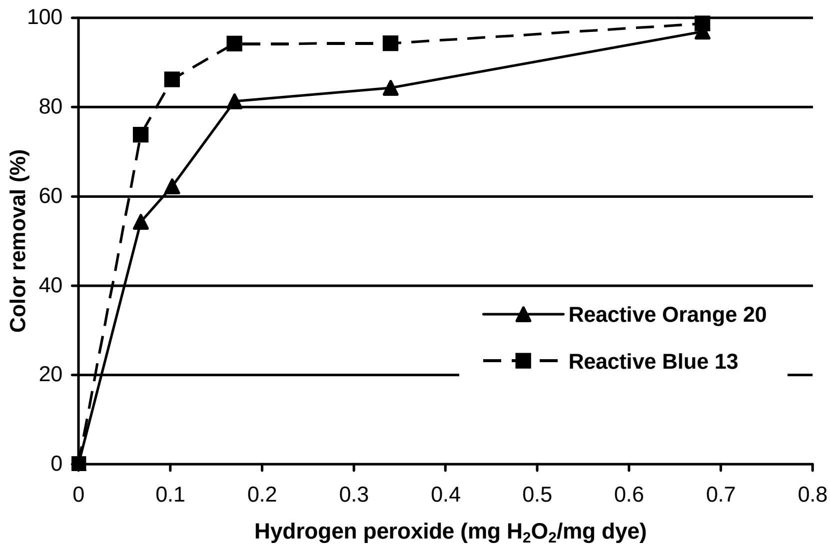


Fig. 2. Effect of hydrogen peroxide doses on color removal at pH 2.5 and 5 mg L^{-1} Fe^{2+}

Oxidation by sodium hypochlorite. The effect of pH of reaction habitat ranging from 3.5 to 9.5 was investigated at 5 mg L^{-1} Fe^{2+} and at selected dose of sodium hypochlorite for both examined dyes. The results are presented in Figure 3.

One can see from Figure 3 that for Reactive Orange 20, pH of reaction habitat cannot be higher than 3.5 because at values pH 4 and higher, color removal was below 20 % whereas at pH 3.5 it was 65 %. Reactive Blue 13 dye was successfully removed for all pH values used. This is why the next experimental trials were carried out for Reactive Orange 20 at pH 3.5 and at two selected pH values 3.5 and 8 for Reactive Blue 13 with various concentrations of ferrous ions. The results are presented in Figure 4.

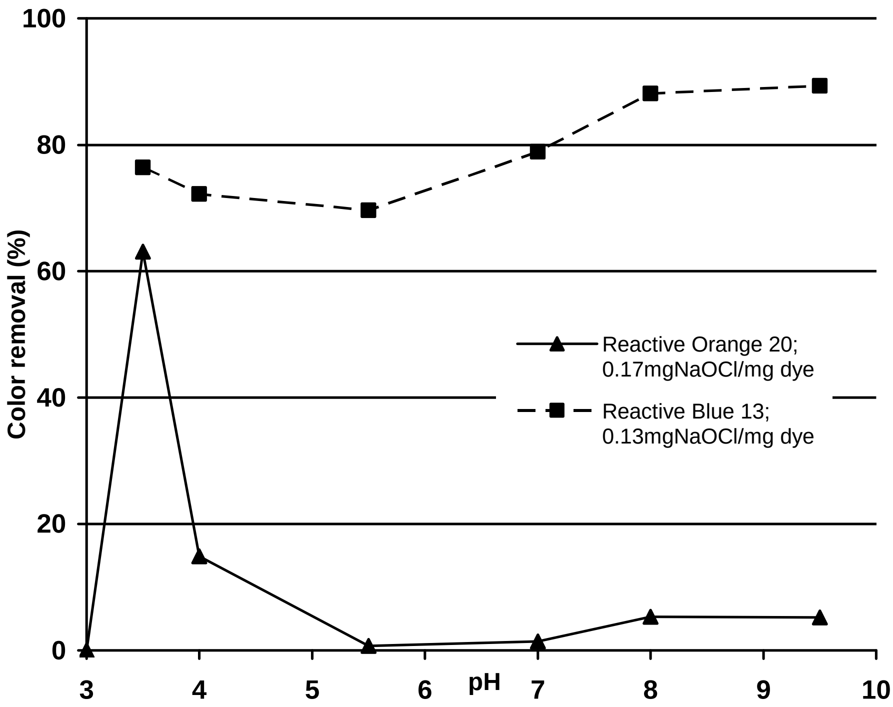


Fig. 3. Effect of pH on color removal by sodium hypochlorite at 5 mg L^{-1} Fe^{2+}

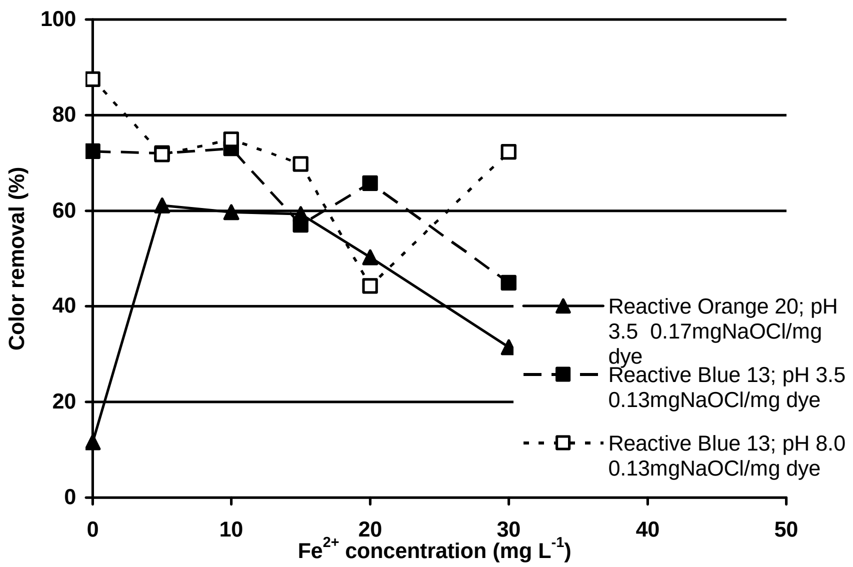


Fig. 4. Effect of ferrous ion catalyst on color removal by sodium hypochlorite at different doses and pH

One can see from Figure 4 that concentrations of Fe^{2+} ions 5–15 mg L^{-1} gave very similar relative high percentage of color removal for Reactive Orange 20. It was finally concluded that 5 mg L^{-1} concentration of ferrous ions were high enough for this dye oxidation.

Reactive Blue 13 was sufficiently discolored without catalyst at pH 8.0 but at pH 3.5 small concentrations of 5–10 mg L^{-1} Fe^{2+} ions probably improved oxidation reaction in a fact the effect was not high. The obtained results can be presumably explained by the presence of Cu in molecule of dye, which might be competitive as a catalyst against ferrous ions in Fenton reaction.

The influence of doses of sodium hypochlorite on color removal was finally investigated at pH 3.5 and 5 mg L^{-1} of catalyst ferrous ions. The results are presented in Figure 5. In the Figure 5 it is shown that for Reactive Blue 13 a smaller dose required of sodium hypochlorite and the percentage of color removal was more efficient than for Reactive Orange 20. It can be explained that oxidation in the case of Reactive Blue 13 by sodium hypochlorite in Fenton process at low pH value is probably improved by Cu present in a molecule of dye.

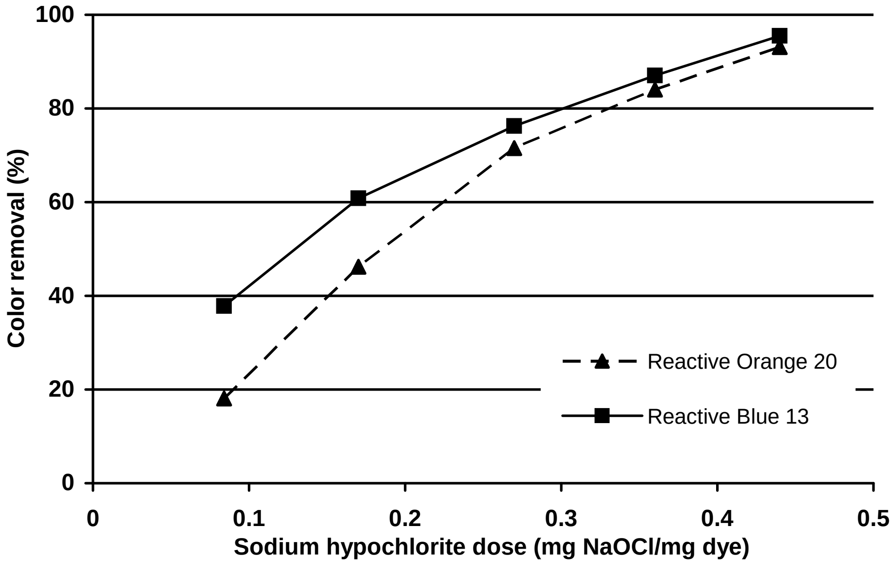


Fig. 5. Effect of sodium hypochlorite dose on color removal at pH 3.5 and 5 mg L^{-1} Fe^{2+}

4. CONCLUSIONS

1. Hydrogen peroxide and sodium hypochlorite caused discoloration of Reactive Orange 20 and Reactive Blue 13 dyes with high efficiency.
2. Both dyes used were oxidized by hydrogen peroxide at pH below 4 in the presence of catalyst ferrous ions. Concentration of catalyst of 5 mg L^{-1} Fe^{2+} was high enough for oxidation.
3. Oxidation by sodium hypochlorite of Reactive Orange 20 was effective at pH below 4, similarly to hydrogen peroxide in the presence of ferrous ion as catalyst.
4. Discoloration of Reactive Blue 13 by NaOCl was sufficient at values of pH below 4 in the presence of Fe^{2+} ions and at values of pH 8 without ferrous ions.
5. Oxidation abilities of sodium hypochlorite were more advantageous than for hydrogen peroxide. However, the AOX by-products of oxidation generated in discoloration process by NaOCl should be taken into consideration what has been reported by M. Jank et al. [6]. The latter will be investigated in further research, which the authors are planning to carry out.

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CURRICULA VITAE

Dr. Eng. Ryszard Tosik, born in Poland in 1943, graduated from the Faculty of Chemistry at Technical University of Łódź, Poland, obtaining MScE degree in 1966, specializing in Chemical Engineering. In 1974 received his Ph.D. degree at the same University. Participated in training periods at Polish Academy of Science, Electrochemistry and Corrosion Division in Warsaw and several chemical factories in Poland. For over 35 years an academic teacher in the Institute of General and Ecological Chemistry of Technical University of Łódź, Poland.

Scientific visits at University of Faro, Portugal and Imperial College of Science, Technology and Medicine in London, UK. Participated in international meetings organized by NATO Advanced Study Institutes (ASIs) and Advanced Research Workshops (ARWs): *New Technologies For Large Water Supply Projects (ASI)s,* 1994 Albena-Varna, Bulgaria; *Controversies Between Water Development and Protection of Environment (ASIs),* 1996 Visegrad, Hungary; *Security of Public Water Supplies (ARWs),* 1998 Tihany, Hungary.

Worked as an expert on corrosion and a senior designer, as well as consulting designer for water and wastewater treatment processes in various Water Project Offices in Poland. Major fields of scientific interest are ranged from investigation on water and wastewater purification with use of Advanced Oxidation Processes (ozone, ozonation with catalysts, hydrogen peroxide, etc.).

He published over 40 original articles on water and wastewater treatment in Polish and international journals, presented many papers, communications and posters on international conferences, e.g. in Faro (Portugal), San Francisco (USA) and Berlin (Germany). Owns five patents in the fields of water and wastewater treatment technologies.

Anna Jóźwiak graduated from the Technical Univesity of Łódź gaining her MScE in 1970. In 1979 she obtained her PhD and at present she works in the Institute of General and Ecological Chemistry (Technical University of Łódź). Her interests mainly concern technology of water treatment and waste disposal.

Magdalena Mitros. Born in Augustów (Poland) in 1977. Graduated from Technical University of Łódź (MScE) – environmental protection in 2002. She is post-graduate student in the Institute of General and Ecological Chemistry of Technical University in Łódź. Her research concerns treatment of wastewater from disposal industry containing organic dyes, with application of oxidation.