Journal of Physical & Theoretical Chemistry
Islamic Azad University of Iran 3 (1)
(2006)
Science and Research Campus
ISSN: 1735-2126

Study of Photooxidative Degradation of Reactive Dyes from Aqueous Solutions by UV/ ClO_2 Process

S. Hashemian[1,2], K. Zare[2,3*]

[1] Islamic Azad University, Department of Chemistry, Yazd branch, Iran
[2] Islamic Azad University, Department of Chemistry, Science and Research Campus, Tehran, Iran
[3] Shahid Beheshti University

ABSTRACT

The color removal of three reactive dyes in an aquatic system without prior treatment was studied. Selected commercial dyes were treated with $NaClO_2$ and UV as oxidation agents. Effects of nature of oxidant, temperature, pH of solutions, concentration of ClO_2^-, contact time of ClO_2^- and UV irradiation were investigated. Optimal ClO_2^- concentration for color removal in the absence of UV irradiation was found to be 20 mg l⁻ for all dyes studied. Combination of UV irradiation and ClO_2^- was found to be more effective. ClO_2^- dosage between 20 mg l⁻ and UV irradiation (15 watts) for color removal than individual oxidant with contact time of 30 minutes was required. The accuracy of method was checked by measuring the COD of the samples. For determination of color removal of samples, Spectrophotometery method was used for measurement of absorbance changes of the samples (ΔA).

Keywords: Oxidation; Color removal; Chlorite; UV; textile Wastewater

* Corresponding author

INTRODUCTION

Color in industrial wastewater is often objectionable and an environmental problem for the dyestuff manufacturing and textile industries. Kuto showed that, Biological treatment; usually do not adequately remove color from textile wastewater [1]. However tertiary treatment such as chemical coagulation, oxidation, adsorption and reverse osmosis are usually effective methods in removing color from textile wastewater. S. V. Mohon and co workers used adsorptionanl chemical coagulation method for color removal of monoazo acid dye from aqueous solutions [2].

Ruey-Sin Juang. et.al studied adsorption behavior of reactive dyes from aqueous solutions on Chitosan [3]. Anuradha Mishra and co worker (2004) used polyacrylamid- grafted plantago phylum mucilage as a flocculant for treatment of textile wastewater [4].

Dean Adams said, chemical oxidation was also found as a very effective method in the treatment of industrial wastewater, especially for removal of odorous colors and toxic organic substances [5].

Jae. Choi. et.al (2004) was used ozone as an oxidation reagent for oxidation of color and COD of acid and reactive dyestuff in wastewater [6]. Shadia El Rafie investigated the decolorizing of dyes with hypochlorite and ozone reagent as oxidizing agent. They examined the effect of pH, temperature and time of treatment on decolorization [7]. Liao [8] and Ince [9] and shu [10] and Yang [11] shown that, Hydrogen peroxide and UV light have also been used successfully in wastewater treatment.

The UV dosage applied to a wastewater is determined by the intensity of UV radiation and contact time. The capability of UV alone as an oxidizing agent for water treatment is not clear.

C. Liao and coworkers reported that when the wastewater is exposures to a 14 watt UV light for 40 minutes, the color is reduced 20 percent [6]. However in other studies, Shu reported that exposure of UV light alone do not lead to significant decolorization of reactive dyes (Black 5 and Acid Red 1 and yellow 23) at various UV intensities and contact times [10]. $NaClO_2$ is water soluble, decomposes at 175^{0}C and used as an oxidizing agent. Chlorite (ClO_2^-) has also oxidative capabilities for color removal. Sodium Chlorite has sufficient oxidizing power to destroy all coloring matter and is not decomposed rapidly by acid or temperature. In addition, UV light in combination with ClO_2^-can be an effective agent to eliminate color from textile wastewaters. In this study effect of UV/ClO_2^- oxidizing agents on elimination of three reactive dyes (blue, red, black) from textile wastewater samples and effluent was investigated. Different parameters including initial ClO_2^- concentration, contact time of ClO_2^-, UV irradiation time, pH and temperature of solutions for determining the optimum conditions for this process, were examined to evaluate their effects on the efficiency of the color removal process.

American Dye Manufactures Institute (ADMI) is an extension of tristimulus method for measuring of color. This method is applicable for colored waters and wastewaters having color characteristics significantly different from platinum-cobalt standards. In this study the results were compared together, therefore instead of ADMI method, Spectrophotometry method was used and an absorbance change of samples was measured (Standard Method 1995, method 2120E) [12].

For accuracy of experiments, %COD reductions of samples also were determined. For determination of Chemical Oxygen Demand (COD) of every dye and effluent Guide direction 5220 C in Standard Methods 1995 was used [12].

EXPERIMENTAL

The UV irradiation used in this study was a 31 centimeter (cm) horizontal bench-scale reactor consisting of a 15 millimeter (mm) diameter quartz tube and a low pressure mercury vapor lamp with a power of 15 watts which emitted ultraviolet irradiation of the wavelength of 254 nanometer (nm). The lamp has a base face length of 29 cm and arc length of 21 cm. Spectrophotometer (Simadzu UV-VIS 160 A with 1cm quartz cells) for measurement of color change was used. A digital dynamic pH meter (M-Series, M-12 by HORIBA) with combined glass electrode was used for measurement of pH.

Commercial reactive dyes (Brilliant red, Indigo Blue, 5 Black) were pro-analysis grade and purchased from Boyakh Saz Co. The dyes were in powder form and proper amount was dissolved in distillated water at room temperature to obtain a stock standard solution of 1000 mg l^{-}), standard solutions were prepared daily by stepwise dilution of 1000 mg l^{-} stock solution and was covered with aluminum foil to avoid degradation by the laboratory fluorescent light.

Effluent discharge was obtained from Yazdbaf Textile factory, which is a commercial dye house and textile manufacturing facility in Yazd.

Sodium chlorite ($NaClO_2$) was supplied by Merck chemical Company (25Wt %). Stock solution of $NaClO_2$ (1000 mg l^{-}) was prepared by dissolving of 0.0905 gram of $NaClO_2$ in water in the 1000 mil flask, diluted standard solutions was prepared daily from stock solution. All other reagents used more of the highest purity available and at least of analytical grade. For the quality control purpose distilled and deionized water was used.

STATISTICAL ANALYSIS

All of results were analyzed by an analysis of variance (ANOVA) on the SPSS for windows program. The analysis of homogeneity of variance according to Duncan test also applied.

RESULTS AND DISCUSSION

Effect of ClO_2^- contact time on color removal from dyes solutions

A constant level of chlorite concentration of 50 mg l^{-}, pH of 7 and room temperature (23 ^{0}C) was maintained during all test procedures. Contact times were varied Time from 1 to 90 minutes. Color reduction was determinated by measurement of the absorbance of the samples before (A_0) and after (A) addition of chlorite ($\Delta A=A-A_0$). The measurement was done at the maximum wavelength of absorbance of each color (λ_{max}).

(λ_{max} red, blue and black colors were 494, 595 and 464 nm respectively). The effect of ClO_2^- contact time on color removal is shown in Figure 1. The results showed that red and blue dyes under test yielded significant decolorization in 25-30 minutes, whereas 5 black and effluent needed longer contact time of 30-40 minutes. The oxidant concentration showed no significant difference ($P>0.05$) when the contact times were longer than these.

Effect of ClO_2^- concentration on color removal from different dye solutions

Chlorite will readily react with organic substances in the standard dye solutions and the effluent. The effect of ClO_2^- concentration was examined at 30 minutes contact time of ClO_2^-, at 23^0C and pH 7.

Figure 2 shows that the concentration of ClO_2^- has a significant effect on dye solutions.

As illustrated, the addition of as little as 20 mg l ˉof chlorite, the blue and red decolorization rates are significant. The rate of decolorization of the black dye and wastewater effluent was much lower than the other colors. Figure 2 shows, with increasing concentration of oxidant up to 25-30 mg lˉ, the reaction rate and the amount of color removal increases, which leveled off concentration. With increases of chlorite concentration more than this among color removal was nearly constant ($P>0.05$). The percentage of black color removal was consistently less than the other colors; in other hand the black dye was more resistant to oxidation process.

For accuracy of experiments, %COD reductions of samples were determined. COD of samples were measured according to Standard Method 1995 (method 5220 C). Table 1 shows the effect of concentration of ClO_2^- on %COD reduction of samples. According to table 1 maximum percent of COD removal in the over of 30 mg lˉ (70 percent) of ClO_2^- was obtained and then nearly was constant.

Effect of temperature on color removal from different dye solutions

To investigate the effect of temperature on the color removal process, a variety of temperatures ranging from 20^0C to 60^0C in the solution were used for dye solutions after adjusting pH levels to a constant 7. Galindo, et al demonstrated that reactions in oxidation are effectively not sensitive to small changes in temperature in the range of 22-45 ^{0}C [13]. The results of this experiment showed that increasing the temperature to 60 ^{0}C with maintaining chlorite concentration and time yielded constant, increased color removal, but chlorite ions were decomposed at higher temperatures (175^{0}C). Therefore in subsequent experiments for high accuracy, simplicity and reaction control, a temperature of 23 ^{0}C was used.

Effect of pH of solutions

The pH and alkality of the dye solution can significantly affect color elimination and the rate of reduction. Hence the effect of different pHs (2-10) on different dye solutions using 1 M HCl and NaOH was investigated. Figure 3 shows the percent of color removal in pH range of 5-8 is higher. It is worthwhile to not that for effluent; the best rate of color reduction was in pH levels of 5-6. When pH increased from 7 to 12 and decrease from 7 to 2 color removal was not significantly ($P>0.05$). However as when an acid is added to an aqueous solution of sodium chlorite, it liberate chlorine dioxide, which has a great corrosive action on the materials of construction including stainless steel, Therefore pH of 7 was used to conduct subsequent experiments.

From COD removal the similar results were obtained.

Effect of UV irradiation time on color removal from different dye solutions

The effect of time of irradiation of UV light at optimum condition and UV power 15 watts was considered by varying the time of irradiation between 0-90 minutes. The color of all of the solutions decreased sharply during the first minute of UV exposure time and then decreased, approximately, in a linear fashion up to the 30 minutes (Figure 4). Further the results showed the blue and red color needed shorter time (25 minutes) than black color and effluent (40 minutes). Duncan test from One-Way ANOVA also confirmed this result. It is important to note that UV treatment alone did not significantly reduce the color intensity of either the standard pure dye solutions or the wastewater effluent (nearly <40 percent) to be considered a success. The color reduction after 25 minute exposure time were negligible ($P>0.05$).

Liao has shown, Contact time required for decolorize various wastewaters in several studies cited in the literature ranged from 30 seconds to 1 hour and other studied also confirmed this results [14].

As the results of Table 2 shows, with UV light alone only nearly 40-50 percent of COD reduced.

Effect of UV time irradiation in presence of oxidant (ClO_2^-) [UV/ClO_2^-] on color removal from different dye solutions

Because each oxidants alone, reduce low percent of dyes (under 50 percent) in optimal condition (room temperature, pH 7 and 20 mg l^- ClO_2^-), the UV irradiation time of dye solutions in presence of oxidant ClO_2^- was investigated. The UV time irradiation was variable between 0-90 minutes. The result of studies is shown in Figure 5. Results suggest that UV/ClO_2^- (20mg l^- of oxidant and 30 minutes of UV irradiation time) will ensure adequate decolorization of effluent. ClO_2^- treatment with UV irradiation was capable of reducing approximately over 80 percent of color from textile wastewater. This results also confirmed by one-way ANOV. Duncan test from ANOVA is shown for high concentration of oxidant and longer contact time of irradiation no significant and P value is more than 0.05. This is probably due to fact that ClO_2^- in water or wastewater converted to Cl_2 and O_2 and heat as follow, whereas in presence of UV irradiation, it converted to free radicals of ClO2, which is stronger oxidizing agent.

$$ClO_2^- \longrightarrow Cl_2 + O_2 + Heat$$
$$ClO_2^- + UV \longrightarrow ClO_2^0$$

As the results were shown in Figure 6, maximum COD removal from samples were similar to the color reduction, in other hand COD reduction was consistent with

Color removal in experiments shown above.

CONCLUSION

The studies revealed that the treatment of dye solutions and effluent by UV/ ClO_2^- is effective in decolorization and degradation of organic components under study.

The highest reduction of color in standard solution and effluent has obtained from ClO_2^- concentration 20-25 mg l⁻ and UV irradiation time 30-40 minute. Increasing the exposure duration in either case did not result in improvement of color reduction in any of the colors, since oxidation occurred in early stages. Determination of optimal ClO_2^- dosage for a particular treatment requires preliminary evaluation of each dye. If the dye structure is known, the theoretical ClO_2^- concentration, which is necessary for removal, can be estimated, but effluent often consists of a mixture of dyes and therefore we have to determine optimum oxidant concentration for each dye separately.

Results also showed that combination of UV and ClO_2^- could reduce higher percent of color from textile wastewater. Probably due to formation of free radicals, this is strong oxidizing agent. The red and blue dye solutions were decolorized more than black dye. The black dye was resistant to the treatment. Therefore combination of UV irradiation and ClO_2^- as an oxidant is effective and suitable for color removal from reactive textile wastewater.

The results also showed pH 7 is suitable for color removal. The effect of temperature was due to higher reaction rate at 60 ^{0}C than 23 ^{0}C as a result of higher reactivity of Chlorite. ClO_2^- could oxidize dyes more efficiently in high temperature but it also is decomposed, therefore in experiments 23 ^{0}C was used. It is notable that the COD reduction yielded similar color removal results.

Table 1. Effect of ClO_2^- dosage on %COD removal of dye solutions and effluent at constant time 15 minutes and room temperature at pH 7

Concentration of ClO_2^- (mgl^{-1})	%CD removal of red color	%COD removal of black color	%COD removal of blue color	%COD removal of effluent
0	0	0	0	0
5	5	5	5	2
10	10	10	10	8
15	20	15	30	25
20	35	20	48	30
25	45	25	65	36
30	47	50	65	44
40	46	50	64	45
50	45	50	60	44
60	45	50	56	40

Table 2. COD removal for varying contact time by UV irradiation for different dye solutions and effluent at constant concentration of ClO_2^- (15 mg l^{-1}) and room temperature at pH 7

Time UV (min)	%COD removal red color	%COD removal black color	%COD removal blue color	%COD removal effluent
0	0	0	0	0
2	3	3	8	2
5	5	4	15	3
7	8	7	25	4
10	10	10	40	5
15	20	20	45	10
20	30	27	50	20
25	35	38	55	40
30	38	40	60	45
40	39	42	65	47
60	40	43	68	48

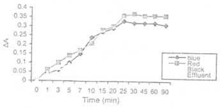

Figure. 1. Effect of contact time of $ClO2^-$ on color reduction in dye solutions and effluent at initial $ClO2^-$ concentration 15 mg l^{-1} at room temperature

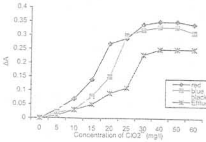

Figure. 2. Effect of $ClO2^-$ dosage on color removal for different color and effluent at room temprature

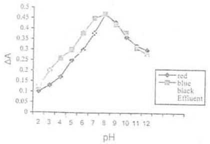

Figure. 3. Effect of pH solutions on color removal from dyes and effluent at concentration of 20 ppm ClO2 and contact time 15 minutes and room temperature

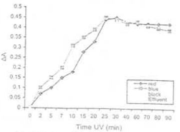

Figure. 4. Effect of UV irradiation on color removal from dyes and effluent at concentration of 15 mg l^{-1} $ClO2^-$ and contact time 15 minutes and room temperature at pH 7

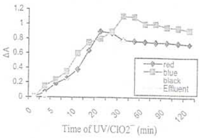

Figure. 5. Effect of UV Irradiation time in presence of $ClO2^-$ on color removal of dyes and effluent at room temperature and pH 7

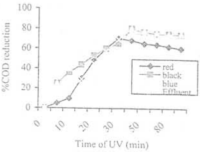

Figure. 6. Effect of UV irradiation on COD removal from dyes and effluent at concentration of 20 mg/l $ClO2^-$ and room temperature at pH 7 at different contact time.

REFERENCES

1- Kuto. W. G., Decolorizing dye wastewater with Fenton s reagent, Wat. Res. 26, 7 (1992) 881.

2- Venkata Mohan. S., Sailaja.P., Srimurali.M., Karthikeyan. J. Environ Eng and Policy. (1999) 149.

3- Ruey-Shin Juang. Etal. J. Chem. Tech. Biotechnol. 70 (1997) 391.

4- Anuradha Mishra. Rajani Srinivasan. Malvika Bajai. Rashmi Dubey. Colloid. Polym. Sci. 282. (2004) 722.

5- Water and Wastewater Examination Manualv. Dean Adams. Second Edition 1991 by Lewis publishers.

6- Jae- Wook Choi, Hyung Keun Song, etal, Korean J. Chem. Eng. 21 (2). (2004). 398.

7- Shadia El Rafie. Research Journal of Chemistry and Environment. 6(1) (2002) 13.

8- Liao C.H. and Gurol M.D. Environ . Sc. & Techinol. 29 (12) (1995) 3007.

9- Ince.N.H and Gonenc, D. T. Environmental Technology. 18. (1997) 179.

10- Shu ,H., Huang, C., Chang, M. Chemosphere.. 29 (1994) 2597.

11- Yang, Y ., Wyatt, D .T .II. , Bahorshky, M.. Textie Chemist and Colorist. (1998) 30.

12- AWWA, APHA, WEF, Standard Methods for the Examination of Water and Wastewater. 19th ed , Washington DC, USA (1995). Method 2120 C, 5220A.5220 B, 2120 E.

13- Golido., Kalt, A., J. Dyes and pigment, 40 (1998) 27.

14- Liao, C., Lu, M.,Yang,Y., Lu, I. Enviromenttal Engineering Science. 17 (2000) 1.