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Contributed Paper

Degradation of Congo Red Dye by Ozonation

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ABSTRACT

The purpose of this study was to investigate the degradation of azo dye in synthetic wastewater by ozonation and to optimize the reaction parameters such as pH, time and type of catalysts which influence the efficiencies of color and COD removal. Congo red dye was selected as model pollutant. Catalytic and non-catalytic ozonation of Congo red dye were carried out in batch reactor with constant ozone flow rate of 36 mg/h. $Cu(NO_3)_2$, $Ni(NO_3)_2$, $Fe(NO_3)_3$, Cu/Al_2O_3 and Cu/SiO_2 were used as catalysts for the catalytic ozonation system. It was observed that over 85% of Congo red could be removed within 1 h for all ozonation conditions. Higher color removal could be achieved when ozonation was carried out in alkaline (pH 10) and acidic (pH 4) condition as compared to in neutral (pH 7) condition. The reduction of COD was more than 60% for both catalytic and non-catalytic ozonation in 2 h. The catalytic ozonation using $Cu(NO_3)_2$ as catalyst showed the highest efficiency as it gave the 90% of color removal in 48 min with 60% of COD reduction. However, with catalyst, efficiencies of color decomposition are higher in alkaline and neutral conditions than in acidic condition. The ozonation of dye was found dominant by pseudo-first-order reaction at room temperature.

Keywords: Ozonation, Decolorization, Congo Red Dye, Azo Dyes, Advance Oxidation Process.

1. INTRODUCTION

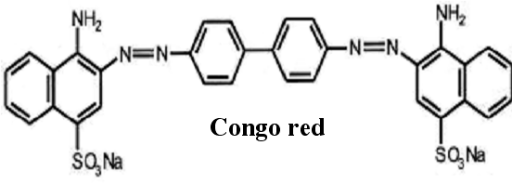
Textile industry is one of the most important industries among those contributing to Thailand's economic development contribution in last few decades. There are about 200,000 tons of dyes uses in textile industry. Designated as water soluble, it was estimated that 10 – 20 % of dye was lost during the dyeing process and released as effluent [1]. The reagents used in textile industry are very diverse in chemical composition. The non-biodegradability of textile wastewater is due to the high content

of dyestuffs, surfactants and other additives, which are generally organic compounds of complex structure [2]. It is difficult to treat these wastewaters by conventional technologies [3].

Congo red dye is one of important azo dyes. Its colored substances have complex chemical structures and high molecular weights. The chemical structure is the sodium salt of benzidinediazo-bis-1-naphtylamine-4-sulfonic acid (Figure 1). It is highly soluble in water and persistent in the environment, once discharged into a natural environment. Thus, the study on Congo red is interesting not only for being possible pollutants of industrial effluents but also because it is a good model of complex pollutants.

In the recent years, ozonation is one of the most attractive alternatives for decolorize dye wastewater. Ozone is an extremely strong oxidant and reacts rapidly with most of organic compounds [4]. Ozone reacts in aqueous solution with various organic and inorganic compounds, either by a direct reaction of molecular ozone or through a radical type reaction involving the hydroxyl radical produced by the ozone decomposition in water.

Ozone and hydroxyl radicals generated in aqueous solution are able to break the aromatic rings [5]. The ozonation process left no chemical sludge in the effluent, combined color removal and COD reduction in one step and is easily operated. Moreover, the residual ozone naturally decomposed to oxygen.



Congo red

Figure 1. The molecular structure of Congo red.

Recently, many catalysts used in catalytic ozonation process have been developed to improve the efficiency of ozonation. This includes transition metals ions, metal oxides and activated carbon.

The objective of the present work is to study the decolorization and COD removal of Congo red, as an azo dye model, in synthetic wastewater. The effects of pH, time and type of catalysts on the efficiencies of color and COD removal were studied.

2. METERIALS AND METHODS

2.1. Materials

Congo red ($C_{32}H_{22}N_6Na_2O_6S_2$; molecular weight: 696.66 g/mol) was purchased from Ajax Finechem. Dye solutions were prepared by dissolving the dye in distilled water. The Congo red solution has the initial pH of 7. The pH was adjusted with ammonium nitrate (NH_4NO_3) and sodium hydroxide (NaOH). $Cu(NO_3)_2$, $Ni(NO_3)_2$, $Fe(NO_3)_3$, Cu/Al_2O_3 and Cu/SiO_2 were used as catalysts for catalytic ozonation.

2.2. Ozonation experiment

The ozone was produced by ozone generator with flow rate of 36 mg/h and fed into the reactor through a porous glass diffuser located at the bottom of the reactor to produce fine bubbles. Ozonation was carried out in a 1,500 ml Pyrex glass reactor. Ozone–oxygen gas stream was continuously fed to the reactor trough a porous gas contributor. The residual ozone in the off–gas was adsorbed by KI solution as shown in Figure 2.

One liter of dye solution with an initial dye concentration of 25 ppm was added into the reactor before starting the reaction. Aligent 8453 UV Spectrophotometric analyses at the wavelength of 500 nm were performed in order to measure the concentration of the dye. Color and COD removal, at steady state, were

determined by the following equations:

$$R_{colour}\,(\%) = \left[\frac{C_{dye,\,o} - C_{dye,\,t}}{C_{dye,\,o}}\right] \times 100 \quad (1)$$

$$R_{COD}\,(\%) = \left[\frac{COD_{\,o} - COD_{\,t}}{COD_{\,o}}\right] \times 100 \quad (2)$$

Where C_{dye} (mg/L) is the dye concentration, COD (mg/L) the chemical oxygen demand and 'o' and't' correspond to initial time and sampling time, respectively. The extent of mineralization of the Congo red was assessed by measuring the COD using the standard acid dichromate method.

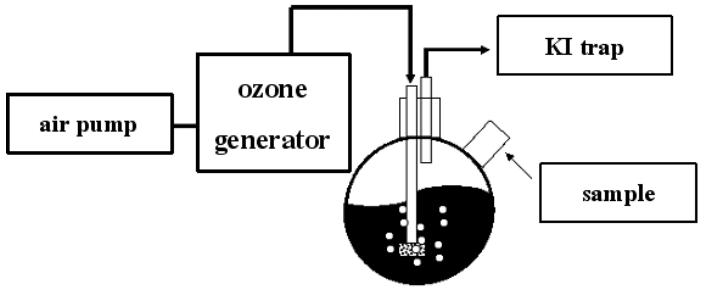


Figure 2. Diagram of ozonation system.

3. RESULTS AND DISCUSSION

3.1. Effect of ozonation on the color removal.

The effect of the reaction time on color removal is displayed in Figure 3 Results in Figure 3 showed that the color reduction occurred very fast achieving around 80% decolorization in 30 min. It should be noted that more than 50% abatement was achieved within the first 6 min. However, after 40 min treatment time, the color reduction did not significantly change and reached 90% reaction after 120 min. As shown above, the ozonation will be a promising process for the degradation of the Congo red.

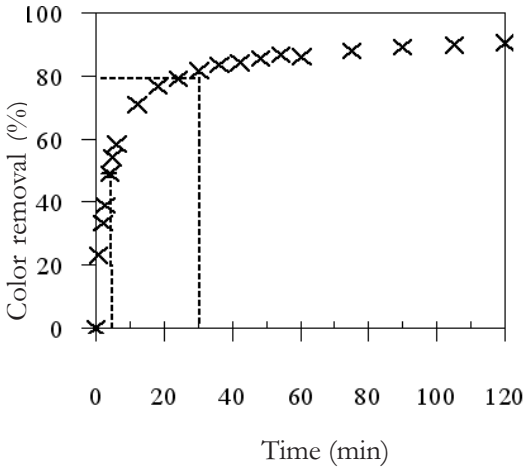


Figure 3. The color removal of Congo red dye over time, pH 7 at room temperature and atmospheric pressure.

3.2. Decolorization of Congo red with different catalysts.

Table 1 showed the results of catalytic ozonation. It was found that without catalysts, color removal reached 50, 70 and 90% within 6, 18 and 120 min., respectively. Of all 5 catalysts tested, $Cu(NO_3)_2$ and Cu/Al_2O_3 were two promising candidates for catalytic ozonation process. When $Cu(NO_3)_2$ and Cu/Al_2O_3 were used as catalysts, the time required for 50% and 70 % color removal was reduced by at least half the time required for non–catalytic process.

3.3. Effect of pH on decolorization during ozonation.

The pH is one of the major factors which may affect treatment efficiency by ozonation. The treatment time for achieving the required percent removal was illustrated in Figure 4. It is clear that the efficiency of color removal increased with increasing pH. 80% color removal was achieved after 24 min and 36 min at pH 10 and 4, respectively. This positive influence of pH on the color removal could be attributed to the presence of reactive radicals. The hydroxyl radicals are formed from ozone decomposition at high pH values, while the molecular ozone remains as the main oxidant at low pH values. It can be explained that the hydroxyl radicals have a higher oxidizing potential than molecular ozone, leading to better decolorization at high pH [4].

It can be seen from Figure 5 that $Cu(NO_3)_2$ catalyst could enhance decolorization in neutral and alkaline conditions. However, the use of $Cu(NO_3)_2$ catalyst did not help improving the decolorization rate in acidic condition.

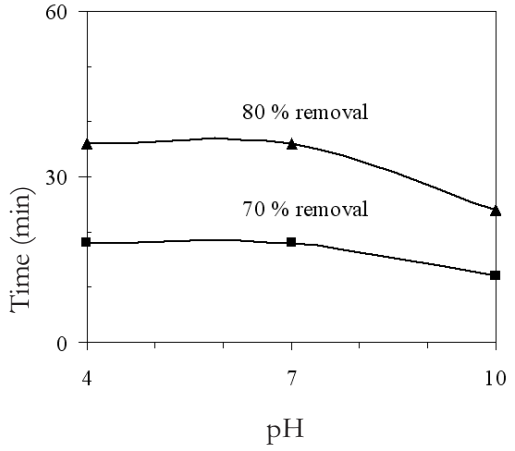


Figure 4. Effect of pH on 70 and 80 percent color removal of Congo red dye.

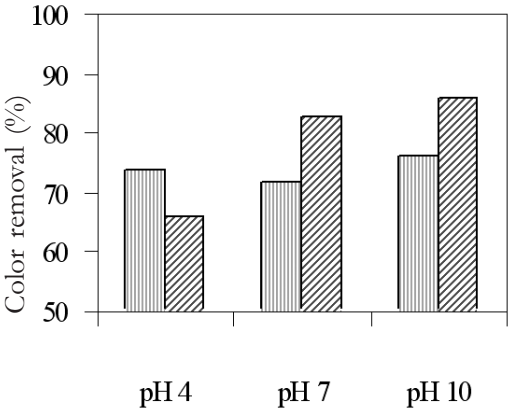


Figure 5. Effect of pH on color removal by ozonation after 20 min reaction time. (No catalyst, with $Cu(NO_3)_2$)

Table 1 Catalytic and non-catalytic decolorization of Congo red dye in synthetic wastewater.

Color removal (%)	Decolorization time (min)					
	without Catalyst	$Cu(NO_3)_2$	$Ni(NO_3)_2$	$Fe(NO_3)_3$	Cu/Al_2O_3	Cu/SiO_2
50	6	2	2	12	3	5
70	18	4	12	42	6	12
90	120	48	120	*	90	90

* Color removal lower than 90%

3.4. Reaction kinetics of ozonation.

It is widely accepted that OH• from ozone decomposition is the important oxidant in ozonation process. Since, ozone was delivered in excess as compared to the dye. The reaction rate equation was therefore described by equation (3).

$$-r_A = -\frac{dC_A}{dt} = kC_A^{\alpha} \qquad (3)$$

Where r_A is the rate of dye decay, C_A is the dye concentration, k is the rate constant, α is the order of reaction respect to dye concentration.

Therefore, equation (3) can be rearranged to the pseudo-first-order equation in equation (4) where k is pseudo-first-order rate constant.

$$\ln(C_{At}/C_{A0}) = -kt \qquad (4)$$

Figure 6 indicated that the reactions with and without catalyst followed the pseudo-first-order

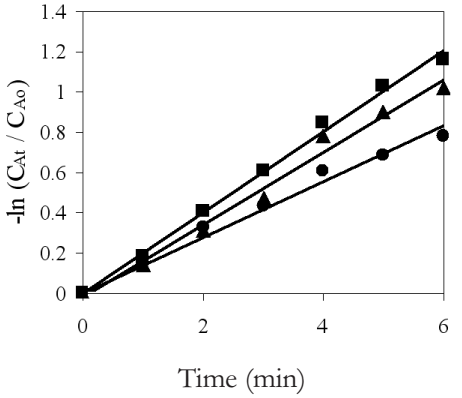


Figure 6. Decolorization of Congo red by ozonation 25 ppm dye concen-tration. (● O_3, ▲ $O_3/CuAl_2O_3$, ■ $O_3/Cu(NO_3)_2$) order reaction with good fitting (R^2 = 0.982- 0.996). The rate constants were 0.1254 min^{-1}, 0.1801 min^{-1} and 0.201 min^{-1} for Ozone, $O_3/CuAl_2O_3$ and $O_3/Cu(NO_3)_2$, respectively.

3.5. COD removal of Congo red effluents.

In this study, the effect of catalytic ozonation using $Cu(NO_3)_2$ and Cu/Al_2O_3 on COD removal was reported. Figure 7 showed that catalysts did not enhance the COD removal efficiency of the ozonation process. More than 60% COD removal was obtained in all conditions, with or without catalysts. The use from Figure 7 and Table 1 suggested that the COD removal did not correlate to the dye color reduction.

It could imply that the catalysts could only enhance the rate of color generating bond cleavage causing the color reduction. However, the catalysts used in this experiment could not lower the activation energy enough to disintegrate the backbone structure of the dye.

4. CONCLUSIONS

Ozone itself is a strong oxidizing agent and has a high efficiency of color removal. In this experiment, ozonation in neutral (pH 7) condition could remove color to more than 50, 70 and 90% within 6, 18 and 120 min. respectively. The efficiency of color removal increased with increasing pH. In catalytic ozonation, $Cu(NO_3)_2$ is the best catalyst as it enhanced the decolorization rate by 3 folds. Furthermore, ozonation process could reduce

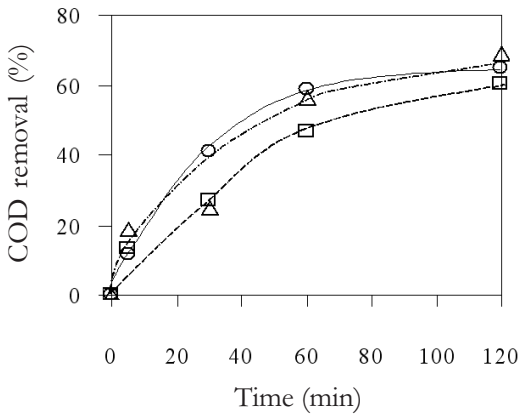


Figure 7. Effect of catalysts on percent COD removal of Congo red dye 25 ppm concentration pH 7. (○ O_3, △ $O_3/CuAl_2O_3$, □ $O_3/Cu(NO_3)_2$)

COD of dye solution to be at lease 60%.

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