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Characteristic of Colour and COD Removal of Azo Dye by Advanced Oxidation Process and Biological Treatment

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Abstract. In this study, the characteristic of COD and colour removal of azo dye by Advanced Oxidation Process (AOP) and biological treatment was evaluated for applying in azo dye industrial effluent treatment. Reactive Red 120 has been selected amongst azo dyes due to its high solubility in aquatic environment. AOP could be improving colour removal of reactive red 120 in comparison to ozonation, due to acceleration of ozone decomposition by Hydrogen Peroxide and eventually enhanced the production of the hydroxyl radical, which is quickly oxidize colour impacting functional group in reactive red 120. The optimum COD removal by AOP was achieved at 1 mg H_2O_2.mg O_3 $^{-1}$. Further addition of hydrogen peroxide could be increasing COD, which probably due to residual H_2O_2 that is not completely react with ozone to produce hydroxyl radical. In the multi-stage ozonation biological treatment, the role of ozonation seems to breakdown the azo dye molecule and created ozonation product that is easily biodegraded in biological treatment. On the other hand, advanced oxidation process tends to decompose ozone and hydrogen peroxide to produce OH radical, and react with azo dye through radical mechanism to completely mineralized azo dye.

Keywords: Azo Dye, Advanced Oxidation Process, Decolourization, biological treatment, Chemical Oxygen Demand

1. Introduction

Wastewater from dye industrial effluent is a complex synthetic organic that should be treating properly to reduce its COD, colour and toxicity [1]. Among the wastewater, azo dyes effluent from textile, plastic, leather, and paper industries are the largest and the most important constituent to be treated [2]. There are some methods used for the treatment of dye-containing wastewater [3]. Coagulation is effective for treatment of insoluble dyestuff wastewater but not so effective for soluble dyestuff wastewater [4, 5]. The adsorption method has difficulties in the treatment of insoluble dyestuff wastewater and it is very difficult to find the desorption process [5, 6]. The chemical method is to oxidize organic materials by oxidizing agents, such as ozone, H_2O_2, UV light or combination of such oxidants that is known as Advanced Oxidation Processes (AOPs). It is well established that AOP is effectively removing colour in azo dye wastewater due to its strong oxidizing property by breaking down the functional group that impacting colour on azo dye [7].

Several research works has been conducted to evaluate the performance of AOP or ozonation in combination with biological treatment to reduce colour and COD in azo dye wastewater. Bose et al. [8] reported that AOPs enhanced the degradation rate of 1, 3, 5-trinitrotriazacyclohexane (RDX) due to increased of hydroxyl radical formation. Muhammad et al [9] compared the treatment of raw and biotreated (upflow anaerobic sludge blanket, UASB) textile dye bath effluent by ozonation and AOPs. Takahashi et al [10] investigated the effects of pre-ozonation and subsequent biological treatment process on the decrease in dissolved organic carbon (DOC) and colour for dyeing wastewater.

Fahmi et al [11] reported that the multi-stage AOP and biological treatment could further improve DOC removal in drinking water sources, due to mineralization of both biodegradable and non-biodegradable DOC

by AOP. However, raw water for drinking water has different characteristic in compare to synthetic organic compound such as azo dye. In other study, it was reported that multi-stage ozonation in combination with biological treatment could further remove refractory synthetic compound such as azo dye in wastewater (12, 13]. The improvement of COD removal in the multi-stage ozonation-biological treatment was attributed by the production of biodegradable fraction of COD.

Some studies reported that azo dye was decolorized rapidly by AOP [5, 8, 9]; however, the role of this oxidizing agent for complete oxidation of azo dye is remaining unclear. Therefore, the characteristic of oxidation product by AOP and biological treatment should be examined to clarify the role of each process (AOP and biological treatment) for azo dye removal. In this study, the characteristic of COD and colour removal of Reactive Red 120 by AOP and biological treatment was evaluated for applying in azo dye industrial effluent treatment.

2. Materials and Methods

2.1. Preparation of Azo Dye Solution

Azo dye used in this study was of analytical grade obtained from Sigma-Aldrich. Reactive Red 120 has been selected due to its high solubility in aquatic environment, which is difficult to decolourize by conventional coagulation/flocculation and physical adsorption. Initial dye concentration was adjusted at 100 mg. L^{-1} by dilution with distilled water.

2.2. AOP and Biological Treatment

AOP selected in this study was the combination of ozone and hydrogen peroxide. Ozone was produced from an A2Z Ozone Generator with maximum capacity of 1 gr. min^{-1} utilizing pure oxygen gas feed. Ozonation of dye samples was carried out using a glass cylinder with a working volume of 2 L equipped with a glass diffuser. Two liters of Reactive Red 120 solution with the concentration of 100 mg. L^{-1} was added into the glass cylinder at pH 7.0. Ozone gas was supplied at various doses ranging from 0.5 - 10 mg O_3.mg^{-1} dye followed by aeration for 20 min to remove residual ozone. Hydrogen peroxide was added at range of 0.2 - 2.0 mg. mg^{-1} O_3 into the glass diffuser before ozonation process. After AOP, water samples were biodegraded by incubating with 1% (v/v) of river water as inoculums for 4 days to remove biodegradable COD.

The effect of ozone and H_2O_2 dose on azo dye color removal was evaluated by varying ozone contact time and initial H_2O_2 concentration. The performance of AOP and biological treatment was evaluate based on colour, and chemical oxygen demand (COD) removal.

In the multi-stage AOP-biological treatment, the solution was oxidized, aerated and biodegraded by the same method as the single-stage treatment. However, after biological treatment, each solution was ozonated again as the previous ozonation and following by biological treatment.

2.3. Analytical Method

Ozone concentration in feed gas was determined by the KI-starch titration [14]. Reactive Red 120 concentration in all samples was determined by Hitachi UV/Vis (U-2810) Spectrophotometer. COD were determined based on procedure derived in Standard method for the examination of water and wastewater [14]. The biodegradable COD is defined as COD fraction removed by biodegradation. The remaining COD after biological treatment is defined as residual COD.

3. Result and Discussion

3.1 Effect of H_2O_2 to O_3 ratio

Figure 1 shows UV-Vis spectrum before and after AOP treatment. The peak for the reactive red 120 was observed at λ_{max} of 535. The specified wavelength peaks were disappeared after AOP at various H_2O_2 to O_3 ratio, which indicated that the azo group of the synthetic dyes was transformed by AOP. Figure 2 shows the percentage of residual colour after AOP treatment at various H_2O_2 to O_3 ratio. As observed, ozonation without hydrogen peroxide (H_2O_2 to O_3 ratio = 0) still able to remove colour up to 99 %. Furthermore, the

addition of hydrogen peroxide at various concentrations could be removing colour completely. Previous result by De Sauza et al [15]) confirmed that colour removal efficiencies were greater than 96 % by ozonation. They verify that the ozonation process as a pre treatment increases the dye degradation. Result presented by Namboodri et al [16] also revealed that ozone able to decolorize all dyes except non soluble disperse and vat dye. On the other hand, in AOP hydrogen peroxide accelerates the decomposition of ozone and enhanced the production of the hydroxyl radical [17]. This radical quickly oxidize colour impacting functional group in azo dye, and consequently the azo dye is decolorized. From these results it is suggested that both ozonation and AOP were strong oxidants that appropriate for decolourization of azo dye.

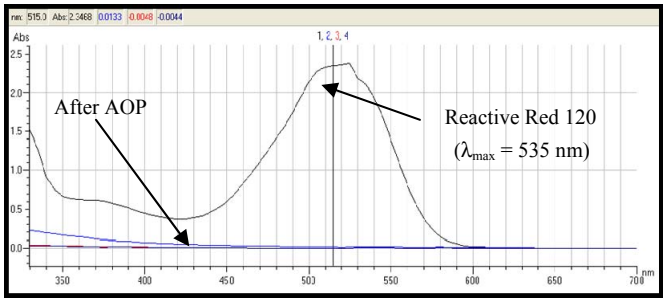


Figure 1. UV-Vis spectrum for reactive red 120 before and after AOP treatment

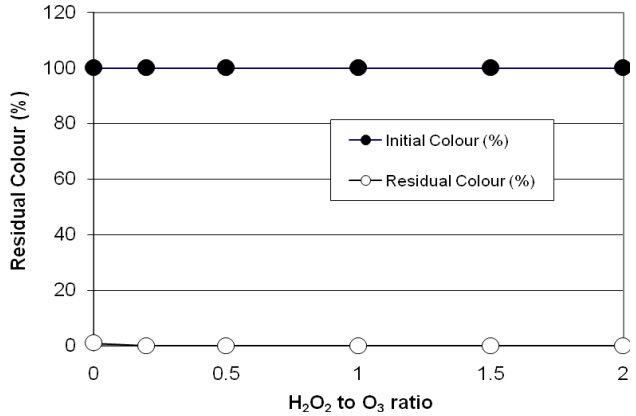


Figure 2. Percentage of residual colour at various H2O2 to O3 ratio

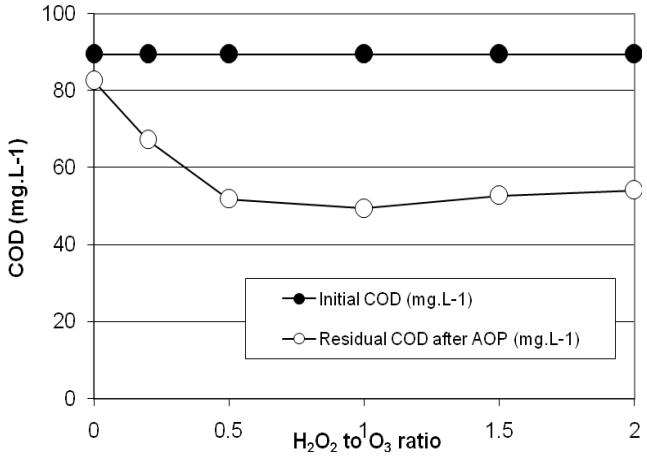
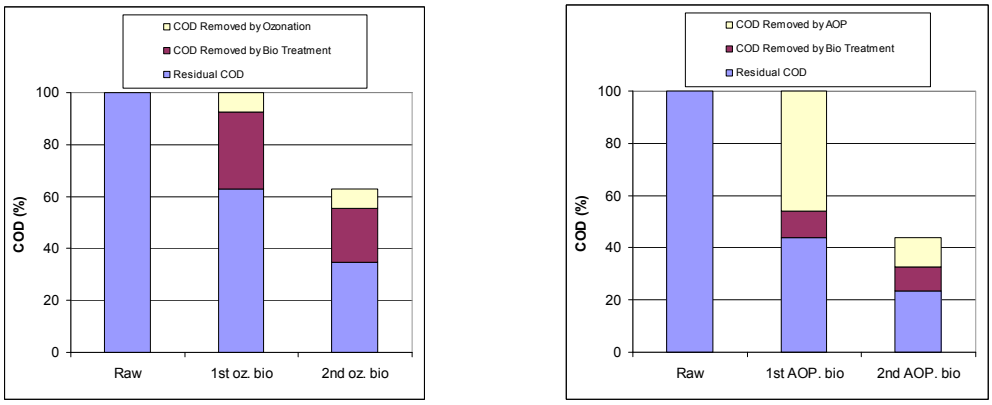


Figure 3. Variation of COD after AOP at various H2O2 to O3 ratio

Figure 3 present the variation of COD after AOP at various H_2O_2 to O_3 ratio. Initial COD value was 89.5 mg. L^{-1}. Ozonation without H_2O_2 addition decreased COD slightly to 82.6 mg. L^{-1}, whereas the addition of hydrogen peroxide from 0.2 - 1 mg H_2O_2.mg O_3 $^{-1}$ significantly decreased COD down to 49.4 mg. L^{-1} at optimum H_2O_2 dose (1 mg H_2O_2.mg O_3 $^{-1}$). However, further addition of hydrogen peroxide at 2 mg H_2O_2/ mg O_3 increasing COD to 54.1 mg/L. The observed high COD values can be partly explained by the presence of H_2O_2, which reacts with the substances used for the determination of COD such as potassium dichromate (VI) which reacts with H2O2 in an acidic medium to yield the unstable, peroxy dichromic acid; being unstable, this immediately degrades into Cr (III) salts. De Sauza [15] reported that there is a trend toward a decrease in COD with increased ozone dose, although occasional increases of COD were observed in the ozonation process due to dye molecules being oxidized resulting in small organic molecular fragments, such as acetic acid, aldehydes, ketones, contributing to the increase in COD during ozonation. In this study, it is expected that COD value would be decreased after AOP. From this experiment the optimum H_2O_2/O_3 ratio was selected at 1 mg H_2O_2/ mg O_3.

3.2 Comparison between Multi-stage Ozonation and AOP

Fig. 4 shows the comparison of COD percentage after multi-stage ozonation biological treatment and AOP biological treatment. In the multi-stage ozonation-biological treatment (fig 4a), 1st ozonation was slightly removed COD in raw wastewater (7.4 %). However, the biodegradable COD was significantly produced in 1st ozonation (29.6 %), and consequently this COD fraction was removed in subsequent biological treatment (1st biological treatment). Similarly, in 2nd ozonation-biological treatment main COD removal was attributed by biodegradable COD, in which final COD value was reduced down to 34.5 %. In the multi-stage ozonation biological treatment, the role of ozonation seems to breakdown the azo dye molecule and created ozonation product that is easily biodegraded in biological treatment. Therefore, ozone was not oxidized azo dye though complete mineralization to produce CO_2 and H_2O. De Sauza et al. [15] recommended ozonation as a pre treatment for combined chemical-biological treatment for azo dye removal. It is a potential process for enhancing colour removal and biodegradability of wastewater containing azo dye, once the appropriate ozonation time is determined. In this context, pre-treatment with ozone is economically desirable due to the lower quantity of ozone required for the mineralization of compounds, and the subsequent biological process will complete the mineralization with lower operational costs than those obtained with chemical processes.



(a) Multi stage Oz. Bio. Treatment (b) Multi stage AOP. Bio. Treatment

Figure 4. Comparison between Multi-stage Ozonation-biological treatment and Multi-stage AOP Biological Treatment

On the other hand, in the multi-stage AOP biological treatment (fig. 4b) 1st AOP removed COD significantly (45.9 %), whereas subsequent biological treatment only removed COD of 10.2 %. In 2nd AOP biological treatment similar trend of removal was observed, in which significant removal of COD was affected by AOP. After 2nd AOP-biological treatment the residual COD was 23.3 %. The result indicated that AOP tend to completely mineralized Azo Dye for COD removal, and slightly produced biodegradable fraction of COD. Advanced Oxidation Process represents a powerful treatment for toxic pollutant such as azo dye in textile waste water Al Kdasi et al. (2004). The addition of hydrogen peroxide and ozone to

wastewater accelerates the decomposition of ozone and enhances production of hydroxyl radical, which is able to oxidize a large spectrum of contaminants in wastewater.

From these observation, it is propose that the reaction between ozone and Azo Dye in aqueous environment resulted in the breakdown of double bond such as C=C and N=N in non biodegradable azo dye and converted it to readily biodegradable by product. It is likely that the reaction mechanism was through direct ozone molecular reaction and the oxidation potential of molecular ozone was not sufficient to completely mineralized azo dye. On the other hand, advanced oxidation process tends to decompose ozone and hydrogen peroxide to produce OH radical, and react with azo dye through radical mechanism to completely mineralized azo dye.

4. Summary and Conclusion

In this study, the characteristic of COD and colour removal of azo dye by AOP and biological treatment was evaluated for applying in azo dye industrial effluent treatment. Reactive Red 120 has been selected amongst azo dyes due to its high solubility in aquatic environment. Based on the result, the following conclusions were derived:

1. AOP could be improving colour removal of reactive red 120 in comparison to ozonation. It is likely, in AOP hydrogen peroxide accelerates the decomposition of ozone and enhanced the production of the hydroxyl radical, which is quickly oxidize colour impacting functional group in reactive red 120.
2. The optimum COD removal by AOP was achieved at 1 mg H_2O_2.mg O_3 $^{-1}$. Further addition of hydrogen peroxide could be increasing COD, which probably due to residual H_2O_2 that is not completely react with ozone to produce hydroxyl radical.
3. In the multi-stage ozonation biological treatment, the role of ozonation seems to breakdown the azo dye molecule and created ozonation product that is easily biodegraded in biological treatment. On the other hand, advanced oxidation process tends to decompose ozone and hydrogen peroxide to produce OH radical, and react with azo dye through radical mechanism to completely mineralized azo dye.

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