Study of Azodyes Degradation By Ozonation and Biological Treatment

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Abstract

Azo-dyes have been largely used in textile industry for dying cellulose and cotton fibers. This class of dyes present a low degree of fixation onto the fibers during dying. Hence, the generated effluent may cause environmental pollution due to high toxicity of chemical components. Owing to their color, the dye cause floral and aesthetic pollution since a small amount is clearly apparent. Azodyes are few or not biodegradable by microorganisms. The very low biodegradability of azodyes is confirmed by biological oxygen demand (BOD). Those are particularly characterized by high chemical oxygen demand (COD), presence of suspended solids and strong color. The aim of study is to suggest techno-economical viable method to discolor the effluent and disintegrate the toxic chemicals into smaller and simple non-toxic molecules. The Ozonation process and biological treatment have been carried out at different conditions for azodyes effluent such as Azoviolet, Congo red, Tartazine.

Keywords: Azodyes, BOD. COD, techno-economical viable method

INTRODUCTION

Amongst complex industrial wastewater with various types of coloring agents, dye wastes are predominant [1]. This wastewater not only toxic to the biological world, but it also has a dark color, which blocks sun light. By these reasons, it causes many problems to the ecosystem [2]. Azo dyes are widely used in textile, plastic, leather, and paper industries as additives [3]. The removal of azo dye, in aquatic environment is important because many azo dyes are toxic to aquatic organisms [4].

There are some methods used for the treatment of dye-containing wastewater [5]. Treatment of insoluble dyestuff wastewater is not so effective for soluble dyestuff wastewater by the desorption process [7], [8]. 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). Most factories use this method to reduce COD and color. But it cannot satisfy the environmental discharge standard by itself alone and the cost is relatively high. The combination of ozonation and biological treatment seems to be promising unit processes to remove residual color, COD and BOD of wastewater containing dye. The reaction between the oxidizing agent with dye in an aqueous environment lead to the decrease in aromaticity and molecular weight which eventually result in an increase in biodegradability and color removal of dye. The biodegradable compound produced during ozonation would be removed by the following biological treatment. Therefore, the improvement of biodegradability is considered to be essential factor that determines the performance of ozonation- biological treatment process.

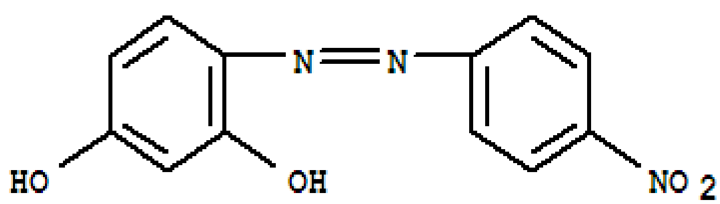
Bose et al. [9] reported that AOPs enhanced the degradation rate of 1,3,5- trinitrotriazacyclohexane due to increase of hydroxyl radical formation. Takahashi et al. [11] investigated the effects of pre-ozonation and subsequent biological treatment process on the decrease in dissolved organic carbon (DOC) and color for dyeing wastewater. Nishijima et al. [12] suggested that ozonation and biological treatment that operating in multistage mode could improve DOC removal in drinking water sources. The improvement of DOC removal in the multi-stage ozonation and Biological treatment process was mainly attributed to the decrease in hydrophobic fraction in raw water [13]. Fahmi et al. [14] 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 ozonation

In this study, decolorization and COD removal of various azo dyes such as Azoviolet, Congo-red, Tartazine in the single-stage ozonation-biological treatment process were evaluated to be applying for wastewater treatment containing azo dye.

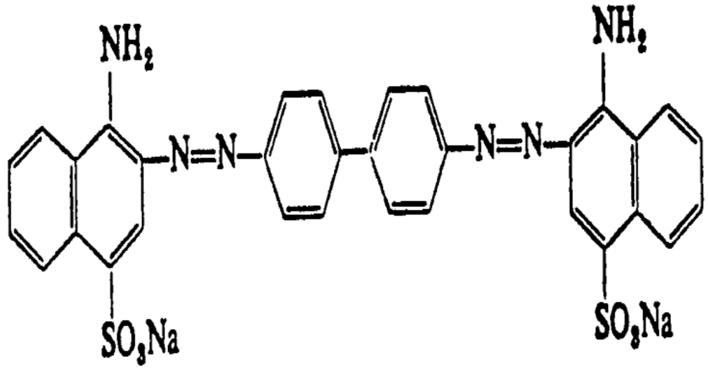
MATERIALS AND METHODS

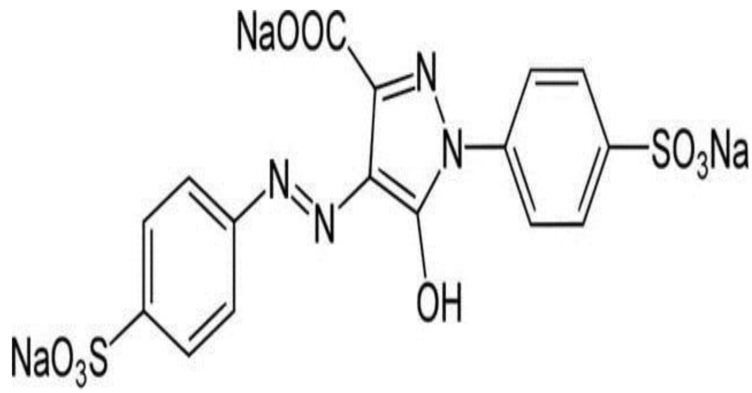
A. Preparation and characterization of Azo Dye Solutions

Azo dyes used were of analytical grade obtained from Loba make. Azoviolet, Congored, Tartazine have been selected amongst azo dyes in performing ozonation and biological treatment due to its high solubility in aquatic environment, which is difficult to decolorize by conventional coagulation/flocculation and physical adsorption. Initial dye concentrations were set at 100 mg. L^{-1} by dilution with distilled water. The characterization of dye was performed based on UV-Vis. adsorption spectra and its functional group.



Azoviolet





Tartazine

B. Ozonation and biological treatment experiments

Ozone was produced from an Eltech Ozone Generator with maximum capacity of 1 g. 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 and a silicon cap. Two liters of dye solution with the concentration of 100 mg L^{-1} was added into the glass cylinder. Ozone gas was supplied at various doses ranging from 0.3-7.2 mg O_3 mg dye^{-1} and following by aeration for 5 min to remove residual ozone. After ozonation, water samples were biodegraded by incubating with 1% (v/v) of river water as inoculums for 4 days to remove biodegradable COD. To compare the performance of the single-stage and multi-stage ozonation-Biological treatment, dye same was ozonated at the same total ozone dose.

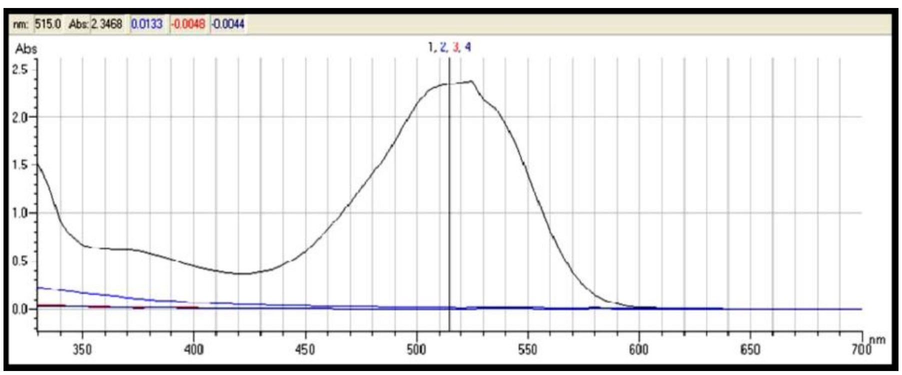
C. Analytical method

Ozone concentration in feed gas was determined by the KI-starch titration [15]. Azo dyes concentration in all samples *λmax* was determined by Systronics UV/Visible Spectro-Photometer (106) at specific wave lengths. COD were determined based on procedure derived in Standard method for the examination of water and wastewater [15]. The biodegradable COD is defined as COD fraction removed by biological treatment. The remaining COD after biological treatment is defined as residual COD.

RESULTS AND DISCUSSION

D. UV-Vis analysis of Azo dyes after Ozonation and Biological treatment.

Figure 1 shows the wavelength of Azoviolet, Congored, Tartazine by UV-Vis Spectrophotometer in synthetic wastewater, after ozonation and after biological treatment. The peaks for the synthetic dye solution were observed at λ_{max} of 535, 510 and 530nm. Azoviolet, Congored, Tartazine. The specified wavelength peaks were disappeared after ozonation, which indicated that the chemical structure of the synthetic dyes was transformed by ozonation. However, subsequent biological treatment seems to have no influence on color removal of azo dyes.



E. Continuous Ozonation and Biological treatment

Figure2.shows color removal efficiency and COD concentration of Azoviolet solution at various Ozone doses. Ozonation at lower ozone dose (0.3 mg O_3. mg dye^{-1}) significantly removed color to 95.8% and increasing ozone dose to 0.6 mg O_3. mg dye^{-1} almost completely removed color. The result indicated that ozone is effective for reducing the color or Azoviolet, which is in agreement with previous result reported by Kuo [7] and Sarasa et al. [16]. On the other hand, COD concentration was gradually decreased from 814 to 17.2 mg. 1^{-1} as ozone dose increased from 0.3 to 7.2 mg O_3 mg dye^{-1}. Higher COD removal at high ozone dose (7.2 mg O_3 mg dye^{-1}) imply that ozonation method is also effective for complete oxidation of organic chemicals containing N=N and aromatic double bonds such as Azoviolet.

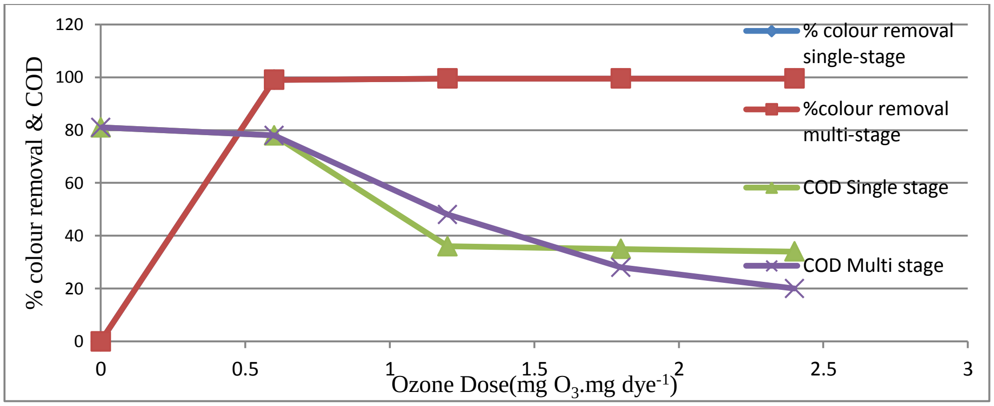


Fig. 2. Color removal efficiency and COD concentration of various Azoviolet, Congored, Tartazine dyes at various ozone dose

Figure 3 shows the variation of COD concentration after ozonation followed by biological treatment. It was observed that originally Azoviolet seems to be completely non-susceptible to biological treatment. COD concentration was slightly decrease by ozonation at lower ozone doses (0.3-0.6 mg O_3 mg dye^{-1}), whereas significant decreased by ozonation and subsequent biological treatment was noted at medium ozone doses (1.2-3.6 mg O_3 mg dye^{-1}). The decreased in COD concentration was contributed simultaneously by ozonation and biological treatment mechanism within the range of these ozone doses. However, COD concentration was mainly removed by ozonation at higher ozone doses (4.8-7.2 mg O_3 mg dye^{-1}). The result indicated that biodegradable fraction of COD could be further oxidized and completely removed by ozonation, in the single-stage ozonation-biological treatment. Consequently, ozone will be competitively consumed by residual COD as well as biodegradable COD if higher ozone dose is applied.

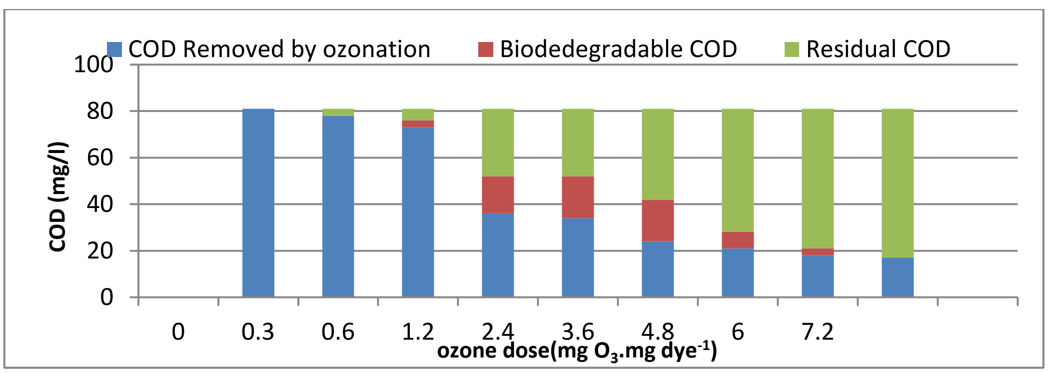


Fig. 3. Variation of COD concentration after ozonation followed by biological treatment for various Azoviolet, Congored, Tartazine dyes

Figure 4 shows the COD concentration after ozonation for various azo dyes. Although the initial concentrations of azo dyes were set at 100 mg. L^{-1}, COD values for various azo dyes were ranging from 80-140 mg. L^{-1}. This variation was due to different in chemical structure and molecular weight of the azo dyes. COD concentration for Azoviolet, Congored, Tartazine were decrease significantly up to ozone dose of 0.6 mg O_3 mg dye^{-1}, whereas further ozonation was not efficient for COD reduction.

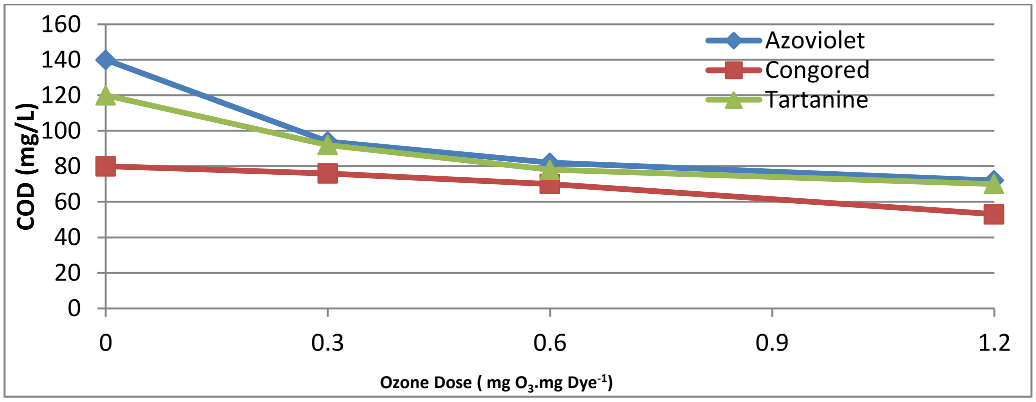


Fig. 4. Variation of COD concentration after ozonation for Azoviolet, Congored, Tartazine.

Figure 5 shows variation of COD concentration after subsequent biological treatment on various azo dyes. At ozone dose of 1.2 mg O_3 mg dye^{-1}, COD value for Azoviolet. After biological treatment respectively. Other azo dyes showed similar trend of reduction after ozonation and biological treatment. These results imply that subsequent biological treatment after ozonation at ozone dose lower than 1.2 mg O_3 mg dye^{-1} was effective for the reduction of COD concentration.

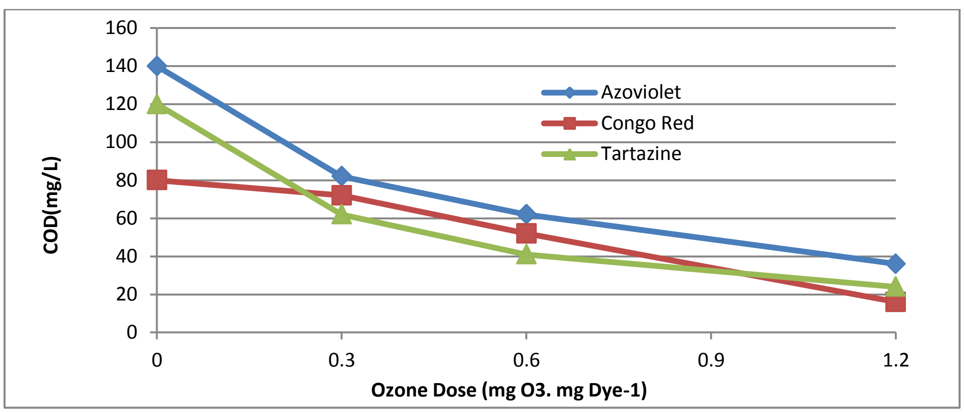


Fig. 5. Variation of COD concentration after biological treatment For Azoviolet, Congored, Tartazine

Table 1 summarized COD removal percentage of various azo dyes after ozonation and biological treatment. The percentage of COD removal increased as the ozone dose increased. COD removal efficiency of azo dyes after ozonation at 1.2 mg O_3 mg dye^{-1} was in the range of 45.7-55.9%. Congored showed the best reduction of COD concentration. After biological treatment, COD removal percentage were further improved up to the range of 76.8-88.9%. It is likely, ozonation of azo dye produced biodegradable fraction of by product that easily removed in biological treatment.

TABLE 1. PERCENTAGE OF COD REMOVAL FOR VARIOUS AZO DYE AFTER OZONATION AND BIOLOGICAL TREATMENT

After Ozonation			
Ozone Dose (mg O_3. mg dye^{-1})	Azoviolet	Congored	Tartazine
0.3	32.4%	7.6%	27.6%
0.6	40.1%	16.0%	41.8%
1.2	48.6%	45.7%	55.9%
After Biological Treatment			
Ozone Dose (mg O_3 mg dye^{-1})	Azoviolet	Congored	Tartazine
0.3	40.4%	12.6%	39.8%
0.6	55.9%	34.8%	84.4%
1.2	76.8%	81.5%	88.9%

C. Single-stage and Multi-stage Ozonation Biological treatment

Figure 6 shows color removal and COD concentration in the single-stage and multi-stage ozonation-biological treatment. It was found that there is no different in color removal between the single-stage and multi-stage ozonation-biological treatment has no significant contribution on color removal. COD concentration decreased from 81 to 53 mgL^{-1}at ozone dose 1.2 mg O_3.mg dye^{-1} in the single-stage ozonation. Contrarily, COD concentration was observed to be continuously decreased in multi-stage ozonation-biological treatment. COD removal in the single stage ozonation-biological treatment and ozonation-biological treatment that repeated for 4 times was 58% and 75% respectively.

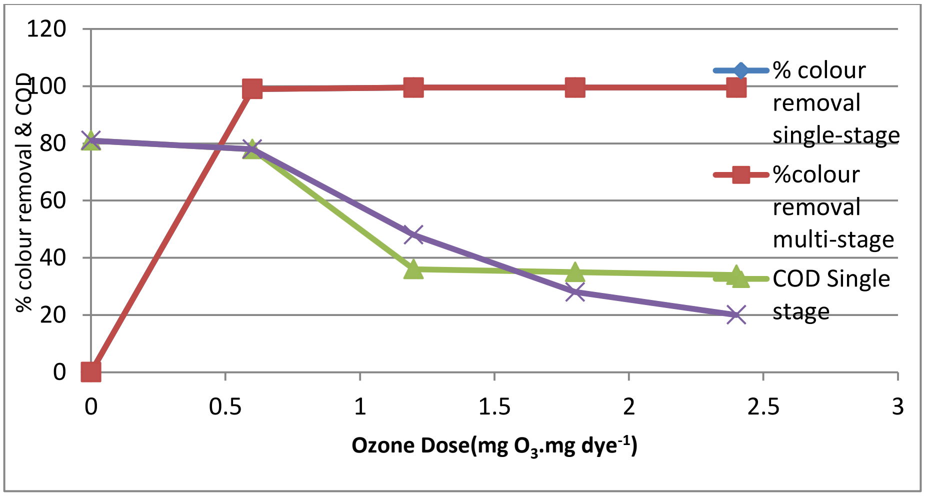
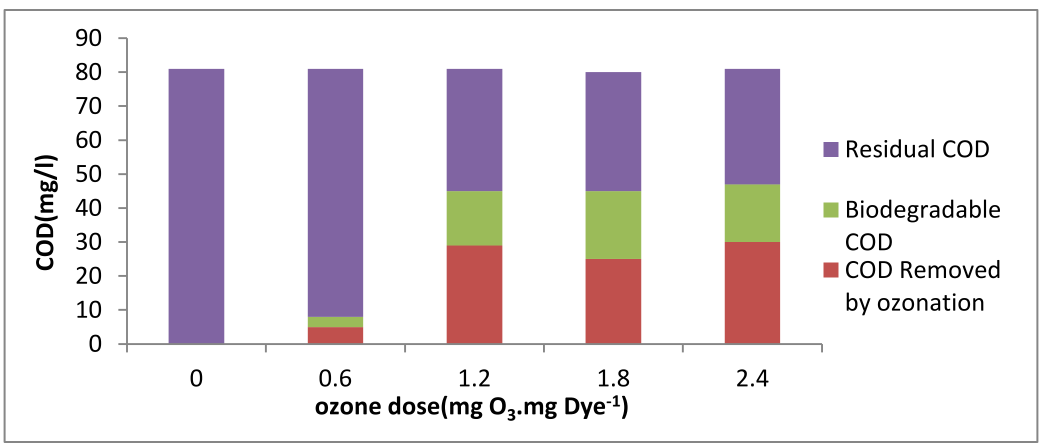


Fig. 6. Color removal & COD concentration in single-stage and multi-stage ozonation-biological treatment.

Figure 7 shows COD concentration in the single-stage and multi-stage ozonation-biological treatment of Azoviolet in the single stage ozonation-biological treatment, complete oxidation was the main mechanism for COD reduction (62.2% at ozone dose 2.4 mg O_3 mg dye^{-1}). on the other hand, biological treatment mechanism seems to be the dominant mechanism in reducing COD concentration in the multi-stage ozonation-biological treatment (67.9% at ozone dose 2.4 mg O_3 mg dye^{-1}).



(a)

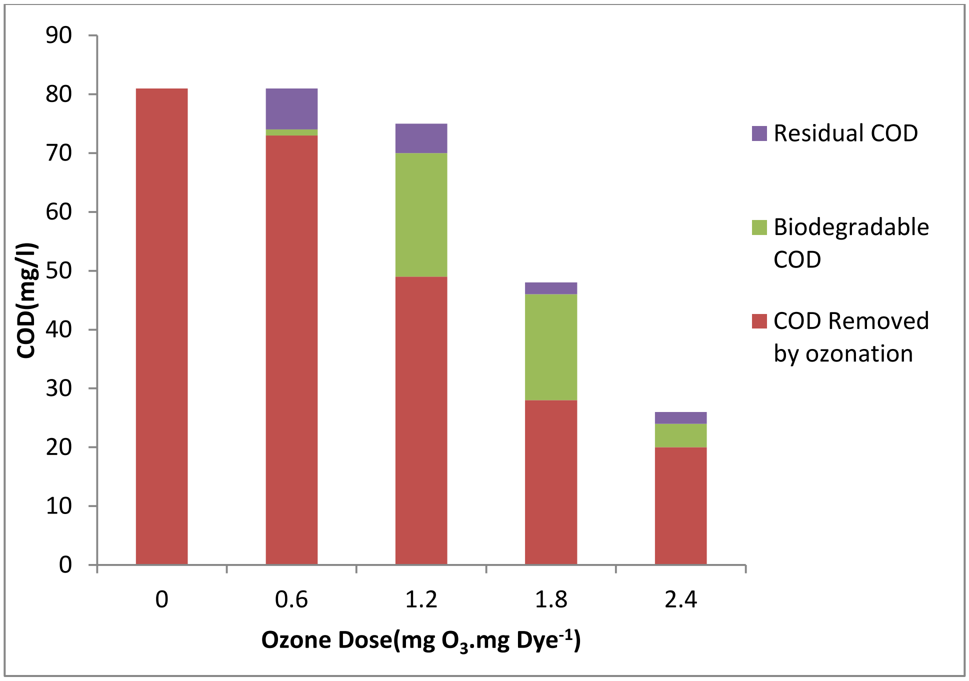


Fig. 7. COD concentration in single-stage ozonation & biological treatment (a) and multi-stage ozonation & biological treatment (b).

Effect of H_2O_2 to O_3 ratio

Figure 8 shows UV-Vis spectrum before and after AOP treatment. The peak for the Azoviolet was observed at λmax 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 9 shows the percentage of residual color 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 color up to 99.8%. Furthermore, the addition of Hydrogen peroxide at various concentrations could be removing color completely. Previous result by De Sauza et al [15] confirmed that color removal efficiencies were greater than 96% by ozonation. They verify that the ozonation process as a pretreatment 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 color 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 decolorization of azo dye.

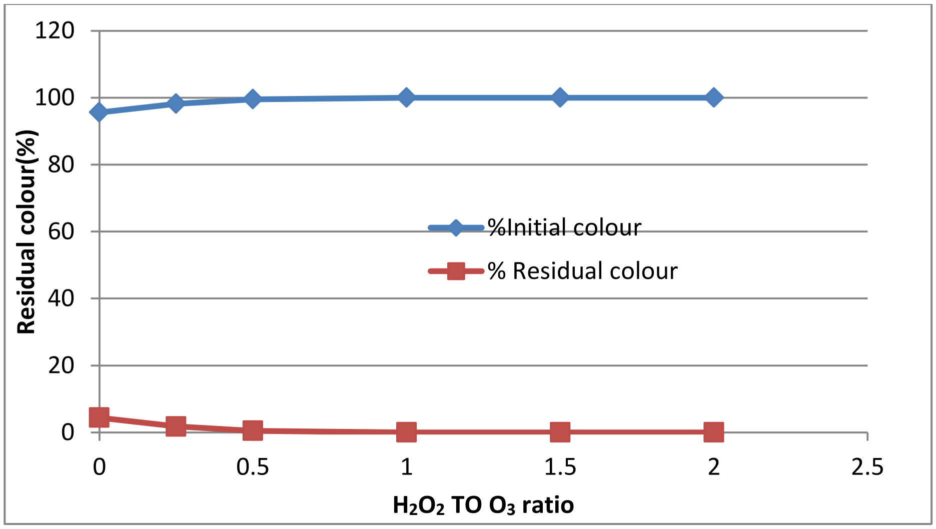


Fig.9. Percentage of residual color at various H_2O_2 to O_3 ratio.

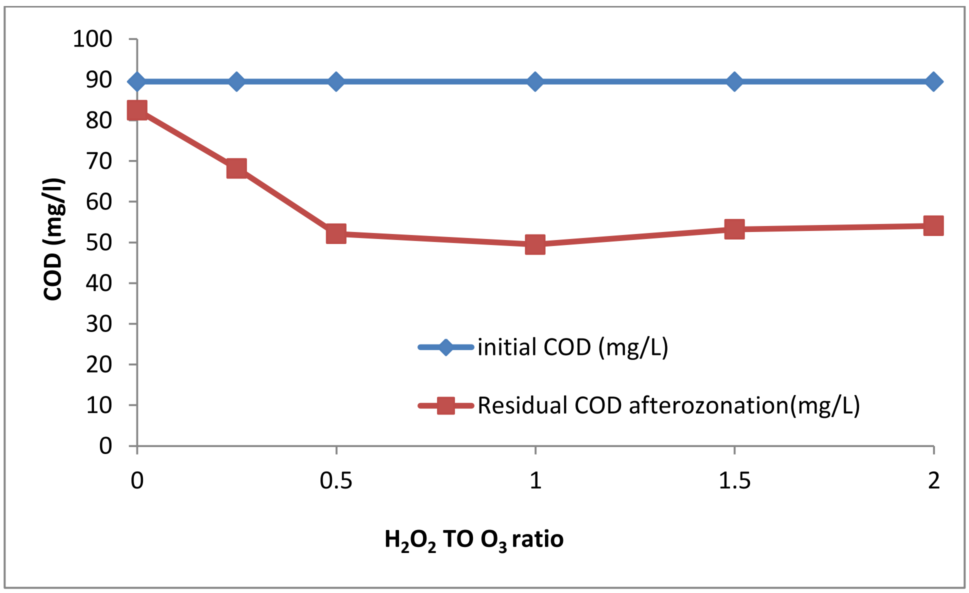


Fig.10. Variation of COD after ozonation at various H_2O_2 to O_3 ratio.

Figure 10 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 decreases COD slightly to 82.6 mg. L^{-1}, whereas the addition of hydrogen peroxide from 0.2-1mg H_2O_2mg O_3^{-1} significantly decreased COD down to 49.4 mg. L^{-1} at optimum H_2O_2 dose (1mg 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/lt. 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 H_2O_2. In an acidic medium to yield the unstable, peroxydichromate 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 1.0 mg H_2O_2./mg O_3.

SUMMARY AND CONCLUSIONS

In this study, decolorization and COD removal of Azoviolet, Congored, Tartazine by ozonation and biological treatment were evaluated to apply for wastewater treatment containing azo dye. The performance of COD and color removal in the single-stage ozonation-biological treatment and multi-stage ozonation-biological treatment. The following findings were obtained:

1. Ozonation transforms the functional group in azo dye to produce more biodegradable by products, which is easily removed by biological treatment.
2. Ozonation is efficient for decolorization of Azoviolet even with lower ozone dose (0.3 mg O_3 mg dye^{-1}). Contrarily, significant decreased in COD concentration was only observed within higher range of ozone doses (1.2 mg O_3 mg dye^{-1}). Higher COD removal at high ozone dose was due complete oxidation of azo dye. The result indicated that biodegradable fraction of COD could be further oxidized and completely removed by ozonation.
3. COD removal in the single-stage ozonation-biological treatment and ozonation-biological treatment that repeated for 4 times was 58% and 75% respectively. The improvement of COD removal in the multi-stage ozonation-biological treatment was attributed to the production of biodegradable fraction of COD.
4. AOP could be improving colour removal of Azodye 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 Azodye.
5. 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.

6. In the multi-stage ozonation biological treatment, the role of ozonation seems to breakdown the azodye 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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