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# Multi-stage Ozonation and Biological Treatment for Removal of Azo Dye Industrial Effluent

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*Abstract*— **In this study, decolourization and COD removal of Reactive Red 120, Remazol Brilliant Blue, Reactive Green 19 and Reactive Black 5 by ozonation and biological treatment were evaluated to apply for wastewater treatment containing azo dye. The performance of COD and colour removal in the single-stage ozonation- biological treatment was also compared with the multi-stage ozonation-biological treatment processes. Ozonation transforms the functional groups in azo dye to produce more biodegradable by products, which is easily removed by biological treatment. Ozonation is efficient for decolourization of Reactive Red 120, Remazol Brilliant Blue, Reactive Green 19 and Reactive Black 5 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 to complete oxidation of azo dye. The result indicated that biodegradable fraction of COD could be further oxidized and completely removed by ozonation. COD removal for Reactive Red 120 in the single stage ozonation-biological treatment and ozonation- biological treatment that repeated for 4 times were 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.**

***Index terms***: **Multi-stage, Azo dye, ozonation, biological treatment,** Chemical Oxygen Demand (COD)

## I. Introduction

Presence of colour and its causative compounds has always been undesirable in water used for either industrial or domestic needs. Different colouring agents like dyes, inorganic pigments, tannins, lignins etch usually impart colour. Amongst complex industrial wastewater with various types of colouring agents, dye wastes are predominant [1]. This wastewater not only toxic to the biological world, but it also has a dark colour, which blocks sun light. By these reasons, it causes many problems to the ecosystem [2]. The number of dyes presently used in textile industry is about 10,000. Among these dyes, azo dyes constitute the largest and the most important class of commercial dyes. Azo dyes are widely used in textile, plastic, leather, and paper industries as additives [3]. The removal of azo dyes 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]. Coagulation is effective for treatment of insoluble dyestuff wastewater but not so effective for soluble dyestuff wastewater [6], [7]. The adsorption method has difficulties in the treatment of insoluble dyestuff wastewater and it is very difficult to find 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 colour. 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 colour, 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 colour 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.

Several research works has been conducted to evaluate the performance of ozonation in combination with biological treatment to reduce dye in wastewater. Bose *et al.* [9] reported that AOPs (the combination of UV/$H_2O_2$, ozone/$H_2O_2$, and UV/ozone) enhanced the degradation rate of 1, 3, 5-trinitrotriazacyclohexane (RDX) due to increased of hydroxyl radical formation. Muhammad et al [10] compared the treatment of raw and biotreated (upflow anaerobic sludge blanket, UASB) textile dye bath effluent by ozonation and AOPs. Takahashi *et al.* [11] investigated the effects of preozonation and subsequent biological treatment process on the decrease in dissolved organic carbon (DOC) and colour for dyeing wastewater. The report indicated that ozonation were significantly removed colour up to 88,6 % and gradually decreased DOC concentration. Subsequent biological treatment was removed DOC significantly.

Nishijima *et al.* [12] suggested that ozonation and biological treatment that operating in multistage mode could improve DOC removal in drinking water sources. The

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improvement of DOC removal in the multi-stage ozonation-biological treatment process was mainly attributed to the decrease in hydrophobic fraction in raw water [13]. In addition, 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 AOP. However, the characteristic of raw water for drinking water is different to synthetic organic compound such as azo dye. Therefore, the performance of multi-stage ozonation in combination with biological treatment to remove refractory synthetic compound such as azo dye in wastewater still remain unclear.

In this study, decolourization and COD removal of various azo dyes such as Reactive Red 120, Remazol Brilliant Blue, Reactive Green 19 and Reactive Black 5 in the single-stage and multi-stage ozonation- biological treatment process were evaluated to be applying for wastewater treatment containing azo dye.

## II. Materials and Methods

### A. *Preparation and characterization of Azo Dye Solutions*

Azo dyes uses were of analytical grade obtained from Sigma-Aldrich. Reactive Red 120, Remazol Brilliant Blue R, Reactive Green 19 and Reactive Black 5 have been selected amongst azo dyes in performing ozonation and biological treatment due to its high solubility in aquatic environment, which is difficult to decolourize 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.

### B. *Ozonation and biological treatment experiments*

Ozone was produced from an A2Z 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 sample was ozonated at the same total ozone dose. In multi-stage treatment, the solution were 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.

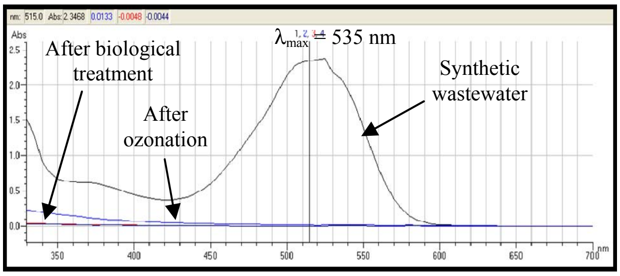
### C. *Analytical methods*

Ozone concentration in feed gas was determined by the KI-starch titration [15]. Azo dyes concentration in all samples was determined by Hitachi UV/Vis (U-2810) Spectrophotometer 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. FTIR was analysis by using RES-10 PERKIN ELMER Spectrum 400 FT-IR FT-NIR Spectrophotometer as to identify the presence of certain functional groups or types of chemical bonds of the dye samples.

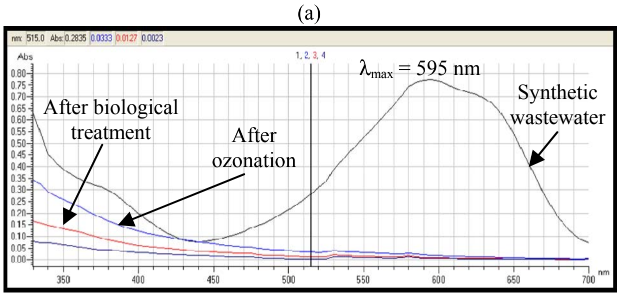
## III. Results and Discussion

### A. *UV-Vis analysis of Azo dyes after ozonation and biological treatment*

Figure 1 shows the wavelength of Reactive Red 120, Remazol Brilliant Blue, Reactive Green 19 and Reactive Black 5 indicated by UV-Vis Spectrophotometer in synthetic wastewater, after ozonation and after biological treatment. The peaks for the synthetic dye solution were observed at $\lambda_{max}$ of 535, 595, 630 and 596 nm for Reactive Red 120, Remazol Brilliant Blue, Reactive Green 19 and Reactive Black 5 respectively. 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 colour removal of azo dyes.




(a)

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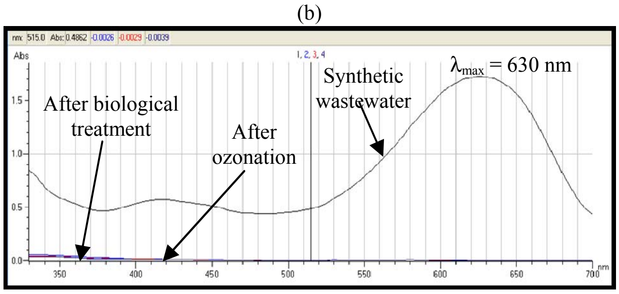
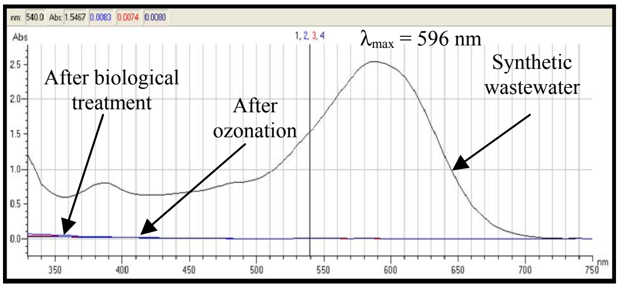



(c)




(d)
Figure 1. Wavelength of various azo dye indicated by UV-Vis Spectrophotometer; (a)Reactive Red 120 (b) Remazol Brilliant Blue (c) Reactive Green 19 (d) Reactive Black 5

## B. *Continuous Ozonation and Biological treatment*

Figure 2 shows colour removal efficiency and COD concentration of Reactive Red 120 solution at various ozone doses. Ozonation at lower ozone dose (0.3 mg $O_3$. mg $dye^{-1}$) significantly removed colour to 95.8 %, and increasing ozone dose to 0.6 mg $O_3$. mg $dye^{-1}$ almost completely removed colour. The result indicated that ozone is effective for reducing the colour of Reactive Red 120, which is in agreement with previous results reported by Kuo [7] and Sarasa *et al.* [16]. On the other hand, COD concentration was gradually decreased from 81 to 17.2 mg. $l^{-1}$ 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 Reactive Red 120 applied in this study.

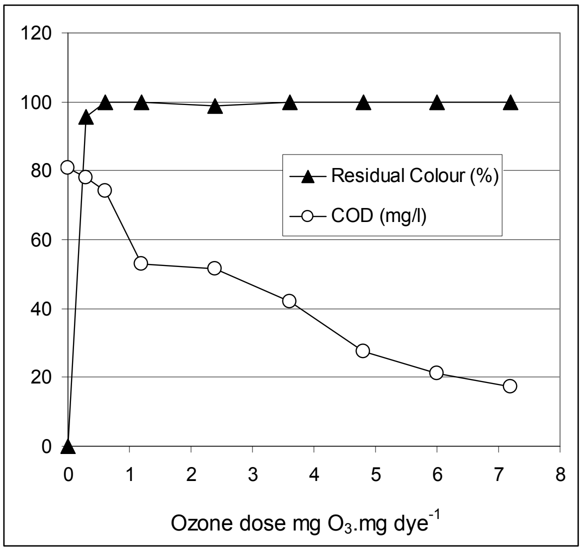



Figure 2. Colour removal efficiency and COD concentration of Reactive Red 120 solution at various ozone doses.

Figure 3 shows the variation of COD concentration after ozonation followed by biological treatment. It was observed that originally Reactive Red 120 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.

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 Remazol Brilliant Blue, Reactive Green 19 and Reactive Black 5 were decreased significantly up to ozone dose of 0.6 mg $O_3$. mg $dye^{-1}$, whereas further ozonation was not efficient for COD reduction. 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 Reactive Red 120 were 81, 44 and 12 mg. $L^{-1}$ for raw synthetic wastewater, sample after ozonation and 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.

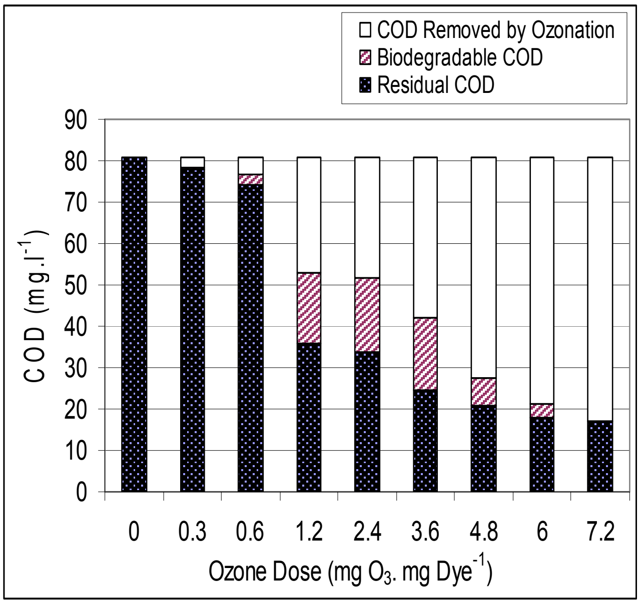



Figure 3. Variation of COD concentration after ozonation followed by biological treatment for Reactive Red 120

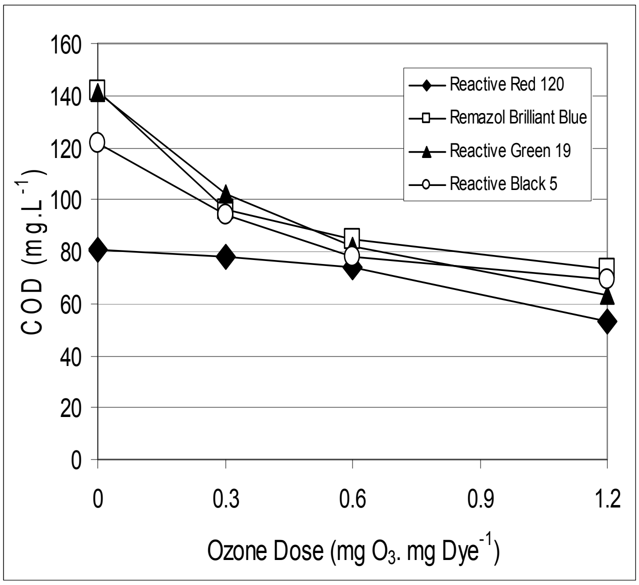



Figure 4. Variation of COD concentration after ozonation for Reactive Red 120, Remazol Brilliant Blue, Reactive Green 19 and Reactive Black 5

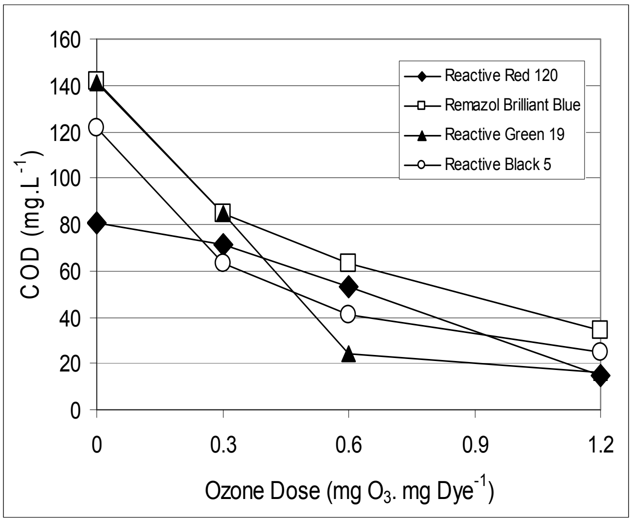



Figure 5. Variation of COD concentration after biological treatment for Reactive Red 120, Remazol Brilliant Blue, Reactive Green 19 and Reactive Black 5

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 43.3 – 55.9 %. Reactive Green 19 showed the best reduction of COD concentration. After biological treatment, COD removal percentage were further improved up to the range of 76.0 – 88.6 %. 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$^{-1}$ dye) | Reactive Red 120 | Remazol Briliant Blue | Reactive Green 19 | Reactive Black 5 |
|---|---|---|---|---|
| 0.3 | 7.4 % | 32.4 % | 27.6 % | 22.9 % |
| 0.6 | 16.0 % | 40.1 % | 41.8 % | 36.1 % |
| 1.2 | 45.7 % | 48.6 % | 55.3 % | 43.4 % |

After Biological treatment

| Ozone Dose (mg $O_3$. mg$^{-1}$ dye) | Reactive Red 120 | Remazol Briliant Blue | Reactive Green 19 | Reactive Black 5 |
|---|---|---|---|---|
| 0.3 | 12.4 % | 40.1 % | 39.7 % | 48.4 % |
| 0.6 | 34.6 % | 55.6 % | 83.0 % | 66.4 % |
| 1.2 | 81.5 % | 76.0 % | 88.6 % | 79.5 % |

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

Figure 6 shows colour removal and COD concentration in the single-stage and multi-stage ozonation-biological treatment. It was found that there is no different in colour removal between the single-stage and multi-stage ozonation-biological treatment, which is confirmed that biological treatment has no significant contribution on colour removal. COD concentration decreased from 81 to 53 mg. l$^{-1}$ at ozone dose 1.2 mg $O_3$. mg dye$^{-1}$ and leveled off between 1.2 – 2.4 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. In previous research work, Nishijima *et al.* [12] reported that multi-stage ozonation-biological treatment could remove more dissolved organic carbon (DOC) in raw water for drinking water by the production of biodegradable fraction of DOC in comparison to the single-stage ozonation-biological treatment for the same total ozonation time.

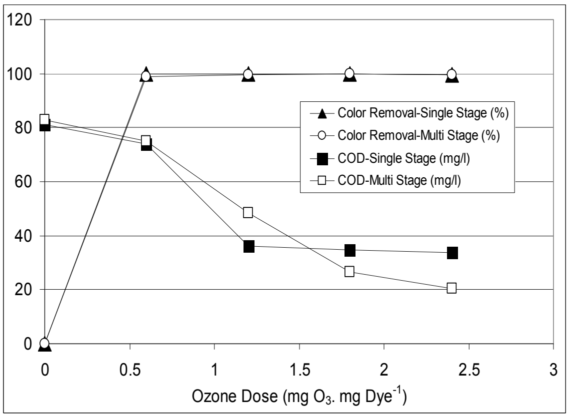
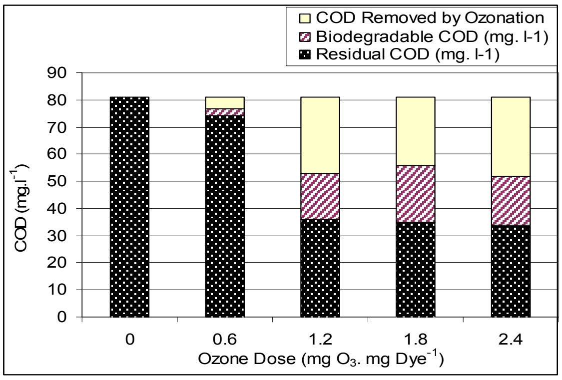
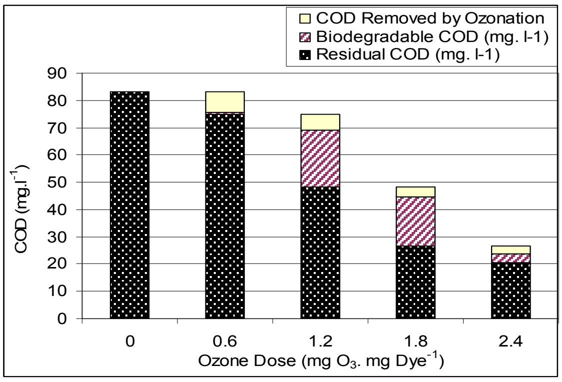



Figure 6. Colour removal and COD concentration in the Single-stage and Multi-stage Ozonation-biological treatment




(a)




(b)

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

Figure 7 shows COD concentration in the single-stage and multi-stage ozonation-biological treatment of Reactive Red 120. 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$^{-1}$). Fahmi *et al.* [13] reported that higher DOC removal for drinking water sources in the multi-stage ozonation and biological treatment was attributed to the production of biodegradable fraction of DOC, which eventually improve DOC removal. It is likely, similar mechanism of DOC removal in drinking water sources is applied to COD removal in wastewater containing azo dye.

### *D. FTIR Analysis*

The results of FTIR analysis for synthetic wastewater, sample after ozonation and after biological treatment of Reactive Red 120 is presented in Figure 8. The colour of the azo dye was given by the azo bond or also called nitrogen to nitrogen double bond (–N=N–) functional group. The peak for azo bond should be presented by the wavelength of 1500 – 1550. In addition, the wavelength for benzene ring and C-O single bond were presented at 1500 – 1700 and 1200 – 1300 nm wavelength, respectively. Based on the peaks obtained, azo bond was detected in raw synthetic wastewater; however, it was disappeared after ozonation and biological treatment. Ozonation and biological treatment also transformed the structure of benzene ring and C-O single bond, which eventually resulted on decolourization of azo dye solution. The result indicated that ozonation was effective in transforming the functional groups present in Reactive Red 120 producing biodegradable product.

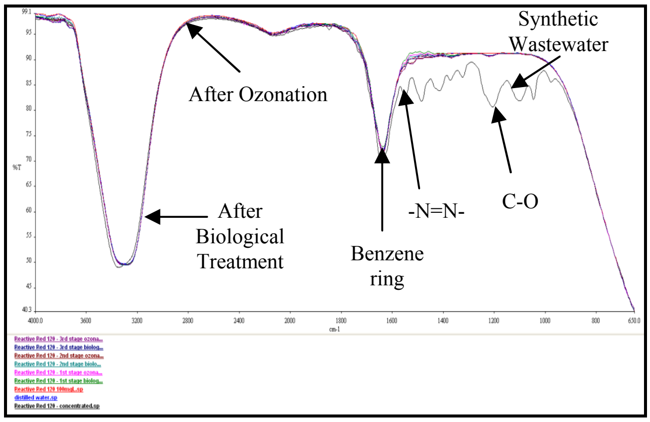



Figure 8. FTIR analysis for transformation of functional group of Reactive Red 120 in the single-stage ozonation and biological treatment

## IV. SUMMARY AND CONCLUSIONS

In this study, decolourization and COD removal of Reactive Red 120, Remazol Brilliant Blue, Reactive Green 19 and Reactive Black 5 by ozonation and biological treatment were evaluated to apply for wastewater treatment containing azo dye. The performance of COD and colour removal in the single-stage ozonation- biological treatment was also compared with the multi-stage ozonation-biological treatment processes. The following findings were obtained:

1) Ozonation transforms the functional groups in azo dye to produce more biodegradable by products, which is easily removed by biological treatment.
2) Ozonation is efficient for decolourization of Reactive Red 120, even with lower ozone dose (0.3 mg O3. mg dye-1). Contrarily, significant decreased in COD concentration was only observed within higher range of ozone doses (1.2 mg O3. 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.

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