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Ozone-assisted Decolorization of Methyl Orange via Homogeneous and Heterogeneous Photocatalysis

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A group of Advanced Oxidation Processes (AOPs) has been investigated for Methyl Orange (MO) oxidation. AOPs were chosen due to their ability to generate hydroxyl radical, •OH. As a result of oxidation, the rapid color removal was observed. However, among the AOPs studied previously, there are not many studies focusing on color removal at near neutral pH. Therefore, the significant of this study is to determine the best system to remove MO at pH 6. This is due to the requirement to discharge water at near neutral pH. It was found that heterogeneous catalytic system (UV/TiO_2) showed better performance compared to homogeneous catalytic system ($UV/Fe^{3+}/H_2O_2$). However, the addition of oxalate into the homogeneous system enhanced the color removal percentage. When both systems were combined with ozone, the complete color removal was achieved. The best system recorded was homogeneous ozonation system ($UV/Fe^{3+}/H_2O_2/O_3$).

Keywords: Advanced Oxidation Processes, Homogeneous, Heterogeneous, Methyl Orange and Ozone

1. INTRODUCTION

Removal of dyes from wastewater has been the subject of interest of many researchers due to known environmental effect of dyestuff to lives and ecosystem. Many of these dyes are soluble in water thus make the removal almost impossible using conventional segregation and filtration method especially at very low concentration. Furthermore, Azo dyes which constitute about 70 % of all dyes are the most recalcitrant to degradation due to their complex structure and strong azo bond [1]. Some studies shows that azo bond (-N=N-) reduction cleavage by azoreductase enzyme produce aromatic amines in the liver and it will cause intestinal cancer [2]. Therefore, the effective methods to treat colored wastewater are crucial demanding.

A variety method such as adsorption, biological degradation, coagulation processes and hypochlorite treatments has been introduced in order to treat colored wastewater. Unfortunately these methods were costly, inefficient and produce secondary pollution as stated by Crini [3]. Therefore, an efficient method that can offer a complete decolorization and mineralization is necessary. Advanced Oxidation Processes (AOPs) has been reported successfully degrade organic pollutant into environmental friendly products [4]. The basic principle of AOPs is based on the generation of reactive radical species such as hydroxyl radicals, •OH that oxidize organic pollutant non-selectively and quickly. The several examples of AOPs that successfully treat reactive dyes were UV, Fenton's reagent, photo-Fenton, UV/H_2O_2, UV/TiO_2 and UV/O_3 [5].

However, most of the AOPs systems studied were focused on the acidic condition. Selvam [6] demonstrated that photo-Fenton and photo-Ferrioxalate (Fe(III)-Oxalate) system were efficient at pH 3. The other researcher, Ashraf [7], used UV/Fe^{2+}/H_2O_2 system to degrade Methyl Red in acidic condition. Similar finding was shown by Pignatello [9], Pérez [10] and Bajt [11]. The studies were restricted to low pH range due to it highly efficient performance of AOP in this range.

Unfortunately, the pH that is suitable for water discharge in Malaysia is pH 6.0-9.0 as stated in Environmental Quality (Industrial Effluent) Regulations 2009 [12]. Therefore, it is significant to study the feasibility of the system to operate at near neutral pH to meet the requirement of environmental friendly water discharge. Corresponding to that, the aim of this study is to evaluate the performance of ozone assisted homogeneous (UV/Fe(III)/H_2O_2) and heterogeneous (UV/TiO_2) catalytic systems in decolorisation of an azo dye (methyl orange) at operation pH 6.

2. EXPERIMENTAL

2.1. Materials

Methyl Orange purchased from BDH Limited was used as target compound in this experiment. $FeCI_3.6H_2O$ (HmBG Chemicals) as iron sources and H_2O_2 30 % w/v (Pancreac) were used for photo-Fenton system. Meanwhile, sodium oxalate supplied from Hamburg Chemical GmbH was used as oxalate sources in photo-Fe(III)-Oxalate system. TiO_2 P-25 (Degussa P25) (80% anatase, 20% rutile) from Degussa were used for photo-TiO_2 system. NaOH (ChemAR) and NH_3 65% (Merck) were used to adjust the reaction mixture pH to near neutral pH. All aqueous solution in this experiment was prepared with deionized water in a Milipore Mili-Q system.

2.2 Experimental procedures and analysis

The methyl orange (MO) removal experiments were carried out in a custom made Pyrex glass cylinder equipped with water circulation jacket. 100 ml of 20 ppm MO was added into the glass cylinder. The irradiation source was 13 W UV-C (UV filter lamp) from Dolphin fixed inside a cylindrical Pyrex tube. In order to make sure the reaction mixture homogenize, air pump from Classica Super X was feed during reaction time. The pH of the reaction mixture was adjusted to pH 6 by using pH Tutor from Eutech Instrument. pH meter was calibrate for every single use. After all the equipment was set up, the UV lamp was turns on for 90 minutes irradiation time.

For homogeneous system (UV/Fe(III)/H_2O_2), 5 mL of Fe(III) at fixed concentration, 2 ppm was added into the glass cylinder simultaneously with the 5 mL of required concentration of H_2O_2. 2 ppm of Fe(III) was chosen due to iron permit limit into water stream is only 2 ppm [15-17] . In order to study the effect of oxalate, 5 mL of desired sodium oxalate concentration was added into the glass cylinder together with Fe(III) and H_2O_2.

In heterogeneous system, TiO_2 slurry was prepared by suspending certain amount of TiO_2 into the glass cylinder containing dyes. The slurries were stirred for 30 minute in dark to ensure TiO_2 was well dispersed in the reaction mixture. For ozone study, the ozone from Ozonizer air purifier, Greentech were feed into the glass cylinder for ozone system studies. The flow rate of ozone was constant at 380 mg/h.

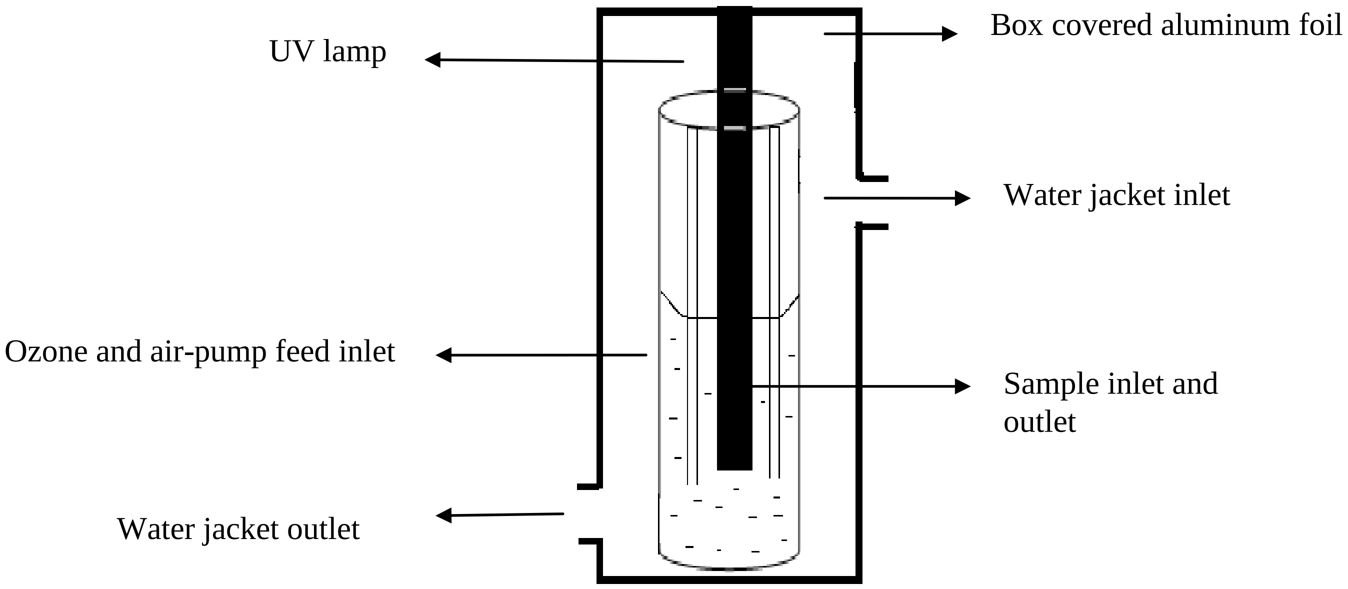

Figure 1. Experimental set up for all systems studied.

The experimental set up is as illustrated in Figure 1. The decolorization of MO were determined by using a UV-Visible spectrophotometer Lambda 20 (Perkin Elmer) at 463 nm. All samples from heterogeneous photocatalysis were filter by using 0.22 μm pore size membrane filter. All analysis was conducted immediately after 15 minute interval sampling to avoid any further reaction.

3. RESULTS AND DISCUSSION

3.1. Homogeneous catalyst

3.1.1. Photo-Fenton and dark Fenton

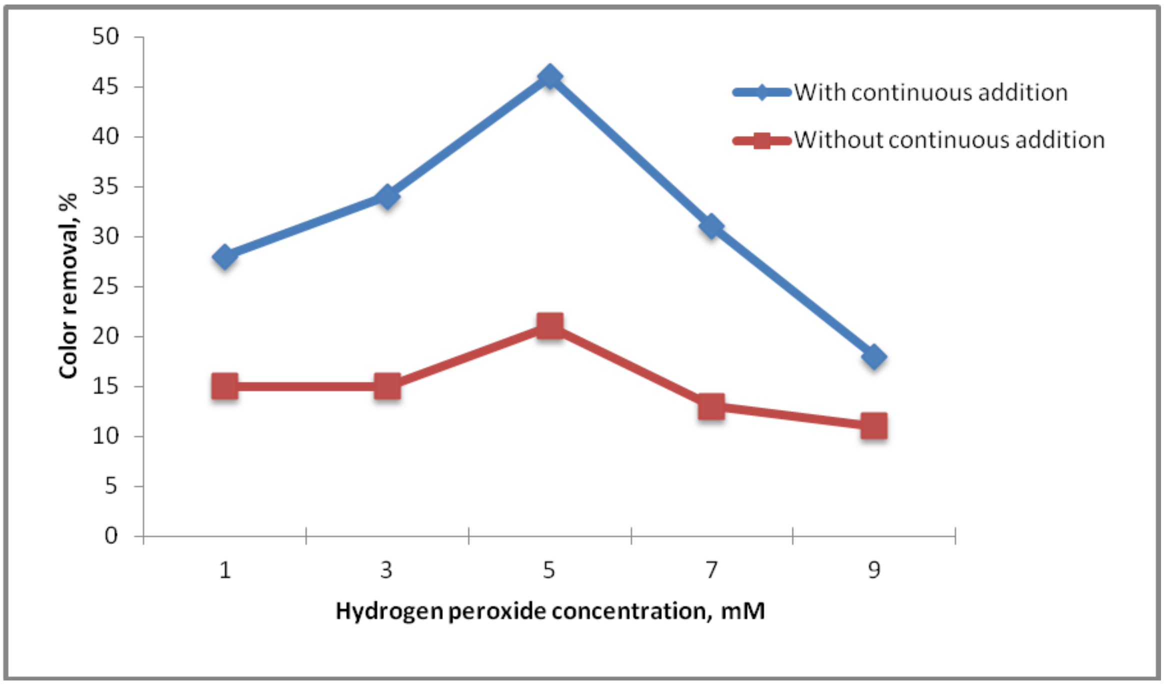

Figure 2. Removal of 20 ppm MO by UV/Fe(III)/H_2O_2 system, with Fe(III) = 2ppm and various H_2O_2 concentration at initial pH ≈ 6

Figure 2 shows the removal percentage at various concentration of H_2O_2. The most effective removal is when 5mM of H_2O_2 was employed. Beyond this concentration, the removal efficiency drop due to reaction between excessive H_2O_2 and •OH as proposed by Fernandez [18] (Eq. (1) and (2).

$$H_2O_2 + \bullet OH \longrightarrow H_2O + HO_2\bullet \quad (1)$$

$$HO_2\bullet + \bullet OH \longrightarrow H_2O + O_2 \quad (2)$$

Since low MO removal recorded, the continuous addition of H_2O_2 in UV/Fe(III)/HO_2 system were carried out. Every 15 minutes, when the sample was taken out for analysis, 5 mL of 5 mM H_2O_2 was added into the system. Almost 30-35 mL of H_2O_2 was used in every system. As a result, the MO removal efficiency was increased from 21% up to 46%. Figure 1 verifies that the continuous addition of H_2O_2 was helps MO removal process. This enhancement could be expected due to the sufficient amount of H_2O_2 provided to involve in equation (3) and (4).

$$Fe^{3+} + H_2O_2 \longrightarrow Fe^{2+} + HO_2\bullet + H^+ \quad (3)$$

$$HO_2\bullet + h\nu \longrightarrow 2\bullet OH + O_2 \quad (4)$$

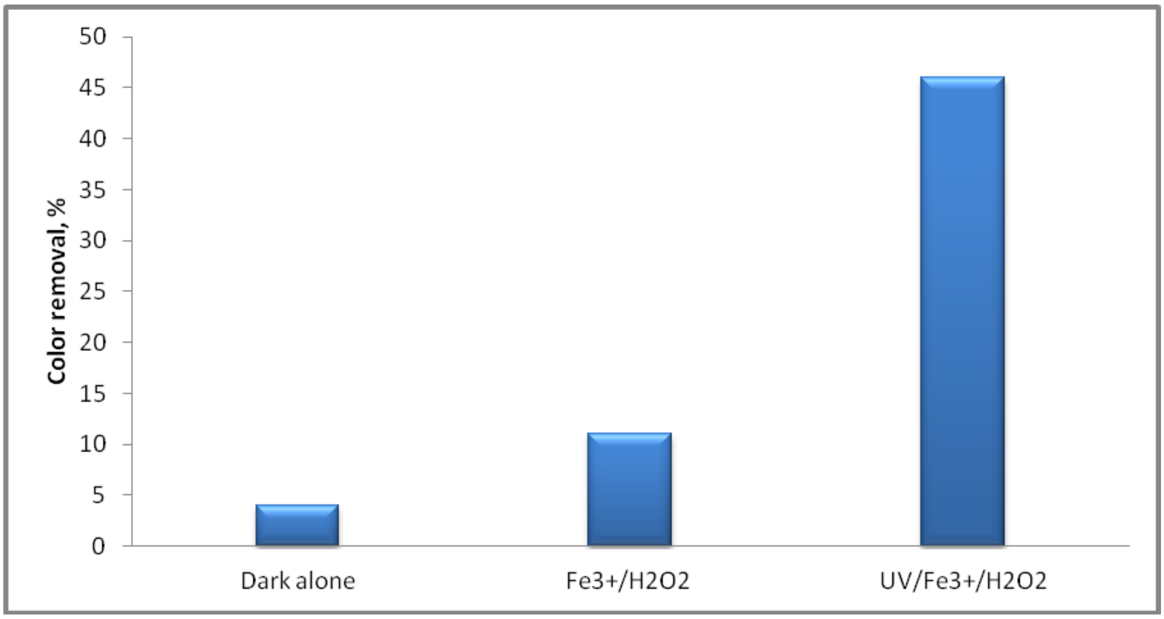

Figure 3. The effect of UV and Fenton's reagent (Fe(III) = 2ppm, H_2O_2 = 5 mM) for 20 ppm MO removal at pH ≈ 6

No enhancement MO removal was recorded for the system with either Fe(III) or H_2O_2 alone. However, when the system introduced with both Fe(III) and H_2O_2, rapid MO removal was obtained as shown in Figure 3. Figure 3 also shows that 46% MO removal was achieved when the system irradiated with UV (UV/Fenton with continuous H_2O_2 addition) compared to only 11% removal in the dark. With irradiation, the destruction rate of chromospheres (λ = 465 nm) was accelerated. This is expected due to the generation of hydroxyl radical from photoreduction of ferric ion to ferrous ion as shown in equation (5). In addition, the production of •OH radical by decomposition of H_2O_2 also was strongly assisted by photolysis process (Eq. (6))[19,21].

$$Fe^{3+} + H_2O + h\nu \longrightarrow Fe^{2+} + \bullet OH + H^+ \quad (5)$$

$$H_2O_2 + h\nu \longrightarrow 2\ \bullet OH \quad (6)$$

3.1.2. Photo-Ferrioxalate

Figure 4 shows the MO removal efficiency enhancement from 46 % to 67 %, with the addition of oxalate. Basically, Ferrioxalate is the chemical actinometer that has been used for decades and the utilization of Ferrioxalate in this study is to enhance the production of •OH. This enhancement was due to photolysis of the ferrioxalate complex and formation of oxalate radical. This radical is very important due to its major contribution in generation of •OH radical.

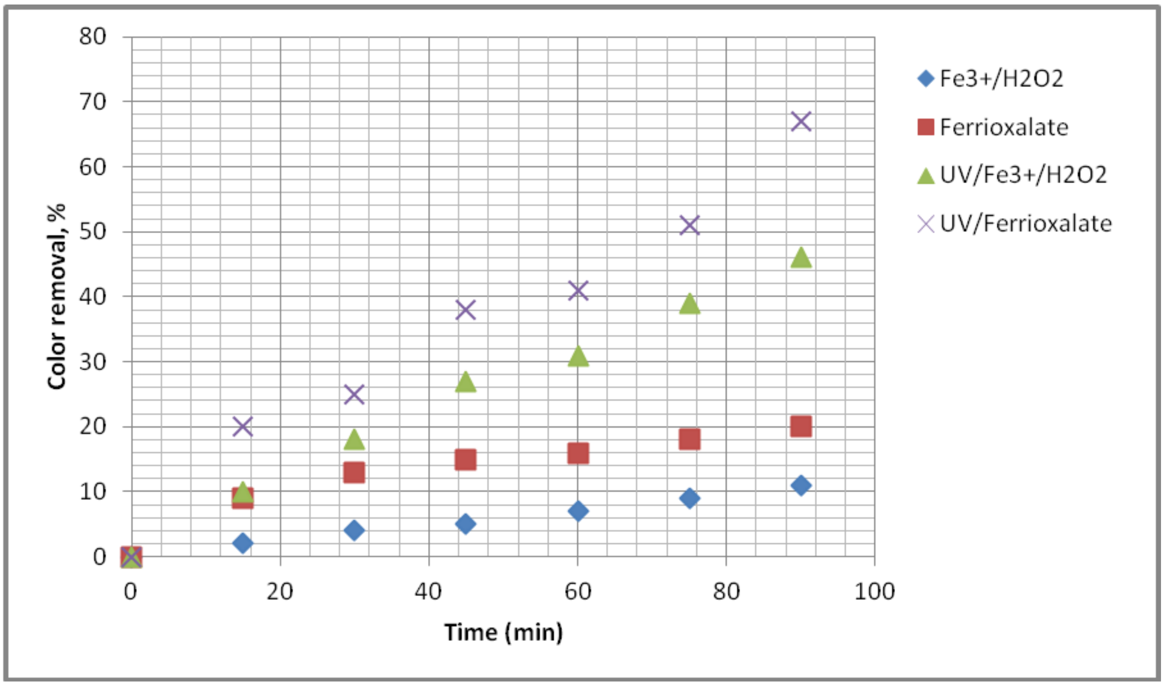

Figure 4. MO removal with different homogeneous systems studied; MO = 20 ppm, Fe(III) = 2 ppm, Oxalate (Ox) = 6 ppm, H_2O_2 = 5 mM at pH ≈ 6

The oxalate radical formed also react with the ferrioxalate complex to produce additional Fe^{2+} (Eq. (8). On the other hand, the oxalate radical also can react with oxygen. As a result, peroxyl radical is produced (Eq. (9)[8]. The protonation of peroxyl radical produced H_2O_2 as shown in equation (10) and (11).

Therefore, the continuous source of Fenton's reagent (Fe^{2+} and H_2O_2) supplied by the photolysis of ferrioxalate could be participate in classical Fenton process (Eq.(12) to ensure continuous generation of •OH radical [6,8].

$$Fe(C_2O_4)_3^{3-} + h\nu \longrightarrow Fe^{2+} + 2C_2O_4^{2-} + C_2O_4^{-} \quad (7)$$

$$C_2O_4^{-} + [Fe(C_2O_4)_3]^{3-} \longrightarrow Fe^{2+} + 3C_2O_4^{2-} + 2CO_2 \quad (8)$$

$$C_2O_4^{-} + O_2 \longrightarrow 2CO_2 + \bullet O_2^{-} \quad (9)$$

$$\bullet O_2^{-} + H^{+} \longrightarrow HO_2\bullet \quad (10)$$

$$2HO_2\bullet \longrightarrow H_2O_2 + O_2 \quad (11)$$

Classical Fenton process:

$$Fe^{2+} + H_2O_2 \longrightarrow Fe^{3+} + OH^{-} + \bullet OH \quad (12)$$

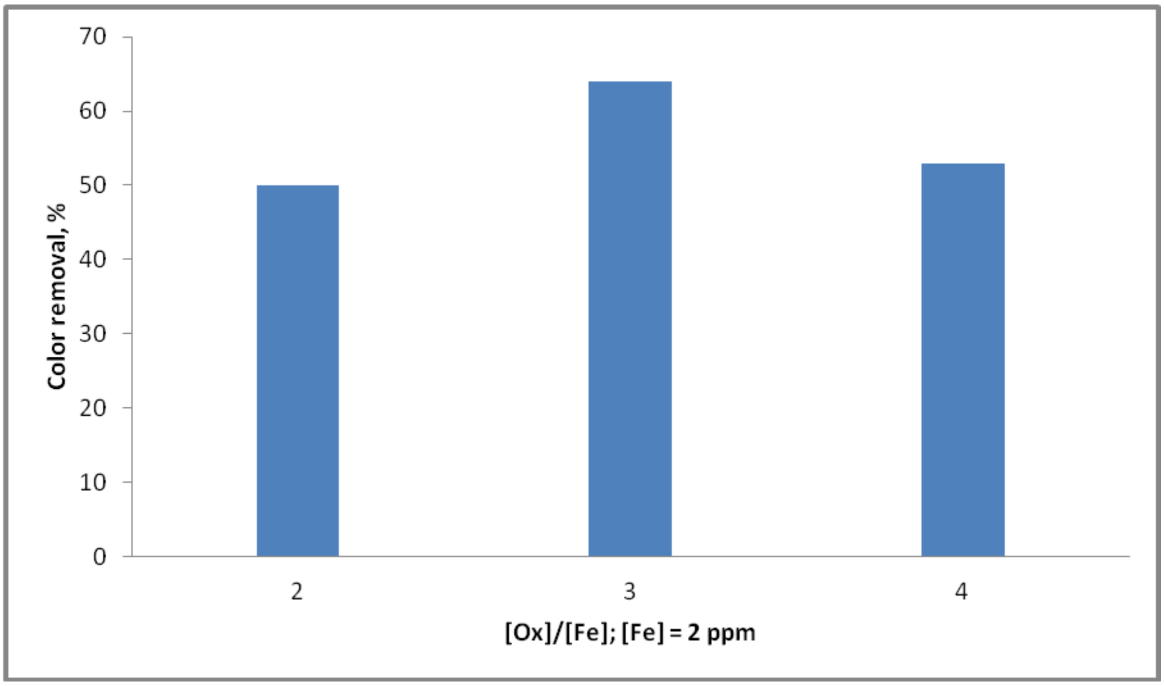

Figure 5. Determination of [Ox]/[Fe^{3+}] concentration ratio, ([Fe^{3+}] = 2 ppm) for decolorization of 20 ppm MO at pH ≈ 6

The concentration ratio of [Ox]/[Fe^{3+}] also plays a role in contributing to the effectiveness of the systems. Various [Ox]/[Fe^{3+}] concentration ratio were studied, based on [Fe^{3+}] = 2 ppm and [Ox]/[Fe^{3+}] = 3 gave an optimum performance as shown in Figure 5. This is because for this concentration ratio, all Fe(III) introduced was expected to complex with the oxalate ions. The limit of ferric ion to complexes is only three.

Table 1. MO removal at different TiO_2 loading (UV/TiO_2). ([MO]= 20 ppm], MO volume = 100mL).

TiO_2 loading (mg/100 mL)	Color removal (%)
5	40.00
10	44.00
20	61.00
20 (No UV)	5.00
30	50.00

Meaning that each ferric ions only able to complex with three oxalate molecules [21]. It is supported by ferrioxalate structure itself, by which its structure is octahedral metal complex with three bidentate oxalate as ligand will bound to an iron centre. Therefore, beyond this limit, the MO removal declined. This is because excess oxalate cannot complex with ferric ion and only become as additional organic compound to compete with MO for •OH radicals.

On the other hand, when the oxalate ions is insufficient to complex with ferric ions for $[Ox]/[Fe^{3+}] < 3$, thus $Fe(OH)_3$ species will formed. This species is less photosensitive compared to Ferrioxalate. Thus, regeneration of ferrous ion is low from the Fe $(OH)_3$ photolysis. As a result, the continuous production of Fenton's reagent was reduced and caused reduction in MO removal performance [21].

Table 1 reveals MO removal from the combination of TiO_2 and UV irradiation. Without UV irradiation, MO removal was only 5.00 %, compared to the presence of UV irradiation which is 61.00 %. The high performance of UV/TiO_2 compared to TiO_2 alone was expected due to TiO_2 active sites that are only can be activated by UV irradiation. The large band gap of TiO_2 (E_{bg}, anatase ≈3.2 eV, E_{bg}, rutile ≈ 3.0 eV) require light of higher energy to generate electrons (e^-) and holes (h^+) in the semiconductor for photocatalysis process and generation of •OH radicals [22].

However, the presence of trapped species such as water and oxygen are highly demanding to prevent the recombination between photogenerated electron and holes. The recombination between these two species will decrease TiO_2 photocatalyst performance of MO decolorization. Generally, the ability of TiO_2 photocatalyst to remove target compound can be explained by equation (13) – (16) [23].

$$TiO_2 + hv \longrightarrow TiO_2\ (e^- + h^+) \quad (13)$$

$$TiO_2\ (h^+) + H_2O \longrightarrow TiO_2 + H^+ + HO\bullet \quad (14)$$

$$TiO_2\ (h^+) + OH^- \longrightarrow TiO_2 + HO\bullet \quad (15)$$

$$TiO_2\ (e^-) + O_2 \longrightarrow TiO_2 + \bullet O_2^- \quad (16)$$

As shown in Table 1, increasing loading of TiO_2 from 5-20 mg/100mL increased the MO removal performance due to the increasing active sites for the reaction. In addition, at 20 mg/100mL TiO_2 is found to be the optimal dosage. However, further increase of the TiO_2 dosage 30 mg/100mL only reduces the photocatalytic performance. This situation can be explained by the failure of the light penetration to the suspended catalyst solution.

When, excess TiO_2 was loaded into the system, the UV light become more difficult to penetrate through the solution even when the UV lamp was placed in vertical geometry inside the solution instead of on the top of the reaction mixture. As a result, photoactivated volume was reduced and certain part of catalyst surface no longer available for photon absorption and dye adsorption. Hence, photocatalytic activity was suppressed [14]. However, the addition of TiO_2 was giving a significant improvement as illustrated in Figure 6.

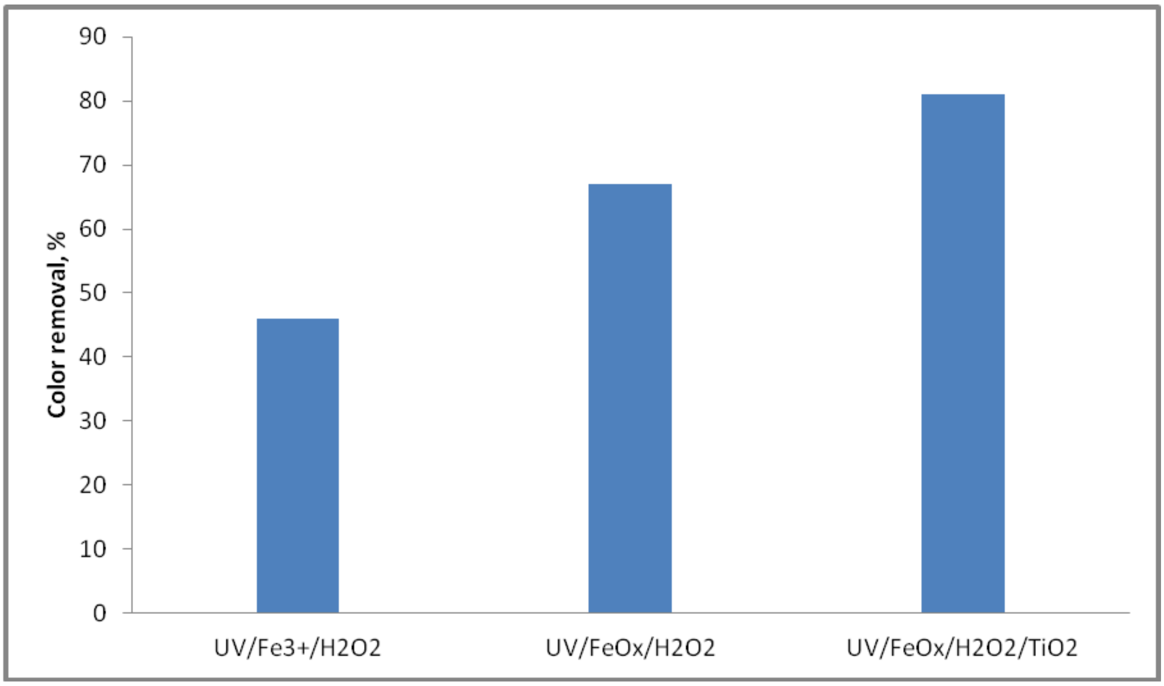

Figure 6. Efficiency of photo Fenton, photo Ferrioxalate and photo Ferrioxalate/TiO_2 systems in MO removal, [MO] = 20 ppm, $[Fe^{3+}]$ = 2 ppm, [oxalate] = 6 ppm, $[H_2O_2]$ = 5mM.

3.3. Effect of ozone combines with homogeneous and heterogeneous catalyst.

Table 2. A comparative study of ozone system for removal of 20 ppm MO (O_3= 380 mg/h, Fe(III) = 2 ppm, H_2O_2 = 5 mM, TiO_2 = 20 mg).

System	Color removal, %	Rate (min^{-1})	R^2
Ozone	97.00	0.011	0.982
Ozone + UV	98.00	0.011	0.984
Ozone + TiO_2 + UV	100	0.016	0.992
Ozone + Ferrioxalate + UV	100	0.022	0.964

Table 2 shows MO removal performance with the present of ozone at fixed flow rate of 380 mg/h. In this study, first order kinetic was applied to show the relation between initial rate and concentration. All systems were well fitted to the first order kinetic as indicated by R^2 value above 0.90. The efficiency of the system was examined based on their rate instead of decolorisation removal. This is because the decolorisation removal was almost similar for all the systems (Table 2).

Based on Table 2, the presence of ozone obviously enhanced MO removal. This situation could be due to two major factors. First, the dissolved ozone in water produces H_2O_2 as shown in equation (17)[23]. H_2O_2 then undergoes photolysis to form •OH radicals (Eq. (6)).

$$O_3 + H_2O + h\nu \longrightarrow H_2O_2 + O_2 \qquad (17)$$

Second, the presence of O_3 in the reaction mixture added another strong oxidant besides •OH radical. This is because ozone has electrochemical oxidation potential of 2.07 V versus 2.80 V for •OH radical [24]. Therefore, it can be speculated that both oxidant react simultaneously in the reaction mixture. As a result, the target pollutant has been oxidized at a faster rate.

3.3.1. Homogeneous ozonation catalytic process

Oxidation-reduction reaction between Fe(III) and ozone that were able generate hydroxyl radical was expected to contribute the most to MO removal. This is due to its capability to produce many desired species for MO removal such as •OH, Fe(II) and H_2O_2. These species are produced by initiation from the reaction between dissolved ozone and Fe(III). The reaction between dissolved ozone and Fe(III) produced •OH radical, Fe(II) ion and some other species (Eq. (18)). The hydrolysis of Fe(II) ion produces additional •OH radical and Fe(III) (Eq. (19)).

Further reaction was expected to occur between Fe(III) and H_2O_2 supplied in this reaction producing hydroperoxyl radical and Fe(II) (Eq. (20)). Lastly, the disproportionation of hydroperoxyl radical produced more •OH radical as shown in equation (11). In addition, some more reaction could be speculated to occur such as the classical Fenton reaction, due to the Fe(II) species produced as in equation (20).

The mechanism for homogeneous ozonation process (Eq. (18)-(21)) has been proposed by Wu [25].

$$Fe^{3+} + O_3 + H_2O \longrightarrow FeO^{2+} + H^+ + HO\bullet + O_2 \tag{18}$$

$$FeO^{2+} + H_2O \longrightarrow Fe^{3+} + HO\bullet + OH^- \tag{19}$$

$$Fe^{3+} + H_2O_2 \longrightarrow Fe^{2+} + HO_2\bullet + H^+ \tag{20}$$

3.3.2 Heterogeneous ozonation catalytic process

As shown in Table 2, irradiated ozonation combined with TiO_2 gives almost complete removal after 90 minutes. This reveals that a lot of hydroxyl radicals were produced from this combination. The reactive hydroxyl radical formed by the reaction between ozone and photogenerated electron as shown in equation (21) to (23). Ozone reacts as a photogenerated electron trap thus avoiding recombination with positive hole [24].

$$O_3 + TiO_2(e^-) \longrightarrow \bullet O_3^- + TiO_2 \tag{21}$$

$$H^+ + \bullet O_3^- \longrightarrow \bullet O_3H \tag{22}$$

$$\bullet O_3H \longrightarrow \bullet OH + O_2 \tag{23}$$

4. CONCLUSION

This study evaluate the effectiveness of ozone in assisting homogeneous (UV/Fe(III)/H_2O_2) and heterogeneous (UV/TiO_2) catalytic systems in MO removal at near neutral pH. The combination of ozone in both catalytic systems was greatly enhancing MO removal performance. However, the best performance was recorded by ozone combine with homogeneous catalytic system as the smallest rate constant achieved.

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