

Using Fenton's Reagents for the Degradation of Diisopropanolamine: Effect of Temperature and pH

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Abstract. Spent DIPA is routinely generated from natural gas absorption columns. It is generated from periodic cleaning of absorption and regeneration columns and during a process upset. The liquid waste containing these absorbents is characterized of having high chemical oxygen demand (COD) in the range of 5,000 to 25,000 mg/L. Based on such loading, the waste is not suitable to be treated via biological treatment. Fenton's reagent was found to be a suitable chemical treatment method. Among the parameters that will affect the treatment efficiency are temperature and pH. Thus for this study, the experimental ranges for temperature and pH: $30^{\circ}\text{C} \leq T \leq 60^{\circ}\text{C}$ and $2 \leq \text{pH} \leq 4$. The molar ratio of reagents, $\text{H}_2\text{O}_2:\text{Fe}^{2+}$ used was 95. The treatment efficiency increases with increasing temperature. The best pH for treatment was 2.5. A simple kinetic study was used to study DIPA degradation. A pseudo first-order reaction rate with respect to concentration of DIPA was found to fit the data collected adequately.

Keywords: Advanced oxidation process (AOP), Fenton's oxidation, Diisopropanolamine, Kinetics

1. Introduction

Diisopropanolamine (DIPA) is used for gas sweetening process. It is commonly used together with sulfolane to remove CO_2 and H_2S in absorbent columns. It was discovered that waste containing DIPA is characteristically having high chemical oxygen demand (COD). A natural gas plant reported that the COD can go up to about 5,000 to a maximum of 25,000 mg/L, depending on the volume of DIPA in the wastewater.

Generally, conventional biological wastewater treatment such as activated sludge is only able to degrade below 1000 mg/L of COD. Thus, an alternative treatment or pre-treatment of the wastewater is required. There are many treatment options available for the removal of pollutants successfully such as stripping, carbon adsorption and membrane process. However, due to cost effectiveness, stringent regulatory limits and process limitations, advanced oxidation process (AOP) is a flexible technique towards enhancing the existing system. AOP is capable of improving the biodegradability of complex or recalcitrant compounds. This process is based on the chemical oxidation technologies that use hydroxyl radical ($\cdot\text{OH}$) generated in situ. The radical oxidizes the organic and/or inorganic contaminants to produce environmentally friendly fragments and eventually to CO_2 and H_2O if sufficient reagents and time are allowed. There are various ways of generating hydroxyl radical. Among the processes known to be effective in removing contaminants from wastewater include ultraviolet (UV) photolysis of ozone (UV/ O_3), UV photolysis of hydrogen peroxide (UV/ H_2O_2), Fenton's reagents ($\text{Fe}^{2+}/\text{H}_2\text{O}_2$), and the photo-Fenton process.

Fenton's reagent consists of hydrogen peroxide (H_2O_2) and Ferrous ions (Fe^{2+}). This method has been used for wastewater treatment that contains organic pollutant such as MTBE [1], aromatic amines [2], pharmaceutical waste [3], petroleum refinery sourwater [4], carpet dyeing wastewater [5] and phenol [6]. All of these studies have successfully treated wastewater to a certain extent and were able to improve its biodegradability using Fenton's reagents.

Production of hydroxyl radicals with these reagents triggers a series of other reactions (Table 1). Reaction (1) is the chain initiation reaction whereby the reactive $\cdot\text{OH}$ is formed. This radical is one of the

strongest oxidants known. Its relative oxidation power ($Cl_2 = 1.0$) has been known as 2.06 [7]. If both $\cdot OH$ and Fe^{2+} ions are in excess, reaction (2) will terminate the chain reaction. Production of hydroperoxyl radicals ($HO_2\cdot$) in reaction (4) plays a role in regeneration of Fe^{2+} ions (5). Regeneration of Fe^{2+} can also happen as shown in (6), albeit at a slower rate. According to Burbano et al. the production superoxide radical ($O_2\cdot^-$) through reaction (7), plays a greater role in the redox cycle of Fe^{2+} and Fe^{3+} . This is based on the reaction constants of reaction (5) and (9).

Table 1: Fenton's oxidation reactions and its rate constants.

Reaction number	Reaction Equation	Rate constants ($M^{-1} s^{-1}$)	References
(1)	$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + \cdot OH + OH^-$	76	[8]
(2)	$\cdot OH + Fe^{2+} \rightarrow Fe^{3+} + OH^-$	3×10^8	[8]
(3)	$\cdot OH + \cdot OH \rightarrow H_2O_2$	5.2×10^9	[10]
(4)	$\cdot OH + H_2O_2 \rightarrow H_2O + HO_2\cdot$	3.3×10^7	[9]
(5)	$Fe^{3+} + HO_2\cdot \rightarrow Fe^{2+} + O_2 + H^+$	3.3×10^5	[10]
(6)	$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2\cdot + H^+$	0.01	[11]
(7)	$HO_2\cdot \rightarrow O_2\cdot^- + H^+$	1.58×10^5	[12]
(8)	$Fe^{2+} + O_2\cdot^- \rightarrow Fe^{3+} + O_2$	1.0×10^7	[1]
(9)	$Fe^{3+} + O_2\cdot^- \xrightarrow{+2H^+} Fe^{2+} + O_2$	1.5×10^8	[1]
(10)	$HO_2\cdot + \cdot OH \rightarrow O_2 + H_2O_2$	1×10^{10}	[13]

Among the parameters that will affect Fenton's oxidation are temperature and initial reaction pH. This study was conducted to see the effects of the said factors on treatment efficiency and kinetic constants. Temperature plays a great role in chemical reaction. Generally by increasing the reaction temperature the reaction rate will increase. However, once the temperature reaches a certain point, some chemical species may be altered consequently the reaction will slow down or stop. For Fenton's oxidation, there are studies [14, 15, 16, 17] that follow the theory. However, some studies [18, 19] demonstrated an on-going increment in pollutant degradation rate as reaction temperature increases. The study materials for the mentioned researches are different. Therefore, it is of interest to determine temperature effect using the same treatment method with DIPA as the study material. It is noted that hydrogen peroxide undergoes self-accelerating decomposition at temperature higher than $60^\circ C$ [20]. The next parameter is pH and it is well known to be a very influential parameter in Fenton's oxidation. This has been studied by many researchers [4, 18, 21, 22]. The variation in initial reaction pH is very small which varies between 2 to 4. At very low pH of less than 2.0, the reaction is slow due to the formation of complex iron species and formation of oxonium ion $[H_3O_2]^+$. Subsequently this will reduce the degradation efficiency. When pH is more than 4.0, the generation of hydroxyl radical is slower because of the formation of Ferric-hydroxo complexes [6], thus decreasing the free iron species in solution. This will inhibit the regeneration of Fe^{2+} . It is also known that the oxidation potential of hydroxyl radical decreases with an increase in pH [23]. In this study, the temperature was set at 30, 40, 50, and $60^\circ C$ and pH at 2.0, 2.5, 3.0, 3.5 and 4.0. Both conditions were set based on the limitations based on the theory discussed above. At the current time, there was no study on DIPA degradation using Fenton's oxidation in any literature. Therefore together with the fact of the existing problems faced by relevant industry related to waste containing DIPA, this study is expected to provide an alternative treatment method.

2. Material and methods

DIPA containing wastewater was prepared synthetically (3 g/L). This concentration was chosen because the equivalent COD is about 5000 mg/L, which is the average concentration of the spent absorbent generated from a LNG plant. A 2-litre jacketed reactor was used and it was connected to a refrigerating bath (Jeio Tech, model no. RW-1025G). The synthetic wastewater was mixed using a magnetic stirrer (Stuart Scientific, model no. SB161-3). Wastewater volume used for each experiment was fixed at 500 mL which was a makeup of the synthetic wastewater and dosage of hydrogen peroxide. The pH of wastewater containing DIPA is about 10 thus it is imperative to do the pH adjustments first using 2 M H_2SO_4 (Mallinckrodt) or/and 10 M NaOH (Merck). This is to avoid conversion of Fe^{2+} to Fe^{3+} at alkaline condition. Then the calculated and weighted amount of $FeSO_4 \cdot 7H_2O$ (Merck) was added followed by a measured volume 30% H_2O_2

(Merck). The measured molarity ratio of the reagents used in this study was determined to be 95 ($\text{H}_2\text{O}_2:\text{Fe}^{2+}$) by using central composite design and response surface methodology. Reaction time started once the H_2O_2 was poured into the reactor. Samples were taken at 0, 1, 2, 5, 10, 15, 20, 30, 45 and 60 minutes time interval and 10 M NaOH was used to stop the reaction [24]. The true concentration of H_2O_2 was determined using the permanganate titration [25]. This was done ensure the dosage remains the same as hydrogen peroxide can degrade easily in storage.

DIPA concentration was analysed using Agilent 1100 HPLC. Column used is YMC Pack Polymer C18 (250 x 6.0 mm I.D.). Eluent used was a combination of 60/40 of 100 mM NaH_2PO_4 and 100 mM of NaOH. The flowrate was set at 1.2 mL/min and temperature was 30°C. UV detector was set at 215 nm and injection volume was 20 μL . The peak was detected at around 8.6 minute.

An understanding of kinetic study is important to provide evidence of reaction mechanisms. Kinetic study explores on how experimental conditions can influence the speed of a chemical reaction. For this study, temperature and pH were used to determine their influence towards Fenton's oxidation. There are two methods for analysing kinetic data, integral and differential method. For this study, the former method will be used. Ramirez et al. [26] simplified the kinetic study by only considering the reaction between the target compound and hydroxyl radical in a batch reactor. In their study, they assume that the reaction is of pseudo first-order. This method is widely used for Fenton's oxidation kinetic study [26, 27, 28].

It is also known the Fenton's oxidation treatment is divided in two-staged reactions [26]. In the first stage the organic compounds are decomposed rapidly and somewhat less rapidly in the second one. The main reason for this observation is that Ferrous ions react very quickly with hydrogen peroxide to produce large amounts of hydroxyl radical (reaction (1)). The in-situ produced $\cdot\text{OH}$ then quickly react with the target compound. This stage is known as the $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ stage. In the second stage which is known as the $\text{Fe}^{3+}/\text{H}_2\text{O}_2$ stage, the reaction is slower due to the slow regeneration of Fe^{2+} from Fe^{3+} (reaction (6)). In this study, kinetic study was done by using data from the second stage only by assuming the reaction order is of pseudo first-order reaction because more than 90% of data falls in the second stage.

3. Results and discussion

3.1. Temperature effect

As mentioned some Fenton's oxidation studies reported that there is an optimum temperature before treatment efficiency drops. It is of interest if this trend takes place for degradation of DIPA using Fenton's oxidation. Fig. 1 shows the effect of temperature on the treatment efficiency. The observed trend is the higher the temperature, the degradation of DIPA increases (up to 100% degradation at 60°C).

There is no optimal temperature found as opposed to some literature reports [14, 15, 16, 17]. Guedes et al. [15] monitored the degradation of cork cooking wastewater at temperatures of 20, 30, 40 and 50°C. It was reported the optimal temperature is 30°C. This finding is the same as [14] and for [16] the optimal temperature is found between 30 to 40°C. Wu et al. [17] on the other hand found the optimum temperature at 45°C. It was explained that increasing the temperature had two opposite effects on the reaction yield. Most probably the generation rate of $\cdot\text{OH}$ is enhanced at a high temperature but when the temperature approaches 60°C, hydrogen peroxide undergoes self-accelerating decomposition. Thus reduces the concentration of $\cdot\text{OH}$. According to [4], there was almost no change in TOC removal efficiency above 40°C. This differs from studies conducted by [18, 19]. Both reported that temperature increment had a positive impact on the degradation of dyes. It was also noted that a shorter reaction period was needed for the decolourization of dye at a higher temperature.

In this study as the temperature goes higher, the degradation is better and faster as demonstrated at 60°C. At 30 minutes DIPA concentration had dropped to 250 mg/L which was about 91.7% DIPA degradation.

3.2. Initial pH effect

As mentioned earlier, reaction pH for Fenton's oxidation should be in between 2 to 4. Some studies reported an optimum pH of 3 [4, 18, 22]. In this study, pH 2.5 is the optimum pH. Studies by [21, 29] gave different optimum pH. Bautista et al. reported an optimum pH of between 2.5 to 3 and Homem et al.

mentioned a pH of 3.5 to 4.5. For degradation of DIPA, Fenton's oxidation optimum initial reaction pH is 2.5 (Fig. 2). This also proves that the theory of acidic initial reaction temperature is firm.

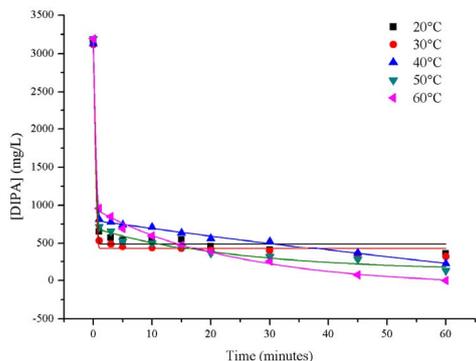


Fig. 1: DIPA degradation trend with respect to temperature ($[\text{H}_2\text{O}_2] = 0.38\text{M}$, $[\text{Fe}^{2+}] = 0.004\text{ M}$ and $\text{pH} = 3$).

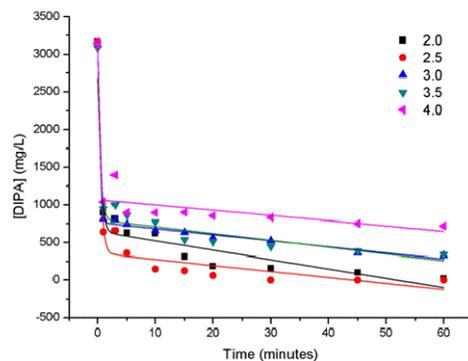


Fig. 2: DIPA degradation trend with respect to pH ($[\text{H}_2\text{O}_2] = 0.38\text{M}$, $[\text{Fe}^{2+}] = 0.004\text{ M}$ and $\text{pH} = 3$).

3.3. Kinetic study

It is assumed that the pseudo first-order kinetic constant remains constant through out the experiment due to the hypothesis of a pseudo steady-state concentration of hydroxyl radical. The kinetic equation is expressed as:

$$(-r_{\text{DIPA}}) = kC_{\cdot\text{OH}}C_{\text{DIPA}} = k_{\text{ap}}C_{\text{DIPA}} \quad (\text{Equation 11})$$

where k_{ap} is an apparent pseudo first-order kinetic constant. The effect of k_{ap} from the physical parameters was determined from the collected data. By integrating and rearranging the equation above to form a linear equation, k_{ap} can be determined. The linear equation is as follows:

$$\ln(C_{\text{DIPA}}/C_{\text{DIPA0}}) = -k_{\text{ap}}t \quad (\text{Equation 12})$$

Figure 3 is an example of the linearised plot for the second stage of Fenton's reaction for temperature effect. The linearised plot shows that the assumption of pseudo first-order kinetic is valid as the data fit accordingly. Similar plot was also found for pH effect.

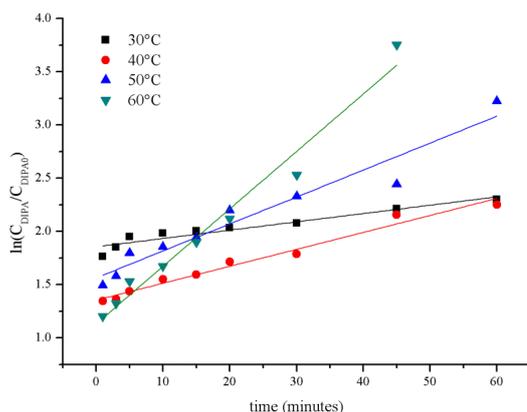


Fig. 3: Linearised DIPA concentration during the second stage at different temperatures.

Table 2 shows the values of k_{ap} for both temperature and pH and its R^2 values. Coefficient of determination, R^2 , is an indicator to how well the equation can be used for prediction. The closer the value is to 1, the better is the fit to the model. From Fig. 3, it is clear that temperature has a strong effect on the degradation of DIPA. The highest pseudo first-order rate constant is at 60°C and the data collected fit well ($R^2 = 0.97$). Similar observations at 60°C were also reported by [26, 28] for orange II dye and nitrobenzene

respectively. It was also noted that the rate constant at 60°C is 85% higher than at 30°C. So it can be concluded that the reaction favours high temperature.

The apparent rate constant is highest at pH 2.5. This is clearly showed by the marked difference in k_{ap} compared to the others. At this pH, the degradation of DIPA was also the highest and fastest (Figure 2). As explained earlier pH lower than 3 causes the formation of iron complex and at higher than 4, the Fe^{3+} precipitates thus decreasing the fraction of soluble iron species. Degradation of DIPA is best at pH 2.5 with k_{ap} of 0.1282. The next closest value of k_{ap} is at pH 2.0 which is 0.0588. The difference is large, which further confirms the best initial reaction pH.

Table 2: Effect of temperature and pH on the apparent pseudo first-order constant (k_{ap}).

Parameter	$k_{ap}(s^{-1})$	R^2
Temperature		
30	0.0078	0.90
40	0.0159	0.97
50	0.0253	0.93
60	0.0542	0.97
pH		
2.0	0.0588	0.95
2.5	0.1282	0.95
3.0	0.0185	0.98
3.5	0.0159	0.85
4.0	0.0060	0.80

4. Conclusion

There was no optimum temperature found for Fenton's degradation of DIPA. The highest degradation was at 60°C. No experiments was carried out beyond that because hydrogen peroxide undergoes self-accelerating decomposition at temperature higher than 60°C. This finding is also supported by the pseudo first-order kinetic constant where k_{ap} at 60°C is 85% higher than at 30°C. Optimum pH was at 2.5. The degradation is faster and this is proven by its k_{ap} which was outstandingly higher than at other pH.

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6. References

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