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Degradation of aniline by liquid ferrate(VI)

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ABSTRACT

In this study, the degradation efficiency of aniline in aqueous solution was investigated at various values of pH, ferrate(VI) dosage, and aqueous solution temperature. Aniline solution was extracted by the liquid–liquid extraction method and analyzed by GC-FID. Aniline was degraded rapidly within 30 s by ferrate(VI). The results indicated that the highest removal efficiency of aniline by liquid ferrate(VI) was found at acidic condition (pH 4.36). In addition, aniline removal efficiency increased with increasing ferrate dosage. The optimum temperature was obtained in 25°C of aqueous solution temperature. The intermediate analysis for the reaction of aniline and ferrate(VI) has been conducted using GC-MS. Nitrobenzene, azobenzene, and ϱ-benzoquinone were identified as reaction intermediates.

Keywords: Liquid ferrate(VI); Aniline; Oxidation; Intermediate study

1. Introduction

In recent years, new harmful pollutants such as non-degradable organic substances and endocrine disruptive substances, which may show various toxicity and carcinogenicity, are produced and consumed due to industrialization and urbanization. This continuously increases pollution loads to a wide range of areas in the environment [1]. Most of the chemical compounds released to the environment are discharged to the atmosphere, and about 0.3% of the total amount is discharged to the water system. However, hazardous materials discharged into the atmosphere can be introduced into the water system such as rivers, lakes, and oceans by rainwater during rainfall, which can be a potential source of water pollution [2,3].

Aniline, the most typical compound in aromatic amines, is a kind of colorless oily liquid with a sweet smell [4]. Aniline is one of the important raw material which is used for producing rubber accelerators, producing intermediate substances for pesticides and making azo and plastic dyes, and this is why it is distributed widely in the environment [5–7]. It is known to be a toxic water pollutant and the most harmful chemical substance to aquatic life because of its high toxicity and accumulation in the environment [8]. It enters the human body by the skin, respiratory tract, and digestion system, resulting in carcinogenic, teratogenic, and mutagenic effects on human beings [9]. As with most amines, aniline is difficult to completely remove by common treatment methods, and it is necessary to use advanced oxidation processes for the treatment of toxic organic compounds. Recently, ferrate(VI) has been studied by many researchers as an oxidizing agent that can effectively treat various kinds of pollutants [10,11]. Ferrate(VI) is a hexavalent iron and can act as a powerful oxidizer and coagulant in the entire pH range. The oxidation–reduction potential of ferrate(VI) in acidic condition is highest (2.2 V) among oxidants (such as ozone, hydrogen peroxide, chlorine dioxide), and in basic condition it has quite high redox potential of 0.7 V [12]. To date, three common synthetic procedures have been developed for the preparation of ferrate(VI): wet oxidation, dry oxidation, and electrolysis method. Recently, the liquid ferrate(VI) which has good stability produced by Sharma's [13] method was developed.

In this study, liquid ferrate(VI) is manufactured based on Sharma's [13] method and investigated [13]. Also, the degradation characteristics of aniline have been studied. The effect

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of parameters such as pH, ferrate dosage, and temperature in aqueous solution has been investigated. Moreover, intermediate products were identified in this study to investigate the mechanism of aniline removal by liquid ferrate(Ⅵ).

2. Materials and methods

2.1. Materials

All chemicals used were of reagent grade or higher purity reagent and were used without further purification. Sodium peroxide (Na_2O_2) and iron(Ⅲ) oxide (Fe_2O_3) were purchased from Alfa Company. They are the main materials in Sharma's liquid ferrate(VI) method. Sodium hypochlorite (NaOCl) and sodium hydroxide (NaOH) were purchased from Junsei Chemical Co., Ltd. (Tokyo, Japan) for the wet oxidation production. Aniline was purchased from Junsei with the purity 99%. The borax ($Na_2B_4O_7 \cdot 10H_2O$) and sodium dihydrogen phosphate dodecahydrate ($Na_2HPO_4 \cdot 12H_2O$) were used in the buffer solution for the determination of ferrate(VI) concentration. These reagents were purchased from the YAKURI pure chemical Co. Ltd., (Japan). Buffer solutions were prepared using water that had been filtrated and passed through an 18 MΩ Milli-Q cm water purification system.

2.2. Methods

2.2.1. Synthesis of liquid ferrate by Sharma's method

The synthesis of liquid ferrate was based on the US Patent 8961921 B2 by Sharma with some modification. The first step to synthesize this ferrate(VI) was heating Fe_2O_3 and Na_2O_2 in 500°C electric furnaces for 30 min and the sample was cooled down as shown in Eq. (1). This step was carried out once more. After that, 2 g of the mixture was mixed and stirred with 60 mL NaOCl and 20 g NaOH added gradually to the reactor as shown in Eq. (2). The mixing process of all the reagents resulted in a dark purple solution which indicated the stable liquid ferrate(VI) had been successfully produced. The solution was then filtered using GF/F filter paper to separate the solution from the solid contaminants.

$$Fe_2O_3 + 3Na_2O_2 \rightarrow NaFeO_2 + 1/2O_2 \quad (1)$$

$$2NaFeO_2 + 3NaOCl + 2NaOH \rightarrow 2Na_2FeO_4 + 3NaCl + H_2O \quad (2)$$

To determine if a certain amount of ferrate was produced in the prepared solution, a buffer solution was used for each experiment. The UV/Vis (Hach, DR 5000) at 505 nm was used to determine the concentration of ferrate(VI) [14].

2.2.2. Degradation experiments

The oxidation experiments were conducted with a 700 mL pyrex glass reactor and performed in a closed zero-head space with a port for sampling, pH probe, thermometer, and ferrate(VI) inlet. Ferrate solutions used in the experiments were stable liquid ferrate produced from the synthesis process.

The 5 mL samples were taken and extracted using a liquid–liquid extraction method with *n*-hexane. Afterward, the aniline concentration remaining after degradation were measured using gas chromatography equipped with HP-5MS column (30 m × 0.25 mm I.D. × 0.25 μm film thickness), and a flame ionization detector (FID) (Fig. 1). The temperatures of the injection port and detector were 200°C and 280°C, respectively. The temperature program began at 35°C and held for 2 min, followed by a 10°C/min ramp until a final temperature of 150°C was reached. The gas chromatography/mass spectrometry (GC/MS) technique was used to analyze intermediate products. GC/MS analysis was performed with mass spectrometer systems (GC/MS-QP2010Plus, Shimadzu, Japan) and an AT-1 capillary column (60 m × 0.32 mm I.D × 1.0 μm film thickness). The injection port temperature was 300°C and the column temperature, initially 35°C, was held constant for 5 min, followed by 8°C/min ramps until 100°C and held for 5 min, 12°C/min ramps until 200°C and held for 5 min, followed by 15°C/min ramps until a final temperature of 250°C was reached. To prevent further degradation by ferrate, the sample taken from the reactor was mixed with 30% NaOH solution and extracted instantly with mechanical vortex mixing.

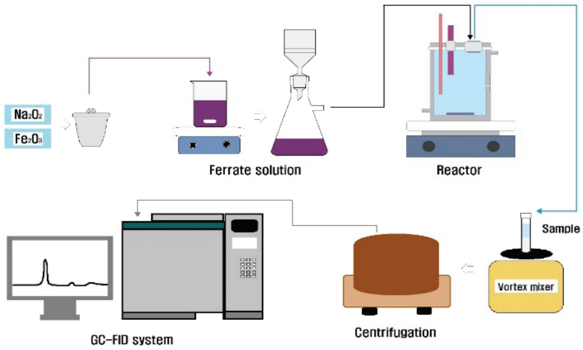


Fig. 1. Schematic diagram for experimental procedure.

3. Results and discussions

3.1. Synthesis of ferrate(VI)

The liquid ferrate synthesized by Sharma's method has been successfully produced with the concentration 78,000–82,000 ppm. A dark purple color was formed as a result of the reaction between an iron source ($NaFeO_2$) with NaOCl and NaOH. The wavelength of ferrate(VI) was in agreement with the previous study by Lee et al. [14], shown in Fig. 2.

3.2. Blank test

To test for clarity for the effect of decomposition by ferrate, a blank test was performed first. The inlet of the reactor was sealed so that the inlet of the external substance or the aqueous solution in the reactor was not volatilized at room temperature and normal pressure. The reaction solution was filled until reaching the headspace of the reactor. The initial concentration of aniline was adjusted to 0.054 mM and the pH was set to neutral. After stirring for 10 min using a magnetic stirrer, samples were taken at regular intervals. As a result, the change of aniline concentration in the sample was lower than 3%. Therefore, the effect of stirring was ignorable.

3.3. Effect of pH

Ferrate(VI) is a powerful oxidant in the entire pH range [15]. Technical literature suggests that ferrate oxidation proceeds more efficiently at pH lower than 10, because the maximum stability of ferrate is at pH 10 [16,17]. To investigate the effect of the pH on the aniline degradation efficiency, the experiments have been carried out at pH 4.36 (acid), 6.37 (neutral), and 10.14 (base). As shown in Fig. 3, the highest aniline removal was observed at pH 4.36 with the removal efficiency of 63.16%. The degradation efficiency was 58.07% and 43.81% at pH 6.37 and pH 10.14, respectively.

The second order reaction rate (K_{app}) values in various pH conditions are shown in Fig. 4. According to previous studies on ferrate(VI) reaction with organic compounds, the second order reaction rate constants have been obtained [18,19]. This method was used to determine all the second order reaction rate value in the experiments. As a result, it was 512.42 $M^{-1} s^{-1}$ at acidic conditions and 452.62 $M^{-1} s^{-1}$, 285.38 $M^{-1} s^{-1}$ at neutral and basic conditions, respectively. Ferrate(VI) has triprotonated ($H_3FeO_4^+$), diprotonated (H_2FeO_4), monoprotonated ($HFeO_4^-$), and deprotonated (FeO_4^{2-}) species existed in the acidic to basic pH conditions [20,21]. For the ferrate at low pH, it is highly unstable and more reactive, thereby ferrate leads to a higher reactivity in acidic conditions [22,23]. In the case of aniline, the reacting ferrate species is $HFeO_4^-$, K_{app} steadily increases even at pH < 7.2 where the $HFeO_4^-$ concentration is at its maximum [19]. Therefore, it is considered that a high decomposition efficiency is observed at pH 4.36 where the $HFeO_4^-$ species has higher concentration.

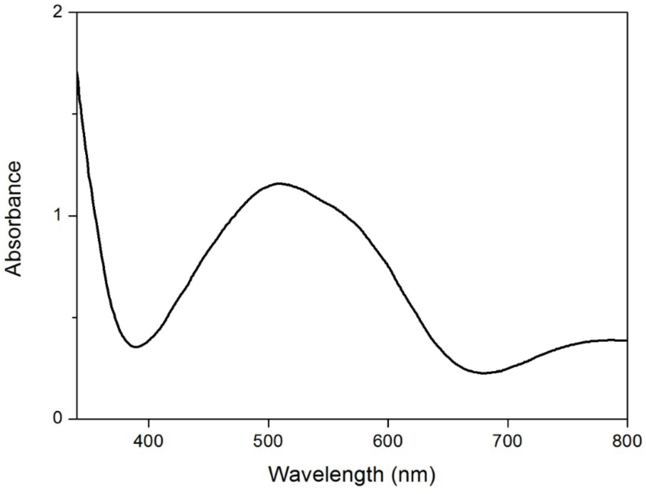


Fig. 2. UV/Vis absorption spectrum of ferrate(Ⅵ) in buffer solution (300 nm – 800 nm).

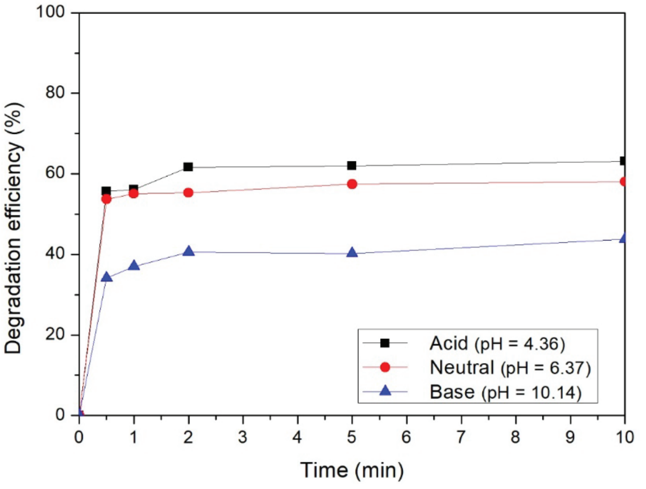


Fig. 3. Degradation in the various pH conditions (experimental conditions: C_0 = 0.0538 mM, ferrate(VI) dosage = 0.02503 mM, temperature = 25°C ± 1°C).

The reaction of ferrate(VI) with organic and inorganic contaminants can occur at different reaction rates and mechanisms [24], the pH may affect the ionization of the target compound and the decomposition using ferrate(VI) may be different depending on the ionization of the target substance [22]. Therefore, it is important to understand the mechanism of reaction with ferrate in the actual water treatment and to find the optimum pH to obtain the maximum decomposition rate.

3.4. Effect of ferrate dose

Ferrate(VI) dose is significant operational parameter which affected ferrate performance to remove organic contaminants [25]. In order to investigate the effect of ferrate dosage, the different concentrations of ferrate are selected from 0.00834 to 0.08344 mM. The effect of the ferrate dosage on the degradation of aniline is shown in Fig. 5. In the solution containing 0.0538 mM of aniline, during a total reaction time of 10 min, the highest removal efficiency was 98.35% with 0.08344 mM of ferrate dose. Aniline was decomposed within 30 s of the reaction. As the dosage of ferrate(VI) increased, the degradation efficiency improved because of the increase of the amount of ferrate available for degradation. This is similar to the results of previous studies [26,27] which considered the reaction between ferrate and many pollutant compounds and confirmed a rapid rate of reaction, typically within minutes.

The rate constant values in the various ferrate doses were calculated and shown in Table 1. The K_{app} values were considered to the molar ratios ($[FeO_4^{2-}]/[\text{aniline}]$) and shown in Fig. 6. The observed K_{app} values increased proportionally

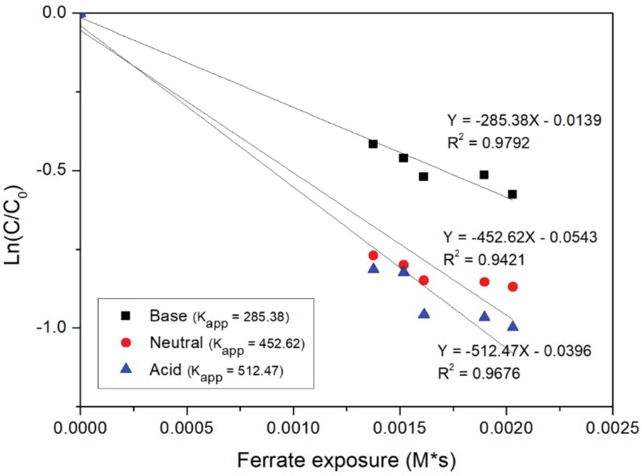


Fig. 4. Plot of ferrate(VI) exposure and ln(C/C_0) for the K_{app} value determination.

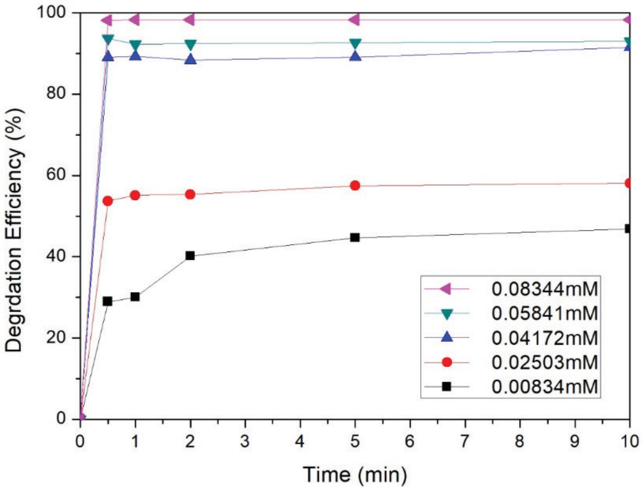


Fig. 5. Degradation in the various ferrate(VI) dosage (experimental conditions: C_0 = 0.0538 mM, pH = neutral (6–7), temperature = 25°C ± 1°C).

Table 1
K_{app} value of aniline in the various dose of ferrate(VI) (experimental conditions: C_0 = 0.0538 mM, pH = neutral (6–7), temperature = 25°C ± 1°C)

Ferrate dose	K_{app} ($M^{-1}\,s^{-1}$)
0.00834 mM	308.72
0.02503 mM	449.19
0.04172 mM	1,223.3
0.05841 mM	1,381.1
0.08344 mM	2,166.1

with increasing of ferrate doses, and K_{app} values obtained from the experiments were 2,166.1 $M^{-1}\,s^{-1}$ for the aniline when the molar ratio was 16:1. Another studies need to be conducted to find the optimal dosage of ferrate which can be added for degradation of target compounds because ferrate in excess dosage will proceed to self-decomposition among ferrates(VI) itself.

3.5. Effect of temperature

Temperature is one of the important factors affecting the removal of contaminants in water using ferrate. The experiments were conducted with temperatures of 10°C, 25°C, 35°C, and 45°C, and applied with a fixed ferrate dose 0.02503 mM. The decomposition efficiency of aniline according to temperature is shown in Fig. 7. In these experiments, the optimal temperature condition for aniline degradation was observed at 25°C with removal efficiency 58.07%. The degradation rates at 10°C, 35°C, and 45°C were 36.92%, 54.41%, and 41.18%, respectively. Generally, in most reactions, the reaction kinetics was enhanced when the temperature increased. In this experiment, however, the decomposition rate was decreased with increasing temperature. Previous studies have also confirmed the homogenous decomposition kinetics of ferrate was enhanced when the temperature increased [28].

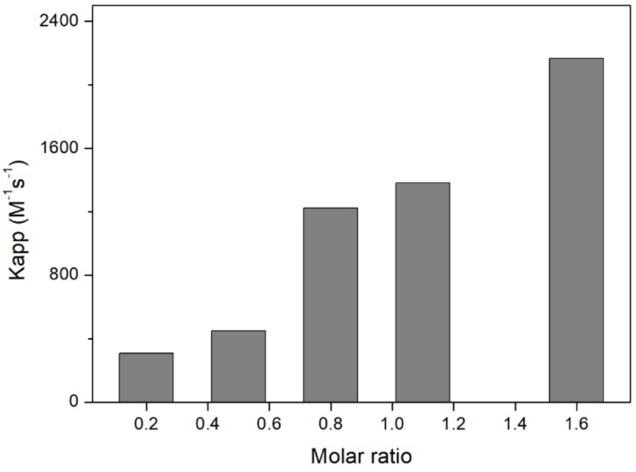


Fig. 6. Relationship between molar ratio and K_{app}.

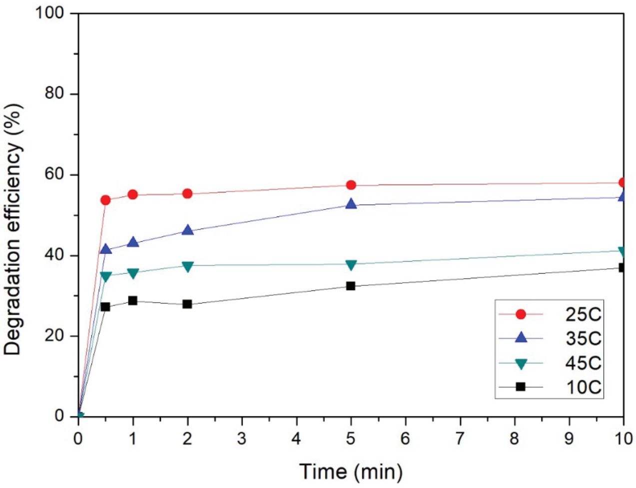


Fig. 7. Degradation at various temperatures (experimental conditions: C_0 = 0.0538 mM, ferrate(VI) dosage = 0.02503 mM, pH = neutral (6–7)).

Table 2 shows the K_{app} in the temperature range from 10°C to 45°C with the highest K_{app} value obtained 449.19 $M^{-1}\,s^{-1}$ in 25°C. Ferrate(VI) at 10°C reacted very slowly due to the low temperature and kinetic energy. On the other hand, ferrate decomposed rapidly at the temperatures 35°C and 45°C since the ferrate was unstable in the high temperature (Fig. 8). Spontaneous decomposition of ferrate will be enhanced when temperature increased [29,30].

In order to investigate the activation energy as a secondary reaction in the decomposition reaction of aniline by ferrate, the decomposition result according to the temperature change of the aqueous solution and the Arrhenius equation was used. The Arrhenius equation of experiment data was used to determine activation energy (Eq. (3)). From the calculation, the activation energy for aniline degradation reaction was 34.131 kJ/mol, when increasing 10°C to 25°C. As the optimum temperature was obtained at 25°C, it is not necessary to spend more energy for treatment of the pollutants using ferrate(VI).

Table 2
K_{app} of aniline at various temperatures (experimental conditions: C_0 = 0.0538 mM, ferrate(VI) dosage = 0.02503 mM, pH = neutral (6–7))

	K_{app} ($M^{-1} s^{-1}$)
10°C	216.43
25°C	449.19
35°C	387.51
45°C	262.70

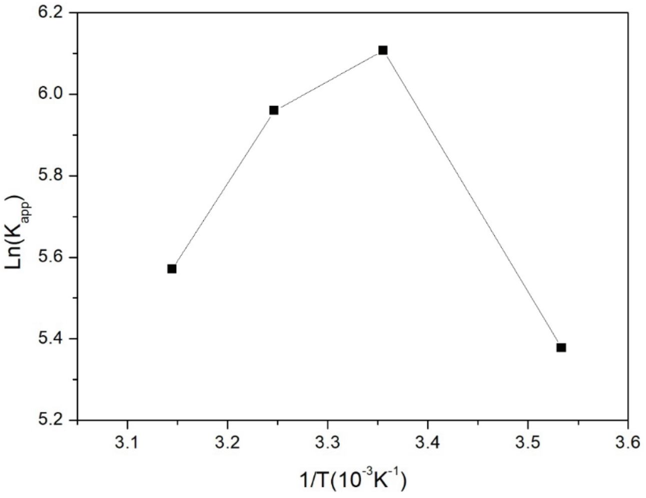
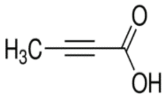
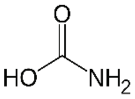
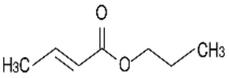
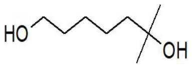
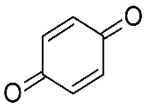
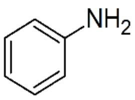
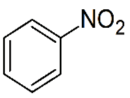
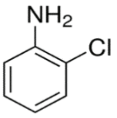
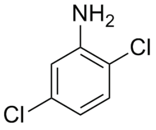
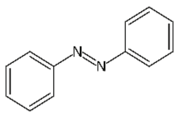


Fig. 8. Relationship between 1/*T* and K_{app} value in the determination of optimal temperature.

$$\ln\frac{\text{rate}_1}{\text{rate}_2} = -\frac{Ea}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \quad (3)$$

Table 3
Intermediate products of aniline from the liquid ferrate(VI) oxidation

Compound name	Structure	R.T (min)
2-Butynoic acid		1.025
Carbamic acid		2.504
Propyl crotonate		13.417
6-Methylheptane-1,6-diol		13.583
p-Benzoquinone		17.049
Aniline		20.314
Nitrobenzene		23.717
o-Chloroaniline		24.826
2,5-Dichloroaniline		27.359
Azobenzene		35.401

3.6. Identification of reaction products

The intermediate products identification of aniline by liquid ferrate(VI) analyzed using GC/MS are shown in Table 3 and the degradation pathway was showed in Fig. 9. The mass spectra were examined with the computer database of the National Institute of Science and Technology Mass Spectral Library. This proposed pathway was based on the previous experiment by many researchers [30–32] which studied the degradation mechanism of aniline by ferrate. Similar intermediate products such as nitrobenzene, azobenzene, and p-benzoquinone have been found in this experiment. Aniline has been found to be readily oxidizable owing to the presence of the NH_2 electron donor group, leading to electrophilic attack at reactive carbons (in the ortho and para positions) on the aromatic ring. Therefore, when aniline reacts with ferrate, oxygen-atom transfer to the aniline may cause azobenzene, nitrobenzene, and formed p-benzoquinone to occur. It partially reacted ring-opening or transfer electrons, then it was proposed that further decomposition of intermediates led to end products such as CO_2 and H_2O (Eq. (2)). The color of the solution was changed into yellowish brown after the addition of liquid ferrate. The observed color changes during oxidative decomposition reaction and this is attributed to the effect of azobenzene [33]. The source of the detected chloride radical in the GC-MS result was from NaOCl (Eq. (1)). This compound was used to synthesize ferrate(VI). Since ferrate(VI) used in this experiment was in-situ liquid ferrate(VI), liquid ferrate(VI) taken directly from the reactor contained –Cl (chlorine radical) as the side product of the reaction [34].

4. Conclusions

In this study, ferrate(VI) was prepared based on Sharma's production method. Also, degradation of aniline by liquid ferrate was conducted under varying conditions (pH, ferrate dosage, and temperature in aqueous solution. The major conclusions of this study are as follows:

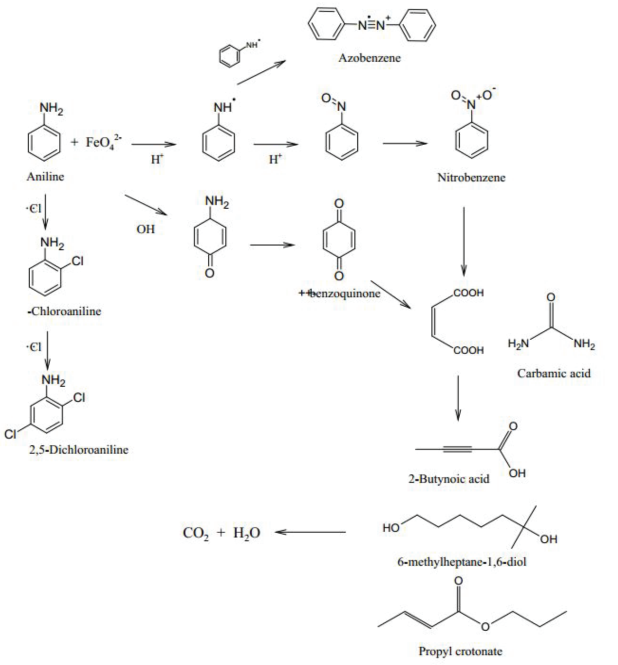


Fig. 9. Degradation pathway of aniline.

1. The liquid ferrate synthesized by Sharma's method has been successfully produced. Aniline in aqueous solution is decomposed within 30 s by ferrate.
2. Degradation of aniline was the highest efficiency in weak acid condition (pH 4.36).
3. The decomposition efficiency of ferrate was increased with increasing the amount of ferrate dose in the neutral condition. The degradation rate of ferrate was found to be 98.35% at 16:1, K_{app} was the highest at 2,166.1 $M^{-1} s^{-1}$.
4. The highest degradation of temperature was observed at 25°C for aniline removal.
5. Nitrobenzene, azobenzene, and p-benzoquinone were identified as the reaction intermediate from the GC/MS analysis. Furthermore, 2-butynoic acid, carbamic acid, and propyl crotonate were detected when the benzene ring was opened.

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