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The Effect of Radical Scavenging Activity on Orange GelbDye Degradation Process Using Fenton's Reagent

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ABSTRACT

Wastewater is exhausted in large volume every year due to the processes of textile industries such as dyeing and finishing processes. Nowadays, more than 50% of dyes used in textile industry are azo-based dyes. Inorganic salts improve the coloration of the dye, which enhances the pollution load of wastewater from textile industries. The main objective of this study was to evaluate the efficiency of degradation of Orange Gelb (OG) dye by Fenton's Reagent of Advanced Oxidation Processes (AOPs). The study also comprises the effect of radical scavengers in different concentrations towards the photochemical treatment of the organic dye by using Fenton process in the presence of ultraviolet (UV) irradiation. A laboratory set-up was designed to evaluate the effectiveness of Fenton's Reagent process in the absence and in the presence of UV irradiation, and also was operated in the presence of radical scavengers. The effects of irradiation time and the addition of different types and concentrations of inorganic salts (NaCl, $NaHCO_3$, $NaNO_3$ and Na_2CO_3) on the degree of degradation efficiency were studied. The results indicated that photo-Fenton's process is more effective than Fenton's process without UV irradiation in dye degradation process. Photo-Fenton's process degrades the dye up to 86%, whereas Fenton's process without UV irradiation only degrades the dye up to 72%. In increasing the Na_2CO_3 and $NaHCO_3$ salts concentration to 1M, the percentage of decolourization decreased to 24% and 18% respectively. While increasing the $NaNO_3$ and NaCl salts concentration to 1M, the percentage decolourization decreased to 80% and 74% respectively. Additionally, it was found that all salts in the experiment could inhibit the efficiency of Orange Gelb (OG) degradation. The degree of their scavenging effects can be ranked from low to high in order of $NaNO_3 < NaCl < Na_2CO_3 < NaHCO_3$.

KEYWORDS: Fenton's Reagent, Azo Dyes, Orange Gelb (OG), Radical Scavenger, Advanced Oxidation Processes.

INTRODUCTION

Wastewater from industrial practices is always a major concern to the environment. The problems arise from the issue that cannot be ignored.Textile industry is one of the most problematic industries among the manufacturing industries. Textile industry generally uses huge quantity of raw water and produces great volume of liquid effluent from its processes. Traditional wastewater treatment technologies were proven to be noticeably unproductive in the treatment of wastewater that contains synthetic dyes [10]. Textile wastewater is normally characterized by its low biodegradability due to the chemical stability of synthetic dyes in the environment. Wastewater generated from the textile industry is contaminated mainly with synthetic dyes [1]. It is estimated that around the world, half million tons of textile dyes are manufactured each year, and nearly 1-10% of it are lost in production and get washed into the stream [14]. From the half million tons of textile dyes, 50% of it are azo-types [4].

Azo dyes are a major class of synthetic dyes which comprising more than 50% of all organic colorants available throughout the world. There is a constant demand in developing more applicable and longer lasting dyes. It must be constantly updated to produce colours that reflect the trend dictated by the changes in social styles and ideas. Brighter, longer lasting colours are regularly required in satisfying the demand [2].Azo dyes are resistant to biodegradation. Hence, conventional biological treatment methods are unproductive in degrading the dye [13]. The high concentration of dyes in discharged water changes the stream colour, and it will lower its aesthetic value. It will also affect the aquatic ecosystem tremendously where azo dye is toxic. The presence of the pollutant in the water system creates serious environmental problem. The discharge of azo dye is a concern due to the colorization of the water. The reflection absorption of sunlight that falling in the water bodies will interfere the growth of bacteria and plants in the water ecosystem [5].

Wastewater that contains a variety of organic and inorganic species would intervene with oxidation reactions of the target pollutant. The inorganic anions such as carbonate, bicarbonate and chloride which are referred to as radical scavengers are very common [7]. Carbonate and bicarbonate ions are frequently found in natural waters,

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while chloride exists in high concentrations in textile industrial wastewater. The conventional processes such as coagulation, flocculation and biological methods adopted for decolouration of effluent containing reactive dyes are no longer able to achieve adequate removal of the colour. From all the treatments available, advanced oxidation process such as oxidation by using Fenton's Reagent has proved to effectively decolorizes almost all dyes [3], as well as for the destruction of a large number of hazardous and organic pollutants [8]. When conventional water treatment processes are incompetent to remove persistent pollutants, advanced oxidation processes (AOPs) are a promising option to remove the pollutant from the contaminated water. AOPs are based on the initiation of a very reactive species such as hydroxyl radicals that can oxidize an extensive range of dyes [10].

Thestudy focused on chemical advanced oxidation processes by using Fenton's Reagent (Fe^{2+}/H_2O_2) with the presence of ultraviolet (UV) irradiation for the treatment. The advanced oxidation processes are competent as they are capable of degrading a broad range of organic pollutants [6]. The target pollutant in the study is Orange Gelb (OG) which is widely used in textile dyeing processes. OG dye is a synthetic azo dye and it is in the form of orange crystalline powder. OG dye is a reactive dye that contains 2 groups SO_3Na, which are soluble in water. The main objective of the study was to evaluate the efficiency of degradation of OG dye by Fenton's Reagent process. The influence of different experimental conditions (Fe^{2+}/H_2O_2, Fe^{2+}/H_2O_2/UV, and the presence of radical scavengers) which affect the efficiency of Fenton's Reagent process [15] in OG dye degradation were investigated.

MATERIALS AND METHODS

Materials

All materials in the experiment were prepared in the laboratory and of analytical grade. The model dye of OG was purchased from its manufacturing company (Acros Organics). The stock solution of the dye (10^{-4} M) was prepared in deionized water and be used throughout the experiment. The instruments used in the experiment were UV-Vis spectrophotometer (UV 1800 Shimadzu) and pH meter (Jenway 3350 pH meter) with Eutech 428 pH electrode.

Methods

The Fenton's oxidation process was operated in three conditions. The first condition is in the absence of UV irradiation (Fenton's Reagent). The second condition is in the presence of UV irradiation (photo-Fenton's reaction). The source of the UV irradiation in the experiment was sunlight. The third condition was the OG dye solution that mixed with anionic scavengers of CO_3^{2-}, HCO_3^-, NO_3^- and Cl^-. The rate of degradation for the condition was also studied.

To study effect of UV irradiation in rate of degradation

0.5L of 10^{-4}M OG solution was poured into an 800ml beaker exposed to sunlight and mixed properly by using a magnetic stirrer, so that the solution will be homogeneous. The initial pH for 10^{-4}M OG solution is 6.70. The pH was controlled by dropping 0.02M H_2SO_4 solution prepared earlier. PH meter was dipped into the solution to ensure the pH is around 3.5. Subsequently, a small amount of sample was pipette from the beaker and run on the UV spectrophotometer. This is a 0 minute on the sample. Afterwards, 50mL H_2O_2 solution and 0.139g of $FeSO_4.7H_2O$ was mixed with the acidified dye solution. A small amount of the sample solution was obtained in a time interval of 1min, 5mins, 10mins, 15mins and 20mins. UV/Vis spectrophotometer was used for monitoring the decolourization of the samples. The above steps were repeated in the absence of sunlight.

To study effect of radical scavengers in rate of degradation

0.5L of 10^{-4}M of OG solution was poured into an 800mL beaker exposed to sunlight and mixed properly by using a magnetic stirrer, so the solution will be homogeneous.PH meter was dipped into the solution to ensure the pH is around 3.5. The pH was controlled by dropping a 0.02M H_2SO_4 solution prepared earlier. Subsequently, a small amount of sample was pipette from the beaker and run on the UV-Vis spectrophotometer. This is a 0 minute on the sample.About50mL H_2O_2 solution, 50mL CO_3^{2-} salt solution and 0.139g of $FeSO_4.7H_2O$ was mixed with the acidified dye solution. A small amount of the sample solution was obtained in a time interval of 1min, 5mins, 10mins, 15mins and 20mins. UV-Vis spectrophotometer was used to monitor the absorbance of the samples. The above steps were repeated by using different concentrations of CO_3^{2-} salt solution which are 10^{-1} M, 10^{-2} M, 10^{-3} M and 10^{-4} M respectively. It followed by the presence of other types of scavengers such as HCO_3^-, NO_3^- and Cl^- salt solution in a concentration of 1M, 10^{-1}M, 10^{-2}M, 10^{-3}M and 10^{-4}M respectively.

RESULTS AND DISCUSSION

Degradation of OG dye in Fenton's Reagent Process as a Control Test

A control test was done by using a 10^{-4}M dye solution. It was reacted with Fenton's Reagent under the presence of UV irradiation, and another test without the presence of UV irradiation where both for 25min. Results

of the efficiency in the dye degradation rate were expressed in percentage (%) which according to the following relationship [9].

$$\% \text{ Degradation} = 1 - \frac{C}{C_o} \times 100\% \quad (1)$$

where Co is the initial OG dye absorbance concentration and C is the absorbance concentration of dye at reaction time. Based on the study, it was proved that Fenton's Reagent effectively degrades the OG dye in a short amount of time. The degradation rate of the dye also increases in the presence of sunlight as the source of UV irradiation. Degradation of OG dye also happens in a dark place but at a lower rate. From the absorbance reading, the percentage degradation efficiency can be calculated by using the percentage degradation formula. The percentage degradation efficiency of OG dye at both conditions by using Fenton's process is shown in Figure 1.

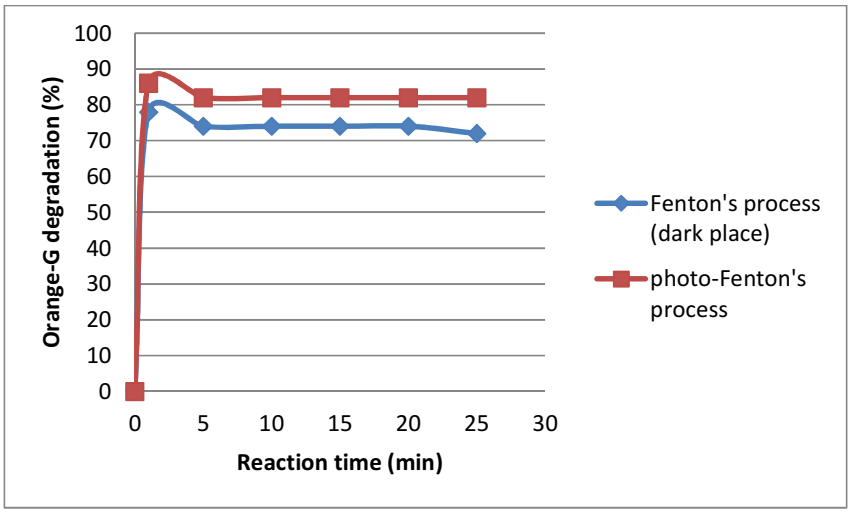

Figure 1: The percentage degradation efficiency of OG dye at 2 different conditions

The reaction causes about 86% of decolourization after reaction time for 1min. It decreases slightly to 82% after reaction time of 25min on UV irradiation exposure under experimental conditions (Fe^{2+}/H_2O_2) at pH3.5. The rapid decolourization of the dye is mainly due to the hydroxyl radical (•OH) which generated by the Fenton's Reagent chemical reaction of iron (Fe^{2+}) catalyst with H_2O.

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

After Fe^{2+} has been reacted, a brown turbidity resulted from the addition causes the recombination of •OH radicals and Fe^{2+} reacts with •OH as a scavenger at 5min to 25min reaction time. Therefore, on further reaction, the rate became almost constant [12].

The reaction of H_2O_2 with UV irradiation also generates •OH which initiate the initial electrophilic cleavage of the dye chromophoric azo (–N=N–) bond.

$$H_2O_2 + h\nu \rightarrow 2OH^{\bullet} \quad (3)$$

$$R_1\text{–N=N–}R_2 + HO^{\bullet} \rightarrow \text{degradation products} \quad (4)$$

However, for 25min of reaction without the exposure of UV irradiation, only about 72% decreased in colour was observed. This is due to the decreased in •OH radicals which act as an oxidizer in oxidizing process and breaking the azo (–N=N–) bond [13]. The results indicated that photo-Fenton's process is more effective in dye degradation process than Fenton's process without UV irradiation.

The Effect of Radical Scavenging Activity of CO_3^{2-}, HCO_3^-, NO_3^- and Cl^- on Fenton's Reagent Process

Five different concentrations of the salts were prepared for theexperiments which are 1M, 10^{-1}M, 10^{-2}M, 10^{-3}M and 10^{-4}M. Different salts of CO_3^{2-}, HCO_3^-, NO_3^- and Cl^-were added respectively with the Fenton's Reagent into the dye solution. The decolourization rates were investigated as some of these anions are thought to act as scavengers of •OH, thereby reducing the degradation effectiveness of the Fenton's Reagent [9].The percentage degradation efficiency of OG dye at the presence of different concentrations of Na_2CO_3 salt is shown in Figure 2.

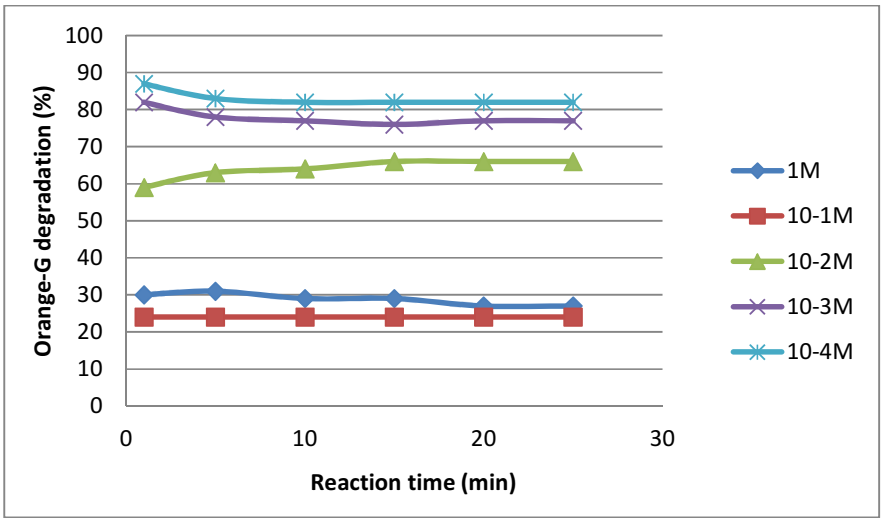

Figure 2:The percentage degradation efficiency of OG dye solution in presence of different concentration of Na_2CO_3 salt

Figure 2 shows that decolourization process was highly inhibited in the presence of Na_2CO_3 in a certain concentration. Increasing the concentration of Na_2CO_3 salt in the dye solution resulted in decreasing efficiency of decolourization. As for the salt concentration of 10^{-2}M, the degradation efficiency was reduced to 59%. The degradation of the dye was retarded, but not as much as in 1M and 10^{-1}M. In the reaction with the addition of 10^{-3}M salt, the degradation efficiency was 82%. The degradation efficiency was only 4% lower than in photo-Fenton's process. It can be concluded that in the presence of 10^{-3}M Na_2CO_3 salt, the degradation efficiency decreased. The degradation efficiency in the addition of 10^{-4}M salt solution showed a quiet similar rate of degradation to a photo-Fenton's process, which was 87% at the reaction time 1min. The results indicated that increasing concentrations of Na_2CO_3 salt in the dye solution reduced the decolourization efficiency down to 24%.The percentage degradation efficiency of OG dye at the presence of different concentrations of $NaHCO_3$ salt is shown in Figure 3.

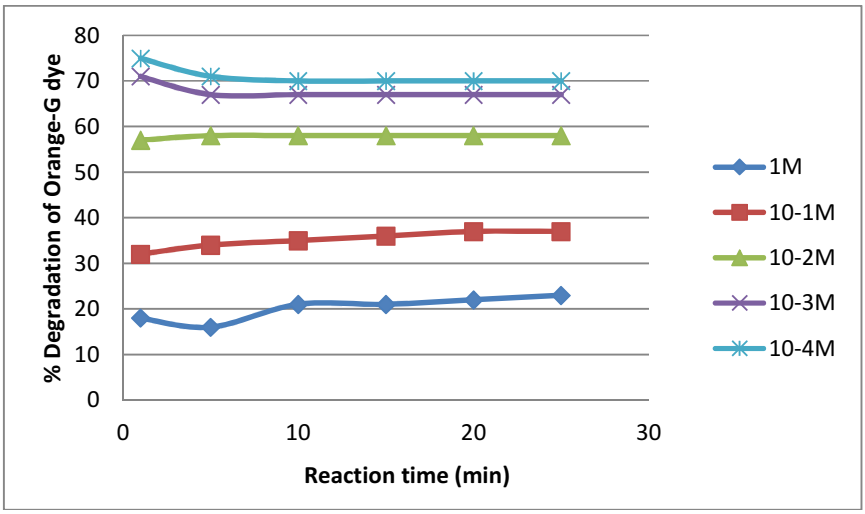

Figure 3: The percentage degradation efficiency of OG dye solution in presence of different concentration of $NaHCO_3$ salt

The result shows that the decolourization process was inhibited in the presence of $NaHCO_3$ in certain concentration which quiet higher than in the presence of Na_2CO_3. In increasing the salt concentration from 10^{-4}M to 1M into the dye solution, the percentage of decolourization decreased to 75% and 18% respectively.

Salt concentration of 1M and 10^{-1}M mainly retarded the degradation process of the dye with the degradation efficiency of 18% and 32% respectively. In the research done by [11], HCO_3^- was proved as $^{\bullet}OH$ scavenger where it showed the decreased in degradation efficiency of the dye with the increasing concentration of the salt. Salt concentration of 10^{-2}M and 10^{-3}M also retarded the degradation process of the dye with the degradation efficiency

of 57% and 71% respectively. The •OH that supposed to initiate the electrophilic cleavage of the dye chromophoric azo (–N=N–) bond and break the bond was scavenged by HCO_3^- [11]. Consequently, the degradation efficiency was reduced significantly. In the reaction with the addition of 10^{-4}M salt, the degradation efficiency was 81%. The degradation efficiency was only 5% lower than in photo-Fenton's process.

The scavenging activity for $NaHCO_3$ was similar to the scavenging activity of Na_2CO_3, which produces the same products [9]. The reaction of the scavenging activity is as follow.

$$HCO_3^- + \bullet OH^- \rightarrow CO^{-3\bullet} + H_2O \quad (5)$$

The results indicated that increasing concentration of $NaHCO_3$ salt in the dye solution resulted in decreasing efficiency of decolourization down to 18%.The percentage degradation efficiency of OG dye at the presence of different concentrations of $NaNO_3$ salt is shown in Figure 4.

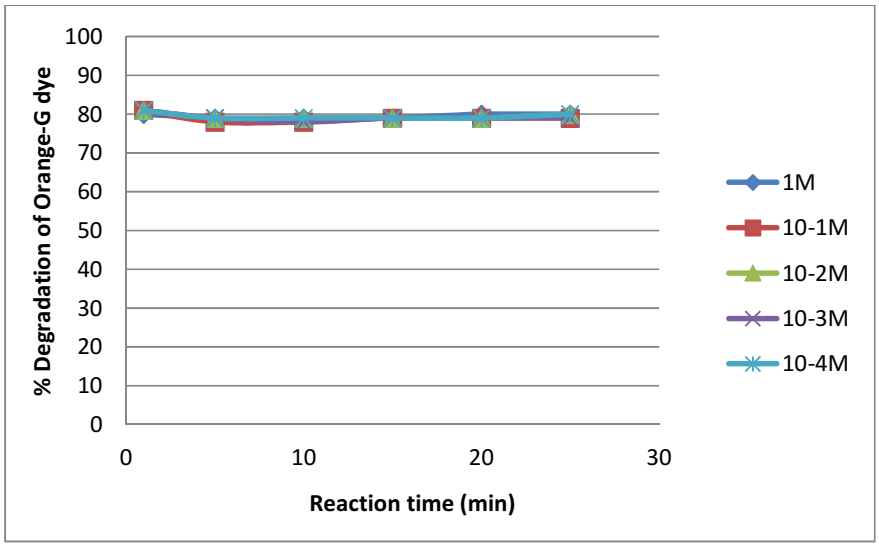

Figure 4:The percentage degradation of OG dye solution in presence of different concentration of $NaNO_3$ salt

As can be seen from Figure 4, the presence of $NaNO_3$ salt barely affects the degradation process of the dye. On increasing the salt concentration to 1M into the dye solution, the percentage of decolourization only decreased to about 80%. Similar degradation efficiency of about 80% can be seen in the concentration of 10^{-1}M, 10^{-2}M, 10^{-3}M and 10^{-4}M.

The results indicated that increasing concentration of $NaNO_3$ salt in the dye solution did not affect the degradation efficiency of the dye. The result was comparable with the research done by [16].The percentage degradation efficiency of OG dye at the presence of different concentrations of NaCl salt is shown in Figure 5.

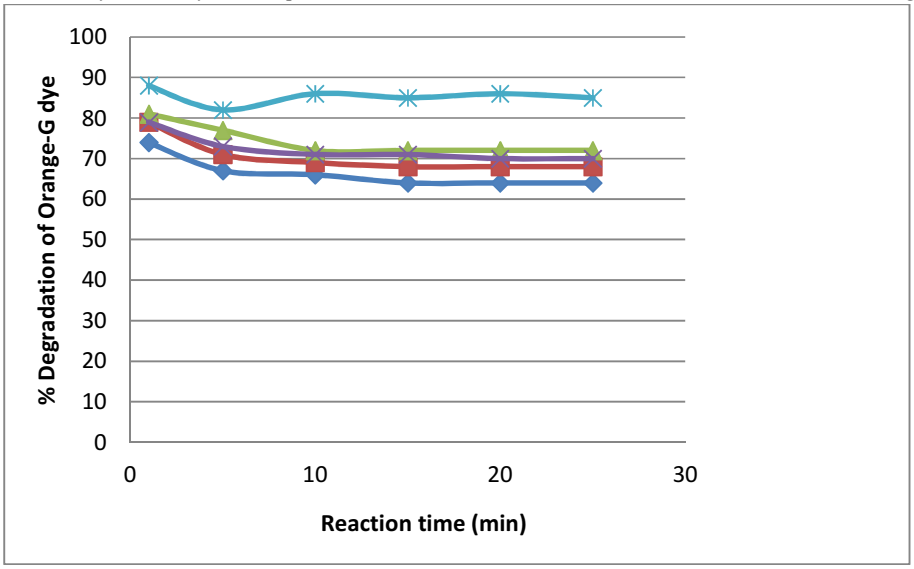

Figure 5: The percentage degradation efficiency of OG dye solution in presence of different concentration of NaCl salt

The result shows that the decolourization process was inhibited in the presence of NaCl in certain concentration. But, it significantly much lower than in the presence of Na_2CO_3 and $NaHCO_3$ salts. Increasing the concentration of NaCl salt in the dye solution resulted in a small decreasing efficiency of decolourization.

At 1M of NaCl salt concentration, only a small decreased in decolourization was observed. The degradation efficiency decreased to 74%. At 10^{-4}M NaCl salt concentration, the decolourization was 88%, higher by 6% compared to the solution with no added salt which was 82%. The result for this type of salt was different compared to all other salts and it was comparable with the research done by [9],which showed the similar trend of degradation by using NaCl salt. The increased in decolourization for the system can be explained by the formation of hypochlorite ion (ClO^-) from chloride ions during the photo-Fenton's process. A possible explanation is that the chloride oxidation reaction was faster than hydrogen peroxide formation, but it seems that hypochlorite is further reacted with the formed hydrogen peroxide. The reaction is as follow [11].

$$ClO^- + H_2O_2 \rightarrow Cl^- + H_2O + O_2 \quad (6)$$

Therefore, these 2 types of oxidation species such as hypochlorite ion and hydrogen peroxide cannot simultaneously exist in the dye solution.The results indicated that increasing concentration of NaCl salt in the dye solution resulted in a small decreasing efficiency of decolourization.

CONCLUSION

The experiment proved that photo-Fenton's process was efficient in the degradation of OG dye solution. The degradation efficiency of photo-Fenton's process was up to 86% in 25min reaction time, whereas the degradation efficiency of Fenton's process without the presence of sunlight irradiation was only up to 78%. The experiment also proved that decolourization of OG dye was retarded in the presence of radical scavengers. Increasing the concentrations of salts in the dye solution reduced the degradation efficiency of the dye, to varying degrees depending on the type of salts used and the concentration of the salts. Additionally, it was found that all salts in the experiment could inhibit the efficiency of OG degradation and the degree of their scavenging effects can be ranked from low to high in an order $NaNO_3 < NaCl < Na_2CO_3 < NaHCO_3$.

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