Silver (II) Mediated Electrochemical Oxidation of Acetic Acid in Nitric Acid Medium

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***Abstract*—Mediated electrochemical oxidation (MEO) is a promising technique for the destruction of organic compounds. In this study, the oxidation of acetic acid to CO_2 was investigated in a nitric acid medium containing electro-regenerated Ag (II) as the mediator, using an undivided cell. The effects of electrolyte concentration, mediator concentration, organic molecule concentration, and temperature on the destruction process were systematically investigated. The destruction efficiency was determined by quantifying the CO_2 produced during the reaction. Real-time CO_2 evolution was monitored using an infrared CO_2 analyzer. Based on CO_2 evolution, the destruction efficiency was found to be 49.6%.**

***Index Terms*—MEO, Undivided cell, CO_2 analyser, Destruction efficiency**

I. INTRODUCTION

Water pollution causes irreversible damage to aquatic ecosystems and poses a significant threat to living organisms. Continuous industrialization has severely degraded water quality in many parts of the world. Although several treatment methods have been developed for the removal of organic contaminants such as dyes and pesticides, many of these approaches suffer from incomplete mineralization and limited recovery.

Advanced oxidation processes (AOPs), which remove pollutants through oxidation, can be achieved via chemical, photochemical, or electrochemical methods. Electrochemical oxidation can occur either through direct anodic oxidation or mediated electrochemical oxidation (MEO). In direct oxidation, organic molecules are oxidized directly at the anode surface. In contrast, MEO involves the use of a metal redox couple to facilitate efficient electron transfer and promote oxidation reactions. Several metal-based redox systems, such as Ag^{2+}/Ag^{+}, Ce^{4+}/Ce^{3+}, Co^{3+}/Co^{2+}, have been employed in MEO due to their high redox potentials. Notably, the Ag^{2+}/Ag^{+} redox couple, with a redox potential of 1.98 V, is capable of oxidizing a wide range of organic compounds under suitable conditions.

A metal ion capable of showing redox behavior in an acidic solution is used for mineralization of organic and then regenerated electrochemically in a closed cycle.

This procedure can be schematically represented as

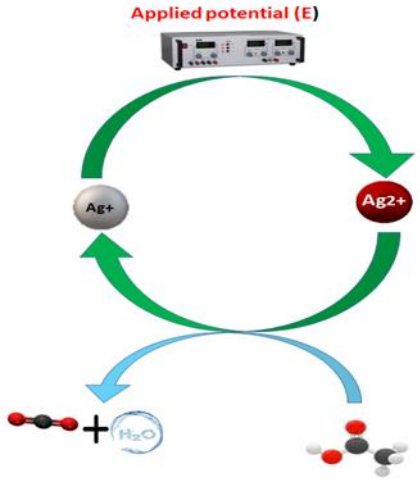

Fig.1 Schematic representation MEO process

The anodic and cathodic reactions can be represented as follows [1-3].

At anode Water is oxidized, and silver ions are electrochemically converted to Ag^{2+}:

$Ag^{+} \rightarrow Ag^{2+} + e^{-}$ $3H_2O \rightarrow ½O_2 + 2H_3O^{+} + 2e^{-}$

Silver(II) ions then form a nitrate complex in nitric acid:

$Ag^{2+} + 2NO_3^{-} \rightarrow Ag(NO_3)_2^{+}$

Silver (II) ions (Ag^{2+}) are extremely powerful oxidizing agents, surpassed only by species such as persulfate, ozone, and fluorine. In nitric acid, silver (II) forms an intense brown solution due to the presence of the $AgNO_3^+$ complex ion. However, the color fades over time depending on the temperature, attributed to the decomposition of Ag^{2+} and the concurrent evolution of oxygen through water oxidation:

$2Ag(NO_3)_2^+ + 3H_2O \rightarrow 2Ag^+ + ½O_2 + 2H_3O^+ + 2NO_3^-$

The reaction of silver (II) with water is critical to the electrochemical oxidation of organic wastes. The process proceeds through multiple intermediate steps, often involving highly reactive species like hydroxyl radicals ($^{\bullet}OH$), which react indiscriminately with organic compounds. Ultimately, organic matter is oxidized to carbon dioxide, carbon monoxide, and water:

One pathway involves:

$2Ag^{2+} + 3H_2O \rightarrow 2Ag^+ + 2H_3O^+ + ½O_2$

Alternatively, hydroxyl radicals may form:

$Ag^{2+} + H_2O \rightarrow Ag^+ + {}^{\bullet}OH + H^+$

Hydroxyl radicals ($^{\bullet}OH$) aggressively attack the organic substrates, oxidizing them to CO_2, CO, H_2O, and inorganic by-products derived from elements such as nitrogen and phosphorus:

$Organics + {}^{\bullet}OH \rightarrow CO_2 + H_2O$

Silver ions (Ag^+) are regenerated at the anode to form Ag^{2+} again, maintaining the cycle. Concurrently, H^+ ions react with nitrate ions to primarily form nitrous acid:

At the Cathode $NO_3^- + 3H^+ + 2e^- \rightarrow HNO_2 + H_2O$

The nitrous acid produced can subsequently be re-oxidized to nitric acid. After oxidation, Ag^{2+} exists in the solution as a dark brown nitrate complex.

The oxidation of an acetic acid substrate by silver (II) ions is represented by the following reaction:

$CH_3COOH + 8AgNO_3^+ + 2H_2O \rightarrow 2CO_2 + 8Ag^+ + 8HNO_3$

1.1 Advantages of MEO process

In the Direct Electrochemical Oxidation (DEO) process, it is nearly impossible to completely suppress the anodic oxidation of water, which reduces the overall efficiency of the process. Additionally, the low mobility of hydrophobic organic pollutants can result in poor mass transfer [4], and electrode surface poisoning by pollutants further complicates the process.

In contrast, the Mediated Electrochemical Oxidation (MEO) process overcomes these limitations. In MEO, a metal ion is electrochemically oxidized in a closed circuit [5-11]. This process has been extensively studied for various systems using metals such as Ag, Ce, Co, and Fe. For instance, Farmer et al. reported the oxidation of ethylene glycol and benzene using silver as the mediator ion [12], and also documented the destruction of chloro-organics using cobalt mediators [13]. The degradation of pesticides with silver mediators has been reported by Galla et al. [14]. However, optimization parameters such as temperature, voltage, feed rate, and flow rate have not been disclosed due to the commercial relevance of the process [15-17].

Although various mediator systems have been investigated, Ag and Ce-based systems have been studied extensively on pilot and larger scales, with only final degradation efficiencies typically reported. The role of the metal ion in MEO is not limited to electron transfer from the electrode surface to the organic molecule; it also mitigates electrode poisoning caused by undegraded organic compounds [18-20]. Several factors influence the efficiency of the MEO process, including:

i. concentration of the metal ion,
ii. stability of the metal ion in aqueous media,
iii. temperature, and
iv. concentration of the acid electrolyte.

Despite numerous studies on the Ag-MEO process for the destruction of organic pollutants, there are limited reports on the degradation of acetic acid and its derivatives. Due to its short chain length, acetic acid is particularly sensitive to oxidation. However, most degradation studies fail to achieve 100% mineralization, often resulting in residual short-chain organic compounds. Therefore, this study employs the Ag-MEO process to investigate the effective destruction of highly refractory acetic acid. The goal is to evaluate critical parameters such as metal ion concentration, ion stability in aqueous media, temperature, and acid electrolyte concentration.

The objective of the present study is to investigate the destruction of acetic acid using silver-mediated electrochemical oxidation (Ag-MEO) and to optimize the process parameters to achieve maximum degradation efficiency.

II. EXPERIMENTAL

2.1 Materials

Silver nitrate (99.8%) from CDH (AR grade) and nitric acid from s.d-fine chemicals were used as received. Double distilled water was used for making the solutions.

2.2 Methods

Electrochemical oxidation was performed in an undivided cell (Fig.2) designed and fabricated in our laboratory. The setup utilized a platinum foil electrode in a nitric acid medium. A 200 mL solution containing 0.5 M $AgNO_3$ dissolved in 6 M nitric acid served as the electrolyte. Continuous stirring of the electrolyte solution was maintained using a magnetic stirrer to ensure uniform mixing.

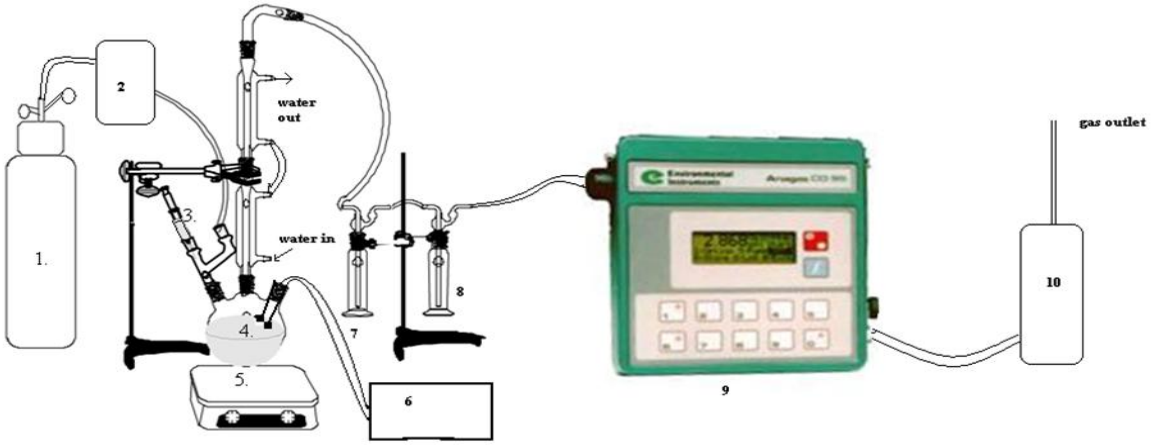

Fig. 2 Schematic Diagram of Mediated Electrochemical Oxidation Experimental Setup

1. Nitrogen cylinder
2. Mass flow controller
3. Syringe containing organic
4. Reaction vessel
5. Magnetic stirrer
6. Power supply unit
7. Copper turnings trap
8. Calcium chloride trap
9. CO_2 gas analyzer
10. Scrubber

The temperature of the reaction vessel was maintained at a constant, pre-set value using water circulation through a double-walled jacket surrounding the vessel. A constant potential was applied using a DC power supply unit (Aplab Limited, Model No. L3260). Prior to each experiment, the CO_2 analyzer was purged with nitrogen to ensure complete removal of residual carbon dioxide, and then connected to the reaction system. The power supply was then switched on for 10 to 15 minutes under a continuous nitrogen flow.

For a typical experimental run, a silver nitrate solution of known concentration in 6 M nitric acid was electrolyzed by applying a constant DC potential of 1.8 V. After 15 minutes of electrolysis, a measured volume of the organic stock solution was injected into the cell. The carbon dioxide evolved during the oxidation of the organic compound was swept out of the cell by a steady stream of nitrogen, regulated using a gas flow controller (Aalborg, USA).

The gas stream passed through NO_2 and moisture traps before reaching the CO_2 analyzer (Anagas CD95, Geotechnical Instruments, UK), which operates on the principle of infrared (IR) absorption. The analyzer provided a direct measurement of CO_2 concentration in parts per million (ppm). The destruction efficiency of the organic compound was calculated by comparing the theoretical amount of CO_2 expected with the actual amount detected during the oxidation process.

In all experiments, the organic compound was introduced in a single dose at the beginning (batch addition), and the CO_2 evolution was monitored and logged at various time intervals.

III. RESULT AND DISCUSSION

3.1 Effect of electrolyte concentration

The CO_2 evolution profile as a function of reaction time for the mediated electrochemical oxidation of 250 ppm acetic acid at different nitric acid concentrations (3M, 6M and 9M) in 0.5M $AgNO_3$ at 65°C is illustrated in Fig. 3. At 3M HNO_3, the CO_2 evolution exhibits a typical pattern an initial rise, followed by a decline, a second peak reaching approximately 4800 ppm, and a final gradual decrease to around 500 ppm by 350 minutes.

When the nitric acid concentration was increased to 6M and 9M, similar trends were observed, though the magnitude of CO_2 evolution was noticeably higher compared to 3M. The profiles for both 6M and 9M nitric acid showed enhanced CO_2 release, indicating improved oxidative degradation of acetic acid. This suggests that increasing the nitric acid concentration enhances the destruction efficiency.

Additionally, it was observed that in the 3M HNO_3 system, metallic silver deposited on the cathode remained more stable and required a brief interruption of power to detach. In contrast, at 6M and 9M, the silver deposits detached more readily during the reaction without any intervention. This indicates that higher nitric acid concentrations not only improve CO_2 evolution and destruction efficiency but also reduce the stability of metallic silver deposits on the cathode.

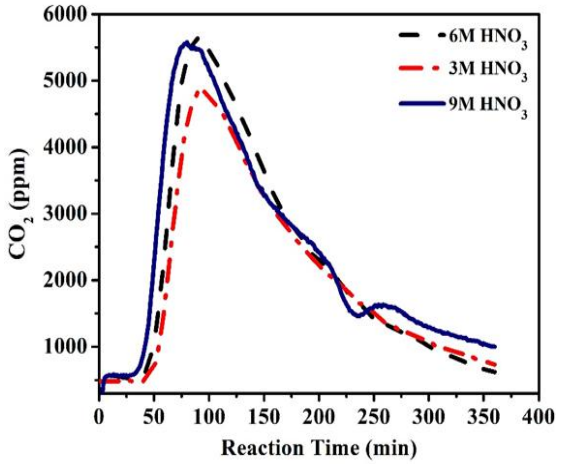

Fig.3 CO_2 evolution profile versus reaction time of Acetic acid in 0.5M $AgNO_3$ + Different HNO_3 concetrations at 70°C

3.2 Effect of temperature

The CO_2 evolution profiles as a function of reaction time for the silver-mediated electrochemical oxidation of acetic acid at different temperatures (40 °C, 55 °C, and 70 °C), using 0.5 M Ag^+ in 6 M HNO_3, are shown in Fig. 4. From the profiles, it is observed that within the first 3-4 minutes after the addition of acetic acid, CO_2 concentration rises to approximately 600 ppm and remains nearly constant up to 45 minutes. After this induction period, the CO_2 concentration increases steadily, reaching a maximum of nearly 5000 ppm at around 75 minutes. This is followed by a gradual decline, and by approximately 200 minutes, the CO_2 levels stabilize at about 500 ppm, which remains constant until the end of the 6-hour reaction period. The non-linear CO_2 evolution pattern suggests the involvement of several oxidation intermediates before complete mineralization to CO_2 occurs. During the initial 3-4 minutes, the injected acetic acid undergoes partial oxidation, generating reactive intermediates. These intermediates are subsequently oxidized to CO_2 over time. It is estimated that around 40-50% of the total oxidation is achieved within the first two hours. At 70 °C, the initial CO_2 evolution rate is significantly higher compared to 40 °C and 55 °C, indicating enhanced reaction kinetics at elevated temperature. However, after approximately 2 hours, the CO_2 profile at 70 °C falls below those at the lower temperatures (Table 1), suggesting that the intermediates are rapidly consumed. This behaviour confirms that destruction efficiency is temperature-dependent, with higher temperatures promoting faster and more complete oxidation (Fig. 6).

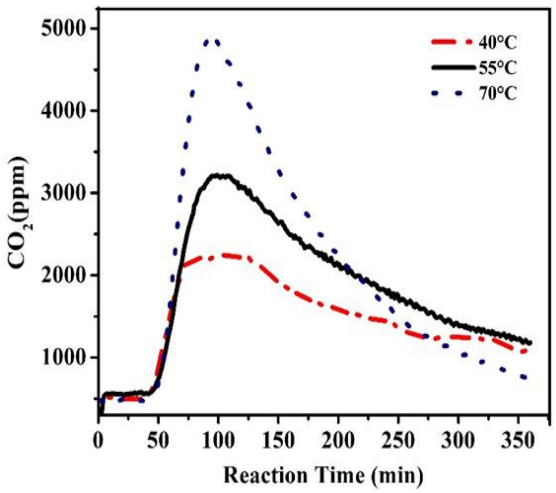

Fig.4 CO_2 evolution profile versus reaction time of Acetic acid at different temperatures in 0.5 M $AgNO_3$ + 6 M HNO_3

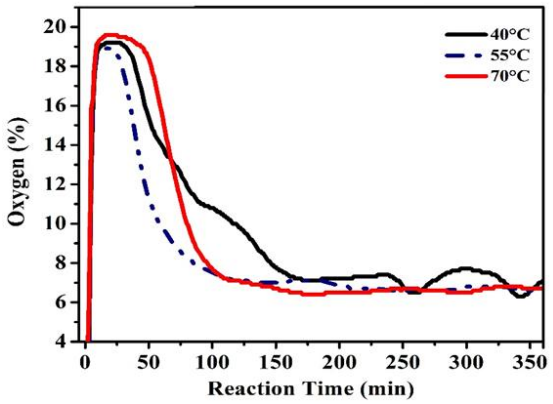

Fig.5 O_2 evolution profile versus reaction time of Acetic acid at different temperatures in 0.5M $AgNO_3$ + 6M HNO_3

Fig. 5 presents the O_2 evolution profiles under the same reaction conditions. At time zero-corresponding to the moment of organic addition-the oxygen concentration is at its minimum. A sharp increase in O_2 evolution is observed shortly after, reaching a peak around 20 minutes, followed by a decline. At approximately 40 minutes, the oxygen concentration reaches a minimum again, coinciding with the onset of rapid CO_2 evolution.

This inverse trend implies that when Ag^{2+} is actively consumed in oxidizing organic intermediates, the competing water oxidation reaction (producing O_2) is minimized. After around 2 hours, when the CO_2 profile plateaus, the O_2 concentration stabilizes at approximately 7-8%, maintaining that level until the reaction concludes.

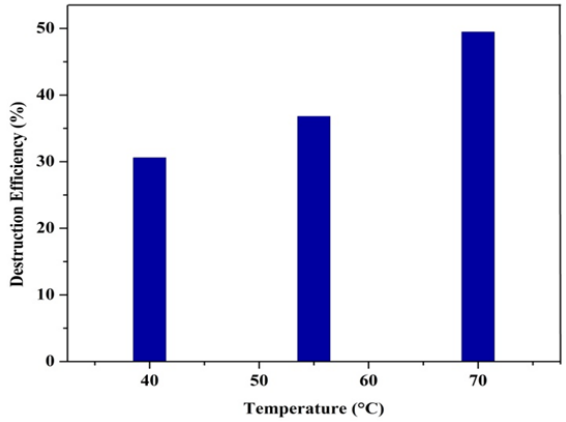

Fig.6 Destruction efficiency of Acetic Acid at different temperatures (40, 55, 70°C) in 0.5M $AgNO_3$ + 6M HNO_3 at 70°C

Temperature (°C)	Destruction Efficiency (%)
40	30.6
55	39.8
70	49.6

Table.1 Destruction efficiency of Acetic Acid at different temperatures in 0.5M $AgNO_3$ + 6M HNO_3

3.3 Effect of mediator concentration

CO_2 evolution profiles versus reaction time for the mediated electrochemical oxidation of 250 ppm Acetic acid at different $AgNO_3$ concentrations (0.1M, 0.3M and 0.5M) with 6M HNO_3 at 70 °C are shown in Fig.7. During the variation of silver concentration, the CO_2 evolution was found to be maximum for 0.5 M $AgNO_3$ and a systematic decrease was observed for 0.3 M and 0.1 M solutions.

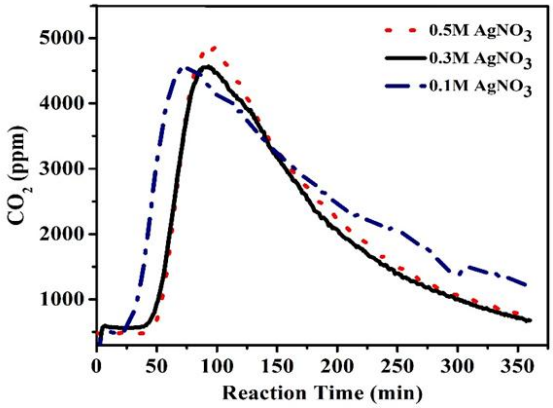

Fig.7 CO_2 evolution profile versus reaction time of Acetic acid at different Mediator ($AgNO_3$) concetrations in 6M HNO_3 at 70°C

IV. CONCLUSION

Silver-mediated electrochemical oxidation was carried out in an undivided cell using platinum sheet electrodes (both anode and cathode) in a nitric acid medium. Owing to the exceptionally high redox potential of the silver (II)/silver(I) couple (1.98 V), silver (II) ions are capable of oxidizing almost any organic compound they encounter. As a model compound representing a class of recalcitrant organics, acetic acid was selected to investigate the influence of various operational parameters.

The effects of mediator ion concentration (Ag^+), electrolyte concentration (HNO_3), and temperature on

the destruction efficiency were systematically studied. It was observed that increasing the temperature enhanced the oxidation efficiency. For instance, at 0.5 M $AgNO_3$ and 6 M HNO_3, the destruction efficiency-based on CO_2 evolution-was calculated to be 49.6%.

When varying nitric acid concentration, the highest destruction efficiency was obtained at 6 M HNO_3. At lower acid concentrations, efficiency decreased, likely due to the deposition of silver on the cathode. Increasing the nitric acid concentration beyond 6M did not yield a significant improvement, indicating that 6M HNO_3 is optimal for the silver-mediated electrochemical oxidation process.

It was also found that increasing the initial organic concentration led to a reduction in destruction efficiency, attributed to the limited availability of silver (II) mediator ions. Temperature variation studies showed that 70 °C provided the highest destruction efficiency.

A comparison of CO_2 evolution data revealed that while approximately 50% of the organic content was removed from the liquid phase, only about 50% was fully mineralized to CO_2. This discrepancy suggests the formation of various intermediates during the oxidation process, which can complicate kinetic analysis. Nevertheless, kinetic constants for different stages of the reaction can be estimated by analyzing specific regions of the CO_2 evolution profiles. Such analysis is currently underway.

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