Destruction of Aniline by Mediated Electrochemical Oxidation Process using Ce(IV) in Nitric Acid – Lab. Scale Study

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INTRODUCTION

To oxidize organic compounds more effectively, an electron transfer mediator, which oxidizes organic compounds in its oxidized state and is itself reduced, may by used. The reduced catalyst is reoxidized at the anode. This process is known as mediated electrochemical oxidation(MEO) [1-3].

As Ce(IV) had been found to be very effective in oxidizing compounds [4], we used Ce(IV) in nitric acid solution as catalysts for oxidation of aniline. Aniline was chosen as a model organic compound for two reasons. First, it is known [4] to undergo a multi-electron (n=28), involving multi-step electron transfer reaction, to form the final products of NH_4, CO_2 and H_2O:

$$C_6H_7N + 12\ H_20 + 28\ Ce(IV) = 6CO_2 + 27\ H^+ + NH_4 + 28\ Ce(III)$$

Secondly, aniline is major by-product in petrol-chemical and coal-tar industrie. Due to many steps and many electrons involved in aniline oxidation, it undergoes a polymerization reaction to form a fairly stable polymer, polyaniline. For this reason, it is difficult to completely oxidize aniline to the final product, CO_2.

With this purpose, the goal of present work was to develop the mini-scale MEO system with the electrochemical monopolar cell of a new design, to apply MEO technology to analyze the destruction of high concentrations of aniline, under different solution temperatures and to compare the theoretical and experimental values of Ce(IV) requirement for aniline destruction.

EXPERIMENTAL

Cerium(III) nitrate, ammonium cerium(IV) nitrate, nitric acid and Aniline (Sigma-Aldrich, Inc, MO, USA) were used as received. Distilled water was used to prepare solutions. Concentration of aniline in an initial solution was 30,000 ppm.

In mini-scale MEO system (Fig. 1.) the electrochemical monopolar cell of a new design had two compartments separated by Nafion membrane [5].

The anode and cathode were in close contact (< 0.2 mm) to a membrane. The area of the anode was equal the area of the cathode and was equal 9 ㎠. The anode and the cathode used iridium coated titanium electrodes of porous type. The volumes of the anolyte and catholyte solutions were 4.5 ml.

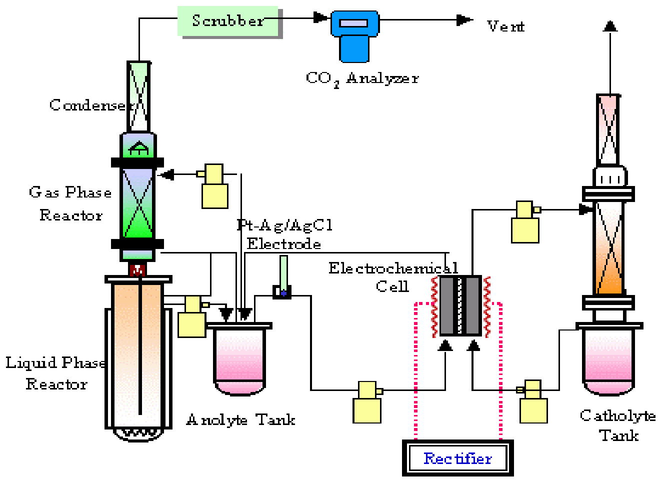

Fig. 1 Schematic diagram of mini-scale MEO system

The anolyte tank volume was of 75 ml. The catholyte tank volume was 200 ml.

The Liquid Phase Reactor had volume of 120 ml. The monopolar cell is nominally operated at an applied current of 6 A. This gives a current density of 0.66 A/㎠. The nominal electrolyte concentrations are 1.0 M Ce(IV) in 3.0 M nitric acid for the anolyte and 4.0 M nitric acid for the catholyte. The flow rate of N_2 was measured by mass flow controller (Instruments & Controls, Inc, USA, AFC 2600-PRO). The concentration of Ce(IV) was measured by ORP Electrode (Thermo Electron Corporation, MA, USA).

In the batch-scale experiments the reactor had volume 250 ml. The concentration of the CO_2 from MEO system was measured by CO_2 analyzer (Environmental Instruments, USA, Anagas CD 95).

RESULTS AND DISCUSSION

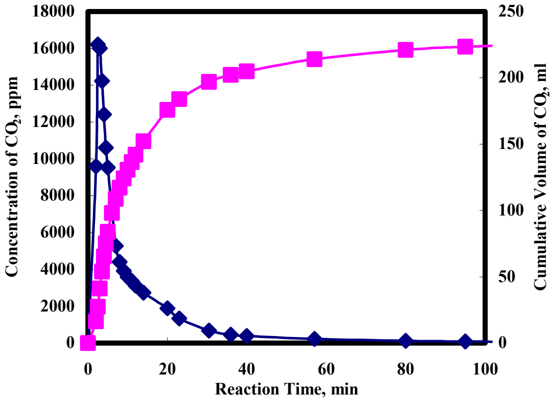

Fig. 2. Evolution of CO_2 during the degradation of 600 ppm aniline at 90 ℃.

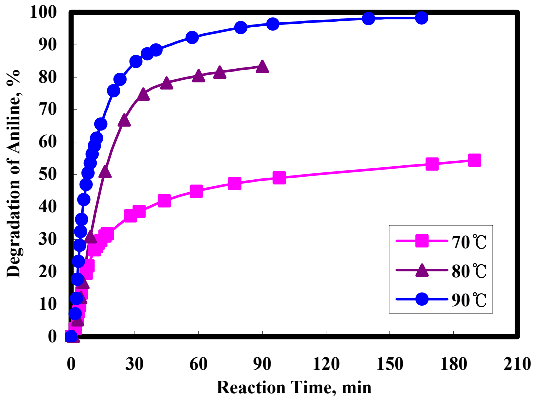

Fig. 3. The degradation of 600 ppm aniline at different temperatures.

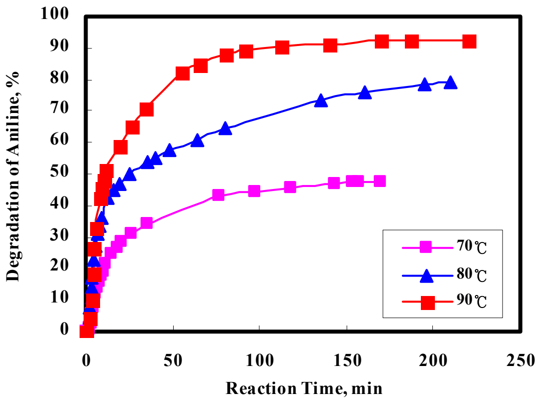

Fig. 4. The degradation of 1200ppm aniline at different temperatures.

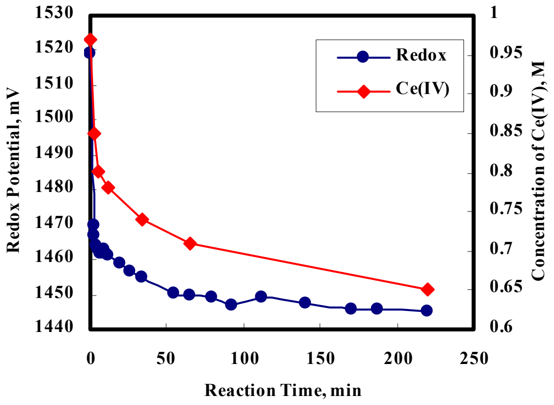

Fig. 5 Redox potential and Ce(IV) concentration under the degradation of 1200 ppm aniline at 90 ℃.

The evolution of CO_2 during destruction of aniline in batch-scale experiments is presented in Fig. 2. The theoretical total volume of CO_2 for complete degradation of 600 ppm aniline can be calculated in 232 ml, but the measured volume of CO_2 was 227ml.

The degradation efficiency of 600 and 1,200 ppm aniline at different temperature is submitted in Fig. 3 and 4 respectively. From the data submitted in Fig. 3 and Fig. 4, it is established that destruction of aniline at temperature of 90 ℃ was more than 90%.

Results of concentration of Ce(IV) from redox potential in anolyte under the degradation of 1200 ppm aniline at 90 ℃ are submitted in Fig. 5.

In order to destruct 1,200 ppm aniline, theoretical concentration of Ce(IV) is required 0.36 M, but 0.32 M Ce(IV) was consumed and 93 % of aniline was destructed within 220 min.

CONCLUSION

The destruction of aniline by mediated electrochemical oxidation process with Ce(IV) was very effective. It is established that destruction of aniline at 90 ℃ was found to be more than 90%.

The results obtained from the redox potential and moles of Ce(IV), testify in favor of the mechanism of destruction of aniline with multi-electron coefficient n=28 ([Ce(IV)]/[Aniline] = 28).

Studies destruction of aniline by mediated electrochemical oxidation process with Ce(IV) in flow liquid reactor are under way in this laboratory.

ACKNOWLEDGMENT

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