

Destruction of Organic Pollutants by Mediated Electrochemical Oxidation Process: Determination of Rate Constants in Continuous Feeding Mode

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Introduction

Mediated Electrochemical Oxidation (MEO) is an emerging and one of the most promising technologies for the destruction of organics as it is capable of completely mineralizing the organics into carbon dioxide and water, without emission of any toxic compounds like dioxins [1]. MEO process offer several advantages: First, the oxidation reaction takes place at ambient temperatures and pressures; second, the products of destruction are contained in the reaction vessel itself with the exception of gases; third, production of secondary waste is minimized and this avoids additional treatment methods.

In MEO process a metal ion in acid medium is oxidized from its lower oxidation state to higher oxidation state and this oxidized species destruct the organic compounds into carbon dioxide and water and itself gets reduced. Therefore, the metal ion is not consumed in the reaction and acts as a mediator. Cerium possesses good oxidizing behaviour due to its high redox potential ($E^{\circ}=1.62$ V) and does not form any insoluble precipitate with chlorine containing compounds. Cerium can be recovered and reused without much loss and therefore it is preferred to other metal ions and hence used in our study.

Many organic pollutants were found in the effluents of several industries such as phenol, benzoquinone, hydroquinone, catechol, maleic acid etc. These organic wastes can be destructed by the application of MEO process in continuous mode with simultaneous cerium(IV) regeneration. In this work the results of continuous process organic destruction with insitu cerium(IV) regeneration were presented. The rate constants were computed by applying our previous model for continuous organic addition and destruction and presented. A comparison of kinetics of batch and continuous process destruction of phenol was attempted.

Experimental

The overall schematic diagram of the continuous MEO process is shown in the Figure 1. It consists of an anolyte, a catholyte and a reactor together with an electrochemical cell [2]. The electrolyte used in the anolyte was 1 M cerium(III) nitrate and 3 M nitric acid, and in the catholyte 4 M nitric acid was taken. The catholyte vessel was provided with a gas scrubber to convert the nitrous oxide vapours into nitric acid. The anolyte and catholyte solutions were circulated through the cell using ceramic pumps. The electrochemical cell consists of an anode and cathode separated by a Nafion 314 membrane. The

anode was made of titanium coated with platinum and cathode was made of titanium (both mesh type). A fluoropolymer sheet (viton) was used as the separator between the electrodes.

The organic destruction experiments were carried out in a continuous stirred tank reactor (CSTR). The reactor and anolyte tanks were filled with cerium(III) solution in nitric acid and oxidised to cerium(IV) before starting organic destruction reaction. The organic solution was continuously fed for 30 min. to the CSTR. The reaction was carried out under specific temperatures using a thermostatic control. The concentration of carbon dioxide produced during the organic destruction was measured continuously using a CO₂ analyser (Environmental Instruments, Anagas CD 98). Carbon dioxide formed was purged by the carrier gas stream (nitrogen) and taken to the analyser. The concentration of CO₂ evolved was converted into volume and used to calculate the destruction efficiency. The liquid samples were analysed for total organic carbon content with a TOC analyzer (Shimadzu, TOC-5000A). The percentage of destruction was calculated from both CO₂ and TOC values.

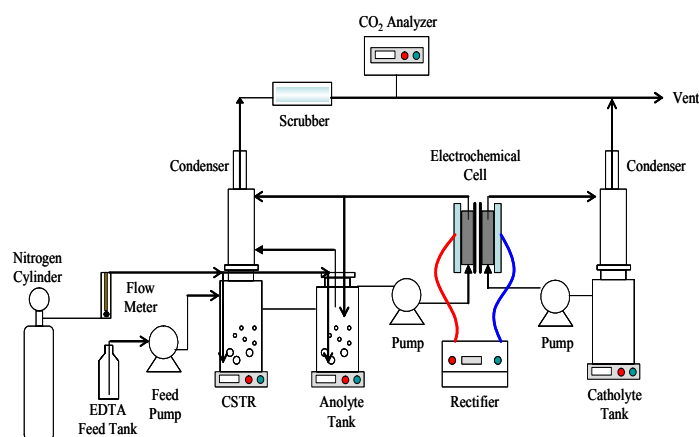


Figure 1. The Schematic Diagram of Continuous MEO process

Results and Discussion

In figure 2 (a), the CO₂ evolution patterns for phenol, hydroquinone, catechol, maleic acid (feed concentrations of 10,000 ppm), and benzoquinone (feed concentration of 2,500 ppm), are shown. It is observed from the figure that as soon as the feeding is stopped the CO₂ evolution starts decreasing. This clearly indicates that the destruction of organic is taking place with very fast rate during its addition and after stopping only little CO₂ evolves from the destruction of remaining organics present. Table 1 shows the destruction efficiency from CO₂ and TOC analyses, the CO₂ analyses always show lower value compared to the TOC as reported by some researchers. In figure 2 (b) the destruction efficiencies for phenol at different temperatures are presented. It can be seen from the figure that the difference in destruction efficiency is within 10% limit.

Table 1. The Mineralisation of Various Organics by Cerium (IV) Mediated Oxidation at 80°C

Organic compound	Feed concentration (ppm)	Destruction Efficiency based on CO ₂ (%)	Destruction Efficiency based on TOC (%)
Phenol	10,000	89.87	99.16
Benzoquinone	2,500	90.63	94.98
Hydroquinone	10,000	93.31	98.92
Catechol	10,000	91.44	99.36
Maleic Acid	10,000	99.20	99.13

In Figure 3 (a) the best fit between modeling and experimental points is shown for optimum k value. The k value was arrived by trial methods and the one with closest to the experimental data was taken as the rate constant of the overall reaction. This was also confirmed by taking the sum of the least square differences for different k values as shown in Figure 3 (b).

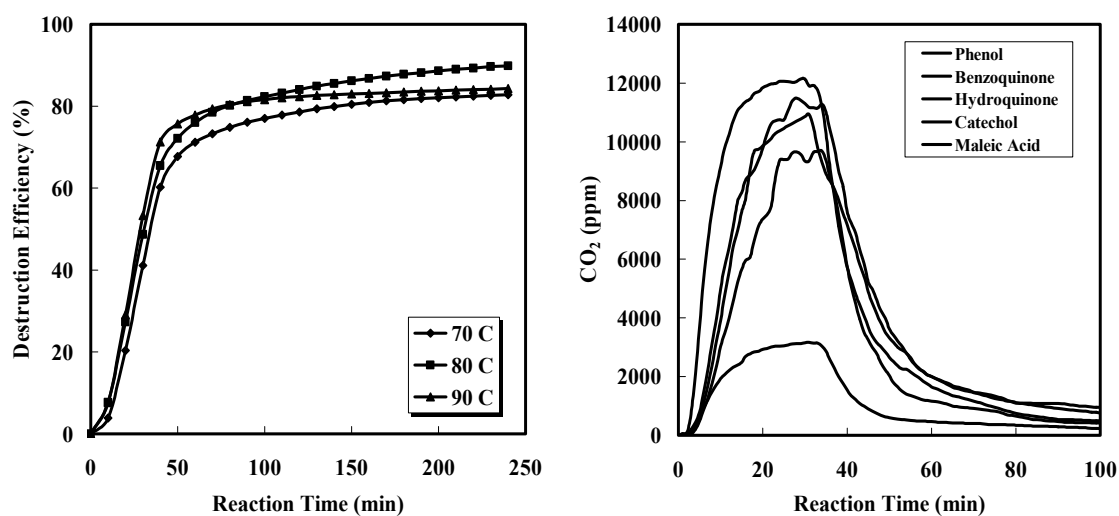


Figure 2. (a) The CO₂ evolution patterns for various organics at 80°C in continuous MEO process, (b) The destruction efficiencies obtained at different temperatures from CO₂ evolution

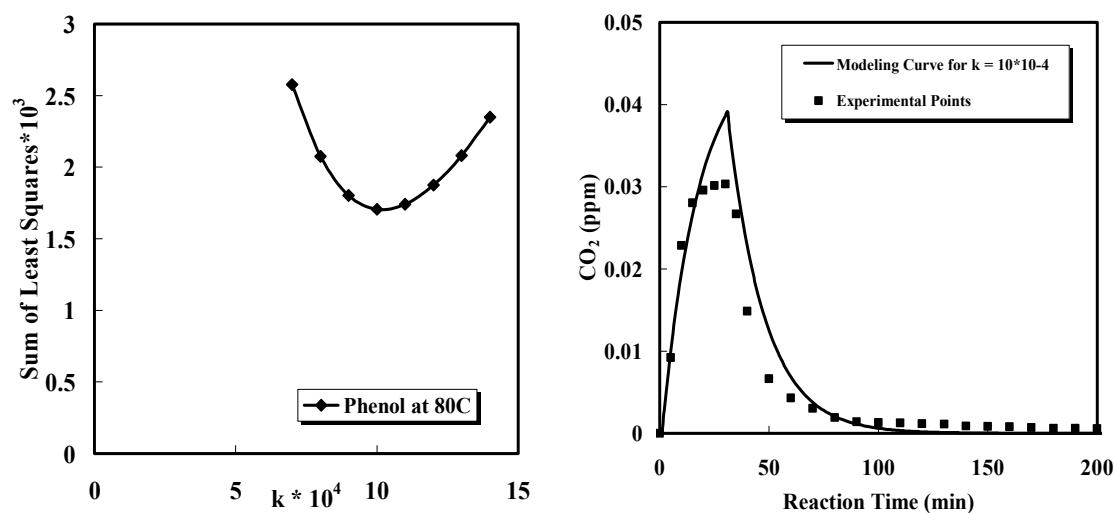


Figure 3. (a) The modeling fit with experimental points for 10,000 ppm phenol at 80° C with 3 ml per min flow rate during continuous MEO process, (b) Curve of sum of least square differences with rate constants to find the closest k value

Conclusions

The continuous mode of mediated electrochemical oxidation process was successfully tested for various organic compounds. A good destruction yield was obtained for all the organics studied. The pseudo first order rate constant for organic destruction was arrived by applying our earlier model to the CO₂ data obtained. The rate constant for continuous process calculated from the model was representing the overall process kinetics.

Acknowledgements

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References

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2. Il Shik Moon, "Electrochemical cell for hybrid mediated oxidation of organic wastes", Korea Patent: 10-2005-0045983, May 31 (2005).