Mediated Electrochemical Oxidation Process: Determination of Rate Constants for the Destruction of Phenol in Batch and Continuous Feeding Modes

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Introduction

Mediated Electrochemical Oxidation (MEO) process 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 carbondioxide 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 carbondioxide 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 (Eº=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, aniline, etc. These organic wastes can be destructed by the application of MEO process in either in batch or in continuous mode of organic addition with simultaneous cerium(IV) regeneration.

In this work the results of phenol destruction with *in situ* cerium(IV) regeneration were presented. The rate constants were calculated by applying the pseudo first order rate equation. A comparison of kinetics of batch and continuous process destruction of phenol was attempted.

Experimental

The overall schematic diagram of the MEO process is shown in the Fig. 1. It consists of an anolyte tank, a catholyte tank 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® 324 membrane. The anode was made of IrO_2/Ti 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 Ce(III) solution in nitric acid and oxidised to Ce(IV) before starting organic destruction reaction. In case of phenol destruction in batch mode the organic was added to the previously prepared oxidizing solution. In the case of continuous organic addition mode the phenol solution was fed for 30 min. to the CSTR while the cell was continuously operated for Ce(IV) regeneration. The reaction was carried out under specific temperatures (70, 80 and 95°C) using a thermostatic control. The concentration of carbon dioxide produced during the organic destruction was measured continuously using a CO_2 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 CO_2 evolved was converted into volume and used to calculate the destruction efficiency. At the end of each reaction the liquid samples were taken and analysed for total organic carbon content with a TOC analyzer (Shimadzu, TOC-5000A). The percentage of destruction was calculated from both CO_2 and TOC values and compared.
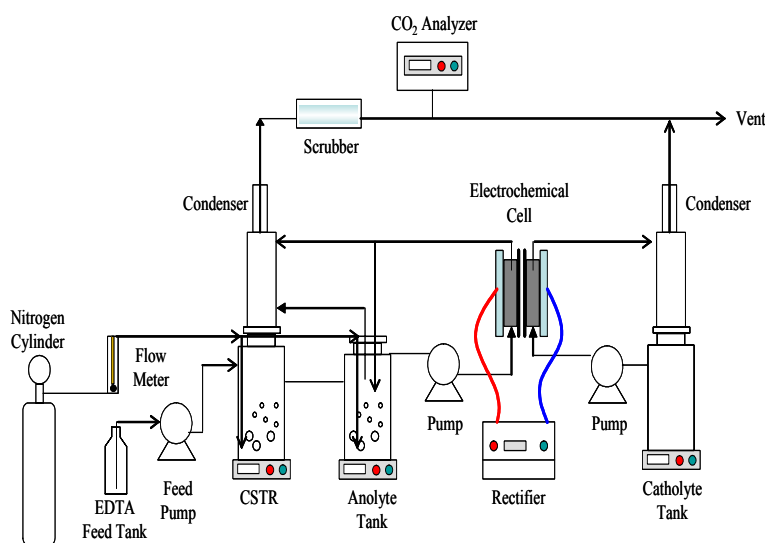

Fig. 1. The Schematic Diagram of Continuous MEO process

Results and Discussion

In fig. 2 (a), the destruction pattern based on total organic carbon removal for phenol in batch mode is shown. It is observed from the figure that the CO_2 evolution starts very quickly after adding organic and with in 5-10 min. starts decreasing. This clearly indicates that the very fast destruction of phenol in MEO process and in case of continuous process the destruction is taking place with very fast rate during its addition and after stopping only little CO_2 evolves from the destruction of remaining organics present. Table 1 shows the destruction efficiency of phenol from CO_2 and TOC analyses, the

CO_2 analyses always show lower value compared to the TOC as reported by some researchers and a similar trend was observed by other researchers in MEO process. 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.

In Fig. 3 (a) the best fit between modeling and experimental points is shown for optimum k value for continuous process of phenol addition. 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 Fig. 3 (b).

Table 1. The Mineralisation of Phenol by Cerium (IV) Mediated Oxidation at 80ºC

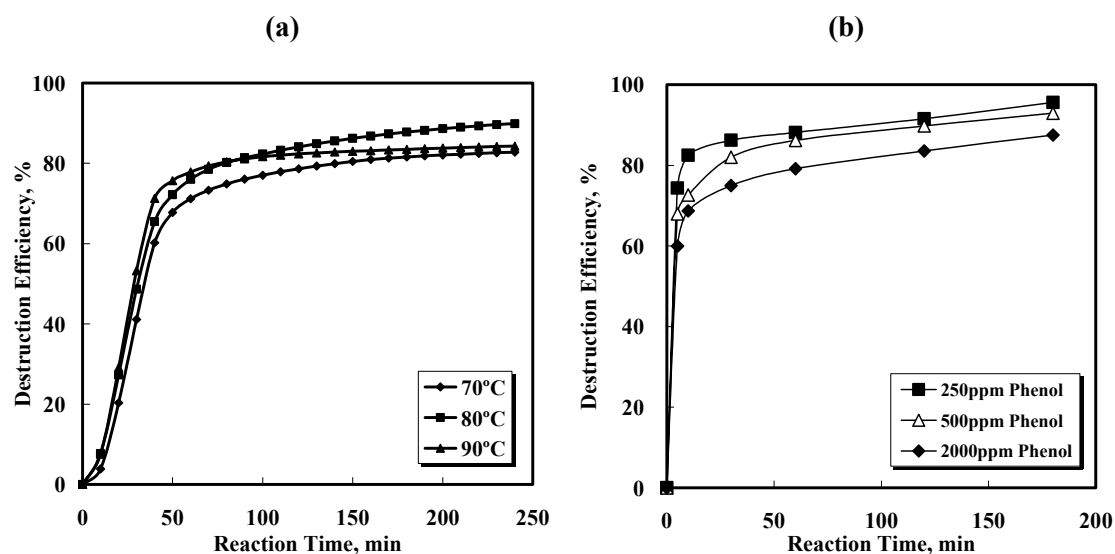| Mode of Addition	Feed concentration (ppm)	Destruction Efficiency based on CO_2 (%)	Destruction Efficiency based on TOC (%)
Continuous	10,000	89	99
Batch	2,500	80	96

Fig. 2. (a) The destruction patterns based on TOC removal for phenol at 80ºC in batch MEO process.
(b) The destruction efficiencies obtained at different temperatures from CO_2 evolution in continuous process
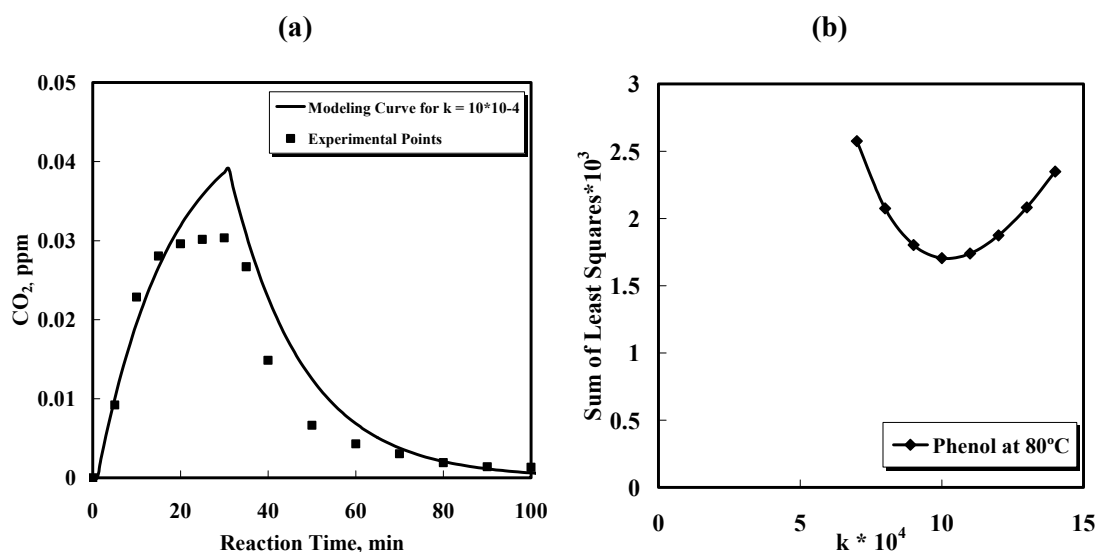
(a) **(b)**

Fig. 3. (a) The modeling fit with experimental points for 10,000 ppm phenol at 80º 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 batch and continuous mode of mediated electrochemical oxidation process was successfully tested for phenol. A good destruction yield was obtained for both types. The pseudo first order rate constant for organic destruction was arrived by applying our earlier model to the CO_2 data obtained. The rate constant for continuous process calculated from the model was representing the overall process kinetics.

Acknowledgements

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).