143a Electrochemical Process for Oxidative Destruction of 4-Chlorophenol

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Phenolic compounds are considered to be one of the major and most difficult pollutants in wastewater to be removed by water treatment processes. They are highly toxic (concentration limit in wastewater is under 0.1mg/L); low biodegradable and can accumulate in living organisms. Phenolic compounds concentrations above 2mg/L are toxic to fish and concentrations between 10 and 100mg/L results in death of aquatic life within 96h. Phenols can be readily chlorinated during water treatment process, and the acceptable concentration limit of chlorophenols in wastewater fell to 0.02mg/L. Some of the large sources of chlorophenol are pulp and paper mills, coke plants, chemical plants, petroleum refineries, plastic manufactures and leachate from municipal waste dumps.

Extensive research had been conducted to remove phenol and its derivatives including 4-chlorophenol. Current treatment processes include carbon adsorption, solvent extraction, biodegradation, advanced oxidation and electrochemical process. The choice mainly depends on the treatment efficiency, reliability, ease of control and economics. Carbon adsorption and solvent extraction can effectively remove 4-chlorophenol from aqueous solutions, but the high cost of carbon regeneration and extraction solvent hindered the large scale application. Advanced oxidation also suffers high operation cost. In case of biological treatment, anaerobic process can not effectively remove 4-chlorophenol from the liquid phase, and the high toxicity of 4-chlorophenol at a concentration as low as 100 ppm can inhibit the growth of anaerobic culture. An aerobic system following the anaerobic one was reported to be able to eliminate all residual chlorophenols including 4-chlorophenol. The choice mainly depends on the treatment efficiency, reliability, ease of control and economics. Electrochemical methods for water treatment have attracted wide attention and recognized to be advantageous due to high efficiency, easy to control, and low costs. The destruction of chlorophenols using electrochemical methods have been studied by other researchers, the influence of such parameters as temperature, pH, initial substance concentration, current density, and electrode material have been investigated. Evaluation of reaction products, electrode fouling and current efficiency were also carried out. However, most investigations were conducted in the low acidic range (pH <4). The purpose of this study is to investigate the electrochemical oxidation of 4-chlorophenol at neutral pH and study the impact of three key parameters on the destruction process, namely, initial concentration, ionic strength of electrolyte and reaction current.

A 780mL electrolytic cell was used in our study. A platinum wire was used as anode (surface area 3.39cm^2) and the cathode material was nickel. The solution was buffered at pH 7 using KH_2PO_4. The influence of the above stated parameters was investigated. Four initial 4-chlorophenol concentrations (25ppm, 50ppm, 100ppm, and 200ppm) and three ionic strengths (0.5M, 1.0M, and 1.5M) were used. NaCl was used as support electrolyte and the current applied ranged from 14.75mA/cm^2 to 88.50mA/cm^2. A Honeywell UDC3000 was used to supply a constant current to the cell. 4-chlorophenol was measured by Agilent 1100 Series HPLC, and Shimadzou TOC-5050 was used to determine TOC removal.

The rate of degradation was found to follow Pseudo first order kinetics. The reaction rate constant ranged from 0.44 to 27.33 hr^{-1} (see Fig 1) for the different reaction conditions studied. Since NaCl was used as electrolyte, two reaction mechanism was proposed: direct attack of the 4-chlorophenol by hydroxyl radical (OH•) and indirect oxidation of 4-chlorophenol by electro generated oxidants such as OCl^-, ClO_3^- or chlorine gas due to the presence of chloride in solution. The reaction rate decreased with the initial 4-chlorophenol concentration (Fig 1), which agreed with results reported by other researchers.

Some brown polymer was found to be formed for experiments with higher initial 4-chlorophenol concentration, indicating an incomplete degradation. Since the initial concentration of 25ppm had the fastest reaction rate, it was selected to investigate the influence of ionic strength. Fig 2 showed the increase of reaction rate constant with the increase of ionic strength. An empirical relationship will be established to predict the reaction rate under different initial concentration, applied current density, and ionic strength and will be presented at the conference.

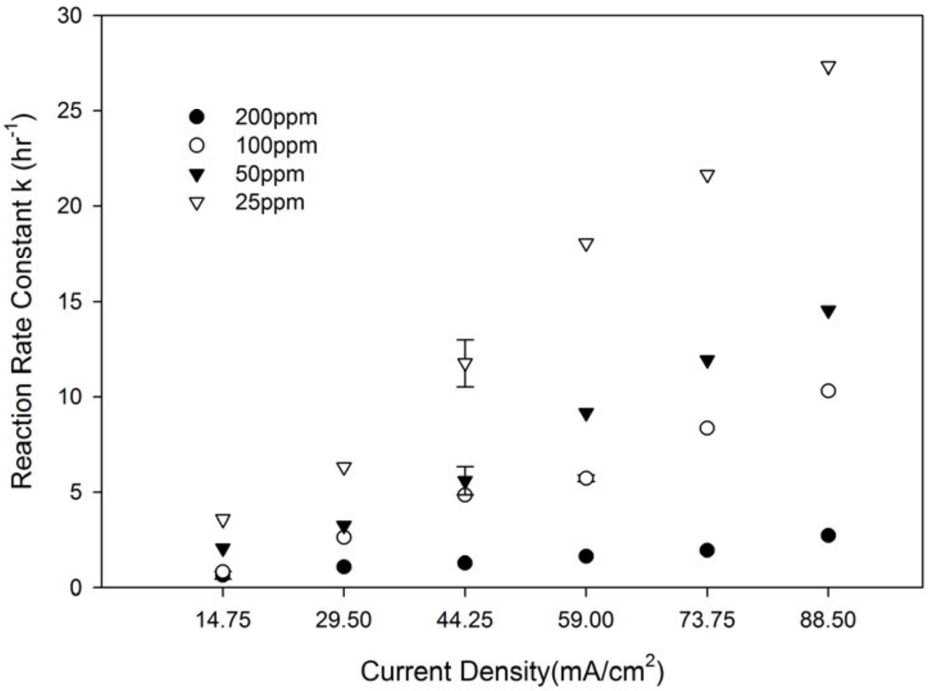

Fig 1. The influence of initial 4-chlorophenol concentration on reaction rate constant k (Ionic strength=1.5M)

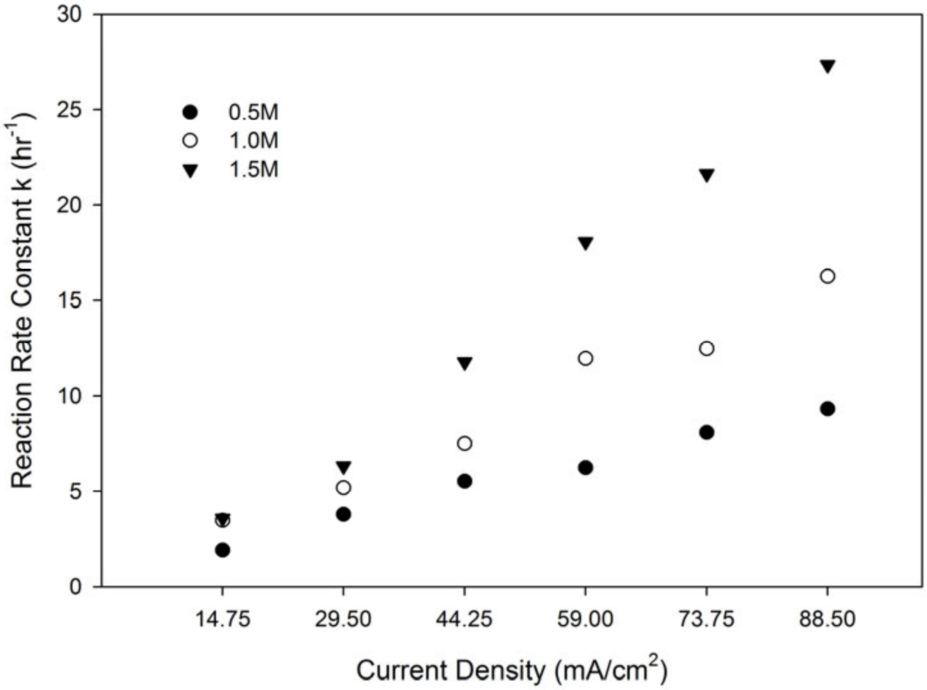

Fig 2. The influence of ionic strength on reaction rate constant k (Initial 4-chlorophenol concentration 25ppm)