Oxidation of Cerium(III) in Nitric acid medium by Ozone for Destruction of Organic Compounds

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Introduction

Ozone is a strong oxidizing agent, capable of participating in many chemical reactions with inorganic and organic substances. Commercially, ozone has been applied as a chemical reagent in synthesis, used for potable water purification, as a disinfectant in sewage treatment, and for the bleaching of natural fibers. Recently there has been an increased interest on ozone activation by metals such as Fe(II), Mn(II), Ni(II), or Co(II) as sulfates. The presence of these metals increase the TOC removal efficiency as compared to ozone alone was reported by many authors. Zinc or copper sulfate, silver nitrate, and chromium trioxide catalyzed ozonation was reported by Abdo et al.,[1] for the treatment of dye effluents. Gracia et al., [2] showed Mn, and Ag catalyzed Ozonation of humic acid substances in water. Andreozzi et al., [3] found that Mn(II) accelerates the oxidation of oxalic acid under acidic conditions. Carie et al., [4] reported the decontamination process for stainless steel by Ce(IV) species in 4M nitric acid in which the reduced cerium is reoxidized by ozone. Ce(IV) ions in acid medium acts as a powerful oxidant and virtually destruct any organic in to CO2 and water. If this high redox species is coupled with ozone either for catalyzing ozone or for regenerating reduced cerium ion then it forms an interesting system of applied research for organic removal and decontamination applications. The first part of this article presents generalities about oxidation of Ce(III) nitrate in nitric acid medium by ozone was investigate. The various parameters like concentration of Ce(III), concentration of nitric acid, ozone flow rate and temperature. The reaction between ozone and cerium containing nitric acid solution was performed in a bubble diffuser and bubble column at room temperature. The kinetics of Ce(III) oxidation by ozone was investigate. The second part focuses on the catalytic Ozonation. After finding the suitable condition for Ce(III) oxidation, this was applied to the phenol destruction.

Experimental Section

The schematic diagram of ozonation system was shown in the Fig 1. The oxygen (2 l/min) was passed into the ozone generator, which produced the ozone-oxygen mixture based on corona discharges. The amount of ozone containing gas mixture was 60 g/h The gas mixture was passed into 1000 ml cerium(III) nitrate in nitric acid solution containing reactor by means of bubble diffuser at a fixed flow rate. The gas mixture flow rate was maintaining by a flow controller. The temperature of

the solution was kept constant at around 25±1°C. During the experiment, Ce(III) was oxidized into Ce(IV) in the presence nitric acid medium. The oxidized of Ce(III) was carried by various experiment conditions like concentration of nitric acid (0.3, 1, 3 and 4M), flow rate of gas mixture (100, 250, 500 and 1000 ml/min) and concentration of Ce(III) (0.01, 0.05 and 0.1M). During oxidation of Cerium, the concentration of Ce(IV) were quantitatively analyzed by titration with ferrous ammonium Sulphate using ferroin as an indicator. Under the suitable conditions of Ce(III) oxidation, the destruction of phenol experiment was carried out. The gas mixture with flow rate of 100 ml/min was passed into 0.05 M cerium(III) nitrate in 0.3 M nitric acid solution for 1 hr. The phenol was added into reaction mixture with the concentration of 250ppm. The gas mixture was continuously passed into the reactor. The destruction of pheol was measured by TOC and concentration of Ce(IV) was determined by titration during the experiment. The gas mixture from outlet was passed through KI solution to destroy any remaining ozone in the gas stream.

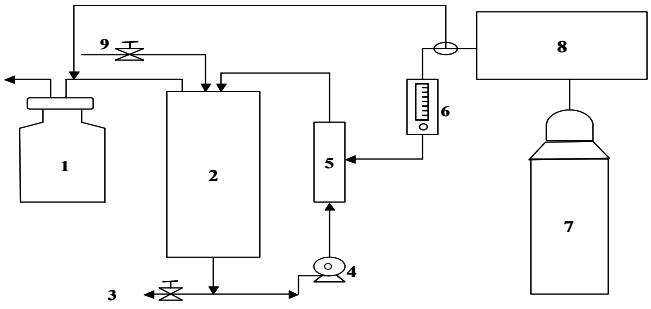

Fig 1. Schematic diagram of ozonation system

Result and Discussion

Effect of initial concentration of Ce(III)

Effects of various initial cerium concentrations (0.01, 0.05 and 0.1M) were studied during the ozonation experiments. Fig. 2(a) and 2(b) shows the percentage formation of Ce (IV) and kinetic of Ce(III) oxidation plot at constant ozone flow rate, initial concentration of nitric acid, and temperature respectively. The percentage formation of Ce(IV) was decreased with increasing the initial concentration of Ce(III) In Fig. 2(b), to plot between ln(C/Co) against reaction time "*t*" was given. From the linear slope, rate of the reaction (k) was determined. The rate constants were calculated with correlation coefficient values of greater than 0.99.

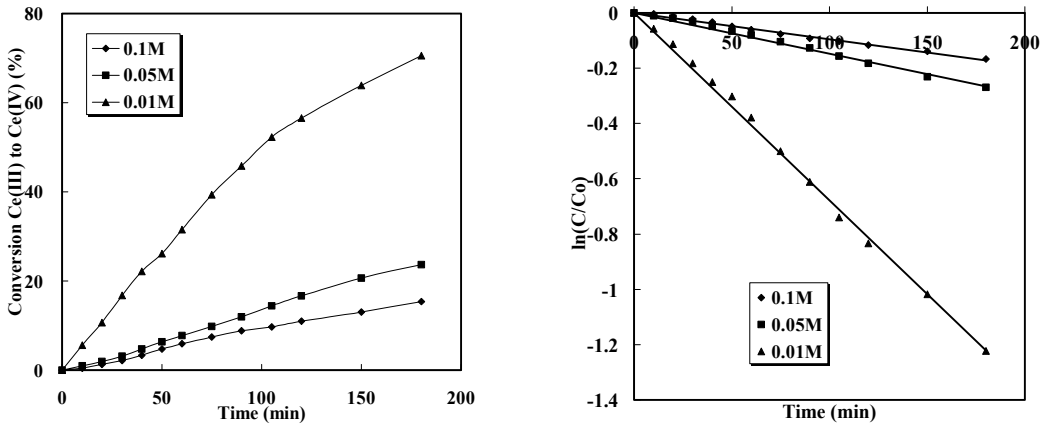

Fig 2. (a) Percentage of Ce(IV) formation with time at different initial conc. of Ce(III). (b) Determination of rate constants for Ce(III) oxidation.(q: 100ml/min, C_{HNO3}: 0.3M and T: 25°C)

Effect of concentration of nitric acid

Fig 3(a) shows the percentage formation of Ce(IV) at different concentration of nitric acid (0.3, 1, 3, and 4M) at constant gas flow rate, initial concentration of Ce(III) and temperature of the system. Fig 3(b) shows the first order plots between ln(C/Co) versus time "*t*" at various concentration of nitric acid. The percentage formation of Ce(IV) and first order rate constants were found to be increased with increasing concentration of nitric acid.

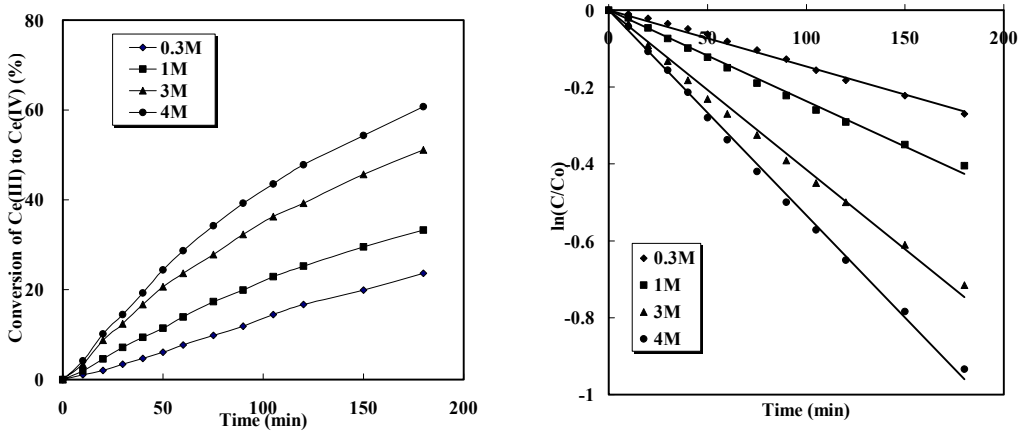

Fig 3 (a) Percentage formation of Ce(IV) with time at different conc. of nitric acid. (b) Determination of first-order rate constants for Ce(III) oxidation. (q: 100ml/min, $C_{Ce(III)}$: 0.05M and T: 25°C)

Effect of Ozone flow rate

Effect of ozone (gas mixture) flow rate on the Ce(III) oxidation was studied under constant initial concentration of Ce(III), Concentration of nitric acid and temperature. Fig 4(a) and 4(b) shows the percentage formation of Ce(IV) and plot $-\ln(C/C_o)$ versus reaction time for different ozone flow rate. From the linear plot the slope (k) was computed. At low flow rates of gas, the linearity of first order

with good correlation coefficient values.

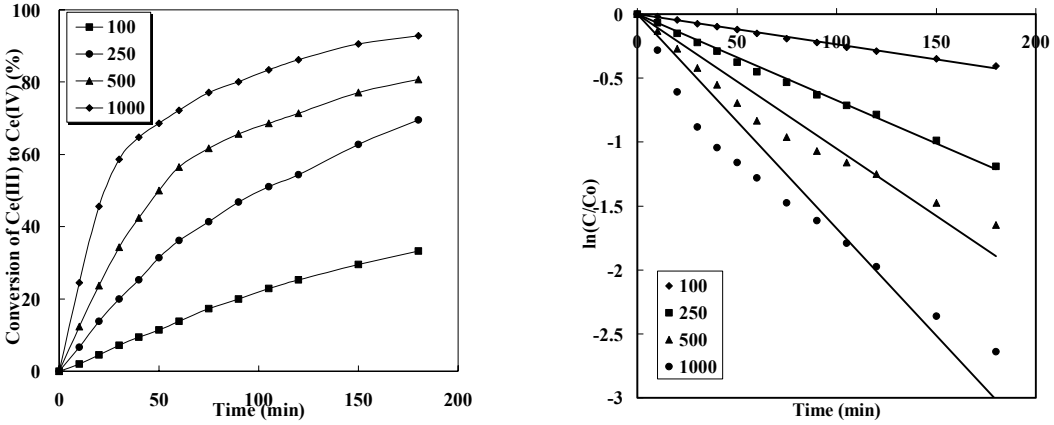

Fig 3 (a) Percentage formation of Ce(IV) with time at different ozone flow rate. (b) Determination of first-order rate constants for Ce(III) oxidation. ($C_{Ce(III)}$: 0.05M, C_{HNO3}: 1M and T: 25°C)

Conclusions

Ozonation was found to be an effective way for the Cerium(III) oxidation and destruction of phenol in the aqueous solution by using bubble column reactor. For the experiments carried out at constant temperature in the aqueous solutions with over a range of the concentration of nitric acid, the first order rate constant increased with increasing nitric acid concentration for Ce(III) oxidation. The bubble column was effective for the destruction of organic from the aqueous solution. The formation of Ce(IV) at higher flow rates was high in bubble column reactor than a bubble diffuser.

Acknowledgement

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References

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