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Effect of additives on ultrasonic degradation of phenol

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Abstract

Sonication for phenol degradation has proved to be an attractive process over the years at least on a laboratory scale but the rates of phenol degradation under sonication have always been quite low. The present work investigates the use of simple additives such as salt and carbon tetrachloride as process intensifying parameters with an aim of reduction in the treatment times and hence the cost of operation. The intermediates formed in the degradation process have been analyzed and it has been observed that these intermediates degrade faster as compared to phenol.

A hybrid technique of ozonation coupled with cavitation has also been investigated with an objective of finding the optimum conditions for the combination of ozonation and cavitation for synergistic effects. Analysis of the intermediates for the combination treatment scheme also indicates that the intermediates (hydroquinone, catechol, resorcinol, maleic acid, acetic acid, oxalic acid, formic acid, etc.) are more biodegradable prompting a possible combination of cavitation with aerobic oxidation for large scale treatment of phenol containing waste.

Keywords: Sonochemistry; Wastewater treatment; Ozonation; Degradation of phenol; Hybrid technique

1. Introduction

Phenol is one of the most common compound found in the effluents of many industries such as petroleum refining and petrochemicals, pharmaceuticals, pesticides, paint and dye industries, organic chemicals manufacturing, etc. If present in even small quantities (of the order of a few ppms), phenol causes toxicity and foul odor to the water. It has been listed as the priority pollutant in the list of EPA (USA). Most of the countries specify the maximum allowable concentration of phenol in the effluent streams to be less than 1 ppm. But degradation of phenol to such low levels has not been possible by conventional biological treatment processes. Lately, there has been a lot of interest in application of the advanced oxidation processes (AOPs) for the removal of phenol from the effluent streams.

Many processes such as membrane separation, wet air oxidation, radiolysis, Fenton oxidation, photocatalytic oxidation, electrochemical oxidation, ozonation, peroxidation [1a,1b] and sonication [2–7] had been used in the past for the degradation of phenol to the required low levels. These processes had been used alone or in combination with other processes to achieve the aim. But all these processes have their inherent limitations such as low rates of degradation, or lower mineralization or high costs of operation or severe operating conditions, etc.

Sonication for phenol degradation has proved to be an attractive process in terms of its normal operating conditions and lower costs. But the rates of phenol degradation under sonication have been very low. There had been some efforts to increase the rates of phenol degradation

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using hybrid techniques [8–15]. Enhancement of ultrasonic degradation rates of phenol using simple additives is a simple but effective method for increasing the rates of degradation. Seymore and Gupta [16] have shown that the rates of ultrasonic degradation of phenol can be increased substantially using simple sodium chloride addition to the aqueous phenol solution. But there have been no detailed reports of phenol degradation with ultrasound using additives such as ozone and carbon tetrachloride. Here in this report we have studied the enhancement in the rates of ultrasonic degradation of phenol using various additives such as salt, carbon tetrachloride and ozone.

2. Experimental

2.1. Materials

Phenol, catechol, hydroquinone, resorcinol, 2-chlorophenol, 4-chlorophenol, and carbon tetrachloride were procured from S.D.Fine-Chem Ltd., Mumbai and were used as received. Phenol and 4-chlorophenol were of laboratory reagent grade and all other chemicals were of analytical reagent grade. All organic acids except maleic acid and malic acid were obtained from S.D.Fine-Chem Ltd. Mumbai and were of analytical grade. Maleic and malic acids were obtained from Himedia Laboratories Ltd. Mumbai. Acetic acid was obtained from Ranbaxy, India. Demineralised water used in all the experimentation and analysis was from Milli-Q Gradient System from Millipore. Oxygen cylinders used were obtained from INOX AIR Products Ltd., Patalganga, India.

2.2. Apparatus

The following equipments have been used in the study.

1. Ultrasonic horn:
   Make: Dakshin
   Frequency: 22 KHz
   Rated output power: 240 W
   Calorimetric efficiency: ~5.2%
   Diameter of stainless steel tip of horn: 2.1 cm
   Surface area of ultrasound irradiating face: 3.46 cm^2.
2. Ultrasonic bath:
   Make: Supersonics
   Frequency: 22 KHz
   Rated output power: 120 W
   Calorimetric efficiency: ~34.69%
   Dimensions of bath: 15 cm × 15 cm × 14 cm
   Surface area of ultrasound irradiating face: 225 cm^2.
3. Ozone generator:
   Make: PCI Ozone Corporation, West Caldwell, New Jersey
   Model: GL-1
   Capacity: 1 lb/day.

2.3. Experimental procedure

The experiments to study the ultrasonic degradation of phenol involved the use of 95 ml of aqueous phenol solution of known concentration of 75 ppm taken in a beaker and were irradiated with ultrasound using Dakshin horn. The solution was irradiated with ultrasound for 15 min and then sonication was stopped for the next 10 min. This process was continued till the solution was irradiated for a predetermined time (1–8 h). The temperature of the solution was kept constant at ~31 ± 2 °C using cold water circulating around the beaker. No effort was made to maintain constant pH during the experiments. The initial pH of phenol solutions was found to be ~6.2.

In the case of experiments with ozone, oxygen ozone mixture was passed at a predetermined rate through a reactor containing 550 ml aqueous phenol solution of ~115 ppm phenol concentration. The concentration of ozone in the ozone–oxygen mixture was ~45.19 ppm (determined by iodometry). Flow rate of the gas mixture passing through the aqueous phenol solution was measured using soap film meter. Samples were taken out at regular intervals from the sampling port. When the ozonation was carried out in the presence of sonication, ozone–oxygen mixture was passed only when ultrasonic horn is ON. Residual ozone from the samples was removed by heating the samples immediately to 70 °C in a water bath. Fig. 1 shows the experimental set up used for the sonication in the presence of ozone.

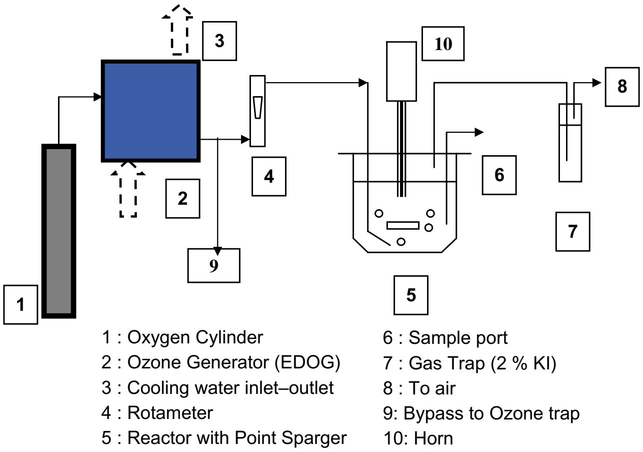

Fig. 1. Ozonation setup.