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Degradation of 4-chloro 2-aminophenol using combined strategies based on ultrasound, photolysis and ozone

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ABSTRACT

The present work investigates the degradation of 4-chloro 2-aminophenol (4C2AP), a highly toxic organic compound, using ultrasonic reactors and combination of ultrasound with photolysis and ozonation for the first time. Two types of ultrasonic reactors viz. ultrasonic horn and ultrasonic bath operating at frequency of 20 kHz and 36 kHz respectively have been used in the work. The effect of initial pH, temperature and power dissipation of the ultrasonic horn on the degradation rate has been investigated. The established optimum parameters of initial pH as 6 (natural pH of the aqueous solution) and temperature as 30 ± 2 °C were then used in the degradation studies using the combined approaches. Kinetic study revealed that degradation of 4C2AP followed first order kinetics for all the treatment approaches investigated in the present work. It has been established that US + UV + O_3 combined process was the most promising method giving maximum degradation of 4C2AP in both ultrasonic horn (complete removal) and bath (89.9%) with synergistic index as 1.98 and 1.29 respectively. The cavitational yield of ultrasonic bath was found to be eighteen times higher as compared to ultrasonic horn implying that configurations with higher overall areas of transducers would be better selection for large scale treatment. Overall, the work has clearly demonstrated that combined approaches could synergistically remove the toxic pollutant (4C2AP).

1. Introduction

Significant development in the industries (chemical, pharmaceuticals etc.) and population growth have also created significant problems related to the environment (air and water pollution) at a level of global concern. The presence of hazardous compounds and toxic wastes in the water streams can result in hazards to human, animal and plant life. Phenol and its derivatives which are used in many chemical, petrochemical and pharmaceutical industries have remarkable contribution to the environmental hazards due to their acute toxicity [1]. 4-Chloro 2-aminophenol (4C2AP) is an intermediate used commonly for the manufacture of dyes and pharmaceuticals. It is a highly toxic organic compound having significant hazardous effects and may be fatal if breathed in, swallowed or absorbed through skin. Absorption into the body may lead to the formation of methemoglobin and at sufficient concentrations, it can result in cyanosis. The partial degradation of 4-chloro-2-nitrophenol (4C2NP) and 3-chloronitrobenzene (3CNB) may also generate 4C2AP [2,3]. Due to the significant toxic effects, it is essential to effectively remove 4C2AP from waste water streams. The conventional waste water treatment schemes namely flocculation/coagulation, membrane separation or elimination by activated carbon adsorption offer considerable limitations. For example, adsorption removes the pollutant from liquid stream but creates a secondary pollutant in terms of adsorbent loaded with the pollutant whereas the biological methods require more time and are less efficient in complete mineralization. The degradation pathway of 4-chloro-2 aminophenol (4C2AP) was studied by Arora et al. [4] in a bioreactor and it was reported that the time required for complete degradation was 36 h. Also in biological treatment schemes, the required preparation of microbes or enzymes needed for the reaction is itself an extensive process so as to avoid contamination with foreign microbes. As the complete and efficient degradation of the pollutants cannot be achieved by either the physical or biological approaches alone, development of new approaches for effluent treatment especially containing toxic compounds such as 4C2AP is essential. The recent approaches applied for the degradation of phenolic compounds include Fenton reaction [5], heterogeneous photo-Fenton process [6], sonochemical degradation [7], photocatalysis [8] and ozonation [9]. A careful analysis of the literature reveals that not much work has been reported for the degradation of chloro and nitro derivates including 4C2AP, which is an emerging contaminant. Considering this aspect the current work has

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targeted on developing efficient treatment scheme for wastewaters containing 4C2AP based on the use of ultrasound.

Passage of ultrasound through the liquid medium generates cavitating conditions such as local hot spots and intense turbulence, which can be important for the wastewater treatment applications. Cavitation also results in generation of hydroxyl radicals having high oxidation potential of 2.87 V based on the decomposition of water molecules [10]. In addition to exploring the application of ultrasound based reactors for the degradation of 4C2AP, the efficacy of combined treatment approach involving ultrasound with photolysis and ozone has also been investigated for the first time. UV photolysis also works on similar principle of free radical attack where the water molecule splits into hydrogen atom and hydroxyl radical due to the passage of UV irradiations. Ozonation works on two reaction mechanisms viz. direct oxidation by molecular ozone having oxidation potential of 2.07 V and indirect oxidation by hydroxyl radicals (formed due to spontaneous decomposition of ozone in aqueous solution under specific conditions of pH or in combination with irradiations). Due to the similarity in the mechanisms of oxidation, the efficiency of cavitation based degradation can be enhanced by coupling with photolysis and/or ozonation. Although in literature, intensification of the degradation of many organic pollutants have been reported by combining cavitation with one or more advanced oxidation techniques such as ozonation and phtolysis [11–15], to the best of our knowledge, the degradation of acutely toxic 4C2AP by any of the combined advanced oxidation methods has not been reported. Also the earlier work has mostly concentrated on laboratory scale investigations and not much work has been presented for comparison of different sonochemical reactor configurations. Thus, the novelty of present work that investigates the degradation of 4C2AP using different configurations of sonochemical reactors (at two scales of operation) is clearly established. The intensification aspects have also been investigated based on the use of combination with ozone and UV irradiation as a supplement to ultrasound based treatment. The work also evaluates the synergistic index for the combination approach and the cavitational yield for different sonochemical reactors to allow easy comparison of the effectiveness of the treatment schemes.

2. Materials and methodology

2.1. Materials

4-Chloro 2-aminophenol was obtained from Sigma-Aldrich. High Performance Liquid Chromatography (HPLC) grade Methanol was obtained from J.T. Baker Chemical Pvt. Ltd. All the other chemicals were obtained from S.D. Fine Chemicals Ltd. Mumbai. Distilled water has been used to prepare aqueous solutions of required concentrations. All the chemicals were used as received from the suppliers without any purification.

2.2. Experimental setup

2.2.1. Ultrasonic horn

Ultrasonic horn procured from Dakshin India Ltd. Mumbai was used in the present work. The horn has an operating frequency of 20 kHz and rated power output of 120 W. The tip diameter of horn is 2.1 cm with an active acoustical vibrational area as 3.46 cm^2. All the experiments were conducted in a 250 ml glass beaker immersed in an ice bath for maintaining constant temperature. The temperature was monitored using a miniature thermocouple sensor attached to a digital indicator. The ultrasonic horn was immersed in the solution from the top of the reactor with a depth of about 5 mm inside the liquid. The on time was set for 7 s and off time for 3 s to allow effective operation of device as per recommendations of the supplier.

2.2.2. Ultrasonic bath

Ultrasonic bath with dimensions of length as 33 cm, width as 20 cm and height as 15 cm was fitted with a transducer of length 24 cm and 3 cm diameter (irradiation area as 205 cm^2) attached to one end of the reactor. Ultrasonic bath has an operating frequency of 36 kHz and rated output power of 150 W. The bath is made up of stainless steel with a drainage valve provided at the bottom of the bath.

2.2.3. Ozonator

A standard ozone generator (model-DOZ400) was procured from Eltech Engineers, Mumbai. A two way bypass valve was attached to the outlet pipe to regulate the ozone flow. The calibration of ozone output was done by standard iodometric titration method [16].

2.2.4. UV cabinet

Photolysis was carried out in a UV chamber having one UV lamp (Philips TUV 8W/G8T5) with power rating of 8 W and dominant wavelength as 254 nm. 250 ml capacity quartz beaker was used for performing the experiments involving photolysis.

2.3. Experimental methodology

2.3.1. Ultrasonic horn

The reactor was filled with 200 ml of aqueous 4C2AP solution of required concentration. The initial pH of the solution was 6 and for the experiments involving the variation of initial pH over the range of 3–8, the pH of solution was adjusted using 0.1 M H_2SO_4 and 0.1 M Phosphate buffer solutions. The effect of temperature was studied over the range 26–38 °C and the rated power of ultrasonic horn was varied from 60 W to 120 W for understanding the effect of power. One parameter at a time approach was used to study the effect of different parameters and the optimum conditions were used in the subsequent investigations. In all the experiments, a magnetic stirrer was used to ensure uniform mixing of the contents. In the case of ozonation experiments, ozone was bubbled in the solution through a ceramic diffuser and the flow rate of ozone was kept constant at 15 mg/h. The combined approach of sono-photolysis, ozone-photolysis, sono-ozonation and the combination of sonication, photolysis and ozonation were studied by performing the experiments in UV chamber with the provision for introduction of ultrasonic horn and ozone. A schematic diagram of the experimental set up has been depicted in Fig. 1. All the experiments were performed in triplicate for a fixed treatment time of 120 min and samples (quantity = 3 ml) were withdrawn at regular intervals for analysis. The data reported in the figures is average of the results obtained for different runs and the variation in the obtained data has been shown as error bars (generally within ±2%).

2.3.2. Ultrasonic bath

The ultrasonic bath was filled with 7 L of aqueous solution of 4C2AP with initial concentration as 20 ppm. A three blade turbine type impeller was used at a speed of 500 rpm for uniform mixing at this scale of operation. The temperature was maintained constant at 30 ± 2 °C by cooling water circulation using peristaltic pump. For studying the combined effect of photolysis along with sonication, the UV tube (8W) fixed on a wooden plate was placed above the reactor and covered with black paper to avoid the diffusion of radiations into the room. Similarly for combined operation of sonication and ozonation, the ozone pipe with ceramic diffuser was dipped inside the reactor. Optimized conditions of pH and temperature were used based on results obtained for the case of ultrasonic