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Photochemical degradation of chlorophenol industry wastewater using peroxy acetic acid (PAA)

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HIGHLIGHTS

- ▶ UV-assisted chlorophenol Industry effluent degradation with peroxy acetic acid.
- ▶ Chlorophenols, COD and chloride ion are reduced to 2 ppm, 127 ppm and 340 ppm.
- ▶ The optimum condition 250 W UV lamp, PAA concentration 4053 ppm and at pH 11.
- ▶ Degradation product reported using GC–MS.

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ABSTRACT

In this present work, photochemical degradation of industrial effluent (collected from GIDC, Surat, India) containing chlorophenols with peroxy acetic acid (PAA) was studied in a batch reactor. It was observed that degradation efficiency dependent on parameters such as UV power, pH and PAA concentration. The optimum condition of UV input, pH and PAA concentration for the treated chlorophenol industry effluent was found to be 250 W, 11 and 4053 ppm. Mineralization of effluent was determined from the chemical oxygen demand (COD) and chloride ion removal data. 97% (reduced to 2 ppm) 4-chlorophenols and 94% COD (reduced to127 ppm) was reduced by UV/PAA process. Chloride ion reduction was 81% (reduced to 340 ppm) at optimized process condition. Samples were analyzed by HPLC, UV spectrophotometer and GC–MS for residual concentration, COD and identification of final degraded products. The degraded compounds obtained were Tridecane, Hexadecane, Tetradecane, Pentadecane, 1,2,4-trimethyl Benzene and 1,3,5-trimethyl Benzene.

1. Introduction

Industry manufacturing chlorophenols and its derivative produces large amount of effluent that contains high concentration of harmful chlorophenols. These are highly poisonous, weakly biodegradable, carcinogenic and retain in the environment for longer period [1]. It is necessary to dispose off these residues in a proper manner following environmental rules and regulations. The permeable discharge limit of chlorophenols in the surface water is 1 ppm and that in marine water 5 ppm. Conventional methods such as biological process, carbon adsorption and chemical oxidation are useful for the removal of chlorophenols. But main disadvantage of these methods is the generation of secondary toxic intermediates [2] and expensive treatment cost when present at very low concentrations in the environment. As a result, alternative treatment technologies are used to mineralize or convert non biodegradable chlorophenol molecules into other degradable compounds. In recent years, advanced oxidation processes (AOPs) are proved as proficient and ideal treatment method for chlorophenol industrial effluent [3]. AOP is defined as the process involving generation and use of powerful transitory species, principally the hydroxyl radical [4]. Among AOPs photochemical method is the most promising method for the degradation of chlorophenols [1]. The reported photochemical method for chlorophenols degradation are heterogeneous photocatalytic oxidation, treatment with ozone (often combined with H_2O_2, UV or both), H_2O_2/UV systems, Fenton, and photo-Fenton type reactions [5]. The UV sources used for the AOPs are low or medium-pressure mercury lamps. However, most chemical bonds cannot be broken directly with only UV due to the limited available wavelengths or absorption bonds of the targeted chlorophenols [6].

Literature review shows that a wide variety of industrial effluents containing chlorophenols are treated by biological [7], photochemical system such as UV/O_3 [8] UV/H_2O_2 [9] UV/TiO_2 [10] and photo-Fenton process [11]. Limited literature is available on degradation of industrial effluent containing mixture of chlorophenols

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by using organic oxidants. Peroxy acetic acid (PAA) is (oxidant) reported for the degradation of refractory compounds and strong oxidant as compared to H_2O_2, methyl ethyl ketone and *p*-nitrobenzoic acid [1]. Thus the present study is undertaken to examine the degradation and subsequent mineralization efficacy of industrial effluent containing chlorophenols (CPs) by organic oxidant PAA. In this work, an attempt has been made to investigate the degradation and mineralization of industrial effluent containing chlorophenols by UV/PAA process. Various factors such as UV input, pH and initial concentration of PAA are varied to study the degradation process. Chemical oxygen demand (COD) and chloride ion content is determined for degree of detoxification. The samples are analyzed by HPLC, UV spectrophotometer and GC–MS for residual concentrations, COD and identification of degraded products.

2. Experimental

2.1. Materials

The oxidant peroxy acetic acid (40%) was obtained from National chemical (Vadodara, India). The solvent acetone (Merck, Mumbai) used for cleaning. Various solutions made in the distilled water, prepared in the laboratory by Millipore (Elix, Bangalore, India). The UV radiation sources were mercury lamp of 18 W, 125 W and 250 W (254 nm) purchased from Zahabi Marketers (Surat, India). Other chemicals like NaOH and H_2SO_4 and potassium dichromate were of analytical grade and used without further purification. The wastewater was collected from local chlorophenol industry (GIDC, Surat). GC–MS analysis was done for identification of CP-congeners in the collected effluent. The CP-congeners were identified as 4-chlorophenol (4CP), 2,4 dichlorophenol (2,4 DCP), 2,6 dichlorophenol (2,6 DCP) and 2,4,6 trichlorophenol (2,4,6 TCP). The characteristic of the collected industrial effluent was as described in Table 1.

2.2. Method

Experiments were carried out in a batch reactor as in Fig. 1. Two cylindrical reactors of quartz glass with 250 ml and 400 ml capacity were used here. The illumination was provided by 18 W, 125 W and 250 W UV lamp. The reaction chamber was filled with the reaction mixture and placed between the reactor wall and UV lamp system. Mixing was done by magnetic stirrer for better degradation result. Reaction vessel was wrapped with aluminum foil. The radiation intensity at the reactor wall or inside the reaction mixture was not measured. But only the consumption power of the mercury lamp was varied. Cooling was provided to the immersion vessel through water cooler pump. Experiments were performed initially with UV/CP-effluent and UV/CP-effluent/PAA system with initial concentration of CPs 142 ppm, COD 2200 ppm, pH 9.5 with initial concentration of PAA 3040 ppm (optimized condition of pH and PAA of synthetic degradation of 4-CP) [1]. UV/CP-effluent results were used as blank for experiments carried out with PAA. For UV/PAA process, peroxy acetic acid at different concentration was used initially. Initial concentration in parts per million (ppm) were as follows: CP-effluent, 142, PAA: 3040, 4053, 6097 and 9116. Remaining experiments of UV/PAA process was conducted with optimized PAA concentration. The pH adjusted at the beginning for further experiments were 4, 7, 9.5 and 12. The pH of the solution was controlled by adding 0.1 N/1.0 N NaOH and 0.1 N/1.0 N H_2SO_4 and measured on digital pH meter (ME-962P, Chandigarh, India). Thereafter the pH was monitored at the time of drawing the samples. All the experiments of UV and UV/PAA system were run for 180 min. Samples were collected and analyze for residual concentration immediately. Experiments were repeated two times to minimize error.

Table 1
Characteristics of industrial effluent.

Parameters	Values
pH	6.5
CP-congeners (4-CP, 2,4 DCP, 2,6 DCP, 2,4,6 TCP)	142 ppm
COD	2200 ppm
Chloride	1800 ppm
Color	Brown

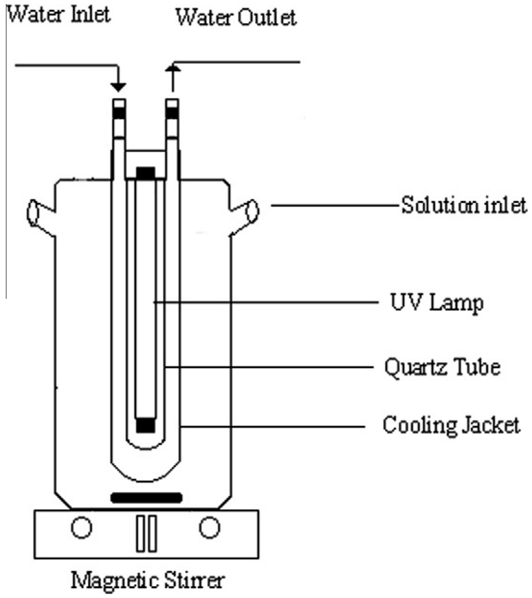

Fig. 1. Experimental set up for UV and UV/PAA process.

2.3. Analysis

Sample analysis was done by HPLC (Shimurzu LC-2010 AHT, Kyoto, Japan) and UV spectrophotometer (DRB 5000, HACH, USA) [12]. The residual concentration of CPs was measured under the following experimental conditions in HPLC analysis: column: Kromasil (250 × 4.6 mm, 5 μm), mobile phase: acetonitrile:water (40:60), pH: 2.6 adjustment using phosphoric acid, flow: 1.0 mL/min, built in UV–Visible detector: 210 nm. A blank run of oxidants alone was performed and compared with initial experimental results to avoid any interference in HPLC analysis. GC–MS analysis was carried out under following experimental condition: temperature programmed: SPLIT-50,60-8-260-30-280-3; carrier gas, helium; flow rate, 1 mL/min; injection volume, 1 μL; solvent delay, 3 min; column HP5MS; column length, 30 m; internal diameter, 0.25 mm; film thickness, 0.2 μm; detector mass spectrometer; mass range scanned, 50–2000 amu. COD analysis was performed using UV spectrophotometer and chloride ion measurement was done by standard methods (9253, Chloride titrimetric method) [12].

3. Results and discussion

3.1. Direct photolysis

Raw effluent used in this study is a combination (Table 1) of chlorophenols (142 ppm) with initial COD and chloride ion concentration as 2200 and 1800 ppm. The degradation of the chlorophenols present in the raw effluent is evaluated on the basis of COD