Separation and Purification Technology 168 (2016) 152–160

Contents lists available at ScienceDirect

Separation and Purification Technology

journal homepage: www.elsevier.com/locate/seppur

Degradation of 4-chloro 2-aminophenol using combined approaches based on microwave and photocatalysis

Arati J. Barik, Somesh V. Kulkarni, Parag R. Gogate *

Chemical Engineering Department, Institute of Chemical Technology, Matunga, Mumbai 400 019, India

ARTICLE INFO

Article history:
Received 4 March 2016
Received in revised form 4 May 2016
Accepted 28 May 2016
Available online 30 May 2016

Keywords:
Microwave irradiation
Photocatalysis
4-Chloro 2-aminophenol
Kinetic analysis
Sequential combination
Toxicity analysis

ABSTRACT

Degradation of 4-chloro 2-aminophenol (4C2AP), a highly toxic organic pollutant, has been investigated using different approaches based on the use of microwave (MW) irradiation, photocatalysis and sequential combination of MW and photocatalysis. Hydrogen peroxide (H_2O_2) has been used as an additive for intensification of the degradation. The effect of important operating parameters such as initial concentration of 4C2AP, initial pH, power dissipation, TiO_2 loading and H_2O_2 loading on the extent of degradation have been investigated. The obtained optimum conditions as initial concentration of 4C2AP as 20 ppm, initial pH as the natural pH of solution, power dissipation of 8 W for UV irradiation, H_2O_2 loading as 300 ppm and TiO_2 loading as 0.1 g/l have been established for photolysis approach and then subsequently used for the sequential combination of MW and UV. It has been established that maximum degradation of 4C2AP as 93.23% is obtained in the sequential approach of MW and UV with optimized TiO_2 and H_2O_2 loadings. The degradation of 4C2AP followed first order kinetics for all the treatment approaches investigated in the present work. The degradation products of 4C2AP have been identified using GC–MS and the toxicity analysis has also been performed using anti-microbial activity test based on agar-well diffusion method for the degradation products as well as the parent pollutant. The obtained results clearly established that the combined process of MW and UV in combination with TiO_2 and H_2O_2 is most effective approach in the degradation of 4C2AP as compared to individual treatment approaches of MW and UV as well as other combined approaches as MW + TiO_2, MW + H_2O_2, UV + TiO_2, UV + H_2O_2, MW + TiO_2 + H_2O_2 and UV + TiO_2 + H_2O_2.

1. Introduction

Phenolic compounds have been widely considered as pollutants having significant environmental impact and commonly detected in surface waters and ground waters. The extensive use and improper disposal practices have led to serious problem of contamination of soil and ground waters. Thus, it is very important to develop effective treatment methods for the degradation of these pollutants [1]. One of the phenolic compounds, 4-chloro 2-aminophenol (4C2AP), is commonly used in dyes and pharmaceutical industries. 4C2AP is highly toxic and has been considered as priority water pollutant with precarious effects on health (harmful to eye, skin, nervous system and blood even at low concentration), as it is readily absorbed by contact with the skin as well as through inhalation of vapors [2]. 4C2AP contained in wastewater must be treated before discharge, which has resulted in a great interest in the study of developing efficient technology for the removal of this toxic pollutant. The conventional disposal methods applied for the removal of phenolic compounds are generally not satisfactory due to the higher stability of phenolic compounds. In recent years, many advanced treatment schemes such as cavitation (ultrasonic cavitation and hydrodynamic cavitation) [3–5], photocatalysis [6], Fenton [7], photo-Fenton [8], wet-air oxidation [9], electrochemical oxidation [10], and ozonation [11] as well as the combined treatments based on different oxidation schemes [12–18] have been applied for the degradation of phenolic pollutants in waste water. Besides these methods, microwave (MW) irradiation can also be effective giving localized higher energy densities and uniform intense heating [19]. The non-thermal effect of absorbed MW energy in a solution reduces the activation energy and weakens the chemical bonds of the organic chemicals [20]. The frequency of MW irradiation varies from 300 GHz to 300 MHz with corresponding variation in wavelengths from 1 mm to 1 m respectively [21]. MW energy (E = 0.4–40 kJ mol^{-1} at ν = 1–100 GHz) has also been reported to be adequate to break the chemical bonds of many organic compounds [22]. For enhanced degradation, MW can be combined with

* Corresponding author.
E-mail address: pr.gogate@ictmumbai.edu.in (P.R. Gogate).

http://dx.doi.org/10.1016/j.seppur.2016.05.050
1383-5866/

suitable process intensifying additives (H_2O_2), catalyst (TiO_2) and other advanced oxidation process such as photocatalysis. Since MW and photocatalysis involve similar mechanism of producing hydroxyl radicals from water, the combined process can give better performance for the degradation of organic pollutants.

A critical analysis of literature reveals some reports of degradation of 4C2AP using advanced oxidation processes. Barik and Gogate [23] investigated the degradation of 4C2AP using combined processes as ultrasound (US) + UV, UV + O_3, US + O_3 and US + UV + O_3 and reported that maximum degradation (99.27%) was obtained in the combined approach of US + UV + O_3 after 2 h of treatment. Arora et al. [24] investigated biodegradation of 4C2AP and reported complete degradation after 36 h of treatment. Barik and Gogate [25] also studied the degradation of 4C2AP using hydrodynamic cavitation (orifice plate with 2 mm hole as cavitating device) in combination with UV and ozone and reported 96.85% degradation of 4C2AP in 2 h of treatment. A detailed analysis of the literature revealed that microwave based treatment approaches have not been investigated for degradation of 4C2AP and hence the present work reports the application of MW irradiation for the degradation of 4C2AP for the first time. The work also reports a novel approach based on the sequential use of MW and UV in the presence of hydrogen peroxide and catalyst TiO_2 for intensifying the degradation. TiO_2 is the most effective and widely acceptable catalyst for photolysis. In the presence of UV energy, the electron-hole pair i.e. conduction band electrons (e^-_{cb}) and valence band holes (h^+_{vb}) are generated on the surface of the catalyst (TiO_2). Valence band holes react with water and the hydroxide ion to produce hydroxyl radicals, while conduction band electrons react with adsorbed molecular oxygen reducing it to superoxide radical anion which, sequentially, reacts with protons to form the peroxide radicals [26]. Thus it is expected that combination approach involving UV/MW energy and catalyst can increase the rate of production of radicals and hence the extent of degradation. The combination approach can also help in reducing the energy requirements for the microwave and UV operations due to the requirement of lower treatment times, which would be very important considering the possible commercial applications. The work also reports the optimisation of operating parameters, kinetic analysis and the identification of the intermediates formed during the degradation process.

2. Materials and methodology

2.1. Materials

4-Chloro 2-aminophenol was procured from Sigma-Aldrich. All the other chemicals such as hydrogen peroxide (30% w/v), titanium dioxide (Anatase, minimum Assay of 99%), sulphuric acid (98%) and sodium hydroxide (98%) of Analytical Reagent (AR) grade were obtained from S.D. Fine Chemicals Ltd. Mumbai. All the chemicals were used as received from the supplier without any purification. Ultrapure Milli-Q deionized water has been used to prepare aqueous solutions of the compound of required concentrations. For toxicity analysis, two gram-positive bacterial strains as *Bacillus licheniformis* and *Lechevalieria aerocolonigenes* and two gram-negative bacteria strains as *Pseudomonas aureofaciens* and *Alcaligenes eutrophus* obtained from the N.R.R.L. culture collection centre, U.S.A. have been used.

2.2. Experimental setup

2.2.1. Microwave oven

A microwave oven (Murphy Richard – Make, Model-MWO 20MS) having the range of rated power output as 136–800 W has been used in the present work. The power dissipation was kept constant at 136 W for all the microwave based experiments. With the help of calorimetric study, the actual power dissipated in the system was observed to be 59.63 W for the supplied power of 136 W giving an energy efficiency of 43.85%.

2.2.2. UV treatment

The UV treatment was based on use of two UV lamps of power 4 W (Philips TUV 4 W/G4T5) and 8 W (Philips TUV 8 W/G8T5) with dominant wavelength as 254 nm. All the UV based experiments were performed using a 250 ml capacity quartz glass beaker.

2.3. Experimental methodology

All the experiments were performed using 200 ml aqueous solution of 4C2AP of required concentration in a 250 ml quartz glass reactor. During UV treatment, the temperature was maintained constant at 30 ± 2 °C using a constant temperature water bath. The effect of initial concentration of the pollutant has been investigated over the range of 20–50 ppm. The effect of UV power on photo-degradation of 4C2AP has been investigated over the range of 4–12 W. For the experiments related to the effect of initial pH over the range of 2–8, the pH of solution was adjusted using 0.1 M H_2SO_4 and 0.1 M NaOH solutions as per the requirement.

For the microwave related experiments, glass reactor with the solution was placed at the centre of the rotating plate directly below the magnetron source. After each irradiation cycle (5 min), it was observed that the temperature of the solution increased to 50 ± 2 °C as measured using a digital thermometer. The solution was then cooled to 30 ± 2 °C using cold water bath and 3 ml samples were withdrawn each time. Owing to limitations of the experimental setup, direct measurement of temperature during reaction was not feasible. The sequential treatment of microwave and UV irradiation was performed maintaining initial temperature as 30 ± 2 °C for each sequential cycle. The other conditions for the sequential operation include optimized initial concentration of 4C2AP as 20 ppm and pH of 6. For every treatment cycle (5 min), the solution has been treated for equal time using each treatment scheme (2.5 min for MW treatment and 2.5 min for UV treatment). In order to intensify the degradation, an oxidizing agent H_2O_2 and catalyst TiO_2 have been used as process intensifying additive at optimized conditions of both UV and microwave. All the experiments were performed for the 30 min of treatment time and samples were withdrawn at periodic intervals of 5 min for analysis.

2.4. Analysis

The concentration of 4C2AP was determined using the High Pressure Liquid Chromatography (HPLC) unit supplied by Agilent Technologies (1200 infinity series), USA. HPLC instrument used in the work comprised of Auto sampler, HPLC pump, UV detector and HPLC column eclipse plus C-18 column having dimensions 2.1 × 50 mm. Mixture of methanol and de-ionized water (70:30 ratio) was used as mobile phase for the analysis at a flow rate of 0.1 ml/min and the wavelength of 292 nm was set for UV detection. The total organic carbon (TOC) content of the samples at optimized treatment conditions was analyzed using ANATOC-II Series TOC analyzer obtained from SGE International Pty. Ltd., Australia. The degradation products of 4C2AP were identified using Thermo-Scientific ISQLT single quadruple gas chromatography–mass spectrometry (GC–MS) unit. The toxicity analysis was performed using antimicrobial test based on agar-well diffusion method considering two gram-positive bacterial strains as *B. licheniformis* and *L. aerocolonigenes* and two gram-negative bacterial strains as *P. aureofaciens* and *A. eutrophus*. Samples collected at regular intervals of time from the experiments giving maximum degradation i.e. the approach of MW + UV + TiO_2 + H_2O_2 (three