

Ultrasound assisted catalytic wet peroxide oxidation of phenol: kinetics and intraparticle diffusion effects

Apostolos N. Nikolopoulos, Olga Igglessi-Markopoulou, Nikolaos Papayannakos *

School of Chemical Engineering, National Technical University of Athens, Zografou Campus, Heroon Polytechniou Str. 9, Athens 15780, Greece

Received 4 February 2004; received in revised form 11 October 2004; accepted 11 October 2004

Available online 25 November 2004

Abstract

The combination of ultrasound irradiation and catalytic wet peroxide oxidation was used as a means to degrade phenol. Direct and indirect irradiation were employed, while experiments in the absence of ultrasound were used as reference. A mixed (Al–Fe) pillared clay named FAZA, was used as a catalyst in the form of powder, extrudates and crushed extrudates. Ultrasound was found to clearly enhance the extrudates performance, increasing the conversion at 4 h by more than 6 times under direct and almost 11 times under indirect irradiation. This observation is attributed to the reduction of diffusion resistance within the catalyst pores. The overall sonication-catalytic wet peroxide oxidation process appears very promising for environmental purposes.

© 2004 Elsevier B.V. All rights reserved.

Keywords: Phenol; Ultrasound; Catalytic wet peroxide oxidation; Kinetics; Intraparticle diffusion effects; Wastewater treatment

1. Introduction

Ultrasound irradiation is a novel advanced oxidation process that has emerged as an answer to the growing need for lower levels of contaminants in wastewater. The sonochemical degradation of a variety of organic contaminants has already been studied. Substrates such as chlorinated hydrocarbons [1,2], carbon tetrachloride [3], CFCs [4], aromatic hydrocarbons [5,6], polycyclic aromatic hydrocarbons [7], PCBs [8], phenolic compounds [9,10], dyes [11], pesticides and herbicides [12,13] and hydrogen sulfide [14] are usually converted to organic acids, carbon dioxide and inorganic ions as final products. Even micro-organisms found in water have been subjected to ultrasonic treatment [15]. Further, it has been shown that the ultrasonic pre-treatment

of sewage sludge can accelerate the subsequent anaerobic digestion [16]. The compounds produced during ultrasonic treatment of contaminants are found to be less toxic, which can then allow biological treatment [17]. The degradation of organic contaminants through acoustic cavitation proceeds through three distinct pathways: (a) oxidation by hydroxyl radicals, (b) pyrolytic decomposition and (c) supercritical water oxidation [18].

The use of heterogeneous catalysts on the other hand, is a very promising way to treat the wastewater streams as it permits treatment under mild temperature and pressure conditions without the necessity of difficult catalyst recovery required in homogeneous catalysis. The catalytic oxidation method employed in the present study involves two powerful features. Firstly, a mixed (Al–Fe) pillared clay named FAZA is used as solid catalyst. This catalyst has already been tested with success in the catalytic degradation of phenol and it was characterised by low leaching and high oxidation activity [19]. Besides, using clays instead of metals or metal oxides as catalysts is environmentally benign, due to the natural origin of

* Corresponding author. Tel.: +30 210 7723239; fax: +30 210 7723155.

E-mail address: npap@chemeng.ntua.gr (N. Papayannakos).

the first and the demanding disposal of the latter. Secondly, the use of hydrogen peroxide as oxidant is also helpful, since no additional pressure is required, as in the case of gaseous oxidants, such as O_2 or O_3 .

It is noteworthy that both ultrasound irradiation and clay catalysts are recognised as examples of “green” techniques [20] and “green” technology [21] respectively.

The aim of the present study is the investigation of the potential benefits of the combined use of ultrasound irradiation and catalytic oxidation for decomposition of phenol, a known and recalcitrant contaminant found in wastewater.

2. Materials and methods

2.1. Materials

Phenol was purchased from Fluka, while methanol and water (HPLC grade) were furnished by J.T. Baker. Hydrogen peroxide was purchased from Merck. Deionised water was used throughout the experiments.

The freshly prepared Al–Fe pillard clay (FAZA) [22] was in the form of powder. Then the FAZA powder was mixed with binders to form a workable paste for extrusion and the calcined cylindrical particles of 1 mm diameter and 2–3 mm length are named extrudates. Since the process for the preparation of the extrudates affects the catalyst intrinsic activity, some of the extrudates were crushed and the particles ($2\mu\text{m}$ average size) were used to evaluate the particles intrinsic activity. A comparison of the FAZA powder and crushed extrudates activity (Table 1) reveals that the extrusion process has a strong effect on the FAZA powder activity, since the crushed extrudates retain only 23.7% of the initial FAZA powder activity. The catalyst specific surface area was $240 \pm 10\text{ m}^2/\text{g}$, while the pore volume was estimated at $0.14\text{ cm}^3/\text{g}$.

2.2. Equipment

A Sonics and Materials Inc. ultrasonic system, model VCX 400, operating at a frequency of 20 kHz with a maximum power output of 400 W, was used to introduce ultrasound (US) into the reaction mixture. Both probe

and cup-horn configurations were employed in order to study the effects of the direct and indirect irradiation respectively. Stirring was achieved by a mechanical stirrer from IKA Labortechnik in the presence of extrudates, while a magnetic stirrer from the same supplier was used in the case of powder or crushed extrudates. The reactions were carried out in a cylindrical glass vessel (65 mm diameter), while in the case of the cup-horn configuration, a vessel (60 mm diameter, 70 mm height) provided by the ultrasound device supplier was used. Samples of the reaction mixture were subjected to HPLC analysis after being filtered through Macherey-Nagel PET filters ($0.2\mu\text{m}$ pore size). A Waters reverse phase C_{18} column was used, while the pump and the UV–Vis detector were supplied by Varian.

2.3. Experimental procedure

Phenol degradation experiments involved an aqueous phenol solution (100 mL , $5 \times 10^{-4}\text{ M}$). The solid catalyst (0.5 g) was suspended in the solution under continuous stirring. After 15 min the addition of hydrogen peroxide was started which corresponded to the initiation of the reaction. Hydrogen peroxide (0.1 M) was added at a rate of 2 mL/h . The pH of the reaction mixture was monitored and maintained between 3.5 and 4, the optimum pH value for the catalyst oxidation activity, according to Barrault et al. [19]. The reactions were carried out for 4 h, unless otherwise stated. The ultrasound source was set to 50% of its quoted maximum power, which corresponded to approx. 30 W, according to calorimetric determination performed in the absence of cooling water for the probe configuration [23]. The Weissler reaction was employed as a chemical dosimeter, leading to the production of 0.6 mmol of I_2 after 30 min of direct sonication and of 0.15 mmol of I_2 during indirect sonication, following the procedure described in [23]. The liquid height in the reactor was 35 mm and the probe

Table 1
Major reaction rate coefficients for the degradation of phenol under sonication and/or catalytic oxidation

Degradation system	Reaction rate coefficient k_1 (min^{-1})
US (probe)	8×10^{-4}
FAZA powder + H_2O_2	1.1×10^{-1}
FAZA crushed extrudates + H_2O_2	2.6×10^{-2}
FAZA extrudates + H_2O_2	4×10^{-4}
FAZA extrudates + H_2O_2 + US (probe)	2.1×10^{-3}
FAZA extrudates + H_2O_2 + US (cup-horn)	1.8×10^{-2}

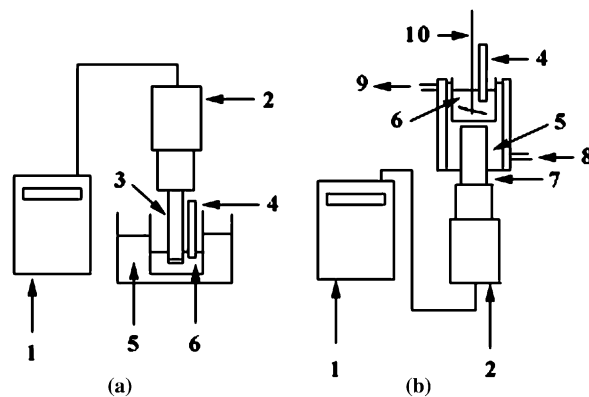


Fig. 1. Experimental set-up. (a) Probe configuration, (b) cup-horn configuration; (1) generator, (2) transducer, (3) probe, (4) temperature indicator, (5) water bath, (6) reaction mixture, (7) horn, (8, 9) inlet and outlet of cooling water, (10) stirrer.

Download English Version:

<https://daneshyari.com/en/article/1270114>

Download Persian Version:

<https://daneshyari.com/article/1270114>

[Daneshyari.com](https://daneshyari.com)