



Relationship between acceleration of hydroxyl radical initiation and increase of multiple-ultrasonic field amount in the process of ultrasound catalytic ozonation for degradation of nitrobenzene in aqueous solution



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ABSTRACT

The synergetic effect between ozone and ultrasound can enhance the degradation of nitrobenzene and removal efficiency of TOC in aqueous solution, and the degradation of nitrobenzene follows the mechanism of hydroxyl radical ($\cdot\text{OH}$) oxidation. Under the same total ultrasonic power input condition, the degradation rate of nitrobenzene (k_{NB}), the volumetric mass transfer coefficient of ozone ($k_{\text{L}a}$), and the initiation rate of $\cdot\text{OH}$ (k_{OH}) increases with introduction of additional ultrasonic field (1–4) in the process of ozone/ultrasound. The increasing amount of ultrasonic fields accelerates the decomposition of ozone, leading to the rapid appearance of the maximum equilibrium value and the decrease in the accumulation concentration of ozone in aqueous solution with the increasing reaction time. The increase in mass transfer of gaseous ozone dissolved into aqueous solution and the acceleration in the decomposition of ozone in aqueous solution synchronously contribute to the increase of $k_{\text{L}a}$. The investigation of mechanism confirms that the increasing amount of ultrasonic fields yields the increase in cavitation activity that improves the mass transfer and decomposition of ozone, resulting in acceleration of $\cdot\text{OH}$ initiation, which determines the degradation of nitrobenzene in aqueous solution.

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1. Introduction

Nitrobenzene is a pale yellow liquid with the odor of bitter almonds, which is used as a raw material for aniline and aniline dyes, intermediate for benzidine, many dyestuffs, and an industrial solvent in polishes. It affects the central nervous system and produces fatigue, headache, vertigo, vomiting, general weakness, unconsciousness, and coma [1]. Therefore, nitrobenzene is considered to be a highly toxic aromatic compound, and is listed as a priority pollutant [2,3]. Consequently, exploration of effective methods for its degradation represents an important research challenge. Various advanced oxidation processes (AOPs), defined

as the oxidation processes which initiate hydroxyl radicals ($\cdot\text{OH}$), have been studied for the degradation of nitrobenzene in aqueous solution because the electron-deficient character of the nitro-group prevents its oxidation by conventional chemical oxidation and its mineralization by microorganisms.

As an attractive and promising AOP, ultrasound catalytic ozonation has been found to be effective for the degradation of a variety of environmentally hazardous pollutants. This combined process overcomes the drawbacks of ozonation alone and ultrasound alone, which are the high cost, only partial oxidation of contaminants, and lesser extent of mineralization. Sonolysis, ozonolysis, and a combination process are used to investigate the degradation of nitrobenzene, 4-nitrophenol, and 4-chlorophenol at frequencies of 20 and 500 kHz, and the correlation of apparent rate enhancement at 20 kHz and retardation at 500 kHz is consistent with a pathway involving the thermolytic destruction of ozone to form atomic oxygen, and atomic oxygen then reacts with water vapor in cavitation bubbles, yielding gas phase $\cdot\text{OH}$ [4]. The results of

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ozonation combined with ultrasound for the removal of tetracycline show that the tetracycline removal follows pseudo-first-order kinetics, and removal rate increases with increasing gaseous ozone concentration, gas flow rate and power density, but decreases with increasing initial tetracycline concentration [5]. Moreover, addition of goethite catalyst can improve further the degradation performance of tetracycline in the system of ozonation/ultrasound [6]. Ultrasonic irradiation in the presence of ozone is demonstrated to be effective for the rapid oxidation of oxalic acid, bioxalate, and oxalate in aqueous solution to CO_2 and H_2O , and the degradation rate of bioxalate exposed simultaneously to ultrasound and ozonation is found to be 16-times faster than predicted by the linear addition of ozonation and ultrasonic irradiation rates [7]. In the presence of ozone accelerates substantially the sonolytic destruction rate of methyl *tert*-butyl ether by a factor of 1.5–3.9 depending on its initial concentration, and the reaction mechanism involves three parallel pathways namely the direct pyrolytic decomposition, the direct reaction with ozone, and the reaction with $\cdot\text{OH}$ [8].

The presence of ozone assists sonodegradation of 2,4,6-trichlorophenol remarkably from 4.1% to 21.9%, and 17.9% TOC reduction is observed using combined operation of ozone and ultrasound [9]. Ozone is much suited for the enhanced degradation of phenol by ultrasound/zero valent iron under alkaline conditions due to the two simultaneously acting effects [10]. In addition, the patented Ozonix[®] technology utilizing the synergistic effects of ozone, hydrodynamic cavitation, acoustic cavitation and electrochemical oxidation/precipitation is a chemical free process that can be used to manage the quality of the supply of raw water, flow-back water, produced and shallow ground fluids and petroleum industry wastewaters. For example, it has been successfully proven while processing recycled fluids at commercial sites on over 750 oil and natural gas wells during hydraulic operations around the United States. Its main mechanism for intensification is expected to be generation of additional oxidation mechanisms and elimination of the mass transfer resistances due to the turbulence generated under cavitating conditions [11].

Multiple-field ultrasound has been used recently with great success to investigate the removal of contaminants from water as compared to single-field ultrasound. It is reported that the cavitation yields (net quantification of the chemical effects) obtained for the degradation of formic acid are order of magnitude higher as compared to the conventional reactors, and a combination of more frequencies can result in better cavitation effects (higher cavitationally active volume and cavitation intensity to enhance the reaction rates) [12]. The results confirm that it is the best to operate the multiple ultrasound sources with no phase difference as it leads to uniform pressure field distribution in the cavitation reactor and hence maximum cavitation activity [13]. Dual-field ultrasound can improve the degradation efficiency of nitrobenzene compared to that of the single field because the combined ultrasonic irradiation causes more efficient mass transfer, leading to increased cavitation activity [14,15]. However, the enhancement efficiency of catalytic ozonation with multiple-field ultrasound has never been researched for the degradation of micro-pollutant in aqueous solution.

The primary objective of this study was to investigate the process characteristics of catalytic ozonation by multiple-field ultrasound from the factors of degradation efficiency of organic micro-pollutant, mass transfer of ozone, and initiation of $\cdot\text{OH}$. The originality of the present study is to reveal the enhancement mechanism of multiple-field ultrasound catalytic ozonation based on the relationship between acceleration of $\cdot\text{OH}$ initiation and increase of multiple-ultrasonic field amount. Nitrobenzene is selected as the target organic compound due to its specific indication efficiency of $\cdot\text{OH}$.

2. Experimental

2.1. Materials and reagents

Nitrobenzene purchased from Beijing Chemical Factory (China) was purified by distillation pretreatment to 99.80%. All solutions were prepared with Milli-Q water purified by a Millipore Q Biocel system ($R = 18.2 \Omega$). All other chemicals used in the experiments were analytical grade reagents and were used without further purification.

2.2. Experimental procedure

The experiments were performed in a semi-continuous ultrasonic reactor depicted schematically in Fig. 1, which was made entirely of stainless steel with a breadth of 11.5 cm, a depth of 11.5 cm and a height of 26.8 cm. The four flattened sides of the reactor were respectively mounted with the four same piezoelectric transducers, each of which was arranged in one side of the reactor and all driven at 28 kHz (A, B, C and D field). The emitting system was connected to a frequency generator and a power supply. The emphasis of the present study is located on the relationship investigation between acceleration of $\cdot\text{OH}$ initiation and increasing amount of multiple-ultrasonic fields under the same total ultrasonic power input condition, namely the total ultrasonic power input was controlled at 120 W either individually (A, the same as B, C or D field) or in combinations (AB (60 W + 60 W), ABC (40 W + 40 W + 40 W) or ABCD (30 W + 30 W + 30 W + 30 W) field). Therefore, typical power intensity and power density were same to the entire individual or combined multiple-field, which were 0.39 W cm^{-2} and 38.5 W L^{-1} , respectively, according to the method described by the previous study [16].

Before the experimental operation, the reactor was pre-ozonated for 4 min to satisfy any ozone demand in the reactor, and then was washed several times with distilled water to exclude any possible side effects. During the degradation experiment, the synthetic solution (4 L) with the nitrobenzene concentration of $50 \mu\text{g L}^{-1}$ was pumped into the reactor by a MP-20R magnetic pump (Shanghai Xishan Pump Co. Ltd., China) and then circulated at a rate of 3.5 L min^{-1} . Ozone was produced from pure oxygen (Harbin Gas Co. Ltd., China, 99.999%) through an XFZ-5 ozone generator (Qinghua Tongli Co. Ltd., China) at a power setting of 40 W, and was subsequently fed into the reactor to contact thoroughly with water samples through a porous titanium plate at its bottom. The total applied ozone in this experiment was controlled at 1.2 mg L^{-1} . Simultaneously, ultrasonic irradiation was operated to combine with the process of ozonation. A cooling system was kept outside the reactor, and cold water was pumped from a thermostatic bath in order to control reaction temperature constantly at 298 K. Water samples were taken from the reactor at various reaction time points to analyze the residual concentration of nitrobenzene. The oxidation reaction was quenched by the addition of a small amount of sodium thiosulphate solution.

In addition, compared to the scavenger effect of buffer solution (HCO_3^- , CO_3^{2-} , H_2PO_4^- , and HPO_4^{2-}), the degradation of trace nitrobenzene (initial concentration $50 \mu\text{g L}^{-1}$) led to a slight conversion of initial pH (6.68–6.79) which could not affect the experiment, and could be neglected. Therefore, the experiments were carried out at initial pH 6.85 in the present study without adding any buffer solution to maintain the pH at a constant value. For the whole study, two duplicate experiments were carried out for residual part of the investigation in order to obtain the accuracy value, namely the data presenting in figures were the average calculated using the three initial values of the experiments, and the experimental errors are less than 5.0%.

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