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Characteristic mechanism of ceramic honeycomb catalytic ozonation enhanced by ultrasound with triple frequencies for the degradation of nitrobenzene in aqueous solution

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ABSTRACT

Ceramic honeycomb catalytic ozonation enhanced by ultrasound with triple frequencies was carried out in semi-continuous mode to investigate the degradation efficiency of nitrobenzene in aqueous solution. The combination process can enhance remarkably the degradation efficiency of nitrobenzene compared to the additive effects of single operations, and the degradation of nitrobenzene follows the mechanism of hydroxyl radical (·OH) oxidation. The enhancement function is even more pronounced in the presence of ultrasound with orthogonal triple frequencies due to the obvious synergetic effect which can accelerate the transformation and the decomposition of ozone, increase the utilization efficiency of ozone, and enhance the initiation of ·OH and the formation of H_2O_2, resulting in the rapid formation of an increasing diversity of byproducts and the higher degree of mineralization of total organic carbon. The investigation of enhanced mechanism indicates the introduction of ultrasound can prevent deactivation by continuously cleaning the surface of catalyst, and can accelerate the cleavage of the bond as well as speed up the diffusion of oxidative intermediate from the heterogeneous surface to the aqueous solution due to the weakening of the bond derived from the ultrasonic shock, leading to the production of the synergetic effect among ozone, ceramic honeycomb and ultrasound.

1. Introduction

The chemical effects of high intensity ultrasound arise from acoustic cavitations of liquids [1]. However, like other advanced oxidation processes (AOPs) or chemical methods, total mineralization is difficult to obtain with ultrasound alone, especially for the treatment of recalcitrant pollutants or mixtures of pollutants [2]. Hence, combinative or hybrid processes involving the use of ultrasound with other AOPs are becoming popular in water treatment since they are found to be more effective in degrading some recalcitrant compounds which are otherwise difficult to handle [3].

Heterogeneous catalytic ozonation, as an alternative technique of AOP, has received much attention in water treatment due to its high oxidation potential [4]. Nitrobenzene, one of the fastest-growing end-use synthetic products of benzene, has been widely dispersed in water and soil, causing great environmental concern [5]. In order to afford the inexpensive and effective processes for the water treatment, various chemical reduction treatment and AOPs have been studied for the degradation of nitrobenzene in aqueous solution, such as Fe^0 reduction [6,7], photocatalysis [8] photoassisted Fenton oxidation [9], and supercritical oxidation [10]. In addition, several researches have been reported on the degradation of nitrobenzene in aqueous solution by the heterogeneous catalytic ozonation processes, including nano-TiO_2, Mn-loaded granular activated carbon (MnO_x/GAC), ceramic honeycomb (CH), Mn–CH, Mn–Cu–K–CH and synthetic goethite [11].

Moreover, it can be found that the presence of ultrasound can enhance the ozonation of nitrobenzene [12]. Many researches have been reported on the removal of contaminants in aqueous solution by the process of ozone/ultrasound, including methyl orange, phenol, *p*-nitrotoluene, aniline, anthraquinone dye, C.I. reactive blue 19, chitosan and pentachlorophenol [13]. However, there is no report on the enhanced heterogeneous catalytic ozonation by ultrasound for the degradation of organic compound, especially the enhancement by ultrasound with different triple-frequency for the trace organic micro-pollutant (μg L^{-1} level).

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The primary objective of this study was to compare the degradation of organic micropollutant in aqueous solution by the different processes, including ultrasound alone, ozone alone and ultrasound/ozone. Nitrobenzene reacts slowly with molecular ozone ($0.09 \pm 0.02\ M^{-1}\ s^{-1}$) [14], while reacts quickly with hydroxyl radical (·OH) ($2.2 \times 10^8\ M^{-1}\ s^{-1}$) [15]. Therefore, nitrobenzene, as a special indicator of ·OH and a major environmental pollutant, is chosen as a target organic compound due to its toxicity of the central nervous system and its refractory nature to conventional chemical oxidation. The originality of the present study was to reveal the characteristic enhanced mechanism based on the investigation of synergistic effect between CH heterogeneous catalytic ozonation and ultrasound with different triple frequencies for the degradation of nitrobenzene in aqueous solution.

2. Experimental

2.1. Materials and reagents

Monoliths of CH (Shanghai Pengyinaihuo Material Factory, China) were used as the catalyst. These blocks have the following characteristics: cylindrical shape with a breadth of 11.4 cm, a depth of 11.4 cm and a height of 1.5 cm, wall thickness 0.4 mm, cell density 300 cells per square inch and weight of a single block of CH was 7.8–8.2 g. Unbuffered synthetic solution was prepared by spiking 50 $\mu g\ L^{-1}$ nitrobenzene (Beijing Chemical Factory, China, purified by distillation pretreatment, 99.80%) in Milli-Q water (Millipore Q Biocel system). All other chemicals used in the experiments were analytical grade reagents, and were used without further purification.

2.2. Experimental procedure

The experiments were carried out in a semi-continuous ultrasonic reactor, as shown 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 four series of piezoelectric transducers, which were arranged in series and all driven at 40, 20, 28 and 28 kHz (A, B,C and D field), respectively. The emitting system was connected to a frequency generator and a power supply, and the ultrasonic power input of every field was 50 W. The emphasis is located on the mechanism investigation of ultrasonic field fixed at the different direction, namely C and D field, for the enhancement efficiency of CH catalytic ozonation in the presence of AB fields because ABD fields is an orthogonal triple frequencies, and ABC fields is composed of an opposite dual frequencies and an orthogonal single frequency. Therefore, typical power intensity and power density were same to ABC and ABD, which were 0.70 $W\ cm^{-2}$ and 48.1 $W\ L^{-1}$, respectively, according to the method described by the previous study [28]. The reactor was sealed during the reaction, and the volume of the atmosphere above the solution in the reactor is 132.25 cm^3, namely 11.5 cm × 11.5 cm × 1.0 cm, which presents no obvious contribution to the experiments. Except for this less volume of atmosphere and ozone, no gases (nitrogen, argon, oxygen) were used to mix and sparge the reaction solution during sonication.

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. The solid catalysts (3 blocks) were fed into the reactor by taking off its coping.

During the degradation experiment, the synthetic solution (4 L) with the nitrobenzene concentration of 50 $\mu g\ L^{-1}$ was pumped into the reactor by a MP-20R magnetic pump (Shanghai Xishan Pump Co. Ltd., China) and then circulated at a rate of 4 $L\ min^{-1}$. 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 CH catalysts and water samples through a porous titanium plate at its bottom. The total applied ozone in this experiment was controlled at 1.0 $mg\ L^{-1}$ (mg ozone/the sample volume). Simultaneously, sonication was performed to combine with the process of CH catalytic ozonation. A cooling system was kept outside the reactor and cold water was

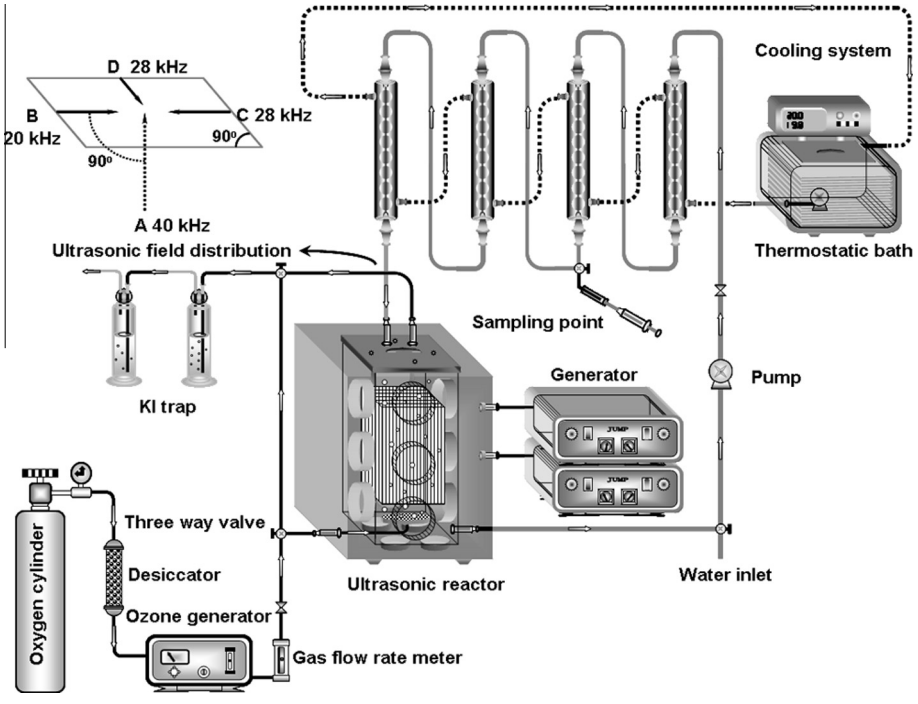

Fig. 1. Schematic of experimental apparatus.

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