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Catalytic ozonation of N,N-dimethylacetamide (DMAC) in aqueous solution using nanoscaled magnetic $CuFe_2O_4$

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ABSTRACT

N,N-dimethylacetamide (DMAC) which is widely used in chemical industry has been listed as a well-known chemical substance. It could cause reproductive toxicity. Therefore, it is urgent to develop methods for degradation of DMAC to minimize its ecological risk. In this study, copper ferrite ($CuFe_2O_4$) magnetic nanoparticles (MNPs) were prepared by sol-gel combustion method for the degradation of DMAC by catalytic ozonation. The results suggest that the synergetic effect between $CuFe_2O_4$ MNPs and O_3 in the $CuFe_2O_4/O_3$ process was significant and the degradation efficiency of DMAC by $CuFe_2O_4/O_3$ process (i.e., 95.4%) was much higher than sole O_3 process (55.4%), sole $CuFe_2O_4$ process (0%), $CuFe_2O_4/O_2$ process (0%), and Fe_2O_3/O_3 process (32.1%), which confirmed the superiority of the $CuFe_2O_4/O_3$ process. In addition, under the optimal conditions, 95.4% removal of the DMAC (200 mg/L), 30.1% removal of COD, 22.3% removal of TOC could be achieved after 120 min treatment by $CuFe_2O_4/O_3$ process. The BOD_5/COD (B/C) ratio was also elevated from 0.03 to 0.33, which indicated the significant improvement of biodegradability. Furthermore, the $CuFe_2O_4$ MNPs showed high catalytic activity, stability and recyclability for DMAC degradation. In particular, leaching of metal ions from reused $CuFe_2O_4$ MNPs was negligible. The radical scavenging experiment certified that the surface hydroxyl groups on $CuFe_2O_4$ MNPs are ozone decomposition sites and the dominant oxide species in $CuFe_2O_4/O_3$ process is $HO^{\cdot}$. Finally, a possible reaction mechanism of $CuFe_2O_4/O_3$ process was proposed according to the present literature and analyses of data. It can be concluded that the high-efficient $CuFe_2O_4/O_3$ process was mainly resulted from the combination of sole ozone oxidation, heterogeneous and homogeneous catalytic ozonation. Therefore, the $CuFe_2O_4/O_3$ process was a simple, nonhazardous, efficient and promising technology for the degradation of DMAC.

1. Introduction

DMAC is a fine industrial solvent for both electrolytes and non-electrolytes. It is widely used for agrochemicals, pharmaceuticals, man-made fibers, industrial coatings, fine chemicals films, paint strippers and other applications [1]. These diverse sources contribute to the presence of DMAC in the environment and a large amount of DMAC is released into the environment during manufacturing and application, even after recovery treatment [2]. Due to its physicochemical properties, DMAC is easily absorbed by inhalation and ingestion and can penetrate the skin [3]. Exposure to DMAC may cause skin irritation, headache, inappetence, fatigue, and hepatic damage. Recently, DMAC has been listed as a well-known chemical substance, which could cause reproductive toxicity [4]. Considering its wide presence, toxicity, and slow rate of degradation, it would lead to an adverse environmental impact on our surroundings and thus endanger public health and welfare if the DMAC wastewater is discharged into the environment directly.

In the literature, there are some studies on the treatment process of DMAC wastewater, such as sorptive microextraction [2], photocatalytic oxidation [4]. However, the application of these processes is still limited due to the operating cost or treatment efficiency. Hence, it is necessary to develop a more cost-effective treatment method to degrade DMAC before it was discharge into the environment. Over the last decade, ozonation has received much attention due to its high oxidation potential on organic matters [5–7]. However, the direct oxidation by ozone alone is relatively slow and selective [8]. The catalytic ozonation has emerged as a powerful technology for the treatment of pollutants in aqueous solution, even for refractory and toxic compounds. Catalytic ozonation includes heterogeneous catalytic ozonation and

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homogeneous catalytic ozonation. However, the application of homogeneous catalytic ozonation in water treatment would require the removal of metal ions from the treated water [9]. Heterogeneous catalytic ozonation due to its higher effectiveness in the degradation of refractory organic pollutants and lower negative influence have obtained an increasing interest in the drinking water and wastewater treatment [10–12]. The most frequently used solid catalysts in ozonation are metal oxides, metals on supports and minerals modified with metals. Several studies have shown that metal oxides can be efficient for the catalytic ozonation of refractory organic pollutants [13–15]. Efficient catalytic ozonation process have been reported via different approaches, such as accelerating $HO^{\cdot}$ production from ozone, enhancing the chemical adsorption of target pollutants on the surface of the catalyst or increasing ozone mass transfer and utilization of ozone [16].

In recent years, the spinel structured ferrites with general formula MFe_2O_4 (M = Mn, Ni, Co, Zn, Mg, Cu, etc.) have attracted extensive attention and have been widely used in many applications due to their unique dielectric, magnetic and optical properties [17–20]. In particular, its magnetic property makes its separation from water very easy. As one of spinel ferrites, $CuFe_2O_4$ as a heterogeneous catalyst has been attracted considerable attention in heterogeneous advanced oxidation processes (AOPs) due to its chemical stability, medium saturation magnetization and mechanical strengths [21,22]. Because its chemical stability of $CuFe_2O_4$, the leaching of heavy metals from the solid phase can be significantly reduced. In addition, the magnetic property of $CuFe_2O_4$ makes its separation from water very easy. Xu et al. and Guan et al. reported that magnetic $CuFe_2O_4$ could effectively activated peroxymonosulfate to produce sulfate free radicals ($SO_4^{\cdot -}$), which is a powerful oxidant with promising applications to degrade refractory organic contaminants [23,24]. Feng et al. reported magnetic $CuFe_2O_4$ spinel nanoparticles can activated H_2O_2 to produce hydroxyl free radicals ($HO^{\cdot}$) and could effectively increase degradation rate of sulfanilamide [25]. Liu et al. also reported $CuFe_2O_4$ can effectively catalytic ozonation of Acid Red B in aqueous solution [26].

To our best knowledge, catalytic ozonation of DMAC with $CuFe_2O_4$ in aqueous solution is rarely reported. In this study, therefore, the $CuFe_2O_4$ MNPs, was prepared by the sol-gel combustion method and applied to catalytic ozonation of DMAC in aqueous solution as the superior active and environment-friendly heterogeneous catalyst. Compared to other preparation methods, sol-gel combustion method can effectively facilitate the mixing of different cations in the complex solutions [27]. Firstly, the performance of different systems for DMAC degradation was evaluated. In addition, the key operating parameters (e.g., catalyst dosage, O_3 flow rate and initial solution pH) of the $CuFe_2O_4/O_3$ process were optimized, respectively. Furthermore, the stability and reusability of the catalyst were estimated. Finally, a possible reaction mechanism was proposed on the basis of the analyses of data and present literature.

2. Materials and methods

2.1. Chemicals

N,N-dimethylacetamide, Cupric nitrate ($Cu(NO_3)_2{\cdot}3H_2O$), Ferric nitrate ($Fe(NO_3)_3{\cdot}9H_2O$), citric acid, sodium hydroxide, sulfuric acid were purchased from Chengdu Kelong chemical reagent factory. All chemicals used in the experiment were of analytical grade and used as received without further purification. Deionized water was used throughout the whole experiment process.

2.2. Preparation of $CuFe_2O_4$ MNPs catalysts

$CuFe_2O_4$ MNPs were prepared by sol-gel combustion method. An aqueous solution of Copper nitrate (0.005 mol), ferric nitrate (0.01 mol) was stirred at 60 °C for 2 h, and then citric acid (0.015 mol) was added. The resultant homogeneous solution was stirred for another 2 h at 60 °C, and then evaporated to remove water. The obtained nitrate-citrate complex gel was calcined at 400 °C for 2 h to decompose the citric acid until fine oxide powders were obtained [27]. For a comparison, CuO and Fe_2O_3 nanoparticles with the comparable particle size with that of $CuFe_2O_4$ MNPs were also prepared by the same method by individually using Copper nitrate and ferric nitrate as precursor, respectively.

2.3. Catalytic ozonation procedure

Batch degradation experiments of DMAC were carried out in a 250 mL flat bottom beaker. Ozone was produced onsite from pure oxygen through an ozone generator, and the inlet concentration of ozone was about 4.6 mg/L. In each semi-batch experiment, 150 mL DMAC aqueous solution (200 mg/L) was transferred into a 250 mL beaker, meanwhile the desired catalysts dosage was added into the beaker. Then, ozone with a desired flow rate was continuously bubbled into the reacting solution through a gas diffuser. To ensure the full fluidization of the catalysts in the reaction solution, the slurry was stirred by a mechanical stirrer with a stirring speed of 300 rpm, which could improve the mass transport rate [28]. The whole experiment process was performed at a running temperature of 25 ± 1 °C by heating in water bath. Water samples were withdrawn at regular intervals and filtered by 0.45 μm one-off syringe filter to ensure the solution was free from suspended particles prior to quantification. To test the recyclability and stability of the $CuFe_2O_4$ MNPs, the particles were collected by magnetic separation after reaction, washed several times with pure water, and dried at 70 °C for 8 h before reuse. Solution pH was precisely adjusted by H_2SO_4 and NaOH in all reaction for the comparison. All the experiments were conducted in triplicate and error bar represented the standard deviation of the replicate experimental data.

2.4. Analytical method

Details pertaining to analytical method in this study are provided in the Supporting Information.

3. Result and discussion

3.1. Characterization of $CuFe_2O_4$ MNPs catalysts

Fig. 1(a) shows the X-ray powder diffraction (XRD) pattern of the fresh $CuFe_2O_4$ MNPs. In the pattern of the $CuFe_2O_4$ MNPs, all of the diffraction peaks matched well with the published XRD pattern of the cuprospinel $CuFe_2O_4$ (PDF # 25-0283), which indicates that the prepared $CuFe_2O_4$ MNPs had great purity. The surface area and the pore structures of $CuFe_2O_4$ MNPs were studied by nitrogen adsorption and desorption isotherms (Fig. 1(b)). The Brunauer-Emmett-Teller (BET) surface area and average pore size of $CuFe_2O_4$ MNPs were 63.03 m^2/g and 11.96 nm.

The SEM image showed that $CuFe_2O_4$ MNPs were mostly quasi-spherical with particle sizes of about 40 nm (see Fig. S2 of Supporting Information). Fig. 2(a) shows that the elemental composition of the fresh $CuFe_2O_4$ MNPs was observed by using energy-dispersive spectrometer (EDS). EDS analysis was used to investigate the chemical composition of the catalyst, which suggests that the $CuFe_2O_4$ MNPs are composed of Cu, Fe and O. Meanwhile, the atomic ration of Cu to Fe was nearly equal to 1:2 in the sample, which was consistent with the molecular formula of the catalyst.

The state of elements in $CuFe_2O_4$ MNPs was determined by XPS (see Fig. 3), in which O, Fe, Cu elements peaks were detected (Fig. 3(a)). From Fig. 3(b), three intense peaks were observed at 932.9 eV (Cu $2p_{3/2}$), 940.2 eV (Cu $2p_{1/2}$) and 942.6 eV (Cu $2p_{1/2}$). The main peak at binding energies of 932.9 eV for Cu $2p_{3/2}$ line was attributed to Cu (II) [29,30]. The presence Fe (III) in $CuFe_2O_4$ MNPs particle was confirmed