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Study on degradation behavior of *N,N*-dimethylacetamide by photocatalytic oxidation in aqueous TiO_2 suspensions

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ABSTRACT

The degradation of *N,N*-dimethylacetamide (DMAC) on the condition of photocatalytic oxidation with the energy/volume ratio of 10 W/0.5 l has been investigated in aqueous solutions containing TiO_2 suspensions as photocatalysts. Focusing on the behavior of photocatalytic degradation of DMAC, the optimal separated conditions of the intermediate products were investigated with the high performance liquid chromatography (HPLC) using mixed eluent (0.4% CH_3COOH:CH_3OH = 92:8 by volume). Meanwhile, the main intermediate products were identified with the liquid chromatography mass-spectrometry (LC/MS). Therefore, the route and inter-relationships among the intermediates in photocatalytic degradation process of DMAC were first proposed. Furthermore, the mineralization degradation of DMAC was illustrated and identified as the final existence of the morphology of N (turning into NO_3^-) in the strong ion exchange column by the multi-dimensional chromatography.

Keywords: DMAC; Photocatalysis; Titanium dioxide; Liquid chromatography; Degradation; Intermediate

1. Introduction

DMAC is a good industrial solvent for both electrolytes and non-electrolytes [1]. It is miscible with water and a variety of organic solvents and enjoys wide applications in the manufacture of coatings, fibres, foils and lacquers, especially in the modern film production industry in recent years [2]. Potential human exposure is through inhalation of vapors or skin contact with the liquid substance in the workplace has a strong irritating effect to eyes, skin and mucous membrane. The occupational exposure limit (TLV) worldwide is accepted at the value of 10 ppm in air, assuming that it may be also safe for women of fertile age [3]. In addition, losses of the toxic substance may lead to an adverse environmental impact on our surroundings and thus endanger public health and welfare [4]. Therefore, the investigation for effective means of breaking down and removing DMAC is of environmental interest to regulating authorities everywhere. With the aggravation of environmental pollution, much attention has been paid to those highly effective and low consumptive techniques on pollution remediation.

Photocatalytic oxidation is one of the emerging technologies for the elimination of organic micro-pollutants because of the efficiency in their mineralization [5]. Several authors have demonstrated the efficiency of such processes and ideally, the end products are carbon dioxide, water, and inorganic mineral ions [6–10]. Solar-powered wastewater treatment using titanium dioxide

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as the heterogeneous photocatalyst is considered a cost-effective alternative to well established oxidation technologies such as ozonolysis or oxidation with hydrogen peroxide under UV illumination.

The process of photochemical degradation and biodegradation of DMAC has been discussed previously [2–4], but still rare, has been reported for mechanism with photocatalyzed degradation of DMAC. Moreover, the common determination results of degradation products with COD and UV absorbance methods hardly provide the important information including the behavior rules and relationships among the main intermediates of photocatalytic degradation process. The present study deals with the photocatalytic degradation of DMAC in the presence of TiO_2 particles and under ultraviolet light. The objectives were: (a) to propose a degradation pathway and to determine the main products by using LC/MS and the analysis techniques of full scanning spectrum with HPLC; (b) to evaluate the process of disappearance and the microscopic degradation behavior of DMAC; (c) to monitor the evolution of mineralization and main inorganic ions. Cost-effective treatments to complete compound mineralization are usually not practicable, and the presence of by-products during and at the end of the water treatment appears to be unavoidable. Therefore, by-product evaluation is the key to optimize each treatment and to maximize the overall process. The identification of possible formation of highly toxic compounds even at low concentrations is essential for the assessment of treated water.

2. Methods

2.1. Materials and chemicals

DMAC of analytical grade (99.5% purity) was purchased from the TCRY Corporation (Tianjin, China). Titanium dioxide (Degussa P-25) was purchased from Degussa Corporation, Germany. It has average particle size of 30 nm and BET specific surface area of 55 $m^2 g^{-1}$. The anatase and rutile percentage was 70% and 30% respectively. Doubly distilled water, filtered through 0.45 μm HA cellulose acetate membranes (Millipore) was used throughout the work. Stock solutions of DMAC (1000 mg l^{-1}) were prepared in water protected from light and stored at 5°C.

2.2. Irradiation procedure

The irradiation of the dispersions was carried out with a homemade photocatalytic apparatus equipped with a GPH212T5VH UVC lamp (10 W) from Heraeus (Hanau, Germany) (Fig. 1). Irradiation experiments of DMAC were carried out on aerated stirred solutions contained in a 500 ml cylindrical Pyrex glass reactor with UV light source in quartz glass sleeve (UV-A or UV-C, light energy:volume = 10 W:0.5 l) under continuous flushing by air at a rate of 0.8 l min^{-1} with pump and inserting needles. Degradations were performed on solutions containing the desired concentration of DMAC (100 mg l^{-1}) and amount of 3 g l^{-1} TiO_2 at natural pH and room temperature. Before being irradiated, the suspensions were allowed to stay in the dark for 60 min under stirring to reach adsorption equilibrium on to semiconductor surface. For the identification of photoproducts, 5 ml of DMAC solutions were sampled and treated by 0.22 μm filtration film and analyzed directly by HPLC and LC/MS. Composition analyses before irradiated were taken as controls, and analytical results of composition at different intervals after irradiated, such as 0.5, 1, 2.5 and 9 h, were compared with those of controls.

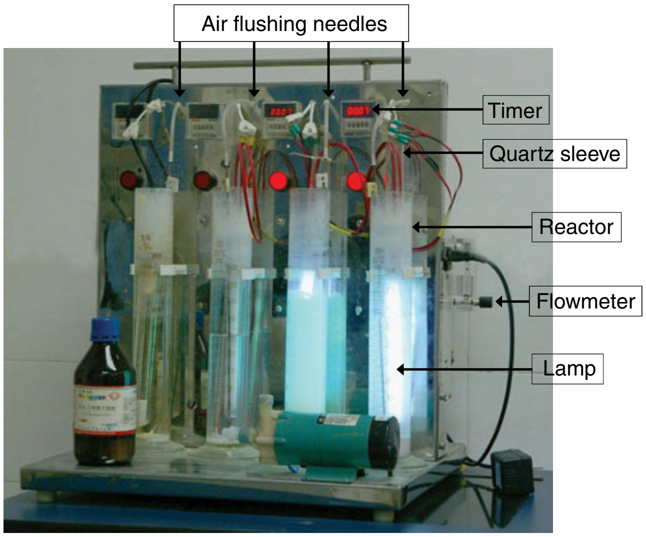

Fig. 1. The homemade photocatalytic apparatus.

2.3. Analytical procedures

2.3.1. Analytical methods

The formation of the intermediates for the photocatalytic oxidation of samples was analyzed with JASCO LC-2010 HPLC equipped with UV-vis Diode array detector and C18 ODS Hypersil column (5 μm, 250 × 4.6 mm) in the reverse phase mode. The HPLC separation was carried out within 10 min using mixed eluent (0.4% $CH_3COOH:CH_3OH = 92:8$ by volume) at injection amount of 20 μl and a flow rate of 1.0 ml min^{-1}. Since acetyl group in DMAC molecule has the absorption at wavelength 200 nm, the absorption spectrum diagram by the full ultraviolet spectral scanning was analyzed in order to get the sensitive response of the degradation intermediates. The intermediates in the photodegradation of the DMAC were identified by Waters Quattro Premier XE UPLC/MS/MS (ESI positive) with daughter scan mode. Optimized conditions were as follows: capillary voltage 0.5 kV, extractor voltage 4 V, desolvation gas (N_2) flow 500 l h^{-1}, cone gas (N_2) flow 50 l h^{-1}, collision gas (Ar) flow 0.2 ml min^{-1}, source temperature 110°C, desolvation temperature 350°C.

2.3.2. Mineralization studies

The concentration of nitrate ion was assayed with JASCO LC-2010 HPLC equipped with Shim-pack IC-A1 (12.5 µm, 100 mm × 4.6 mm i.d.) anion exchange column. The eluent was a mixture of phosphate buffer (5.0 mm) and methanol (the mass fraction of 2%) at pH 6.7 and a flow rate of 1.5 ml min^{-1}. Due to the same DAD detector, analytical results of A1 and C18 column can be compared to each other to identify the final mineralization product. Meanwhile chemical method (*N*-naphthylethylenediamine dihydrochloride spectrophotometric method) was used to detect existence of NO_2^-.

2.3.3. Degradation pathway evaluation

Identification of possible intermediate products during the photocatalytic reaction is the best way to understand the pathways of photocatalytic degradation reaction. To identify the possible intermediate products during the photocatalytic degradation, UPLC/MS/MS (ESI positive) experiments were conducted. The irradiated solutions of DMAC at different time intervals were observed. Major intermediates during the degradation process were proposed by using m/z values of molecular ions fragments.

3. Results and discussion

3.1. Chromatographic condition optimization

In the process of chromatography separation of DMAC degradation product, composition of mobile phase (methanol and water), flow rate and column temperature were optimized to get better HPLC chromatographic resolution. The results showed that the HPLC separation effect was very stable to flow and temperature while the methanol content of mobile phase would lead to improve peak shape and efficiency of separation. The HPLC can offer better separation effect when methanol content was less than 8% in mobile phase. Furthermore, acetic acid solution was added as polar modifier to adjust retention time of degradation product. Finally, the optimal separation mobile phase of 0.4% CH_3COOH/CH_3OH (92/8 by volume) was chosen to obtain the best separation efficiency.

3.2. Chromatographic behavior of the degradation products of DMAC

HPLC chromatogram of 0, 1, 2.5 and 9 h irradiated samples are shown in Figs. 2(a)–(d). Fig. 2(a) represented chromatogram of sample not treated with UV-C for the mentioned conditions of analysis in Section 2. DMAC was identified because of the single peak in the chromatogram at the retention time of 6.92 min ($T^{6.92}$). Chromatogram of products degraded for 1 h was shown in Fig. 2(b). The peaks of intermediates were observed at the retention time of 2.15, 4.08, 4.38 and 5.92 min, respectively. The intensity of DMAC peak ($T^{6.92}$) decreased while at the same time intensity of the primary intermediate peak ($T^{5.92}$) increased observably. After 2.5-h irradiation, the intensity of intermediate peak ($T^{4.08}$) increased markedly while the peak of DMAC and the weak peak ($T^{4.38}$) disappeared (Fig. 2(c)). With the photocatalytic degradation reaction carrying on, intermediate peaks faded away except peak $T^{2.15}$ as shown in Fig. 2(d). However, there are still several peaks that were not identified but could be regarded as untransformed components since their concentration virtually unchanged with the reaction time. These intermediates were further confirmed by UPLC/MS/MS analysis.

In order to evaluate the temperature effects of the above experiments, degradation efficiencies of DMAC after 1 h irradiated were tested under different temperature

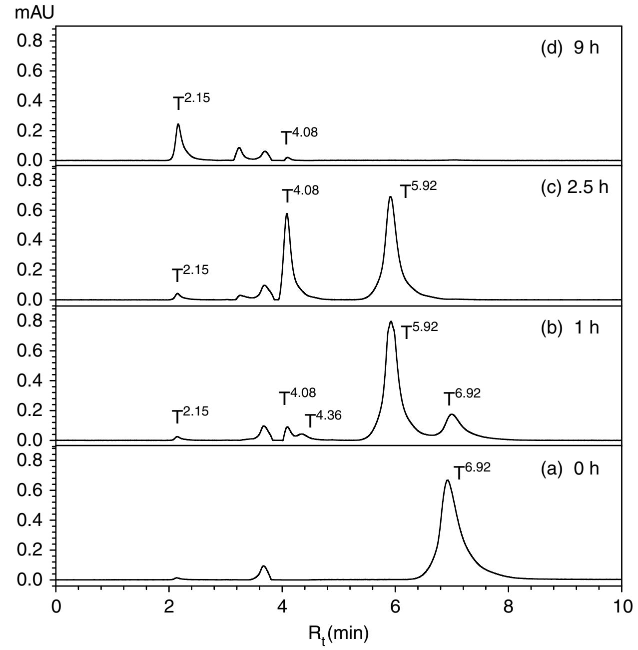

Fig. 2. HPLC chromatogram of degraded samples of different time intervals: (a) 0 h, (b) 1 h, (c) 2.5 h and (d) 9 h. Peaks labeled with code correspond to the identified degradation intermediates (*see* Table 1).

Table 1
Mass spectrometry analysis results of major photocatalytic products of DMAC

DMAC–intermediate products	Peak	Characteristic ions (m/z ES+)
DMAC	$T^{6.92}$	88(100), 46(96), 43(60)
N-methylacetamide	$T^{5.92}$	74(100), 43(23)
N-methyl-*N*-hydroxymethylacetamide	$T^{4.36}$	104(15), 61(15), 44(98)
Acetamide	$T^{4.08}$	60(100), 43(36)

(10°C, 20°C and 30°C, respectively). Experimental results show that the temperature factor on the influence of the catalytic degradation is not significant. Therefore, the experimental results in this paper were obtained at room temperature (19–22°C).

3.3. Proposed pathway for the degradation of DMAC

The DMAC and major degradation intermediate products were identified by interpretation of the mass spectra after 1 h of irradiation. Table 1 lists the mass spectrometry analysis results of the main products. Mass spectra of degradation intermediate products were showed in Fig. 3. Compound $T^{6.92}$ was identified as the DMAC molecular with molecular ion peak at m/z = 88. The daughter ion peaks at m/z = 46 and 43 which were associated with main fragments of dimethylamino and acetyl group from DMAC, respectively. Compound $T^{5.92}$ was identified as the dealkylated derivative, exhibited molecular ion peak at m/z = 74 which corresponded to the characteristic loss of methyl group. The daughter ion peaks at m/z = 43, which had lower relative abundance, were associated with fragments of acetyl from the parent ion. Compound $T^{4.36}$ was identified as the hydroxylation derivative, presented quasi-molecular ion peak at m/z = 104 with lower relative abundance which referred to the instable characteristic of methyl hydroxylation. The daughter ion peaks at m/z = 61 and 44 showed that it might exist fragments from C–N bond rupture of *N*-methyl-*N*-hydroxymethylacetamide. Finally, Compound $T^{4.08}$ was identified as the acetamide with molecular ion peak at m/z = 60, which the fragment ions at m/z = 43 exhibited fragments of acetyl from demethylation steps.

Based on the previous structure identification of the organic intermediates, a possible pathway of photocatalytic degradation of DMAC was proposed in Fig. 4. The degradation process of DMAC is consistent with the data report previously [3].

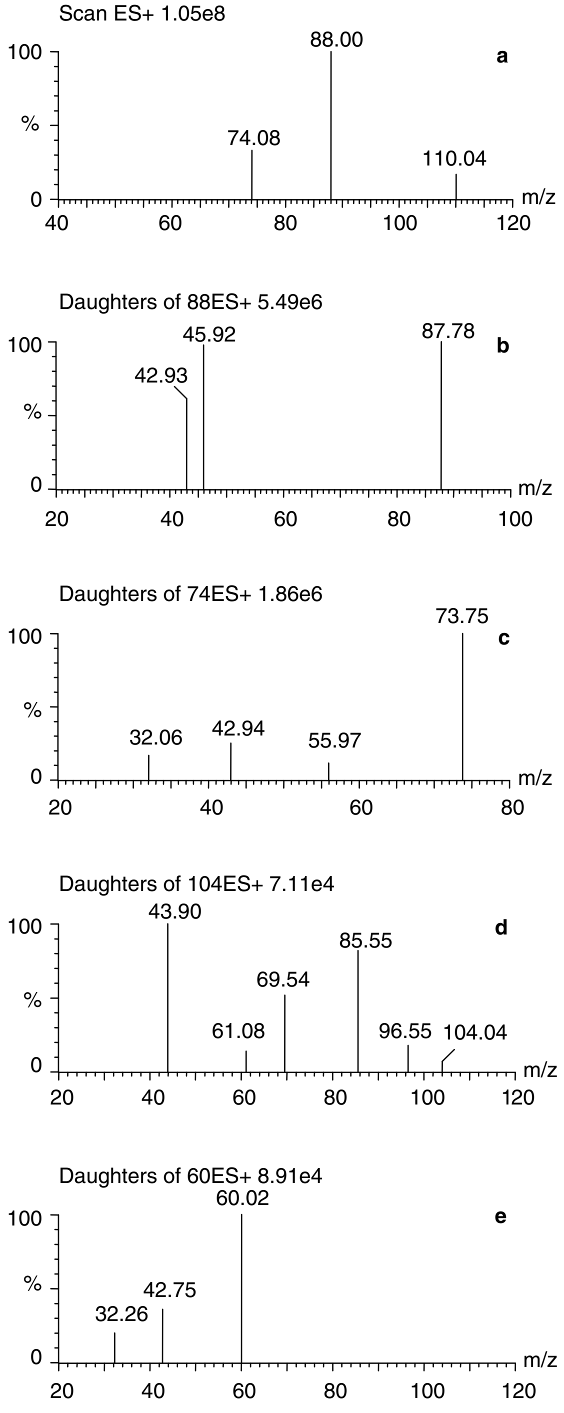

Fig. 3. Mass spectra of the compounds obtained after 1 h of irradiation. (a) Full-scan mass spectrum of the sample, (b) daughter scan mass spectrum of the peak $T^{6.92}$, (c) daughter scan mass spectrum of the peak $T^{5.92}$, (d) daughter scan spectrum for the peak $T^{4.38}$, (e) daughter scan spectrum for the peak $T^{4.08}$.

3.4. Evolution of the mineralization

Photocatalytic oxidation is one of the advanced technologies for the elimination of organic compounds based on oxidation action of radicals and positive hole. These generated radicals, which further react with organic compound to achieve complete mineralization with the formation of carbon dioxide, water, and nitrate with elemental nitrogen. Under the present experimental

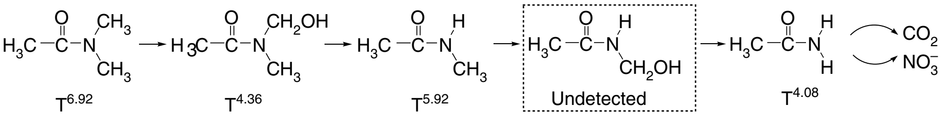

Fig. 4. Proposed photocatalytic degradation route of DMAC.

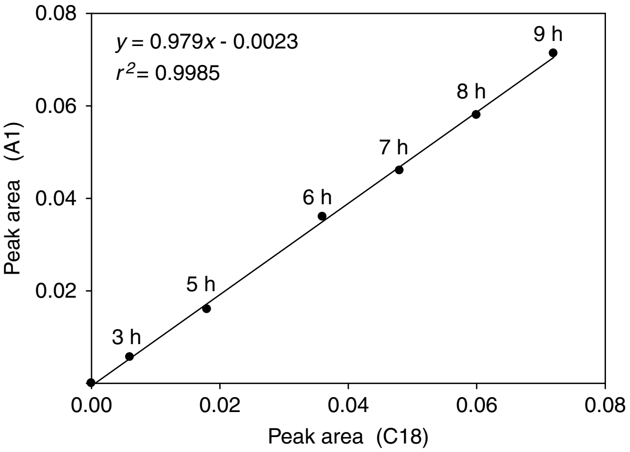

Fig. 5. Fitted relation of the peak area of nitrate between A1 column and C18 column for the same sample with different degradation time intervals.

conditions, the quantitative conversion of nitrogen to nitrate would be achieved after long degradation periods (more than 9 h) for DMAC, which was expressed as the peak of $T^{2.15}$ in HPLC chromatogram (Fig. 2). The characteristics of the compound in peak $T^{2.15}$ on A1 column was in conformity with those of nitrate reference standard sample. The *N*-naphthylethylenediamine dihydrochloride colorimetric method was adopted to further confirm that the nitrite did not exist in final products. Moreover, the responses of the compound in peak $T^{2.15}$ were compared both of A1 and of C18 column. The results showed that the increases of peak area had a good linear relationship (Fig. 5). As suggested above the peak $T^{2.15}$ (Fig. 2) represented NO_3^-, which was the mineralization end product in photocatalytic degradation process of DMAC.

4. Conclusions

The photocatalytic purification of water containing the DMAC has been performed in TiO_2 aqueous suspensions. The present works suggested that TiO_2 photocatalysis should be an effective technique for the destruction of the typical non-proton polar solvent in aqueous solutions. The generation and changes of main intermediates produced after degradation with different intervals have been analyzed by HPLC with the optimal separated conditions, which demonstrated to convert high concentration DMAC to inorganic compounds through photocatalysis degradation with low intensity light source. The organic intermediates were further identified by LC/MS techniques. Based on these findings we proposed degradation route of DMAC and its behavior in photocatalytic degradation process. Further study on mineralization oxidation showed that the fate of element N in DMAC was mineralized to NO_3^- in the strong anion exchange column by the multi-dimensional chromatography.

Acknowledgements

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References

[1] S. Swaroopa, P. Sughoshb and G. Ramanathanc, Biomineralization of N,N-dimethylformamide by Paracoccus sp. strain DMF, J. Hazard. Mater., 171 (2009) 268–272.

[2] H. Zhang, J.Y. Jiang, Y.X. Zhou and X.M. Chen, Adsorption and photodegradation of N,N-dimethylacetamide on suspended sediment particles in water, Res. J. Environ. Sci., 22(8) (2009) 902–906. In Chinese.

[3] E. Menegola, M.L. Broccia, M. Prati and E. Gianini, In vitro embryotoxicity study of N,N-dimethylacetamide and its main metabolite N-monomethylacetamide, Toxicol. in Vitro, 13 (1999) 409–415.

[4] A. Princivalle, F. Pasini and L. Perbellini, S-(acetamidomethyl) mercapturic acid (AMMA): A new biomarker for occupational exposure to N,N-dimethylacetamide, J. Chromatogr. B: Analyt. Technol. Biomed. Life Sci., 878(27) (2010) 2515–2519.

[5] E. Pelizzetti, Concluding remarks on heterogeneous solar photocatalysis, Sol. Energy Mater. Sol. Cells, 38 (1995) 453–457.

[6] P.A. Bianco, M. Vincenti, A. Banciotto and E. Pramauro, Photocatalytic and photolytic transformation of chloramben in aqueous solutions, Appl. Catal. B., 22 (1999) 149–158.

[7] D. Bahnemann, J. Cunningham, M.A. Fox, E. Pelizzetti, P. Pichat and N. Serpone, Photocatalytic treatment of waters, Aquatic and Surface Photochemistry, Boca Raton, FL: Lewis Pubs, 1994, p. 261–316.

[8] J.M. Hermann, Heterogeneous photocatalysis: fundamentals and applications to the removal of various types of aqueous pollutants. Catal. Today, 53 (1999) 115–129.

[9] E. Pelizzetti, E. Pramauro, C. Minero, N. Serpone and E. Borgarello, Photodegradation of organic pollutants in aquatic systems catalyzed by semiconductors, Photocatalysis and Environment: Trends and Applications, NATOASI Series, Dordrecht, The Netherlands: Kluwer, 1988, p. 469–497.

[10] I.K. Konstantinou, V.A. Sakkas and T.A. Albanis, Photocatalytic degradation of propachlor in aqueous TiO_2 suspensions. Determination of the reaction pathway and identification of intermediate products by various analytical methods, Water Res., 36 (2002) 2733–2742.