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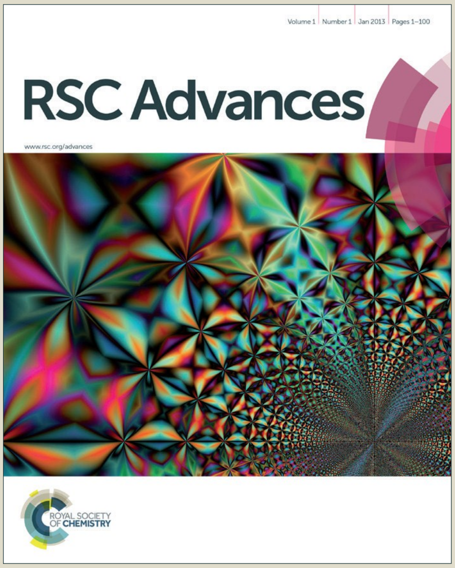

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Catalyst for the Degradation of 1,1-dimethylhydrazine and its By-product N-Nitrosodimethylamine in Propellant Wastewater

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Abstract

The three-component metal catalyst was prepared and used in the process of catalytic wet peroxide oxidation (CWPO) for the degradation of unsymmetrical dimethylhydrazine (UDMH) in propellant wastewater with H_2O_2. It was structurally characterized by scanning electron spectroscopy (SEM), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and energy-dispersive X-ray (EDX), and its catalytic activity was evaluated with the indexes such as the efficiency of UDMH degradation and chemical oxygen demand (COD) removal, the concentration of ammonia (NH_3-N), formaldehyde (HCHO), total nitrogen (TN) , total organic carbon (TOC) and N-Nitrosodimethylamine (NDMA). Besides, the reaction system was traced by UV-Vis full wavelength scanning spectroscopy and liquid chromatography-mass spectroscopy (LC-MS). As a result, it was observed that the degradation mechanism was created by ·OH attacking the amino group and homocoupling in UDMH with the mutual transformation of active ingredient Cu $^{II/I}$. Based on the investigation of reaction factors(H_2O_2 dosage, temperature, catalyst dosage, pH and the initial concentration of UDMH) focusing on the removal of NDMA, the optimal conditions for CWPO with three-component metal catalyst were determined. The high treatable concentration of UDMH (500 mg/L), rapid rate and good reusability with the high efficiency of UDMH degradation and COD removal (99.9 % in 10 min and 94.6 % in 30 min, respectively) and the low concentration of NDMA were the plausible performance of present catalyst.

Keywords: High concentration of UDMH, Three-component metal catalyst, CWPO,

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Degradation mechanism, NDMA.

1. Introduction

As the principal component of liquid rocket propellant, unsymmetrical dimethylhydrazine (1,1-dimethylhydrazine, UDMH) is widely used in the launching tests of missiles and satellites due to its good thermal stability, large combustion heat and high specific impulse[1, 2]. With the rapid development of aerospace industry, the huge consumption of UDMH unfortunately results in a large amount of waste water. In the past, it was discharged without any treatment because UDMH is readily oxidized in the air. However, nowadays it is found that the possible compounds derived from the degradation of UDMH are suspected to be harmful to the environment and human health[3]. As an example, among them, N-Nitrosodimethylamine (NDMA) is extremely dangerous because it is a potent carcinogen[4, 5]. Numerous methods have been tried to deplete it, including physical and chemical treatment, and photocatalytic degradation. However, the degradation efficiency is still unsatisfactory, let alone many shortcomings of those approaches[1, 2, 6-10]. For example, the traditional physical techniques known for the UDMH removal such as the adsorption by activated carbon, ion exchange[6] and incineration are not appropriate for the treatment of UDMH wastewater due to the regeneration issues of activated carbon and ion exchange resins as well as the pollution problems caused by incineration. Chemical treatment with chloramines, fenton, ozone, heterogeneous catalytic oxidation may be used for the removal of UDMH from water [2, 7-9]. However, these methods are mainly disadvantageous to generate N-nitrosodimethylamine

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(NDMA), an intermediate of UDMH oxidation[10]. It is even more toxic than UDMH. Photocatalysis, such as O_3/UV and H_2O_2/UV, is reported as an efficient method for the degradation of UDMH with the merit minimizing the formation of NDMA[1]. A mechanism of degradation of UDMH by H_2O_2 is suggested as following (Eq. 1～17),

$$H_2O_2 \rightarrow 2\cdot OH \qquad (1)$$

$$H_2O_2 + \cdot OH \rightarrow \cdot OOH + H_2O \qquad (2)$$

$$\cdot OH + \cdot OOH \rightarrow O_2 + H_2O \qquad (3)$$

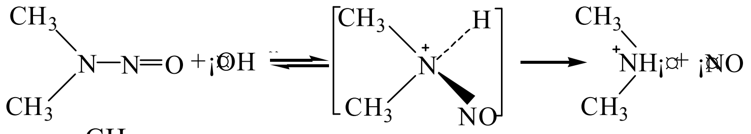
$$2H_2O_2 \rightarrow 2H_2O + O_2 \qquad (4)$$

$$(CH_3)_2NNH_2 + \cdot OH \rightarrow (CH_3)_2NN\cdot H + H_2O \qquad (5)$$

$$(CH_3)_2NN\cdot H + \cdot OOH \rightarrow (CH_3)_2NN(H)OOH \qquad (6)$$

$$(CH_3)_2NN(H)OOH \rightarrow (CH_3)_2NN^{-}OOH + H^{+} \qquad (7)$$

$$(CH_3)_2NN^{-}OOH \rightarrow (CH_3)_2NN=O + OH^{-} \qquad (8)$$



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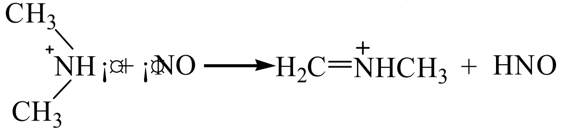

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$$H_2C{=}\overset{+}{N}HCH_3 + H_2O \longrightarrow CH_3NH_2 + HCHO + H^{+} \qquad (11)$$

$$(CH_3)_2NN\cdot H + \cdot OH \rightarrow (CH_3)_2N=N + H_2O \qquad (12)$$

$$2(CH_3)_2N=N \leftrightarrow (CH_3)_2NN=NN(CH_3)_2 \qquad (13)$$

$$(CH_3)_2N=N \rightarrow CH_3N=N + \cdot CH_3 \qquad (14)$$

$$CH_3N=N \rightarrow \cdot CH_3 + N_2 \qquad (15)$$

$$\cdot CH_3 + \cdot OH \rightarrow CH_3OH \qquad (16)$$

$$CH_3OH + \cdot OH \rightarrow HCHO \qquad (17)$$

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However, for the large-scale industrial applications, the low concentration of UDMH in wastewater makes these methods inefficient. Therefore, the destruction of the sub-standard UDMH becomes a very urgent task with a new catalytic system, and also the main topic of this paper.

Comprehensively taking account of the factors such as the degradation efficiency, by-products, cost and capacity of treatment, and also employing eco-friendly H_2O_2 as the oxidant, the catalytic wet peroxide oxidation (CWPO) is considered as the most potential method for the practical applications and attractive to many researchers[11]. It is reported that Cu $^{\mathrm{II}}$ was an effective ion to promote UDMH decomposition by homocoupling reaction of UDMH with the mutual transformation of active ingredient Cu $^{\mathrm{II/I}}$ (Eq. 18 and Eq. 19)[12]. Moreover, the capacity of Cu $^{\mathrm{II}}$ for breaking UDMH molecules down is significantly enhanced by increasing hydrogen peroxide[13]. On the other hand, it is well-known that amides can be reduced to the corresponding inorganic amines in the presence of Zn $^{\mathrm{II}}$ catalysts under mild conditions, and Ni $^{\mathrm{II}}$ is a stronger hydrogenation catalyst to promote degradation of NDMA(Eq. 20～22)[14-16]. Therefore, in order to promote the performance of catalyst in the decomposition of UDMH, simultaneously the ability of decomposing NDMA, it may be a good choice to combine Cu $^{\mathrm{II}}$ with Ni $^{\mathrm{II}}$ and Zn $^{\mathrm{II}}$ to make a multi-component catalyst. Adding Zn $^{\mathrm{II}}$ and Ni $^{\mathrm{II}}$ into Cu $^{\mathrm{II}}$ catalyst, a possible mechanism of degrading UDMH may be figured out as following,

$$5\left(CH_3\right)_2 NNH_2 + 16Cu^{2+} \rightarrow 2(CH_3)NN = CH - N = N(CH_3)_2^{+} + 16Cu^{+} + 14H^{+} + N_2 \quad (18)$$

$$4Cu^{+} + O_2 + 4H^{+} \rightarrow 4Cu^{2+} + 2H_2O \qquad (19)$$

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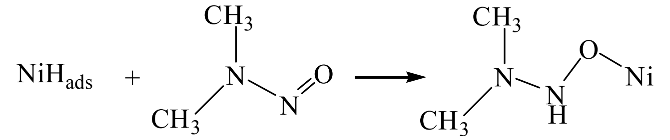
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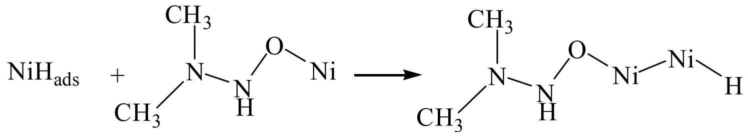
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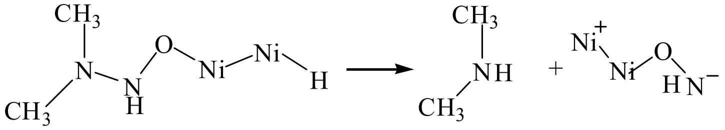
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This is right the purpose of present research, in which the catalytic properties of CuO-ZnO-NiO/γ-Al_2O_3 were tested in the oxidation of UDMH with H_2O_2.

2. Experimental

2.1. Materials and reagents

Aluminium (□) sulphate decahydrate ($Al_2(SO_4)_3 \cdot 18H_2O$), Dimethylamine borane ($(CH_3)_2NHBH_3$, DMAB), Polyethylene glycol (PEG200(1000), Copper(□) nitrate trihydrate ($Cu(NO_3)_2 \cdot 3H_2O$), Zinc(□) nitrate hexahydrate ($Zn(NO_3)_2 \cdot 6H_2O$), Nickel(□) nitrate hexahydrate($Ni(NO_3)_2 \cdot 6H_2O$), hydrogen peroxide (H_2O_2, 30 %, wt %), and ethanol (AR) were all purchased from Sinopharm Chemical Reagent Co. Ltd, and used without any further treatment. Distilled water was used for all the experiments.

2.2. Preparation of γ-Al_2O_3 and CuO/ZnO/NiO/γ-Al_2O_3 nanoparticles

γ-Al_2O_3 and CuO/ZnO/NiO/γ-Al_2O_3 nanoparticles were prepared in accordance with Ref [17]. Namely, 15.0 g PEG 1000 and 150 mL PEG 200 as a surfactant were added into the aqueous solution consisted of $Al_2(SO_4)_3 \cdot 18H_2O$ (33.3 g), DMAB

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(118.0 g) and 500 mL distilled water in a 1000 mL three-necked round bottom flask with heat jacket. After stirring for 30 min with an anchor-type mechanical stirrer, the reaction was performed at 80 °C for 1 h, and then, rapidly cooled to room temperature with flowing tap water. The resultant white precipitate was separated by centrifugation and washed trice with distilled water and ethanol. After dried at 80 °C for 12 h in air, the product was ground to powders and calcined at 950 °C for 2 h.

The same process was applied to prepare the CuO/ZnO/NiO/γ-Al_2O_3 nanoparticles with the altered recipe. The aqueous solution was formulated with $Cu(NO_3)_2{\cdot}3H_2O$ (0.32 g) , $Zn(NO_3)_2{\cdot}6H_2O$ (0.37 g) and $Ni(NO_3)_2{\cdot}6H_2O$ (0.39 g) in water.

2.3. Characterization of catalysts

X-ray diffraction (XRD, Rigaku Miniflex 600) using Cu K_α was employed to analyze the structure of catalyst at 2θ angle from 5° to 80°. The surface elements and their states were analyzed by X-ray photoelectron spectroscopy (XPS, Thermo ESCALAB-250) with Al Ka (1486.6 eV) irradiation source. A scanning electron microscopy (SEM, Hitachi S-4800) was applied to discover the surface morphology and energy-dispersive X-ray (EDX, Hitachi S-4800) to evaluate the chemical composition on the catalyst surface.

2.4. Catalytic wet peroxide oxidation

The catalytic oxidation of UDMH was carried out in a 250 mL three-necked round bottom flask with 100 mL 500 mg/L of simulated UDMH wastewater, 1 g

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CuO-ZnO-NiO/γ-Al_2O_3 catalyst and 4 mL H_2O_2(30 %, wt %). In order to avoid the loss of volatile UDMH by evaporating in the experiments, and keep the reaction temperature at constant as well, a total reflux system and thermostatic water-bath were employed. The reaction solution, 10 mL, sampled at given time intervals was treated by adding MnO_2 to remove the H_2O_2 residual, and then centrifuging for 10 min at 3,000 rpm to separate the catalyst from the aqueous solution. Both of the catalyst and aqueous solution were analyzed to evaluate the performance of catalyst such as the percentage conversion of UDMH and removal efficiency of chemical oxygen demand (COD). UDMH concentration was determined by spectrophotometry with sodium amino ferrocyanide according to Chinese standard GB/T 14376-93, whilst the COD was detected by a standard method using COD reagents. They were calculated over the following equations:

$$UDMH\ \deg radation\ efficiency(\%) = \frac{(C_0 - C_t)}{C_0} \times 100\%$$

$$COD\ \deg radation\ efficiency(\%) = \frac{(COD_0 - COD_t)}{COD_0} \times 100\%$$

Where C_0 and COD_0 are the initial UDMH and COD concentration (mg/L) of the UDMH wastewater, C_t and COD_t are the UDMH and COD concentration (mg/L) at time t.

The component variation of reaction system was monitored by a UV-visible spectrophotometer, where the solutions sampled at different time intervals and treated with MnO_2 were used. The amount of total nitrogen (TN), ammonia (NH_3-N) and formaldehyde (HCHO) in the reaction system were determined respectively

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according to Chinese standard HJ 636-2012, HJ 535-2009 and HJ 601-2011. The amount of main intermediate NDMA was detected by high-performance liquid chromatography (HPLC) [18] and other intermediate products were evaluated by liquid chromatography–mass spectrometry (LC-MS)[19]. Total amount of organic carbon （TOC）was measured by TOC analyzer[20].

In the experiments of degrading UDMH, the effect of different variables including H_2O_2 dosage (0-6 mL), reaction temperature (25-70 °C), catalyst dosage (0-1.5 g), initial pH value (4-10) and initial UDMH concentration (200-1000 mg/L) were investigated. Catalyst recycling experiment was implemented to detect the stability and reusability of the synthesized catalyst.

3. Results and Discussions

First of all, it should be remarked that the components of catalyst were determined by a series of preliminary experiments including single component (Cu^{II}), two-component (Cu^{II}-Zn^{II} and Cu^{II}-Ni^{II}) and three-component catalysts. When single component and two-component were supported on γ-Al_2O_3, the degradation efficiency of UDMH and COD were not ideal, namely that couldn't meet the national emission standards of UDMH content and COD, in addition NDMA content was relatively high. The efficiency of three-component was the best. Since those data were regardless to the content of this paper, for succinctness and also the secrecy of patent, they were excluded.

3.1. Catalysts characteristics

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In order to evaluate the effects of loading Cu, Zn and Ni, as an example, the SEM images of γ-Al_2O_3 and a typical CuO/ZnO/NiO/γ-Al_2O_3 are presented respectively in Figure 1 at different magnifications. The support, γ-Al_2O_3, appears as irregular shape of alumina particles (a) and has a large gap (A) leading to a strong adsorption. When copper, zinc and nickel oxides at low loadings were impregnated, no significant change could be observed in the shape (b).

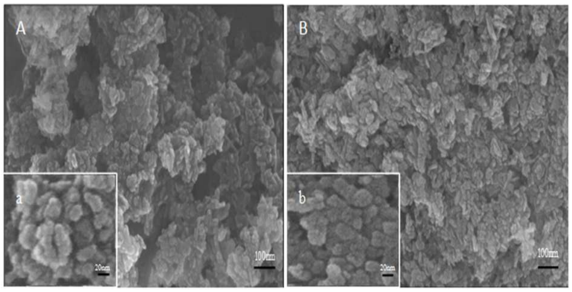

Figure 1. SEM images of γ-Al_2O_3 (A, a) and CuO/ZnO/NiO/γ-Al_2O_3 (B, b) catalysts at different magnification.

The surface distribution of elements was identified by EDX. As shown in Figure 2, Cu, Zn and Ni peaks can be clearly seen from Fig. 2b. Moreover, the mass fraction of these elements doped on γ-Al_2O_3 is basically identical with the nominal content. It indicated that copper，zinc and nickel atoms are dominantly distributed on the surface of γ-Al_2O_3.

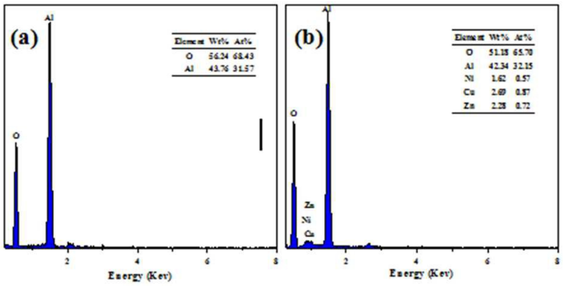

Figure 2. EDX patterns of γ-Al_2O_3 and CuO/ZnO/NiO/γ-Al_2O_3 catalysts.

The XRD patterns of γ-Al_2O_3 and CuO/ZnO/NiO/γ-Al_2O_3 are exhibited in

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Figure 3. The characteristic peaks peculiar to γ-Al_2O_3, i.e. 2θ=37.38°, 45.86° and 67.16°, were observed [17, 21]. It indicated that γ-Al_2O_3 was prepared successfully. When copper, zinc and nickel atoms were introduced into γ-Al_2O_3, as shown in Fig. 3, no significant change was found in the XRD pattern. It indicated that the lattice of γ-Al_2O_3 was not interfered with the addition of Cu, Zn and Ni. Additionally, the diffraction from the crystalline CuO, ZnO and NiO was not observed in the spectrum. All the above results evidenced that Cu, Zn and Ni were highly dispersed and adsorbed on the surface of γ-Al_2O_3[22]. The loading mass percentage was too low to form the independent crystalline phase.

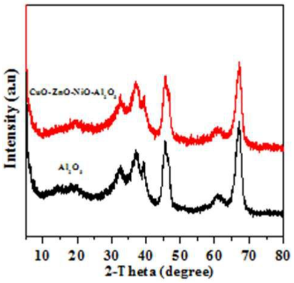

Figure 3. XRD patterns of γ-Al_2O_3 and CuO/ZnO/NiO/γ-Al_2O_3 catalysts.

In order to evaluate the performance of metal ions during the reaction, XPS of catalyst at pro- and post-reaction were also carried out. As shown in Fig. 4 that the valence of three elements of the catalyst have not changed before and during reaction, the binding energy at about 856.1 eV and 862.1 eV were observed, assigned to the main

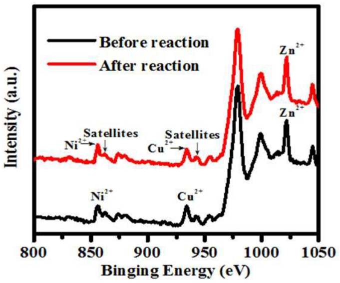

Figure 4. XPS spectra of CuO/ZnO/NiO/γ-Al_2O_3 catalyst at pro- and post-reaction.

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line of $Ni^{2+}(2p_{3/2})$ and its satellite, respectively[23]. The Figure 4 also displays the Cu XPS spectra (930–970 eV) and the Zn XPS spectra (1016–1028 eV). The characteristic peaks peculiar to $Cu^{2+}(2p_{3/2})$ and $Zn^{2+}(2p_{3/2})$, i.e. BE=933.3 eV and 1021.9 eV, were observed[24, 25]. This result suggests that the catalyst itself is not changed and only plays the role in changing the reaction rate during the reaction.

3.2. Trials of UDMH catalytic oxidation

As described in the section of introduction, the UDMH and COD are readily removed from the wastewater by various means. However, the removal of NDMA derived from the decomposition of UDMH is hard. Therefore, in order to test the performance of CuO/ZnO/NiO/γ-Al_2O_3 catalyst, a preliminary experiment was carried out by dropwise adding H_2O_2 with peristaltic pump. The conditions are: UDMH: 500 mg/L, H_2O_2: 4 mL, catalyst: 1 g, pH: 8.5, 60 °C, and the UV-vis full wavelength scanning was carried out to trace the reaction process. However, it should be remarked that, since no peak appears from 500 to 800 nm, only the spectra in the range from 200 to 500 nm wavelength is selected. As shown in Figure 5, it is characterized as the disappearance of peak of 0 time at 215 nm within only 2 min, instead, the platform peak from 220 nm to 280 nm appeared during the catalyzed reaction. Moreover, the broadness of platform peak gradually becomes small and smooth, companying with decrease of absorbance strength from 5 to 30 minutes. Furthermore, a special peak in the vicinity

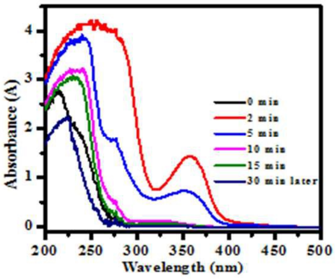

Figure 5. UV-vis full wavelength scanning under different times

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of 350 nm with high absorbance suddenly appears at the reaction time 2 min. In addition, this peak becomes weak at 5 minutes, and finally disappears at 10 minutes. This result qualitatively indicated that UDMH immediately reacted in the system, turning into the unstable intermediate compounds.

In order to further clarify the intermediate compounds, ESI (+) mass spectroscopy was carried out with solution of UDMH oxidation sampled at 5 minutes. As shown in Figure 6, with the original UDMH solution, only two substances, i.e. UDMH and NDMA, were observed. However, a lot of substances was found in the solution sampled at 5 min. Among them, the possible oxidation intermediate products of UDMH reported in the references were detected, such as N-nitrosodimethylamine (NDMA), 1,1-dimethylguanidine (DMG), 1-Formyl-2,2-dimethylhydrazineand1(FDMH), and 1,4,4-tetramethyl-2-tetrazene (TMT)[12, 19, 26]. The fragment intensity ratios are presented in Table 1. These products further explained the emergence of platform and special peak in Figure 5. Besides, it confirmed the mechanism of degradation that hydroxyl radicals mainly attacked the amino group of UDMH molecule. Of course, all of these substances would be further oxidized to the corresponding small molecules

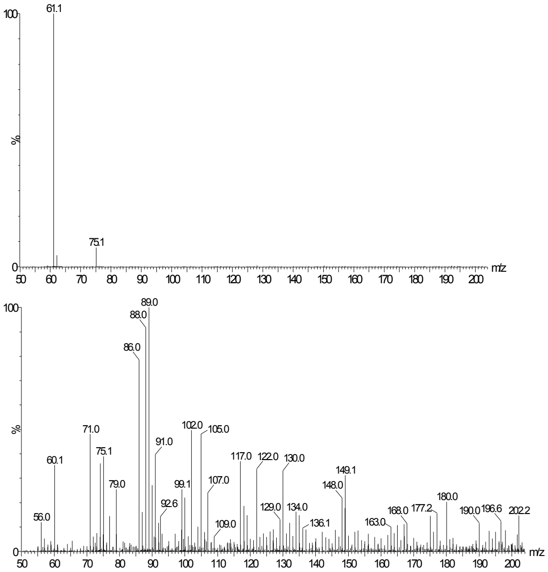

Figure 6. ESI (+) mass spectra of original UDMH and products of UDMH oxidation in 5 minutes.

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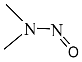
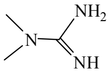
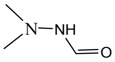
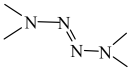
which were not reflected in the mass spectrum because of small molecular weight. For example NDMA and TMT were broken down into methylamine and formaldehyde respectively by Eq. 9～11 and Eq. 12～17 [13, 27, 28]. Additionally, reminiscent of Figure 5, it can be conclude that UDMH and most of its subsequent intermediate products could be thoroughly degraded by the present catalyst.

Table 1. Possible oxidation intermediate products of UDMH in 5 minutes

The substance name	Structural formula	Molecular weight	Precursor ion m/z	Fragment intensity ratio
N-nitrosodimethylamine		74.1	75.1	38.5
1,1-dimethylguanidine		87.1	88	92.5
1-Formyl-2,2-dimethylhydrazine		88.1	89	100
1,1,4,4-tetramethyl-2-tetrazene		116.2	117	37

On the basis of the unique amino group of UDMH, in order to further illustrate the degradation of UDMH, the quality indexes of wastewater treatment such as NH_3-N, TN and TOC were separately detected. The results are shown in Figure 7, including the variation of main byproducts of UDMH decomposition, NDMA (Eq. 5～8) [11-13] and HCHO(Eq. 9～17)[13, 27, 28] according to the mechanism described in the part of introduction. It is clear that, in general, all the indexes decreased as the reaction proceeded, except that of NDMA. The content of NDMA increased from 0 to 5 min. After leveled off in 5 min, it gradually decreased to a stable value at 30th min. The

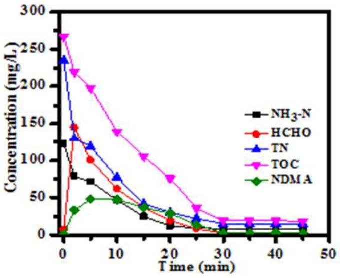


Figure 7. The change of NH_3-N, HCHO, TN, TOC, NDMA in the process of UDMH oxidation.

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concentration of NH_3-N, TN and TOC decreased rapidly at first 2 minutes, and then declined slowly. Meanwhile HCHO suddenly appeared at 2 min. Its content decreased gradually and finally reached equilibrium. These results indicated that UDMH was degraded readily by present catalytic system. And also, the mechanism of degradation as ours induced in the part of introduction was correct due to the generation of NDMA in the process of degradation.

Figure 8 shows the variation of COD and degradation efficiency of UDMH in the reaction. As shown in Figure 8, with the increase of reaction time, the degradation efficiency of UDMH increased rapidly. It reached more than 98.7 % merely in 10 minutes. However, for the COD removal efficiency, it is fairly time expended. It reached 95.0 % in 30 minutes until attained the national standard of emission level which is as low as 50 mg/L. At a glimpse of the curve, three stages are obvious, i.e. the rapid increase from 0 to 10 min, the leveled off stage from 10 to 20 min and finally rapid increase from 20 to 30 min. The first stage (rapid increase) is likely ascribed to the removal of COD in the original wastewater with a little amount of H_2O_2. The second stage (leveled off) is possibly attributed to the generation of intermediates. As discussed above, UDMH was decomposed readily in a few minutes, but a large amount of various intermediate compounds was produced in the system. Therefore, the leveled off stage implies that, at least, the intermediate compounds are hard to be decompose such as

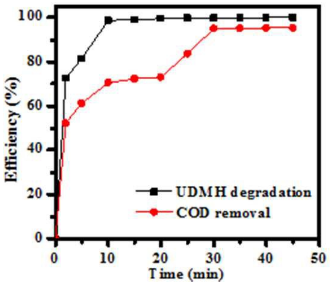

Figure 8. UDMH and COD degradation efficiency under different times

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NDMA shown in Figure 7 under the present catalytic conditions. Certainly, reminiscent of dropwise addition of H_2O_2, it is also apparent that the inadequate amount of H_2O_2 was a possible reason. As shown in Fig. 8, the efficiency of COD removal rapidly increased from 20 to 30 min after this stage. This result indicated that the concentration of H_2O_2 was the main factor to improve the COD removal efficiency. Anyway, the level of COD was finally decreased to the level required by the standard. This was a great result encouraging us to do the further research.

Summarizing all the data reflected by the figures, it is reasonable that with the increase of concentration of H_2O_2 and the reaction time, oxidation of ·OH from H_2O_2 improved increasingly. UDMH and the intermediate products could be relatively thoroughly degraded. Moreover, compared with the fenton method[1] and photocatalysis method[29], the present process was advantageous to save time and achieve the higher degradation efficiency. For example, by present process, it only took 30 minutes to attain ca 98% of the degradation efficiency, whereas by the above-mentioned methods, more than 1 h was needed and those degradation efficiencies was lower than ours under the same concentration of UDMH wastewater. Therefore, the combination of the $CuO/ZnO/NiO/\gamma\text{-}Al_2O_3$ catalyst and H_2O_2 was a good choice to treat the UDMH wastewater. The following optimization was carried out to achieve more desirable results and meet emissions standards of NDMA.

3.2.2 Effect of H_2O_2 dosage

The degradation efficiency of UDMH is closely related to the powerful oxidization of ·OH derived from H_2O_2 (Eq. 1)[11]. Theoretically, the total amount of

H_2O_2 is 0.75 mL for completely oxidizing 100 mL, 500 mg/L of UDMH to the volatile substances. However, it is reported that the amount as much as more than several times the stoichiometric ratio of H_2O_2 was needed in most cases due to the inadequate applicability[2]. Figure 9 (a and b) presents the effects of H_2O_2 dosage on the catalytic degradation of UDMH in wastewater and the generation of intermediate product (NDMA) by using our catalyst and CWPO process. It is clear that, with only 1 mL H_2O_2, UDMH was completely degraded, but the COD removal efficiency (Fig. 9a) was aggrandized gradually as the volume of H_2O_2 increased from 0 to 6 mL. It attained to a maximum value, 96.5%, as 6 mL H_2O_2 was added. In contrast, as shown in Fig. 9b, the concentration of NDMA attained to the maximum value only expending 1 mL H_2O_2. This result was coincident to the former shown in Fig. 8, further confirming that the main product of UDMH oxidation was NDMA. However, a problem arises that why the excessive H_2O_2 is needed. It is possibly ascribed to a factor that the intermediate products of UDMH oxidation are much more difficult to be oxidized than UDMH by H_2O_2. Since the oxidation rate of intermediate products is slow, the scavenging effect occurs as shown in Eq. 2～3 and Eq. 5 [11, 13]. Some of hydroxyl radicals reacted with H_2O_2 and UDMH to produce ·OOH (Eq. 2 and Eq. 5). It quenches ·OH to form O_2 (Eq. 3), giving rise to severe loss of H_2O_2. Consequently, excessive amount of H_2O_2 is required to complement the loss of ·OH. This explanation is supported by the oxidation of NDMA. As shown in Fig. 9b, with the increase of H_2O_2, NDMA content rose fleetly from 2.2 mg/L to 38.0 mg/L, and then decreased gradually to a stable value of 2.4 mg/L. According to the mechanism, ·OH

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attacks amino group of UDMH according to the reactions (Eq. 5～8)[1, 27], thereby UDMH was transferred into NDMA. The concentration of NDMA reached the maximum value, ca 40 mg/L, when 1 mL H_2O_2 was added. It indicated that UDMH was mostly transferred into NDMA. Therefore, the excessive amount of H_2O_2 was actually applied to oxidize NDMA. This result further confirmed that, as shown in Fig. 9b, NDMA contributed the main part of COD after UDMH was exhausted.

Taking all the factors such as the efficiency of UDMH degradation and COD removal as well as the generated content of NDMA into consideration, comprehensively the optimal volume for CWPO of 100 mL, 500 mg/L of UDMH wastewater was determined, i.e. 5 mL of H_2O_2, which was about 6.7 times as much as the theoretical dosage.

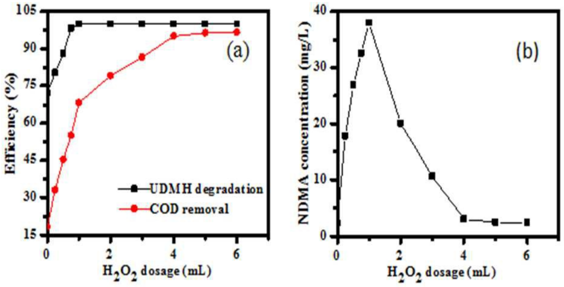

Figure 9. Effect of H_2O_2 dose on catalytic oxidation of UDMH by CuO/ZnO/NiO/γ-Al_2O_3 catalyst: (a) UDMH and COD degradation efficiency; (b) NDMA concentration (UDMH: 500 mg/L; temperature: 60 °C; catalyst: 1 g; pH: 8.5; time:30 min).

3.2.3. Effect of temperature

The generation of ·OH is restricted directly by the temperature. The effect of temperature on degradation of UDMH and the generation of intermediate product (NDMA) was shown in Figure 10 (a and b). Obviously from 25 °C to 70 °C, both the

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efficiency of UDMH degradation and COD removal (Fig. 10a) increased, whilst the concentration of intermediate product (NDMA) declined gradually (Fig. 10b) with the increase of temperature. For example, at 25 °C, the efficiency of UDMH degradation was only 80 %, whilst the percentage of COD removal was about 46 %. The concentration of NDMA was as high as 75 mg/L. It indicated that, at low temperatures, neither UDMH nor intermediate products such as NDMA were not completely degraded for H_2O_2 not being converted to ·OH. At 40 °C, UDMH was almost completely degraded, whereas efficiency of COD removal was only 63.8 %. Meanwhile, the concentration of NDMA decreased to a half concentration of NDMA as that at 25 °C because of part of intermediate product(NDMA) being oxidized to methylamine and formaldehyde by extra ·OH (Eq. 9～11)[27, 28]. When the temperature rose to 65 °C and 70 °C, all indexes such as the efficiency of UDMH degradation, COD removal and NDMA content were satisfied according to the standard. This is due to the fact that the generation of ·OH by H_2O_2 (Eq. 1) is much easier and faster at higher temperature, resulting in the improvement of the oxidation efficiency of UDMH and intermediate product (Eq. 9～11) . Therefore, higher temperature was beneficial to the degradation of UDMH. But too much high temperature didn’t necessarily contributed to the improvement of the degradation performance because the thermal decomposition of H_2O_2 (Eq. 4) was severe , leading to a low utilization of H_2O_2[11]. In order to achieve less energy consumption, resources saving and the excellent degradation effect, 65 °C should be the best temperature for catalytic degradation of UDMH wastewater by $CuO/ZnO/NiO/\gamma\text{-}Al_2O_3$ with H_2O_2 as oxidant.

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Compared with $Cu_xMg_{1-x}Cr_2O_4/\gamma\text{-}Al_2O_3$ catalyst system[9], the UDMH molecular can be completely transformed into the deep oxidation products CO_2, H_2O and N_2 and don't produce secondary pollutants. However, the low concentration of UDMH in wastewater and harsh conditions such high temperature makes this method inefficient. Therefore, the mild reaction condition of the catalyst is necessary for the industrial requirements.

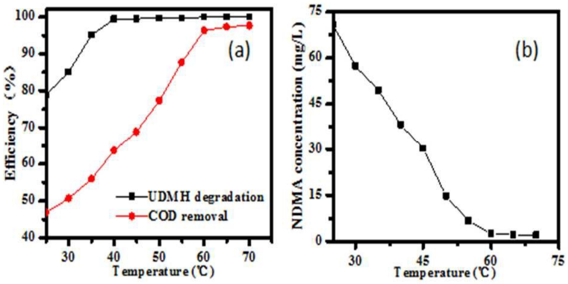

Figure 10. Effect of temperature on catalytic oxidation of UDMH by $CuO/ZnO/NiO/\gamma\text{-}Al_2O_3$ catalyst: (a) UDMH and COD degradation efficiency; (b) NDMA concentration (UDMH: 500 mg/L; H_2O_2: 5 mL; catalyst: 1 g; pH: 8.5; time:30 min).

3.2.4 Effect of catalyst dosage

The effect of catalyst dosage on the catalytic degradation of UDMH wastewater and the generation of intermediate product (NDMA) are shown in Figure 11 (a and b). It was inferred that catalyst dosage was of great importance for the efficiency of UDMH degradation and COD removal. When the catalyst dosage was increased from 0 g to 1.0 g, the efficiency of UDMH degradation and COD removal increased from 69.1 % to nearly 100 % and 54.6 % to 97.5 %, respectively (Fig. 11a). Meanwhile, the concentration of NDMA decreased from 30 to 2.4 mg/L. These results proved that the present catalyst was effective in CWPO to degrade UDMH and its main intermediate product, NDMA, by H_2O_2. 1.0 g $CuO/ZnO/NiO/\gamma\text{-}Al_2O_3$ catalyst was appropriate in

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the present system. Since the present catalyst containing Zn ^{II} and Ni ^{II}, amides were reduced to the corresponding amines under the mild conditions[16]. Furthermore, nickel is a stronger hydrogenation catalyst, attacking the N-N bond of NDMA to form DMA (Eq. 20 ~ 22)[15] and ·NO, which subsequently converted to methylamine, formaldehyde (Eq. 11) and ammonia through sequential electron transfer steps. Two important aspects of the copper-facilitated reaction are changed in copper oxidation sites and the relative accessibility of the Cu^{2+} LUMO orbital[14], thereby leading copper, zinc and nickel to be more accessible to the NDMA molecules in the solution. Therefore, catalyst dosage was an considerably important factor for the catalytic degradation of UDMH wastewater due to forming strong oxidizing ·OH by catalytic decomposition of H_2O_2 (Eq. 1) and generating coupling reaction through the generation and disappearance of active ingredient Cu^{2+} (Eq. 18 and Eq. 19) [12].

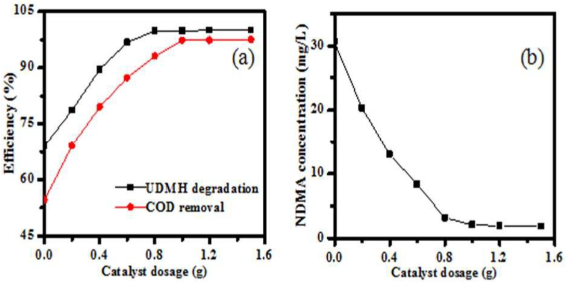

Figure 11. Effect of catalyst dosage on catalytic oxidation of UDMH by CuO/ZnO/NiO/γ-Al_2O_3 catalyst: (a) UDMH and COD degradation efficiency; (b) NDMA concentration (UDMH: 500 mg/L; H_2O_2: 5.0 mL; temperature: 65 °C; pH: 8.5; time: 30 min).

3.2.5. Effect of initial pH

The simulation of initial pH of UDMH wastewater ranging from 4 to 10 was carried out by adding the diluted solutions of sulfuric acid and sodium hydroxide for the purpose to evaluate the influence of pH on the degradation performance. The

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results are reflected in Figure 12 (a and b). An apparent feature was that the generation of NDMA was greatly affected by pH values (Fig. 12b). The optimal degradation efficiency was obtained at the pH of 7.5, the UDMH conversion and COD removal reached 99.9 % and 94.6 %, meanwhile NDMA content was about 0.45 mg/L after 30 minutes. Lower and higher pH values were not beneficial to the degradation of UDMH. When the initial pH of UDMH solution was sour, the COD and UDMH degradation efficiency generally showed an andante upward trend. Under heavily acidic conditions the degradation of UDMH was severely prevented which could be attributed to inhibition of reaction of Cu^{2+} and UDMH (Eq. 18) and relative stability of H_2O_2 which was not easily decomposed into hydroxyl radicals. However, acidic conditions was favorable to restrain the transformation of UDMH to NDMA (Eq. 7)[30, 31].

In addition, the strong alkaline circumstance was also not suitable for the degradation of UDMH wastewater and inhibiting formation of NDMA. It was explained that zinc oxide and aluminium oxide reacting with sodium hydroxide became the ZnO_2^{2-} and AlO_2^- which resulted in significantly reducing activity of the catalyst and breaking support of catalysts. Moreover H_2O_2 readily reacting with sodium hydroxide generated H_2O. What's more alkaline conditions promoted the generation of NDMA. Heavily acidic and alkaline conditions were not only beneficial to the degradation of UDMH and recovery of catalyst. Thus, near-neutral pH conditions were more suitable for catalytic oxidation of UDMH wastewater. It turned out that the pH 7.5 was the optimum for the total UDMH oxidation since the reaction

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rate was relatively high as well as the UDMH mineralization degree. As we know, with the fenton method[1, 8], the catalyst was efficient under the acidic conditions. In the alkaline solution, the fenton reagents would be deactive. Therefore, the catalyst developed in this paper is necessarily a complement for the industrial requirements.

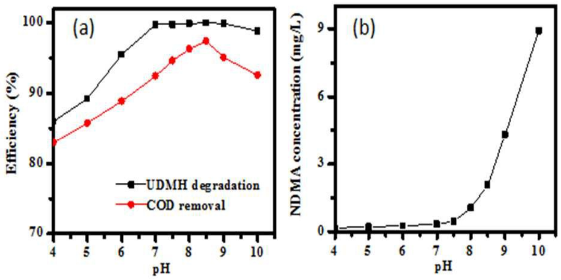

Figure 12. Effect of pH value on catalytic oxidation of UDMH by CuO/ZnO/NiO/γ-Al_2O_3 catalyst: (a) UDMH and COD degradation efficiency; (b) NDMA concentration (UDMH: 500 mg/L; H_2O_2: 5.0 mL; temperature: 65 °C; catalyst: 1 g; time:30 min).

3.2.6. Effect of initial concentration of simulated UDMH wastewater

The initial concentration of UDMH was adjusted within the range of 200–1000 mg/L and the experiments were performed to meet the emission Standards by all kinds of industries. As shown in Figure 13a, both the efficiency of UDMH degradation and COD removal ware inversely proportional to their initial concentrations. As the initial concentration increased from 200 to 1000 mg/L, they decreased from ca 100 % to 95.5 % and 96.5 % to 85.4 %, respectively. However, the concentration of NDMA increased constantly (Fig. 13b). These results were natural since the concentration of H_2O_2 was constant. Anyway, comprehensively considered all the indexes, when the initial concentration of UDMH was lower than 500 mg/L, the reaction conditions presented in Figure 13 were relatively appropriate to treat UDMH wastewater. It meant that, by the present catalyst and CWPO, the treatable

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maximum concentration of UDMH in wastewater was 500 mg/L. It was much higher than the upper limitation by photocatalysis[29], 200 mg/L, let alone the highest efficiency of photocatalysis was less than 90%. Anyway, this value, 500mg/L, is satisfactory industrially in most cases as we know.

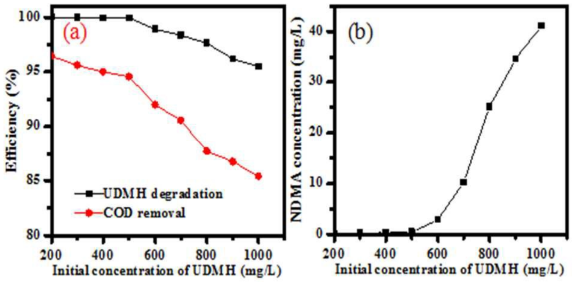

Figure 13. Effect of initial concentration of UDMH on catalytic oxidation of UDMH by CuO/ZnO/NiO/γ-Al_2O_3 catalyst: (a) UDMH and COD degradation efficiency; (b) NDMA concentration (H_2O_2: 5 mL; temperature: 65 °C; catalyst: 1 g; pH:7.5; time:30 min).

4. Reusability of CuO/ZnO/NiO/γ-Al_2O_3

Reusability of catalyst is a key factor to determine the feasibility of a catalyst[32]. Hence, in order to investigate the reusability of catalyst, the experiments were designed as follows. The catalyst powder after each reaction was recycled by centrifugation, and then dried. Five runs were conducted to evaluate the long-term reusability of CuO/ZnO/NiO/γ-Al_2O_3 with the optimal conditions discussed above. The results are listed in Table 2. It is clear that the little decrease of both efficiency of UDMH degradation and COD removal were observed after five runs reaction, but the values were acceptable. The concentration of NDMA remained in the water slightly increased (Table 2). Two reasons are cited to explain the above conditions. At first, it can be speculated that a thimbleful of catalyst was lost inevitably in the process of recycling catalyst. Secondly, a portion of elements was leached in aqueous solution,

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resulting in lower activity. The content of main active ingredient Cu^{2+} was detected. It was observed that it was less than 5% of copper loadings after twenty runs reaction, indicating a negligible leaching. Although these factors somehow influenced the catalytic activity, the synthesized $CuO/ZnO/NiO/\gamma\text{-}Al_2O_3$ kept relatively high activity at least in five runs and the catalytic efficiency was satisfactory. It is plausible compared with the methods using ion as a catalyst[2, 12].

Table 2. The indicators of the UDMH oxidation after reusing.

Repeating times	1	2	3	4	5
UDMH conversion (%)	99.9	99.5	99.0	98.7	98.1
COD removal (%)	94.6	93.8	92.4	91.1	90.7
NDMA content (mg/L)	0.45	1.26	2.04	3.05	3.92

5. Conclusions

Three-component metal catalyst ($CuO/ZnO/NiO/\gamma\text{-}Al_2O_3$) was prepared by the method of impregnation-calcination. The structural analysis by XRD, SEM and EDX indicated that the surface morphology of $\gamma\text{-}Al_2O_3$ nanoparticles was maintained at pre- and post-treatment, whilst CuO, ZnO and NiO were dispersed on the surface of $\gamma\text{-}Al_2O_3$ nanoparticle without any aggregation. It was firstly used as a catalyst in the process of catalytic wet peroxide oxidation (CWPO) for the degradation of unsymmetrical dimethylhydrazine (UDMH) in propellant wastewater with H_2O_2. As a result, UDMH was degraded rapidly and efficiently due to the highly active ·OH derived from H_2O_2. However, a key problem in the process arose from the removal of COD. Tracing the process of CWPO with the full scan UV-Vis and ESI (+) mass spectroscopy, it was found that a hard degradable compound, NDMA, was created by

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the degradation of UDMH. The path of NDMA generation was suggested that the hydroxyl radical (·OH) attacked mainly amino group of UDMH and Cu^{2+}. UDMH generated coupling reaction through the generation and disappearance of active ingredient Cu^{2+}. Based on the investigation of reaction factors, i.e. H_2O_2 dosage, temperature, pH of wastewater, catalyst dosage and the initial concentration of UDMH. The optimal conditions for CWPO with $CuO/ZnO/NiO/\gamma\text{-}Al_2O_3$ were determined, namely for the wastewater containing 500 mg/L UDMH, the H_2O_2 dosage was 5 mL, catalyst, 1.0 g, pH 7.5, temperature, 65℃. Under these conditions, the maximal treatable concentration of UDMH was 500 mg/L, with which the high efficiency of UDMH degradation and COD removal (99.9 % in 10 min and 94.6 % in 30 min, respectively) and the low concentration of NDMA (0.45 mg/L) were obtained. Moreover, the catalyst activity less changed after recycling for 5 times, indicating a good reusability. According to the Chinese standards for wastewater emission, by the present catalyst and CWPO process, the levels of UDMH and COD were qualified, but the concentration of NDMA was still a little higher than that of standards. Hence, the further improvement of this catalyst is required in the future.

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