Supplementary data for:

Contrasting mechanisms of UDMH degradation by MnO_2 and Mn_2O_3 under microwave assistance: Electronic structure, Surface adsorption and Catalytic reaction

Jiepeng Wang, Siyu He, Zhe Wang, Yunlong Deng, Jielei Hao, Xuqian Wang, Yongkui Zhang*

Department of Pharmaceutical & Biological Engineering, School of Chemical Engineering, Sichuan University, Chengdu 610065, China

Corresponding author:

Xuqian Wang, Yongkui Zhang

Department of Pharmaceutical & Biological Engineering, School of Chemical Engineering, Sichuan University, Chengdu 610065, China

Tel.: +86-28-85405221

Email: zhangyongkui@scu.edu.cn (Y. Zhang)

Text S1 Test methods

1. Determination of chemical oxygen demand (COD) - dichromate method

The COD of UDMH wastewater before and after degradation was determined according to the (GB 11914-89 Determination Method for Chemical Oxygen Demand in Water Quality according to the National Standards of the People's Republic of China). The specific operation procedure was as follows:

1.5 mL water sample was taken into a 10 mL digestion tube, then 0.5 mL mercury sulfate-masking agent, 1.5 mL potassium dichromate digestion solution, and 2.5 mL silver sulfate catalyst solution were added into sequence too. After mixing, the digestion tubes were thermally treated in an intelligent digestion instrument (TDR-25A) at 165 ^{o}C for 15 min, and then placed for cooling. The absorbance of the digestion solution was measured by ultraviolet visible spectrophotometer at 600 nm.

2. Determination of formaldehyde content - acetylacetone spectrophotometry

A pipette gun was used to add 2 mL of solution to be tested into a 25 mL volumetric flask, then deionized water was used to reach calibration line. After shaking well, 2.5 mL acetylacetone solution was added. The volumetric bottle was placed in a water bath at 65 ^{o}C for 15 min, then removed and cooled to room temperature. The absorbance of the solution was measured by UV-vis spectrophotometer using a quartz cuvette with an optical path of 1 cm at 414 nm wavelength and deionized water as a blank solution.

3. Determination of dimethyl hydrazine - amino-ferrous sodium cyanide spectrophotometric method

The UDMH of UDMH wastewater before and after degradation was determined according to the (GB/T 14376-1993 Water quality - Determination of partial dimethylhydrazine - sodium amino

ferrocyanide spectrophotometric method). The specific operation procedure was as follows:

2 mL of the solution was taken to be tested into a 25 mL volumetric flask and the solution was diluted with deionized water to the scale line. 1 mL citrate buffer was added to the solution, then 1 mL Sodium ferrocyanide amino (TPF) color developer was added after 30 s. After mixing well, the volumetric flask was kept warm in 25 ^{o}C water bath for 1 h. The absorbance of the solution was measured by UV-vis spectrophotometer using a quartz cuvette with an optical path of 1 cm at a wavelength of 500 nm with deionized water as a blank solution.

4. Test method for ammonia nitrogen

Appropriate amount of water sample pretreated by flocculation and precipitation (for that ammonia content would not exceed 0.1mg) was added into a 50 mL colorimetric tube, then the solution was diluted to mark line by deionized water. Then 1.0 mL potassium sodium tartrate solution of 500 g L^{-1} was added. Appropriate amount of deionized water was added to a 50 mL colorimetric tube, and a certain amount of 1mol L^{-1} sodium hydroxide solution was added to neutralize boric acid. And then the solution was diluted to the mark. Then 1.5 mL of Nachter reagent was added and the solution was mixed well. After 10 min, the absorbance was measured in the same step as the calibration curve.

5. Determination methods of NDMH and FDMH

The concentrations of NDMA and FDMH were quantitatively determined by HPLC on a C18 column (250 mm×4.6 mm, packing size 5 m, Supelco). Mobile phase was the mixture solution of acetonitrile and water (5:95, V/V), total flow rate was 1 mL min^{-1}, and detection wavelength was 230 nm and 235 nm, respectively [1].

6. UV full wavelength scanning conditions

Ultraviolet spectroscopy could determine the structure information of reactants and products in the degradation process and is widely used in the detection of organic pollutants. The full wavelength of some products degraded by UDMH was shown in Table S2 [2]. In this study, UV full-wavelength scanning method was used to analyze and detect the degradation solution of UDMH under different reaction conditions. And the residual concentrations of several major degradation products were evaluated. The scanning wavelength range was 190-600 nm.

7. Text method for Mn^{2+}

Inductively coupled plasma emission spectrometer (ICP-OES) is a highly sensitive instrument for elemental analysis, which is widely used in the detection of trace elements. In this study, ICP-OES method was used to analyze and detect manganese ions in UDMH degradation solution under different reaction conditions.

Text S2 SPME-GC-MS detect

Due to the low concentration of various intermediates after reaction, solid phase microextraction was used in this study to extract and enrich the degraded intermediates of UDMH, and then qualitative analysis was conducted by GC-MS. Specific steps were as follows：

(1) SPME: The sample was transferred to a 10 mL headspace bottle and then 1 g NaCl was added. Polyacrylate (PA) solid phase microextraction head was used for solid phase microextraction fiber, and adsorption temperature was room temperature, adsorption time was 40 min, magnetic stirring speed was 800 rpm, desorption temperature was 250 ^{o}C, desorption time was 3 min.

(2) GC - MS: DB-5 MS capillary column (30 m×0.25 mm×0.25 μm, Agilent, J&W Scientific) was used, split ratio was 10:1, carrier gas was high purity helium gas and flow rate was 1 mL min^{-1}. Heating procedure: keep at 40 ^{o}C for 5 min, and then heat up at 30 ^{o}C min^{-1} for 180 ^{o}C and keep for 2 min, and next heat up at 50 ^{o}C min^{-1} for 280 ^{o}C and keep for 2 min. Ion source temperature was 220 ^{o}C, and interface temperature was 280 ^{o}C. Scan m/z range was 20-500.

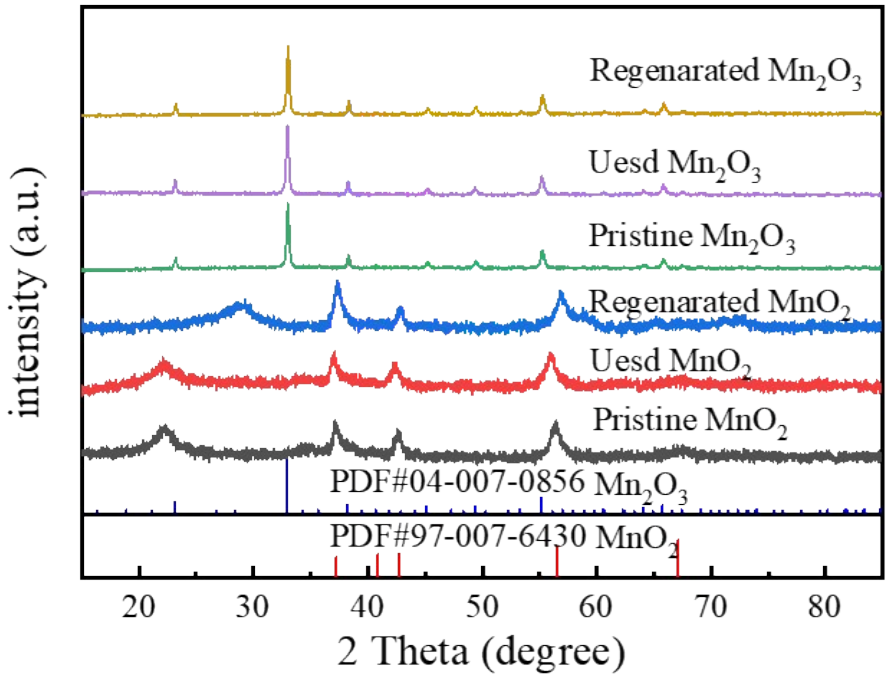


Fig. S1 Comparative XRD analysis between MnO_2 and Mn_2O_3

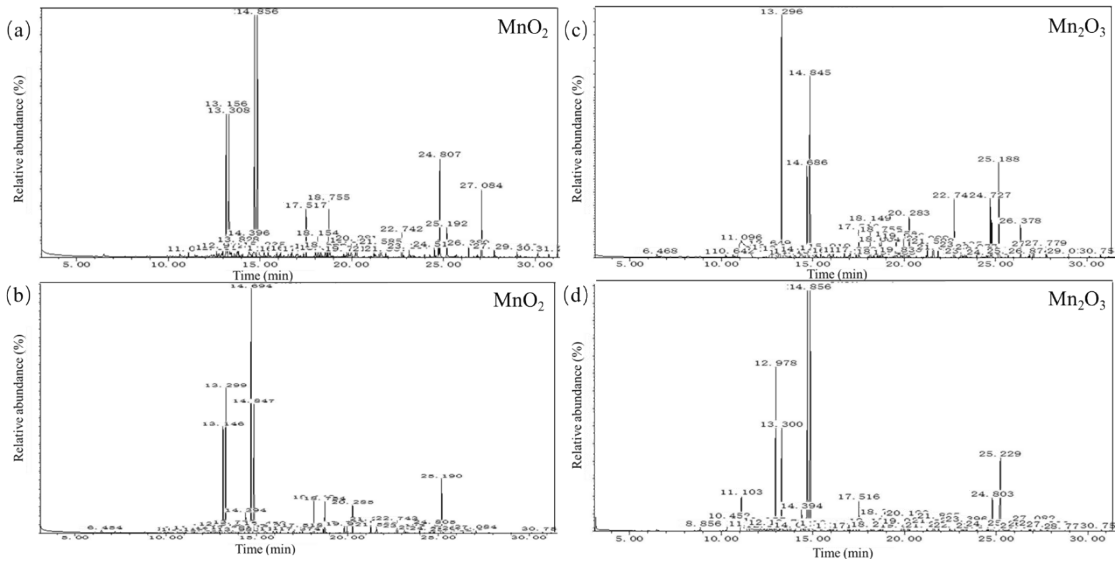


Fig. S2 Total ions chromatograms of the products from UDMH degradation under reaction for 5 min (a, c) and 60 min (b, d).

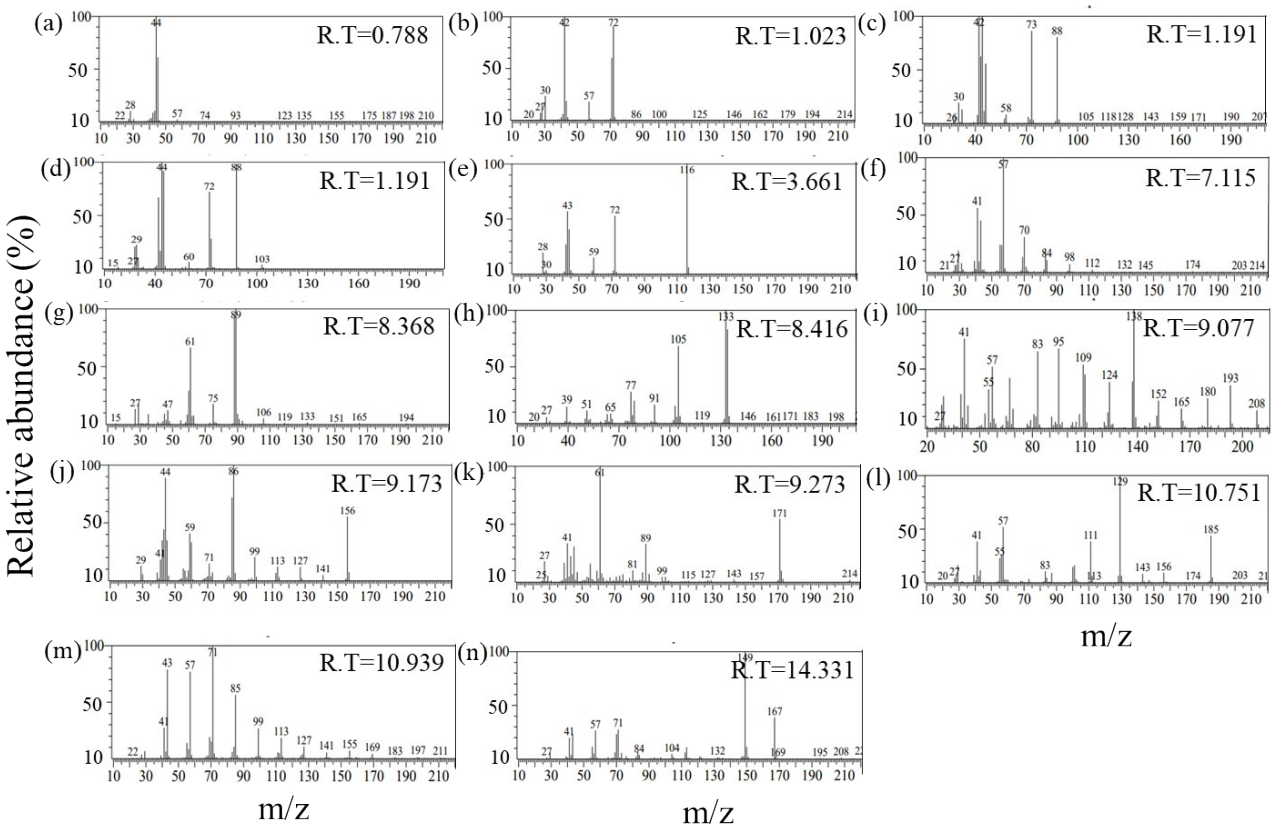


Fig. S3 Mass spectra of the products from UDMH degradation.

Table S1 The main parameters of UDMH solution

Parameters	Concentration of UDMH (mg L^{-1})	Concentration of COD (mg L^{-1})	Concentration of HCHO (mg L^{-1})	Initial pH
UDMH	250	543.05	2.72	6.04

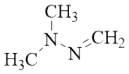
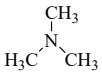
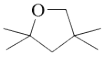
Table S2 The experimental parameters of reaction condition optimization

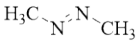
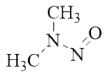
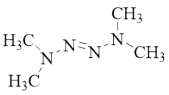
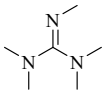
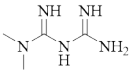
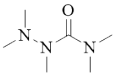
Parameters	Dosage of MnO_2 or Mn_2O_3 (mmol L^{-1})	Power of MV (W)	pH	Reaction time (min)
Dosage of MnO_2 or Mn_2O_3 (mmol L^{-1})	1/5/20/40/100/200/400	250	5	30
pH	5	250	1/3/5/7/9/11	30
Reaction time (min)	MnO_2 40 Mn_2O_3 100	250	MnO_2 9 Mn_2O_3 7	1/5/10/15/20/30 /60/120

Table S3 UV characteristic absorption wavelength for UDMH wastewater degradation products

Products	Characteristic absorption wavelength (nm)
NDMA	230
FDMH	235
TMT	280
$(CH_3)_2NN{=}CHN{=}NCH_3$	320
$(CH_3)_2NN{=}CHN{=}N(CH_3)_2^+$	360

Table S4 Possible intermediates of UDMH degradation

No.	Compound name	m/z	Tentative structure	Detected	Reported in/by
l^*_1/L^*_3	FDMH	72		√	3
l_2	formaldehyde	30	HCHO	√	3
l_3	trimethylamine	89		√	4
$l_4/p^*_8/P^*_7$	Tetramethyl tetrahydrofuran	128		√	4

l_5/p_6	N-methyl ethylamine	58		√	4
l_6	Penta methyl pyrrole	138		√	4
l_7/L_7	N-methylformamide	73		√	4
L_1/P_8	Dimethyl diazene	60		√	5
$L_2/p_3/P_3$	NDMA	74		√	3
L_4/P_9	Tetramethyl tetrazene	116		√	5
L_5	1, 1, 2, 3, 3-pentamethylguanidine	130		√	4
L_6	Formamide	45		√	6
$L_8/p_7/P_6$	1, 1-dimethyl guanidine	88		√	4
$L_9/p_2/P_2$	Pentamethylhydrazine amide	146		√	4
$L_{10}/p_5/P_5$	2H-pyrazole-3-amine	83		√	4
p_1/P_2	Dimethylamine	43		√	4

* For Mn_2O_3 degradation products, lowercase symbols (l_x) represent intermediates at 5 minutes, while uppercase symbols (L_x) denote products at 60 minutes. For MnO_2 degradation products, lowercase symbols (p_x) indicate intermediates at 5 minutes, and uppercase symbols (P_x) signify final products at 60 minutes.

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