A study on Kinetics of Mn$_2$O$_3$ catalytic oxidation about Supercritical (near) critical water of POPs

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Abstract: Supercritical(near) critical water oxidation is a green and efficient method developed in recent years for the treatment of organic waste. The kinetics of Mn$_2$O$_3$ catalytic degradation of persistent organic pollutants (POPs) in Supercritical(near) critical water was studied. The reaction order, apparent activation energy and the feedback of three factors on catalytic degradation were determined. The experiment shows that under the conditions of temperature 280~360℃, pressure 6.9~20.3mpa and reaction time 5~30min, Mn$_2$O$_3$ and hydrogen peroxide are used as the oxygen source without the catalyst. 4,4'-dibromobiphenyl has a reaction order of 1.71, Apparent activation energy 46.56 kJ/mol; Mn$_2$O$_3$ catalyst was used, the reaction order of 4,4'-dibromobiphenyl was 1.79, and the apparent activation energy was 37.89 kJ/mol. Therefore, Mn$_2$O$_3$ as a catalyst can significantly degrade the activation energy of POPs in near-critical water.

1. The introduction

When water is in the high-temperature and high-pressure state above the critical point (374℃, 22.1Mpa), it is called Supercritical(near) critical water. Supercritical water has variable density, low surface tension, low viscosity and high diffusion coefficient$^{[1-3]}$. Supercritical water oxidation technology can be used in the treatment of various toxic substances and waste water. There are many reports on the development and application of supercritical water oxidation technology. The main treatment objects include: phenol$^{[4]}$, trichloroacetaldehyde, nitrobenzene, tert-butanol$^{[5]}$, naphthal$^{[6]}$, diaminoethylene dioxime, cyanogen and melamine$^{[7]}$, DDT, polychlorinated biphenyl, dioxins$^{[8]}$, explosive wastewater$^{[9]}$, papermaking wastewater$^{[10]}$, organic fermentation wastewater$^{[11]}$, nitrification process wastewater$^{[12]}$, organophosphorus pesticides$^{[13-14]}$ and plastics$^{[15]}$ and so on. Supercritical water oxidation technology has high treatment efficiency and low treatment cost$^{[16]}$. It is economically and technically feasible and has a broad development prospect. Supercritical water oxidation (swo) is a green and efficient method for the treatment of organic waste developed in recent years. Listed in the national key technology of one of the big six “energy and the environment”, the SCWO listed as the most promising waste disposal technology, the scientist Paul w. Hart said: “given the SCWO method has many advantages, and use it to replace the incineration method is full of vitality.”

This study mainly studied the kinetics of Mn$_2$O$_3$ catalytic degradation of persistent organic pollutants (POPs) in near-critical water, and determined the feedback of three factors, including reaction order, apparent activation energy and pre-index factor, on catalytic degradation.

2. The experiment content
2.1 Experimental instruments
High-pressure reaction kettle: Hai’an huada petroleum instrument co., LTD
High efficiency and energy saving industrial resistance furnace: 10kw, Kaifeng teda electric furnace technology co., LTD
Electric thermostatic blast drying oven: dgg-9070b, Shanghai senxin industrial instrument co., LTD
Electronic balance: ab104-n, mettler Toledo instrument Shanghai co., LTD
Ultrasonic cleaner: QT10260, Tianjin ripu electronic instrument co., LTD
Vacuum pump: 2xz-2, Shanghai vacuum pump factory
Muffle furnace: sxl-1208, Shanghai jinghong experimental equipment co., LTD
Digital regulator: XMTD, Shanghai huihai electrical equipment co., LTD
Integrated thermal analyzer: STA 409 PC, neisch instrument company, Germany
X ray diffractometer: D’max-2200, science corporation, Japan

2.2 The raw material
4,4’-dibromobiphenyl: yantai jiumu chemical co., LTD
Manganese dioxide: analytically pure, Shanghai tongya chemical technology development co. LTD
Hydrogen peroxide solution: analytically pure, Shanghai sinopyrine chemical reagent co. LTD
Silver sulfate: analytically pure, Shanghai fine chemical materials research institute
Concentrated sulfuric acid: analytically pure, Shanghai sinopyrine chemical reagent co. LTD
7-Hydrated ferrous sulfate: Shanghai shanhai engineering group experiment no.2 plant
Artificial zeolite: 20~40 mesh, Shanghai reagent 5 factory
Deionized water: made in laboratory.

2.3 experimental process

2.3.1 preparation of catalysts
MnO₃; Zinc heteropoly. Mn₃O₇ catalyst is sold by the MnO₂ powder, through molding, drying, roasting, crushing and other steps.

2.3.2 oxidative degradation of 4,4’-DBB
The intermittent agitation-free high-pressure stainless steel reactor was used as a device for the oxidation and degradation of 4,4’-DBB, with a volume of 100ml. The liquid product was calculated according to the K₂Cr₂O₇ method in national standard 11914-89, and the chemical oxygen demand (COD) value was taken as the evaluation index.

2.3.3 determination of chemical oxygen demand (COD)
Accurately absorb 20.00ml of evenly stirred sample (if the sample is less than 20.00ml, it can be diluted to 20.00ml), 10.00mlK₂Cr₂O₇ standard solution, put it in a reflux conical bottle containing grinding port, then add several small zeolites or glass beads, mix the ingredients in conical bottle evenly through shock. Start the timer from the boiling of the liquid, reheat and reflux for 2h.

If the COD value of the water sample is too high, you can first take 1/10 of the required volume in the above steps for measurement, and then gradually reduce the content of the water sample, until the measured solution is not green, the volume of the water sample used at this time should be the required volume for analysis of the water sample. In the process of water sample dilution, the volume of water sample absorbed shall not be less than 5.00ml. For water samples with high COD value, progressive dilution and multiple dilution can be carried out. If the content of Cl- in the water sample is greater than 30mg/L, 0.4g HgSO₄ should be placed in the reflux conical flask first, and then 20.00ml water sample or diluted water sample should be added for determination.

After reflux, the liquid was cooled to room temperature, and the outer wall of the condensing tube was washed with 90ml deionized water, and the reflux conical bottle was removed. If the total volume
of the liquid is too large, the titration end point will be fuzzy, affecting the determination results. So the total volume of the solution should be less than 140 milliliters.

After the solution is thoroughly cooled, drop 3 drops of ferrous spirit indicator and titrate the sample through the standard solution of ferrous ammonium sulfate. When the color of the solution changes from yellow to turquoise to reddish brown, record the volume of the titrant used.

20.00ml deionized water was taken for the above steps as the blank contrast experiment, and the volume of titrant used in the blank test was accurately recorded.

Calculate the COD value of the water sample

\[
\text{COD}_{\text{Cr}} (\text{mg/L}) = (V_0 - V_1) \times C \times 8 \times 1000 / V
\]

Where: 
- \(C\) -- concentration of titrant, namely the standard solution of ammonium ferrous sulfate, mol/L;
- \(V_0\) -- the volume of the standard solution of ammonium ferrous sulfate required for blank experiment, ml;
- \(V_1\) -- volume of the standard solution of ammonium ferrous sulfate required for water sample determination, ml;
- \(V\) -- volume of water sample used in the experiment, ml;

2.3.4 establishment of kinetics equation of degradation reaction

Firstly, the experimental data are preprocessed to improve the fitting accuracy. Then experimental data input to the main interface, in the use of MATLAB simulation toolbox (MATLAB7.0→Start→Toolboxes→CurveFitting Tool) for data processing, customized nonlinear fitting, as shown in figure 1.

![Figure 1 the Create Custom Equation dialog box](image)

3. Results and discussion

3.1 kinetic analysis of non-catalytic cracking reaction

The experimental data of non-catalytic degradation reaction kinetics are shown in table 1.

| Residence time /min | COD (mg/L) | 320°C | 340°C | 350°C | 360°C |
|---------------------|------------|-------|-------|-------|-------|
| 5                   | 347.2      | 283   | 239.5 | 214.8 |
| 10                  | 228        | 154.2 | 122.5 | 98.7  |
| 15                  | 157.2      | 119.2 | 89.5  | 67.3  |
| 20                  | 85.4       | 65.7  | 52.9  | 42.2  |
| 25                  | 62.6       | 48.6  | 23.6  | 12.6  |
| 30                  | 49.3       | 31.4  | 12.8  | 3.3   |

Because the oxidation reaction in the near critical state of water produces more intermediate products, reflecting a more complex situation, easy to be affected by many factors and interference. The power exponential equation method is not affected by the intermediate reaction and the products, but only
depends on the concentration of reactants and the reaction temperature. Therefore, the power exponential equation method is adopted in this paper for the kinetic study of the reaction. In the process of this reaction, the organic matter content can be characterized by chemical oxygen demand, so the content of pollutants in the macroscopic dynamics study can be characterized by chemical oxygen demand after the reaction, and the change of chemical oxygen demand can be characterized by the oxidation reaction process. Thus, the following dynamic expression can be obtained:

\[
\frac{d[COD]}{dt} = k[COD]^a[H_2O_2]^b
\]  

(1)

Where: a, b respectively represent the reaction series of COD and \( H_2O_2 \).

Since the oxidant (\( H_2O_2 \)) is excessive in the near critical water oxidation reaction, the concentration of the oxidant \( [H_2O_2] \) in the reaction process can be considered as a constant, so \( [H_2O_2]^b \) can be incorporated into \( k_1 \), then equation (1) is converted into

\[
\frac{d[COD]}{dt} = k [COD]^a
\]  

(2)

After the determination of initial chemical oxygen demand \( [COD]_0=3628 \) mg/L, the initial conditions were applied: \( t=0, [COD]_0=3628 \) mg/L, and when \( a\neq1 \), the integral of equation (2) was:

\[
[COD] = 3628[1 + 3628^{a-1}k(a-1)t]^{1/(a-1)}
\]  

(3)

According to the experimental data in table 1, equation (3) is fitted to get figure 2. Through regression analysis, \( a=1.71 \) can be obtained, and the reaction rate under different temperatures is constant \( k \). The specific data are shown in table 2.

**Table 2 Relationship between temperature and reaction rate constant**

| T/℃  | 320   | 340   | 350   | 360   |
|------|-------|-------|-------|-------|
| k×10³ | 1.057 | 1.358 | 1.655 | 1.915 |

Fig2 non catalyzed kinetic data fitting chart
According to the Arrhenius formula,

\[ k = Ae^{-\frac{E_a}{RT}} \]  

Arrhenius formula can be converted into the following formula:

\[ \ln k = -\frac{E_a}{RT} + \ln A \]  

Where \( A \) is the preexponential factor and \( E_a \) is the reaction activation energy.

\( \ln k \) and \( -\frac{-1\times10^3}{T} \) were used to draw the figure, and the results were shown in figure 3. According to the slope of the line, the reaction activation energy \( E_a = 46.56 \text{ kJ/mol} \), and the preexponential factor \( A = 13.09 \).

Fig 3 non catalytic conditions of LNK and \(-T^{-1}\times10^3\) relationships

| COD (mg/L) | 320°C | 340°C | 350°C | 360°C |
|-----------|--------|--------|--------|--------|
| 5         | 208.6  | 180    | 148.5  | 115.9  |
| 10        | 118    | 83     | 70.5   | 61.4   |
| 15        | 63.5   | 41.2   | 32.4   | 23.7   |
| 20        | 32.64  | 25.7   | 20.5   | 15.2   |
| 25        | 22.6   | 18.6   | 13.9   | 3.6    |
| 30        | 17.3   | 11.4   | 2.8    | 0      |

3.2 kinetic analysis of MnO₃ catalytic degradation reaction

Experimental data of MnO₃ catalytic degradation reaction kinetics are shown in table 3.

Under the catalysis of near-critical water oxidation, the following kinetic expression is obtained:

\[ -\frac{d(COD)}{dt} = k_i[COD]^a[H_2O_2]^b[M]^c \]  

In the formula, \( a, b \) and \( c \) respectively represent the reaction series of COD, \( H_2O_2 \) and \( M \) (catalyst).

The regression study was carried out through formula 3 of the test data in table 1, and the value of \( a \) calculated in figure 4 was obtained (\( a = 1.71 \)), and then the value of the reaction rate constant \( k \) under different temperature conditions was obtained. The specific calculation is shown in table 4.
Fig. 4 fitting diagram of kinetic data under Mn$_2$O$_3$ catalysis
(a) 320°C (b) 340°C (c) 350°C (d) 360°C

Table 4 relationship between temperature and reaction rate constant

| T/°C | k×10$^3$ |
|------|----------|
| 320  | 5.261    |
| 340  | 6.178    |
| 350  | 7.202    |
| 360  | 8.681    |

LNK and (-T$^{-1}×10^3$) were used to draw the figure, and the results were shown in figure 5. Just like non-catalytic oxidation, the reaction activation energy Ea= 37.89 kJ/mol could be calculated based on the slope of the line.

Fig. 5 relationship between LNK and -T$^{-1}×10^3$ catalyzed by Mn$_2$O$_3$

4. Conclusion
Under the conditions of temperature 280~360°C, pressure 6.9~20.3mpa and reaction time 5~30min, Mn$_2$O$_3$ and hydrogen peroxide were used as oxygen sources to study the kinetics of catalytic oxidation of 4,4'-dibromobiphenyl by near-critical water. Through MATLAB software fitting, it was found that:
(1) without catalyst, the reaction order of 4,4'-dibromobiphenyl is 1.71, with apparent activation energy of 46.56 kJ/mol.

(2) MnO₃ catalyst was used, the reaction order of 4,4'-dibromobiphenyl was 1.79, and the apparent activation energy was 37.89 kJ/mol.

(3) activation energy of MnO₃ as catalyst can significantly degrade POPs in near-critical water.

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