Kinetic Model of Organics Degradation of Reverse Osmosis Concentrate by UV/H₂O₂ Processing

Xiaoli Ye* Haijun Sun, Shan Gao, Lei Qiao
Wuhan Second Ship Design and Research Institute, Wuhan, China

*Corresponding author e-mail: 172513406@qq.com

Abstract. The contrast experiments showed that H₂O₂ was difficult to oxidize organics while Ultraviolet light direct photolysis could decompose organics partially. However, the UV/H₂O₂ system could significantly enhance the degradation of organics efficiency due to the synergetic effect between UV radiation and oxidation. The degradation process accorded approximately with the quasi-first-order kinetics. A simplified kinetic model of degrading organics in reverse osmosis concentrate (ROC) streams by UV/H₂O₂ method is established using related theories of the steady state approximation and pseudo-first order kinetic model. The simulation results of the model is basically consistent with the experimental results, and the error is maintained below 10%.

1. Introduction
Reverse osmosis (RO) technology has been used increasingly in the seawater and brackish water desalination, wastewater reclamation and other fields, which provides 70%-75% high-quality reclaimed water with environmental and economic benefits. However, about 25%-30% reverse osmosis concentrate (ROC) is generated consequently, and the pollutants concentration in ROC can be 2~3 times higher than that in RO influent. Generally, those organic pollutants are refractory dissolved organic matter (DOM), and maybe contain some environmental priority pollutants.

Ultraviolet photo catalytic oxidation process has a lot of advantages over other processes, including high oxidation ability, low selectivity, complete reaction and no waste produced, etc. UV/ H₂O₂ process produces highly oxidizing hydroxyl radicals (·OH), the redox potential is 2.80 V, which is higher than the reduction potential of ozone (2.07 V), hydrogen peroxide (1.77 V), and chlorine (1.30 V). It can completely mineralize or partially decompose most of the organic matter in water, and has broad application prospects [1]. This study used UV/ H₂O₂ photo oxidation degradation to treat the reverse osmosis concentrated water of a coal-to-olefins plant, and the ROC of a coal-to-olefins plant is taken as the research object, and raised a simplified reaction kinetics model with the test results, in order to provide a theoretical reference for the application of this technology in practical engineering.

2. Experimental
2.1. Materials
The ROC was collected from the RO process of a coal-to-olefins plant which used a coupling technique of intermediate chemical desalination and secondary reverse osmosis. The water quality of the ROC is summarized in Table1.
Table 1. Main characteristic of the ROC samples

| Parameters             | Values     | Parameters     | Values     |
|------------------------|------------|---------------|------------|
| pH                     | 7.95~8.22  | Cl (mg/L)     | 5301.2     |
| Conductivity (μS/cm)   | 9800~11000 | SO42-(mg/L)   | 4916.9     |
| COD (mg/L)             | 200.2      | NO 3-(mg/L)   | 529.6      |
| TOC (mg/L)             | 33.25      | Alkalinity (mg/L) | 224.6 |

2.2. Photochemical experiments

Experiments were carried out in a 1L (effective volume) stainless steel cylindrical reactor with a sampling hole on the top. A 10W low pressure mercury lamp, emitting at 254 nm was used. Aqueous solutions were stirred by a magnetic bar (200 r/min) throughout the experiments in order to remain homogeneous. Before each experiment, the lamp was warmed up for 15 min to ensure stable lamp-output.

In a typical photochemical experiment, 500 ml of ROC were put in the reactor and, for UV/H2O2 experiments, the appropriate amount of H2O2 was added. Afterwards, the warmed up UV-lamp was introduced into the reactor and, at given times, a 5 ml sample was taken and immediately analyzed by total organic carbon analyzer.

2.3. Analytical method

For the samples from the degradation process, the total organic carbon (TOC) was measured by a TOC analyzer (TOC-L CPN, Shimadzu Corporation). Samples were filtered (0.45 micron cellulose acetate) prior to the TOC analyses.

3. Results and discussion

3.1. UV, H2O2, UV/H2O2 Treatment of the ROC

Experiments of the ROC organics degraded by UV alone, H2O2 alone and combined UV/H2O2 processes were carried out respectively. As we can see, the removal rate of TOC are respectively 13%, less than 1% and 86% when used UV, H2O2 and UV/H2O2. The results shown in Figure 1 indicated that it was difficult to be oxidized by hydrogen peroxide alone. However, UV photolysis process could remove only a small fraction of TOC after 360min of reaction time. Furthermore, the presence of H2O2 significantly increased the degradation of MC-RR compared with UV radiation alone. It could be concluded that there existed synergetic effect between UV photolysis and hydrogen peroxide oxidation [2].

The experimental data were fitted with pseudo-first-order, and the fitted kinetic parameters were presented in Table 2. Where $k$ was the observed pseudo-first-order. R² was the corresponding correlation coefficient. Although the degradation of organics using combined UV/H2O2 system was a complicated oxidation process, the results showed that it could be described approximately with the pseudo-first-order. It was apparent that the rate constants of the combined UV/H2O2 oxidation of organics were higher than that of single H2O2 oxidation plus UV photolysis, which meant that the degradation of organics were significantly accelerated under the combined UV/H2O2 process. This also proved that hydroxyl radical generated during the reaction.
Figure 1. Influence of different reaction systems on degradation performance of organics
(=10mmol/L, pH=7.95~8.22 , single UV lamp ,t=25±1°C,200r/min)

Table 2. Degradation kinetics of different reaction systems of organics

| different reaction systems | Pseudo-first order kinetic equation | k / min\(^{-1}\) | R\(^2\) |
|----------------------------|------------------------------------|----------------|--------|
| \(\text{H}_2\text{O}_2\)     | \(\ln (\text{TOC}_0/\text{TOC})=2.0 \times 10^{-5} t\) | \(2.0 \times 10^{-5}\) | 0.8733 |
| UV                        | \(\ln (\text{TOC}_0/\text{TOC})=2.0 \times 10^{-4} t\) | \(2.0 \times 10^{-4}\) | 0.9791 |
| UV/\(\text{H}_2\text{O}_2\) | \(\ln (\text{TOC}_0/\text{TOC})=0.0062 t\) | 0.0062        | 0.9471 |

3.2. Effect of Initial \(\text{H}_2\text{O}_2\) Concentration

Experiments of organics degraded was conducted with varying the initial concentration of \(\text{H}_2\text{O}_2\) from 0 to 20 mmol/L. The results were presented in Figure 2. As shown in Figure 2, the degradation rate increased nonlinearly with increasing \(\text{H}_2\text{O}_2\) dosage. However, with the continuous increase in the initial \(\text{H}_2\text{O}_2\) concentration, especially beyond 10 mmol/L, the degradation rate of organics declined slightly.

Figure 2. Effect of initial \(\text{H}_2\text{O}_2\) concentration on the degradation of organics
(pH=7.95~8.22,single UV lamp, t=25±1°C , 200r/min)

Applying the pseudo-first-order rate reaction, the oxidation kinetics of organics at different initial \(\text{H}_2\text{O}_2\) concentrations was also studied under the UV/ \(\text{H}_2\text{O}_2\) process and the fitted kinetic parameters were
listed in Table 3. This proved that the effect of increasing H₂O₂ concentration was the most essential for the degradation of organics attributed to the powerful oxidation species of hydroxyl radical amount increased from the decomposition of increasing H₂O₂. It has been proved that H₂O₂ acts as both promoter and scavenger of HO• [3]. According to reaction (7), H₂O₂ can produce HO• under UV radiation. Additionally, according to reaction (10), H₂O₂ reacts with the HO• to form HO₂•, which has lower oxidation performance compared with HO•. In the excess of H₂O₂, competitive reactions occurred.

| C[H₂O₂] / mmol/L | pseudo-first order kinetic equation | k / min⁻¹ | R² |
|------------------|-----------------------------------|-----------|----|
| 0.0              | Ln (TOC₀/TOC) = 0.0002 t          | 0.0002    | 0.8596 |
| 1.0              | Ln (TOC₀/TOC) = 0.0020 t          | 0.0020    | 0.9839 |
| 2.0              | Ln (TOC₀/TOC) = 0.0028 t          | 0.0028    | 0.9785 |
| 5.0              | Ln (TOC₀/TOC) = 0.0040 t          | 0.0040    | 0.9718 |
| 10.0             | Ln (TOC₀/TOC) = 0.0070 t          | 0.0055    | 0.9595 |
| 20.0             | Ln (TOC₀/TOC) = 0.0059 t          | 0.0050    | 0.9480 |

3.3. Establishment of Kinetic Model

Effect of UV / H₂O₂ oxidation of organics attributed to UV photolysis, H₂O₂ and HO• oxidation (ignoring the oxidation of other oxidizing radicals in the process) [4]. H₂O₂ oxidation proved to be negligible (Table 1). Applying the pseudo-first-order rate reaction, the oxidation kinetic equations of organics can be expressed as:

\[
r_{\text{UV/H}_2\text{O}_2} = -\frac{dC_R}{dt} = k_{\text{obs}} C_R = (k_{w} + k_{\text{HO•}})C_R
\]

3.3.1. UV radiation

Organics(R) absorbed ultraviolet light and turned into an excited state (R*), then converted to a reaction intermediate (R₁) [5].

\[
R \xrightarrow{k_1} R^* \xrightarrow{k_2} R_1
\]

The rate of UV photolysis reaction of organics is:

\[
r_{\text{UV}} = k_{\text{UV}} C_R = k_1 C_R - k_{-1} C_{R^*}
\]

Applying the steady state hypothesis (i.e., the concentration of R* is constant), then:

\[
\frac{dC_{R^*}}{dt} = -k_1 C_R + k_{-1} C_{R^*} + k_2 C_{R^*} = 0
\]

Solve this C_{R^*}, substituting equation (3) for the reaction rate equation of UV photolysis:

\[
r_{\text{UV}} = k_{\text{UV}} C_R = \frac{k_1 k_2}{k_1 + k_2} C_R
\]
\[ k_{UV} = \frac{k_1 k_2}{k_1 + k_2} \]  

(6)

k1, k2 and K2 related to light intensity, en light intensity is constant, \( \frac{k_1 k_2}{k_1 + k_2} \) is a constant [6].

### 3.3.2. •OH oxidation

The primary and principal step for the UV/H2O2 degradation has been postulated as the initial attack by photon to H2O2 and the formation of •OH. The •OH then undergo radical-chain reaction with the organics, and product are formed.

\[ \text{H}_2\text{O}_2 \xrightarrow{k_v}{k_1} 2 \cdot \text{OH} \]

(7)

\[ \text{R} + \cdot\text{OH} \xrightarrow{k_2} \text{R-OH} \]

(8)

The reaction of •OH oxidation of organics can be expressed as:

\[ r_{\text{•OH}} = k_{\cdot\text{OH}} C_R = k_4 C_{\cdot\text{OH}} C_R \]

(9)

Other reactions involved are given below [7–9]:

\[ \text{H}_2\text{O}_2 + \cdot\text{OH} \xrightarrow{k_3=2.7 \times 10^7 \text{M}^{-1}\text{s}^{-1}} \text{HO}_2 \cdot + \text{H}_2\text{O} \]

(10)

\[ \text{H}_2\text{O}_2 + \text{HO}_2 \cdot \xrightarrow{k_3=3.0 \text{M}^{-1}\text{s}^{-1}} \text{OH} + \text{O}_2 + \text{H}_2\text{O} \]

(11)

\[ \text{HO}_2 \cdot + \cdot\text{OH} \xrightarrow{k_5=7.5 \times 10^7 \text{M}^{-1}\text{s}^{-1}} \text{OH}^+ + \text{HO}_2 \cdot \]

(12)

\[ \text{HO}_2 \cdot + \cdot\text{OH} \xrightarrow{k_6=7.1 \times 10^7 \text{M}^{-1}\text{s}^{-1}} \text{H}_2\text{O} + \cdot\text{O}_2 \]

(13)

\[ \text{Cl}^- + \cdot\text{OH} \xrightarrow{k_7=4.3 \times 10^7 \text{M}^{-1}\text{s}^{-1}} \text{ClO}^- \cdot \]

(14)

\[ \text{ClO}^- \cdot \xrightarrow{k_8=6.1 \times 10^7 \text{M}^{-1}\text{s}^{-1}} \text{Cl}^- + \cdot\text{OH} \]

(15)

Assume that the concentration of chloride was a constant. In addition, the data demonstrated that the rate of reaction (16) and (17) were not different largely and located on the same magnitude. Therefore, it can be assumed that the concentration of •OH in the reaction of reaction (16) and (17) was constant. Now, the rate of •OH and HO2• are:

\[ \frac{dC_{\cdot\text{OH}}}{dt} = -2k_1 C_{\cdot\text{HO}_2} + k_4 C_{\cdot\text{OH}} C_R + k_5 C_{\cdot\text{OH}} C_{\cdot\text{OH}} - k_6 C_{\cdot\text{HO}_2} C_{\cdot\text{OH}} - k_7 C_{\cdot\text{HO}_2} C_{\cdot\text{OH}} + k_8 C_{\cdot\text{HO}_2} C_{\cdot\text{OH}} \]

(16)

\[ \frac{dC_{\cdot\text{HO}_2}}{dt} = -k_1 C_{\cdot\text{HO}_2} C_{\cdot\text{OH}} + k_6 C_{\cdot\text{HO}_2} C_{\cdot\text{OH}} - k_7 C_{\cdot\text{HO}_2} C_{\cdot\text{OH}} + k_8 C_{\cdot\text{HO}_2} C_{\cdot\text{OH}} \]

(17)

With steady state hypothesis, ie:
\[
\frac{dC_{\text{cde}}} {dt} = \frac{dC_{\text{mno}}} {dt} = 0
\]  
(18)

Simultaneous (16), (17) and (18), it can be concluded:

\[
C_{\text{cde}} = \frac{2(k_1 + k_6C_{\text{H}}O_2)C_{\text{H}}O_2}{k_2C_R + 2k_6C_{\text{H}}O_2 + 2k_7C_{\text{H}}O_2}
\]  
(19)

Compared to the reaction constant \(k_1\) the and \(k_6\) are too small to ignore. The concentration of organics in the same reaction system is constant, so it can be assumed \(A = k_4C_R\); Assuming that the concentration of \(\text{HO}_2\) only related to the concentration of \(\text{H}_2\text{O}_2\), so it can be assumed \(B = 2k_7C_{\text{H}}O_2\). Equation (19) can be further simplified to:

\[
C_{\text{cde}} = \frac{2k_4C_{\text{H}}O_2}{A + B + 2k_6C_{\text{H}}O_2}
\]  
(20)

\[
k_{\text{cde}} = k_4C_{\text{cde}} = \frac{2k_4k_6C_{\text{H}}O_2}{A + B + 2k_6C_{\text{H}}O_2}
\]  
(21)

Therefore, the total apparent rate constant \(k_{\text{obs}}\) is:

\[
k_{\text{obs}} = \frac{k_1k_2}{k_3 + k_2} + \frac{2k_1k_6}{k_6 + (A + B)/C_{\text{H}}O_2}
\]  
(22)

Assume that the function of \(k_{\text{obs}}\) is related to \(\text{H}_2\text{O}_2\) concentration:

\[
k_{\text{obs}} = k\left(C_{\text{H}}O_2\right)^\alpha
\]  
(23)

Simultaneous logarithms on both sides, that is:

\[
\ln k_{\text{obs}} = \alpha \ln(C_{\text{H}}O_2) + \ln k
\]  
(24)

Under the same conditions, the oxidation rate constant of organics were shown in Table 2, with varying the initial concentration of \(\text{H}_2\text{O}_2\) from 0 to 10 mmol/L. Figure 3 is made with \(\ln C_{\text{H}}O_2\) as abscissas and \(\ln k_{\text{obs}}\) as ordinate.
Figure 3. Relationship between the total apparent rate constant and initial concentration of H$_2$O$_2$.

Compare coefficient and it can be concluded:

$$k_{obs} = 0.002203 C_{H_2O_2}^{0.4325}$$  \hspace{1cm} (25)

Substituting Equation (25) into Equation (1) for integration, the kinetic equation of organics in the UV/ H$_2$O$_2$ oxidation process is:

$$\ln \frac{C_{R_1}}{C_{R_0}} = 0.002203 C_{H_2O_2}^{0.4325} t$$  \hspace{1cm} (26)

3.4. Model verification test

The comparison between simulation results and experimental results were shown in Figure 4. As can be seen from Figure 4, the simulation results of the kinetic model for the oxidation process of organics was basically consistent with the experimental results.

Figure 4. Comparison of experimental results of the organics degradation with simulation results ($C_{H_2O_2}=10$mmol/L, pH=7.95~8.22, single UV lamp, t=25±1°C,200r/min)

The slight deviation exists because the model derivation process is partially simplified. However, in general, when the light intensity and the initial concentration of H$_2$O$_2$ are fixed, the quasi-first-order
reaction kinetic model can be used to describe the process of organics degradation. Which provided a theoretical reference for the design of water treatment projects under similar water quality conditions.

4. Conclusion
The following conclusions can be drawn from the results of the experiments.

Firstly, the contrast experiments showed that the oxidation of organics efficiency enhanced significantly due to the synergetic effect between UV radiation and oxidation.

Secondly, degradation of Organics in ROC followed the pseudo-first-order kinetics under the experimental conditions.

Thirdly, with the increase of hydrogen peroxide concentration, the reaction rate rises increased first and then decreased.

Lastly, a simplified kinetic model of degrading organics in ROC by UV/ H2O2 method is established using related theories of the steady state approximation and pseudo-first order kinetic model. The relationship between the observed rate constants and the concentration of H2O2 can be described as follows: 

\[ k_{obs} = 0.002205C_{H_2O_2}^{0.4325} \]

The simulation results of the model basically agree well with experimental results.

Symbol (Nomenclature)

- \( C_r, C_{r0}, C_{r*}, C_{r-OH} \) Represent the concentration of organics at any given moment, initial, excited state and intermediate state in ROC, mg/L;
- \( C_{H_2O_2}, C_{H_2O_2,0} \) Represent the concentration of H2O2 at any given moment and initial, mmol/L;
- \( C_x \) Represent the concentration of \( x \) (intermediate) concentration, mol\cdotL\(^{-1}\);
- \( r_x \) Represent the reaction rate of \( X \), mg\cdotL\(^{-1}\)\cdots\(^{-1}\);
- \( k_x \) Represent the reaction rate constant of \( X \), s\(^{-1}\) or mol\cdotL\(^{-1}\)\cdots\(^{-1}\).

References

[1] Li, S. F., Wang, L., & Huang, J. L. (2004). Removing organic substance in water by UV/H2O2 system. Journal of Harbin Institute of Technology, 36 (12), 1686-89.
[2] Andreozzi, R., Caprio, V., Insola, A., & Marotta, R. (2000). The oxidation of metol (n-methyl-p-aminophenol) in aqueous solution by UV/H2O2, photolysis. Water Research,34 (2), 463 - 472.
[3] Glaze, W. H., Kang, J. W., & Chapin, D. H. (1987). The chemistry of water treatment processes involving ozone, hydrogen peroxide and ultraviolet radiation. Ozone Sci Eng, 9 (4), 335-352.
[4] De, A. K., Chaudhuri, B., Bhattacharjee, S., & Dutta, B. K. (1999). Estimation of \( \cdot \)oh radical reaction rate constants for phenol and chlorinated phenols using UV/H2O2 photo-oxidation. Journal of Hazardous Materials, 64 (1), 91 - 104.
[5] Aránguiz, J., Prado, J., Chamarro, E., & Esplugas, S. (1995). Kinetics of the ud degradation of atrazine in aqueous solution in the presence of hydrogen peroxide. Journal of Photochemistry & Photobiology A Chemistry, 88 (1), 65-74.
[6] Crittenden, J. C., Hu, S., Hand, D. W., & Green, S. A. (1999). A kinetic model for H2O2/UV process in a completely mixed batch reactor. Water Research, 33 (10), 2315 - 2328.
[7] Grebel, J. E., Pignatello, J. J, & Mitch, W. A. (2010). Effect of halide ions and carbonates on organic contaminant degradation by hydroxyl radical-based advanced oxidation processes in saline waters. Environmental Science & Technology, 44(17), 6822.
[8] El-Dein, A. M., Libra, J. A., & Wiesmann, U. (2003). Mechanism and kinetic model for the decolorization of the azo dye reactive black 5 by hydrogen peroxide and uv radiation. Chemosphere, 52 (6), 1069 - 77.
[9] Kiwi, J., Lopez, A., & Nadtochenko, V. (2000). Mechanism and kinetics of the OH-radical intervention during fenton oxidation in the presence of a significant amount of radical scavenger (Cl\(^-\)). Environmental Science & Technology, 34 (11), 2162 - 2168.