Refractory petrochemical wastewater treatment by K$_2$S$_2$O$_8$ assisted photocatalysis

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**Abstract**

The K$_2$S$_2$O$_8$ assisted photocatalytic system was applied for treating refractory petrochemical wastewater. Co-TiO$_2$/zeolite catalyst synthesized by sol-gel method was demonstrated to possess a good activity towards mineralization of the refractory petrochemical wastewater in the K$_2$S$_2$O$_8$ assisted photocatalytic system. Orthogonal design was employed to optimize the reaction parameters, according to the results, K$_2$S$_2$O$_8$ dosage was the most prominent impact factor. More experiments were conducted to further enhance the COD removal efficiency. In consideration of both efficiency and costs, the petrochemical wastewater was treated in the K$_2$S$_2$O$_8$ assisted photocatalytic system at pH 4, K$_2$S$_2$O$_8$ dosage 2.03 g/L, catalyst amount 250 g/L with irradiation by 1 lamp and aeration. The COD removal efficiency reached up to 93.4% with a rate constant of $1.14 \times 10^{-2}$ per min, and Co-TiO$_2$/zeolite showed a good stability towards the K$_2$S$_2$O$_8$ assisted photocatalytic degradation of petrochemical wastewater.

**Keywords:** Refractory petrochemical wastewater, K$_2$S$_2$O$_8$ assisted photocatalysis, Co-TiO$_2$/zeolite, Sulfate radical

1. Introduction

The petrochemical industry, which produces various primary and synthetic organic chemicals by using oil or gas byproducts as major raw materials, has become an important pillar industry in China's economy (Li et al., 2011). However, the rapid development of petrochemical industry has brought a series of environmental problems, threatening human health and ecological balance. Petrochemical wastewater is a kind of wastewater with high COD concentration, low biodegradability (Liu et al., 2014) and ecotoxicity. Additionally, the water even become more complex when several wastewater joined together forming the integrated petrochemical wastewater. Due to the complexity and refractory of the petrochemical wastewater, traditional treatment cannot make the effluent to meet the discharge standard, the research of advanced treatment technologies has become a focus recently.

Biological processes (Pigram and MacDonald, 2001; Herrero and Stuckey, 2015; Jiang et al., 2015; Shamsudin and Majid, 2017a), coagulation (Zheng et al., 2014), catalytic vacuum distillation (Yan et al., 2010), electrochemical methods (Santos et al., 2014) and supercritical water gasification (Hanedar et al., 2017) have been employed to treat wastewater from petrochemical industry. However, the operational costs are relatively high. Among all these processes, advanced oxidation processes (AOPs) are more desirable because they can oxidize and degrade the pollutants non-selectively, thus mineralize the organic compounds and reduce COD. Hydroxyl radical (\( \cdot OH, E_0 = 2.8 \text{ eV} \)) is well known as a major reactive oxygen species in AOPs (Huang et al., 2001; Kwan and Voelker, 2003; Matta et al., 2007; Shamsudin et al., 2017b). As with hydroxyl radical, sulfate radical (\( \cdot SO_4 \)) is also a strong oxidant with high redox potential (\( E_0 = 2.5–3.1 \text{ eV} \)) (Neta et al., 1988), and sulfate radical-based oxidation processes have received much attention for its efficient destruction of organic contaminants in recent years (Lutze et al., 2015a; Yang et al., 2015; He et al., 2014). \( \cdot SO_4 \) reacts with many organic compounds at nearly diffusion controlled rates, which are comparable to \( \cdot OH \), and it is less influenced by competing constituents in practical application (Gara et al., 2008; Lutze et al., 2015b) compared with \( \cdot OH \), such as alkalinity and natural organic matter (NOM), implying that \( \cdot SO_4 \) is more favorable to destruct refractory organic contaminants. As an alternative to \( H_2O_2 \), persulfate (\( S_2O_8^{2-} \)) has been studied for its activation and possible applications in degrading contaminants via producing \( \cdot SO_4 \) (Jo et al., 2014; Ali et al., 2017).
Titanium dioxide (TiO₂) has been extensively utilized as a heterogeneous catalyst in photocatalysis processes. When TiO₂ absorbs UV light, photo-induced TiO₂ is generated and electrons are excited from the valence band of TiO₂ to the exciting band, which results in electron-hole pairs (Mousanejad et al., 2014), as shown in chemical Eq. (1.1).

\[
\text{Co-TiO}_2 + \text{hv (UV light)} \rightarrow \text{TiO}_2 (h^*_\text{vb}) + \text{TiO}_2 (e^-) \quad (1.1)
\]

In this case, oxygen molecules can act as electron acceptors to form superoxide ions (O₂⁻), hydroxyl ions or water molecules can function as electron donors to produce hydroxyl radical, and S₂O₈²⁻ can be activated to generate SO₄²⁻, the process can be denoted as follows.

\[
\begin{align*}
\text{O}_2^+ + e^- & \rightarrow \cdot \text{O}_2^- \quad (1.2) \\
\cdot \text{O}_2^- & + e^- \rightarrow \cdot \text{O}_2 \quad (1.3) \\
\cdot \text{O}_2^- + \text{H}^+ & \rightarrow \cdot \text{OH} \quad (1.4) \\
\text{OH}^- + h^*_\text{vb} & \rightarrow \cdot \text{OH} \quad (1.5) \\
\text{H}_2\text{O} + h^*_\text{vb} & \rightarrow \cdot \text{OH} + \text{H}^+ \quad (1.6) \\
\text{S}_2\text{O}_8^2^- + e^- & \rightarrow \cdot \text{SO}_4^- + \text{SO}_3^- \quad (1.7) \\
\cdot \text{SO}_4^- + e^- & \rightarrow \cdot \text{SO}_4 \quad (1.8) \\
\cdot \text{SO}_4^- + \text{H}_2\text{O} & \rightarrow \text{SO}_4^2^- + \cdot \text{OH} + \text{H}^+ \quad (1.9)
\end{align*}
\]

Enhanced COD removal efficiency can be obtained attributing to the various generated radicals (Eqs. (1.10) and (1.12)).

\[
\begin{align*}
\cdot \text{OH} + \cdot \text{H}^+ + \text{organic pollutant} & \rightarrow \text{H}_2\text{O} + \text{CO}_2 \quad (1.10) \\
\cdot \text{OH} + \text{organic pollutant} & \rightarrow \text{H}_2\text{O} + \text{CO}_2 \quad (1.11) \\
\cdot \text{SO}_4^- + \text{organic pollutant} & \rightarrow \text{SO}_4^2^- + \text{H}_2\text{O} + \text{CO}_2 \quad (1.12)
\end{align*}
\]

To the best of our knowledge, few reports were published on K₂S₂O₈ assisted photocatalysis as an advanced oxidation technology. The objective of this study is to prepare a TiO₂-based catalyst for activating K₂S₂O₈ in a photocatalytic process, thus producing \( \cdot \text{SO}_4^- \) to destruct refractory organic contaminants in the petrochemical wastewater. Co was doped in the catalyst to enhance photocatalytic activity, meanwhile, Co was reported to have a catalytic activity towards K₂S₂O₈ oxidation reaction. Considering the issue of the catalyst reclamation, zeolite was selected as catalyst support. First, the K₂S₂O₈ assisted photocatalysis activity of different catalysts were tested and compared, then orthogonal design (OD) was employed to determine the most crucial factor and optimize the COD removal efficiency of the petrochemical wastewater. More contrast experiments were conducted to further investigate and analysis the optimum condition.

2. Materials and methods

2.1. Materials and chemicals

Zeolite (Na₂O·Al₂O₃·3SiO₂·yH₂O), Tetrabutyl orthotititanate (AR) and Polyethylene glycol (AR, average Mn 2000) were purchased from Tianjin Guangfu Fine Chemical Research Institute, China. Co (NO₃)₂·6H₂O (AR) was obtained from Guangdong Guanghua Sci-Tech Co., Ltd, China. Absolute ethanol (AR) was purchased from Hunan Huilong Reagent Co., Ltd, China. Acetylacetone (AR) were purchased from Tianjing Kemiu Chemical Reagent Co., Ltd, China. Acetic acid (AR) and K₂S₂O₈ (AR) were obtained from Sinopharm Chemical Reagent Co., Ltd, Hunan, China. H₂SO₄ (AR) was purchased from Zhuzhou Xing Kong Hua Bo Co., Ltd, China. All chemicals were used as received without further purification. Deionized water was used throughout this study.

2.2. Preparation of the catalyst

The catalyst was prepared according to our previous work. Before used as a support, zeolite was calcined at 950 °C in a chamber electric oven for 2 h, after cooled, it was rinsed with deionized water for 3 times, afterwards, the zeolite was dried at 200 °C and kept for further use.

The sol-gel method was used to synthesize the prepolymer. The procedure was as follows: 200 mL ethanol, 2 mL acetic acid, 7.8 mL acetylacetone and 50 mL tetrabutyl orthotititanate were added into a 500 mL 4-neck flask which was heated in a water bath, and the solution was stirred uniformly. Then 3.4 mL 0.5 M Co(NO₃)₂ solution and 34 mL ethanol were mixed and added into a 125 mL constant pressure funnel. Afterwards, the mixed solution was dropped into the flask from the funnel at a certain flow rate, the dropping process continued for 1 h. Subsequently, 2 g polyethylene glycol 2000 was added, and the bathing temperature was rised to 80 °C, keep the temperature for 1 h. The product was kept for further use after cooling down.

The Co-doped TiO₂/zeolite catalyst was prepared using the immersion process. The treated zeolite support was immersed in the synthesized prepolymer for 0.5 h, after draining the excess pre-polymer, the prepolymer-capped zeolite was dired in oven and calcined at 400 °C for 2 h to obtain Co-doped TiO₂/zeolite.

2.3. Batch experiment

Petrochemical wastewater with a COD concentration of 1050 mg/L obtained from Hunan Jianchang Petrochemical Co., Ltd was used as target wastewater for each batch test. As the zeolite is porous, its adsorption function may have an influence on COD removal efficiency, the zeolite was immersed and saturated in the petrochemical wastewater before each experiment. The photocatalysis experiments were carried out with a photoreactor set up, which consisted of a cylindrical vessel, a low-pressure mercury lamp settled in the center of the vessel and two other lamps symmetrically located on inner wall of the vessel to supply irradiation, all the lamps emitting mainly at 254 nm. In each experiment, 800 mL of the petrochemical wastewater was measured into the reactor, and the pH was adjust to 3 followed by the addition of a certain amount of 0.2 M K₂S₂O₈. Afterwards, a certain amount of the catalyst was added into the reactor. To start the reaction, irradiation by UV light was applied.

2.4. Analysis

Chemical oxygen demand (COD) of the petrochemical wastewater was determined by potassium dichromate reflux method following the standard procedure. The degraded petrochemical wastewater after certain time intervals were collected, and the Chemical oxygen demand (COD) was determined by potassium dichromate reflux method following the standard procedure (A.D. Eaton 2005). Corresponding concentration were calculated with the help of the equation found from calibration graph, and COD removal efficiency was calculated as follow:

\[
\text{COD removal efficiency} = \left( \frac{\text{COD}_0 - \text{COD}_t}{\text{COD}_0} \right) \times 100\% \quad (2.1)
\]

where COD₀ represent origin COD value of petrochemical wastewater as received, COD₀ refers to COD value after treated at a certain time.
3. Results and discussion

3.1. Catalyst performance

To compare the catalytic activity of different catalysts, contrast experiments were performed. Fig. 1 shows COD removal efficiency of the petrochemical wastewater treated without catalyst and with different catalysts, including zeolite, TiO$_2$/zeolite, and Co-doped TiO$_2$/zeolite. It can be seen from the figure that the pseudo-first order dynamic model could primely fit all the experimental data. Compared with no catalyst, all the three types of catalysts showed an enhanced performance towards COD reduce of the petrochemical wastewater. Pure zeolite has a similar catalytic activity with no catalyst after saturated by petrochemical wastewater, indicating that pure zeolite is almost inactive towards photocatalysis. Co-TiO$_2$/zeolite exhibited the best efficiency of approach 60%, demonstrating that Co doping promoted the catalytic activity of the catalyst.

In the K$_2$S$_2$O$_8$-assisted photocatalysis system, TiO$_2$ is a well-known photocatalyst, which contribute to the generation of OH. However, the rapid recombination of electron-hole pairs in UV/TiO$_2$ system is a great barrier. Co doping may solve this problem, as introducing various transition metals into TiO$_2$ lattice is found increased as K$_2$S$_2$O$_8$ dosage was increased, indicating that the utilization of photon has reached the maximum value, and the excessive photo cannot be used. Acidic pH is selected in the OD experiments as it is favored for the generation of OH. From the results, no big difference in COD removal efficiency was observed with different pH, indicating acidic environment is appropriate for the reaction. Catalyst amount is also an important influence factor, but it didn't mean the more the better. Excessive catalysts may cause active sites covered as the result that the catalysts were stacked together.

Orthogonal design was employed to optimize the treatment efficiency of the K$_2$S$_2$O$_8$ assisted photocatalysis. Many factors have influences on COD removal efficiency. Oxidant dosage is an important factor, as it offers the source of SO$_4^-$, which is a main electron acceptor in the system affecting the extent of reaction. Light intensity has a direct connection with catalytic efficiency, as effective photon number in unit volume is a direct factor affecting reaction rate. pH condition has an influence on the generation of OH, which is also a main electron acceptor in the system. Additionally, the amount of active sites is determined by the catalyst amount. Thus, concerning about the influence of oxidant dosage, light intensity, pH and catalyst amount, a L$_9$(3$^4$) orthogonal experiment of four factors and three levels was adopted to primarily optimize the photo-chemical oxidation of the petrochemical wastewater, with final COD values determined after each treatment as the indexes. All the parameters range were selected according to previous literatures. The detailed orthogonal experiments and related results are listed in Tables 1 and 2 respectively.

![Fig. 1. COD removal efficiency on different catalysts. pH = 3, catalyst amount: 375 g/L, K$_2$S$_2$O$_8$ dosage: 3.38 g/L with 2 lamp irradiation and aeration.](image)

### Table 1

| Factors                  | K$_2$S$_2$O$_8$ dosage, g/L | Light intensity | pH | Catalyst amount, g/L |
|--------------------------|-----------------------------|----------------|-----|----------------------|
| 1                        | 0.68                        | 1 Lamp         | 2   | 125                  |
| 2                        | 2.03                        | 2 Lamp         | 3   | 250                  |
| 3                        | 3.38                        | 3 Lamp         | 4   | 375                  |

By variance analysis, the order of influence for photocatalytic activity is K$_2$S$_2$O$_8$ dosage, catalyst amount, light intensity, and pH. The optimum experiment condition is: K$_2$S$_2$O$_8$ dosage 3.38 g/L, catalyst amount 250 g/L, irradiated by 3 lamp in the solution with pH = 4. COD removal efficiency was visibly influenced by K$_2$S$_2$O$_8$ dosage. In our experiment range, COD removal efficiency increased as K$_2$S$_2$O$_8$ dosage was increased, indicating that the K$_2$S$_2$O$_8$ dosage didn't reach the optimum value. Light intensity didn't exhibit significant influence on COD removal efficiency, mainly because the utilization of photon has reached the maximum value, and the excessive photo cannot be used. Acidic pH is selected in the OD experiments as it is favored for the generation of OH. From the results, no big difference in COD removal efficiency was observed with different pH, indicating acidic environment is appropriate for the reaction. Catalyst amount is also an important influence factor, but it didn’t mean the more the better. Excessive catalysts may cause active sites covered as the result that the catalysts were stacked together.

More experiments were conducted to further enhance the COD removal efficiency of the K$_2$S$_2$O$_8$ assisted photocatalysis.

3.3. Influence of K$_2$S$_2$O$_8$ dosage

The data analysis listed in Table 2 indicates that the oxidant dosage is the predominant factor amongst the selected four factors, COD removal efficiency improved with the increasing of the oxidant dosage, however, the cost also increased. The optimization of the K$_2$S$_2$O$_8$ assisted photocatalysis process seeks to minimize the oxidant dosage in consideration of the cost requirement. Thus, we compared the COD removal efficiency with different dosage of K$_2$S$_2$O$_8$, and the results were shown in Fig. 2.

The results indicated that the efficiency of COD removal was enhanced as the concentration of K$_2$S$_2$O$_8$ increased. This is attributed to the high concentration of SO$_4^-$ radicals in the medium generated from the Co catalytic decompose and photocatalysis of K$_2$S$_2$O$_8$. However, it was observed that the increase rate of COD removal efficiency was slowed down obviously as K$_2$S$_2$O$_8$ dosage increased. Considering the cost of K$_2$S$_2$O$_8$, the optimum K$_2$S$_2$O$_8$ dosage was determined to be 2.03 g/L.

3.4. Influence of aeration

Besides oxidant dosage, light intensity, pH and catalyst amount, aeration may also be a factor that affects the K$_2$S$_2$O$_8$ assisted photocatalysis via improving the hydraulic condition and the dissolved oxygen concentration. Thus, the influence of aeration was investigated and the results were reflected in Fig. 3.

Results indicated that the application of aeration would accelerate the COD removal efficiency mainly because it can cause a dis-
turbance in the solution, allowing sufficient contacts between radicals and organic pollutants, thus improve the utilization of the active radicals.

3.5. Influence of reaction time

As can be seen in Figs. 1–3, COD removal efficiency increased obviously even after react for 120 min. Thus, experiment was conducted with longer reaction time under optimum condition for further study. Fig. 4 reflects the curve of COD removal efficiency at

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Table 2
Results of orthogonal experiment.

| Factors experiment | A   | B   | C   | D   | COD, mg/L |
|--------------------|-----|-----|-----|-----|-----------|
| 1                  | 1   | 1   | 1   | 1   | 732       |
| 2                  | 1   | 2   | 2   | 2   | 632       |
| 3                  | 1   | 3   | 3   | 3   | 626       |
| 4                  | 2   | 1   | 2   | 3   | 607       |
| 5                  | 2   | 2   | 1   | 2   | 586       |
| 6                  | 2   | 3   | 3   | 3   | 503       |
| 7                  | 3   | 1   | 3   | 2   | 422       |
| 8                  | 3   | 2   | 1   | 3   | 436       |
| 9                  | 3   | 3   | 2   | 1   | 445       |

| i (total index) of 1 level | 1990 | 1761 | 1671 | 1763 |
| ii (total index) of 2 level | 1696 | 1654 | 1684 | 1557 |
| iii (total index) of 3 level | 1303 | 1574 | 1634 | 1669 |
| I = i/3 | 663 | 587 | 557 | 588 |
| II = ii/3 | 565 | 551 | 561 | 519 |
| III = iii/3 | 434 | 525 | 545 | 556 |

Range analysis | 229 | 62 | 16 | 69 |

The order of influence: A > D > B > C
Optimum levels: A3B3C3D2

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Fig. 2. COD removal efficiency with different K2S2O8 dosage. pH = 4, Catalyst amount 250 g/L, reaction time 120 min.

Fig. 3. Influence of aeration on COD removal efficiency. pH = 4, Catalyst amount 250 g/L, K2S2O8 dosage: 2.03 g/L, reaction time 120 min.

Fig. 4. COD removal efficiency at different time interval. pH = 4, Catalyst amount 250 g/L, K2S2O8 dosage: 2.03 g/L, irradiated by 1 lamp with aeration.

Fig. 5. Life test of Co-TiO2/zeolite. pH = 4, Catalyst amount 250 g/L, K2S2O8 dosage: 2.03 g/L, reaction time, 240 min, irradiated by 1 lamp with aeration.
different reaction time. In the beginning, COD removal efficiency raised significantly as the reaction progress. After reacted for a period of time, the COD removal efficiency began to increase slowly along with reaction time, and the curve became much more flat. After a 4-h treatment, COD removal efficiency reached 93.4%. In consideration of the cost, 4 h is enough for the \( \text{K}_2\text{S}_2\text{O}_8 \) assisted photocatalysis. The rate constant of the \( \text{K}_2\text{S}_2\text{O}_8 \) assisted photocatalysis was also calculated according to pseudo-first-order kinetics, the kinetic curve was shown in Fig. 4 (dash line), and the calculated rate constant (slope of the blue dashed curve in Fig. 4) was 1.14 \times 10^{-2} \text{ per min.}

### 3.6. Life test of catalysts

Cycle experiments were conducted under the optimum conditions to evaluate the catalyst service life. The catalyst was not rinsed and regenerated all through the process, and the wastewater was replaced by the original petrochemical wastewater every 240 min. Result was showed in Fig. 5, it can been seen that Co-TiO\(_2\)/zeolite showed good stability towards COD removal of petrochemical wastewater, no significant drop in COD removal efficiency was observed from the cycle experiment.

### 4. Conclusion

In summary, a sulfate radical based AOP was adopted in this paper to reduce COD of petrochemical wastewater. The sulfate radical was generated from \( \text{K}_2\text{S}_2\text{O}_8 \) through photocatalysis and Co-catalytic decompose. Co-TiO\(_2\)/zeolite catalyst was prepared for the reaction, it exhibited an enhanced activity towards the \( \text{K}_2\text{S}_2\text{O}_8 \) assisted photocatalysis. Considering both efficiency and costs, the optimum condition for the \( \text{K}_2\text{S}_2\text{O}_8 \) assisted photocatalysis is: \( \text{K}_2\text{S}_2\text{O}_8 \) dosage 2.03 g/L, catalyst amount 250 g/L, pH = 4, irradiated by 1 lamp with aeration. Under the optimum condition, the COD removal efficiency of the refractory petrochemical wastewater treated by \( \text{K}_2\text{S}_2\text{O}_8 \) assisted photocatalysis can reach up to 93.4% with a rate constant of 1.14 \times 10^{-2} \text{ per min.}

The Co-TiO\(_2\)/zeolite catalyst showed a perfect stability. Results demonstrated that the catalyst and the \( \text{K}_2\text{S}_2\text{O}_8 \) assisted photocatalysis technology are promising in refinery wastewater treatment. More experiments should be conducted to optimize the synthesis condition Co-TiO\(_2\)/zeolite to further improve the performance of the \( \text{K}_2\text{S}_2\text{O}_8 \) assisted photocatalysis treatment.

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