Original article

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 1.14×10^{-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.

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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 rencently.

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 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 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$_2$O$_2$, persulfate (S$_2$O$_8^-$) 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)
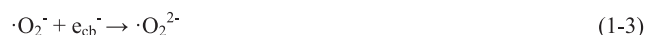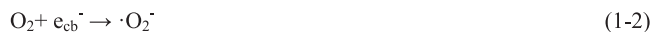

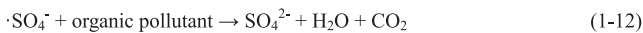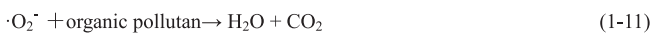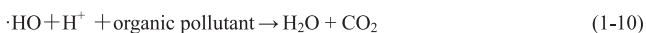
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Titanium dioxide (TiO_2) has been extensively utilized as a heterogeneous catalyst in photocatalysis processes. When TiO_2 absorbs UV light, photo-induced TiO_2 is generated and electrons are excited from the valence band of TiO_2 to the exciting band, which results in electron-hole pairs (Mousanejad et al., 2014), as shown in chemical Eq. (1.1).

$$Co\text{-}TiO_2 + hv \text{ (UV light)} \rightarrow TiO_2 \ (h_{vb}^+) + TiO_2 \ (e_{cb}^-) \qquad (1.1)$$
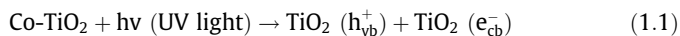
In this case, oxygen molecules can act as electron acceptors to form superoxide ions ($\cdot O_2^-$), hydroxyl ions or water molecules can function as electron donors to produce hydroxyl radical, and $S_2O_8^-$ can be activated to generate $\cdot SO_4^-$, the process can be denoted as follows.

$$O_2 + e_{cb}^- \rightarrow \cdot O_2^- \qquad (1\text{-}2)$$

$$\cdot O_2^- + e_{cb}^- \rightarrow \cdot O_2^{2-} \qquad (1\text{-}3)$$

$$\cdot O_2^- + H^+ \rightarrow \cdot HO_2 \qquad (1\text{-}4)$$

$$OH^- + h_{vb}^+ \rightarrow \cdot OH \qquad (1\text{-}5)$$

$$H_2O + h_{vb}^+ \rightarrow \cdot OH + H^+ \qquad (1\text{-}6)$$

$$S_2O_8^- + e_{cb}^- \rightarrow \cdot SO_4^- + SO_4^- \qquad (1\text{-}7)$$

$$\cdot SO_4^- + e_{cb}^- \rightarrow SO_4^{2-} \qquad (1\text{-}8)$$

$$\cdot SO_4^- + H_2O \rightarrow SO_4^{2-} + \cdot OH + H^+ \qquad (1\text{-}9)$$

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

$$\cdot HO + H^+ + \text{organic pollutant} \rightarrow H_2O + CO_2 \qquad (1\text{-}10)$$

$$\cdot O_2^- + \text{organic pollutan} \rightarrow H_2O + CO_2 \qquad (1\text{-}11)$$

$$\cdot SO_4^- + \text{organic pollutant} \rightarrow SO_4^{2-} + H_2O + CO_2 \qquad (1\text{-}12)$$

To the best of our knowledge, few reports were published on $K_2S_2O_8$ assisted photocatalysis as an advanced oxidation technology. The objective of this study is to prepare a TiO_2-based catalyst for activating $K_2S_2O_8$ in a photocatalytic process, thus producing $\cdot SO_4^-$ 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 $K_2S_2O_8$ oxidation reaction. Considering the issue of the catalyst reclamation, zeolite was selected as catalyst support. First, the $K_2S_2O_8$ 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. Meterials and methods

2.1. Meterials and chemicals

Zeolite ($Na_2O \cdot Al_2O_3 \cdot xSiO_2 \cdot yH_2O$), Tetrabutyl orthotitanate (AR) and Polyethylene glycol (AR, average Mn 2000) were purchased from Tianjin Guangfu Fine Chemical Research Institute, China. Co $(NO_3)_2 \cdot 6H_2O$ (AR) was obtained from Guangdong Guanghua Sci-Tech Co., Ltd, China. Absolute ethanol (AR) was purchased from Hunan Huihong Reagent Co., Ltd, China. Acetylacetone (AR) were purchased from Tianjing Kemiou Chemical Reagent Co., Ltd, China. Acetic acid (AR) and $K_2S_2O_8$ (AR) were obtained from Sinopharm Chemical Reagent Co., Ltd, Hunan, China. H_2SO_4 (AR) was purchased from Zhuzhou Xing Kong Hua Bo Co., Ltd, China. All chem-

icals 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 orthotitanate 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 $Co(NO_3)_2$ 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 TiO_2/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 prepolymer, the prepolymer-capped zeolite was dired in oven and calcined at 400 °C for 2 h to obtain Co-doped TiO_2/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 photocatlysis 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 $K_2S_2O_8$. 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:

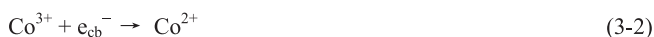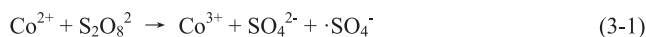$$\text{COD removal efficiency} = (COD_0 - COD_t)/COD_0 \times 100\% \qquad (2.1)$$

where COD_0 represent origin COD value of petrochemical wastewater as received, COD_t 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$_8$-assistant 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 effective for energy band reconstruction and band-gap narrowing (Tong et al., 2012). And Co also played an important role in transfer K$_2$S$_2$O$_8$ into ·SO$_4^-$, which showed a ·SO$_4^-$ based Fenton-like reaction activity (Eqs. (3.1) and (3.2)).

$$Co^{2+} + S_2O_8{}^2 \rightarrow Co^{3+} + SO_4{}^{2-} + ·SO_4^- \qquad (3\text{-}1)$$

$$Co^{3+} + e_{cb}{}^- \rightarrow Co^{2+} \qquad (3\text{-}2)$$

3.2. OD of the experiments

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,
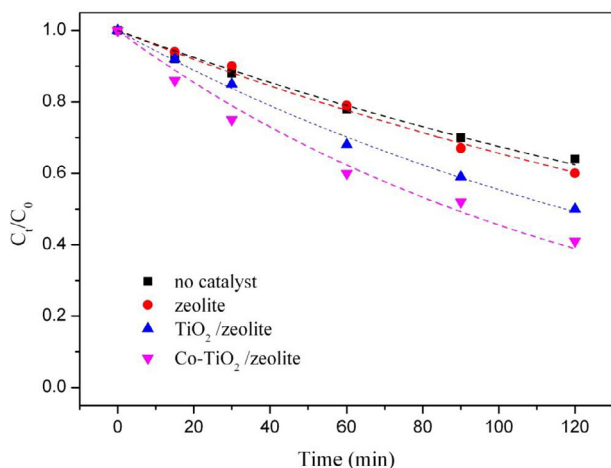

Fig. 1. COD removal efficiency on different catalysts. pH = 3, catalyst amount: 375 g/L, K$_2$S$_2$O$_8$ dosage: 3.38 g/L with 2 lamp irradiation and aeration.

Table 1
Three levels of every factor in orthogonal experiment.

Factors levels	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

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.

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.
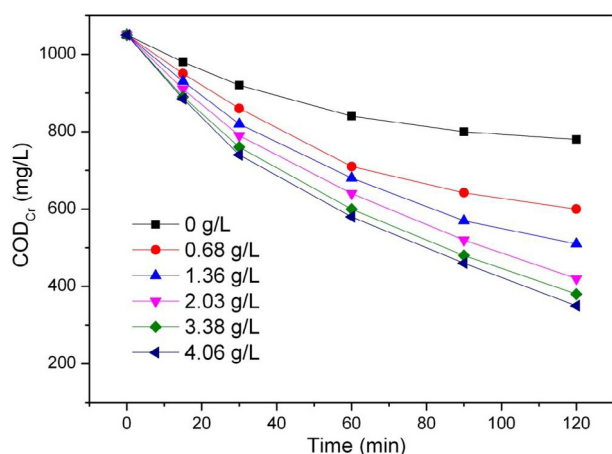
3.4. Influence of aeration

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-

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	3	1	586
6	2	3	1	2	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
Optmum levels: $A_3B_3C_3D_2$

Fig. 2. COD removal efficiency with different $K_2S_2O_8$ dosage. pH = 4, Catalyst amount 250 g/L, reaction time 120 min.
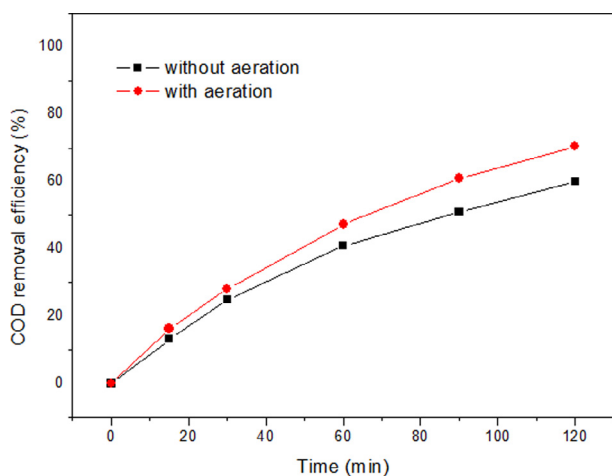

Fig. 3. Influence of aeration on COD removal efficiency. pH = 4, Catalyst amount 250 g/L, $K_2S_2O_8$ dosage: 2.03 g/L, reaction time 120 min.

turbance in the solution, allowing sufficient contacts between radials 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
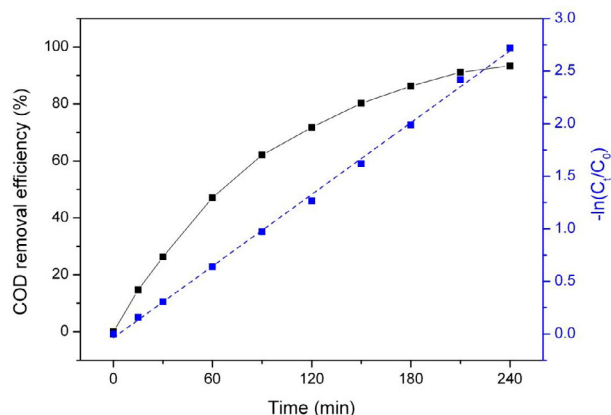
Fig. 4. COD removal efficiency at different time interval. pH = 4, Catalyst amount 250 g/L, $K_2S_2O_8$ dosage: 2.03 g/L, irradiated by 1 lamp with aeration.
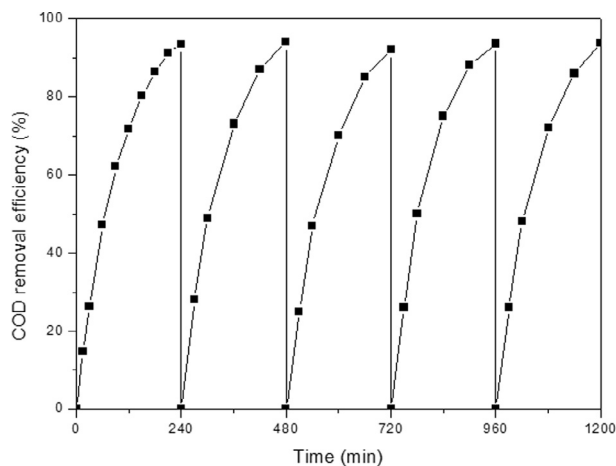
Fig. 5. Life test of Co-TiO₂/zeolite. pH = 4, Catalyst amount 250 g/L, $K_2S_2O_8$ dosage: 2.03 g/L, reaction time, 240 min, irradiated by 1 lamp with aeration.

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 $K_2S_2O_8$ assisted photocatalysis. The rate constant of the $K_2S_2O_8$ 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 1.14×10^{-2} 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 $K_2S_2O_8$ through photocatalysis and Co-catalytic decompose. Co-TiO_2/zeolite catalyst was prepared for the reaction, it exhibited an enhanced activity towards the $K_2S_2O_8$ assisted photocatalysis. Considering both efficiency and costs, the optimum condition for the $K_2S_2O_8$ assisted photocatalysis is: $K_2S_2O_8$ 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 $K_2S_2O_8$ assisted photocatalysis can reached up to 93.4% with a rate constant of 1.14×10^{-2} per min, and the Co-TiO_2/zeolite catalyst showed a perfect stability. Results demonstrated that the catalyst and the $K_2S_2O_8$ assisted photocatalysis technology are promising in refractory wastewater treatment. More experiments should be conducted to optimize the synthesis condition Co-TiO_2/zeolite to further improve the performance of the $K_2S_2O_8$ assisted photocatalysis treatment.

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