Research Paper

Photo-assisted heterogeneous Fenton-like process for treatment of PNP wastewater

F. C. Ban, X. T. Zheng and H. Y. Zhang

ABSTRACT

The purpose of this study was to investigate the effect of photo-assisted heterogeneous Fenton on p-nitrophenol (PNP) wastewater treatment by a homemade reactor. Supported Fe-Ce/Al₂O₃ was used as a catalyst and H₂O₂ as an oxidant to treat simulated p-nitrophenol wastewater under ultraviolet light. The effects of H₂O₂ dosage, catalyst dosage, initial solution pH value, reaction temperature and reaction time on the removal rate of p-nitrophenol in a photo-assisted heterogeneous Fenton system were determined. According to the relation between the concentration of each component and time, the relation curve is fitted, and then the kinetic equation is established. Finally, we obtained the optimum process conditions to achieve the PNP wastewater removal rate of 98.7%. The degradation of the photo-assisted heterogeneous Fenton method conforms to the first-order kinetic model, and the kinetic equation is LnC₀ – LnC = –kt. Therefore, photo-assisted heterogeneous Fenton treatment of PNP wastewater is effective and can be used in the treatment of refractory wastewater.

Key words | dynamics, Fe-Ce/Al₂O₃ catalyst, heterogeneous Fenton-like, P-nitrophenol, synergistic effect

INTRODUCTION

China is a developing country. In recent years, with the continuous progress of modern industry, all walks of life have made considerable development. The people’s living standards have been significantly improved. At the same time, the people’s awareness of the protection of the natural environment is constantly improving, and their desire and expectation for the vast blue sea and blue sky are becoming more and more urgent. China’s water environment has also attracted more and more attention from all walks of life. But the same problems exist in many developing and middle-income countries. At present, China’s water environment has many problems, such as widespread water pollution, many hidden dangers of water environment security, and relatively backward water pollution control. P-nitrophenol is a representative of a typical refractory industrial and agricultural wastewater, which is discharged into water without effective treatment, causing serious harm to people’s physical property and the natural ecological environment (Bergendahl & Thies 2004). P-nitrophenol is listed as a ‘priority pollutant control’ by the US environmental protection agency (EPA) and Chinese environmental protection authorities (Duan et al. 2010). In the comprehensive sewage discharge standard, it is defined as the second class pollutant and a strict standard is set for its discharge concentration. Therefore, our study took p-nitrophenol wastewater as an example. The aim is to provide a solution to all the existing problems in the treatment of refractory organic wastewater. What we are doing is contributing our share to sewage treatment in all developing countries like China.

The sodium salt of p-nitrophenol (PNP) is an intermediate in many chemical industries. PNP is highly toxic and
corrosive, and if its wastewater can not be treated properly, it can damage the environment. Conventional water treatment methods adopted at home and abroad such as adsorption, extraction, and biological methods are difficult to effectively use, while advanced oxidation methods (AOPs) are widely used in the treatment of organic wastewater for their universality and high efficiency of refractory organics (David et al. 2018). The Fenton system is simple in operation, rapid in response, and mild in conditions (Zeng et al. 2015). However, the traditional Fenton method still has many shortcomings, such as low utilization of H2O2, small application range of pH, and difficulty in recycling catalysts. The Fenton system has been used in light, electricity, microwave, and ultrasound to treat the refractory wastewater, which achieved good results. Other metal ions (Hassan & Hameed 2014) instead of Fe2+ Fenton-like technology have also become a hot topic. Heterogeneous Fenton-like oxidation is a technique in which one or several metal ions are immobilized on a carrier to form a solid catalyst containing metal ions instead of Fe2+ in solution (Zhou 2010). The solid catalyst is easy to separate and recover, and it solves the problem that the homogeneous Fenton reaction produces refractory iron mud. Combined with the above methods, the introduction of ultraviolet light (Meng et al. 2010) in the heterogeneous Fenton-like system not only catalyzes the decomposition of H2O2 but also improves the efficiency of conversion of Fe3+ to Fe2+ and enhances the catalytic effect. The author prepared a heterogeneous Fenton-like catalyst Fe-Ce/Al2O3 to remove PNP from water under the synergistic effect of ultraviolet light. The removal effect of PNP by photo-assisted heterogeneous Fenton-like method was investigated by a series of single-factor experiments. The optimum process conditions were obtained, and the removal effect of PNP by different reaction systems was compared. The stability and service life of the catalyst were also investigated.

MATERIALS AND METHODS

Catalyst preparation

The catalyst for the test was prepared using the following production method: taking the appropriate amount of Al2O3 particles and immersing them in NaOH solution with 5% mass fraction for 30 min. Washed with distilled water and soaked for 24 h, drained, placed in an oven at 105 °C for 3 h, and then calcined in a muffle furnace at 350 °C for 3 h, dry and spare. 25 g of activated Al2O3 particles were placed in a 100 mL mixed solution containing 0.3 mol/L Fe(NO3)3, 30% by mass of Ce(NO3)3 and 0.3% by mass of oxalic acid in a constant temperature water bath at 25 °C. After immersion for 25 h, it was washed with deionized water, filtered, dried in an oven at 105 °C, and finally calcined in a muffle furnace at 350 °C for 3 h to obtain a heterogeneous Fenton-like catalyst Fe-Ce/Al2O3. A part of the catalyst was taken as samples, which were put into a scanning electron microscope (SEM) and specific surface area analyzer (BET) for detection, and the test results were output.

Specific surface area analysis

The pore size distribution and specific surface area of Fe-Ce/Al2O3 catalyst and support were analyzed by the BET test. The specific surface area (SSA, m2 g−1) of the catalyst sample was determined by the NOVA1000 specific surface area analyzer of Kona instruments, USA. Before the test, the samples were treated with 100 °C vacuum degassing.

Surface topography analysis

The surface morphology and particle dispersion state of the catalyst were analyzed by SEM. The XL-30 ESEM FEG scanning electron microscope produced by the FEI company in the Netherlands was used in the experiment. The test sample is a solid powder. Apply a small amount of the sample to the conductive tape with a toothpick and fix it on the sample table for testing. Fe-Ce/Al2O3 catalyst needs to be treated with gold spray before surface morphology analysis. The analysis was carried out under the condition that the acceleration voltage was 15,000 V and the amplification was 3,500–10,000 times.

Experimental methods

In this study, photo-assisted heterogeneous Fenton catalyst Fe-Ce/Al2O3 was used to treat refractory organic matter
p-nitrophenol (PNP). The purpose of degradation of PNP in water was realized under the synergistic effect of ultraviolet light and self-made catalyst. First, 0.2 g Analytical Reagent p-nitrophenol was dissolved in 500 ml deionized water, and then the volume was fixed to 1 L to obtain the simulated PNP wastewater with a concentration of 200 mg/L. Through a single-factor test, the effects of different influencing factors and reaction systems on simulated PNP wastewater treatment were studied. The standard conditions for controlling the influencing factors in the experiment were: the mass concentration of PNP simulated wastewater was 200 mg/L, the dosage of H2O2 was 150 mmol/L, the dosage of catalyst was 50 g/L, the pH was 4, the temperature was 25 °C, and the reaction time was 90 min. PNP was measured every 15 min and the removal rate was calculated. For example, when examining the effect of temperature, other conditions are controlled in the established standard value, and only the temperature size is changed to investigate its effect on the processing effect of PNP.

PNP and COD were determined by spectrophotometry, and the removal rate of PNP and COD were calculated:

\[ \eta_p = \frac{C_{p0} - C_{pt}}{C_{p0}} \times 100\% \quad (1) \]

In the equation, \( \eta_p \) is PNP removal rate, \( C_{p0} \) is PNP measurements (mg/L) at 0 moment, \( C_{pt} \) is PNP measurements (mg/L) at \( t \) moment:

\[ \eta = \frac{C_0 - C_t}{C_0} \times 100\% \quad (2) \]

In the equation, \( \eta \) is PNP removal rate, \( C_0 \) is COD measurements (mg/L) at 0 moment, \( C_t \) is COD measurements (mg/L) at \( t \) moment.

Then, the catalytic mechanism was studied. By comparing the degradation effects of four reaction systems of UV/H2O2, UV/catalyst, H2O2/catalyst and UV/H2O2/catalyst on p-nitrophenol, the reaction mechanism of the system was discussed. Lastly, the kinetic model of degradation of p-nitrophenol wastewater by photo-assisted heterogeneous Fenton method was established. By analyzing the relationship between the concentration of each component and time, the chemical reaction rate and kinetic effect of the system were determined.

**RESULTS AND DISCUSSION**

**Microscopic characterization of the catalyst**

**SEM surface topography analysis**

The surface structure of the activated Al2O3 particle carrier and the Fe-Ce/Al2O3 catalyst were analyzed by SEM, as shown in Figure 1.

It can be seen from Figure 1 that the activated Al2O3 particle carrier has a smooth and flat block shape with loose distribution and metallic luster, while the Fe-Ce/Al2O3 catalyst particles are larger and the surface is rougher and tightly agglomerated. This is because Fe3+ and Ce3+ cover the surface of the carrier, increasing the surface area and changing the physical properties of the surface, while more uniformly binding the particles.

**BET specific surface area analysis**

The specific surface area of the activated Al2O3 particle carrier and the Fe-Ce/Al2O3 catalyst were analyzed by BET, as shown in Table 1.

It can be seen from Table 1 that the specific surface area, total pore volume and average pore diameter of the Fe-Ce/Al2O3 catalyst are reduced compared with the Al2O3 carrier, because Fe^{3+} and Ce^{3+} are coated on the surface of the carrier, resulting in a smaller specific surface area. At the same time, the pores of the particles are filled, resulting in a smaller pore volume and smaller pore diameter.

**Factors influencing the photo-assisted heterogeneous Fenton-like reaction**

**Effect of H2O2 dosage on PNP treatment**

It can be seen from Figure 2 that when the dosage of H2O2 is 50–150 mmol/L, the removal rate of PNP increases with the increase of H2O2 dosage. When the dosage of H2O2 was
150 mmol/L and the reaction was carried out for 90 min, the PNP removal rate reached 92.6%. Thereafter, the dosage of H₂O₂ was continuously increased, and the removal rate of PNP decreased slightly. When the concentration of H₂O₂ is low, increasing the dosage can increase the ·OH and the reaction rate becomes faster. However, H₂O₂ can interact with the active site on the catalyst surface to generate ·OH and react with ·OH (Zhang et al. 2006), when the concentration of H₂O₂ is too high, H₂O₂ will consume part of ·OH, resulting in a lower degradation rate, while high concentration of H₂O₂ will also dissolve the catalyst and reduce the catalytic efficiency.

### Effect of catalyst dosage on PNP treatment

It can be seen from Figure 3 that when the catalyst dosage is 30–100 g/L, the removal rate of PNP increases with the...
increase of catalyst dosage. When the catalyst dosage is 100 g/L and the reaction is 60 min, the PNP removal rate reaches 89.3%, and the PNP removal rate reaches 98.7% when the reaction is 90 min. After that, the dose of the catalyst was continuously increased, and the PNP removal rate decreased slightly.

Increasing the dosage of the catalyst will provide more active sites for H₂O₂ (Chen et al. 2014), increase the amount of ·OH, and accelerate the degradation of PNP. However, excessive addition of the catalyst leads to an excess of the active site, causing self-quenching reaction, lowering the utilization rate of H₂O₂, and lowering the degradation efficiency.

**Effect of initial pH of solution on PNP treatment**

As can be seen from Figure 4, as the initial pH increases, the removal rate of each phase of the PNP decreases. The initial pH = 3, the PNP removal rate reached 90% when the reaction was 45 min, and the PNP was almost completely removed after 60 min of reaction; the initial pH = 4, the PNP removal rate was close to the pH = 3 level when the reaction was 90 min; pH = 4–7, the PNP removal rate reached over 80% when the reaction was 90 min, and then the initial pH was increased to 8, and the removal rate was reduced to 73.5%. In the acidic environment, Fe³⁺ and Ce³⁺ are easily present in the form of ions, which is beneficial to the conversion of H₂O₂ to ·OH (Feng et al. 2006). The photo-assisted heterogeneous Fenton-like catalyst system increases the pH range of the Fenton system and controls the initial pH of the reaction to 4 based on cost reduction.

**Effect of reaction temperature on PNP treatment**

The experimental results show that the PNP removal rate is 37.9% at 30 min and 15 °C, and the PNP removal rate is 95.8% at 65 °C. The PNP removal rate increases with temperature. At 90 min, the PNP removal rates at 15 °C and 25 °C reached 94.6% and 98.7%, respectively. There was no significant difference in the PNP removal rate between 25 °C and 75 °C. The removal rate of PNP at 75 °C was slightly lower than that at 65 °C. The increase in temperature causes the collision of H₂O₂ with the catalyst more frequently, which accelerates the decomposition of H₂O₂. When the temperature is above 25 °C, the activity of ·OH is high, but when the temperature rises to 75 °C, H₂O₂ is decomposed by heat, resulting in a decrease in PNP removal rate. In addition, when the reaction temperature is too high, the energy consumption is large, and the equipment is required to be high, and the reaction temperature is selected to be 25 °C for the purpose of energy-saving, emission reduction, and cost reduction (Figure 5).

**Effect of reaction time on PNP treatment**

The experimental results show that the removal rate of PNP increases rapidly from 0 to 60 min, and reaches 88.9% at
60 min. After 60 min, the reaction tends to be balanced. After 90 min, the removal rate remains basically unchanged. At 120 min, it reaches 98.7%. When the reaction time was 0 ~ 90 min, the COD removal rate increased steadily. The COD removal rate reached 69.4% at 90 min, and the removal rate remained unchanged after 90 min. The COD removal rate was 72.9% at 120 min. In the initial stage of the reaction, with the decomposition of H2O2, the ·OH in the system increased, and the removal rate of PNP and COD increased rapidly. As the reaction progressed, H2O2 was gradually consumed, the ·OH content continued to decrease, and the degradation rates of PNP and COD gradually became balanced. At the same time, the removal rate of PNP is always higher than the COD removal rate, indicating that ·OH does not directly degrade PNP to CO2 and H2O, but decomposes a part of PNP into intermediate products, such as hydroquinone, p-aminophenol, benzoquinone, etc. (Zhang 2009; Figure 6).

Removal of PNP by different reaction systems

At present, there are still differences in the reaction mechanism of the photo-assisted heterogeneous Fenton-like catalyst system. It is widely recognized that organic matter diffuses from the liquid state to the catalyst, is catalytically degraded and then desorbed into the liquid state (Navalon et al. 2010). In order to compare the removal effect of PNP on different reaction systems, PNP was removed by UV/catalyst, UV/H2O2, catalyst, and UV/H2O2/catalyst. The result is shown in Figure 7.

It can be seen from Figure 7 that the removal rate of PNP by the UV/catalyst system is only 2.5%, the removal rate of PNP by the UV/H2O2 system is 10.8%, and the removal rate of PNP by the H2O2/catalyst system is 76.8%, while the removal rate of PNP by UV/H2O2/ catalyst system was over 98%. H2O2 plays an oxidizing role in the catalytic oxidation process, and PNP is not oxidatively degraded without H2O2. The UV/H2O2 system has a low removal rate. The removal rate is greatly improved after
the addition of the catalyst, and the H₂O₂/catalyst system has a good removal rate, indicating that the solid supported catalyst plays a key role in improving the PNP removal rate, which indirectly proves the rationality of the guess. The PNP removal rate of the UV/H₂O₂/catalyst system is greater than the sum of the removal rates of the UV/H₂O₂ system and the H₂O₂/catalyst system, indicating that the UV light and the catalyst have good synergistic effects.

Catalyst stability

Catalysts undergo various physical and chemical changes in the reaction system, resulting in a decrease in activity, a decrease in catalytic efficiency, and a decrease in the removal rate of organic matter (Li 2014). The supported catalyst with the particle Al₂O₃ as the carrier is clogged with the pores after repeated use, the number of surface active sites is reduced, the active component is lost, and the activity of the catalyst is decreased. The catalytic effect of the Fe-Ce/Al₂O₃ catalyst after repeated use was studied. Control reaction conditions: PNP simulated wastewater concentration of 200 mg/L, H₂O₂ dosage of 150 mmol/L, catalyst dosage of 100 g/L, pH of 4, temperature of 25°C, and a reaction time of 90 min. After the completion of the reaction, the catalyst was repeatedly washed, filtered, dried, and reused. The experimental results show that the PNP removal rate decreases with the increase in the number of reactions. From the first to the fourth time, the PNP removal rate decreased slightly. The PNP removal rate reached 90% at 90 min, and the PNP removal rate decreased slightly to 83.2% when the fifth time was repeated. The Fe-Ce/Al₂O₃ catalyst can resist the reaction erosion better, thus maintaining its own physical and chemical properties, and has good stability. It has no qualitative change after repeated use for 5 times, and still maintains a good catalytic effect.

ESTABLISHMENT OF KINETIC MODEL FOR DEGRADATION OF P-NITROPHENOL WASTEWATER BY PHOTO-ASSISTED HETEROGENEOUS FENTON-LIKE PROCESS

The kinetic model of degradation of p-nitrophenol wastewater by photo-assisted heterogeneous Fenton method is established through experiments, which can not only provide an in-depth understanding of the catalytic mechanism of the method but also provide a method to strengthen the process, to improve the efficiency of this method in industrial wastewater treatment and to provide useful data for future research. On the one hand, the process of dynamics research is the indirect study of experimental mechanisms. On the other hand, it is the study of chemical reaction rates. By studying the relationship between the reaction rate of photo-assisted heterogeneous Fenton reaction and the amount of hydrogen peroxide added to the solution, the amount of catalyst added to the solution, and the pH value of the initial solution, the activation energy required for the reaction was obtained. Therefore, the important index to judge the catalytic activity of a catalyst is reaction activation energy.

According to the catalytic mechanism of section 3, the reaction of photo-assisted heterogeneous Fenton-like reaction to generate hydroxyl radicals is as follows:

\[
\begin{align*}
Fe^{2+} + H_2O_2 &\rightarrow Fe^{3+} + OH^- + HO^+ \\
Fe^{3+} + H_2O_2 &\rightarrow FeO_2H^2+ + H^+ \\
Fe^{3+} + HO_2^- &\rightarrow Fe^{2+} + H^+ + O_2 \\
Fe^{3+} + H_2O_2 + UV &\rightarrow OH^- + Fe^{2+} + H^+ 
\end{align*}
\] (3) (4) (5) (6)

In the photo-assisted heterogeneous Fenton-like system, H₂O₂ first reacts with metal ions on the active center of the catalyst to produce ⋅OH, and the resulting ⋅OH oxidizes p-nitrophenol and its intermediates in the reaction solution. At the same time, the generated ⋅OH generates O₂ under the catalytic action of the catalyst, and the consumption of the partial ⋅OH is caused.

The photo-assisted heterogeneous Fenton-like system has a very fast reaction rate, which is much higher than the direct photolysis reaction of p-nitrophenol and its intermediates. Therefore, the direct photolysis of p-nitrophenol can be neglected, and it is considered that the degradation of p-nitrophenol and its intermediate products is carried out by the ⋅OH generated by the system.
In summary, the rate equation of the reaction can be expressed as:

$$- \frac{dC}{dt} = kC^n_1C^n_2$$  \hfill (7)

In the equation:

- $C^n_1$ = concentration of ·OH in solution
- $C^n_2$ = concentration of PNP in solution
- $k$ = reaction rate constant
- $p,n$ = reaction series
- $t$ = Reaction time

In the process of studying the kinetics of photo-assisted heterogeneous Fenton-like oxidation degradation of organic wastewater, the research object is mostly a single organic matter in solution. In the reaction, organic matter is converted into intermediate substances. ·OH hydroxyl radicals have the characteristics of strong oxidizing ability and fast reaction rate, and have no specificity. ·OH has a short period of time during the reaction, and $C^n_1$ is regarded as a constant in order to impair the interference caused by the intermediate product of p-nitrophenol during the reaction (Malik & Saha 2003; Dantas et al. 2006).

So the above formula can be expressed as:

$$- \frac{dC}{dt} = kC^n$$  \hfill (8)

Discussion and analysis:

When $n = 0$, a zero-order reaction rate equation can be obtained, and the integral of formula (8) is obtained:

$$- \frac{dC}{dt} = kC^n$$  \hfill (9)

When $n = 1$, the first-order reaction rate equation can be obtained, and the integral of formula (9) is obtained:

$$\ln\frac{C}{C_0} = -kt$$  \hfill (10)

When $n = 2$, the second-order reaction rate equation can be obtained, and the integral of formula (10) is obtained:

$$\frac{1}{C} - \frac{1}{C_0} = kt$$  \hfill (11)

To establish a kinetic equation for the treatment of p-nitrophenol wastewater by photo-assisted heterogeneous Fenton-like, the reaction orders should be verified first. Based on the experimental data and the derived reaction rate equation, the relationship between the degradation concentration of p-nitrophenol and the reaction time under different reaction orders is determined. Analyzing and comparing the graphs, the degree of fitting of the graph is the coefficient of linear correlation. The determination of the reaction order is based on the best correlation value in the graph. According to the above theory, the drawings are separately made.

Test reaction conditions: prepare 100 mL of 200 mg/L p-nitrophenol solution, adjust the initial pH value of 4, H$_2$O$_2$ dosage is 150 mmol/L, the catalyst dosage is 100 g/L, control room temperature is 25°C. The effect of the removal of p-nitrophenol was investigated by changing the reaction time, and the total reaction time was 100 min. During the reaction, the concentration of p-nitrophenol was measured every 20 min, and the removal rate of p-nitrophenol in the wastewater was calculated. The experimental results are shown in Table 2 below, and the well-fitted p-nitrophenol rate equation was selected based on image analysis.

According to Table 2, figures of $C_0$-$C$, $\ln(C_0/C)$, $1/C$-$1/C_0$ are drawn. The figures are shown below.

The $R^2$ of the equation in the figure indicates the degree of fitting. The larger the $R^2$, the closer to 1 indicates that the fitting of the equation is better. It is indirectly indicated that the kinetic equations in the equation of the equation are more consistent with the study of this experiment. It can be seen from the figure that when the kinetics of degrading p-nitrophenol is analyzed, the correlation of $\ln(C_0/C)$ versus time t is the highest, and the R-value is closer to 1. There is a

| Time (min) | C  | $C_0$ | $\ln(C_0/C)$ | $1/C - 1/C_0$ |
|-----------|----|------|--------------|---------------|
| 15        | 160.81 | 39.19 | 0.218        | 0.001         |
| 30        | 114.33 | 85.67 | 0.559        | 0.004         |
| 45        | 58.37  | 141.63 | 1.232       | 0.012         |
| 60        | 23.56  | 176.44 | 2.139       | 0.037         |
| 75        | 10.70  | 189.3 | 2.928        | 0.088         |
| 90        | 4.77   | 195.23 | 3.736       | 0.205         |
linear relationship between the points in the figure, and the reaction rate constant $k$ is the slope obtained by linear fitting. It is indicated that the degradation mechanism of p-nitrophenol conforms to the first-order kinetic model (Figures 8, 9 and 10).

**CONCLUSION**

We conducted a complete experimental study on the degradation of PNP wastewater. During the study, analysis showed that the active ingredients Fe$^{3+}$ and Ce$^{3+}$ covered the surface of the Al$_2$O$_3$ carrier and filled the particle channel. The surface of the supported catalyst was rough with a certain pore structure, and the specific surface area was 228.95 m$^2$/g. It is beneficial to treat organic wastewater catalytically in the heterogeneous Fenton system. Then, the single factor experiment shows that the photoassisted heterogeneous Fenton catalyst system is effective in treating PNP wastewater. The optimal process conditions were as follows: to treat the simulated wastewater with a mass concentration of 100 mL PNP of 200 mg/L, 15 mmol H$_2$O$_2$ and 10 g Fe-Ce/Al$_2$O$_3$ were added, the control pH was 4, the temperature was 25°C, and the reaction time was 120 min. At this point, the removal rate of PNP reached the maximum, 98.7%, and the removal rate of COD reached 72.9%. Finally, a model for degradation of p-nitrophenol wastewater by photo-assisted heterogeneous Fenton method was established. The results show that it conforms to the first-order dynamic equation, which indicates that it meets the needs of engineering practice. The study confirmed that it is feasible and effective to treat p-nitrophenol wastewater by UV and catalyst.

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First received 16 July 2019; accepted in revised form 10 January 2020. Available online 6 February 2020.