Rapid determination of dye concentration in wastewater by TiO₂-KMnO₄ synergistic photocatalytic oxidation system

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Abstract. A new method for the determination of dye concentration based on photocatalytic oxidation digestion and spectrophotometry was established by using KMnO₄ synergistic TiO₂ photocatalytic oxidation and methyl orange solution as simulated dye wastewater. The mechanism of photocatalytic oxidation for the determination of dye concentration was discussed, and the optimal reaction conditions for dye digestion were investigated. The optimal digestion conditions were as follows: solution pH 1.5, TiO₂ amount 1.0 g/L, KMnO₄ initial concentration 10.0 mmol/L, solution temperature 80 °C, ultraviolet light irradiation time 10 min. Compared with potassium dichromate reflux method or potassium permanganate method, the photocatalytic digestion method of TiO₂–KMnO₄ synergistic system is more rapid, efficient, economical and environmentally friendly, which provides a new idea for the determination of dye concentration in wastewater.

1. Introduction

With the rapid development of textile industry, the variety and quantity of dyes are increasing day by day, and dye wastewater has become one of the key sources of pollution in the water system, which causes great harm to the ecological environment and drinking water. The research of dyes degradation, mainly catalytic degradation, has become the main work of dye wastewater treatment in recent years, and some achievements have been made[1-7].

In the process of dye wastewater treatment and water quality monitoring, the degradation degree of dye is usually judged by chemical oxygen demand (COD). Potassium dichromate method and potassium permanganate method are the two most commonly used methods to determine COD value, each of them has its advantages and disadvantages[8].

Potassium dichromate reflux method is to first oxidize and digest organic water sample by high temperature reflux of K₂Cr₂O₇ solution, and then quantitative analyze by chemical titration and calculate the COD value. The results of this method are reliable and reproducible, but the operation is troublesome, time-consuming and electricity-consuming, the water sample needs to be heated and refluxed for 2 hours. A large amount of concentrated sulfuric acid needs to be consumed, expensive silver sulfate needs to be used as catalyst, and highly toxic mercury sulfate needs to be used to mask the interference of chloride ion, and so on.

The analysis period of potassium permanganate method is shorter than that of potassium dichromate method, and the digestion process is relatively simpler. There is no need to reflux and use the catalyst, but the organic matter in water can not be completely oxidized, the oxidation rate is low, so there is a certain gap between the measured value and the true value, and the accuracy is low.
There are also studies using spectroscopic sensing technology for water sample monitoring\cite{9, 10}. Compared with the traditional analysis methods, spectral analysis technology has the obvious advantages of continuous monitoring, on-line monitoring and rapid detection. However, it is only suitable for fixed-point and real-time monitoring of COD in environmental water samples with known and fixed components, and is not suitable for dye wastewater with unknown and complex components. Therefore, it is of great practical significance to develop new ideas and develop a rapid, sensitive and environmentally friendly method for the determination of dye concentration.

Photocatalysis is a kind of advanced oxidation technology, and the photocatalysis technology has obvious advantages especially when the organic pollutants in water are difficult to be degraded by other methods. As a deep purification technology, the photocatalysis can completely mineralize various organic substances into non-toxic carbon dioxide and water. So photocatalysis is more and more applied to environmental pollution treatment, and is becoming a hot spot technology for treating the dye waste water difficult to be degraded at present. Photocatalysis, since it can efficiently and deeply oxidize and degrade the dye, can this technique be used for the digestion of water samples in the determination of dye concentration? Thereby it can overcome the shortcoming of long-time heating reflux in the potassium dichromate method or the low oxidation rate in the potassium permanganate method.

In the early stage, we used the synergistic photocatalytic oxidation effect of TiO$_2$-K$_2$Cr$_2$O$_7$ to establish a simple and sensitive method for the rapid determination of dye concentration based on the reduction of Cr$_2$O$_7^{2-}$ to Cr (III) and then spectrophotometric determination of the residual Cr$_2$O$_7^{2-}$ \cite{11,12}. In this paper, we used methyl orange solution as the simulated dye wastewater, and used the photocatalytic effect of TiO$_2$, simultaneously used KMnO$_4$ as an electron trapping agent to strengthen the synergistic oxidation in the system. So that the oxidation of dye and the reduction of MnO$_4^-$ can be carried out according to stoichiometric ratio, then the amount of dye can be obtained by the determination of remaining MnO$_4^-$ by spectrophotometry.

2. Experimental

2.1. Instruments and reagents
Jasco ultraviolet-visible spectrophotometer, HANNA HI98128 water-proof pocket pH meter, WFH-203B three-use ultraviolet analyzer, WCLG-1 micro magnetic stirrer, TGL-16G desktop high-speed centrifuge, FA2204B electronic balance, millipre synergy UV ultrapure water device.

Titanium dioxide (Degussa P25, BET surface area 50 ±15 m$^2$/g, primary particle size 21 nm, compaction density 130 g/L, ratio of anatase to rutile type is about 80:20). Methyl orange (C$_{14}$H$_{14}$N$_{3}$NaO$_3$S, relative molecular mass 327.34), potassium permanganate (KMnO$_4$, relative molecular mass 158.03), concentrated sulfuric acid (H$_2$SO$_4$, relative molecular mass 98.08), these reagents were all analytical pure. The water used in the experiment was ultra-pure water.

2.2. Experimental methods
In the reaction vessel, KMnO$_4$ solution, TiO$_2$ and a certain amount of simulated dye waste water methyl orange solution were added in above sequence, and the solution was stirred at a certain reaction temperature for several minutes. The volume of the reaction solution was maintained at 40 mL and the pH was adjusted with H$_2$SO$_4$ solution. The high-speed centrifugation was carried out after a certain time of the 254 nm ultraviolet light irradiation. 1 mL of the supernatant was pipetted to a 25 mL colorimetric tube and diluted to volume. Using water as a reference, the absorbance value A was measured at a wavelength of 525 nm, which was the absorbance value of the remaining MnO$_4^-$ in the solution.

The typical reaction conditions of photocatalytic oxidation digestion experiment were as follows: the initial concentration of KMnO$_4$ was 10.0 mmol/L, TiO$_2$ was added in an amount of 1.0 g/L, the initial pH value was 1.5, the solution temperature was 80 °C, and the light irradiation was 10 min. The
Absorbance of MnO$_4^-$ before photocatalysis was set to be as $A_0$, and the variation value of absorbance $\Delta A$ was calculated, where $\Delta A = A_0 - A$.

The standard curve was performed with the concentration of the standard methyl orange series solution and the corresponding $\Delta A$ value, and the methyl orange concentration of the actual water sample could be obtained according to the curve.

3. Results and discussion

3.1. Synergistic photocatalytic oxidation mechanism

Nano TiO$_2$ generates highly active holes/electron pairs under the irradiation of ultraviolet light. Holes (h$^+$) react with water to form $\cdot$OH, and both holes and $\cdot$OH have strong oxidizing ability, which can react with organic compound dyes adsorbed on the surface of TiO$_2$, and oxidize the dye to CO$_2$ and H$_2$O. The KMnO$_4$ coexisting in the solution is reduced by accepting photogenerated electrons on the surface of TiO$_2$ as an electron acceptor, thereby the chance of recombination of photogenerated electrons and holes is reduced, the oxidizing ability of the synergy system is improved.

Since the reduction of KMnO$_4$ and the oxidative degradation of the dye are synergistically carried out in a stoichiometric relationship, the concentration of the dye in the water sample can be indirectly determined by measuring the change value of the concentration of KMnO$_4$ in the system. The main reactions of the system are as follows:

\[
\begin{align*}
\text{TiO}_2 + \text{hv} & \rightarrow \text{h}^+ + \text{e}^- \\
\text{H}_2\text{O} + \text{h}^+ & \rightarrow \cdot\text{OH} + \text{H}^+ \\
\cdot\text{OH} \text{ or } \text{h}^+ + \text{organics} & \rightarrow \cdot\cdot\cdot\rightarrow \text{CO}_2 + \text{H}_2\text{O} \\
\text{MnO}_4^- + 8 \text{H}^+ + 5 \text{e}^- & \rightarrow \text{Mn}^{2+} + 4 \text{H}_2\text{O}
\end{align*}
\]

3.2. Selection of solution pH

The oxidant KMnO$_4$ can only have strong oxidizing ability under certain acidity conditions. Under the fixed condition of KMnO$_4$ initial concentration 6.0 mmol/L, methyl orange 40 mg/L, TiO$_2$ amount 1.0 g/L and the solution temperature 80 °C, the effect of pH value on the change value of MnO$_4^-$ absorbance ($\Delta A$) was investigated by ultraviolet irradiation for 10 min. The results are shown in figure 1.

It can be seen from the figure that as the pH value of the solution decreased, $\Delta A$ gradually increased, that is, the low pH was beneficial to improve the overall oxidizing ability of the photocatalytic system. Because the TiO$_2$ surface was positively charged under acidic condition, which was more favourable for the adsorption of MnO$_4^-$, thereby the recombination of the holes and the electron pairs on the surface of TiO$_2$ was inhibited. However, when the solution was strongly acidic, the concentration of H$^+$ in the solution was greatly increased, so that it consumed too much e$^-$ amounts and indirectly affected the generation of the $\cdot$OH, thereby the reaction rate was affected. So that when the pH was 1.5, the results of promotion and inhibition reached a peak value, the best experiment result was at pH 1.5. Therefore, 1.5 was selected as the most optimal pH value of the system.

![Figure 1. Effect of solution pH on MnO$_4^-$ absorbance change value ($\Delta A$)](image-url)
3.3. Selection of TiO$_2$ photocatalyst amount

The standard oxidation-reduction potential of MnO$_4^-$ is 1.51 V (MnO$_4^-$ + 8 H$^+$ + 5 e$^-$ → Mn$^{2+}$ + 4 H$_2$O), and its oxidizing ability is weaker than that of ·OH (2.7 V). Therefore, the oxidation of organic matter by this system is mainly heterogeneous photocatalytic oxidation of nano TiO$_2$. In photocatalytic reaction, the amount of catalyst is also an important problem.

In order to study the effect of TiO$_2$ amount on the performance of photocatalytic synergistic oxidation degradation of methyl orange, the initial concentration of KMnO$_4$ was fixed at 6.0 mmol/L, the concentration of methyl orange was 40 mg/L, the pH of the solution was 1.5, the temperature of solution was 80 °C. The effect of TiO$_2$ amount on the change value of MnO$_4^-$ absorbance (ΔA) was investigated by ultraviolet irradiation for 10 min.

As shown in figure 2, as the amount of TiO$_2$ increased, ΔA increased, which was beneficial to the determination. However, if the amount of TiO$_2$ was too large, the suspended particles would affect the penetration of ultraviolet light in the solution, the holes and electron pairs in the bottom or deep solution could not be excited to generate smoothly to participate in the digestion of methyl orange, so that the reaction was only carried out in the surface or shallower layer, the photocatalytic effect of TiO$_2$ decreased and the ΔA value dropped, thereby the reaction efficiency was affected. Therefore, 1.0 g/L was selected as the most optimal TiO$_2$ amount of the system.

![Figure 2. Effect of TiO$_2$ photocatalyst amount on MnO$_4^-$ absorbance change value (ΔA)](image)

3.4. Selection of initial concentration of KMnO$_4$

In the process of photocatalytic degradation of organic matter by nano TiO$_2$, the oxidant KMnO$_4$ was used as an electron trapping agent to prevent the recombination of photogenerated electrons and holes to improve the photocatalytic degradation ability of the synergistic system.
Under the condition of methyl orange concentration 40 mg/L, TiO$_2$ amount 1.0 g/L, the pH value of the solution 1.5, solution temperature 80 °C, ultraviolet light irradiation for 10 min, the effect of initial concentration of KMnO$_4$ on MnO$_4^-$ absorbance change value (ΔA) was investigated.

It can be seen from figure 3, that ΔA increased with the increase of the initial concentration of KMnO$_4$. When the initial concentration of KMnO$_4$ reached 10.0 mmol/L, ΔA reached the maximum and then decreased slightly. Therefore, 10.0 mmol/L was selected as the initial of KMnO$_4$.

3.5. Selection of solution temperature

Although the activation energy of photocatalytic reaction comes from photonic energy, the temperature of the solution can also affect the collision rate between the dye molecule and photocatalyst. Figure 4 shows the variation of MnO$_4^-$ absorbance change value (ΔA) at different temperature after ultraviolet light irradiation for 10 min, and the initial concentration of KMnO$_4$ was 10.0 mmol/L, the concentration of methyl orange was 40 mg/L, the amount of TiO$_2$ was 1.0 g/L, and the pH of the solution was 1.5.

The results show that with the increase of solution temperature, the collision opportunity between the photocatalyst TiO$_2$ particles and the reactant methyl orange increased, and the photocatalytic oxidation rate increased, thus the oxidizing ability of the synergistic system was enhanced. However, too high temperature would cause a large number of evaporation of the reaction solution, therefore the temperature of the reaction solution was selected at 80 °C.

![Figure 4. Effect of solution temperature on MnO$_4^-$ absorbance change value (ΔA)](image)

3.6. Selection of ultraviolet light irradiation time

The effect of ultraviolet light irradiation time on the of MnO$_4^-$ change value (ΔA) was studied under the condition that the initial concentration of KMnO$_4$ was 10.0 mmol/L, the concentration of methyl orange was 40 mg/L, the amount of TiO$_2$ was 1.0 g/L, the pH value of the solution was 1.5, and the temperature of the solution was 80 °C, the result is shown in figure 5.

As can be seen from the figure, under the given condition, ΔA increased with the extension of the irradiation time. When the irradiation time reached 10 min, ΔA reached a stable value, that is, the stability of the overall oxidizing ability of the photocatalytic system was achieved. Therefore, 10 min was selected as the time of the photocatalytic degradation.

In summary, the optimal reaction conditions for oxidation and detection of dye methyl orange concentration were as follows: solution pH 1.5, TiO$_2$ amount 1.0 g/L, KMnO$_4$ initial concentration 10.0 mmol/L, solution temperature 80 °C, ultraviolet light irradiation time 10 min.
3.7. Standard curve

In the above selected oxidation system, different concentrations of standard methyl orange solution were added for photocatalytic oxidation digestion, and the change value of MnO$_4^-$ absorbance (ΔA) before and after the reaction was measured. The values of ΔA and methyl orange concentration was plotted to obtain a standard curve, the results are shown in figure 6.

It can be seen that under the conditions selected in this experiment, there was a good linear relationship between ΔA value and methyl orange concentration value of 10-120 mg/L. The corresponding linear equation was $y=0.0041x+0.1421$, and the correlation coefficient $R^2=0.9959$.

4. Conclusion

Under the condition of ultraviolet light irradiation, TiO$_2$-KMnO$_4$ had obvious photocatalytic digestion effect on methyl orange simulated wastewater. The experimental results show that:

(1) The initial pH value of the solution, the amount of TiO$_2$, the initial concentration of KMnO$_4$, the temperature of the solution and the ultraviolet light irradiation time all can affect the digestion of the dye.

(2) The optimal digestion conditions were obtained as follows: solution pH 1.5, TiO$_2$ amount 1.0 g/L, initial concentration of KMnO$_4$ 10.0 mmol/L, solution temperature 80 °C, irradiation time 10 min. The change of MnO$_4^-$ absorbance was determined by spectrophotometry, so that the dye concentration can be obtained indirectly.

(3) Based on the principle that KMnO$_4$ can obtain photogenerated electrons to improve the photocatalytic oxidizing ability of semiconductor, a new method for the determination of dye concentration by spectrophotometry with nano TiO$_2$-KMnO$_4$ synergistic system for photocatalytic
digested wastewater was established. This method has the characteristics of fast (only 10 min light digestion, greatly shortening the measurement time), sensitive (the synergistic system has higher oxidation performance, so the detection limit is lower and the sensitivity is higher) and environmentally friendly (avoiding the use of precious silver salt and mercury sulfate, and will not cause secondary pollution). It is of great value to be popularized.

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