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Study on Removal of the Dye Eosin with Combined Effect of Ferrate and Light

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This paper studied the oxidative degradation of the dye eosin by the combined effect of ferrate and light, mainly investigated the effects of light intensity, reaction temperature, amount of ferrate added, initial concentration of eosin etc. on the degradation rate of dyes, and tried to explore the degradation mechanism of the dye. The study found that light and ferrate have a synergy effect on the oxidative degradation of dyes. Increasing the light intensity and increasing the amount of ferrate added can significantly increase the removal rate of eosin; the influence of reaction temperature and initial concentration of eosin on the final eosin removal rate is complicated, and there are optimal reaction temperature and the initial concentration of eosin. By studying the UV-visible absorption curves of eosin at different time during the degradation reaction, it can be found that no new product formed during the reaction. It is inferred that the eosin is eventually oxidized into smaller molecules such as carbon dioxide and water.

1. Introduction

With the rapid development of the dyestuff industry, the variety and quantity of dyes are increasing. While enriching our color world, the wastewater of dyes also brings serious pollution to the environment. High-chroma printing and dyeing wastewater is currently recognized as harmful industrial wastewater, and its color can cause visual unpleasant to the people, its components contain organic substances that are difficult to biodegrade, such as dyes and dye intermediates. The decolorization and degradation treatment of dye wastewater is a worldwide difficulty and hot spot, and has become an important issue in the current environmental protection field. Dye wastewater has the characteristics of large amount, diversified, deep chroma, high toxicity, and complex components, and is not easily biodegraded (Jin, 1990).

The treatment of dye wastewater began in the 1970s. It has developed adsorption, flocculation, chemical oxidation, photocatalytic oxidation, biological oxidation and other processing techniques (Ji and Chen, 2016; Chaleshtori et al., 2013; Wu et al., 2016). Ferrate is a strong oxidant, and its oxidation-reduction potential is as high as 2.20 eV under acidic conditions. It is a kind of green water treatment agent integrating oxidation, disinfection, sterilization and flocculation (Xia et al., 2004; Mohammad et al., 2009; Luo et al., 2008). The use of ferrate for oxidation to remove pollutants in water is a research hotspot in the field of water treatment both at home and abroad. In this paper, as a model contaminant, eosin Y (hereinafter referred to as “eosin”) was used to investigate the oxidation behavior of dyes by the method of combining ferrate with light irradiation. The influences of light intensity, reaction temperature, reaction time, amount of reagent and other factors on the degradation rate of the dye eosin were investigated, and the degradation mechanism of the dyestuff was also explored.

2. Experiment

2.1 Experimental materials

K_2FeO_4 was prepared according to the method described in (Luo et al., 2008) and its purity was about 99%. Other reagents required in the experiment are: Sodium sulfite, Eosin Y, and HCl, all were analytically pure

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(AR) and purchased from Tianjin Kemiou Chemical Reagent Co., Ltd.

2.2 Experimental instruments

Persee TU-1901 spectrophotometer (Beijing Persee General Instrument Co., Ltd.); light source using PL5-5XE300 xenon lamp light source (Perfectlight Technology Co., Ltd.), continuously adjustable power; HJ-3 magnetic stirrer (Jintan Xinghang Instrument Factory).

2.3 Experimental Methods

The K_2FeO_4 oxidation dye experiment is carried out in a 300-mL quartz reactor, the reactor is directly under the xenon light source and the electrical power is controlled at 0-300W. The reactor is filled with a certain volume of 0.2 m•mol•L^{-1} K_2FeO_4 solution and a volume of 100 mL eosin dye solution with a concentration of 20 mg•L^{-1}. The magnetic stirring makes the reaction system maintain a uniform concentration, using constant-temperature water to circulate in the reactor jacket to ensure that the temperature of the reaction system is constant. The reaction has carried out for a predetermined time, 10 ml of the solution is taken with a pipette and sodium sulfite is added to terminate the reaction, and the absorbance of the filtrate is measured at 515 nm (the maximum absorption wavelength of eosin).

3. Experimental results and discussion

Figure 1 shows the removal rate of eosin under three situations at 20°C (i.e., light only, ferrate only, light and ferrate treatment), the added ferrate amount is 2ml, and the power of the light source is 300 W. It can be seen from the figure that when we only use the light, it has a very low removal rate of eosin, and the concentration of the solution may even increase when the time reaches 20 min. This is due to evaporation of the eosin solution. When we only use the ferrate solution, eosin can be degraded to a certain extent, when the oxidation time is 20 minutes, the removal rate of eosin can reach about 30%. When using ferrate solution with the same concentration and combining with the light, the removal rate can be effectively improved, and the removal rate of eosin can reach about 50% when the reaction time is 20 minutes, which shows that the light and the ferrate solution have a synergy effect. The reaction rate of the system can be estimated from the removal rate of eosin at the same time, it can be seen from the figure that the combination of light and ferrate solution leads to an increase in the reaction rate, which is related to the formation of a certain concentration of Fe (V) in the reaction system [8].

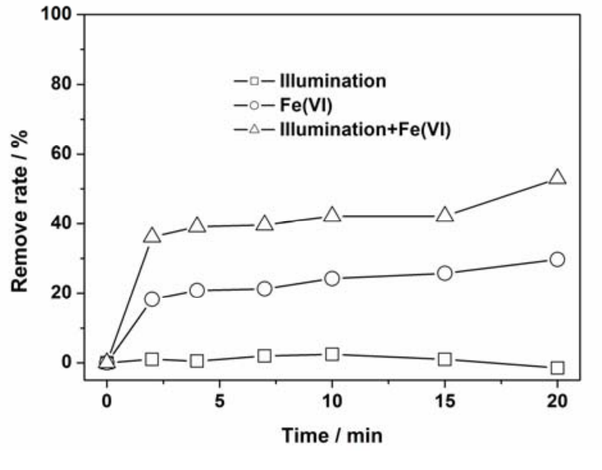

Figure 1: Change of removal rate of eosin with time under different experimental conditions

The light emitted by a xenon light source is similar to sunlight, and about 5% of it is ultraviolet light. In many studies (Winkelmann et al., 2008; Yuan et al., 2008; Chen, 2012), it has been confirmed that UV light has a synergy effect on the oxidizability of ferrate due to the fact that UV light can promote the conversion of Fe(VI) into Fe(V) and Fe(IV). The reaction mechanism is that Fe(VI) gets one electron to continuously generate Fe(V) which has stronger activity, and Fe(V) further obtains an electron to form Fe(IV) (reaction mechanism is shown in Eq 1, 2 respectively).

$$Fe(VI) + e^- \rightarrow Fe(V) \tag{1}$$

$$Fe(V) + e^- \rightarrow Fe(IV) \tag{2}$$

Fe(V) can be generated and detected by pulse radiolysis under alkaline conditions. It has very strong oxidizability and extremely high reaction rate. Its reaction rate constant is about 10^4 times that of Fe(VI) (Nadine et al., 2008; Sharma et al., 2008). It is because of its stronger oxidizability and higher reaction rate that the removal rate of the dye in the system is effectively improved. This is similar to the results of studies using this effect to remove contaminants such as organic phosphorus and phenol.

Fix the volume of added ferrate at 2 mL, changing the power of the light source to further compare the degradation of eosin under different light intensity (see Figure 2). It can be seen from the figure, as the power of the light source increases, the rate of the reaction and the final removal rate of eosin are both significantly increased. This is due to the increase in the electric power of the light source and the corresponding increase in the light intensity, which is conducive to the synergy effect with ferrate and the generation of higher-concentration Fe(V), thereby increasing the reaction rate and making the reaction more thorough.

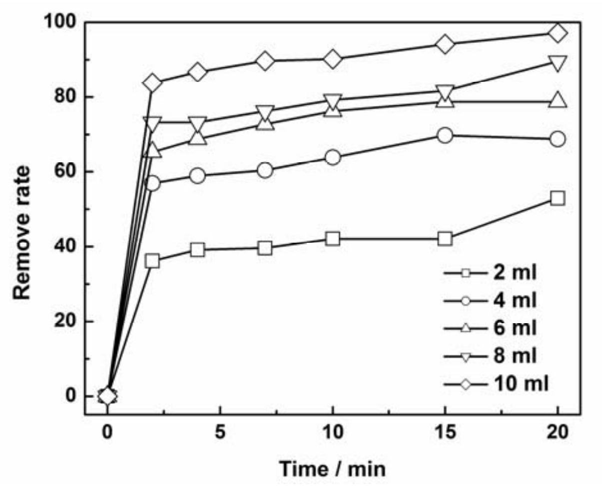

Figure 2: Effect of different light intensity on the removal rate of eosin

Figure 3 shows the effect of the added ferrate volume on the removal rate when fixing the light source power at 300W. From the figure we can know that, the removal rate of eosin increases significantly with the increase of ferrate volume, 2 ml of ferrate can make the removal rate of eosin ultimately reach 50%, when the volume of ferrate is increased to 10 ml, the removal rate can be increased to more than 95%. It can also be seen from the figure that the change of the removal rate decreases obviously after 2 min, indicating that the reaction is close to equilibrium. In the redox reaction, the redox potentials of the oxidized and reduced states are related to their concentration (more precisely, the "activity"). The relationship between the redox potential and the concentration can be calculated according to the Nernst equation (Equation 3), where φ is the electrode redox potential, φ^θ is the redox potential under standard conditions, R is the ideal gas constant, and T is absolute temperature, n is the number of electrons gained or lost during the reaction, F is the Faraday constant, ao and ar are the redox potentials of the oxidizing and reducing agent, respectively. Increasing the concentration of ferrate can increase the ao value, so as to increase the redox potential and the oxidizability. Therefore, the increase of ferrate solution amount actually increases the concentration of oxidizing agent, so as to increase its redox potential and enhance the oxidizability, and finally the removal rate of the dye eosin is improved; the equilibrium of reaction ultimately depends on the comparison of the redox potential of oxidizing and reducing agent. When the two are equal, the system reaches equilibrium. With the progress of the redox reaction, the concentration ao of the ferrate oxide state gradually decreases, and the concentration ar of the reduced state increases, thus causing the reduction of the redox potential φ of the ferrate. When the redox potential φ of the oxidizing and the reducing agent are close to each other, the reaction is close to equilibrium. Reflecting in the figure, the removal rate of dye basically reaches a balance, and then changes little with time.

$$\varphi = \varphi^\theta + \frac{RT}{nF} Ln \frac{a_0}{a_r} \tag{3}$$

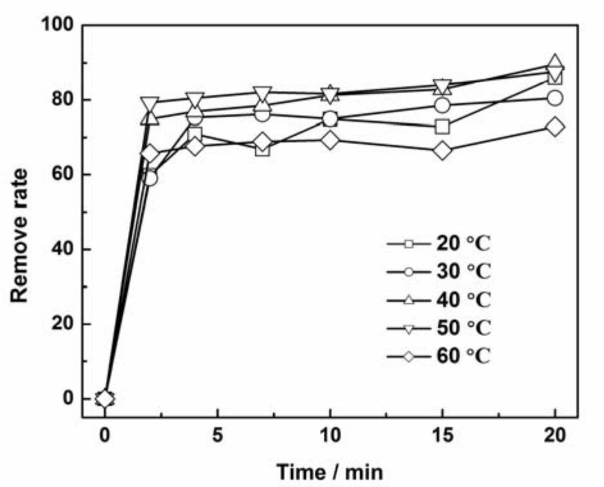

Figure 3: Effect of different ferrate amount on the removal rate of eosin

Figure 4 shows the effect of reaction temperature on the removal rate of eosin. We examined the effect of temperature on the removal rate of eosin in the temperature range of 20°C-60°C. The results showed that the temperature had little effect on the reaction rate and the final eosin removal rate. The removal rate increased slightly with the increase of reaction temperature from 20°C to 50°C, but the removal rate decreased at 60°C. This is very different from the effect of increasing ferrate concentration in Figure 3, which shows that the effect of temperature on the reaction is more complicated. On the one hand, the increase of the reaction temperature has a positive effect on accelerating the reaction rate. According to the Arrhenius equation (Equation 4), it can be known that the reaction rate k is exponentially related to the temperature T. The increase of temperature is equivalent to accelerate the random movement of the molecules and increase the proportion of activated molecules, thus increasing the probability of collision between oxidizing and reducing agent molecules; on the other hand, the increase of reaction temperature is unfavorable to the stability of ferrate, it’s because high temperature will accelerate the decomposition of the ferrate itself; in addition, the synergy action of UV-light and ferrate can produce Fe(V) with stronger oxidizability and faster oxidation rate. The production of Fe(V) may cause the leveling effect, which counteracts the effect of temperature increase. Fe(V) is more unstable than Fe(VI), and the decomposition of Fe(V) is faster.

$$k = Ae^{-Ea/RT} \tag{4}$$

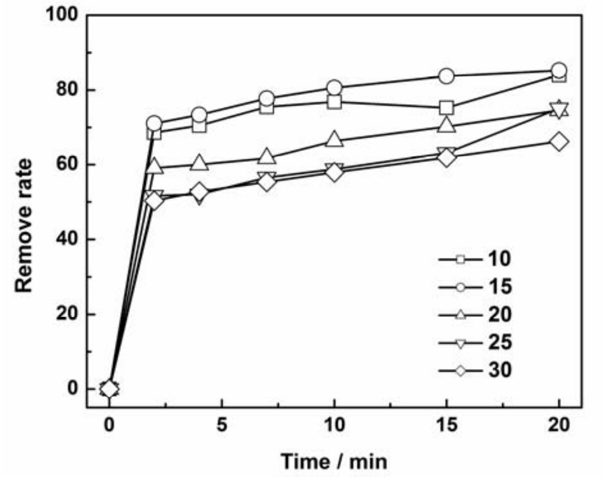

Figure 4: Effect of different reaction temperatures on the removal rate of eosin

Figure 5 shows the effect of the initial concentration of eosin on the removal rate. Similar to the effect of temperature, the effect of the initial concentration of the reducing agent on the reaction rate and the removal rate is not one-way, it also has a trend of increasing first and decreasing later, which is different from the reaction of the dye with ferrate. In this paper, in addition to the oxidizing agent ferrate, we also added an auxiliary means of light, and the degree of light attenuation in the solution and the penetration depth of light are closely related to the concentration of the solution. High concentration of the solution will aggravate the attenuation of light, resulting in a significant reduction in penetration depth and ineffective synergy. In the lower concentration range, appropriately increasing the concentration of the dye will increase the concentration of the reactant molecules. Since most reactions of this type are first-order reactions, the reaction rate increases with the concentration of the reactants; generally, the final removal rate also increases with the initial concentration.

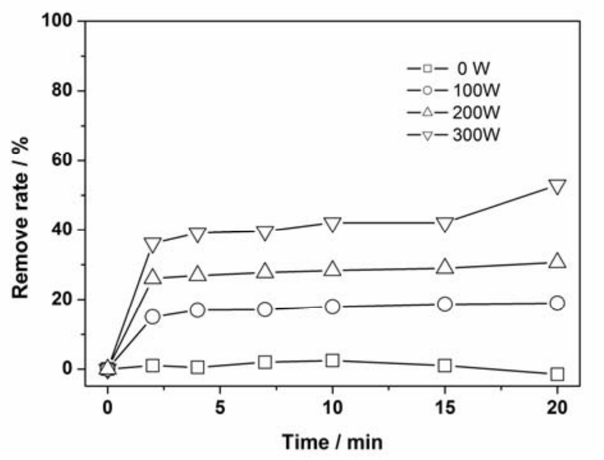

Figure 5: Effect of initial concentration of eosin on the removal rate

The UV-visible absorption spectrum of the eosin degradation process is shown in Figure 6. Most of the dye molecules have complex conjugated structures, and the different functional groups make the dye molecules have different absorption peaks in the ultraviolet and visible regions. Structures such as benzene rings and naphthalene rings generally generate absorption peaks in the ultraviolet region, and the bulkier conjugated structure may cause absorption peaks in the visible region. Eosin has three UV absorption peaks near 254 nm, 300 nm, and 343 nm. The absorption peak at 254 nm comes from the π-π* transition of the benzene ring (Xia et al., 2004); the absorption peaks at 300 nm and 343 nm are presumed to be from the n-π* transition; the absorption peak at 515 nm is the largest, and it is a characteristic absorption peak of eosin, which comes from the absorption of the entire molecule conjugated structure. It can be seen from the figure that all the absorption peaks of eosin decreased rapidly with the time, and the reaction has basically completed after 2 min. This is similar to the results reflected in Figure 2, Figure 3 and Figure 4. In addition, we can see there are no other absorption peaks in the figure, indicating that no other intermediate products are produced during the degradation reaction, and eventually the eosin is oxidized and degraded to smaller molecules such as carbon dioxide and water.

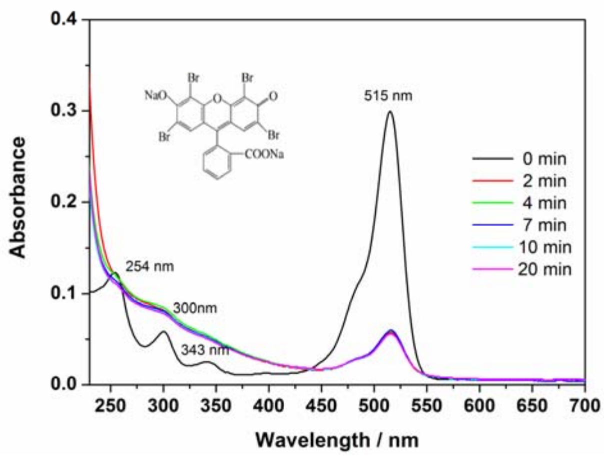

Figure 6: UV-visible absorption spectrum of eosin degradation process

4. Conclusion

This paper uses the ferrate combining with light, and by changing the light intensity, reaction temperature, the amount of ferrate added, the initial concentration of eosin and other conditions, it explores the oxidation degradation of the dye eosin and tries to discuss the degradation mechanism of eosin. The study draws the following conclusions:

(1) Light and ferrate have a synergy effect on the oxidative degradation of dyes, it’s because the UN-light can induce ferrate to produce Fe(V), which has stronger oxidizability and faster reaction rate;

(2) Increasing the light intensity and increasing the amount of ferrate added can significantly increase the removal rate of eosin, which can be attributed to that more photons were used to produce Fe(V), while the increase in ferrate concentration can also increase redox potential;

(3) The effect of reaction temperature and initial concentration of eosin on the final removal rate is more complex. In addition to the reaction rate, the reaction temperature can accelerate the decomposition of Fe(VI) and Fe(V), and the two determine the progress of the reaction together. In addition to affecting the reaction rate, the initial concentration of eosin may also cause the attenuation of light waves and the change of penetration depth. In summary, there is an optimal reaction temperature and initial concentration of eosin.

(4) By studying the UV-visible absorption curve of eosin, it can be found that no new product is formed during the reaction, and it is presumed that it is eventually oxidized into smaller molecules such as carbon dioxide and water.

Acknowledgements

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References

Chaleshtori M.Z., Hosseini M., Edalatpour R., Masud S.M.S., Chianelli R.R., 2013, New porous titanium-niobium oxide for photocatalytic degradation of bromocresol green dye in aqueous solution, Mater Res Bull, 48(10), 3961-3967, DOI: 10.1016/j.materresbull.2013.06.014

Chen G.M., 2012, Total site integration, Master's Thesis, Huazhong University of Science and Technology, Wuhan, PRC.

Ji Y.P., Chen X.L., 2016, Synthesis of BiOI Nanomaterials and Its Light Driven Photocatalytic Degradation towards Bromocresol Green, Environmental Science and Technology, 39, 31-35.

Jin X.C., 1990, Pollution chemistry of organic compounds, Tsinghua University Press, Beijing, PRC.

Luo Z.Y., Zhang S.T., Deng Y., Zheng Z.G., 2008, Preparation of Potassium Ferrate(VI) and Its Practical Application in Water Treatment, Technology of Water Treatment, 34, 40-42.

Mohammad A., Jiang J.Q., Cecile S., 2009, On-line production of ferrate with an electrochemical method and its potential application for wastewater treatment – A review, Jounal of Environmental Management, 90(3), 1350-1356, DOI: 10.1016/j.jenvman.2008.10.001

Nadine N.N., Virender K.S., Diane C., 2008, Reactivity of Ferrate (V) with Aminopolycarboxylates in Alkaline Medium: A Premix Pulse Radiolysis, Inorganica Chimica Acta, 361(4), 1041-1046, DOI: 10.1016/j.ica.2007.07.019

Sharma V.K., Yngard R.A., Cabelli D.E., Baum J.C., 2008, Ferrate(vi) and ferrate(v) oxidation of cyanide, thiocyanate, and copper(i) cyanide. Radiation Physics & Chemistry, 77(6), 761-767, DOI: 10.1016/j.radphyschem.2007.11.004

Winkelmann K., Sharma V.K., Lin Y., Shreve K.A., Winkelmann C., Hoisington L.J., 2008, Reduction of ferrate (VI) and oxidation of cyanante in a Fe(VI)-TiO2-UV-NCO- system,Chemosphere, 72(11), 1694-1699, DOI: 10.1016/j.chemosphere.2008.05.008

Wu C.N., Zhao Q.Y., Song J., Fang T., Bao C., Kong Z., Sun B., Zhang R., Yang H., 2016, Study on PAC Addition on Retarding Membrane Fouling for Printing and Dying Wastewater Treatment by Hybrid Dynamic Membrane Bioreactor, Environmental Science and Technology, 39, 123-127.

Xia Q.Y., Lin Z.H., Zheng X., Chen Z., 2004, Study of Degradation of Azo Dyes Treated by Ferrate, Journal of Fujian Normal University (Natural Science Edition), 20, 50-53.

Yuan B.L., Li X.Z., Nigel G., 2008, Aqueous Oxidation of Dimethyl Phthalate in a Fe(VI)-TiO2-UV Reaction System, Water Research, 42(6-7), 1413-1420, DOI: 10.1016/j.watres.2007.10.010