Fenton Oxidation of different molecular Polyethylene Glycol Model Wastewater

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Abstract. Fenton Oxidation of the polyethylene glycol model wastewater was studied. The experimental conditions were optimized with COD (Chemical Oxygen Demand) removal rate as the indication, and used the organic model wastewater containing different molecular weight PEG. The experimental results showed that: PEG with the same concentration and different molecular weights were investigated under the same oxidation condition. Fenton oxidation of the polyethylene glycol model wastewater can be up to 50% at the condition of pH=3 and the best dosage of H_2O_2/Fe^{2+}; COD removal rate of the PEG2000 was degraded 82% in the conditions, PEG4000 was 62.3%, PEG6000 was lower at the same conditions, was 59.3%, PEG10000 was 61.2%.

1. Introduction

Chemical wastewater is a kind of waste water which is difficult to be biodegraded. At present, most of the treatment of chemical waste water is treated by chemical method before biodegradation. Polyethylene glycol is widely used in industrial production and life, especially for the application of polyethylene glycol with different molecular weights. In general, polyethylene glycol is a kind of compound which is difficult to be treated by biochemical treatment [1], especially when the molecular weight of polyethylene glycol is greater than 400. At present, the treatment of polyethylene glycol is mainly treated by chemical oxidation and biological methods. Kecun Ma [2] et al used Fenton oxidation process to treat refractory chemical wastewater and Fenton oxidation and biological combined treatment process to treat this kind of wastewater. Under the best experimental conditions, the treatment of waste water treatment has achieved the ideal treatment effect, and it can remove certain NH_3-N [2,3]. Fenton oxidation and Fenton like oxidation are widely used in the difficult to degrade chemical waste water. In the process of waste water treatment, a large amount of .OH has been produced under the catalysis of ferrous metal. It has a good economic applicability and operable for the treatment of refractory organic matter [4]. Imamura et al. [6] chose non catalysis and wet catalytic oxidation to degrade polyethylene glycol with different molecular weights. The TOC removal efficiency was best when the molecular weight was about 2000, and the low molecular weight PEG was easier to be decomposed than the high molecular weight PEG [5-8]. The Fenton oxidation process

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is used to treat the photovoltaic industry wastewater containing polyethylene glycol, and Liu Yu's Fenton reagent method is used to treat the photovoltaic industry wastewater [9]. Under the different experimental factors, the wastewater treatment has achieved good results. It has a good application foundation for the pretreatment of the more difficult biodegradable wastewater. It used ozonation of PEG200, PEG1000, PEG6000, PEG10000, PEG20000 [10]; TiO_2 /Ti catalytic oxidation conditions were investigated in the process of photo catalyzing PEG) simulated wastewater [11]. Fenton oxidation of PEG conditions were investigated [12-15].

Polyethylene glycol is a class of polymers, forming substances of different molecular weight. Although there are some studies on the chemical treatment of polyethylene glycol, there are few reports on different molecular weights. For the polyethylene glycol with a molecular weight greater than 400, it is difficult to biodegrade. In order to improve its biodegradability, the author [15] has done a Fenton oxidation experiment with a molecular weight of 200,400, 1000 and 2000 of polyethylene glycol. In order to further study the Fenton experiment with different molecular weights, the Fenton method was used to oxidize PEG2000-10000 as the object of study. After the oxidation of polyethylene glycol with molecular weight greater than 400, it is easy to be biodegradable and provides a basis for further treatment of photovoltaic industry wastewater containing polyethylene glycol. The critical and the optimum operating conditions estimated.

2. Experiment

2.1. Experimental materials and reagents
Polyethylene glycol (PEG2000-10000), potassium dichromate, Tianjin Da Mao Chemical Reagent Factory; 30% hydrogen peroxide, Guangzhou Chemical Reagent Factory; ferrous sulfate, ammonium ferrous sulfate, Fu-chen chemical reagent plant in Tianjin city; sulphuric acid, and Guangzhou chemical reagent two plant; all the drugs are analytically pure. Deionized water is made by the laboratory of environmental science and engineering, Qi Lu University of Technology.

2.2. Experimental Instruments
MY3000-6M six joint mixer, Gang Jiang Mei Yu Instrument Co., Ltd.; pH acidity meter, Qingdao Ren He Xing Experimental Technology Co., Ltd.; electronic balance, Shanghai Precision Scientific Instruments Co., Ltd.; COD thermostat heater, Qingdao De Jia Li Technology Co.

2.3. Experimental Method
By using synthetic polyethylene glycol wastewater, the 500 mL polyethylene glycol simulated wastewater with a mass concentration of 10 g/L was prepared in the 1000 mL beaker. The pH value was adjusted with 1 mol/L H_2SO_4, and a certain amount of $FeSO_4.2H_2O$ and 30% H_2O_2 were added to the oxidation experiment. The pH of waste water was determined by acidity instrument of Qingdao Ren-He Instrument Co. Ltd. and COD was determined by potassium dichromate method was determined [16].

3. Results and Analysis

3.1. Determination of the reaction time of Fenton oxidation
As can be seen from Fig. 1 the COD removal rate increases with the increase of oxidation time at the pH is 3, when the value of hydrogen peroxide and ferrous sulfate is calculated. In the 90 minutes period of the reaction, the COD removal rate of the model water increases rapidly at the reaction time. The reaction is basically linear relation, and it is going up, but the COD removal rate of water sample decreases from 90 minutes to 120 minutes. The COD removal rate is reduced, which can be attributed to the decrease of COD removal rate due to the reduction of the reaction rate or the production of some intermediate [12], which is difficult to be oxidized by .OH during the reaction. When the time reached 90 minutes, the degradation rate of COD was the best, but when the reaction time increased to

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120 minutes, the removal rate of COD decreased, thus the optimum time for Fenton oxidation was 90 minutes.

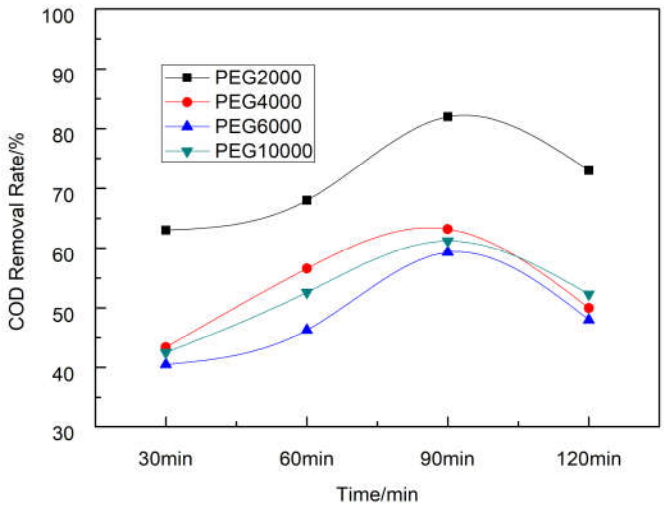

Fig. 1 COD removal rate of PEG with different molecular weights

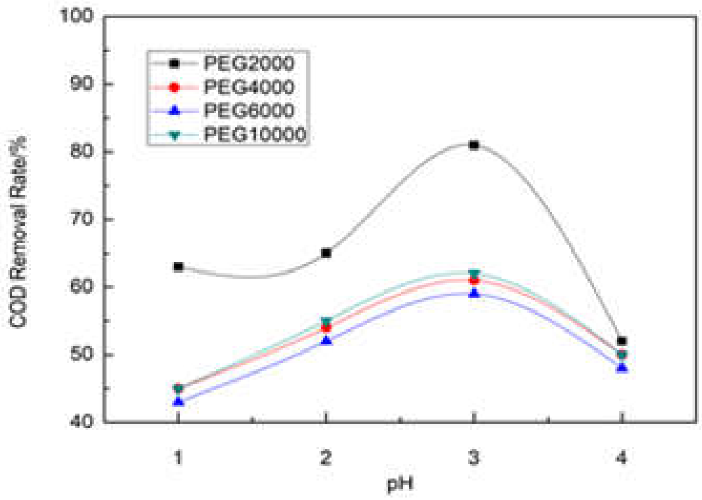

Fig. 2 COD removal efficiency of the different MW PEGs with pH curve

3.2. Effect of pH value on degradation of Polyethylene Glycol Simulated Wastewater with different molecular weights

When the time of oxidation reaction is 90 minutes, the COD removal rate of polyethylene glycol waste water with different molecular weight at different pH conditions is shown from Fig. 2. The removal efficiency of COD is best at pH=3 and the removal rates of COD are 81%, 62%, 61% and 59% respectively. When the pH value rises to 4, the value of COD removal rate decreases rapidly. The degradation rate of COD decreases to 50% at pH=4. In the Fenton oxidation system, the pH value is the best in 2-3. When the pH value is greater than 3.5, the Fe^{2+} will be oxidized to Fe^{3+}, and the iron hydroxide precipitate is formed in the solution, which increases the amount of ferrous sulfate and reduces the treatment effect of the wastewater. Therefore, in the process of treatment, when the pH is generally 3, the best removal effect can be achieved. The Fenton method only works well under acidic conditions. When pH is greater than 4, Fe^{2+} can't catalyze H_2O_2 and production .OH. In this experiment, the COD removal rate reaches the best effect. When pH is equal to 3, and the change is more obvious than 3. So the best pH value of this experiment is 3. The result of this experiment is consistent with the previous results.

3.3. Effect of H_2O_2 on degradation of Polyethylene Glycol Simulated Wastewater with different molecular weights

As shown in Fig. 3 when the optimum pH is 3 and the optimum oxidation time is 90min, the removal rate COD is increased with the increase of H_2O_2 dosage, and the removal rate is best when the dosage is 1.5 mL/L, and the COD removal rate begins to decrease when the dosage continues to increase. Thus, the optimum dosage of the 1.5 mL/LH_2O_2 can be determined. With the increase of H_2O_2 dosage, the COD removal rate of wastewater increased first and then decreased. It can be seen that the amount of H_2O_2 has a very important effect on the removal rate of COD: when the amount of H_2O_2 is low, it produces less OH. As the amount of H_2O_2 increases, the production of the. OH is also increased, as the produced. OH can oxidize organic matter, so the removal rate of COD is higher. However, when the amount of H_2O_2 is too large, some H_2O_2 can't be decomposed effectively, which leads to the reduction of the treatment effect. At the same time, excessive H_2O_2 in the solution will be oxidized to false COD in the determination of COD, resulting in the decrease of the COD removal rate.

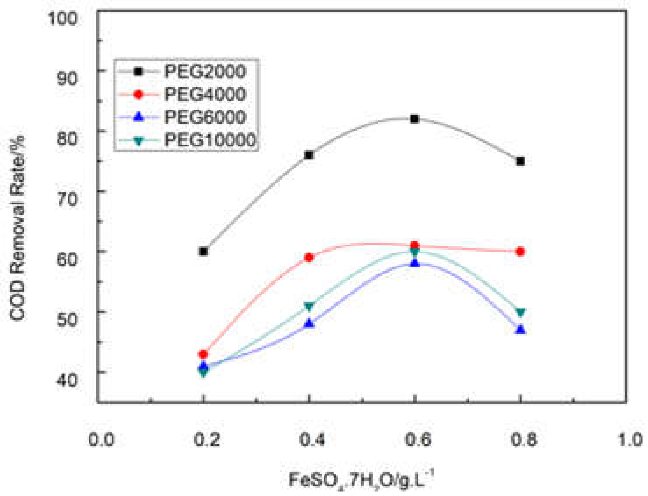

Fig. 3 COD removal efficiency of the different MW PEGs with dosage of the H_2O_2

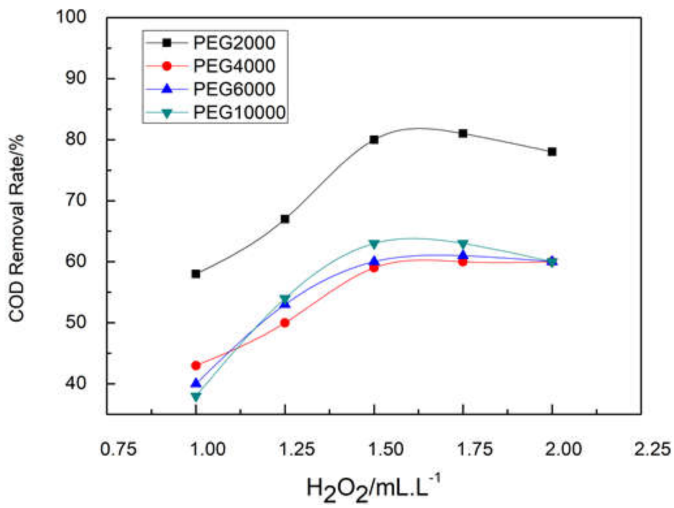

Fig. 4 COD removal efficiency of the different MW PEGs with dosage of the $FeSO_4.7H_2O$

3.4. Effect of $FeSO_4$ on degradation of Polyethylene Glycol Simulated Wastewater with different molecular weights

According to previous studies, it is determined that when the dosage of pH 3 and 30% hydrogen peroxide is 1.5ml, and the dosage of ferrous sulfate is 0.1 g, 0.2 g, 0.3 g and 0.4 g, the degradation results of Polyethylene Glycol Simulated Wastewater with different molecular weights are shown in Fig.4., after the optimum pH is 3 and the optimum oxygenation time is 90 min, with ferrous sulfate cast In addition, the removal rate of COD also increased. When the dosage reached 0.6 g/L, the COD removal rate of the polyethylene glycol with different molecular weight reached the maximum, while the COD removal rate decreased when the dosage was added, and the Fenton reaction mechanism [13] showed that when the Fe^{2+} dosage was too small, the reaction was not conducive to the production of initial OH; But when the amount of Fe^{2+} is too high, it will appear in the initial reaction, and H_2O_2 produces a large amount of OH, while some of the OH has not been able to react with the organic matter in the wastewater, which leads to the decrease of the utilization of H_2O_2. In addition, the reaction of Fe^{2+} and ·OH will decrease and the concentration of OH will be reduced. Considering the actual operation cost and processing effect, the best dosage of 0.6 g/L for $FeSO_4$ can be determined.

4. Results and discussion

The Fenton oxidation method was used to treat polyethylene glycol with different molecular weights. The results showed that the best treatment effect and cost were achieved when the initial pH value was 3, the dosage of ferrous sulfate and hydrogen peroxide was 0.6 g/L and 1.5 mL/L respectively.

The degradation of PEG solutions with different molecular weights at the same concentration shows that polyethylene glycol solutions with molecular weights of 2000 and 10000 in PEG solutions with molecular weights of 2000, 4000, 6000 and 10000 are easier to degrade, and the highest COD removal rate is different under the different reaction conditions, while the molecular weight is 6000 and 4000. Polyethylene glycol solution is relatively difficult to be degraded. The oxidation degradation and degradation effect of Fenton oxidation method for polyethylene glycol with different molecular weight are compared for the first time. It has a good application and research significance for improving the biodegradability of high molecular weight.

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