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Study on pretreatment of regeneration papermaking wastewater by intensified micro-electrolysis

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ABSTRACT

In this paper, using the method of H_2O_2 – micro-electrolysis / MnO_2 to treat the papermaking waste water, the effect of initial pH of raw water, total iron and carbon, proportion of iron and carbon, hydraulic retention time, the amount of MnO_2 as well as H_2O_2 dosing quantity in micro—electrolysis unit were investigated. The results show that the initial pH was 3.0, the dosage of iron and carbon was 20 g/L, the MnO_2 dosage was 2.5 g/L, H_2O_2 dosing quantity is 0.55 g/L, the proportion of iron and carbon was 1:1 and the reaction time was 50 min, under these conditions, the removal rates of COD、SS、ammonia nitrogen, total phosphorus and BOD_5 were reached to 88%, 98.4%, 85%, 98% and 52% . At the same time, biodegradability increased from 0.32 to 0.81, the pollution load of subsequent biochemical treatment process was reduced.

Key words: Regenerated papermaking wastewater; Micro- electrolysis; MnO_2; H_2O_2

INTRODUCTION

Waste paper pulp papermaking wastewater contains a large number of small fibers, resins, dyes, chemical and mechanical impurities, the pollution load of COD、BOD_5 and chromaticity of wastewater is big, and difficult to directly biodegradation. Existing treatment technologies mainly include physical and chemical method, oxidation method and biochemical method and combination technology processing method [1-3]. In this paper, H_2O_2-Micro-electrolysis/MnO_2 combined process regenerated wastewater, micro-electrolysis method has the following characteristics: low operating cost, good treatment effect and the advantages of "using waste treat waste [4-13], macromolecular organic matter can be broken down into easy degradation of small molecules, in order to improve the wastewater biological sex. Plus manganese dioxide catalyst can reduce activation energy reaction, provide reaction place, and strengthen the result of micro- electrolysis treatment. Adding H_2O_2 Of micro-electrolysis reaction is equivalent to wastewater treatment provides a micro electrolysis - Fenton coupling technology, improve the effect of the degradation process. After the pretreatment process, wastewater meets the requirements of the subsequent biochemical process and creates the conditions for the utilization of papermaking wastewater.

For regenerated papermaking wastewater treatment object, this paper discusses the pH, the dosage of iron, carbon, iron carbon ratio, reaction time, the amount of MnO_2, H_2O_2 dosing quantity and other factors on the treatment effect, determine the appropriate reaction conditions, at present there is little to apply the technology in the study of regenerated papermaking wastewater treatment.

EXPERIMENTAL SECTION

1.1 Materials preparation

The experiment used reagents are analytically pure. For machining scrap iron scrap , with the mass fraction of 10%

sodium hydroxide solution before use soak 20min, to remove the iron surface oil, and then the mass fraction of 5% hydrochloric acid solution soak 10min, remove the iron oxide surface , conduct activation treatment , and finally rinse clean with tap water [8]. Activated carbon (Shanghai National Medicine Group), Wastewater fully soaked before using activated carbon to eliminate interference generated by its adsorption.

The experiment water regenerated papermaking wastewater from Shandong Paper Co. renewable papermaking wastewater. The quality of wastewater after treated by the grille, regulation pool and primary sedimentation tank treatment as follow: the COD, SS, ammonia nitrogen and total phosphorus were 5865 mg/L, 1259 mg/L. 30.36 mg/L, 9.23 mg/L, and the initial pH was 7.0, BOD_5 is 1841mg/L, B/C is 0.32.

1.2 Experimental device and method

This pretreatment reaction device adopts the 90 mm diameter, organic glass column height of 450 mm, lower part uses the air pump aeration. The whole reaction process temperature is controlled by the constant temperature water tank.

According to certain proportion mixing activated carbon and pretreated iron filings in the organic glass column, join the wastewater to be treated, under the condition of air 150 l/h, changes in reaction time, pH, Changes in reaction time, pH, the amount of iron and carbon, iron-carbon ratio, MnO_2 amount, H_2O_2 dosage and other reaction, Still some time, sampled for COD and other pollutants after the reaction.

1.3 Analysis

COD: Potassium dichromate method (GB/T11914-1989); BOD_5: Dilution and seeding method (HJ505-2009); Ammonia nitrogen: Nessler's reagent spectrophotometry ((HJ535-2009)); Total phosphorus: Anti-Mo-Sb spectrophotometry method (GB/T11893-1989); SS: Weight method (GB/T11901-1989).

RESULTS AND DISCUSSION

2.1 Effect of MnO_2

When pH was 3.0, the dosage of iron and carbon was 20 g/L, the proportion of iron and carbon was 3:1, the reaction time was 40 min , MnO_2 was respectively added 0 g/L, 1 g/L, 1.25 g/L, 1.5 g/L, 2 g/L, 2.5 g/L, 3 g/L, 3.5 g/L, 4 g/L, 4.5 g/L, 5 g/L , /L, 0.75 g/L, a research on the manganese catalysis of MnO_2 on micro-electrolysis catalysis of wastewater treatment system, The results of is shown in Fig.1.

It can be observed from Fig. 1 that with the increase of the amount of MnO_2, micro electrolysis wastewater COD removal rate increases, when the amount of MnO_2 is 2.5 g/L, the COD removal rate reached 77%, compared with the separate system of micro electrolysis treatment increased by 14.5%, the main reason is to reduce the join of MnO_2 reaction activation energy, improve the ability of wastewater oxidation reduction, and MnO_2 itself have adsorption ability, can remove contaminants in wastewater, for micro electrolysis reaction carrier [14, 15]. Continue to increase, for the amount of MnO_2 wastewater COD removal rate began to reduce, and reduce the speed faster, its main reason is that when the amount of MnO_2 is large, the presence of manganese dioxide hindered the effective contact of iron and carbon, micro electrolysis reaction is reduced, wastewater treatment effect.

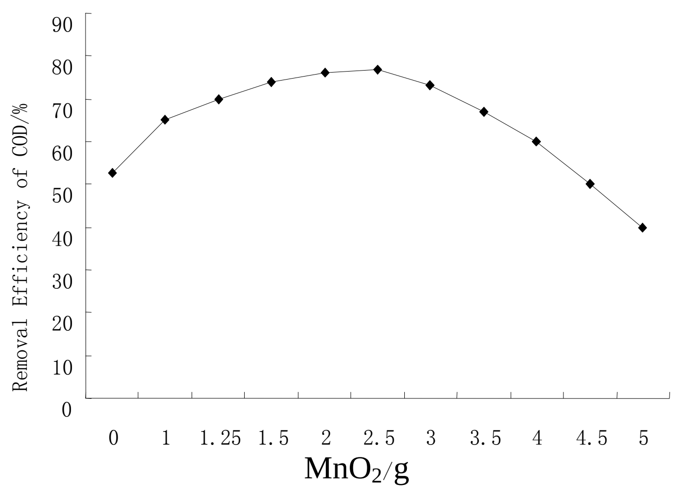

Fig.1 Effect of MnO2dosage on COD removal of wastewater

2.2 effect of H_2O_2 treatment micro-electrolytic MnO_2 / waste water treatment system

2.2.1 Effect of H_2O_2 dosing quantity

When pH was 3.0, the dosage of iron and carbon was 20 g/L, the reaction time was 40 min ,the MnO_2 dosage was 2.5 g/L, the proportion of iron and carbon was 3:1, H_2O_2 dosing quantity were 0.25 g/L, 0.35 g/L, 0.45 g/L, 0. 55 g/L, 0.65 g/L, 0.75 g/L. The results of is shown in Fig.2.

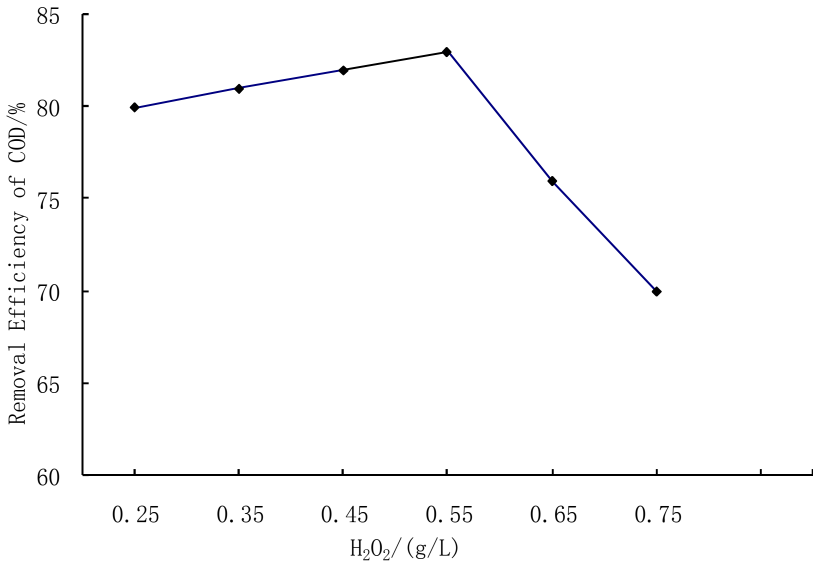

Fig.2 Effect of H_2O_2 dosage on COD removal of wastewater

The figure 2 shows that with the increase of H_2O_2 dosing quantity, the removal rate of COD of wastewater increases, When H_2O_2 dosing quantity is 0.55 g/L, the maximum removal rate reached 83%. Then continue to increase, the removal rate of COD began to decline, the reason is that H_2O_2 dosing excessive, excessive H_2O_2 directly make Fe^{2+} oxidized to Fe^{3+}, consumes of the H_2O_2 and inhibits the generation of · OH, at the same time, reduce pollutants degradation rate. In addition, the residual H_2O_2 also interferes with the determination of COD of the water. Experiment select H_2O_2 appropriate dosing quantity is 0.55 g/L.

2.2.2 Effect of iron carbon ratio

When pH was 3.0, the dosage of iron and carbon was 20 g/L, the reaction time was 40 min ,the MnO_2 dosage was 2.5 g/L, H_2O_2 dosing quantity is 0.55 g/L, the proportion of iron and carbon was 4:1、3:1、2:1、1:1、1:2、1:3、1:4, the influence is shown in Fig.3.

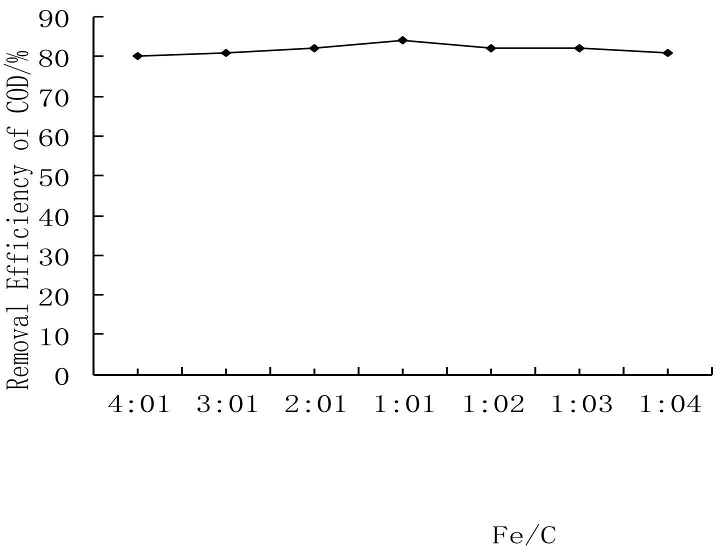

Fig. 3 Effect of Fe/C ratio on COD removal of wastewater

The Fig. 3 shows that the ratio of Fe/C on COD removal rate is not big, when Fe/C ratio 1:1, produce the largest number of battery, the best effect, the removal rate of COD reached a peak of 84%. Fe/C than the big surplus will cause iron filings, the rest of the iron filings participate in the displacement reaction of H^+, increase the invalid iron dissolution, and activated carbon is too little, iron carbon bed support and porosity were lower, easy to jam and harden, unfavorable to the operation of the reactor; Fe/C than hours, due to the decreases of scrap iron to make a substantial reduction in the number of scrap iron internal battery, was also make full use of and activated carbon formation on the surface of iron filings micro battery, system internal micro battery quantity limits, so increasing the amount of active carbon, treatment effect will decline. Therefore, the appropriate experiment of Fe/C ratio is 1:1.

2.2.3. Effect of pH

When the dosage of iron and carbon was 20 g/L, the reaction time was 40 min, the MnO_2 dosage was 2.5 g/L, H_2O_2 dosing quantity is 0.55 g/L, the proportion of iron and carbon was 1:1, and the influence of different initial pH of the treatment effect is shown in Fig.4.

The Fig.4 shows that under the condition of acid, with the increase of pH, the removal rate of COD increases, when pH was 3.0, the treatment has the best effect. When the pH is less than 3, iron reacts with acid to form hydrogen large cover on the surface of iron filings, reduced the effective surface area of iron filings, reduces the galvanic effect, so that the treatment effect decline. And the pH of solution is too low, can destroy flocculation body, make the chromaticity of solution increase with the elevating of Fe^{2+} and Fe^{3+}. When pH greater than 3, concentration of H^+ decreases gradually, and the effect of cathode reaction also fall. So the suitable pH is 3.

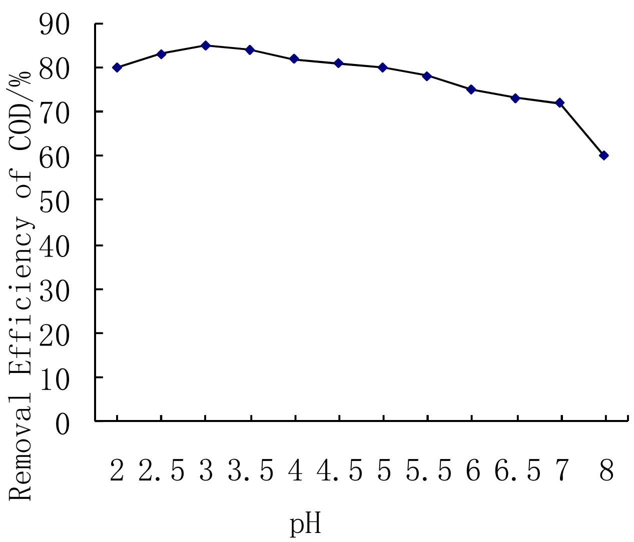

Fig.4 Effect of pH on COD removal of wastewater

2.2.4. The effect of reaction time

When the initial pH was 3.0, the dosage of iron and carbon was 20 g/L, the MnO_2 dosage was 2.5 g/L, H_2O_2 dosing quantity is 0.55 g/L, the proportion of iron and carbon was 1:1, the influence of reaction time on the micro electrolysis reaction as shown in Fig.5.

It can be seen that with the increase of reaction time, the removal rate of COD and the chromaticity is increasing. When the reaction time up to 50 min, the removal rate of COD reached 88%. More than 50 min, the removal rate of COD and chromaticity no longer change even lower. The reason is that longer reaction time can make fully the products of electrode reaction and pollutants in the wastewater for electrochemical, adsorption and flocculation. But too long reaction time is will make more Fe^{2+} oxidized to Fe^{3+}, increase the chromaticity, reaction time is too long can lead to the sediment deposition in the waste water in the gap between packing and covering on the surface of iron and carbon, hindered the contact and inhibit reaction. And the extension of reaction time, will increase the volume of the reactor, the building area, construction costs and equipment investment cost. Thus the best reaction time is 50 min.

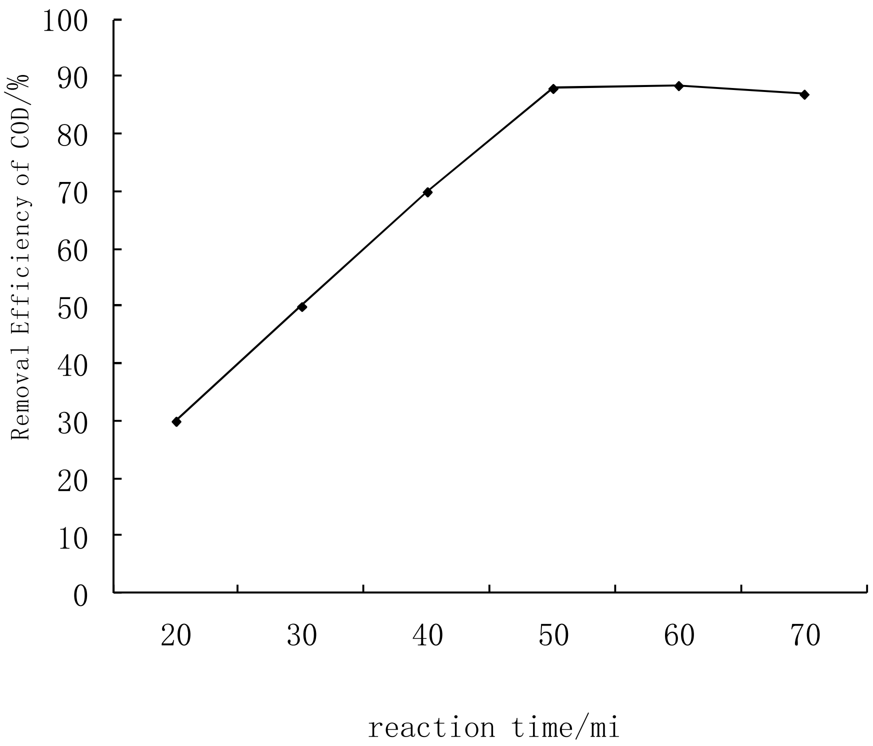

Fig.5 Effect of reaction time on COD removal of wastewater

2.3 Analysis of water quality treated by H_2O_2 - micro electrolysis/MnO_2

2.3.1 Ultraviolet spectrum analysis

Ultraviolet spectrum analysis wastewater treated by H_2O_2- micro electrolysis/MnO_2. The results show that before the wastewater treatment absorption peaks have many and large range .the 190-210 nm of peak band has a strong absorption. After wastewater treatment, the 200-230 nm absorption peak obvious disappear, 230-270 nm absorption peak increases, it illustrates that the reaction has made some pollutants into easily degradable material.

2.3.2 Water quality after treatment by H_2O_2 - micro electrolytic/ MnO_2

Analysis quality of water treated by H_2O_2 - micro electrolysis/MnO_2 under the appropriate conditions, After the reaction, the COD, SS, ammonia nitrogen and total phosphorus were 704mg/L, 20 mg/L. 4.55mg/L, 0.21mg/L, and the initial pH was 8.0, BOD_5 is 870 mg/L, BOD_5/COD is 0.81. The removal rates of COD, SS, ammonia nitrogen, total phosphorus, and BOD_5 were reached to 88%, 98.4%, 85%, 98% and 52%. Biodegradability increased from 0.32 to 0.8. At the same time, the pollution load of subsequent biochemical treatment process was reduced and conducive to further biochemical degradation reaction.

CONCLUSION

H_2O_2-micro-electrolysis/MnO_2 process was used to pretreat wastewater of regenerate paper. The optimal condition of the process was determined. The results show that the pH is 3.0, the dosage of iron and carbon was 20 g/L, the MnO_2 dosage was 2.5 g/L, H_2O_2 dosing quantity is 0.55 g/L, the proportion of iron and carbon was 1:1 and the reaction time was 50 min. After the reaction, the COD、 SS、 ammonia nitrogen and total phosphorus were 704mg/L, 20 mg/L. 4.55mg/L, 0.21mg/L, and the initial pH was 8.0, BOD_5 is 870 mg/L, BOD_5/COD is 0.81. This process creates the conditions for the subsequent biochemical treatment.

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