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Treatment of Dye Wastewater by Flocculation and Sedimentation-Micro-electrolysis-Fenton Oxidation Process

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This paper adopts the flocculation and sedimentation-micro-electrolysis-Fenton oxidation process to treat dye wastewater. The optimized treatment conditions are as follows: in the flocculation and sedimentation stage, the PAC and PAM dosages should both be 1ml/L, in the micro-electrolysis stage, the influent should be of pH3.5, and the hydraulic retention time should be 6h, and in the Fenton reaction, the dosage of H_2O_2 should be 0.6ml/L. The results of operation for 15 consecutive days under the optimal conditions show that the combined process can reduce the COD in the raw water from over 1500mg/L to below 1000mg/L, and that the system can obviously increase the biodegradability (BOD_5/COD) of the raw water.

1. Introduction

Due to complex composition, high chroma, high COD, and poor biodegradability, dye wastewater is a type of industrial wastewater that is currently difficult to treat (Ou et al., 2015). This wastewater poses great threats to major water bodies and human health (Papić et al., 2004; Jung et al., 2015). In recent years, the iron-carbon micro-electrolysis technology has been widely applied in the treatment of dye wastewater because it has integrated redox, coagulation, adsorption, co-precipitation, and micro-electric field concentration effects (Ju et al., 2011), and the equipment have simple structures, cover small areas and are easy to operate with low capital and operating costs and low energy consumption (Yang et al., 2009; Li et al., 2010), and in addition, the technology can greatly improve the biodegradability of wastewater (Zhao et al., 2010; Saidi et al., 2014).

Han et al., (2016) used the activated carbon mixed with iron scrap left in machining as the micro-electrolysis packing to treat dye wastewater, with the COD and chroma removal rates being up to 73% and 98.5%, respectively. After micro-electrolysis, the molecular structure of the azo dyes is damaged, so the biodegradability of wastewater is greatly improved. Fu et al., (2010) used zero-valent iron/activated carbon micro-electrolysis combined with microwave discharge electrodeless lamp/sodium hypochlorite to treat simulated azo dye wastewater containing Reactive Red 195 and found that the azo bond of the dye is interrupted by the micro-electrolysis process. This combined process reached a chroma removal rate of up to 100% and a COD removal rate of 82%. Among the operating conditions, the initial reaction pH value, iron-carbon ratio and particle size of iron scrap have great impacts on the treatment result. Yang et al., (2014) used iron-carbon micro-electrolysis to treat wastewater containing amino silicone polymers. Amino silicone emulsions are often used in fabric softening and printing. They found that low initial pH and iron-carbon ratio can enhance the removal of COD in the amino silicone emulsion wastewater by micro-electrolysis. With the increase of the treatment time, the surfaces of iron scrap and activated carbon are covered by the amino silicone polymer, leading to the decrease of the treatment efficiency. Zhang et al., (2014) used an ozone aerated iron-carbon micro-electrolysis filter to treat the azo dye RR2 wastewater and found that the chroma of wastewater could be completely removed, and that the TOC removal rate could be up to 82%. When this process is used to treat wastewater within a large pH range, the removal effects are not much different. The optimal treatment pH is 9. The oxidation of ozone, the catalytic oxidation of Fe^{2+}/Fe^{3+} and the redox actions of electro-reduction and electro-oxidation play the main roles in this process. The catalytic action of Fe^{2+}/Fe^{3+} can induce the transformation of Fe^{2+} and Fe^{3+}, and can also reduce the dissolution rate of zero valent iron.

The micro-electrolysis reactions can be represented as follows (Fan et al., 2009):

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Anode (oxidation): $2Fe-4e^{-} \rightarrow 2Fe^{2+}$, E^{0} $(Fe^{2+}/Fe) = -0.44$ V (1)

Cathode (reduction): $2H^{+} + 2e^{-} \rightarrow 2[H] \rightarrow H_2$, E^{0} $(H^{+}/H_2) = 0$ V (Acidic) (2)

$O_2 + 4H^{+} + 4e^{-} \rightarrow 2H_2O$, E^{0} $(O_2/H_2O) = +1.23$ V (Acidic) (3)

$O_2 + 2H_2O + 4e^{-} \rightarrow 4OH^{-}$, E^{0} $(O_2/OH^{-}) = +0.40$ V (Neutral to alkaline) (4)

From the above experimental results, it can be seen that the micro-electrolysis process has high treatment efficiency, but in actual application, the efficiency is often not as good as expected. Therefore, it remains to be further studied as how to effectively combine micro-electrolysis with other processes to make this technology fully exert its effects. This paper studies the effects of the flocculation and sedimentation-micro-electrolysis-Fenton oxidation process on treatment of dye wastewater, hoping to provide some technical guidance for the efficient treatment of such wastewater.

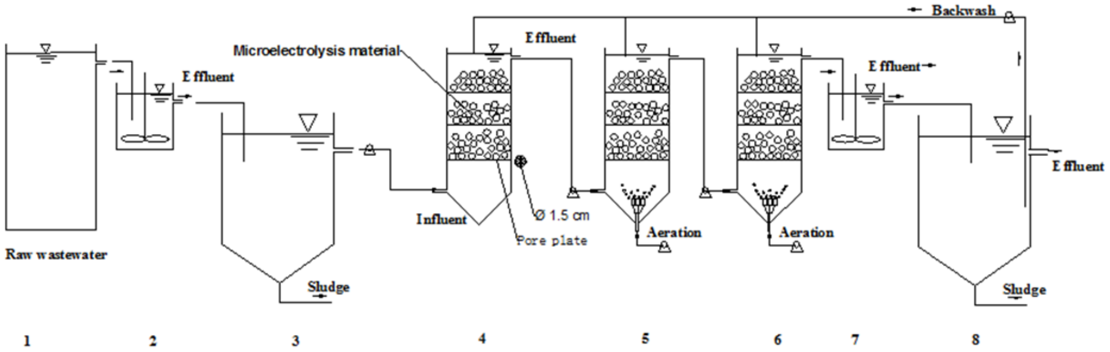
2. Materials and methods

2.1 Materials

The dye wastewater has a COD of 1000-4000mg/L, a BOD of 100-800mg/L and a chromaticity 200-300 times. Porous material sintered at high temperature is used for the iron-carbon micro-electrolysis. This material contains a large amount of fine pores, allowing gas and liquid to circulate through the small channels in the material. The specific surface area is $38.27m^2/g$, the porosity 65% and the density 1300 kg/m^3 (Wang et al., 2016). The ration of 1:1 of Fe:C (mass ratio) was selected in our paper. The less C cathode could not exert the best micro-electrolysis efficiency while the more C cathode might inhabit much more space and cumbered the reaction.

2.2 Test equipment and methods

As show in Figure 1, after the pH adjustment in the header tank, the raw water is gravity-fed into 1# coagulating basin, where polyaluminum chloride solution (10% PAC solution) and polyacrylamide solution (1‰ PAM solution) are added. The water in 1# coagulating basin flow by gravity into the primary settling tank, where it precipitates. The supernatant flows out from the upper part of the tank, and the sludge flows out from the bottom.



(1) pH header tank, (2) 1# coagulating basin, (3) primary settling tank, (4) 1# micro-electrolysis column(5.6 L), (5) 2# micro-electrolysis column(5.6 L), (6) 3# micro-electrolysis column(5.6 L), (7) 2# coagulating basin, (8) secondary settling tank ; In 1# and 2# coagulating basins, there are automatic dosing system. PAC and PAM are added into 1# coagulating basin and hydrogen peroxide and soda lime are added into 2# coagulating basin.

Figure 1: Flocculation and sedimentation-micro-electrolysis-Fenton oxidation process

The supernatant in the primary settling tank is sent into 1# micro-electrolysis column from its bottom by a peristaltic pump and flows out from the top. The upper part of the micro-electrolysis column is provided with a backwash water distributor. Inside the micro-electrolysis column, there are three support plates, each of which is an orifice plate, with a pore diameter of 1.5cm. Each support plate is covered with the normalized iron-carbon micro-electrolysis material, with the elliptical diameters being 3-5 cm. The dosage of the micro-electrolysis material is $250kg/m^3$. The hydraulic retention time of the wastewater in 1# micro-electrolysis column is controlled at around 6 hours. Anoxic micro-electrolysis reduction reaction can effectively reduce the pollutants. The effluent from 1# micro-electrolysis column is sent to 2# micro-electrolysis column from the bottom by a peristaltic pump and flows out from the top. 2# micro-electrolysis column is equipped with an aeration device at the bottom for aerated micro-electrolysis, which is different from 1# micro-electrolysis column, where no aeration device is provided. 1# micro-electrolysis column is mainly used for reduction in micro-electrolysis, and 2# and 3# micro-electrolysis columns are used for oxidation in micro-electrolysis. The final effluent of micro-electrolysis flows by gravity into 2# coagulating basin, where 30% H_2O_2 is first added, and after a certain reaction time, soda lime is added to adjust the pH to about 8. At this point, the Fenton reaction can be terminated and efficiently flocculate with the newly formed Fe^{3+}. The water in 2# coagulating basin flows by gravity into the secondary settling tank and settles there. The supernatant flows out from the upper part of the tank and the sludge flows out from the bottom. Part of the supernatant from the secondary settling tank is sent by a peristaltic pump into the upper part of the micro-electrolysis column as backwash water.

2.3 Analysis methods

COD is determined by the 5B-3C rapid tester; the pH value is determined by the PHS-3C acidimeter and BOD_5 is determined by the dilution inoculation method (GB/T7488-1987) (State Environmental Protection Administration of China, 2002).

3. Results and discussion

3.1 Determination of PAC and PAM dosages

The author added 500mL of dye wastewater sample into a 500mL beaker, placed it on a six-joint mixer, and added PAC into it during stirring, with a rotating speed of 100r/min. After coagulation for 10min, the author quickly continued to quickly stir it for 1min, and then slowly stir it 10 min. After 20min of standing, the author took the supernatant and determined COD, as shown in Figure.2.

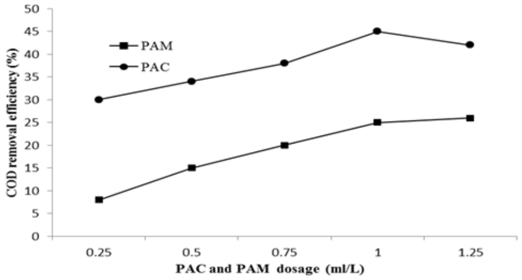


Figure 2: Impact of PAM dosage on the wastewater treatment result

It can be seen from Figure 2 that when the PAC dosage was 1ml/L, the treatment result was the best. Based on the 1ml/L PAC dosage, the PAC dosage was optimized. The COD removal rate first decreased and then increased with the increase in PAM dosage. When the PAM dosage was 1.0ml, the COD removal rate could be up to 45%. Therefore, in the flocculation and sedimentation stage, the process is to first add 1ml/L of the coagulant - PAC solution first, and then add 1ml/L of PAM solution. After this process, the SS in the wastewater was drastically reduced, mitigating the blockage of the pores in the micro-electrolysis material, prolonging the backwash time of the micro-electrolysis section, and saving part of the operating costs.

3.2 Effects of influent pH in micro-electrolysis

The test results are shown in Figure 3.

The hydraulic retention time was controlled to 6 h to observe the effects of the influent pH on the wastewater treatment result by the iron-carbon micro-electrolysis pretreatment system. As can be seen from Figure.3, the COD removal rate increased as the influent pH decreased. When the pH was 2.5, the removal rate of COD was about 75%, and when the pH was 3.5, the COD removal rate was about 65%. The lower the pH value is, the faster the electrode reaction will proceed, and the more conducive it will be to the realization of various micro-electrolysis effects. However, if the pH value is too low, the scrap iron consumption will increase, so the iron content in water will increase and the effluent chroma will be high, and what is more, the low pH value will change the form of the product, destroying the flocs generated after the reaction. Therefore, the initial pH value is usually controlled at the slightly low level. Considering the large consumption of iron in the low-pH condition, which would lead to high operating costs, it was determined that the pH value of the wastewater be set at 3.5.

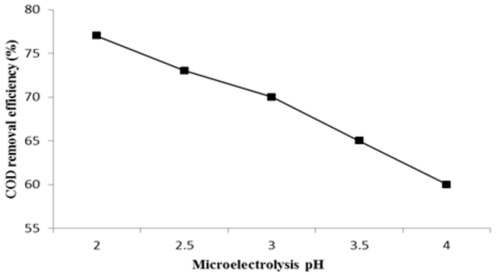


Figure 3: Effects of pH in micro-electrolysis on the wastewater treatment result

3.3 Determination of the hydraulic retention time

The author controlled the retention time of wastewater in the reactor at 2, 4, 6, 8 and 10h, and measured its COD and pH value after the effluent became stable. The test results are shown in Figure 4. The COD in the raw water was 541.9mg/L (the same below).

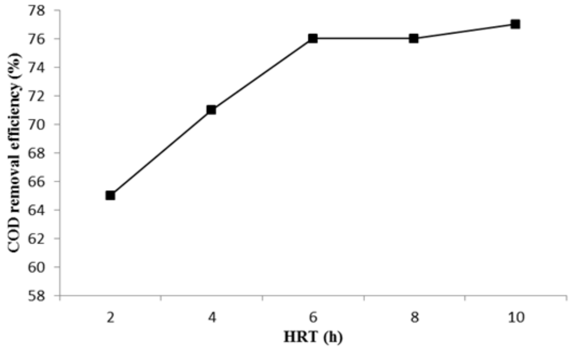


Figure 4: Effects of retention time on the wastewater treatment result

As shown in Figure 4, when the hydraulic retention time was less than 6h, the COD removal rate increased linearly with time, and after 6h, it did not increase significantly. Therefore, the retention time was set at 6h.

3.4 Determination of the H_2O_2 dosage

In micro-electrolysis, under acidic conditions, a lot of Fe^{2+} can be generated at the anode, which can react with H_2O_2 to form the Fenton reagent and further generate hydroxyl radicals (OH·). OH· is a strong oxidant, which can effectively remove the organic matters in dyes and increase the biodegradability of the wastewater.

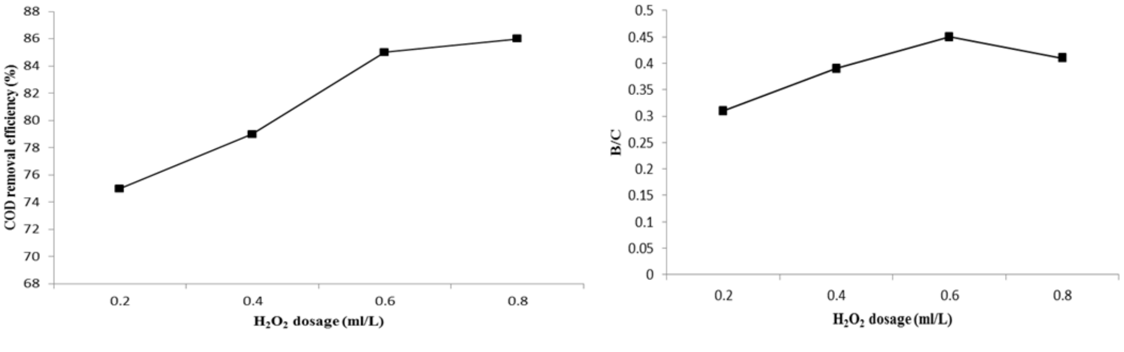


Figure 5: Effects of H_2O_2 dosage on wastewater treatment result

As can be seen from Figure 5, when the dosage of H_2O_2 was 0.6ml/L, the removal rate of COD was about 85%, and with the increase of H_2O_2, the COD removal rate did not increase obviously. Therefore, the dosage of H_2O_2 was set at 0.6ml/L, and under this dosage, BOD_5/COD also reached the maximum – increasing from 0.20 in the raw water to 0.45.

The results show that the optimal treatment conditions are as follows: in the flocculation and sedimentation stage, PAC and PAM dosages should both be 1ml/L, in micro-electrolysis, the influent pH should be 3.5, and the hydraulic retention time should be 6h. In Fenton reaction, the H_2O_2 dosage should be 0.6ml/L.

3.5 Removal of COD in dye wastewater by the continuous treatment system

The COD concentrations in all effluents are shown in Figure 6.

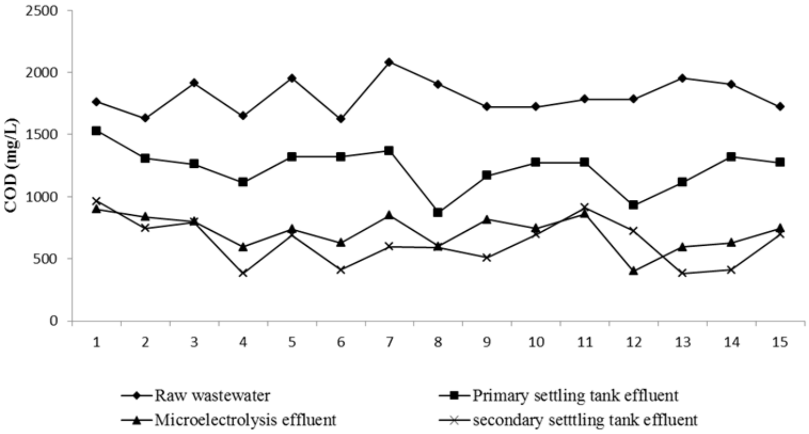


Figure 6: Overall process treatment results of COD in the wastewater

Figure 6 shows the changes in the COD removal rate over the time during the 15 consecutive days of iron-carbon micro-electrolysis reaction. the effluent COD removal efficiency varies with operating time. The COD concentration of the micro-electrolysis effluent in the whole continuous system was lower than that after the coagulation and sedimentation. The latter remained basically at about 30% while after the iron-carbon micro-electrolysis treatment, the COD removal rate remained at about 60%. After micro-electrolysis, the coupled Fenton method had little effect on the removal of COD, probably because after the Fenton reaction, the refractory macromolecular organic compounds were degraded into low molecular ones. The original macromolecular organic compounds that are not easily oxidized were not detected while the low molecular ones could be oxidized during the COD testing and thus could be easily detected. So in terms of the contribution to the COD removal rate, micro-electrolysis in the combined process plays a leading role in wastewater treatment.

3.6 Improvements to the dye wastewater biodegradability by the continuous treatment system

Dye wastewater has poor biodegradability mainly due to the fact that the CODs in dye wastewater are mainly macromolecular organic compounds that cannot be metabolized and decomposed by microorganisms. At present, the usual practice is to degrade macromolecular organic compounds into low molecular ones through oxidation to enhance biodegradability. Table 1 shows how well the continuous treatment system of iron-carbon micro-electrolysis coupled with Fenton improved the biodegradability of wastewater.

Table 1: Improvements in the biodegradability of wastewater

Day(s) / Item	1	5	15
Influent B/C	0.15	0.2	0.18
Effluent B/C	0.35	0.40	0.32

It can be seen from Table 1 that BOD_5/COD in the system effluent was much better than that in the raw water, indicating that this is an ideal pretreatment process. The advanced Fenton oxidation process can form extremely oxidative OH·, which can degrade the vast majority of macromolecular organic compounds into low molecular ones. This shows that Fenton can effectively oxidize organic compounds, which further improves the biodegradability of wastewater.

4. Conclusion

After single-factor optimization, the optimized treatment conditions are summarized as follows: the PAC and PAM dosages should both be 1ml/L, in micro-electrolysis, the influent should be of pH3.5, and the hydraulic retention time should be 6h, and in the Fenton reaction, the dosage of H_2O_2 should be 0.6ml/L. After continuous operation for 15 days, the micro-electrolysis treatment system maintained a COD removal rate of over 60%. In the combined process, micro-electrolysis plays the dominant role in wastewater treatment. Flocculation and sedimentation is the secondary, and the Fenton oxidation is the worse but which further improves the biodegradability of wastewater.

Acknowledgments

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