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Study of Pretreatment of PVC Paste Resin Wastewater by Process Integration of Microeletrolysis-Fenton

YU-PING HU[1,2], SHUANG-FEI WANG[1,*], ZHUO-YUAN ZOU[2] and HUA YANG[2]

[1]Institute of Light Industry and Food Engineering of Guangxi University, Nanning, P.R. China
[2]Guangxi University for Nationalities, Key Laboratory of Chemical and Biological Transforming Process, University of Guangxi, Nanning, P.R. China

*Corresponding author: Fax: +86 0771 3264900; Tel: +86 0771 2173625; E-mail: wangshuangfei1963@hotmail.com

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In this paper, PVC paste resin (PPVC) wastewater is dealed with process integration of microeletrolysis-fenton. The influences of the pH, the Fe/C weight ratio, the residence time and the dosage of H_2O_2 on the COD reduction efficiency are considered. The optimal conditions of the treatment were determined as follows: pH = 3,HRT = 180 min, m_{Fe}:m_C = 3:1, V = 3.0 mL/L. Compared with the single micro-electrolysis, the combined process can improve the COD reduction rate of 34.57 %, reduce the amount of H_2O_2 and the cost of wastewater treatment.

Key Words: PPVC wastewater, Fe-C micro-electrolysis, Fenton oxidation, COD.

INTRODUCTION

An annual output of 140,000 tons of PVC is produced in a chemical plant in Nanning, Guangxi, China. According to raw materials and process analysis, in the PVC production process, the average water consumption is about 9.8 t/t PVC paste resin. PVC paste resin waste is a kind of industrial wastewater that is difficult to treat. It contains large amounts of refractory organic pollutants, low concentration of ammonia, high concentrations of organic matter, poor biodegradability and high salt content. Such wastewater is difficult to be controlled by biological methods. Currently, there is still no successful case in China[1]. In order to improve the biodegradability of wastewater, before the biological treatment, it must be pretreated by advanced oxidation methods that can transform the poor biochemical degradable organic matter into the more easily degradable organic matter[2].

Nowadays, chemical treatment methods known as advanced oxidation processes (AOPs) have been used for pollutant abatement due to the high oxidative power of the HO˙ radical[3-6],the main reactive species generated by such processes, but the high electrical energy demand or the consumption of chemical reagents are come on problems among all the advanced oxidation processes. So finding a new low-cost and efficient PPVC wastewater treatment methods is essential.

EXPERIMENTAL

Quality of wastewater: In this experiment, wastewater comes from a PVC paste resin workshop of Nanning Chemical Industry Co., Ltd. Wastewater emissions are about 3760 m^3/d. After sampling and monitoring,quality of wastewater is listed in Table-1.

TABLE-1
QUALITY OF PPVC WASTEWATER

CODCr (mg/L)	BOD5 (mg/L)	NH_3-N (mg/L)	Turbidity NTU	SS (mg/L)	p H	Temp. (ºC)
800-1200	80-120	7-16	60-100	80-160	6.5-8.5	65-70

It can be seen from Table-1, wastewater COD is high, ammonia is low, pH is alkaline, BOD/COD is in the range of 0.07-0.15, which means its biodegradability is poor.

Digester, micropore aerator, furnace, PHS-3C precision pH meter,UV751-GD UV-visible spectrophotometer, FA2004N electronic balance, U-3010 UV spectrophotometer, (Shanghai Precision and Scientific Instrument Co., Ltd.), 78HW-1-type temperature magnetic stirrer.

Iron particles (average particle size of 2-4 mm); carbon (average particle size of 2-3 mm); Hydrogen peroxide (technical grade, 27.5 %); 2 mol/LNaOH solution, $FeSO_4$ (AR), H_2SO_4(AR), HNO_3(AR), CaO(AR), NaOH(AR), $AgNO_3$(AR), $Na_2S_2O_3$(AR), starch indicator, *etc*. (AR)

Iron cleaning: To clean oil on the surface on iron, we use the mass fraction of 10 % sodium hydroxide solution to soak scrap metal scrap for 1 h scrap metal shavings soaked with hydrochloric acid solution for 10 min to remove surface rust on iron. Then we use flowing water to wash iron filings until the pH of the washed water is near neutral.

Carbon particles cleaning: We crush scrap graphite into particles whose size is 2-3 mm and clean ash with the flow of water until Washed water becomes clear.

PVC paste resin wastewater treatment: Take 250 mL of PVC paste resin wastewater, adjust the pH of the solution to a certain value with 10 % NaOH or 10 % H_2SO_4 and then add pretreated iron-carbon fillers to cause the reaction. After a period of reaction time, the solution needs to be stay still for 0.5 h to form the stable stratification.Take the supernatant and survey COD to determine the best pH value,the best HRT and the best iron-carbon ratio.Then add H_2O_2, observe the changes of COD reduction.

Detection method

COD monitoring: (GB 11914-89) Rapid digestion method; pH monitoring: Glass electrode method; COD reduction = (1-treated-water COD/Untreated wastewater COD) × 100 %.

RESULTS AND DISCUSSION

Influence of pH: Take seven wastewater samples, adjust the pH value of 1.0, 2.0, 3.0, 4.0, 5.0, 6.0, 7.0. m_{Fe}:m_C = 3:1, HRT = 180 min. Experimental results are shown in Fig. 1.

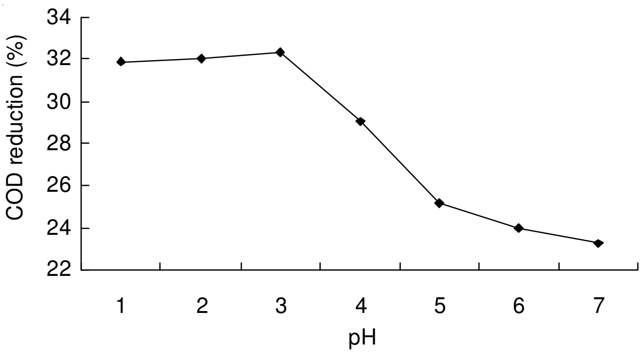

Fig. 1. Influence of pH on COD reduction

From the Fig. 1, we can see that with the increase of pH, COD reduction rate decreased. Reasons are the following: (1) When the pH value is low,the existence of a large number of H^+ makes the response quickly when leaving the line. Under acidic conditions, H^+ can get two electrons to become a new eco [H]. This new eco-[H] has a high chemical activity. It can change the structure and properties of many organic compounds of wastewater. (2) Low pH value will increase the potential difference between the original battery to promote the electrode reaction. Improve the COD reduction rate.

When the iron-carbon forms the original battery, acidic environment is favourable for electrolytic iron. However, if the pH is too low, it will not only accelerate the corrosion of iron, but also cause the waste because of the cost of a lot of acid. Furthermore, too low pH is not conducive to form the flocculation substance $Fe(OH)_3$. In summary, the best pH value is 3.

Influence of residence time: Residence time is an important factor that can affect the micro-electrolysis treatment. It directly related to the micro-electrolysis process. Take four wastewater samples under the conditions that pH = 3, m_{Fe}:m_C = 3:1. The reaction were carried out for 1, 2, 3, 4 and 5 h respectively. The COD reduction rate is shown in Fig. 2.

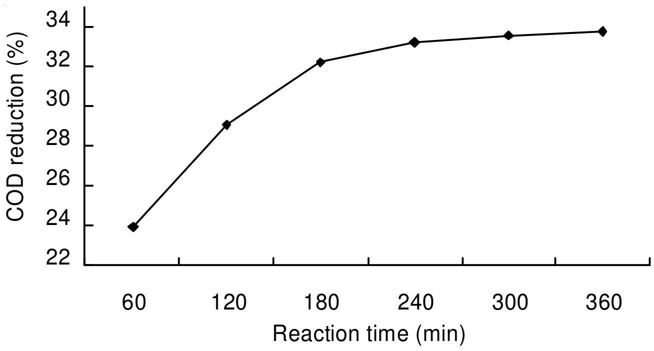

Fig. 2. Influence of reaction time on COD reduction

Fig. 2 showed that when the reaction time is less than 3 h, COD reduction rate increased rapidly with the increased reaction time. But when it reached to 3 h, COD reduction rate did not increase significantly. The reasons are: the longer time the iron contacts with wastewater, the reaction between them will be more adquate. However, if the residence time is too long, the output of wastewater will contain large amounts of iron and the sediments deposited on the iron surface will delay the ongoing process of micro-electrolysis. Therefore, in the latter process, with the time extended, the increase of COD reduction rate is not obvious. Thus, the best response time is 3 h.

Influence of iron-carbon ratio: Micro-electrolytic oxidation-reduction reaction occurs between the iron-carbon electrodes, therefore, the iron-carbon ratio has great influence on the COD reduction rate. Take four wastewater samples, under the conditions of pH = 3, HRT = 3 h and four fixed iron-carbon ratios 1:1, 2:1, 3:1 and 4:1, respectively. The results were shown in Fig. 3.

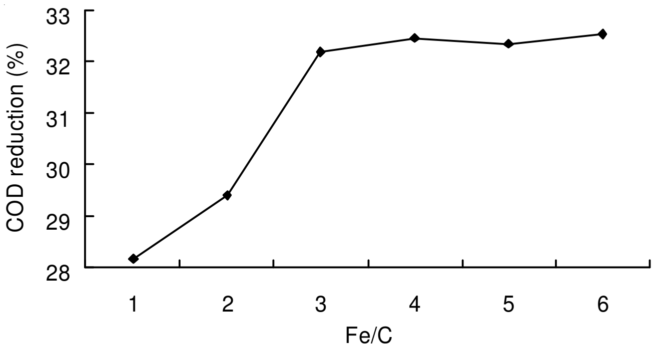

Fig. 3. Influence of Fe/C on COD reduction

Fig. 3 showed that the COD reduction rate increased with the increase in iron-carbon mass ratio. When the iron-carbon ratio is less than 3:1, COD reduction rate increased rapidly with the iron-carbon ratio increased. But when it reached to 3:1, the increase COD reduction rate slowed down. It is because the original micro-cell reaction will happen inside the iron impurities. When adding the activated carbon, the iron and activated carbon particles are supposed to form a galvanic cell, which will make the iron filings corrosion by both the original micro-cell and the galvanic cell. It will accelerate the electrode reaction and improve the processing efficiency. Reaction will speed up quickly with the increase in carbon content. The COD reduction rate gradually increased with the increased number of primary cells in the system. The number of the original battery will reached its limit when the activated carbon reaches a certain number, this time the COD reduction rate will remain basically unchanged. Thus, the best iron-carbon ratio is 3:1

Influence of H_2O_2: PVC paste resin wastewater COD = 978 mg/L. Take seven 1000 mL wastewater samples, under the conditions of pH = 3, HRT = 3 h and m_{Fe}: m_C = 3:1, add 0 mL, 1 mL, 2 mL, 3 mL, 4 mL, 5 mL, 6 mL H_2O_2 solution (c = 27.5 %) in the samples, respectively, calculate the COD reduction efficiency. The results are shown in Fig. 4.

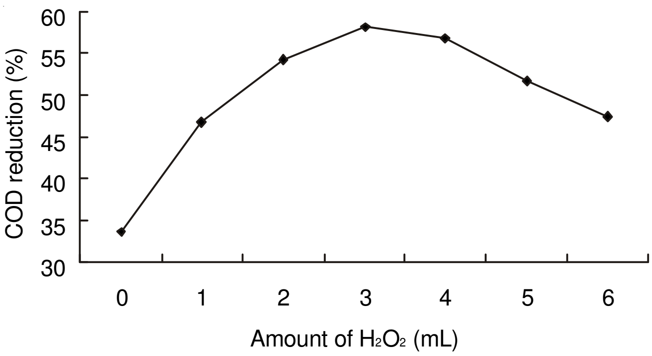

Fig. 4. Influence of amoun of H_2O_2 on COD reduction

It can be seen from the Fig. 4 that the COD reduction rate of PVC paste resin wastewater was 23.53 % with the simple micro-electrolysis method. However, after adding H_2O_2, the removal efficiency is significantly improved. The reason may be that in the micro-electrolysis process, large amounts of Fe^{2+} can be produced and Fenton reaction will occur between Fe^{2+} and H_2O_2 after adding H_2O_2, which can cause further oxidation and decomposition of the organic pollutants in wastewater and improve treatment efficiency[7,8].

Furthermore, the influence of the added amount of H_2O_2 on COD reduction rate can be considered. Within a certain range, $HO^{\cdot}$ concentration was gradually increased with the increase in the amount of H_2O_2, COD reduction rate also increase. When the added amount of H_2O_2 (mass fraction 27.5 %) is 3 mL/L, The highest COD reduction efficiency 58.10 % can be achieved. When the amount of H_2O_2 added was more than 3 mL/L, COD reduction rate decreased. The reason is that according to the Fenton reaction, excess H_2O_2 can react with $HO^{\cdot}$ and reduce the concentration of $HO^{\cdot}$ in the solution. At the same time, too high concentrations of H_2O_2 can not produce more $HO^{\cdot}$. Moreover, H_2O_2 will oxidize Fe^{2+} to Fe^{3+} at the beginning in such conditions, which will inhibited the production of $HO^{\cdot}$ to reduce the COD reduction efficiency. In determination process of COD, H_2O_2 will be broken down into O_2 to increase effluent COD to certain extent[9]. Considering the treatment effect and operating costs, we determine the added amount of H_2O_2 is 3 mL/L.

Conclusion

• PVC paste resin wastewater was treated by micro-electrolysis. According to the experimental results, we determined the optimal conditions for micro-electrolysis process were pH = 3, HRT = 180 min, m_{Fe}: m_C = 3:1.

• Wastewater was treated with the single micro-electrolysis method and the microeletrolysis-Fenton integration process method, respectively. The experimental results show that the COD reduction rate of single micro-electrolysis was 23.53 %, COD reduction rate of microeletrolysis-Fenton integration process was 58.10 %. The removal efficiency can be increased by 34.57 % with the latter method.

• It is found by experiment that with the combination of micro-electrolysis-Fenton process, the best added amount of H_2O_2 is V = 3 mL/L wastewater. Either too small or too large amounts is not conducive to the removal of COD in wastewater.

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