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Treatment of anthraquinone dye wastewater by hydrolytic acidification-aerobic process

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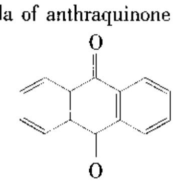
Abstract: Experiment on microbial degradation with two kinds of biological process, hydrolytic acidification-aerobic process and aerobic process was conducted to treat the anthraquinone dye wastewater with COD_{Cr} concentration of 400 mg/L and chroma 800. The experimental result demonstrated that the hydrolytic-aerobic process could raise the biodegradability of anthraquinone dye wastewater effectively. The effluent COD_{Cr} can reach 120—170 mg/L and chroma 150 which is superior to that from simple aerobic process.

Keywords: anthraquinone dye wastewater; hydrolysis; aerobic; biological treatment

Introduction

The textile printing and dyeing wastewater is a kind of industrial wastewater which is hard to be treated, and especially the dyeing wastewater containing reductive dyestuff as the anthraquinone dyestuff is more difficult to treat. It is reported by the literature that, the anthraquinone dyestuff is the substitution and derivative of anthraquinone, and a reductive and hydrophobic dyestuff (The Beijing Environment and Equipment Research Center, Beijing Environment Protection Technology Institute, the National Municipal Environmental Pollution Control Engineer and Technology Research Center, 2000). Anthraquinone is a kind of polyaromatic compound, hard to be oxidized, and bad biodegradability.

The structural formula of anthraquinone is as follows:



The BOD/COD of the anthraquinone dye wastewater is relatively low, and the organics such as the anthraquinone belongs to the refractory materials, which is the difficulty in the industrial wastewater treatment domain. For long times, the physico-chemical technology is always used to treat this kind of wastewater in the engineer (Zan, 1997; Lu, 2000). The technologies mainly used are coagulation, adsorption, and ozone primary treatment, and so on. Among of them, the micro-battery and ozone primary treatment could destroy the molecular structure of the dyestuff molecule effectively, improve the biodegradability of wastewater, and remove the chroma of wastewater rather effectively.

However, these technologies above-mentioned need high cost, cause seriously secondary pollution, and are hard to reach the emission standard the nation provided. Therefore, in the light of the anthraquinone dye wastewater which is a kind of industrial wastewater with bad biochemical characteristics, it is important in the engineering practice to search a kind of effective technology with high efficiency, low treatment cost, low secondary pollution.

1 The quality of experimental raw water

The experimental water is the anthraquinone dye wastewater produced practically by certain foreign capital textile factory in the Shanghai Waigaoqiao Protective Tariff Zone, and its main contaminants are: dyestuff, resin, and washing assistant. The main component of dyestuff is the anthraquinone material.

The quality of wastewater is shown in the Table 1.

Table 1 Quality of wastewater

COD_{Cr}, mg/L	BOD/COD	TN, mg/L	TP, mg/L	Chroma, times	pH
400	0.05	16.73	0.90	800	7

2 Discussion of wastewater treatment technology

As the physico-chemical technologies for the anthraquinone dye wastewater make bad treatment effect, seriously secondly pollution, and need high cost, it is considered using the biochemical technologies to treat this wastewater. The anthraquinone dye wastewater has bad biodegradability; therefore, the difficulty of treating this wastewater by biochemical technologies is how to improve the biodegradability of wastewater.

Anaerobic acidification is a kind of new biological primary treatment technology. Considering that the grow velocity of the methane former, the hydrolysis bacteria, and the acid former are different from each other, use the rinse function when water flowing to restrain the propagate of methane former in the reactor, control the anaerobic treatment in the first stage of the anaerobic treatment which need short react time, that means with the function of the hydrolysis bacteria, and the acid former, the nonsolvable organics hydrolyze into the solvable organics, the nonbiodegradable big-molecule materials were changed into biodegradable small-molecule materials. Taking the anaerobic hydrolysis as the primary treatment of biochemical treatment, could raise the biodegradability of wastewater, and decrease the load of subsequent biological treatment, so it is utilized extensively in the treating of the nonbiodegradable industrial wastewater. For the dyeing wastewater that has high chroma, the hydrolysis could destroy the chromophoric group of the dyestuff molecule, and remove its chroma effectively. Therefore, the hydrolytic-anaerobic aerobic process is a good biochemical technology for the anthraquinone dye wastewater.

3 The equipment of biochemical experiment and testing methods

The equipment of biochemical experiment is shown in Fig.1.

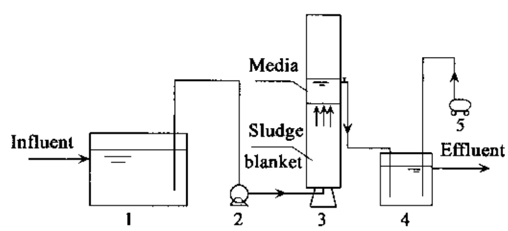


Fig.1 Pilot for biochemical experiment

1. tank; 2. measuring pump; 3. hydrolysis reaction column; 4. aerobic reaction tank; 5. small-sized aerator

In Fig.1 "3" is the hydrolysis equipment, and it is made up by a Plexiglas column which inside diameter is 8 cm, height is 1 m. The elastic packing is filled under the outlet. "4" is the aerobic reaction equipment, made by a 1000 ml tall beaker, where the diffusion units of small-sized aerator stretch into.

The measurement method is shown in Table 2.

Table 2 Measurement method

No.	Item	Measure method	No.	Item	Measure method
1	Flux	Volume	4	BOD_5	Diluting
2	COD_{Cr}	Standard	5	Temperature	Thermometer
3	NH_4-N	Distillation	6	SS	Weight

4 Experimental study on the anaerobic acidification-aerobic process

4.1 The aerobic experiment of influent

Judging from the quality determination of influent, the nitrogen and phosphorus nutrition is not sufficient, so nitrogen and phosphorus must be added in proportion into all of the influent water used for biochemical experiment. The aerobic experiment is operated in a 1000 ml beaker, for 24 h successively. The return sludge from the secondary settling tank of municipal sewage plant is get to be inoculated and acclimated. The retention time of the aerobic experiments is 12, 24, 36, 48 h respectively, and the experimental results are shown in Fig.2 and Fig.3.

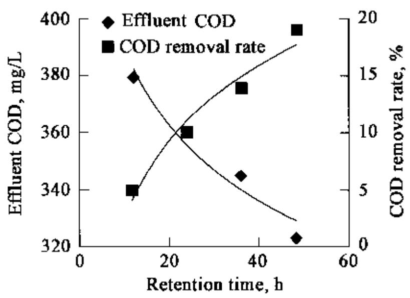


Fig.2 The COD removal rate of influent in the aerobic process

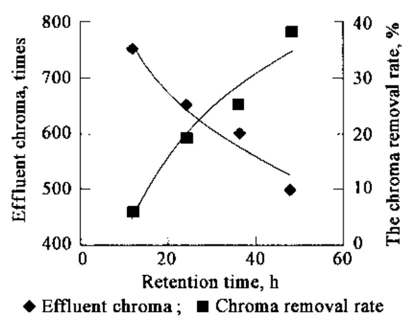


Fig.3 The chroma removal rate of influent in the aerobic process

4.2 The hydrolytic acidification experiment

The sludge in hydrolytic tank of the sewage plant is getting to be inoculated, and fill the experimental column with it. The influent way of hydrolytic tank is upflow, and the elastic solid packing is filled over the sludge to stop its running off. The influent of hydrolytic column is from a creeping pump, and it runs for 24 h successively. There are three engineering conditions: $T = 30$, 60 and 90 h. The hydrolytic equipment got to regular operation after 2 weeks. It is observed that the sludge in the column is dense, and there are little air bubbles rising occasionally, which indicated that trace methane is produced, and the hydrolytic system had got into the stable operation stage. The effluent quality of anaerobic hydrolysis is shown in Fig.4 and Fig.5.

4.3 The aerobic experiment of the hydrolytic column effluent

The effluent of anaerobic hydrolytic column is treated by aerobic process. The effluent of the hydrolytic column are treated separately with aerobic experiments whose retention time are 3, 6, 12 h. The experimental results are shown in Fig.6 and Fig.7.

4.4 The change of the sludge concentration in hydrolytic column

The height of the filling sludge in the hydrolytic column initially is 80 cm. When the system run for 1 month, the effluent is stable, and the

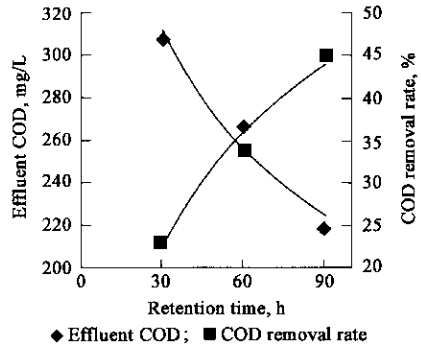


Fig.4 The removal rate of COD in the hydrolytic process

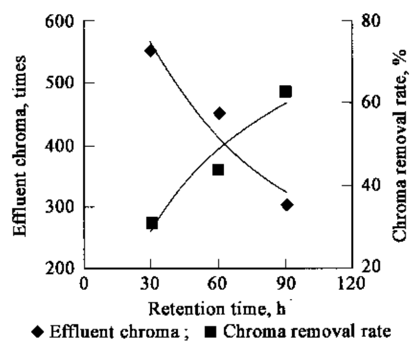


Fig.5 The removal rate of chroma in the hydrolytic process

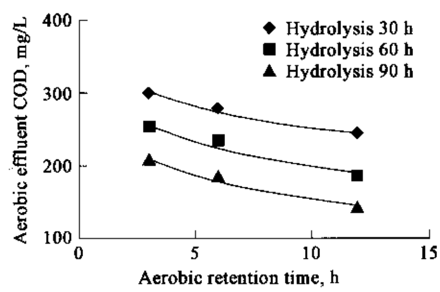


Fig.6 The COD in the effluent of hydrolytic-aerobic process

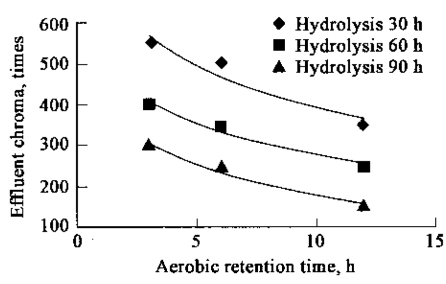


Fig.7 The chroma in the effluent of hydrolytic-aerobic process

height of sludge layer falls to 67 cm; when run for 2 month, the height of sludge layer falls to 60 cm, but compared with that of 1 month ago, the sludge concentration increases a little, while the amount of sludge does not. The change of sludge concentration in the experiment is shown in Table 3.

Table 3 Concentration of hydrolytic sludge

	Index	30 h	60 h	90 h
Initially	MLSS, g/L	30	30	30
	VSS/SS, %	0.75	0.75	0.75
1 month later	MLSS, g/L	26.9	26.0	25.3
	VSS/SS, %	59	55	52
2 month later	MLSS, g/L	28.7	27.5	26.1
	VSS/SS, %	60	56	50

4.5 The discussion of experimental results

The COD_{Cr} removal of influent after simple aerobic biochemical process is limitary. When treated with aerobic process for four kinds of retention time: 12, 24, 36, 48 h, the effluent quality does not differ greatly, the effluent COD_{Cr} is 323—379 mg/L; the effluent chroma is 500—750, the removal rates of COD_{Cr} and chroma are both low. When the aeration time increases from 12 h to 48 h, the effluent quality is improved, but its effect is not evident, which indicates that, the wastewater contains a large number of nonbiodegradable materials, simply extending the aeration time is not very helpful to improve the effluent quality.

After long time of anaerobic hydrolytic process, the quality of wastewater changes evidently. The effluent COD_{Cr} is about 220 when the retention time is 90 h; the effluent COD_{Cr} is about 264 when the retention time is 60 h, and they are both lower than the effluent COD_{Cr} when the retention time is 30 h(307 mg/L); the effluent chroma is decreased from 550 when retention time is 30 h to 300 when retention time is 90 h. The retention time of hydrolysis in the experiment is much longer than the retention time of hydrolysis process for regular industrial wastewater. The experimental results indicated that, the retention time is the main controlling parameter in the anaerobic hydrolytic reaction, and prolonging the retention time of anaerobic hydrolytic reaction is effective to improve the removal rate of COD_{Cr} and chroma.

Results of the contrastive experiments with hydrolytic acidification-aerobic process and aerobic process indicated that the former effect is superior to the latter evidently, especially when treated with hydrolytic process, the COD_{Cr} and chroma are both removed evidently. That means, although the contaminant as the anthraquinone in the wastewater belongs to the refractory organics, the hydrolytic acidification for long time make important effect on improving the wastewater quality; at the same time, the hydrolytic acidification also decreases the organic load of wastewater, and create beneficial condition for the subsequent aerobic treatment.

For the same aerobic treatment time, the longer the former hydrolytic retention time is, the better the effluent quality of subsequent aerobic treatment is. Judging from the experiment, after anaerobic hydrolytic process for 90 h and aerobic process for 12 h to the anthraquinone dyeing wastewater, the effluent COD_{Cr} lowers to about 140 mg/L, the removal rate of COD_{Cr} is above 63%, the effluent chroma lowers to 150, and the removal rate of chroma is above 81%.

The experiment indicated that the hydraulic retention time of the two stage process for the anthraquinone dyeing wastewater: anaerobic hydrolysis and aerobic aeration, exceeds the regular wastewater biological treatment greatly. The sludge retention time of the experiment with anaerobic hydrolytic process is much longer than the hydraulic retention time, and the sludge has enough time for decomposition again, and changes into soluble COD_{Cr} and some gas. For the subsequent aerobic treatment, as the aeration time is long, the endogenous respiration phenomenon of sludge is evident. Therefore, after 2 month of small-scale test, the amount of sludge in the hydrolytic reactor and aerobic reactor have not changed basically, with little sludge produced.

5 Conclusions

Hydrolytic acidification process could transform the big-molecule organics of polyaromatic compound aromatic as the anthraquinone into the biodegradable small-molecule materials, destroy the chromophoric group of dyestuff molecule, and decrease the chroma of wastewater effectively. After the anaerobic acidification primary treatment, the organic load of wastewater is decreased, the quality of wastewater is improved evidently, and it create beneficial condition for the subsequent aerobic treatment.

Using aerobic aeration process to treat the anthraquinone dyeing wastewater, when the aeration time is longer than 12 h, it is not very helpful to improving the effluent quality by exceeding the aeration time; while it could raise the removal rate of COD_{Cr} and chroma by exceeding the retention time of anaerobic hydrolytic process greatly.

After the anaerobic hydrolytic process for 90 h and aerobic process for 12 h to the anthraquinone dyeing wastewater, the effluent COD_{Cr} could falls to about 140 mg/L, with the removal rate above 63%, the effluent chroma is decrease from 800 of influent to 150, with the removal rate above 81%.

Adopting the hydrolytic-anaerobic aerobic process to treat the anthraquinone dyeing wastewater, has the advantages of high treatment efficiency, convenient operation and manage, low energy consuming, low sludge product, low operation cost, and so on. However, as the hydraulic retention time of the biochemical treatment is relatively long, the occupy space of the treatment system is relatively big.

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