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Petro-chemical wastewater treatment by biological process

GUAN Wei-sheng, LEI Zi-xue, ZHU Jun-huang

(Institute of Environmental Engineering, Xi'an Highway University, Xi'an 710064, China)

Abstract: In order to study the feasibility of treating petro-chemical wastewater by the combination of anaerobic and aerobic biological process, a research of treating wastewater in UASB reactor and aeration basin has been conducted. The test results shows that under moderate temperature, with 5.2 kgCOD/($m^3 \cdot d$) volumetric load of COD_{Cr} in the UASB reactor and 24h of HRT, 85% removal rate of BOD_5 and 83% of COD_{Cr} and 1.34 m^3/($m^3 \cdot d$) volumetric gas production rate can be obtained respectively. The aerobic biodegradability can be increased by 20%—30% after the petro-chemical wastewater has been treated by anaerobic process. As Ns = 0.45 kgCOD/(kgMLSS·d), HRT = 4h in the aeration tank, 94% removal rate of BOD_5, 93% of COD_{Cr}, 98.8% total removal rate of COD_{Cr} and 99% removal rate of BOD_5 can be reached.

Key words: anaerobic-aerobic process; petro-chemical wastewater; wastewater treatment

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In the course of oil refining, organic wastewater with high concentration of emulsified oil and phenol is produced, so far, the methods of physicochemical and aerobic biochemical processes are usually adopted home and abroad for the treatment of such wastewater (National Environmental Protection Bureau, 1992; Knoblock, 1993; Trobisch, 1992). However, as the wastewater contains uneasily degradated emulsified oil and organic matters, the existing treatment procedures are often characterized by high cost and can not meet the requirements of industrial wastewater disposal standard. The author has improved the aerobic biodegradation property of the petro-chemical wastewater by anaerobic biological process at first so that the wastewater can be treated by the succeeding aerobic biological process smoothly.

1 Testing materials and methodology

1.1 Testing wastewater

In the production of such final products as gasoline, kerosene and diesel, of such base oils as engine oil and lubricating oil with the ordinary depressurized devices or in the production process in catalytic cracking workshops, the mixed wastewater may be produced. Such wastewater was therefore taken from Lanzhou Petro-chemical Oil Refinery for testing. The main parameters of the water quality after pretreatment are as shown in Table 1.

Table 1 Main parameters after pretreatment

COD, mg/L	BOD_5, mg/L	TOC, mg/L	Emulsified oil, mg/L	Volatile phenol, mg/L	Sulfide, mg/L	pH
5200	3160	2943	90	760	46	6.5—8.0

1.2 Methods for the analysis of water quality

Methods used in the analysis of water quality included potassium dichromate method for COD_{Cr}, method of gravimetric analysis for oil, method of iodimetry for volatile phenol, method of biological oxidation for BOD_5, method of volumetric analysis for sulfide and method of precision acidimeter for pH value.

1.3 Technological process and equipment

The technological process is as shown in Fig. 1. The system is designed to treat 65.5L of wastewater per day. The wastewater first flows into the UASB reactor from the high level water tank, then partially into the aeration sedimentation basin. The effluent is drained after sedimentation and solid-liquid separation. The UASB reactor is made of ϕ200 PVC plastic pipe and polymethyl methacrylate. The volume of the reacting zone is 65.5L and that of the sedimentation and solid-liquid separation zone is 23L. Heating water circulation and indirect heating techniques are applied to control the temperature of reacting zone at 35±2℃. The aerobic treatment is carried out in the completely mixed aeration basin made of plastic plate, where the volume of the reacting zone is 4L and that of the precipitation zone is 2L.

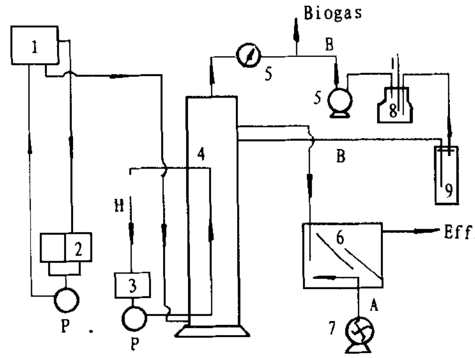

Fig.1 Experiment settings
1. high level water tank; 2. water distributing box; 3. water heating tank; 4. UASB reactor; 5. gas meter; 6. aeration sedimentation basin; 7. air compressor; 8. water trap; 9. water sealer; H: hot water pipe; B: biogas pipe; A: air pipe

1.4 Materials and methodology

The inoculating sludge in the UASB reactor and that in the aeration sedimentation basin were taken from the drained water in the moderate anaerobic digesting tank and mixed water in the aeration sedimentation basin respectively in Xi'an Water Treatment Plant. From the beginning of the test, 7L of granular activated carbon was put into the UASB reactor per week with a succession of 3 week, while 10g of $FeSO_4$ was put in it once every week through out the test.

The testing was divided into two phases, i.e., the starting one and the operating one. The first one last three weeks in which the sludge was cultured and tamed. The second one last 90 days when the organic loads in the UASB reactor and the aeration sedimentation basin were increased.

2 Test results and discussion

2.1 Operation parameters of the two phases biological treatment

The operation parameters of anaerobic and aerobic biological treatment can be seen in Table 2.

Table 2 Operation parameters of anaerobic-aerobic system

Operational parameters	HRT, h	Sludge concentration, g/L	Return sludge flow ratio, %	Dissolved oxygen, mg/L	Reaction temperature, ℃
UASB(phase)	24	60		0—0.05	35±2
Aeration basin	3.0—4.0	1.5—3.0	50—100	0.7—2.5	Normal

2.2 Anaerobic phase

A test of 90 day continuous stable operation was conducted. The final organic volumetric load remained at 5.2 kgCOD/(m^3·d) and the average treatment result of the stable operation are tabulated in Table 3. The result shows that on the average, removal of 1 kgCOD can produce 0.31 m^3 of marsh gas containing 67% of methane and 30% of CO_2, the volumetric gas production rate is

1.34 $m^3/(m^3 \cdot d)$.

Table 3 Average data of UASB reactor in stable operation

Inflow, L/h	Volumetric load, $kgCOD/(m^3 \cdot d)$	HRT, h	COD_{Cr}, mg/L inf.	eff.	rem., %	BOD_5, mg/L inf.	eff.	rem., %	TOC, mg/L inf.	eff.	rem., %	Oil, mg/L inf.	eff.	rem., %	Sulfide, mg/L inf.	eff.	rem. %
2.73	5.20	24.0	5200	885.0	83	3160	474	85	2943	364.8	90	8.0	8.0	91.1	46	2.0	95.6

Note: inf. stands for influent; eff. for effluent and rem. for removal rate

The relationships between Fr, COD_{Cr} and oil removal rate are as shown in Fig.2. It can be seen that if Fr$<$3 $kgCOD/(m^3 \cdot d)$, oil and COD_{Cr} removal rate $>$90%; if Fr $>$5.5 $kgCOD/(m^3 \cdot d)$, oil removal rate falls to less than 80%.

The relationships between HRT, COD_{Cr} and oil removal rate are plotted in Fig.3. It is evident that if HRT = 15—20h, COD_{Cr} and oil removal rate $<$75%; if HRT = 24h, the oil removal rate rises up to more than 80%.

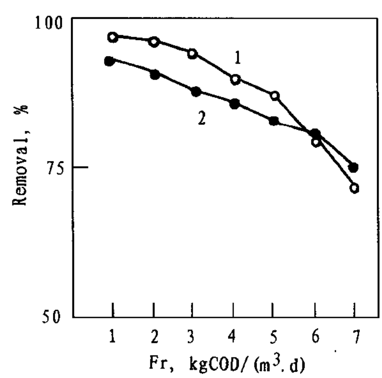

Fig.2 Relationships between Fr, COD_{Cr} and oil removal rate
1. oil removal rate 2. COD_{Cr} removal rate

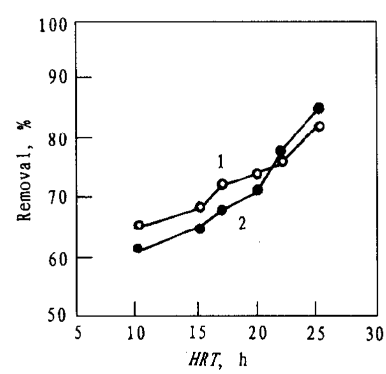

Fig.3 Relationships between HRT, COD_{Cr} and oil removal rate
1. oil removal rate 2. COD_{Cr} removal rate

It can be seen from Table 3 that it is very effective to use anaerobic organic matters to remove emulsified oil for its concentration after pretreatment is only 120 mg/L. When its concentration in the UASB reactor is less than 120 mg/L and the volumetric load is kept under 5.2 $kgCOD/(m^3 \cdot d)$, the oil removal rate in the reactor will be above 90%, while volumetric load is kept under 3 $kgCOD/(m^3 \cdot d)$, the oil removal rate in the reactor will be above 95%.

The removal rates of several organic matters in UASB reactor under stable operation are tabulated in Table 4, where five organic polluting materials are hard to be degradated and removed under general conditions (Jin, 1997). The results in Table 4 show that anaerobic organic matter is highly capable of decomposing and degradating organic matters hard to be degradated by aerobic biochemical process.

Table 4 Degradation rate of several kinds of organic matters in UASB reactors

Methylphenol, C_7H_8O, mg/L			Dimethylphenol, $C_8H_{10}O$, mg/L			Ethylphenol, $C_8H_{10}O$, mg/L			Methylethylphenol, $C_9H_{12}O$, mg/L			Trimethylphenol $C_9H_{12}O$, mg/L		
inf.	eff.	rem., %	inf.	eff.	rem., %	inf.	eff.	rem., %	inf.	eff.	rem., %	inf.	eff.	rem., %
3.0	0.01	99.7	2.6	0.15	94.2	0.87	—	100	0.31	0.01	96.8	0.42	0.06	85.7

Note: —. undetected

2.3 Aerobic phase

The effluent in the UASB reactor goes into the completely mixed aeration basin for aerobic bio-treatment. The data from the aeration basin test are shown in Table 5.

Table 5 Test results of aerobic biological treatment

Water treated, L, h	COD_{Cr}, mg/L inf.	eff.	rem, %	BOD_5, mg/L inf.	eff.	rem., %	TOC, mg/L inf.	eff.	rem., %	Oil, mg/L inf.	eff.	rem. %	DO, mg/L	SVI	Aeration time, h
1.0	885.5	64.5	92.7	474.0	30.2	93.7	364.8	24.2	93.4	8.0	0.3	96.3	2.2	80	4.0

Note: the sludge loading is the aeration basin in 0.45 kgCOD/(kgMLSS·d)

Based on the above anaerobic-aerobic test, a comparison aerobic test was conducted for petrochemical wastewater with and without anaerobic treatment under the same conditions. Completely mixed aeration basin was adopted in the test. The volume of the reacting zone was 4L and that of the sedimentation and solid-liquid separation zone was 2L. The treatment capacity was 1.0/h and the period of aeration was 4h. The sludge load in the aeration basin was 0.45 kgCOD/(kgMLSS·d). The dissolved oxygen concentration was controlled at 2—3 mg/L. The whole test last 65 days. The comparison test results are as shown in Fig. 4. It evident that after anaerobic treatment, the aerobic biochemical treating capacity can be increased by 20%—30% and that the removal rate of organics from the wastewater with aerobic treatment has been considerably improved.

2.4 Discussion

A certain amount of granular activated carbon was put into the UASB reactor because it has some catalytic effect (Zheng, 1988) on anaerobic fermentation and can improve the transparency at the top layer of the water in the reactor, besides, it can cause the microorganism in the reactor to be adsorbed onto the surface of the carbon. Since it has certain retaining effect on the anaerobic sludge, a high concentration of anaerobic activated sludge is always kept in the reacting area, with the formation of the granular sludge layer. As a result, the anaerobic activated sludge will stay longer in the reactor so that the organic polluting materials and microorganism can get closely contacted which is advantageous for the degradation and removal of polluting materials.

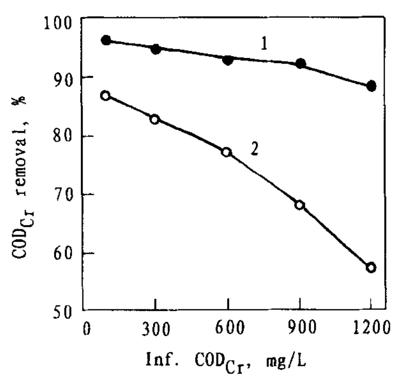

Fig. 4 COD_{Cr} removal of two sorts of wastewater by aerobic biological treatment
1. UASB effluent; 2. diluted water

When an appropriate amount of Fe^{2+} is added at the start and during the operation of UASB reactor, the activity of anaerobic organism can be improved (Hu, 1988). It has been shown that if the sulfide concentration is above 100 mg/L, the anaerobic fermentation will be retarded, especially in methane fermentation. During the trial operation, the sulfide concentration in the UASB was kept under 80 mg/L. A suitable amount of sulfide is favorable for the composition of cellular materials and the growth of germs. In the test, therefore, the sulfate and organosulphate in the wastewater were transferred into S^{2-}, which, after reacting with Fe^{2+}, produced FeS. Because FeS could speed up the formation of granular sludge, granular sludge was formed after about 40 days operation by putting granular carbon and $FeSO_4$ in the reactor. The accumulation of granular sludge caused a large quantity of methanogens with higher bioactivity to be produced in the UASB reactor. Meanwhile, as the granular sludge could build up thicker organic membrane structure to offer a nice environment for methanogens production, a stable operation of the UASB reactor was maintained.

The results in the anaerobic test (Table 4) and aerobic test (Fig. 4) show that after anaerobic treatment of petrochemical wastewater with high concentration of organism, the treating capacity of aerobic biochemical process can be greatly improved. This is because with anaerobic treatment, the organic matters in the wastewater have been partly degradated and removed, and the molecular structure of some organic matters has also been changed considerably. Especially some organic matters difficult to be degradated by aerobic microorganism have been transferred to the easily decomposed ones (Min, 1993). Therefore, it is practical and feasible both in technique and economics to adopt the method of treating petro-chemical wastewater with the combination of anaerobic and aerobic biological processes.

3 Conclusions

The anaerobic and aerobic biological process is not only applicable to the treatment of city wastewater, but also effective in treating petro-chemical wastewater with high concentration of organism. Under the condition that in the influent water, COD_{Cr} amounts to 5200 mg/L; BOD_5 to 3160 mg/L; TOC to 2743 mg/L; emulsified oil to 90 mg/L; volatile phenol to 760 mg/L, after wastewater remains in the whole system for 28 hours, in the effluent water, COD_{Cr} drops to 64.5 mg/L; BOD_5 to 28 mg/L; TOC to 24.2 mg/L; emulsified oil to 0.3 mg/L; volatile phenol to 0.3 mg/L; sulfide to 0.7 mg/L.

Petro-chemical wastewater hard to be treated by the usual methods can be effectively treated by the combination of anaerobic and aerobic biological processes. Further more, this combinative method has some remarkable environmental and economical advantages.

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