Coal Chemical Wastewater Heterogeneous Catalytic Oxidation Pretreatment Pilot Scale Test

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Abstract. A chemical enterprise in northwest China mainly produces 1, 4-butane diol, PTMEG and other chemical raw materials, with high concentration of waste water pollutants, low biochemical properties, strong biological toxicity and difficult to biodegrade. The pilot system constructed a chemical flocculation precipitation - heterogeneous catalytic oxidation - UASB - multistage aerobic - MBR system for treating BDO and PTMEG wastewater. The pilot system operates stably and efficiently, and the effluent meets the national sewage comprehensive discharge standard (GB8978-2002) grade A standard.

1. Introduction

As an important organic fine chemical raw material, 1, 4-butane diol is widely used in medicine, chemical industry, and textile, and papermaking, automobile and daily chemical industry [1]. At present, the commonly used production process is alkynes’ aldehyde method, and the products are 1, 4-butane diol (BDO), 1, 4-butane diol (BYD), polytetrahydrofuran (PTMEG), etc. Among them, tetrahydrofuran (THF) and PTMEG are toxic, heterocyclic organic compounds, which are hard to be degraded from structural analysis and have great harm to human health [2-3]. When the concentration of THF in wastewater reaches 200mg/L, anaerobic microbes are significantly inhibited and the amount of gas produced decreases sharply [4].

BDO, PTMEG production wastewater treatment technology is currently used combination of UASB + aerobic process, there are following drawbacks: (1) anaerobic (UASB) reactor in waste water with tetrahydrofuran, Polytetrahydrofuran, biological toxicity of formaldehyde suppression, system operating not stably, easy acidification, efficiency of pollutants removal is low, the aerobic system load is too high, discharge water quality can’t meet the standard [1] [5]. (2) High Sludge Organic Loading Rate of aerobic biochemical system, high yield of daily biological sludge, high cost of sludge disposal. (3) The impact load of water quality and water amount is large, and the operation stability of the system is poor, so the effluent cannot meet the national first-level A emission standard.

Zuo yan and Liu jing studied the treatment of poly tetrahydrofuran wastewater by iron iron-carbon micro-electrolysis, research shows that the Fe - C dosing amount to 30 g/l, pH value of 3, the reaction time of 120 min, COD removal rate as high as 75%, the conditions were created for the subsequent biochemical treatment of polytetrahydrofuran wastewater [6]. However, when the iron-carbon catalyst is operated under low pH conditions, the reaction time is long, the amount of iron elution is large, a large amount of iron mud is generated, and the iron-carbon filler is easily blocked, the backwashing frequency is high, and the filler replacement period is short. Therefore, it is necessary to select a
heterogeneous catalytic oxidation process with good catalytic oxidation effect, stable operation and low yield of chemical sludge for the treatment of BDO wastewater [7-8].

The pilot system constructed chemical flocculation precipitation-heterogeneous catalytic oxidation -UASB- multistage aerobic -MBR and three typical heterogeneous catalysts were screened for the process pilot. As a pretreatment process of biochemical system, heterogeneous catalytic oxidation unit decomposes refractory and biotoxic substances and simultaneously degrades COD, this pilot process mainly has the following advantages: (1) Chemical flocculation and sedimentation will reduce the suspended matter in the wastewater to below 50mg/L, avoiding the blockage of the filler caused by the high concentration of suspended solids and the phenomenon of mud running in the anaerobic system. (2) Heterogeneous catalytic oxidation partially oxidizes organic pollutants in raw water, and provides conditions for oxidative destruction of PTMEG, THF, and formaldehyde molecular structures, high wastewater B/C values, and stable operation of anaerobic reactors and subsequent systems. (3) Heterogeneous catalytic oxidation controls the oxidation of organic pollutants in raw water through the addition of oxidants, and controls the organic load of inlet water in the biochemical system. (4) use of activated carbon load transition metal catalyst with efficient and stable treatment effect, the reaction time is only 30 min or so, less chemical sludge production, catalyst there is no phenomenon of harden, backwash frequency is low, less waste of catalyzer. (5) The combined process has strong anti-impact load capacity, stable operation, and wide application range. The effluent meets the national First Grade Standard of GB 8978-2002.

2. Materials and methods

2.1. Materials
The pilot wastewater comes from BDO and PTMEG production workshops of a chemical enterprise in northwest China. The mixed wastewater quality is as follows: COD 6000~12000 mg/L, BOD5 596~1800 mg/L, B/C 0.083~0.11, pH 6~9, salt content 0.06wt%. The main effluent discharge and pollutant concentration are shown in table 1.

| No | parameter | Flow | Concentration | toxicity | Biodegradation | pretreatment |
|----|-----------|------|---------------|----------|----------------|--------------|
| 1  | BDO       | 20m3/h | 1800 mg/L     | N        | Easy           | N            |
| 2  | BYD       | 15m3/h | 200 mg/L      | N        | Difficult      | Y            |
| 3  | HCHO      | 10m3/h | 3600 mg/L     | Y        | Bacteriostatic | Y            |
| 4  | PT/THF    | 8m3/h  | 3700mg/L      | Y        | Bacteriostatic | Y            |

The fillers of the pilot system were iron filings, carbon powder fillers, iron carbon sintering fillers and activated carbon loading transition metal fillers respectively, which were used for catalytic oxidation treatment of BDO's mixed wastewater.

2.2. Methods
The pilot system includes chemical flocculation precipitation unit, catalytic oxidation unit, biochemical unit and sludge disposal unit. The process flow is shown in figure 1.
The design scale of the pilot system is 1t/d, and the water samples come from the mixed waste water produced by the BOD production enterprise. The COD of the pilot water samples is about 9000mg/L. The anaerobic system inoculation sludge was taken from the existing anaerobic reactor of the production enterprise, and the aerobic system inoculation sludge was taken from the secondary sedimentation tank. The main unit design parameters of the pilot system are shown in table 2.

### Table 2. Main unit design parameters of pilot system.

| Items                | pH  | SS(mg/L) | DO(mg/L) | HRT(h) |
|----------------------|-----|----------|----------|--------|
| Flocculation unit    | 6–9 | -        | -        | 0.3    |
| Catalytic oxidation unit | 3–5 | ≤50      | 1–3      | 0.5    |
| UASB                 | 7.2–7.5 | ≤50      | ≤0.1    | 8      |
| Aerobic unit         | 6–9 | ≤50      | 2–4      | 6      |

The catalytic oxidation unit adopts heterogeneous catalysis, pH control for 3 ~ 5 [3], hydrogen peroxide solution dosing quantity is 1.05 ~ 1.2 times of the amount of COD removal, the reaction time control for 30 min, through controlling the quantity of hydrogen peroxide solution dosing control of COD removal in the raw water, The control of Catalytic unit removal efficiency is 50 ~ 80%. COD in anaerobic water inlet is controlled 2000~3000mg/L, and volume load is 4.5kg/m3, while sludge load of aerobic system is 0.075–0.12kg / MLvss.

### 3. Results and Discussion

#### 3.1. Results

##### 3.1.1 Pilot test results of iron filings and carbon powder fillers. Two kinds of heterogeneous catalytic materials of iron and carbon system were used in the pilot test, namely "iron chip, carbon powder" filler and iron carbon sintering filler respectively, for the catalytic oxidation pretreatment of BOD mixed wastewater.

In the catalytic reaction of traditional iron carbon heterogeneous fillers, there are large amount of iron chip dissolution, easy blocked, influence on mass transfer [3], high frequency of backwashing and unstable operation effect. The specific running results are shown in figures 2 and 3.
Figure 2. Analysis of intermediate test results of catalytic oxidation of "iron powder + activated carbon powder".

The catalytic oxidation treatment wastewater of "iron powder + activated carbon powder" is BDO's mixed wastewater with a COD of 9000mg/L. In the first 5 hours of the initial reaction, the removal of organic pollution by activated carbon is mainly adsorptive, with a high removal rate of about 75-90% [8]. After the stable operation of the system, the interval of backwashing is about 5h. The removal rate of COD is reduced from 60% to 20%, and the average removal rate is less than 40%.

Figure 3. Analysis of intermediate test results of catalytic oxidation of "iron carbon sintering filler".

The iron-carbon sintered filler catalyzed the oxidation of BDO mixed wastewater. The treatment effect was better than that of iron powder and carbon powder filler. The time interval of backwashing was about 5h, the COD removal rate was reduced from 75% to 25%, and the average removal rate was about 47%.

3.1.2 Experimental results of activated carbon supported transition metal catalyst fillers. Activated carbon-supported transition metal catalytic oxidation first removes pollutants by adsorption of activated carbon, catalytic activity of catalytic groups on the surface of activated carbon, oxidation of
chemical oxides, and the process of adsorption and catalytic oxidation of pollutants[4]. The COD removal rate of BDO mixed wastewater in pilot scale operation test is \( \geq 50\% \), which improves the treatment effect of pretreatment system stability, maneuverability, reduces the operation difficulty and workload, and can be better used in engineering. The specific running results are shown in figures 4.

![Figure 4. Analysis of removal efficiency of COD by heterogeneous catalytic oxidation on activated carbon.](image)

During the pilot system linkage operation process, BDO mixed wastewater, COD is about 9000 mg/L, the average COD of the effluent by the heterogeneous catalytic oxidation unit is about 2940 mg/L, the removal rate of COD decreased from 86% to 51%, and the removal efficiency of COD by heterogeneous catalytic oxidation unit is about 67%.

The COD effluent of anaerobic reactor is 460~620mg/L, the removal rate is about 75%, and that of aerobic biochemical system is 30~46mg/L.

3.2. Discussion

3.2.1 Analysis of catalyst selection. The ferrocarbon heterogeneous catalyst has unstable operation effect, high yield of chemical sludge and easy blockage of slabs. It is not suitable for catalytic oxidation pretreatment of high concentration organic wastewater.

During the wastewater pilot unit operation, activated carbon supports transition metal catalyst, the catalyst can be operated continuously and efficiently for 80 hours without backwashing. Stable treatment effect is good, the average removal efficiency is about 60%, pilot system stable effluent COD remains under 50 mg/L. Activated carbon load transition metal catalyst is a catalyst suitable for heterogeneous catalytic oxidation of BDO wastewater and has good catalytic effect, strong maneuverability, a small amount of sludge production and easy to realize automation.

3.2.2 Summary of pilot run analysis. The chemical flocculation precipitation - heterogeneous catalytic oxidation -UASB- multi - stage aerobic -MBR combined system pilot operation, the expected functions of all sections of the pilot test are realized, and the pilot technique in the treatment of macromolecules, BDO wastewater with biological toxicity of operation can be realized in the process of high efficiency and stable operation, the final stable water meet the national standard "standard of sewage comprehensive discharge" level 1 A. The results as shown in table 3.
Table 3. Main unit design parameters of pilot system.

| Items                      | waste water | catalytic oxidation | UASB          | Aerobic unit |
|----------------------------|-------------|---------------------|---------------|--------------|
| COD(mg/L)                  | 5000        | 1800~2000           | 460~620       | 30~46        |
| removal rate               | -           | 60~80%              | 74~77%        | 90~95%       |

4. Conclusion

(1) Micro-electrolytic catalyst composed of iron filings and carbon powder, iron-iron sintering catalyst for treating high concentration organic wastewater, the serious iron dissolved, much chemical sludge production, treatment effect is not stable, easy to harden and does not apply to high concentration organic wastewater treatment.

(2) Activated carbon supported transition metal heterogeneous catalytic oxidation can achieve tetrahydrofuran, the destruction and chain scission of the molecular structure of polymer and formaldehyde, eliminate the toxicity inhibition effect of toxic and harmful substances on biochemical system, and greatly improve the biochemical nature of influent water quality of biochemical system.

(3) Constructed chemical flocculation precipitation - heterogeneous catalytic oxidation - UASB - stage aerobic - MBR combined system can efficiently and stably treat high-pollution, high-toxicity organic wastewater generated in BDO, PTMEG production process and downstream product production process, effluent COD ≤ 50mg/L, meeting the national final effluent stability and meeting the national ‘Sewage Integrated Emission Standard’ Level A Standard.

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