A Study of Refractory Industrial Wastewater Treatment by Fe/C Microelectrolysis Combining with Multiphase Fluid Catalytic Oxidation

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Abstract. Refractory industrial wastewater used to be high strength in diversified organic pollution and biotoxicity. It is becoming a formidable global environmental issue. This study revealed a novel process of Fe/C microelectrolysis combining with multiphase fluid catalytic oxidation to treat high strength industrial wastewater (take pharmaceutical wastewater as an example). Different catalysts were investigated to optimize the operation parameters. The results showed that the average COD removal rate of single microelectrolysis in pharmaceutical wastewater was 23.1%. After microelectrolysis treatment, the B/C was improved from 0.11 to 0.23. The PVA pellets were set as the fluidized catalysts with activated carbon (AC), TiO$_2$ and MnO$_2$, respectively. The AC, TiO$_2$ and MnO$_2$ could significantly promote the COD degradation of pharmaceutical wastewater. When combining with multiphase fluid catalytic oxidation, the PVA/MnO$_2$ indicated a higher COD removal efficiency of 51.6% with 0.4%H$_2$O$_2$ addition, the effluent B/C was 0.34.

Introduction

With the rapid development of global economy, the society industrialization is moving forward constantly. Massive quantity of industrial wastewater discharged with varieties of chemical compounds, including toxic and refractory pollutions which become a widely concerned environmental issue. The clear negative impacts on ecosystems, and the potential to endanger the health of the general public make it import to address the problem urgently, especially in developing countries$^{[1,2]}$. Because of the biotoxicity and recalcitrance of the industrial wastewater, it could not be treated via biological system directly. The complex chemicals would limit the growth and propagation of activated sludge microbes, and break down the whole bio-system$^{[3,4]}$. Thus, the refractory wastewater need a suitable pretreatment to decrease its COD concentration, reduce the biotoxicity and enhance the biodegradability. Fenton, microelectrolysis, wet catalytic oxidation (WCO) were the commonly advanced oxidation processes put into industrial wastewater pretreatment. However, microelectrolysis was not such a preferable option due to the low efficiency. Fenton reaction needs a high reagent cost and will produce mounts of sludge. WCO process requires much energy and high-level reactor, causing more running cost. Hence, WCO is unsuited for large-scale application$^{[5]}$. In this study, a novel multiphase fluid catalytic oxidation (MFCO) technology was combined with microelectrolysis to pretreat refractory industrial wastewater in order to get a higher COD removal rate. The different catalysts were compared, the operation parameters were optimized as well.

Methods and Materials

Refractory Industrial Wastewater

The refractory industrial wastewater was obtained in regulating tank of pharmaceutical factory. The average COD was 17472±4189mg/L while the average pH was 2.73±0.62. Amides, esters, heterocyclics were the main organic pollutions. The B/C was lower than 0.12.
Experiment Set Up

**Microelectrolysis Test.** The microelectrolysis reaction was taken in beakers. Iron and carbon powders were squeezed into ellipsoid (d=2~5cm) with binder and several metal oxides, and sintered at high temperature as Fe/C fillers. The accumulation volume of Fe/C in beaker was 70%. Before using, the fillers were cleaned by sulfuric acid solution (pH<4.0) for three times. The HRT and gas water ratio were controlled at 2h and 5:1, respectively. Since the low pH of raw water, the microelectrolysis experiment was run without pH adjusted. The wastewater subsequently entered into MFCO reactor after microelectrolysis treatment.

**Multiphase Fluid Catalytic Oxidation Reactor and Catalysts.** A schematic diagram of the multiphase fluid catalytic oxidation system is shown in Figure 1. A custom-designed columnar reactor (φ100mm×700mm) was made of polymethyl methacrylate with a net cavity volume of 5.0L. A three-phase separator was set in the top of the reactor to avoid the catalysts running out. The reactor was connected with a aerating pump to ensure the catalysts keeping fluidifying through forceful aeration. Moreover, the hydrogen peroxide was dosed as oxidant at the beginning.

The spherical catalysts were made by polyvinyl alcohol (PVA) and boric acid cross-linking reaction with activated carbon (AC), titanium dioxide (TiO$_2$) and manganese dioxide (MnO$_2$) addition, respectively, and the products were solidified into pellets (d<5mm). The AC, TiO$_2$ and MnO$_2$ mass ratio to PVA were 3:1. After preparation, these fluid catalysts were rinsed by distilled water for three times and soaked overnight. The different spherical catalysts were filled within 50% volume ratio of the MFCO reactor, respectively. A reactor without catalyst filling was operated as control group. When reaction finished, the effluent was adjusted to pH=8.0 for flocculation and precipitation by 0.3%PAC and 0.1%PAM addition. Afterwards, the supernatant was used for detecting. During the experiment, the optimal HRT and H$_2$O$_2$ addition were examined.

![Figure 1. Schematic diagram of multiphase fluid catalytic oxidation system (1-three-phase separator, 2-catalyst package, 3-aerating pump, 4-sample connection).](image)

Analytic Methods

The effluent was diluted by distilled water for analysis. The COD was determined by dichromate titration described in National Standard (GB119189-89). BOD$_5$ was assayed by inoculation dilution method (after 5 days). A portable pH meter (Rex PHS-3C, Shanghai) was used for pH monitoring. The available content of hydrogen peroxide in oxidizing agent was 27.5%. All tests were carried under room temperature.

Results and Discussions

**Refractory Wastewater Treated by Microelectrolysis**

Table 1 shows the COD removal of pharmaceutical wastewater by microelectrolysis oxidation. The average COD removal rate was 23.1% through multiple experiments. And the pH and B/C raised
from 2.73 to 4.83 and 0.11 to 0.23, respectively. The acidity of the raw wastewater could be conducive to microelectrolysis reaction\textsuperscript{[6]}. Iron and carbon in microelectrolysis fillers formed numerous primary cells and release electron and ferrous ion. The concentration of Fe\textsuperscript{2+} species increased to 114±23mg/L. Along with aeration, this process generated much activated radicals such as [O], [H] and [OH]\textsuperscript{[7,8]}, which could oxidize and break the chemical bonds of resistant organics, causing biodegradability enhancement. Meanwhile, due to the damage of Fe/C fillers, AC/Fe powder scattered into bulk solution. This led to an increase of SS to 28.4mg/L. However, when the AC and zero-valent iron entered into MFCO, this could furtherly promote the oxidation and absorption of pollutants. Subsequently, the SS would be settled as sediment by flocculating to separate. On the other hand, the effluent ammonia concentration increased from 243mg/L to 339mg/L. This indicated the organic amine pollutants were decomposed effectively.

Table 1. The effect of microelectrolysis treatment on pharmaceutical wastewater.

| Index | Inflow | Effluent |
|-------|--------|----------|
| pH    | 2.73±0.62 | 4.83±0.41 |
| COD   | 17472±4189mg/L | 13558±3047mg/L |
| B/C   | 0.11±0.02 | 0.23±0.04 |
| Fe\textsuperscript{2+} | - | 174±23mg/L |
| SS    | - | 28.4±5.3mg/L |
| NH\textsubscript{3}-N | 243±25mg/L | 339±42mg/L |

Effect of MFCO on Wastewater Treatment

Effect of Catalyst Type. As mentioned above, mounts of Fe\textsuperscript{2+} were dissolved into aqueous phase during microelectrolysis. The effluent of microelectrolysis oxidation flowed into MFCO reactor with H\textsubscript{2}O\textsubscript{2} addition. The occurrence of Fe\textsuperscript{2+} and H\textsubscript{2}O\textsubscript{2} caused intense Fenton process, according to Eq. (1), which creating high oxidative hydroxyl radical (•OH)\textsuperscript{[9]}.\n
\[
Fe^{2+} + H_{2}O_{2} \rightarrow Fe^{3+} + HO• + HO^{-} \tag{1}
\]

Figure 2 shows the COD (inflow COD=14258 mg/L) degradation in MFCO system with different catalysts. Comparing to the control, the PVA pellets with catalysts could compose the resistant organics more effective. The effluent COD concentration decreased with operating time and mainly degraded in 2 hours. The final COD concentrations were control for 12151 mg/L, AC/PVA for 10625 mg/L, TiO\textsubscript{2}/PVA for 9613 mg/L and MnO\textsubscript{2}/PVA for 9231 mg/L, respectively. The significant COD reduction owed to 3 reasons: (1) the existence of PVA pellets adequately mixed the solution with aeration; (2) the PVA pellets surface provided a better reaction medium for Fenton chemistry and pollutants oxidation; (3) the catalysts in PVA pellets could catalyze H\textsubscript{2}O\textsubscript{2} for more oxidative radicals generation. AC is a common adsorbent and catalyst used in wastewater treatment. When mixed into PVA pellets, it could accelerate H\textsubscript{2}O\textsubscript{2} decomposed into [H] and •OH and hold organics by absorption\textsuperscript{[10]}. On the other hand, TiO\textsubscript{2} in PVA pellets formed TiO\textsubscript{2}/H\textsubscript{2}O\textsubscript{2}/UV fenton-like system to heighten the COD degradation\textsuperscript{[11]} due to the MFCO reactor was diaphanous. For MnO\textsubscript{2}, it could urge on the decomposition of H\textsubscript{2}O\textsubscript{2} more effectively. And make the products participate in refractory organics by intensive fluidization state.

In the meantime, the B/C was found to be further enhanced than microelectrolysis. After MFCO treatment, the B/C ratios of control, AC/PVA, TiO\textsubscript{2}/PVA and MnO\textsubscript{2}/PVA were 0.27, 0.29, 0.33 and 0.34.

Table 2. The effect of catalytic type on B/C.

| Catalytic type | Inflow B/C | Effluent B/C |
|---------------|------------|--------------|
| Control       | 0.21       | 0.27         |
| AC            | 0.33       | 0.29         |
| TiO\textsubscript{2} | 0.33     | 0.34         |
| MnO\textsubscript{2} | 0.34     |              |
Figure 2. COD removal in MFCO systems with different catalysts (H$_2$O$_2$ dosage for 0.2%v/v).

**Effect of H$_2$O$_2$ Addition.** Many researches indicated the dosage of H$_2$O$_2$ could directly impact on the generation of activated oxidative radicals$^{[12]}$. The results in Figure 3 showed more COD reduction with more H$_2$O$_2$ addition. The highest COD removal rates were 17% for control, 26.7% for AC/PVA, 35.4% for TiO$_2$/PVA and 38.6% for MnO$_2$/PVA, respectively. After the Fenton reaction of H$_2$O$_2$ and Fe$^{2+}$ in bulk solution, the redundant H$_2$O$_2$ was utilized by the PVA catalyst for great oxidative radicals production. Therefore, the pollutants were degraded more completely. However, when H$_2$O$_2$ dosage was 0.4%, the effluent COD increased. This may be due to the surplus H$_2$O$_2$ contribution.

![Figure 3](image3.png)  
Figure 3. Effect of H$_2$O$_2$ addition on COD removal (HRT=2h).

**MFCO Operation under Optimal Condition.** The COD changes of MFCO under optimal condition were revealed in Figure 4 (MnO$_2$/PVA as catalyst, H$_2$O$_2$ addition with 0.4%). After 2h catalytic oxidation, the COD removal rate reached over 36% and the trend became slow. Till the end, the COD removal rate was 38.6%. Totally, 51.6% COD was degraded by “microelectrolysis+MFCO” process. Meanwhile, the concentration of Fe$^{2+}$ decreased while the pH increased rapidly during initial 2h. It indicated the fenton oxidation in MFCO system fully occurred in the first 2h. The H$_2$O$_2$ consumption led higher pH. Most organics undegraded in microelectrolysis system were oxygenolysised by MFCO reaction. Moreover, the rest COD compositions would give a favor to sequent biological treatment$^{[13]}$. 

![Figure 4](image4.png)
Conclusions

This study presented a novel advanced oxidation process of microelectrolysis+MFCO for refractory wastewater treatment. PVA pellets were mixed with types of materials for fluid catalysts. In MFCO system, liquid, solid and gas demonstrated highly fluidization. Thus, fenton oxidation was significantly promoted result in high efficient COD reduction. The single microelectrolysis got a COD degradation rate of 23.1%, and B/C was enhanced to 0.23. Catalyst in MFCO could improve the fenton chemistry with an efficiency MnO₂>TiO₂>AC>control. The optimal operating condition of MFCO were 0.4%H₂O₂ addition and HRT for over 2h with MnO₂/PVA. After microelectrolysis and MFCO treating, the highest COD removal rate was 51.6% and effluent B/C was 0.34. The biodegradability of pharmaceutical wastewater was significantly enhanced. Summarily, microelectrolysis+MFCO is a preferred option for refractory industrial wastewater treatment.

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