Application of advanced oxidation process combining anaerobic granular sludge on refractory industrial wastewater treatment

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Abstract. An AOPs of Fe/C micro-electrolysis (FCME) and Fenton oxidation (FO) was combined with anaerobic granular sludge (AGS) to treat recalcitrant pharmaceutical wastewater in this study. The AOPs showed significant COD reduction during both FCME and FO. For influent COD=9000~11000mg/L, the pretreatment effluent COD could reach below 5500mg/L under 0.6% H2O2 adding condition. And the B/C of pharmaceutical wastewater was improved from 0.11 to 0.37. The subsequent AGS treatment in EGSB got a COD removal rate of 87.1%. The extracellular polymeric substance (EPS) and mean diameter detection demonstrated high stability of EGSB. AOPs with AGS is supposed to be a better option for recalcitrant wastewater treatment process.

1. Introduction

Industrial pollution is a commonly concerned environmental issue, particularly for the refractory wastewater treatment. Many toxic and nonbiodegradable compounds exist in the industrial wastewater[1], like pharmaceutical wastewater, pesticide wastewater, dyeing wastewater, etc. Thus, the treatment of such industrial influent is especially challenging due to the inhibitory properties of complex chemicals. Once these pollutants were not efficiently decomposed and discharged into the surface water, it would cause badly ecological emergency and human health risks. To deal with the refractory industrial wastewater, anaerobic digestion and advanced oxidation processes (AOPs) were usually chosen as the necessary solutions.

Anaerobic digestion has been used to treat domestic wastewater as well as industrial wastewater for decades[2-4]. It is a necessary process of wastewater treatment in biological system. Comparing with aerobic treatment, the advantages of anaerobic treatment can be described as: (1)lower energy requirement; (2)lower macro/micro-nutrients needing; (3)lower biological solid waste production, (4)higher organic loading rates and toxic or xenobiotic compounds suffering and (5)generating valuable biogas for energy recovery[5,6]. However, the traditional anaerobic treatment need a long start-up period, a long hydraulic retention time (HRT) and a large floor area. When the upflow anaerobic sludge blanket was developed in 1970s, the disadvantages of traditional anaerobic process had been overcome. Under the hydraulic shear force, the suspended anaerobic sludge could be aggregated in to dense and rapidly settling anaerobic granular sludge (AGS). AGS has a high-rate of
organic matters degradation, and has been popularly applied in treating high strength industrial wastewaters from brewery, food processing, pharmaceuticals, landfill leachate and so on\textsuperscript{[7-9]}. However, the AGS did not suit to treat recalcitrant wastewater directly.

Recently, advanced oxidation processes (AOPs) were developed as indispensable methods for high strength and refractory wastewater treatment, such as fenton, photocatalytic, wet oxidation, electro-chemical oxidation. These processes could produce a large number of highly oxidized active radicals to disintegrate the recalcitrant organic compounds. AOPs were recognized to reduce the COD concentration and increase the B/C rate of high strength wastewater. Therefore, the coupling treatment of AOPs allows improvement in the biodegradability of recalcitrant wastewater and reduction of toxicity of wastewaters, making the wastewater suitable for subsequent biological treatment\textsuperscript{[10]}. Among the AOPs, Fe/C microelectrolysis and Fenton oxidation were the preferred choices because of their low cost, easy operation and high efficiency. Su et al. studied the Fenton-like pretreatment and AGS to treat cephalexin, and got a COD removal rate of over 90\%\textsuperscript{[11]}. Zhou et al. investigated ultra-high concentration organic wastewater treatment by Fe-C micro-electrolysis and biological process\textsuperscript{[12]}. The results showed the COD could be reduced from more than 150,000 mg/L to ~500 mg/L.

Currently, the research on Fe/C micro-electrolysis and Fenton oxidation with AGS for refractory pharmaceutical wastewater treatment has been minimally reported. So in this work, we demonstrated the performance of Fe/C and Fenton oxidation combining with AGS biological process to treat high strength and recalcitrant pharmaceutical wastewater, and optimized the operation conditions to get a high stable pollutants removal rate. Specifically,

2. Materials and methods

2.1 Wastewater source, AOPs oxidants and sludge inoculum

The recalcitrant pharmaceutical wastewater was taken from the regulating reservoir of a neurodrug producing company in Xuzhou, Jiangsu. The characteristics of the wastewater were shown in Table 1. Fe/C micro-electrolysis followed with Fenton oxidation was set as the AOP. The micro-electrolysis packing was purchased from Longantai Environmental Protection Technology Co., Ltd in Shandong. The Fenton oxidant was H\textsubscript{2}O\textsubscript{2} with available contents of 27.5\% v/v. Besides, 30\% NaOH solution and 5 mol/L H\textsubscript{2}SO\textsubscript{4} were used for pH adjusting during the advanced oxidation reaction. The AGS was inoculated from a UASB of Qianjiang brewery in Hangzhou, the volatile suspended solid and total solid were 18.53 g/L and 21.38 g/L.

| Parameter                        | Value range          |
|----------------------------------|----------------------|
| pH                               | 4.3–5.5              |
| Chemical oxygen demand (COD)     | 9300–14000 mg/L      |
| Biochemical oxygen demand (BOD\textsubscript{5}) | 780–1350 mg/L       |
| Ammonia nitrogen (NH\textsubscript{3}-N) | 110–180 mg/L       |
| Total phosphorus (TP)            | 10–25 mg/L           |
| Total dissolved solids (TDS)      | 3300–5400 mg/L       |

2.2 AOPs reactors and operation conditions

The AOP set-up diagram was shown in Fig. 1. Tow oxidizing towers made of polymethyl methacrylate with volume of 5L respectively was used for Fe/C micro-electrolysis and Fenton reaction. Fe/C packing accumulation filling rate was 70\% of the tower volume. The pH of wastewater was adjusted to 3.0–3.5 by 5 mol/L H\textsubscript{2}SO\textsubscript{4} and then pumped into the micro-electrolysis tower(MET). The effluent of MET subsequently flowed into Fenton tower within H\textsubscript{2}O\textsubscript{2} addition. The AOP was operated along with low intensity of aeration all the time. After AOP pretreatment, the wastewater was adjusted to pH value 8–8.5 for iron ions removal and flocculent precipitation with PAC and PAM adding. The supernatant was stored in a cistern for biological treatment by AGS. The HRT of ME was the same as
Fenton oxidation, for 2h.

Fig. 1 Schematic of the recalcitrant pharmaceutical wastewater treatment system

2.3 Biological experiment set-up
An expanded granular sludge bed (EGSB) of 3.52L effective volume (7-cm diameter, 100-cm height) was used for anaerobic treatment. The inoculum sludge concentration in EGSB was 25 g/L. Before used, the AGS was cultivated for 1 week in EGSB with glucose (8000 mg/L COD), nitrogen, phosphorus and trace elements addition (C:N:P=500:5:1). Then the pretreated pharmaceutical wastewater was pumped into EGSB. The HRT was controlled in 12~24h and the recirculation reflux ratio was 15 L/h. The reactor was maintained under mesophilic condition throughout their operations and they ran for about 60 days. The effluent sampled to analysis each day.

2.4 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). The ammonia nitrogen was evaluated according to APHA(2012)[13]. The AGS was sampled from the top, middle and bottom to analyze its characteristics, respectively. The extracellular polymeric substance (EPS) was extracted by the method described by Yang et al.[14], and analyzing concentrations of polysaccharides and proteins using method mentioned by Feng et al. 2014[15]. The average diameter of AGS was monitored on a laser dispersion particle size distribution analyzer (LS-909E, Omcc) and by observation on an Olympus CX31 microscope.

3. Results and discussions

3.1 Performance of AOPs treating pharmaceutical wastewater
The COD removal of pharmaceutical wastewater within AOPs treatment was shown in Fig. 2a. It showed a relatively constant removal efficiency of COD after operating for 3h. The average effluent COD of Fe/C and Fenton were 6661 mg/L and 5130 mg/L, respectively. And the COD removal rates were 37.7% and 51.9%. The theory of Fe/C micro-electrolysis was based on potential difference between iron and carbon in electrolyte. At a low pH condition (pH=3.0~3.5 in this work), Fe and C in micro-electrolysis fillers formed countless microscopic galvanic cells and produced mounts of electronics. On the other hand, moderate aeration could contribute to the Fe corrosion and compete as the electron acceptor to lead H$_2$O$_2$ generation[16]. When the high density of electronics met hydron and oxygen molecules, several reactions occurred (Eq. 1-4). Fe/C micro-electrolysis can enhance structural transformation of the organic pollutants due to the high potential difference between Fe and C[17]. The generating Fe$^{2+}$ will trigger subsequent Fenton reaction without pH adjustment. During the Fenton reaction, within H$_2$O$_2$ addition(0.2% v/v), Fe$^{2+}$ was oxidized by H$_2$O$_2$ to Fe$^{3+}$ along with
hydroxyl radical generation (Eq. 5). Hydroxyl radical could oxidize most of the organic compounds, particularly for recalcitrant ones. Therefore, the B/C were improved significantly by Fe/C and Fenton (Fig. 2b). The Fe/C process enhanced B/C from 0.11 to 0.26, and further to 0.31 after Fenton reaction. The higher B/C would benefit to the organics biodegradation by the subsequent AGS bio-process.

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\begin{align*}
\text{Anode (iron)} & \quad \text{Fe} - 2e \rightarrow \text{Fe}^{2+} & \quad \text{E}_0(\text{Fe}/\text{Fe}^{2+}) = 0.4V \quad (1) \\
\text{Cathode (carbon)} & \quad 2H^+ + 2e \rightarrow 2[H] \rightarrow H_2 & \quad \text{E}_0(H^+/H_2) = 0V \quad (2) \\
O_2 + 4H^+ + 4e & \rightarrow 2H_2O & \quad \text{E}_0(O_2) = 1.23V \quad (3) \\
O_2 + 2H_2O + 4e & \rightarrow 4OH^- & \quad \text{E}_0(O_2/OH^-) = 0.41V \quad (4) \\
\text{Fe}^{3+} + H_2O_2 & \rightarrow \text{Fe}^{3+} + OH^- + \bullet OH & \quad (5)
\end{align*}
\]

![Graph showing COD and B/C over time](image)

Fig. 2 The performance of Fe/C micro-electrolysis and Fenton oxidation in pharmaceutical wastewater pretreatment

![Graph showing B/C ratio](image)

Fig. 3 The effect of H$_2$O$_2$ dosage on COD removal and BOD improvement

Meanwhile, the dosage of H$_2$O$_2$ in fenton reaction could significantly effect on COD removal efficiency and the B/C ratio. In Fig. 3, the COD removal efficiency increased with the increase of H$_2$O$_2$ addition. The COD removal rate of 0.2%, 0.4%, 0.6% H$_2$O$_2$ dosage were 41.6%, 47.3% and 49.7%, respectively. Also, the BOD$_5$ reached the highest concentration of 2038 mg/L within 0.6% H$_2$O$_2$ addition while B/C was 0.37. H$_2$O$_2$ is the key of •OH producing in Fenton reaction and the dosage of H$_2$O$_2$ decides the yield of •OH directly. However, the superfluous H$_2$O$_2$ addition would scavenge the generated hydroxyl radical and formed less reactive radical HO$_2^*$ shown in Eq. 6$^{[18]}$. At same time, the excess H$_2$O$_2$ once flowed into the subsequent biosystem, it could make a negative
impact on microbes growth. Much H$_2$O$_2$ addition would take a higher cost as well. Consequently, the expected dosage of H$_2$O$_2$ was less than 0.6%.

$$H_2O_2 + \bullet OH \rightarrow H_2O + HO_2 \bullet$$  \hspace{1cm} (6)

3.2 EGSB performance on pharmaceutical wastewater treatment

The original wastewater COD was 10000–12000 mg/L. After AOPs treatment, the supernatant (COD=5000~7000 mg/L) of coagulation precipitation was pumped into EGSB. The EGSB were fed with nutrient solution for 1 week before setting up (see in section 2.3).

Fig. 4 shows the COD removal of pretreated pharmaceutical wastewater in EGSB. During the initial 10 d of the experiment (HRT=10h), the effluent COD rapidly reduced from 6000 mg/L to 2000 mg/L. This can be attributed to the time taken by the microorganisms to acclimatize due to the change of the environmental conditions\(^{[19]}\). The effluent COD became stable after 10 days since the AGS had adapted the pharmaceutical wastewater. When the HRT=15h and 20h, the COD of effluent got lower average concentrations of 1090 mg/L and 771 mg/L, respectively. The highest COD removal rate was 87.1% at HRT=20h condition. The favorable treatment efficiency attributed to the biodegradability enhancement of wastewater by AOPs. Moreover, the HRT exert in addition key hydraulic selection pressure on the AGS. Enough retention time provides adequate contact chance of organics and anaerobic microbes. Sheldon and Erdogan found the optimal HRT of EGSB for soft drink industrial wastewater (COD≈3000 mg/L) to be 12h\(^{[20]}\). For higher concentration wastewater, the HRT needs increasing.

![Fig. 4 The COD changes of EGSB for pretreated pharmaceutical wastewater treatment](image)

EPS plays a very important role in forming and maintaining anaerobic granules. Usually, under high toxicity condition, the EPS of sludge would reduce due to the loss of microbial activity\(^{[21]}\). In this work, the mean EPS concentrations of AGS during different stage were listed in Table 2. The EPS concentration firstly reduced from 41.1mg/g VSS to 26.3mg/g VSS, then increased to 30.2mg/g VSS during 20~40d and to 38.9mg/g VSS during 40~60d. The mainly reason for EPS reduction might be that microorganisms excrete EPS substance into external environment to provide a formidable protective defense against the toxic pollutants\(^{[19]}\). As the AGS gradually accommodated the current wastewater, the microorganisms started to rebuild themselves and produce more EPS. This result demonstrated that the toxicity of pharmaceutical wastewater was reduced by the AOPs pre-treatment as well. Meanwhile, the mean diameter of AGS increased from 0.84mm to 1.22mm, along with COD removal rate increasing. The diameter of AGS was mainly connected to the hydraulic shear force, inorganic composition and sludge carrier. The up flow velocity in EGSB was 3.9m·h$^{-1}$, which matched to Faria’s study\(^{[22]}\). The electrolyte addition in AOPs and in wastewater provided a suitable condition for AGS growth (NaCl, CaCl$_2$, etc.).
Table 2 The characteristics of AGS and COD removal rate at different operation stages

| Time       | HRT | EPS       | Mean diameter | COD removal rate |
|------------|-----|-----------|---------------|------------------|
| Initial    | -   | 41.1mg/g VSS | 1.03mm        | -                |
| 10~20d     | 10h | 26.3mg/g VSS | 0.84mm        | 73.2%            |
| 20~40d     | 15h | 30.2mg/g VSS | 1.01mm        | 81.6%            |
| 40~60d     | 20h | 38.9mg/g VSS | 1.22mm        | 87.1%            |

4. Conclusions
Through the above research, it is found that Fe/C micro-electrolysis and Fenton oxidation could efficiently decrease the COD of refractory pharmaceutical wastewater and improve its biodegradability. The highest COD removal rate was 51.7%. EGSB reactor could subsequently decompose the pre-treated wastewater, and the effluent COD was lower than 800 mg/L. The total COD removal rate of was over 92%. Besides, the AGS in EGSB kept an integrated form. These results demonstrated AOPs combining AGS was a preferred method for recalcitrant wastewater.

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