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The feasibility of using combined Fenton-SBR for antibiotic wastewater treatment

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ABSTRACT

The first part of this study examined the effect of operating conditions on Fenton pretreatment of an antibiotic wastewater containing amoxicillin and cloxacillin. The optimum H_2O_2/COD and H_2O_2/Fe^{2+} molar ratios were 2.5 and 20, respectively. Under the optimum operating conditions, complete degradation of the antibiotics occurred in 1 min. In the second part of this study, a bench-scale SBR was operated for 239 days and fed with Fenton-treated wastewater under different operating conditions. BOD_5/COD ratio below 0.40 of the Fenton-treated wastewater had negative effect on the SBR performance. Hydraulic retention time (HRT) of 12 h was found suitable for the SBR and increasing HRT to 24 and 48 h did not significantly improve the SBR efficiency. Statistical analysis (two-way ANOVA) was made on the results to optimize the H_2O_2/Fe^{2+} molar ratio and Fenton reaction time and it was found possible to reduce the Fe^{2+} dose and increase the Fenton reaction time. Under the best operating conditions (H_2O_2/COD molar ratio 2.5, H_2O_2/Fe^{2+} molar ratio 150, Fenton reaction time 120 min and HRT 12 h), the combined Fenton-SBR process efficiency was 89% for sCOD removal and the SBR effluent met the discharge standards. Combined Fenton-SBR is a feasible process for antibiotic wastewater treatment.

1. Introduction

Pharmaceutical compounds including antibiotics and other drugs have been observed in the aquatic environment. These compounds have been detected in surface water [1–3], ground water [3], sewage effluents [4, 5], and even in drinking water [6]. Pharmaceutical compounds can reach the aquatic environment through various sources such as pharmaceutical industry, hospital effluent and excretion from humans and livestock [5, 7, 8].

Among all the pharmaceutical drugs that cause contamination of the environment, antibiotics occupy an important place due to their high consumption rates in both veterinary and human medicine. A problem that may be created by the presence of antibiotics at low concentration in the environment is the development of antibiotic resistant bacteria [9]. In recent years, the incidence of antibiotic resistant bacteria has increased and it is believed that the increase is due to the use of antibiotics [10]. Furthermore, the presence of antibiotics in wastewaters has increased in the past years and their abatement is a challenge.

Advanced oxidation processes (AOPs) are effective in the degradation of most pollutants in wastewater [11]. Oxidation with Fenton's reagent is based on ferrous ion, hydrogen peroxide and hydroxyl radical produced by the catalytic decomposition of hydrogen peroxide in acidic solution [12]. Fenton's reagent has been reported to be effective in the treatment of recalcitrant industrial wastewaters — 76 and 95% COD removal was achieved for amoxicillin wastewater [13] and semiconductor wastewater [14], respectively.

Combining AOP and biological process has received attention in recent years as a promising alternative treatment of recalcitrant wastewater. Using AOP pretreatment is important to improve the biodegradability and produce an effluent that can be treated biologically [15]. Combined Fenton-sequencing batch reactor (SBR) process has been reported to be effective in the treatment of recalcitrant wastewater such as azo dyes [16], semiconductor wastewater [14] and pharmaceutical wastewater [17]. In combined Fenton-SBR process, the degradation by-products of Fenton pretreatment are more readily biodegradable and thus improve the efficiency of SBR.

Sequencing batch reactor (SBR) is a wastewater treatment process based on the principles of the activated sludge process. The operation cycle is divided into five phases: filling, aeration-reaction, settling, decantation and idle. SBR has been successfully employed in the treatment of both municipal and industrial wastewater [18].

In our previous work, degradation of amoxicillin, ampicillin and cloxacillin antibiotics in aqueous solution using Fenton [19], photo-Fenton [20, 21], TiO_2 photocatalysis [22] and ZnO photocatalysis [23] was studied. In addition, technical and economic comparisons among different AOPs as well as simulation of Fenton process for treatment of antibiotic aqueous solution were made [24, 25]. Recently, feasibility of using combined UV/H_2O_2/TiO_2-SBR and photo-Fenton-SBR processes for antibiotic wastewater treatment have been reported [26, 27]. The first part of this

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study examined the effect of operating conditions (H_2O_2/COD molar ratio and H_2O_2/Fe^{2+} molar ratio) on Fenton pretreatment of an antibiotic wastewater containing amoxicillin and cloxacillin. The second part of this study examined the feasibility of using combined Fenton-SBR treatment of the antibiotic wastewater. Effect of Fenton-treated wastewater characteristics under different Fenton operating conditions and SBR hydraulic retention time (HRT) on SBR and combined process efficiency were also evaluated.

2. Materials and methods

2.1. Antibiotics and chemicals

Analytical grade of amoxicillin (AMX) was purchased from Sigma and cloxacillin (CLX) from Fluka, and was used to construct HPLC analytical curves for determination of antibiotic concentration. Potassium dihydrogen phosphate (KH_2PO_4) was purchased from Fluka and acetonitrile HPLC grade from Sigma. Hydrogen peroxide (30% w/w) and ferrous sulfate ($FeSO_4 \cdot 7H_2O$) were purchased from R & M Marketing, Essex, U.K.

2.2. Antibiotic wastewater

Antibiotic wastewater used in this study was obtained from a local antibiotic industry producing amoxicillin and cloxacillin. The antibiotic wastewater characteristics are summarized in Table 1.

2.3. Analytical methods

Antibiotic concentration was determined by HPLC (Agilent 1100 Series), equipped with micro-vacuum degasser (Agilent 1100 Series), quaternary pumps, diode array and multiple wavelength detector (DAD) (Agilent 1100 Series), at wavelength 204 nm. The data were recorded by Chemstation software. The column was ZORBAX SB-C18 (4.6 mm × 150 mm, 5 μm) and the column temperature was set at 60 °C. Mobile phase was made up of 55% buffer solution (0.025 M KH_2PO_4 in ultra purified water) and 45% acetonitrile, and flow rate 0.5 mL/min. Ions present in raw wastewater such as SO_4^{2-} and Cl^- were determined by an ion chromatograph (Metrohm). The eluent phase consisted of 3.2 mM Na_2CO_3 and 1.0 mM $NaHCO_3$. The analytical column was METROSEP A SUPP 5–150 (4.0 mm × 150 mm, 5 μm). The flow rate was 0.7 mL/min and the temperature was 20 °C. Total phosphorus (TP), ammonia nitrogen (NH_3–N), nitrate nitrogen (NO_3^-–N) and chemical oxygen demand (COD) were determined according to the Standard Methods [28]. The sample was filtered through 0.45 μm membrane filter for determination of soluble chemical oxygen demand (sCOD). When the sample contained hydrogen peroxide (H_2O_2), to reduce interference in COD determination pH was increased to above 10 to decompose hydrogen peroxide to oxygen and water [29]. The pH was measured using a pH meter (HACH sensION 4) and a pH probe (HACH platinum series pH electrode model 51910, HACH Company, USA). Biodegradability was measured by 5-day biochemical oxygen demand (BOD_5) test according to the Standard Methods [28]. Dissolved oxygen (DO) was measured by an YSI 5000 dissolved oxygen meter. The seed for BOD_5 test was obtained from a municipal wastewater treatment plant. TOC analyzer (Model 1010; O & I Analytical) was used for determining dissolved organic carbon (DOC). Determination of total suspended solids (TSS) and volatile suspended solids (VSS) were carried out according to the Standard Methods [28].

2.4. Experimental setup and procedure

Fig. 1 shows a schematic of the combined Fenton-SBR process. The treatment was accomplished in two stages, Fenton process as stage 1 and aerobic sequencing batch reactor (SBR) as stage 2.

2.4.1. Stage 1: Fenton process

Batch experiments were conducted using a 2.2 L Pyrex reactor with 2000 mL of the antibiotic wastewater. The required amount of iron ($FeSO_4 \cdot 7H_2O$) was added to the wastewater and mixed by a magnetic stirrer to ensure complete homogeneity during the reaction. Thereafter, necessary amount of hydrogen peroxide (H_2O_2) was added to the mixture with simultaneous adjustment to the required pH value by H_2SO_4. The time at which hydrogen peroxide was added to the mixture was considered the beginning of the experiment. The reaction was allowed to continue for the required time. Thereafter, pH was increased to above 10 for iron precipitation and decomposing residual H_2O_2 [29]. Precipitated iron was separated from the reactor and the supernatant was used to feed the SBR after pH adjustment to 6.8–7.2. Samples were taken and filtered through a 0.45 μm membrane syringe filter for determination of soluble chemical oxygen demand (sCOD), biochemical oxygen demand (BOD_5) and dissolved organic carbon (DOC), and filtered through a 0.20 μm membrane syringe filter for measurement of antibiotic concentration by HPLC.

2.4.2. Stage 2: aerobic sequencing batch reactor (SBR)

The operating liquid volume of the 2-L SBR was 1.5 L and depth 20 cm. The reactor was equipped with an air pump and air diffuser to keep DO above 3 mg/L, and stirring plate and stirrer bar (200 rpm) for mixing. Feeding and decanting were performed using two peristaltic pumps. The cycle period was divided into five phases: filling (0.25 h), aeration-reaction (variable), settling (1.25 h), decanting (0.25 h) and idle (0.25 h). The cycle was repeated 6–9 times as necessary to allow cell acclimation and/or to obtain repetitive results. Daily analysis of sCOD and DOC of influent and effluent was carried out. Concentration of mixed liquor suspended solids (MLSS) and mixed liquor volatile suspended solids (MLVSS) were monitored throughout the operation.

2.4.3. Start up of SBR

The SBR was inoculated with 200 mL of sludge from the aeration tank of a municipal wastewater treatment plant. Concentration of MLSS in the reactor after inoculation was 2300 mg/L. For acclimation of the biomass, an HRT 2 of days was used and the Fenton-treated antibiotic wastewater was mixed with domestic wastewater at ratios of

Table 1
Antibiotic wastewater characteristics.

Parameter	Value	Number of samples	Range	Parameter	Number of samples	Value
Amoxicillin (mg/L)	138 ± 5	4	145–131	TP (mg/L)	1	7.5
Cloxacillin (mg/L)	84 ± 4	4	91–78	NO_3^-–N (mg/L)	1	5.1
COD (mg/L)	675 ± 20	30	710–620	NH_3–N (mg/L)	1	11.1
sCOD (mg/L)	575 ± 20	30	520–600	SO_4^{2-} (mg/L)	1	0.7
DOC (mg/L)	145 ± 5	22	155–138	Cl^- (mg/L)	1	5.92
BOD_5(mg/L)	70 ± 10	15	89–55	Turbidity (NTU)	1	45
pH	6.8	–	6.7–6.9	Conductivity (μS/cm)	1	125
TSS (mg/L)	70 ± 5	5	85–62			