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Treatment of recalcitrant organic silicone wastewater by fluidized-bed Fenton process

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A B S T R A C T

To achieve an enhanced degradation of recalcitrant organic silicone wastewater in the fluidized-bed Fenton process was attempted using three different carrier substrates [quartz sand, brick particles and granular activated carbon (GAC)]. Quartz sand was determined as the best carrier substrate due to better reactor bed expansion, fluidized state and pollutant removal rate than the brick particles and GAC. The iron oxide components such as FeOOH, FeO, Fe_2O_3, and Fe_3O_4 were found on the surface of coated quartz sand using X-ray diffraction (XRD) analysis. The optimal hydraulic retention time (HRT) of 60 min was determined based on COD and TOC removal rate. Further, the optimal operating conditions of pH 3.5, H_2O_2/COD (mass ratio) 2.6:1, H_2O_2/Fe^{2+} (molar ratio) 13.6:1 and quartz sand filling rate of 35% were determined by the orthogonal experiments for the recalcitrant treatment. In the fluidized-bed Fenton process treated effluent COD value was 40 mg/L and TOC value was 20 mg/L, with a removal rate of 95% and 85%, respectively. Compared to the traditional Fenton process the COD and TOC removal rates were found to increase by 20% and 15% respectively. Furthermore, the total iron removal rate was higher than conventional Fenton process, which significantly reduced the iron concentration in effluent.

1. Introduction

The organic silicone has numerous potential industrial applications such as in cosmetic, rubber coating purpose and also used as an antifoam agent in fermentation processes [1,2]. Due to the vast important applications of silicone, the production of silicone is increased hugely worldwide. At present the construction and expansion of organic silicone monomer production plants are augmented in China, and thus resulted in the production of huge quantity of silicone wastewater.

Silicone wastewater is containing huge concentration of organic halide (AOX), silicone polymers, organic pollutants (benzene and toluene), chemical oxygen demand (COD), total organic carbon (TOC), and other toxic metals, which makes this wastewater as non-biodegradable (recalcitrant) in nature. Most of the small-scale silicone manufacturing industries use the biological treatment process, which lead to incomplete removal of organic compounds from the wastewater. Direct release of partially treated wastewater into municipal wastewater treatment plant (WWTP) is hugely affecting the performance of municipal WWTP operational process. Releasing this wastewater into the receiving environments causes a huge problem in the aquatic environment and health of humans. To attain wastewater discharge standards and protect environment, other processes like chemical precipitation, adsorption, flocculation, coagulation, ozonation [3], oxidation and Fenton oxidation process were widely used for further treatment of recalcitrant wastewater [4,5].

The conventional Fenton (Fe^{2+}/H_2O_2) process has been widely used to treat the recalcitrant wastewater due to its strong oxidation property, low capital cost, easy operation and formation of non-toxic by-products [6]. However, increased utilization rate of Fe^{2+} and H_2O_2, reduced production of ferric hydroxide [$Fe(OH)_3$] waste sludge in Fenton process are being paid more attention.

Hence, the objective of this study is to use FB-Fenton to treat the silicone effluent wastewater, which was collected from outlet of conventional activated sludge process, with high content of residual recalcitrant organic compounds. Formation of iron oxide components on the surface of fluidized carrier, optimization of operational parameters to attain increased organic compounds removal rate and ferric sludge waste removal were evaluated.

FB-Fenton was successfully used in degradation of azo-dye [7], nitrobenzene [8,9], textile wastewater [10], 2,4-dichlorophenol [11], adsorption of metals like Cu^{2+} [13], and also used in treatment

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of chemicals like aniline [14], monoethanolamine and phosphate [15], acetaminophen [16], o-toluidine [17], and 2,6-DMA [18]. This study reports the first time use of FB-Fenton process for the treatment of silicone effluent wastewater. This treatment was attempted due to its combined homogeneous Fenton oxidation (Fe^{2+}/H_2O_2), heterogeneous oxidation (H_2O_2/FeOOH) process, fluidized bed crystallization, and reductive dissolution of iron oxides. Fluidized-bed could promote both the chemical reaction and mass transfer rate, due to close contact between the different phases in the fluidized-bed and its continuous operation, which augments the organic removal rate. Furthermore, the generated Fe^{3+} could crystallize or precipitate and grow on the carrier surface, which reduces the ferric hydroxide sludge [12].

2. Materials and methods

2.1. Wastewater collection

The silicone wastewater used in this study was collected from the effluent (treated wastewater from Silicone Rubber Chemical Plant of Hangzhou city, Zhejiang, China) after the conventional activated sludge treatment process. The collected wastewater was immediately used for the sample characteristics and within 6 h of sample collection the experiments were conducted. The collected wastewater characteristics (Table 1) such as COD, BOD_5, TOC, pH, and turbidity measurements were conducted.

2.2. Materials procurement

The analytical reagents NaOH (5 mol/L) and H_2SO_4 (3.1 mol/L) were purchased from WenZhou Chemical Co., Ltd, China. The ferrous sulfate ($FeSO_4{\cdot}7H_2SO_4$) and hydrogen peroxide (H_2O_2, 30%) were purchased from JiangSu Fine Chemical Co., Ltd, JiangSu, China. The quartz sand, brick particles and granular activated carbon (GAC) were used as fluidized (carrier) materials. The diameters of the three carriers used were 0.5, 0.8 and 0.7 mm, respectively. All three carriers had been soaked in water for 24 h before use. All chemicals used in this study were of analytical grade.

2.3. Fluidized-bed reactor setup

The experimental apparatus operated in this study was shown in Fig. 1. The reactor was made of plexiglass column with a diameter of 8 cm and a height of 78 cm. The total volume of the reactor was 3.92 L. The reactor bottom was packed with a ceramsite (2–5 mm in size) up to 6 cm height and then topped with 14 cm height of carrier substrate prior to conduct the experiment.

It is important to mention here that, in this study we have evaluated three kind of carrier substrates (quartz sand, GAC and brick particles) in order to investigate the improvement in the reactor performance and pollutants removal capacity from the silicone effluent wastewater. The characteristics of carrier substrates used were as follows: quartz sand (0.5 mm in size, colorless in nature), GAC (0.7 mm in size, black granular) and bricks particles were obtained from near the University (ZJUT, Hangzhou, China) construction sites (0.8 mm in size, brown).

Table 1
Characteristics of wastewater used in this experimental study.

Wastewater characteristics	Range
COD	370–490 mg/L
TOC	80–120 mg/L
BOD_5	0
Turbidity	7.36–14.2 NTU
pH	6.3–7.5

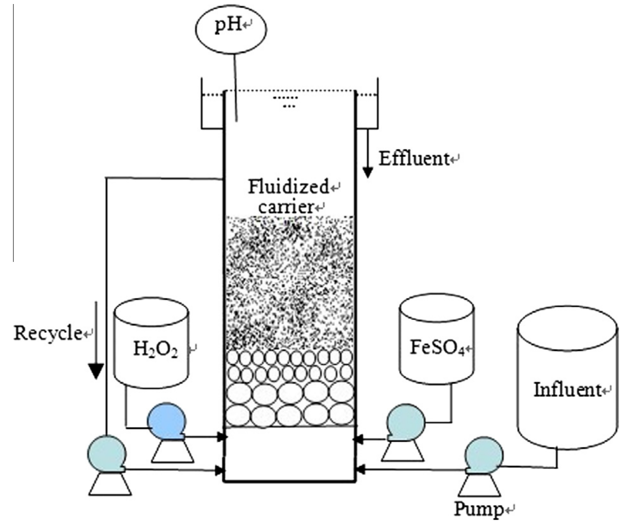

Fig. 1. The schematic diagram of fluidized-bed Fenton.

Once the reactor was filled with one kind of carrier substrate the wastewater was introduced into the bottom of the reactor via peristaltic pump. The initial wastewater pH (6.3–7.5) was adjusted to reactor operating pH of 3.5. Then, the Fenton reagent was pumped into the reactor from the bottom side using a micro-peristaltic pump with a flow rate of 3 mL/h. The internal circulation rate was maintained 4 times higher than the influent feeding rate in order to maintain 50% more bed expansion in the reactor. A stable pH of 3.5 was maintained in the reactor by adding H_2SO_4 or NaOH during the process operation.

Complete coating of various carrier substrates (quartz sand, GAC and brick particles) with Iron oxide was achieved in the reactor. The coating period was varied with each carrier substrate in a reactor-operating period of 8 to 18 days. In case of quartz sand the complete coating was attained at 12 days, whereas in the brick particles and GAC, the complete coating was obtained in 8 and 18 days, respectively.

2.4. Experimental methods

2.4.1. Coating of carrier substrates

The complete coating of carrier substrates with Iron oxides was achieved in the silicone wastewater. The influent wastewater was pumped at a rate of 0.6 L/h, which contained COD 390 mg/L, H_2O_2/Fe^{2+} (molar ratio) 1:2 and maintained a stable pH of 3.5. In order to achieve a complete and uniform coating of carrier substrates with iron oxide in a shorter time period a small quantity (1–2 g) of iron powder (Fe_3O_4) was introduced in the reactor manually. The reactor was operated in a similar condition as mentioned above by varying the three kinds of carrier substrates (quartz sand, GAC and brick particles), except the time required for the complete coating of iron oxides on the surface of each carrier.

After the carrier was completely coated with iron oxides, the best carrier substrate was selected based on following aspects, such as time required for complete coating, bed expansion rate, the fluidized state, and the COD and TOC removal rate (at the optimal conditions). Further, the complete coating of carrier substrates were validated by examining the surface of carrier substrates before and after coating by 3D microscope, SEM and XRD analysis.