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Remedying acidification and deterioration of aerobic post-treatment of digested effluent by using zero-valent iron



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G R A P H I C A L A B S T R A C T



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ABSTRACT

This study presents a novel strategy for remedying acidification and improving the removal efficiency of pollutants from digested effluent by using Zero-Valent Iron (iron scraps) in a sequencing batch reactor. Through this strategy, the pH increased from 5.7 (mixed liquid in the reactor without added ZVI) to 7.8 (reactors with added ZVI) because of Fe^0 oxidation and NO_3^- reduction. The removal efficiencies of COD increased from 11.5% to 77.5% because of oxidation of ferric ion and 'OH produced in chemical reactions of ZVI with oxygen and because of flocculation of iron ions. The removal efficiencies of total nitrogen rose from 1.83% to 93.3% probably because of autotrophic denitrification using electron donors produced by the corrosion of iron, as well as the favorable conditions for anammox due to iron ions. Total phosphorus increased from -25.8% to 77.1% because of the increase in pH and the precipitation with iron ions.

1. Introduction

In some areas, small pig farms have rapidly expanded into large centralized livestock farms in recent years, resulting in the production of abundant animal feces and urine in small geographic areas and causing serious environmental problems. In areas around livestock farms, swine wastewater has been considered a major pollution source. Anaerobic digestion has been commonly used to treat swine wastewater with high levels of organic pollutants because it can remove organic pollutants effectively, reduce the organic load for post-treatment, and produce biogas (Bernet and Béline, 2009; Yang et al., 2016). Digested effluent from the anaerobic digestion still contains considerable

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amounts of organic matter, phosphorus, and high concentrations of ammonia. Aerobic post-treatment is thus required to remove N, P, and residual organic matter in order to meet discharge standardsfor land-limited swine farms. However, a number of difficulties have been encountered with aerobic post-treatment. The performance of direct aerobic treatment of digested effluent is very poor, having removal efficiency of 10%–60% and 50%–80% for COD and $\rm NH_4^+$ -N, respectively. Little of the total phosphorus (TP) was removed because of the acidification during aerobic treatment (Deng et al., 2008; Urbinati and Oliveira, 2014).

The acidification in aerobic treatment process is due to imbalance of alkalinity in the nitrification/denitrification process. In aerobic biological treatment systems, three main factors affect the alkalinity balance: influent alkali, consumption of alkali by the conversion of ammonia nitrogen in the nitrification phase, and production of alkali in the denitrification phase. When the alkalinity of the influent and the alkali produced in denitrification cannot balance the alkali consumed in nitrification, the pH decreases. Solutions to the acidification problems include addition of alkali (Anup et al., 2013; Deng et al., 2008), direct increase of the pH; and addition of organic electron donors such as glucose (Kuo et al., 2015), methanol (Bortone et al., 1992), acetate (Obaja et al., 2003), or raw swine wastewater (Deng et al., 2008; Yang et al., 2016). Addition of organic electron donors to the digested effluent can promote biological denitrification, resulting in production of enough alkali. However, the costs of added alkali and organic electron donors such as glucose, methanol, and acetate are high. The addition of raw swine wastewater would decrease the production of biogas and increase aeration.

Autotrophic denitrification, which uses inorganic matter such as sulfur compounds (Mohseni-Bandpi et al., 2013), hydrogen (Rezania et al., 2007), or zero-valent iron (ZVI) (Wang et al., 2012) as electron donors, has attracted much attention because of its low sludge production and good applicability to wastewater with low C/N ratio. Compared with the agents used in several methods that support autotrophic denitrification, hydrogen and sulfur compounds has relatively high cost and disadvantages (the explosive properties of hydrogen, for example) that limit their large-scale use (Wang et al., 2012). Autotrophic denitrification using ZVI has been studied by many groups because of its low cost (Deng et al., 2016; Yi et al., 2010; Zhang et al., 2010). They have demonstrated that nitrate and nitrite can be completely reduced by metallic iron under anoxic and aerobic conditions. However, ferrous hydroxide and other protective layers of the Fe⁰ surface chemically inhibit the reaction. Nevertheless, nitrate can be reduced into ammonia by ZVI. To our knowledge, ZVI has been used in previous studies only to remove nitrate and nitrite. Little attention has been paid to the removal of ammonia using Fe⁰. In particular, remedying the acidification and improving the removal efficiency of organic material, nitrogen, and phosphorus in aerobic post-treatment of digested effluent have not been reported.

Iron scraps (IS) are a major type of solid waste that are generated by steel plants and machine-processing factories, and they cost nearly one-third the price of iron (Deng et al., 2016; Siciliano, 2015). According to current government regulations, unused IS must be recovered by steel mills (Deng et al., 2016). In this regard, the reuse of IS in autotrophic

denitrification can reduce the cost of nitrogen removal while simultaneously reducing the amount of IS.

In the current work, we propose a remedial method for the acidification and the deterioration of aerobic post-treatment of digested effluent by adding IS to a sequencing batch reactor (SBR). The improvement of the removal efficiency of pollutants from the digested effluent from a swine farm was investigated. The findings of this work may provide a novel method for the complete removal of ammonia nitrogen, as well as the simultaneous removal of organic material, nitrogen, and phosphorus from wastewater with low COD/N ratio.

2. Materials and methods

2.1. Aerobic reactor

Aerobic treatment of digested effluent was accomplished in SBRs. Each SBR consisted of an acrylic container (12 cm diameter, 100 cm height) having a total volume of 11.3 L and a working volume of 10 L. Air was supplied using an air compressor (model ACO-001; Guangdong Ri Sheng Group Co. Ltd., Raoping, China) connected to an aeration stone placed at the bottom of the reactor. A peristaltic pump (model BQ50-1J-A; Baoding Longer Precision Pump Co., Ltd., Baoding, China) was used for feeding influent and discharging effluent.

2.2. Materials

2.2.1. Sludge

The aerobic seed sludge of the SBR was from the aeration tank of a wastewater treatment plant in Shuangliu County in Sichuan Province, China.

2.2.2. Wastewater

We used the digested effluent of swine wastewater as model wastewater. The digested effluent was collected from a biogas plant that treats swine wastewater in Jianyang County, Sichuan Province.

2.2.3. Iron scraps (IS)

ZVI in this experiment was IS collected from a mechanical processing factory. It had low specific surface area, a length of 50-100 mm, a width of 1-5 mm, and a thickness of 1-2 mm. Its chemical composition is shown in Table 1.

2.3. Experimental design

A 20 L aerobic reactor was inoculated with 2 L of aerobic sludge. At first, the digested effluent was treated in an aerobic reactor until the mixed liquid was acidified. The acidified liquid was then equally divided into two parts. Every part was transferred into a SBR (Fig. 1a). The concentration of biomass in the reactor was 1727 mg/L. Afterward, 200 g of iron scraps (IS) was transferred to the bottom of one SBR. This SBR is referred to an IS reactor; the other SBR (without IS) is referred to a CG reactor. Aeration was regulated to guarantee a dissolved oxygen (DO) concentration greater than 2.0 mg/L at the end of the aeration stage. Each reactor had two 12 h sequences daily, each consisting of

Table 1

The chemical composition of the iron scraps and sludge (%).

*										
Item	Fe	0	С	Р	Ca	Si	Mg	К	S	Т
Iron scraps before reaction Iron scraps after reaction Sludge of CG [*] Sludge of IS ^{**} :	96.52 45.34 1.72 15.14	0 35.44 33.71 42.19	3.48 10.90 42.5 21.65	0 3.11 2.54 6.88	0 2.2 16.41 11.08	0 1.04 0.53 0.75	0 0.81 1.16 1.15	0 0 0.37 0.44	0 0.43 0.77 0.54	100 99.27 99.34 99.82

 * CG: Control reactor without added iron scraps

** IS: Treatment reactor with added iron scraps

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