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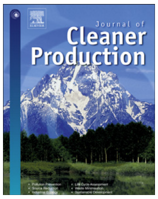

Improving the dewaterability of citric acid wastewater sludge by Fenton treatment

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ABSTRACT

The citric acid wastewater treatment produces a large quantity of sludge, which contains more organic matter and is more difficult to be dewatered by mechanical devices, compared to the municipal wastewater sludge. Fenton conditioning was a highly effective and affordable approach to improving the dewaterability of citric acid wastewater sludge while preserving the fertilizing properties. The optimal condition of Fenton treatment was pH 5.0, H_2O_2 dose of 20 mg g^{-1} dry solids, and Fe^{2+} dose of 80 mg g^{-1} dry solids. Capillary suction time was reduced from 19.3 s to 10.7 s, and the water content of sludge cake was reduced from 85.3% to 73.8% under this condition. There was no significant difference in capillary suction time and the water content of sludge cake reduction by Fenton treatment between the lab-scale and scale-up experiments. The mechanism investigations of extracellular polymeric substances, zeta-potential, particles size, and morphological changes of the sludge samples conditioned by Fenton treatment under the optimal condition demonstrated that the enhanced coagulation by Fenton treatment was the mechanism dominating the sludge dewaterability improvement. Most critically to the citric acid wastewater sludge, the majority of fertilizing properties of the sludge were preserved after Fenton treatment. The volatile suspended solids, total organic carbon, total nitrogen, potassium and phosphorus were mostly maintained in the solid phase. The cost of Fenton reagents under the optimal condition was approximately 49 US$/t dry solids, which made Fenton treatment a cost reasonable approach to citric acid wastewater sludge conditioning.

1. Introduction

Citric acid is a tricarboxylic acid ($C_6H_8O_7 \cdot H_2O$), which is widely used in food, beverage, cleaning product, and some metallurgical and dyeing industries (Angumeenal and Venkappayya, 2013). The global demand of citric acid exceeded 2 million tons in 2015, ranking it the top employed organic acid in the world (Ciriminna et al., 2017). Citric acid is produced through fermentation processes of crops such as corns and yams, associated with the production of 50–60 tons of wastewater per ton citric acid (Li et al., 2013). The wastewater from citric acid production contains a higher biochemical oxygen demand (BOD) than municipal wastewater, resulting in a high volume of sludge throughout the activated sludge processes. This waste sludge is also more difficult to dewater because of the high organic content (Skinner et al., 2015). The large volume of wet sludge thus brings considerable difficulties in transportation and disposal, and results in a high management cost, hence increasing sludge dewaterability is crucial.

The sludge dewatering has been regarded as the most cost intensive step in wastewater treatment, as it accounts for 50–60% of the operating cost (Egemen et al., 2001). A conventional sludge conditioning process using organic polymers facilitates the flocculation and sedimentation of solid particles in sludge by charge neutralization and adsorption, and improves sludge dewatering effectiveness and efficiency (Mowla et al., 2013). However, high

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Abbreviations

BOD	Biochemical oxygen demand
$^{\cdot}$OH	Hydroxyl radicals
Wsc	Water content of sludge cake
DS	Dry solids
TSS	Total suspended solids
VSS	Volatile suspended solids
S/COD	Soluble/ Chemical oxygen demand
CST	Capillary suction time
RSM	Response surface methodology
BBD	Box-Behnken Design
EPS	Extracellular polymeric substances
S-EPS	Slime extracellular polymeric substances
LB-EPS	Loosely bound extracellular polymeric substances
TB-EPS	Tightly bound extracellular polymeric substances
SEM	Scanning electron microscope
TOC	Total organic carbon
ANOVA	Analysis of variance
TS	Total solids
VS	Volatile solids

moisture content (as high as 80%) still remains in the dewatered sludge through mechanical dewatering devices (Citeau et al., 2011). Polymer application is also limited because of the adverse effects on the environment and human health (Bolto and Gregory, 2007).

Fenton treatment had been given great attention as it may work as a strong oxidant by producing hydroxyl radicals (·OH) through iron-catalyzed decomposition of H_2O_2, or serve as a coagulant when the added Fe^{2+} reaches a higher level than H_2O_2 (Neyens and Baeyens, 2003). Fenton treatment has been widely applied in wastewater treatment to remove recalcitrant organic matter (Rodriguez et al., 2016; Pliego et al., 2015). Moreover, its application in waste management has also been identified. For example, Fenton treatment was reported to successfully stabilize anaerobic digestate of municipal solid waste (Quina et al., 2015) and wastewater activated sludge (Gholikandi et al., 2017). In addition, a few studies have demonstrated that Fenton treatment was able to improve the dewaterability of municipal wastewater sludge. It was reported that the water content of sludge cake (W_{sc}) of 71.3–75.1% could be achieved by the addition of Fenton reagents at concentrations of 720 mg g^{-1} dry solids (DS) Fe^{2+} and 360 mg g^{-1} DS H_2O_2 (He et al., 2015), or at pH 2.0–2.5 (Lu et al., 2003). In combination with other regents, e.g., lime and/or skeleton builders or surfactants, the required amount of Fenton reagents reduced and W_{sc} could be reduced further to less than 60% (Liu et al., 2013; Zhang et al., 2014; Mo et al., 2015; Yu et al., 2016; Xing et al., 2017).

Despite that Fenton treatment has been demonstrated to be effective for municipal wastewater sludge conditioning, its potential for citric acid wastewater sludge conditioning has never been validated. With the higher organic load in the citric acid wastewater, the property of its sludge can be quite different from that of municipal wastewaters', resulting in discrepancies in Fenton treatment outcomes. In addition, as the dewatered citric acid wastewater sludge is mainly sent for making fertilizers, additional materials (i.e. lime or surfactants) during the conditioning process which may lead to secondary pollution must be avoided. Moreover, preservation of the fertilizing properties during the sludge conditioning is of primary concerns. Therefore, an understanding of Fenton treatment on the above issues, and an optimization of Fenton treatment conditions are essential for validating its application for conditioning citric acid wastewater sludge.

The objectives of this study are to (a) investigate the efficacy of Fenton treatment on improvement of the dewaterability of the citric acid wastewater sludge, (b) examine the mechanisms of Fenton treatment on conditioning the citric acid wastewater sludge, (c) validate the fertilizing property preservation of the conditioned sludge, and (d) analyze the cost of the reagents.

2. Material and methods

2.1. Sludge samples and chemicals

Raw sludge samples were collected from the secondary sedimentation tank from a citric acid production company in Shandong province, China. Samples were stored at 4 °C before use. The supernatant was decanted, and the dense gravity thickened sludge was used. Raw sludge was homogenized by rapid mixing before sample collection for measurements and experiments. The properties of raw sludge were illustrated in Table 1. The measurements of water content, total suspended solids (TSS), volatile suspended solids (VSS), and soluble chemical oxygen demand (SCOD) were conducted in accordance with the Standard Methods (American Public Health Association, 2005). The capillary suction time (CST) and W_{sc} were measured as described in Section 2.2.3.

In the lab-scale and scale-up experiments, sulfuric acid (H_2SO_4) (analytical grade) and sodium hydroxide (NaOH) (analytical grade) were used for pH adjustment. Ferrous sulfate heptahydrate ($FeSO_4·7H_2O$) (analytical grade) and hydrogen peroxide (H_2O_2) (30% wt, analytical grade) were used as Fenton reagents. Chemicals were purchased from Sinopharm Chemical Reagent Co. Ltd., China. The pH was determined using a digital pH meter (HQ440d, Hach, USA).

2.2. Experimental procedures

2.2.1. Lab-scale experiments

The homogenized raw sludge with a volume of 100 mL was poured into a 250 mL beaker, with the addition of 4 mol L^{-1} H_2SO_4 for pH adjustment. A desired amount of $FeSO_4·7H_2O$ was then added and stirred for 3 min at 200 rpm. The Fenton reaction was subsequently initiated by the addition of H_2O_2, with the stirring of 200 rpm for 60 min. Upon completion of the reaction, the sample was neutralized to pH 7.2–7.3 using 4 mol L^{-1} NaOH. The factorial design with 3-factor 3-level using Box-Behnken Design (BBD) (Montgomery, 1991) with the response of CST reduction is shown in Table 2. Due to the health and safety considerations in the citric acid wastewater treatment processes, corrosively acidic reaction conditions were strongly advised to be avoided. Despite that Fenton reaction was reported to be more effective at lower pHs (pH 2–3) (Neyens et al., 2002; Mo et al., 2015), a few studies claimed that Fenton conditioning was also effective at near neutral pH (Liu et al., 2012; Tony et al., 2008; Yu et al., 2016). The pH range was thus set to be 5.0–7.0 for the BBD experiment. Preliminary experiments showed that Fe^{2+} doses higher than 80 mg g^{-1} DS resulted in brownish color and increasing thickness of the sludge. Although the limits of iron in discharged sludge and in organic fertilizers are not regulated in China, the highest level of Fe^{2+} dose was controlled at 80 mg g^{-1} DS for the BBD experiment, from the esthetic and human perceptive perspectives. The statistical analysis was processed using the Design Expert 8.0.6 software (Stat-Ease Inc.).

2.2.2. Scale-up experiments

The optimal treatment condition obtained by the BBD experiment was applied in a scale-up lab experiment using a 12-L polyethylene reactor. Homogenized raw sludge with a volume of 10 L was added into the reactor, followed by pH adjustment and the addition of $FeSO_4$ $7H_2O$. Mixing was started by two aeration