Chemical Engineering Journal 272 (2015) 128–134

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

A Fenton-like process for the enhanced activated sludge dewatering

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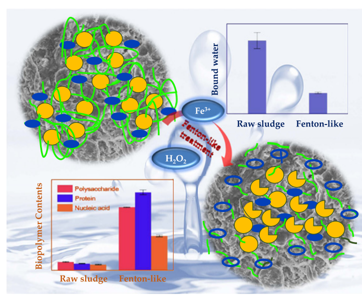
HIGHLIGHTS

- A Fenton-like reaction was proposed as an effective sludge dewatering process.
- Uniform design was used to optimize this sludge dewatering process.
- The mechanism for the enhanced dewatering performance was elucidated.

GRAPHICAL ABSTRACT



The mechanism of the enhanced sludge dewatering by Fenton -like treatment

ARTICLE INFO

Article history:
Received 29 November 2014
Received in revised form 7 March 2015
Accepted 9 March 2015
Available online 16 March 2015

Keywords:
Activated sludge
Dewatering
Extracellular polymeric substances (EPS)
Fenton-like peroxidation
Uniform design

ABSTRACT

The presence of high moisture content in sewage sludge aggravates the disposal costs and restricts its application. Sewage sludge is traditionally conditioned by dosing organic/inorganic chemicals. However, after the treatment, the moisture content and inorganic solid mass remain to be a high level. In this work, a Fenton-like dewatering process, i.e., a combination of sulfuric acid, hydrogen peroxide and ferric sulfate, was developed. Uniform design was used to optimize the composite conditions, and the effects of Fenton-like treatment on sludge dewatering were examined. The results show that, after the treatment of the Fenton-like reaction, the moisture content of sludge cake and the dry solid mass decreased from 80.0% to 66.1% and from 12.9 to 10.6 g/L, respectively. The mechanism for the enhanced dewatering performance was explored, and the degradation of abundant extracellular polymeric substances, the lysis of the sludge cells, and the release of bound water and typical metals within the sludge flocs were found to be mainly responsible for the enhanced dewatering performance. In addition, a surface thermodynamic analysis with the extended DLVO theory shows that the higher hydrophobicity and the less stable sludge flocs also contributed to the decrease in moisture content. Our results confirm that such a Fenton-like treatment exhibited excellent performance in enhancing sludge dewatering and metal leaching and is a promising pretreatment approach for sludge disposal.

1. Introduction

Huge quantities of waste sewage sludge generated from municipal wastewater treatment plants has attracted wide concerns as the transport of large volumes of excess sludge and the subsequent disposal cause great economic and environmental burden [1]. In many wastewater treatment processes, dewatering operation is the bottleneck of their sludge disposal systems. The water content of raw sludge is about 99%, and could be reduced to about 80% after the sludge treatment with the traditional chemical conditioners. Also, the increased volume of dewatered sludge after inorganic conditioner treatment is a problem to be resolved. Dewatering sludge to a high DS% (percentage dry solids content) of 40% or above is crucial for the cost-effective reduction in volume. Thus, reducing moisture content and sludge inorganic

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http://dx.doi.org/10.1016/j.cej.2015.03.034
1385-8947/

substances mass through conditioning before mechanical dewatering is essential for the further sludge disposal. However, it is well known that it is very difficult to further dewater sewage sludge [1–3].

For a few decades, efforts have been made to improving the sludge dewaterability and revealing its mechanisms. It is found that the extracellular polymeric substances (EPS), which occupy a significant fraction of sludge mass, play a key role in binding a large volume of water (i.e., bound water) [2,4,5]. The negatively charged EPS network plays a significant role in maintaining hydrated sludge structure and could effectively prevent the release of water and internal components (e.g., heavy metals) [6]. As a result, dewatered sludge cake contains a high moisture contents and a large sludge mass to dispose [4,7,8]. Therefore, the degradation of EPS and the lysis of sludge micro-organisms are found to be significant in enhancing the release of water from sludge flocs [9]. Many conditioning techniques, such as ultrasonic pretreatment [10], microwave irradiation and thermochemical [11], etc., have been introduced to degrade EPS and promote sludge dewatering.

Among the conditioning techniques, Fenton reaction involves powerful chemical oxidation and can degrades EPS, and thus have been studied and proven to be effective in sludge dewatering [12,13]. The powerful oxidizing ability generated from the following reaction:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^{\cdot} + OH^- \quad (1)$$

Moreover, the newly formed ferric ions may catalyze hydrogen peroxide, the reactions are shown in Eqs. (2) and (3):

$$Fe^{3+} + H_2O_2 \leftrightarrow Fe{-}OOH^{2+} + H^+ \quad (2)$$

$$Fe{-}OOH^{2+} \rightarrow HO_2^{\cdot} + Fe^{2+} \quad (3)$$

Drawbacks associated with the use of Fenton's reagent, even with the use of common chemical polyelectrolytes such as cationic polyacrylamide (CPAM), are the high moisture content and inorganic solid mass, which are unfavorable for the subsequent disposal or reutilization of the dewatered sludge cake [3].

Compared to the Fenton reaction, Fenton-like reactions mainly refer to the reaction of hydrogen peroxide with ferric ions, as shown in Reactions (2) and (3) [14]. Previous studies have demonstrated that Fenton-like peroxide could oxidize pollutants such as chlorophenoxy herbicide and trichloroethene [15,16]. Besides, it could effectively degrade bacteria, resulting in the disinfection of wastewater effluents [17]. This indicates that the Fenton-like reactions have a high oxidicability. However, information about the utilization of Fenton-like reactions for sludge dewatering is very limited. The effects of Fenton-like reactions on sludge moisture content and dry solid mass are largely unknown.

In this work, Fenton-like reaction was introduced to enhance sludge dewatering performance. Sulfuric acid (H_2SO_4) was used to adjust pH, hydrogen peroxide (H_2O_2) was added to reduce odors, degrade biopolymers, and subsequently release the bound water and metals within sludge. In addition, ferric sulfate ($Fe_2(SO_4)_3$) was dosed to speed up the filtration and maximize the metal solubilization. To optimize the dosage of Fenton-like conditioner, the uniform design (UD) was employed with the water content of sludge cake as the response [18]. To provide more insights into the dewatering mechanism, the release of biopolymers from sludge, the bound water content in dewatered sludge cake and the typical metal leaching were analyzed. Extended-DLVO approach was also introduced to quantify the impacts of different treatments on sludge aggregation and dewatering behaviors from a thermodynamic point of view. Our results verify that the Fenton-like conditioner could reduce the water content obviously and promote the release of metals. Also, the degradation of abundant EPS and the lysis of the sludge cells were proven to be mainly responsible for the release of bound water and metals, which is beneficial for the agricultural application of sludge cake.

2. Materials and methods

2.1. Chemicals and raw sludge

$Fe_2(SO_4)_3$, H_2O_2 (30%), H_2SO_4 (98%), perchloric acid ($HClO_4$), hydrofluoric acid (HF) and nitric acid (HNO_3) purchased from Shanghai Chemical Reagent Co., China, were of analytical reagent grade and used without further purification. Raw activated sludge was collected from sludge digestion tanks in the Wangtang Municipal Wastewater Treatment Plant (Hefei, China), which has a capacity of 180,000 m^3 of wastewater per day. To minimize the microbial activity, the collected sludge samples were stored in a refrigerator at 4 °C until future use (less than 2 weeks). The characteristics of the raw activated sludge were measured in triplicate and the average values are shown in Table 1.

2.2. Sludge conditioning and dewatering

For each conditioning test, H_2SO_4 at a concentration of 1 M was added to a 100 mL portion of sludge to adjust the pH to the designed value. Then, H_2O_2 was dosed into the mixture. After magnetic stirred at 100 rpm for 2 h, a known amount of $Fe_2(SO_4)_3$ was added to the oxidized sludge, and the mixture was stirred at the same speed for 1 h. When the Fenton-like peroxidation was completed, the sludge was dewatered by the Buchner funnel test [19]. The specific resistance to filtration (SRF), the time to filter (TTF), volatile suspended solids (VSS) and the water content of the dewatered sludge cake were measured to characterize the filterability of the sludge samples. The SRF (m/kg) was measured based on a previous report [20]. The TTF (s) is defined as the time required to collect half of the volume of the raw sludge sample, and measured using a reported method [19]. The VSS was determined by dried sludge cake in 600 °C ovens according to the Standard Methods [21]. The moisture content of the filtered sludge cake was calculated according to the following equation: $(W_1 - W_2)/W_1 \times 100\%$, where W_1 is the weight of wet cake after filtration and W_2 is the weight of filter cake dried at 105 °C for 2.5 h [21].

2.3. UD of the experiments

UD was used for the optimization of the Fenton-like reaction for dewatering. This is a simple but powerful statistic tool to study more factors with relatively fewer experimental trials [18,22,23]. Fe^{3+} dosage (X_1), H_2O_2 dosage (X_2) and pH (X_3) were chosen as three independent variables in sludge dewatering process. The effects of the three variables on the response value of water content (%) of sludge cake were examined. There were 4 levels for pH and 6 levels for the other two factors. In order to improve the accuracy, a U_{12} ($6^2 \times 4$) mixed-level uniform design was selected. Table 2 presents the range and levels of each factor. It should be stressed that in our pre-experiments, when the concentration of H_2O_2 exceeded 373 mg/g DS, the moisture content of sludge cake

Table 1
Characteristics of the raw activated sludge.

pH	6.7 ± 0.1
Total solids (%)	1.29 ± 0.08
Volatile suspended solids (VSS, g/g DS)	0.56 ± 0.03
Specific resistance to filtration (SRF, $\times 10^{13}$ m/kg)	8.16 ± 0.11
The time to filter (TTF, s)	80 ± 5
Water content (%)	80.0 ± 1.5