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Short Communication

Characterizing the fluorescent products of waste activated sludge in dissolved organic matter following ultrasound assisted ozone pretreatments

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HIGHLIGHTS

- Ozone/US combined pretreatment achieves a maximal sludge reduction ratio of 40.14%.
- Ozone/US combined pretreatment could induce more DOMs released from WAS.
- This combined-lysis technology provide more DOMs in subsequent biological processes.
- EEM technique was a high available tool for assessing components changed in WAS.

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ABSTRACT

This study investigated the effects of ozone and ultrasound (US) pretreatments, both individually and combined, on waste activated sludge reduction. Batch tests were conducted first to optimize the individual ozone and US pretreatments. Maximum sludge reduction ratios of 10.89% and 23% were obtained at 0.15 g O_3/g total solids ozone dose and 1.5 W/mL US energy density, respectively. The combined ozone and US pretreatments were studied using response surface methodology. A maximum sludge reduction ratio of 40.14% was achieved by the combined ozone/US pretreatment with an ozone dose of 0.154 g O_3/g total solids and an US energy density of 1.445 W/mL. The analysis of the dissolved organic matter by three-dimensional excitation–emission matrix fluorescence spectroscopy showed that the combined pretreatment was superior to the individual ozone and US pretreatments, and also demonstrated the synergetic effect of these two combined pretreatments.

1. Introduction

The activated sludge process is widely used in both municipal and industrial wastewater treatment plants. During this process, a considerable amount of waste activated sludge (WAS) is produced (Yang et al., 2011). The handling of WAS is currently one of the most significant challenges in biological wastewater treatment processes. Furthermore, because of environmental, economic, legal and even social constraints, primary disposal methods for WAS such as landfilling, incineration and use in agriculture have become restricted (Chen et al., 2002). Therefore, the development of new, environmentally responsible methods to manage the WAS problem are of great concern.

Recently, WAS pretreatment methods such as thermal, microwave, alkaline, ultrasonic, and ozone oxidation pretreatments have been used to reduce the amount of WAS, and a range of acceptable results have been reported to date (Cai et al., 2004; Guo et al., 2008; Chu et al., 2009; Xiao and Liu, 2009). Of these pretreatment methods, ultrasound (US) pretreatment is recognized as a potential high-efficiency pretreatment technique which has no impact on the environment (Guo et al., 2011). Consequently, US pretreatment is considered to be an effective and promising pretreatment method (Tiehm et al., 2001). However, US pretreatment, on its own, has disadvantages. When the US pretreatment is applied to the WAS, the majority of the ultrasonic energy is absorbed by the liquid (Xu et al., 2010), so that less ultrasonic energy is available to the WAS, resulting in a high energy consumption. Consequently, various strategies have been considered to increase the US efficiency. Ozone is a powerful oxidant and disinfectant which is already used in wastewater and waste sludge treatment processes (Bougrier

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et al., 2006). With ozone oxidation, the sludge ozonation process generally follows a three step pathway: (1) the sequential decomposition reactions of floc disintegration; (2) solubilization; and (3) the subsequent oxidation and mineralization of the released organics into carbon dioxide (Chu et al., 2009). When US is combined with ozone pretreatment, an advanced oxidation technology could result (Yang et al., 2012). Thus, a combined pretreatment could decrease the energy use requirements and enhance WAS disintegration.

In this study, the effect of individual ozone and US pretreatments on WAS reduction were first investigated, and the synergetic effect of this combined pretreatment was also studied using central composite design (CCD) and response surface methodology (RSM). Three-dimensional excitation–emission matrix (3D-EEM) fluorescence spectroscopy was used to characterize the dissolved organic matter (DOM) in the WAS after different pretreatment methods. The optimized controlled conditions determined in this study should offer important reference values for any subsequent studies.

2. Methods

2.1. Single factor tests

The experimental apparatus used in this study was the same as used by Yang et al. (2012). The characteristics of the WAS used in this study are shown in the Supplementary Information (SI). To study the optimal conditions for sludge reduction, various ozone doses were applied at 0.05, 0.075, 0.10, 0.15, and 0.20 g O_3/g total solids (TS); and a range of US energy densities were investigated at 0.3, 0.6, 0.9, 1.2, and 1.5 W/mL. The detailed operational process was also specified in the previous study (Yang et al., 2012). During the single-factor tests, each experiment was conducted for 1 h and measurements were taken every 10 min. In the subsequent orthogonal experiments, RSM was used to design and calculate the optimum independent variables and experimental responses, and the detailed operation steps were shown in SI.

The DOM concentrations of the sludge samples (with different pretreatments under optimal conditions) were measured to compare the changes in the WAS composition by EEM fluorescence spectroscopy. All samples were analyzed in triplicate and the overall experiments were conducted at room temperature.

To determine the amount of WAS reduction, an appropriate factor to evaluate the WAS reduction yield needs to be chosen. In this study, the WAS reduction yield was defined as the sludge reduction ratio (%) (Eq. (1)):

$$\text{Sludge reduction ratio} = \frac{\Delta \mathrm{TS}}{\mathrm{TS}_{\text{initial}}} \times 100\% \tag{1}$$

where $\mathrm{TS}_{\text{initial}}$ is the initial total solids (TS), $\mathrm{TS}_{\text{final}}$ is the final (pretreated sludge sample) total solids (TS), and $\Delta\mathrm{TS} = \mathrm{TS}_{\text{initial}} - \mathrm{TS}_{\text{final}}$.

3. Results and discussion

3.1. Analysis of single factor tests

As shown in Fig. S1a, the sludge reduction ratio increased from 4.90% to 10.89% as the ozone dose increased from 0.05 to 0.15 g O_3/g TS. However, when the ozone dose exceeded 0.15 g O_3/g TS, the sludge reduction ratio began to decline. Sludge ozonation is reported to be a complicated process. First, the ozone reacts with the soluble fraction of the sludge, and then subsequently oxidizes the particulate fraction. As the ozone dose increases, more intracellular substances would be released into the liquid, so that the soluble fraction has a screening effect on any particulate matter being attacked by ozone. This screening effect would result in little improvement in sludge solubilization (Cesbron et al., 2003). Additionally, it is suggested that the increasing amount of radical scavengers released from the microorganism cells might inhibit future indirect reactions with ozone (Yan et al., 2009). Consequently, to achieve a cost-effective technology, it is important to optimize the ozone dose. In this study, an ozone dose of 0.15 g O_3/g TS was determined to be the optimal level.

Fig. S1b shows that WAS reduction increased from 6.13% to 23% as the US energy densities increased from 0.3 to 1.5 W/mL, although the increasing trend slowed when the US energy density exceeded 0.9 W/mL. As shown in Fig. S1b, sludge reduction ratios of 19.24%, 21.56% and 23% were obtained at US energy densities of 0.9, 1.2 and 1.5 W/mL, respectively. Further increasing the US energy density would induce larger volume micro-bubble cavities, but is unlikely to significantly enhance the sludge reduction, and may result in wasted energy. Therefore, the ideal parameters for the individual pretreatments in this study were 0.15 g O_3/g TS ozone and 1.5 W/mL US energy density.

3.2. Analysis of orthogonal experiments

3.2.1. Optimization of operating variables and their reciprocal analysis

The design matrix determined by the CCD of the RSM, and the mean experimental sludge reduction ratio results are shown in Table S2. In the following quadratic equation, X_1 represents the ozone dose, X_2 represents the US energy density, and Y_{ACTUAL} is the response value. The sludge reduction ratio (Y_{ACTUAL}, %) was regarded as a function of the ozone dose and the US energy density. The quadratic regression equation for the sludge reduction ratio is given in Eq. (2):

$$\begin{aligned} Y_{\text{ACTUAL}} = {} & -33.98047 + 319.04061X_1 + 69.10886X_2 \\ & - 25.83333X_1X_2 - 914.50000X_1^2 - 22.93056X_2^2 \end{aligned} \tag{2}$$

An analysis of variance (ANOVA) was used to determine the significance of the quadratic model and the experimental results, as shown in Table S3. Based on the statistical analysis (Table S3), the linear model terms (x_1 and x_2) and quadratic model terms (${x_1}^2$ and ${x_2}^2$) were all significant at the 95% confidence level, indicating that the model is statistically significant and useful. However, the combined effect of ozone and US on the response model, with a P-value of 0.3115 (related to a model x_1x_2 value greater than 0.05) was not significant at the 95% confidence level.

To better describe the combined effect of the two pretreatments, the model was modified. In the modified model, the non-significant model term (x_1x_2) was reduced, and a modified quadratic polynomial equation is shown in Eq. (3):

$$\begin{aligned} Y_{\text{ACTUAL}} = {} & -29.33047 + 288.04061X_1 + 65.23386X_2 \\ & - 914.50000X_1^2 - 22.93056X_2^2 \end{aligned} \tag{3}$$

Based on the modified experimental model equation (Table S4), both the R^2 (0.9707) and the "adjR^2" values (0.9561) were close to 1, indicating a good agreement between the experimental and modeled results. A high F-value of 66.30 indicates that the model is significant. The linear model terms (x_1 and x_2), the combined model term (x_1x_2) and the quadratic model terms (${x_1}^2$ and ${x_2}^2$) were all significant at 95% confidence level, indicating that the modified model was more significant and accurate. From the ANOVA analysis, the modified model could accurately predict the sludge reduction ratio.

To obtain the optimal values for the ozone dose and US energy density, a numerical method was used to solve the modified quadratic equation (Eq. (3)). The optimal values determined for X_1 and X_2 were an ozone dose of 0.154 g O_3/g TS and an US energy