Multivariate analysis of sludge disintegration by microwave–hydrogen peroxide pretreatment process

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HIGHLIGHTS
• Investigation of TSS, H₂O₂ dosage, pH and interactions on MW sludge pretreatment.
• Quadratic models were drawn for 16 response variables with good predictive ability.
• Models could optimize the treatment process for multiple disintegration objectives.

ABSTRACT
Microwave irradiation (with H₂O₂) has been shown to offer considerable advantages owing to its flexible control, low overall cost, and resulting higher soluble chemical oxygen demand (SCOD); accordingly, the method has been proposed recently as a means of improving sludge disintegration. However, the key factor controlling this sludge pretreatment process, pH, has received insufficient attention to date. To address this, the response surface approach (central composite design) was applied to evaluate the effects of total suspended solids (TSS, 2–20 g/L), pH (4–10), and H₂O₂ dosage (0–2 w/w) and their interactions on 16 response variables (e.g., SCOD released, pH, H₂O₂ remaining). The results demonstrated that all three factors affect sludge disintegration significantly, and no pronounced interactions between response variables were observed during disintegration, except for three variables (TCOD, TSS remaining, and H₂O₂ remaining). Quadratic predictive models were constructed for all 16 response variables (R²: 0.871–0.991). Taking soluble chemical oxygen demand (SCOD) as an example, the model and coefficients derived above were able to predict the performance of microwave pretreatment (enhanced by H₂O₂ and pH adjustment) from previously published studies. The predictive models developed were able to optimize the treatment process for multiple disintegration objectives.

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1. Introduction
Conventional biological wastewater treatment processes, when applied widely, produce vast amounts of waste activated sludge (WAS), the treatment and disposal of which are difficult and expensive for municipal wastewater treatment plants (WWTPs). However, WAS is gaining prominence as a potential bio-resource, although sludge reutilization is impeded by factors such as the protective cell walls and matrix of extracellular polymeric substance (EPS). To overcome these obstacles, sludge pretreatment technologies have been developed incrementally in several previous studies [1,2]. Pretreated sludge has been demonstrated to be suitable for many purposes, including the following: (1) enhancing anaerobic digestion of WAS to improve biogas production [3–5] or energy recovery by microbial fuel cells [6]; (2) recovering nutrients (nitrogen and phosphorus) or material resources (e.g., proteins, VFAs for the production of polyhydroxyalkanoates) from sludge [7]; (3) improving sludge dewatering to promote reduction in sludge volume or sludge disinfection [8]; and (4) reducing sludge production by cryptic growth [9,10].

Methods for sludge disintegration by mechanical [11], thermal [12], and chemical [13] treatment have been proposed previously. Microwave (MW) pretreatment, which offers advantages such as the rapid application of direct heat and reduction of energy losses, is an alternative method to conventional thermal pretreatment and has garnered increasing attention recently [14,15]. In particular, microwave pretreatment was found to be superior to thermal treatment in terms of sludge solubilization and biogas production [16]. Moreover, changes in the dipole orientation of polar molecules occur during microwave irradiation, producing athermal

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(or non-thermal) effects [17]. For the solubilization of waste activated sludge, the effectiveness of microwave irradiation is affected by several factors, which have been investigated extensively [3]; such factors include MW output power [10,18], target temperature [19], and sludge concentrations [20,21]. However, investigation of these factors through conventional “change one factor at a time” methods have some shortcomings, including that these methods are laborious, time-consuming, and incapable of obtaining true optimal values owing to their inability to consider interactions among variables. Therefore, three-factor fixed-effect analysis of variance (ANOVA) determination has been adopted to evaluate the effects of high temperature (110–175 °C), MW intensity (1.25 and 3.75 C/min), and sludge concentration (6 and 11.85%) on the solubilization of sludge [22]; the interaction of these factors was found to be significant at the 94% confidence interval. Moreover, the effects of heating pretreatment on the degree of solubilization of waste activated sludge are investigated using response surface analysis [21], and the conditions required to produce a maximum solubilization degree of 17.9% were predicted to be 400 W (output power 400–1600 W), 102 °C (target temperature 60–120 °C), and 2.3% TS (total solid concentration, 1–3%).

The addition of H2O2 in a closed-vessel MW digestion system has been reported to enhance the pretreatment of sludge markedly [23], and such advanced oxidation processes (AOPs) appear to offer promise as suitable technologies for the minimization [24] and pasteurization and stabilization [25] of excess sludge. A H2O2 dosing strategy to inhibit the adverse effects of catalase at low temperatures in an open system was developed in our previous work [26]. To optimize the microwave-enhanced advanced oxidation process (MW/H2O2–AOP), screening experiments (four factors: temperature, hydrogen peroxide dosage, mixing, and solids concentration) were conducted [20]: appropriate solids disintegration and nutrient release were determined to occur at 120 °C and 0.80 g H2O2/g dry sludge. Yin et al. [27] found initial sludge TS content and hydrogen peroxide dosage were the most significant factors controlling nutrient solubilization (i.e., more significant than heating temperature and heating time), maximum solubilization was obtained for 2.5% TS, 2 wt% hydrogen peroxide, and 5 min of microwave heating at 120 °C.

Microwave–H2O2 has been reported to perform better in substrate degradation under acidic and neutral conditions [28]. Moreover, the effects of acids (e.g., HCl and H2SO4) on sludge disintegration have been shown to enhance the release of ammonia [29]. Microwave-enhanced advanced oxidation processes have been adopted previously for the treatment of dairy manure at low pH [30]; such low-pH methods are known to offer advantages such as enhanced phosphorous release and promotion of the dewatering of sludge [31]. Conversely, combined MW irradiation (160 °C) with an alkaline pretreatment method (using NaOH, pH ∼12.5) demonstrated that this technique could increase the solubilization ratio (in terms of SCOD/TCOD) to 0.37 [3].

Recently, Hong et al. [28] found that the degradation of rhodamine B (RhB) and methylene blue (MB) in the MW–H2O2 system was very competitive at extreme alkaline pH, suggesting that this may be an appropriate means of promoting degrada-
tion under highly alkaline conditions; this result is encouraging for the development of MW–H2O2 technology in alkaline wastewater treatment. Similarly, it has been shown that high pH may enhance the MW thermal effect, making MW techniques more suitable for application in sludge disintegration [15]. However, few studies to date have investigated the microwave–H2O2 system under alkali conditions.

A priori, and on the basis of a literature survey on MW and AOPs [23–28], TSS, H2O2, and pH were known to be the critical factors controlling sludge disintegration at mild temperatures (100 °C) [32]: however, the effect of pH (from acidic to basic) has not yet been fully recognized. In addition, the interactions among these three factors remain unclear. Moreover, the majority of previous researches have focused on the treatment of target sludge, neglecting the behavior of the oxidant H2O2 during this process. In practical engineering applications of this technology, it is always designed to achieve multi-objectives for the sludge disintegration unit; for example, the sludge can be treated to release more organic matter and less heavy metal. If recovery of N/P in the form of struvite is to be considered, phosphate and ammonia (and Mg2+) release should be maximized, whereas the release of Ca2+ (which acts as an inhibitor) should be minimized. Therefore, there is great demand for a unifying predictive model that incorporates the above aspects of sludge pretreatment and will allow simultaneous quantitative evaluation of sludge disintegration and optimization of MW–H2O2 sludge pretreatment by pH adjustment for multi-objectives.

Response surface methodology (RSM) is a powerful statistical tool used to construct models and evaluate the influences of several individual factors and their interactions simultaneously. Accordingly, RSM has emerged as an important tool in the study of multifactor interaction. Typically, predictive models have been used to analyze and optimize operation parameters, thus allowing desirable responses to be attained while reducing the number of experiments.

The present study adopted multivariate analysis to investigate sludge disintegration and aimed to achieve the following: (1) investigate the effects of pH in isolation and in conjunction with uniform initial sludge concentration and H2O2 dosage, and assess the interactions among these factors during sludge disintegration based on RSM and 16 response variables; and (2) construct a unifying model to predict sludge solubilization and H2O2 usage, thus providing a simple way to estimate optimal values for multiple sludge pretreatment objectives.

2. Materials and methods

2.1. Raw materials

The WAS was obtained from returned sludge from the secondary settling tank of the Fangzhuang municipal wastewater treatment plant (WWTP), with a design capacity of 40,000 m3/day, in Beijing, China. This WWTP was an A2/O process plant and operated with sludge retention time (SRT) of approximately 15 days. The high VSS to TSS ratio in the sludge (79%) indicates that it consisted mainly of organic substances. Waste activated sludge was centrifuged before use and washed three times to avoid the interference of soluble matter. The sludge was stored at concentrations of 3% at 4 °C and diluted with distilled water prior to use to provide various set concentrations.

2.2. Experimental design

The effects of the studied variables (TSS, pH, H2O2 dosage) and their interactions on the response variables were investigated using a central composite design (CCD) method. The CCD method adopted allows the development of mathematical equations. TSS (X1), pH (X2), and the H2O2 to sludge ratio (X3) were varied over the ranges 3–20 g/L, 2–12, and 0–2 (w/w), respectively, with corresponding central values of 11.5 g/L (X1), 7 (X2), and 1.0 (X3). Xi denotes the real value of the three variables according to the experimental design (Table 1, actual values). The parameters were standardized according to the following equation.

\[ x_i = \frac{X_i - X_o}{\Delta X_i} \quad (1) \]

where \( x_i \) was the coded value of the variable \( X_i \), \( X_o \) was the value of \( X_i \) at the center point of the investigated area, and \( \Delta X_i \) was the
step change value. The matrix was a factorial design matrix with 16 response variables, four axial points, and three central points (Table 1).

The 16 response variables can be grouped into three categories: (1) sludge disintegration and organic matter released (SCOD released, TCODremaining and TSSremaining in the mixture, TOC of sludge disintegration and organic matter released (SCOD), and metals (K, Ca, Mg, Cu, and Zn) released. Each response variable Y was assessed as a function of three first-order effects (x1, x2, and x3), three interaction effects (x1x2, x1x3, and x2x3), and three second-order effects (x1^2, x2^2, and x3^2) and can be described as follows:

\[ Y = \beta_0 + \beta_1 x_1 + \beta_2 x_2 + \beta_3 x_3 + \beta_11 x_1^2 + \beta_22 x_2^2 + \beta_33 x_3^2 + \beta_12 x_1 x_2 + \beta_13 x_1 x_3 + \beta_23 x_2 x_3 \]  

(2)

where Y was the response variable (e.g., the percentage of sludge disintegrated or the amount of H2O2 remaining) and \( \beta_i \) were coefficients. The variables and response variables were analyzed using the response surface analysis function of the Design-Expert software package and the SPSS software package (version 11.0, SPSS Inc., USA).

2.3. Experimental setup and treatment procedures

Sludge pretreatment was conducted using a customized industrial microwave oven (Baoding Julong Microwave Energy Equipment Co. Ltd., China), based on our own design. The oven was operated at 600 W (maximum power: 1200 W) at a frequency of 2450 MHz and was equipped with a paddle-type agitation and a thermocouple temperature sensor to monitor temperatures in real time. A schematic diagram and photograph of the experimental setup are presented in the Figs. S-1 and S-2 in supplementary information.

The volume of treated sludge was 300 mL. The pH of sludge was adjusted using 1 mol/L H2SO4 or NaOH before heating by microwave. To offset the effects of the enzyme catalase on degradation of H2O2, the sludge was firstly preheated to 60°C by microwave irradiation, then dosed with preset amounts of hydrogen peroxide (A.R., 30%, w/w), and heating was continued until the temperature reached 100°C; then, the sludge was cooled in a water bath before analysis. The total heating process was conducted over a period of 5 min, as has been reported elsewhere [26]. The sludge treatment procedure is summarized in Fig. S-3 in the supplementary information.

2.4. Analysis

The filtrate obtained by passing samples through a 0.45 μm membrane was used to measure the concentrations of soluble substances. The concentration of residual H2O2 in sludge samples was determined according to the colorimetric method with Ti [26]. The residual H2O2 in the WAS was assumed to interfere strongly with the results of COD measurement; therefore, COD values were determined after removal of residual H2O2 by adding catalase (Sigma CS9322). Total COD (TCOD), soluble COD (SCOD), TSS, VSS, ammonium, and total phosphorus (TP) were determined according to standard methods [33]. Heavy metal contents were analyzed by inductively coupled plasma atomic emission spectroscopy (ICP–AES; Optima 2000, PerkinElmer Co., USA), and soluble TOC was determined using a TOC–VCPH analyzer (Shimadzu, Japan).

3. Results and discussion

3.1. Performance of sludge disintegration by the MW–H2O2 process

The results obtained in this study for all experimental conditions were listed in Table 2. For all 16 variables studied, these
results were subjected to analysis of variance (ANOVA) to determine second-order equations that incorporated the interactions between the three variables, and the coefficients \((\beta_0, \beta_1-\beta_3)\) for each variable were calculated and fitted to quadratic models. The ANOVA F-value describes the significance of individual factors and their interactions, whereas the F-value illustrates the significance of the coefficient. The increase of SCOD in bulk solution has been shown to be an ideal [14] and priority index for evaluating the disruption of complex WAS floc structures and reutilization of sludge. Prediction of released SCOD is a key issue in the further research and complex WAS floc structures and reutilization of sludge. Prediction of released SCOD is a key issue in the further research and complex WAS floc structures and reutilization of sludge. Analysis of variance (ANOVA) showed that the models (Table 3) were statistically good (i.e., the probability for the regression is significant at 95% for \(p < 0.0001\)). The predicted values are relatively close to the observed values \((R^2 = 0.98)\), indicating that the developed model successfully describes the correlation between the factors and the SCOD released. Moreover, \(x_1, x_2, x_3,\) and \(x_4\) were all found to be significant. The adequate precision value (Table 3) was adopted as a measure of the signal-to-noise ratio; in particular, it compares the range of predicted values at the design points to the average prediction error. Here, this value was found to be 19.99, which indicates an adequate signal, considering that a ratio greater than 4 was desirable [34].

For SCOD released, the coefficient of variance (CV) was found to be 8.75%; thus, the model can be considered to predict the observed data reasonably well, indicating good model reproducibility. The coefficients of the quadratic model in Eq. (2) were calculated by least-squares multi-linear regression analysis, and the model’s goodness of fit was investigated by determining the \(R^2\) coefficient. The resulting quadratic model can be considered suitable to describe the impacts of the three selected variables (TSS, pH, and ratio of H\(_2\)O\(_2\) to sludge) during sludge disintegration by AOP incorporating MW and H\(_2\)O\(_2\).

Based on Eq. (2) and Table 4, Eqs. (3) and (4) were produced for coded and actual SCOD released, respectively.

\[
\text{SCOD} = 2826.26 + 1040.65x_1 + 498.01x_2 + 439.24x_3 + 192.41x_1x_2 - 87.44x_1x_3 + 158.54x_2x_3 + 191.75x_1^2 - 8.51x_2^2 - 78.17x_3^2 \quad (3)
\]

\[
\text{SCOD} = 1544.07 - 145.63 \times TSS - 79.76 \times pH - 197.72 \times H_2O_2 + 21.34 \times TSS \times pH + 29.34 \times TSS \times H_2O_2 + 150.23 \times pH \times H_2O_2 + 7.51 \times TSS^2 - 2.68 \times pH^2 - 223.33 \times H_2O_2^2 \quad (4)
\]

Eq. (4) represents the actual factors in their original units. According to Eq. (3), the highest values of \(\beta_i\) were found between TSS concentration and SCOD released, suggesting that the release of organic matter is controlled primarily by sludge concentration. Moreover, all values of \(\beta_i\) were positive, indicating that the amount of organic matter released increases with increasing sludge concentration, H\(_2\)O\(_2\) dosage, and pH. The low values of \(\beta_i\) indicate that the effects of interaction among the selected variables are not pronounced, which is supported by the F-values obtained when interaction between variables was considered (Table 3).

To verify the representativeness and applicability of the model, experimental results in this and other studies were compared with the model-predicted values. Treatment temperature was not considered as a controlling factor in this study, because this research aimed primarily to investigate an atmospheric pressure system; however, it has been shown previously that 100 °C is the optimal temperature [26], considering the cost involved in the complex operation of the sealing and anti-explosion system, which is a prerequisite for pretreatment at 120 °C. As the performance of sludge disruption at 120 °C was similar to that at 100 °C under the experimental conditions considered here [35], it is possible to extend the applicability of this model to the medium temperatures (e.g., 120 °C) within a pressured system. For the treatment material, sewage sludge and the extracted activated sludge cells (which are EPS-free [36]) were compared together, and SCOD released was selected to allow comparison between previously published results. Studies investigating the effects of the MW–H\(_2\)O\(_2\) sludge pretreatment process on SCOD release were selected carefully (Fig. 1), and suggest that the interference of residual H\(_2\)O\(_2\) that could be removed by catalase [26] or sodium carbonate [37] should be considered. The predicted results were calculated according to Eqs. (1) and (3) (associated data and calculations are presented in the supporting information). Although the treatment conditions for the three main treatment factors varied widely, the predicted SCOD released corresponded well to the experimental data (Fig. 1).

The Pearson correlation coefficient between the data obtained from published studies and the predictive model was 0.916, with a significance level of 0.99, according to the reference line (Fig. 1). However, TSS was found to vary between studies, and pH and H\(_2\)O\(_2\) dosages have not always been investigated accurately. Nevertheless, the developed model ties these variables together well, providing a link between different treatment techniques with different TSS, pH, and H\(_2\)O\(_2\) dosage.

### 3.2. Quadratic models for all response variables

Using the same analysis procedure used to describe the amount of SCOD released, a quadratic model incorporating the other 15 response variables was constructed based on the results listed in Table 2. The regression coefficients and relevant statistical parameters of all 16 response variables were obtained from the ANOVA for the predictive models of sludge disintegration, as shown in Table 4. An independent predictive model was constructed for each selected response variable by substituting into Eq. (2). According to the ANOVA analysis, the regression models were significant with respect to a preset confidence level \((p < 0.05)\). In this study, \(R^2\) ranged from 0.864 (for NH\(_4\)-N released) to 0.991 for TCOD\(_{\text{remaining}}\) in solution) and demonstrated a good fit between the quadratic model and the experimental data.

The relative contribution of each variable \((x_i, x_{ij}, x_i^2)\) to each dependent response variable \((Y_i - Y_{16})\) can be measured directly by the respective coefficient in the fitted model. The positive
coefficients in the fitted models for $Y_1$–$Y_{16}$ indicate that the degree of sludge disintegration is closely related to the rate of change of factors $x_3$ (i.e., the H$_2$O$_2$ to sludge ratio) and $x_2$ (pH). Moreover, based on these results, the contributions of three first-order effects ($x_1$, $x_2$, $x_3$), three interaction effects ($x_1 x_2$, $x_1 x_3$, and $x_2 x_3$), and three second-order effects ($x_1^2$, $x_2^2$, and $x_3^2$) to the results were ranked based on the obtained coefficients, i.e., the values obtained for $\beta_i$. In Table 4, the coefficients obtained for all 16 models provide information about the influence of each independent variable on each response variable. For example, for TN released, the coefficient for coded TSS ($x_3$) is 49.28; this is the largest coefficient obtained, suggesting that TSS is the dominant factor controlling the amount of TN released in these selected ranges for all factors.

Several previous studies have considered model simulation of MW sludge pretreatment [15,21,22,38,39]. For example, Yang et al. [38] constructed a quadratic model to investigate the effects of combined alkaline and microwave pretreatment with two variables (different pH and specific energy input by RSM). Similarly, Abelleira et al. [39] determined the effect of thermal treatment and hydrogen peroxide (H$_2$O$_2$) addition on sludge solubilization and organic matter removal by RSM. Because these empirical models were second-order polynomial models, they were validated satisfactorily, with high $R^2$ values (i.e., >0.9). The unifying model developed in the present study was possible to simulate the versatile uses of the MW irradiation technique in sludge treatment, e.g., MW, MW–H$_2$O$_2$, MW–acid MW–alkaline and recently proposed MW–H$_2$O$_2$–alkaline. Response variables of this model covered the characteristics of sludge, sludge treatment process indicators, nutrients and metals released. This unifying (AOP) model was verified by experimental data obtained from the existing literature [20,26,29,31,35,36], which was provided in Table S-1 in supplementary information. This model can be used as a tool to predict the microwave (or hybrid) treatment performance for any given values of TSS, H$_2$O$_2$, and pH. It was also possible to compare treatment procedure with same factors among different studies. For example, the plotting of data points (Fig. 1) below the reference line (for the 120 °C treatment) [35] suggests that the method described here performs better than mild MW treatment. Thus, the model can be used for both empirical estimation and the design of the microwave–hydrogen peroxide pretreatment process in future.

### 3.3. Optimization of the MW–H$_2$O$_2$ process for organic matter release

To improve understanding of the parameter of SCOD released in bulk solution, the predictive models have been presented as three-dimensional response surface plots and contour plots (Fig. 2). Pairs were formed from the variables ($x_1$, $x_2$, and $x_3$), keeping the third variable fixed at its central value, e.g., the ratio of H$_2$O$_2$ to TSS was maintained constant while sludge pH was varied. When being held constant, the H$_2$O$_2$ ratio, TSS, and pH were 1, 11.5 g/L, and 7, respectively. The results suggest that the released SCOD increased in response to high sludge concentrations and H$_2$O$_2$ dosages. The maximum COD released appeared in the corner of the matrix, coinciding with higher TSS, pH, and H$_2$O$_2$ dosage. The $p$-value of model effects $x_1 x_2$, $x_1 x_3$, $x_2 x_3$ were greater than 0.05 (0.0729, 0.3682, 0.1258 respectively), indicating that the interaction between the three variables (TSS, H$_2$O$_2$ ratio and initial pH) did not have a significant effect on the COD released.

In the present study, based on the optimization of H$_2$O$_2$ content and pH for the microwave-based pretreatment, the optimal values of these three parameters fell within the experimental range. The percentage of sludge disintegration increases monotonically with increasing energy input, H$_2$O$_2$ dose, and pH. The recommended values for TSS, the H$_2$O$_2$ to sludge ratio, and pH were determined to be
20 g/L, 2, and 10, respectively; these optimal values were verified by experimental study (Fig. 1), and fall within the boundaries of experimental conditions.

TSS was found to be a key factor for most of the response variables in this study (Table 4), for example, the maximum SCOD/TCOD (0.468) was achieved in the lowest TSS (Run 9). The coefficient $\beta_1$ for SCOD/TCOD was $-0.045$, it indicated that low sludge concentration was better than high sludge concentration for improvement of SCOD/TCOD ratio under mild temperature. This result is consistent with results and a linear model reported previously in the literature [21]. They found TSS (or water content) was the most important factor that influenced the solubilization of solid materials [40]. However, water has a high thermal capacity and can absorb more energy with a relatively small increase in temperature. More energy would be consumed in raising the temperature of water at higher water contents, which decreases the efficiency of energy in the solubilization of solids. Thus, increasing the concentration of sludge treated can significantly reduce energy consumption and overall operating costs, especially in large-scale applications. The maximum sludge concentrations achieved to date for microwave pretreatment in closed-vessel systems were as high as 34 g/L [40] and 118.5 g/L [22]; such high sludge concentrations typically require less energy consumption per unit of dry sludge. Thus, high TSS is recommended considering the economic feasibility of MW–H$_2$O$_2$ technology. The results of the present study suggest that the dosage of H$_2$O$_2$ has little effect on the amount of residual H$_2$O$_2$ after treatment, suggesting that H$_2$O$_2$ takes part in the reaction only partially. Although H$_2$O$_2$ is stable under acidic conditions but active under alkaline conditions, where it decomposes easily [42], over 72% of H$_2$O$_2$ remained in bulk solution in all runs of the present study. Therefore, the amount of H$_2$O$_2$ used is critical in determining the overall performances and the total costs of the pretreatment technology.

H$_2$O$_2$ dosage is known to play an important role in breaking down the structure of sludge and increasing the amount of organic matter released into bulk solution [20,26,41]. Because of the catalase in sludge, H$_2$O$_2$ cannot be used as other oxidant O$_3$ or Cl$_2$ to solubilize the sludge directly, and usually used together with Fe as Fenton reaction [34]. In a previous study, catalase activity was suppressed in microwave treatment firstly, then microwave facilitated the hydroxyl radicals (OH·) formation through the decomposition of H$_2$O$_2$, enhancing both the oxidation and particulate COD disintegration of WAS samples [14]. For example, sewage sludge was found to release 46.8% of TCOD after MW–H$_2$O$_2$ treatment for 5 min (run 9 in Table 2); conversely, only 11.6% of SCOD was released for MW treatment only (100°C, Run 13) without H$_2$O$_2$. Kenge et al. [20] recommended that the ratio of H$_2$O$_2$ to sludge (w/w) be set to 0.8. The model derived in this study thus provides a convenient way to predict the effects of the H$_2$O$_2$ dosage and their relation to the cost of the pretreatment process. Yet the fate of H$_2$O$_2$ has received little attention in previous studies of MW–H$_2$O$_2$ technology. The results of the present study suggest that the dosage of H$_2$O$_2$ has little effect on the amount of residual H$_2$O$_2$ after treatment, suggesting that H$_2$O$_2$ takes part in the reaction only partially. Although H$_2$O$_2$ is stable under acidic conditions but active under alkaline conditions, where it decomposes easily [42], over 72% of H$_2$O$_2$ remained in bulk solution in all runs of the present study. Therefore, the amount of H$_2$O$_2$ used is critical in determining the overall performances and the total costs of the pretreatment technology.

High pH appears to be effective in increasing the percentage of sludge disintegration, whereas low pH was found to be effective in reducing the amount of H$_2$O$_2$ consumed (Table 4); moreover, low pH was found to be favorable for the release of heavy metals and resulted in decreases in VSS/TSS for the treated sludge particles. Previous studies have shown that microwave–H$_2$O$_2$ or microwave-only pretreatment of sludge can enhance the release of NH$_4^+$–N and PO$_4^{3−}$–P in acidic solutions [43]. PH adjustment without MW irradiation (especially alkaline treatment) could also effectively solubilize particulate organic matter in the sludge [44]. However, the treatment always takes several hours or more (typically, 3–24 h) to complete. When combined with microwave disintegration methods, this treatment was found to be highly efficient and rapid (typically completed within 30 min), the organic matter released could be enhanced to the 25.0% at pH 10 (Run 12, Table 2). The success of pH adjustment treatment depends on two main mechanisms: chemical degradation and ionization of hydroxyl groups [44]. A high extreme of pH leads to increased negative charge of
Fig. 2. Two- and three-dimensional contour plots of the quadratic model for SCOD released with respect to \( \text{H}_2\text{O}_2 \) dosage, initial pH, and TSS. The 3D surface plots use color to distinguish changes in response, whereas the density of the lines in the contour plots represents the rate of change of the parallel contour line, such that higher densities correspond to faster rates of change.
bacterial surfaces, and the stability of H$_2$O$_2$ is influenced strongly by pH. During the MW–H$_2$O$_2$ oxidation, the rate of generation and consumption of hydroxyl radicals (which form at pH > 8) is strongly influenced by pH. The MW pretreatment facilitates the hydrolysis of polymer and compounds with poor biodegradability [45] to produce simpler compounds that can be more readily biodegradable [46]. In the present study, the final pH of pretreated sludge was found to be notably lower than the initial pH (Table 2), possibly owing to dissolution of carboxylic acids and volatile fatty acids generated by complex organic matter in association with cell lysis [47,48] in the initial high-pH group. Thus, the final pH of slurry may remain within the natural range, which will be beneficial for subsequent treatment of sludge. In the group without pH control, weak acidic products (e.g., VFA) [49] generated by MW–H$_2$O$_2$ treatment may disturb the further post treatment of sludge. Nevertheless, the mechanisms by which pH affects the microwave–H$_2$O$_2$ sludge pretreatment process require further research.

3.4. Optimization of the MW–H$_2$O$_2$ process for multi-objectives

The empirical validation for this experiment was satisfactory (Fig. 1). In particular, the results suggest that, to achieve optimal conditions generally, focus should be placed primarily on solubilization conducted under mild conditions (i.e., H$_2$O$_2$ < [1.4, 2.0]; pH < 8 [8,10]). Moreover, the model acquired from the response surfaces discussed in the previous sections provides an effective strategy to optimize the microwave/hydrogen peroxide/pH pretreatment process for multiple objectives, including anaerobic digestion, sludge leaching, and nutrient recovery. This optimization was conducted separately for each response variable (Fig. 3). The optimal treatment conditions can be decided in practice based on general predictive models and cost–benefit analysis, considering the price of the energy and H$_2$O$_2$ required for pretreatment and the economic benefits gained from sludge pretreatment. Cost–benefit analysis parameters may vary depending on the intended use. For example, recovery of resources may require more intensive treatment than sludge reduction (e.g., by requiring sludge to be transported back to aeration tanks), and the costs of the additional treatment must be taken into consideration.

The optimized treatment conditions for different responses can be clustered into three groups: (1) points including (SCOD$_{max}$, TN$_{max}$, TOC$_{max}$), which represent the degree of sludge disintegration and plot in the region of high TSS, high H$_2$O$_2$, and high pH, accompanied by H$_2$O$_2$ consumption and TSS reduction; (2) points indicating the degree of disintegration of the sludge itself (VSS/TSS$_{min}$, SCOD/TCOD$_{max}$), which lie in areas of high H$_2$O$_2$ and high pH; (3) and points based on the amounts of nutrients (except TN) and metals released, where the optimal operating conditions correspond to low pH and low H$_2$O$_2$.

Generally, every response is associated with optimal operating conditions (involving $x_1$, $x_2$, and $x_3$). Field engineering reutilization applications (e.g., sludge reduction, material recovery, heavy metal leaching) have multiple engineering objectives, such that there may often be conflict between various treatment requirements, e.g., between struvite recovery (low pH, low H$_2$O$_2$ dosage) and enhancing anaerobic digestion (high pH, high H$_2$O$_2$ dosage). In fact, conflict may arise even for a single treatment objective: for example, to enhance the denitrification process for an external carbon source, maximum COD release (high pH and H$_2$O$_2$ dosage) and minimum ammonia release (low pH and H$_2$O$_2$ dosage) are desired. However, few previous studies have attempted to integrate the optimization of individual parameters into a framework for groups of optimal parameters designed to meet multiple objectives. To address this, the response can be optimized using the Design-Expert software and Modde 9.0 [39] to attribute different weights to the response variables depending on their purpose and based on model predictions (i.e., Eq. (2) and the coefficients from Table 4). Such optimization can help meet the varying requirements of sludge disintegration, even under restrictions imposed by multiple objectives.

To retain advantages over other competing sludge pretreatment techniques (e.g., mechanical, ultrasonic, ozone) and ensure favorable results in full-scale applications, microwave (and hybrid microwave) pretreatment processes must offer better performance for multiple engineering objectives simultaneously. In this context, RSM could provide a powerful tool to determine optimal conditions for such integrated multiple objectives. These models will be particularly useful in future studies of MW-enhanced advanced oxidation processes.

4. Conclusions

(1) The effects of pH (especially alkaline) on SCOD released in microwave–hydrogen peroxide pretreatment were found to be pronounced, and pH was shown to play an important role in determining the percentage of H$_2$O$_2$ utilized.

(2) Quadratic models were built based on statistical analysis using the RSM approach, and were found to fit the data from this experiment and the literature well; in particular, analysis of variance returned a high coefficient of determination (0.871–0.992) for all 16 response variables. The predictive model developed here was shown to be capable of optimizing the treatment process for multiple disintegration objectives.

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