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

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HIGHLIGHTS

- Investigation of TSS, H_2O_2 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.

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ABSTRACT

Microwave irradiation (with H_2O_2) 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 H_2O_2 dosage (0–2 w/w) and their interactions on 16 response variables (e.g., $SCOD_{released}$, pH, $H_2O_2_{remaining}$). 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 $H_2O_2_{remaining}$). Quadratic predictive models were constructed for all 16 response variables (R^2 : 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 H_2O_2 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 degradation 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 (X_1), pH (X_2), and the H₂O₂ to sludge ratio (X_3) 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 (X_1), 7 (X_2), and 1.0 (X_3). X_i 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.

$$x_i = \frac{X_i - X_i^0}{\Delta X_i} \quad (1)$$

where x_i was the coded value of the variable X_i , X_i^0 was the value of X_i at the center point of the investigated area, and ΔX_i was the

Table 1
Matrix of experimental design and results.

Run	Coded values			Actual values		
	TSS (x_1)	pH (x_2)	H ₂ O ₂ (x_3)	TSS (X_1 , g/L)	pH (X_2)	H ₂ O ₂ (X_3)
1	−1	−1	−1	6.44	5.22	0.40
2	1	−1	−1	16.55	5.22	0.40
3	−1	1	−1	6.44	8.78	0.40
4	1	1	−1	16.55	8.78	0.40
5	−1	−1	1	6.44	5.22	1.59
6	1	−1	1	16.55	5.22	1.59
7	−1	1	1	6.44	8.78	1.59
8	1	1	1	16.55	8.78	1.59
9	−1.68	0	0	3.00	7.00	1.00
10	1.68	0	0	20.00	7.00	1.00
11	0	−1.68	0	11.50	4.00	1.00
12	0	1.68	0	11.50	10.00	1.00
13	0	0	−1.68	11.50	7.00	0.00
14	0	0	1.68	11.50	7.00	2.00
15	0	0	0	11.50	7.00	1.00
16	0	0	0	11.50	7.00	1.00
17	0	0	0	11.50	7.00	1.00

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, TCOD_{remaining} and TSS_{remaining} in the mixture, TOC of bulk solution, derived index of SCOD/TCOD); (2) process indicators (i.e., percentage of H₂O₂_{remaining} and pH value); and (3) nutrients (released ammonia, TN, and TP in bulk solution) and metals (K, Ca, Mg, Cu, and Zn) released. Each response variable Y was assessed as a function of three first-order effects (x_1 , x_2 , and 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) and can be described as follows:

$$Y = \beta_0 + \beta_1 x_1 + \beta_2 x_2 + \beta_3 x_3 + \beta_{11} x_1^2 + \beta_{22} x_2^2 + \beta_{33} x_3^2 + \beta_{12} x_1 x_2 + \beta_{13} x_1 x_3 + \beta_{23} x_2 x_3 \quad (2)$$

where Y was the response variable (e.g., the percentage of sludge disintegrated or the amount of H₂O₂_{remaining}) and β_i and β_{ij} 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.).

Table 2
Experimental parameters, results, and data analysis in the CCD design for sludge pretreatment by MW–H₂O₂.

Run	SCOD (mg/L)	TCOD (mg/L)	TOC (mg/L)	TSS (g/L)	SCOD/TCOD	VSS/TSS	pH	H ₂ O ₂ _{remaining} (%)	NH ₄ ⁺ –N (mg/L)	TN (mg/L)	TP (mg/L)	K (mg/L)	Ca (mg/L)	Mg (mg/L)	Cu (mg/L)	Zn (mg/L)
1	1342	8029	418.11	5.13	0.172	0.74	4.97	92	40.93	44.16	53.15	40.07	38.27	76.43	0.16	1.11
2	3152	18,994	1220.51	13.39	0.157	0.72	5.18	88	65.70	112.83	82.10	89.10	69.77	147.50	0.34	1.38
3	2007	6884	684.33	5.01	0.257	0.66	7.05	83	27.15	55.34	41.38	37.97	6.81	41.09	0.30	0.33
4	4125	15,670	1654.82	11.54	0.206	0.66	6.33	90	60.12	142.24	62.40	71.62	13.49	81.23	0.50	0.34
5	1736	7992	570.24	4.76	0.223	0.73	4.95	96	35.44	60.06	51.38	38.92	34.45	68.36	0.19	1.15
6	3436	15,269	1395.24	10.01	0.172	0.71	4.94	85	57.19	138.76	81.19	72.24	54.01	123.29	0.36	1.51
7	2574	6687	902.15	4.47	0.330	0.64	6.28	87	39.81	85.16	47.95	35.11	8.81	40.07	0.26	0.24
8	5504	14,992	2200.30	9.10	0.275	0.62	5.75	75	53.50	200.23	76.29	72.57	24.00	91.01	0.46	0.44
9	1699	3393	296.04	2.02	0.468	0.67	6.53	95	15.45	28.75	37.19	12.95	5.58	22.84	0.18	0.26
10	5061	17,197	1745.24	12.30	0.209	0.69	5.69	72	47.60	221.19	72.30	63.38	26.47	87.61	0.59	0.55
11	2143	14,678	802.42	8.55	0.154	0.74	4.39	94	57.05	85.91	79.98	72.56	69.76	138.95	0.33	2.69
12	3485	10,886	1300.29	6.38	0.250	0.58	6.77	73	58.58	123.93	53.00	75.73	7.70	57.15	0.38	0.16
13	1613	12,782	585.66	11.10	0.116	0.70	7.36	–	33.50	57.58	52.85	59.89	5.57	49.55	0.09	0.19
14	3620	10,664	1436.73	5.90	0.260	0.61	5.67	84	48.05	145.06	67.55	61.69	20.79	84.56	0.35	0.51
15	2906	11,132	1100.03	7.40	0.209	0.65	6.05	80	55.39	106.45	58.31	57.98	15.73	76.99	0.29	0.35
16	2832	10,713	1040.98	7.81	0.204	0.65	6.09	81	49.26	102.15	53.56	56.35	14.17	72.96	0.24	0.32
17	2857	10,442	1087.26	7.61	0.205	0.65	6.15	82	49.17	102.31	56.59	57.24	14.96	76.11	0.29	0.21

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 agitator and a thermocouple temperature sensor to monitor temperatures in real time. A schematic diagram and photograph of the experimental set-up 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 C9322). 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 (β_0, β_1 – β_{23}) 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 *P*-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 application; it was conducted based on the results obtained and the simulation conducted according to Eq. (2). 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_1^2 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_2O_2 to sludge) during sludge disintegration by AOP incorporating MW and H_2O_2 .

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

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

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

Eq. (4) represents the actual factors in their original units. According to Eq. (3), the highest values of β_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 β_i were positive, indicating that the amount of organic matter released increases with increasing sludge concentration, H_2O_2 dosage, and pH. The low values of β_{ij} 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

Table 3

Analysis of variance tables for SCOD released in bulk solution.

Source	Sum of squares	Df	Mean square	<i>F</i> -value	<i>P</i> -value
Model	22,024,707.94	9.00	2,447,189.77	36.76	<0.0001
x_1 (TSS)	14,789,601.05	1.00	14,789,601.05	222.17	<0.0001
x_2 (pH)	3,387,046.67	1.00	3,387,046.67	50.88	0.0002
x_3 (H_2O_2)	2,634,780.63	1.00	2,634,780.63	39.58	0.0004
$x_1 x_2$	296,161.32	1.00	296,161.32	4.45	0.0729
$x_1 x_3$	61,584.71	1.00	61,584.71	0.93	0.3682
$x_2 x_3$	201,088.97	1.00	201,088.97	3.02	0.1258
x_1^2	414,516.35	1.00	414,516.35	6.23	0.0413
x_2^2	817.07	1.00	817.07	0.01	0.9149
x_3^2	68,890.69	1.00	68,890.69	1.03	0.3429
Residual	465,972.88	7.00	66,567.55		
Lack of fit	463,142.73	5.00	92,628.55	65.46	0.0151
Pure error	2830.15	2.00	1415.08		
Cor. total	22,490,680.82	16.00			
Std. dev.	258.01			R^2	0.98
Mean	2946.67			CV (%)	8.76
Adeq. precision	19.99			PRESS	3,694,847

Df: degrees of freedom; Cor. total: totals of all information corrected for the mean; Adeq. precision: adequate precision; PRESS: predicted residual error sum of squares.

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 extent 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_2O_2 sludge pretreatment process on SCOD release were selected carefully (Fig. 1), and suggest that the interference of residual H_2O_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_2O_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_2O_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_1 – Y_{16}) can be measured directly by the respective coefficient in the fitted model. The positive

Table 4
Coefficients of models and statistical parameters for response variables.

Response	SCOD (mg/L)	TCOD (mg/L)	TOC (mg/L)	TSS _{remaining} (g/L)	SCOD/ TCOD	VSS/TSS	pH	H ₂ O ₂ remaining (%)	NH ₄ ⁺ -N (mg/L)	TN (mg/L)	TP (mg/L)	K (μg/L)	Ca (μg/L)	Mg (μg/L)	Cu (μg/L)	Zn (μg/L)
β_0	2862.3	10751.9	1069.3	7.593	0.207	0.648	6.122	82.305	50.98	104.021	56.073	57.224.1	14,432.2	74,687.2	274,774	289,996
β_1	1040.6 ^a	4287.3 ^a	463.7 ^a	3.072 ^a	-0.045 ^a	-0.002	-0.180	-4.545 ^a	10.78	49.278 ^a	12.241 ^a	17,447.2 ^a	7911.9 ^a	23,870.7 ^a	105,755 ^a	97,544
β_2	498.0 ^a	-910.2 ^a	195.9 ^a	-0.499 ^a	0.037 ^a	-0.043 ^a	0.686 ^a	-4.170 ^a	-1.18	13.993 ^a	-6.237 ^a	-1298.5	-18,141.3 ^a	-21,948.7 ^a	39,437	-589,555 ^a
β_3	439.2 ^a	-600.3 ^a	184.6 ^a	-1.133 ^a	0.033 ^a	-0.017 ^a	-0.326 ^a	-1.418	1.21	20.266 ^a	3.112 ^a	-1239.0	1356.9	2590.0 ^a	30,636	51,828
β_{12}	192.4	-143.9 ^a	80.2	-0.294	-0.005	0.002	-0.181	1.729	0.017	6.825	-1.175	-1405.3	-3649.0	-4363.2	6,508	-52,030
β_{13}	87.7	-521.0	43.8	-0.614	-0.005	-0.004	-0.004	-2.907 ^a	-2.79	4.775	1.023	-1486.5	-428.4	-668.0	-0.516	33,914
β_{23}	158.5	361.0	54.6	0.096 ^a	0.010	-0.005	-0.136	-1.680	2.50	5.748	2.893	2011.4	4008.4	5130.6	-16,303	-20,924
β_{11}	191.8 ^a	-129.0	3.9	-0.111	0.042 ^a	0.015 ^a	-0.081	1.898	-5.96	6.218	-0.223	-6844.3 ^a	2174.4	-4828.9	38,481	51,857
β_{22}	-8.5	750.4 ^a	14.8	-0.003	-0.006	0.008	0.268 ^a	0.662	3.33	-0.871	3.930 ^a	5877.5 ^a	10,202.2 ^a	10,312.0 ^a	28,723	412,55 ^a
β_{33}	-78.2	376.0	0.6	0.363	-0.011	0.005	0.062	0.884	-2.69	-2.144	1.706	1154.7	1169.6	-648.0	-19,547	32,135
R ²	0.979	0.991	0.969	0.986	0.871	0.926	0.920	0.928	0.906	0.974	0.968	0.968	0.946	0.929	0.884	0.959

Note: β_k is defined in Eq. (2).

^a This factor is significant at the 95% confidence level.

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 H₂O₂ 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 β_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_1) 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 (H₂O₂) 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 R² 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–H₂O₂, MW–acid MW–alkaline and recently proposed MW–H₂O₂–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, H₂O₂, 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–H₂O₂ 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 H₂O₂ to TSS was maintained constant while sludge pH was varied. When being held constant, the H₂O₂ 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 H₂O₂ dosages. The maximum COD released appeared in the corner of the matrix, coinciding with higher TSS, pH, and H₂O₂ 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, H₂O₂ ratio and initial pH) did not have a significant effect on the COD released.

In the present study, based on the optimization of H₂O₂ 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, H₂O₂ dose, and pH. The recommended values for TSS, the H₂O₂ to sludge ratio, and pH were determined to be

Fig. 1. Verification of values predicted by RSM with respect to observed SCOD released.

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 β_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 pre-treatment process. In the hybrid process (with H_2O_2) of an open system, the control and elimination of overflowing foam requires further study, particularly when used to treat very high concentrations of sludge owing to the of undesirable heavy foam.

H_2O_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_2O_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 ($OH\cdot$) formation through the decomposition

of H_2O_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_2O_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_2O_2 . Kenge et al. [20] recommended that the ratio of H_2O_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_2O_2 dosage and their relation to the cost of the pretreatment process. Yet the fate of H_2O_2 has received little attention in previous studies of MW- H_2O_2 technology. The results of the present study suggest that the dosage of H_2O_2 has little effect on the amount of residual H_2O_2 after treatment, suggesting that H_2O_2 takes part in the reaction only partially. Although H_2O_2 is stable under acidic conditions but active under alkaline conditions, where it decomposes easily [42], over 72% of H_2O_2 remained in bulk solution in all runs of the present study. Therefore, the amount of H_2O_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_2O_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_2O_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 H_2O_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.

Fig. 3. The optimal conditions for 16 response variables. (Red dots) organic matters and nutrient in solution, (green dots) metals in solution, (light blue dots) treated sludge properties, (yellow dots) TCOD of mixture, pH and H_2O_2 in solution, min and max in parentheses represent the optimal condition for the maximum or minimum values of this variables. (For interpretation of the references to color in this legend, the reader is referred to the web version of the article.)

bacterial surfaces, and the stability of H_2O_2 is influenced strongly by pH. During the MW– H_2O_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_2O_2 treatment may disturb the further post treatment of sludge. Nevertheless, the mechanisms by which pH affects the microwave– H_2O_2 sludge pretreatment process require further research.

3.4. Optimization of the MW– H_2O_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., $H_2O_2 \in [1.4, 2.0]$; $pH \in [8, 10]$). 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_2O_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_2O_2 , and high pH, accompanied by H_2O_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_2O_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_2O_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_2O_2 dosage) and enhancing anaerobic digestion (high pH, high H_2O_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_2O_2 dosage) and minimum ammonia release (low pH and H_2O_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_2O_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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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.jhazmat.2014.10.022>.

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