NSFC

ISSN 1001-0742
CN 11-2629/X

2012

Volume 24
Number 12

JOURNAL OF ENVIRONMENTAL SCIENCES

ELSEVIER

Science Press

Sponsored by
Research Center for Eco-Environmental Sciences
Chinese Academy of Sciences

ISSN 1001–0742 **Journal of Environmental Sciences** Vol. 24 No. 12 2012

CONTENTS

Aquatic environment

Atmospheric environment

Terrestrial environment

Environmental biology

Environmental health and toxicology

Environmental catalysis and materials

Environmental analytical methods

Serial parameter: CN 11-2629/X*1989*m*170*en*P*21*2012-12

Available online at www.sciencedirect.com
ScienceDirect
Journal of Environmental Sciences 2012, 24(12) 2060–2067

JOURNAL OF
ENVIRONMENTAL
SCIENCES
ISSN 1001-0742
CN 11-2629/X
www.jesc.ac.cn

Optimization of H_2O_2 dosage in microwave-H_2O_2 process for sludge pretreatment with uniform design method

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Received 28 November 2011; revised 02 September 2012; accepted 06 October 2012

Abstract

A microwave-H_2O_2 process for sludge pretreatment exhibited high efficiencies of releasing organics, nitrogen, and phosphorus, but large quantities of H_2O_2 residues were detected. A uniform design method was thus employed in this study to further optimize H_2O_2 dosage by investigating effects of pH and H_2O_2 dosage on the amount of H_2O_2 residue and releases of organics, nitrogen, and phosphorus. A regression model was established with pH and H_2O_2 dosage as the independent variables, and H_2O_2 residue and releases of organics, nitrogen, and phosphorus as the dependent variables. In the optimized microwave-H_2O_2 process, the pH value of the sludge was firstly adjusted to 11.0, then the sludge was heated to 80°C and H_2O_2 was dosed at a H_2O_2:mixed liquor suspended solids (MLSS) ratio of 0.2, and the sludge was finally heated to 100°C by microwave irradiation. Compared to the microwave-H_2O_2 process without optimization, the H_2O_2 dosage and the utilization rate of H_2O_2 in the optimized microwave-H_2O_2 process were reduced by 80% and greatly improved by 3.87 times, respectively, when the H_2O_2:MLSS dosage ratio was decreased from 1.0 to 0.2, resulting in nearly the same release rate of soluble chemical oxygen demand in the microwave-H_2O_2 process without optimization at H_2O_2:MLSS ratio of 0.5.

Key words: H_2O_2 dosage; uniform design method; microwave; optimization; sludge pretreatment

DOI: 10.1016/S1001-0742(11)60998-4

Introduction

Along with the rapid socioeconomic development of China, the sewage treatment rate and numbers of municipal wastewater treatment plants (WWTPs) are sharply increasing. The amount of municipal sewage treated daily increased to 102.62 million m^3 in 2010 from 80.91 million m^3 in 2005, and the municipal sewage treatment rate rose to 76.9% in 2010 from 48.4% in 2005 (National Bureau of Statistics of China, 2006, 2011). The treatment and disposal of sewage sludge, which is a byproduct of biological wastewater treatment, is thus becoming a big challenge for municipal WWTPs in China.

The costs of excess sludge treatment and disposal are about 20%–40% (and may be as high as 60%) of the total operating costs of WWTPs, and make a key impact on the application of biological wastewater treatment technology (Low and Chase, 1999). Hence, the current legal constraints, rising costs, and public sensitivity of sewage sludge disposal have provided considerable impetus to explore and develop strategies and technologies for the minimization of sludge production (Wei et al., 2003a). Many methods have been developed for sludge reduction, mainly based on the mechanisms of lysis-cryptic growth, uncoupling metabolism, maintenance metabolism, and predation on bacteria (Low and Chase, 1999; Liu and Tay, 2001; Wei et al., 2003a, 2003b). Sludge reduction technologies based on the lysis-cryptic growth mechanism, such as sludge reduction with ozone pretreatment or thermal pretreatment, show great potential for practical application. In addition, anaerobic sludge digestion is another way to achieve both sludge reduction and resources recovery as it is safe, environmental friendly and low cost (Weemaes et al., 2000). It is well known that almost all of the phosphorus and organic matter (mainly carbohydrates, proteins, and lipids) are contained in tight extracellular polymeric substances (EPS) in the sludge and the cell walls of microorganisms. Obviously, sludge pretreatment becomes the key step for both sludge reduction based on the lysis-cryptic growth mechanism and enhancement of anaerobic sludge digestion. Therefore, recently many researchers have focused on sludge pretreatment technologies mainly based on physical, chemical, and biological methods and their combinations for minimization of sludge production, improvement of sludge dewaterability and enhancement of sludge anaerobic digestion (Neyens and Baeyens, 2003; Odegaard, 2004; Cacho et al., 2006; Cacho and Suidan, 2006; Bordeleau and Droste, 2011; Chi et

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al., 2011; Coelho et al., 2011; Tyagi and Lo, 2011), and notably the hybrid sludge pretreatment technologies endow with promising outcomes through neutralizing the associated drawbacks with individual pretreatment techniques. As one of the most promising technologies, e.g., microwave pretreatment was proved to be the most effective for enhancing methane potential of pulp mill waste sludge, compared with ultrasonic and chemo-mechanical methods (Saha et al., 2011), studies of microwave technology and its combined processes for sludge pretreatment have received increasing attention in recent years. Microwave with pressure seal (Liao et al., 2005a), microwave under ambient pressure conditions (Cheng, 2008; Cheng et al., 2010; Yan et al., 2009), microwave-acid, microwave-alkali (Cheng, 2008; Cheng et al., 2009; Doğan and Sanin, 2009; Yan, 2010; Chi et al., 2011; Chang et al., 2012; Erden, 2012), microwave-H_2O_2 process (Eskicioglu et al., 2006, 2007, 2009; Liao et al., 2005a; 2005b; Lo et al., 2008; Wang, 2009; Wang et al., 2009a, 2009b; Wong et al., 2006a, 2006b; Yu et al., 2010a, 2010b) have been used to improve sludge disintegration and sludge disinfection, among which the microwave-H_2O_2 (MW-H_2O_2) process has been shown to be the most effective. Although some studies have focused on improving the lysis efficiency of sludge pretreated by microwave and combined processes, few studies have investigated decreasing the costs of microwave and its combined processes for sludge pretreatment, such as saving dosages of chemicals by optimizing these processes.

A new H_2O_2 dosing strategy for sludge pretreatment by the MW-H_2O_2 process was developed in previous study considering temperature sensitive of catalase (H_2O_2:H_2O_2-oxidoreductase, EC 1.11.1.6) in sludge (Wang et al., 2009a). Waste activated sludge was firstly heated to 80°C by microwave irradiation, then dosed with H_2O_2 at a H_2O_2:mixed liquor suspended solids (MLSS) ratio of 0.5–1.0, and continuously heated to 100°C by microwave irradiation, so that both the H_2O_2 utilization and sludge lysis efficiency were significantly improved. A laboratory test of sludge reduction for a conventional activated sludge (CAS) process was carried out by returning the sludge pretreated by the MW-H_2O_2 process with this new H_2O_2 dosing strategy into the aeration tank. The sludge reduction was found to be significant, i.e. the sludge yield (0.05 g TSS/g $COD_{removed}$) of the experimental group was much less than that of the control (0.12 g TSS/g $COD_{removed}$) (Wang, 2009). However, the H_2O_2 dosage was still very high and resulted in a high level of residual H_2O_2 in the pretreated sludge, hindering practical application of the MW-H_2O_2 advanced oxidation process for sludge reduction and resources recovery.

Previous studies also showed that alkaline conditions were helpful in improving the release efficiencies of organic matter, nitrogen, and phosphorus, as well as reducing H_2O_2 residues in sludge pretreated by the MW-H_2O_2 process (Wang, 2009; Yan, 2010). The chemical oxygen demand (COD) release rate for sludge pretreated by the MW-H_2O_2 process increased from 20.4% at pH 7.0 to 35.6% at pH 11.0. The uniform design method on the basis of the orthogonal design method is firstly established by Chinese mathematicians Kaitai Fang and Yuan Wang through combining the number theory with multivariate statistics, and usually applied for a multi-factor and multi-level experimental design approach (Li and Hu, 2005; Zhao, 2006). Compared with the traditional orthogonal design method, the uniform design method is capable of selecting experimental points uniformly in the experimental region and highly representative in the experimental domain, so that higher reliability can be achieved with the same number of tests (Li and Hu, 2005; Zhao, 2006). As an efficient way for optimizing various processes, the uniform design method is widely used in materials preparation, membrane fabrication and wastewater treatment (Leung et al., 2000; Li et al., 2003; Wang et al., 2012). Therefore, the purpose of this study was to further optimize the H_2O_2 dosage in the MW-H_2O_2 process with the uniform design method, by investigating the effects of pH and H_2O_2 dosage on both H_2O_2 residues and releases of organic matter, nitrogen, and phosphorus from sludge pretreated by the MW-H_2O_2 process.

1 Materials and methods

1.1 Experimental setup and sludge

A lab-scale industrial microwave reactor operating at 2450 MHz was designed by our research group and made by Julong Co. Ltd. (Baoding, China). It has about 25 L of cavity volume, and is equipped with a lift mixer and a thermocouple temperature sensor. The power of the microwave reactor can be steplessly adjusted in the range of 0–1000 W, but the microwave reactor was operated at 600 W and 50 r/min of the agitation rate, respectively, on the basis of results from previous studies (Cheng, 2008; Yan, 2010). H_2O_2 (A.R., 30%, W/W) at a density of 1.12 g/mL and a concentration of 336,000 mg/L was used in this study.

The waste activated sludge was obtained from Qinghe municipal WWTP with an A^2/O activated sludge process in Beijing, China. The design capacity of this WWTP is 400,000 m^3/day, and the sludge age is maintained at 20 days. In this study, the waste activated sludge was firstly passed through a 60-mesh screen and then adjusted to an approximate MLSS concentration of 20 g/L for batch testing (Table 1).

1.2 Experimental methods

According to the uniform design method, a $U8^*(8^5)$ uniform design table was used in this study, in which the number of factors was set to 2 with a uniformity deviation (D) of 0.1445. Eight uniformly distributed combinations of pH values and H_2O_2:MLSS ratios were tested. Table 2 shows parameters used to optimize the MW-H_2O_2 advanced oxidation process for sludge pretreatment. Each test was carried out in duplicate.

The effects of pH and H_2O_2 dosage on the H_2O_2 residue and releases of organic matter, nitrogen, and phosphorus from the sludge pretreated by the MW-H_2O_2 process

Table 1 Characteristics of the waste activated sludge

Site	MLSS (mg/L)	SCOD (mg/L)	NH_4^+-N* (mg/L)	PO_4^{3-}-P* (mg/L)	pH
Qinghe WWTP	18821.4 ± 283.3	172.4 ± 8.7	21.75 ± 1.31	5.89 ± 0.85	7.40 ± 0.01
RCEES STS**	11878.0 ± 370.5	36.0 ± 1.0	3.18 ± 0.42	2.63 ± 0.22	6.25 ± 0.01

* Concentrations of NH_4^+-N and PO_4^{3-}-P were determined in the supernatant of the raw sludge; ** sewage treatment station (STS) at Research Center for Eco-Environmental Sciences (RCEES), Chinese Academy of Sciences.
MLSS: mixed liquor suspended solids; SCOD: soluble chemical oxygen demand.

Table 2 Experiments for optimizing the microwave-H_2O_2 process by the uniform design method*

Series No.	Experimental conditions	
	Adjusted pH	H_2O_2:MLSS ratio
1	1 (7.5)	4 (0.5)
2	2 (8.0)	8 (0.9)
3	3 (8.5)	3 (0.4)
4	4 (9.0)	7 (0.8)
5	5 (9.5)	2 (0.3)
6	6 (10.0)	6 (0.7)
7	7 (10.5)	1 (0.2)
8	8 (11.0)	5 (0.6)

* Values in brackets are the values of the pH and H_2O_2:MLSS ratios.

were analyzed by the regression analysis. The regression analysis of the experimental data was carried out by the simplex and step-back methods using the Uniform Design software (Ver. 3.0, Uniform Design, China). The pH values and H_2O_2:MLSS ratios were as the independent variables (x, y), respectively, and the H_2O_2 residue ($H_2O_{2\text{-res}}$), total organic carbon (TOC), inorganic carbon (IC), ammonia nitrogen (NH_4^+-N), orthophosphate phosphorus (PO_4^{3-}-P), total nitrogen (TN), and total phosphorus (TP) were as the dependent variables (z). After optimizing the MW-H_2O_2 process, the release efficiencies of organic matter, nitrogen, and phosphorus from the sludge pretreated by the MW-H_2O_2 process with and without optimization were compared by batch experiments. Test 1 (without optimization):sludge was firstly heated to 80°C with microwave irradiation, then dosed H_2O_2 at a H_2O_2:MLSS ratio of 1.0, and continuously heated to 100°C with microwave irradiation. Test 2 (without optimization): sludge was pretreated the same as that in Test 1, but H_2O_2 was dosed at a H_2O_2:MLSS ratio of 0.5. Test 3 (with optimization): the pH value of the sludge was firstly adjusted to 11.0 by addition of 5.0 mol/L NaOH solution, and then the sludge was treated as that in Test 1, but H_2O_2 was dosed at a H_2O_2:MLSS ratio of 0.2. In these batch experiments to validate the optimized MW-H_2O_2 process, the waste activated sludge was obtained from a sewage treatment station (STS) operating with a vertical circulation oxidation ditch at a capacity of 200 m^3/day in Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences. The characteristics of the sludge are listed in Table 1.

1.3 Analysis

The concentration of residual H_2O_2 in the sludge samples was determined by a colorimetric method with Ti (Eisenberg, 1943). It is necessary to remove the residual H_2O_2 before analyzing all indicators except $H_2O_{2\text{-res}}$ considering the residual H_2O_2 would affect the determination of some parameters, such as TOC (Wang, 2009). In this study manganese dioxide (MnO_2) was used for catalytic decomposition of the residual H_2O_2 in the sludge samples (Wang, 2009). The concentrations of soluble TOC and soluble IC were determined by a TOC-VCPH analyzer (Shimadzu, Japan). The total chemical oxygen demand (TCOD) concentration of the waste activated sludge and SCOD concentration of the filtrate were determined by a DR2800 spectrophotometer (HACH, USA). The concentrations of TN, TP, NH_4^+-N, PO_4^{3-}-P, MLSS, and mixed liquor volatile suspended solids (MLVSS) were measured according to APHA methods (APHA, 2005).

2 Results and discussion

2.1 Regression analysis

Experimental results and coefficients for each parameter predicted by the regression model (Eq. (1)) are listed and compared in Tables 3 and 4, respectively.

$$z(H_2O_{2\text{-res}}) = p_1 + p_2x + p_3x^2 + p_4x^3 + p_5x^4 + p_6x^5 + p_7\ln y + p_8(\ln y)^2 + p_9(\ln y)^3 \quad (1)$$

To explain the regression model, an analysis of the H_2O_2 residual concentration ($H_2O_{2\text{-res}}$) was selected as an example. As shown in Eq. (1), $H_2O_{2\text{-res}}$ as the dependent variable (z) was fitted to the pH value and H_2O_2:MLSS ratio as independent variables x and y, respectively, and the values of p_1–p_9 in Eq. (1) were –8.46E+05, 3.76E+05, –5.77E+04, 3.29E+03, 1.99E–02, –4.20E+00, 1.08E+04, 1.11E+03, and –7.04E+02, respectively.

Obviously, the z value (e.g., $H_2O_{2\text{-res}}$, TOC, IC) can be predicted for non-test point combinations of the independent variables (x, y) within their definition ranges by Eq. (1). In order to investigate the accuracy of the regression model, several combinations of independent variables (x, y) within the ranges were selected for validation tests, and the calculated values (z) were compared with the experimental values. As shown in Fig. 1, the average of the ratios of the calculated values to the experimental values was 0.9946, indicating the high accuracy of the regression model. As shown in Fig. 2, the $H_2O_{2\text{-res}}$ concentration decreased with the increased pH value and the decreased H_2O_2:MLSS ratio. However, the H_2O_2:MLSS ratio had more significant impact on the $H_2O_{2\text{-res}}$ concentration.

As shown in Fig. 2, the results clearly showed that all concentrations of TOC, NH_4^+-N, PO_4^{3-}-P, TN, and TP increased with increases in both the pH value and H_2O_2:MLSS ratio. At the same H_2O_2 dosage, a high pH value improved the release efficiencies of organic matter, nitrogen, and phosphorus. For the same pH value, concentrations of TOC, NH_4^+-N, PO_4^{3-}-P, TN, and TP

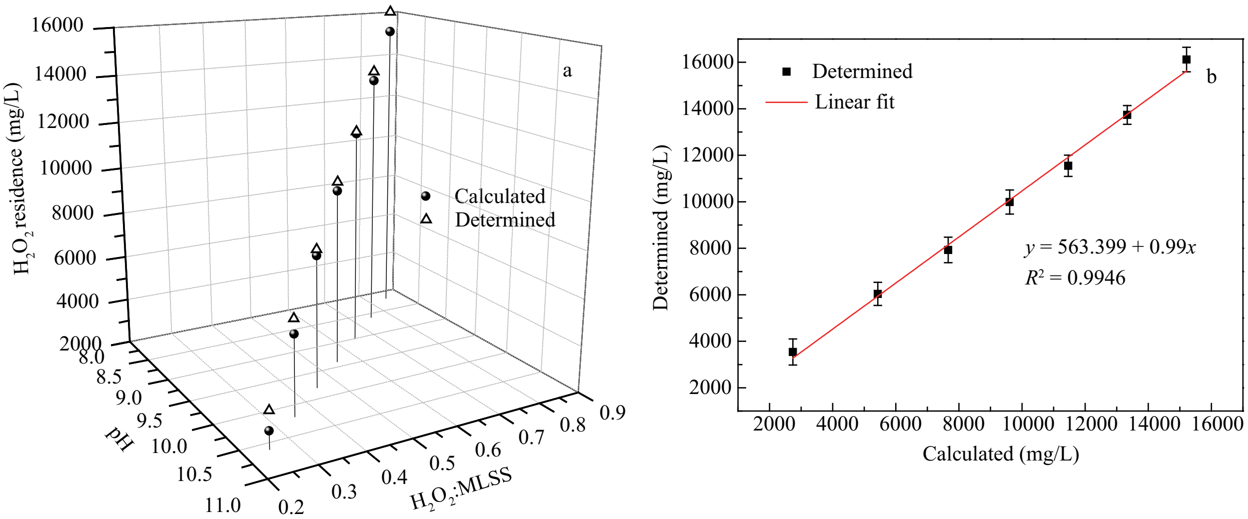

Fig. 1 Comparison of the calculated values of residual H_2O_2 with the experimental ones. (a) visual comparison; (b) ratios of the experimental value to the calculated value.

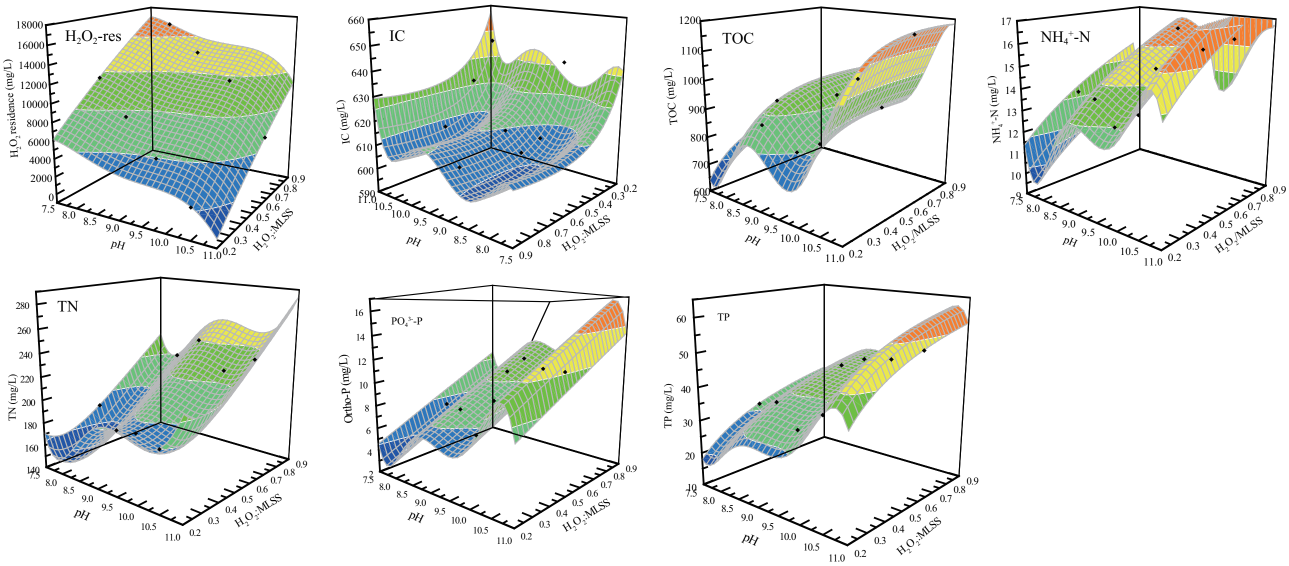

Fig. 2 Changes in calculated H_2O_2, IC, TOC, NH_4^+-N, TN, PO_4^{3-}-P, and TP concentrations (z) with pH value (x) and H_2O_2:MLSS ratio (y) based on the regression model.

released were increased with the increase of H_2O_2:MLSS ratio. It was reported that microwave heating would increase the decomposition of H_2O_2 into hydroxyl radicals and therefore enhance the oxidation process when H_2O_2 was applied simultaneously with either conventional or microwave heating (Yu et al., 2010a, 2010b; Eskicioglu et al., 2008). Additionally, Yu et al. (2010a, 2010b) found that release of organic matters was firstly increased with the increase of H_2O_2 dosage at the same temperature, and then decreased as further increase of H_2O_2 dosage. These results indicated that it would be necessary to optimize the H_2O_2 dosage of the MW-H_2O_2 process.

There are three main reasons for the greater oxidative effect of H_2O_2 under alkaline conditions during sludge pretreatment by the MW-H_2O_2 process in this study. Firstly, the activity of catalase (H_2O_2:H_2O_2-oxidoreductase, EC 1.11.1.6) is greatly inhibited by both temperature over 40°C and alkaline conditions. Catalase, a terminal respiratory enzyme, is present in all aerobic living cells and can break down H_2O_2 into water and molecular oxygen via a two-electron transfer mechanism, thus protecting cells from damage caused by reactive oxygen species. Peroxisomes are widely found in all aerobic living cells, and catalase accounts for about 40% of total peroxidase enzymes. Due to temperature sensitive, the catalase is active at the low temperature (5–35°C) and gradually inactive beyond 40°C (Gabbita and Hzuang, 1984; Wang et al., 2009a). A novel H_2O_2 dosing strategy in the MW-H_2O_2

Table 4 Coefficients of each parameter predicted by the regression model of Eq. (1)

Parameter	Root mean square residual	Residual sum of squares	Correlation coefficient	Coefficient of determination
$H_2O_{2\text{-res}}$	1.43E-03	1.64E-05	1.0000	1.0000
TOC	3.86E-04	1.19E-06	1.0000	1.0000
IC	6.29E-05	3.17E-08	1.0000	1.0000
TC	1.12E-04	9.96E-08	1.0000	1.0000
NH_4^+-N	1.57E-05	1.97E-09	1.0000	1.0000
TN	3.67E-04	1.08E-06	1.0000	1.0000
PO_4^{3-}-P	1.32E-07	1.40E-13	1.0000	1.0000
TP	3.58E-05	1.02E-08	1.0000	1.0000

Table 3 Experimental results of parameters by the uniform design method (Average ± S.D.)

Parameter	Series No.							
	1	2	3	4	5	6	7	8
H_2O_2:MLSS	0.5	0.9	0.4	0.8	0.3	0.7	0.2	0.6
Adjusted pH	7.50	8.00	8.50	9.00	9.50	10.00	10.50	11.00
pH after pretreatment	6.91 ± 0.08	6.77 ± 0.13	7.09 ± 0.14	6.88 ± 0.03	7.43 ± 0.06	7.44 ± 0.11	8.07 ± 0.14	7.91 ± 0.11
$H_2O_{2\text{-res}}$ (mg/L)	11170.89 ± 678.71	16124.69 ± 620.21	8073.31 ± 218.56	13500.63 ± 803.05	5299.18 ± 448.42	11318.05 ± 480.43	2471.14 ± 205.98	6477.89 ± 544.54
TOC (mg/L)	784.32 ± 93.97	849.97 ± 142.58	928.39 ± 197.75	958.10 ± 145.48	805.07 ± 103.76	895.73 ± 154.35	895.53 ± 119.80	1178.2 ± 151.97
IC (mg/L)	611.06 ± 23.02	607.11 ± 21.35	604.87 ± 17.13	604.60 ± 18.80	624.97 ± 25.82	610.73 ± 21.93	633.52 ± 41.01	628.05 ± 44.31
TC (mg/L)	1395.39 ± 112.53	1457.08 ± 134.67	1533.26 ± 214.79	1562.70 ± 231.52	1430.04 ± 119.09	1473.13 ± 137.13	1529.05 ± 155.17	1806.29 ± 115.75
NH_4^+-N (mg/L)	13.25 ± 0.74	13.84 ± 0.12	13.50 ± 0.61	16.32 ± 0.83	12.91 ± 0.36	15.69 ± 1.08	14.14 ± 1.03	16.52 ± 1.12
TN (mg/L)	213.58 ± 8.26	248.99 ± 21.04	196.58 ± 11.18	254.34 ± 16.40	192.98 ± 19.75	241.04 ± 16.99	204.83 ± 17.60	260.09 ± 13.40
PO_4^{3-}-P (mg/L)	6.97 ± 0.41	9.04 ± 1.16	7.57 ± 1.57	11.12 ± 1.12	6.51 ± 0.71	11.02 ± 1.50	10.46 ± 1.66	11.61 ± 1.49
TP (mg/L)	29.94 ± 3.00	38.17 ± 3.37	35.28 ± 4.76	43.93 ± 4.37	32.34 ± 3.65	47.48 ± 6.41	41.73 ± 4.37	53.46 ± 3.06

process was thus developed for reducing H_2O_2 dosage (Wang et al., 2009a). Although the catalase displayed a wide range of tolerance pH (6 and 9), the maximum catalase activity occurred at pH value of 7.0 as shown in Fig. 3 (Gabbita and Hzuang, 1984). In this study, the decomposition of H_2O_2 met with the first order kinetics when pH was in the range of 5.0–7.0 (Fig. 3). Obviously, the activity of catalase in this study was sharply inhibited with increases in both pH and temperature, thus resulting in little decomposition of H_2O_2 by catalase. Secondly, the combination of pH value and heating in this study can promote the decomposition of H_2O_2 into hydroxyl radicals (OH·) and superoxide ions (O_2^-·), and then enhance the oxidation process. Due to its weak acidity, H_2O_2 is stable under acidic conditions, but becomes unstable under alkaline conditions and can be easily decomposed into OH· and O_2^-· (Gould, 1985; Glaze et al., 1987; Qiang, 2002). Additionally, when the temperature is in the range of 60–80°C, the decomposition rate of H_2O_2 into OH· is known to rise linearly (Mo, 2008). Therefore, an effective way of releasing more OH· and O_2^-· through H_2O_2 decomposition would be to adjust the pH value to alkaline condition and heat the sludge to 80°C, thereby improving the utilization efficiency and oxidative effect of H_2O_2 during sludge pretreatment by the MW-H_2O_2 advanced oxidation process. Thirdly, in previous studies (Wang, 2009; Wang et al., 2009a; Yan, 2010; Eskicioglu et al., 2008; Doğan and Sanin, 2009; Chang et al., 2011), a synergistic effect occurred in sludge pretreated by a combination of microwave irradiation and alkaline conditions that promoted sludge disintegration. In this study, the pH value was firstly adjusted to 11.0 before sludge pretreatment by the MW-H_2O_2 advanced oxidation process, and this enhanced the effects of oxidation and disintegration of the sludge caused by H_2O_2 and/or OH·. In the study of Erdincler and Vesilind (2000), alkali was shown to react with cell walls and membranes in a variety of ways, e.g. saponification which occurred between the alkali and the fatty acids of cell membranes can change the permeability of cell membranes and damage the cell walls or structure of the membranes. In a summary, the addition of alkali can not only promote structural damage within the sludge and increase the release of particulate organic matter, but also promote the decomposition of H_2O_2 into OH· and O_2^-· (Fig. 4). Meanwhile the dosing H_2O_2 can significantly increase the permeability and fluidity of cell membranes, thus their combination results in a synergistic effect to enhance sludge disintegration.

While IC showed no significant change with pH variation, it decreased with an increase in the H_2O_2:MLSS ratio, which further reflected the oxidative decomposition of organic substances by the MW-H_2O_2 advanced oxidation process. The transformation of organic matter mainly involves dissolution and mineralization during the sludge pretreatment by the MW-H_2O_2 process. Mineralization indicates the generation of CO_2, and dissolution indicates the formation of soluble low-molecular-weight organics from particulate high-molecular-weight organics. Comparing IC and TOC in Fig. 2, as the H_2O_2:MLSS ratio increased, the increase in TOC concentration was much higher than

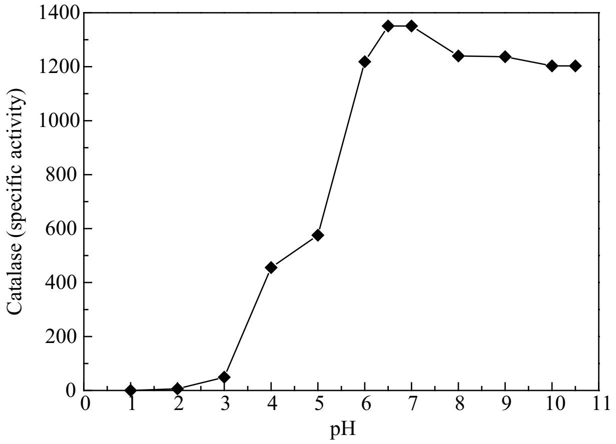

Fig. 3 Catalase activity of activated sludge vs. pH value.

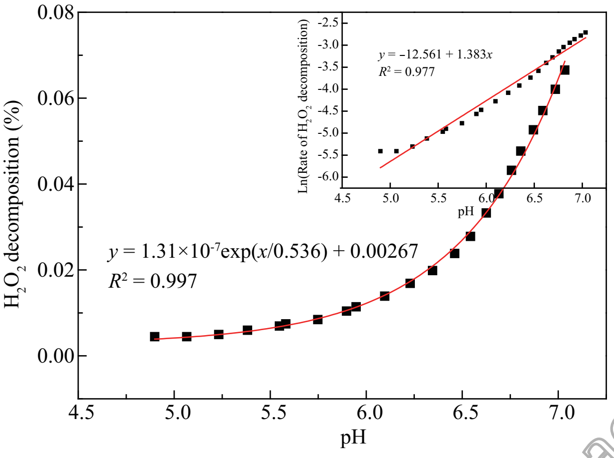

Fig. 4 Rates of decomposition of H_2O_2 vs. pH value.

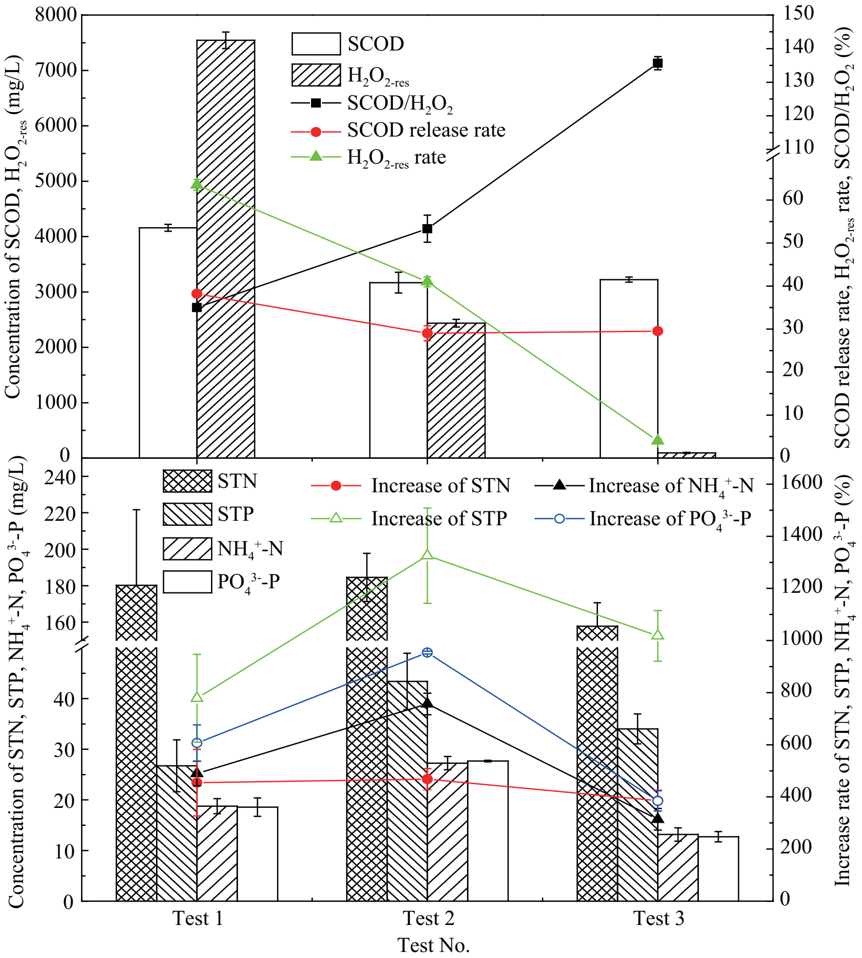

Fig. 5 Comparison of SCOD, NH_4^+-N/soluble total nitrogen (STN), PO_4^{3-}-P/soluble total phosphorus (STP), and $H_2O_{2\text{-res}}$ concentrations with and without optimization (the ratios of H_2O_2:MLSS for Test 1, 2 and 3 were 1.0, 0.5, and 0.2, respectively).

the decrease in IC concentration, indicating that most of the organic substances in the sludge were converted into low-molecule-weight organics and only a small quantity of soluble organics in the sludge were mineralized into CO_2. This result can not only prevent deterioration by sludge dewatering, but also promote the efficiency of sludge reduction or sludge anaerobic digestion.

2.2 Optimization of sludge pretreatment by the MW-H_2O_2 process

For the purposes of sludge post-treatment processes such as anaerobic digestion, high concentrations of nutrients and soluble organics need to be present at the end of sludge pretreatment. Therefore, the released TOC, TP, and TN and the residual H_2O_2 after sludge pretreatment by the MW-H_2O_2 process were set as optimization indices. The optimization directions of the released TOC, TP, and TN were set as positive and that of the residual H_2O_2 was set as negative. Equation (2) was established:

$$Z = Z_1 + Z_2 + Z_3 - Z_4 \qquad (2)$$

where, Z_1, Z_2, Z_3, and Z_4 are the indices of TOC, TP, TN, and $H_2O_{2\text{-res}}$, respectively. The regression model of Eq. (1) was substituted into the above mentioned variables within their definition ranges, and then the optimal values of the solution using the Michael Marquardt (Levenberg-Marquardt) and global optimization methods were obtained as x = 11, y = 0.2. This result showed the optimized operational conditions of the MW-H_2O_2 advanced oxidation process for sludge pretreatment as follows: the pH value of the sludge was firstly adjusted to 11.0, then the sludge was heated to 80°C with microwave irradiation and H_2O_2 was dosed at a H_2O_2:MLSS ratio of 0.2, and finally the sludge was continuously heated to 100°C with microwave irradiation.

2.3 Release rate of C, N, P in the optimized MW-H_2O_2 process

As shown in Fig. 5, when the H_2O_2:MLSS ratio was decreased from 1.0 (Test 1) to 0.5 (Test 2), the percentage of $H_2O_{2\text{-res}}$ decreased from 63.5% to 41.0%, the SCOD decreased from 4158 to 3168 mg/L, and the SCOD release rate decreased from 38.2% to 29.0%, whereas the concentrations of NH_4^+-N, PO_4^{3-}-P, and soluble total phosphorus (STP) all increased (e.g. NH_4^+-N increased from 18.76 to 27.25 mg/L, STP increased from 26.74 to 43.49 mg/L). When the H_2O_2:MLSS ratio was optimized at 0.2 (Test 3) and the pH was 11.0, the released SCOD concentration and rate from the sludge were 3223 mg/L and 29.5%, respectively, approximately the same as the SCOD released in Test 2 (H_2O_2:MLSS = 0.5), and the concentrations of NH_4^+-N, STN, PO_4^{3-}P, and STP were slightly less than those in Test 1 (H_2O_2:MLSS = 0.5), but the percentage of $H_2O_{2\text{-res}}$ decreased significantly from 63.5% (Test 1) and 41.0% (Test 2) to 4.0% (Test 3) with optimization. Therefore, with optimization, not only was the H_2O_2 dosage sharply reduced by 80% (H_2O_2:MLSS ratio reduced from 1.0 to 0.2), but also the release rate of SCOD was nearly the same as that without optimization (at a H_2O_2:MLSS ratio of 0.5). In addition, the sludge disintegration performance of this optimized MW-H_2O_2 process based on the released SCOD rate (29.5%) was higher than that (28%) of sludge pretreated in the MW-H_2O_2 process (at 120°C, 1 g H_2O_2/g MLSS) (Eskicioglu et al., 2008). Although the release rate of SCOD increased with a high dosage of H_2O_2 (H_2O_2:MLSS ratio greater than 0.5, such as Test 1), the utilization efficiency of H_2O_2 (measured by SCOD:H_2O_2 ratio) was only 35.0% in Test 1, which was much lower than those of in Test 2 (53.3%) and Test 3 (135.7%). It is clear that, with optimization, the sharply decreased H_2O_2 dosage can greatly reduce the cost of H_2O_2 in the sludge pretreatment by the MW- H_2O_2 advanced oxidation process.

3 Conclusions

Results clearly showed that the uniform design method was feasible and an effective way of optimizing the MW-H_2O_2 advanced oxidation process for sludge pretreatment. The optimized MW-H_2O_2 advanced oxidation process for sludge pretreatment was as the following: the pH value of the sludge was firstly adjusted to 11.0, the sludge was heated to 80°C with microwave irradiation, and then H_2O_2 was added at a H_2O_2:MLSS ratio of 0.2, and the sludge was continuously heated to 100°C with microwave irradiation.

With optimization, the H_2O_2 dosage was sharply reduced by 80% and the utilization rate of H_2O_2 was greatly improved by 3.87 times when the H_2O_2:MLSS ratio was decreased from 1.0 to 0.2, nearly the same release rate of SCOD was achieved as that without optimization at a H_2O_2:MLSS ratio of 0.5.

Acknowledgments

This work was supported by the National Natural Science Foundation of China (No. 51008297), the Hi-Tech Research and Development Program (863) of China (No. 2007AA06Z347) and the National Major Science & Technology Projects for Water Pollution Control and Management (No. 2012ZX07202-005).

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Journal of Environmental Sciences (Established in 1989)
Vol. 24　No. 12　2012

Supervised by Chinese Academy of Sciences
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Edited by Editorial Office of Journal of Environmental Sciences (JES)
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Tel: 86-10-62920553; http://www.jesc.ac.cn
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http://www.elsevier.com/locate/jes
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ISSN 1001-0742
9 771001 074123 12>