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Study on the reuse of municipal sludge treated with wet oxidation coupled with alkali hydrolysis

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ABSTRACT

In thus study, municipal sludge was treated by wet oxidation coupled with alkali hydrolysis for recycling as a carbon source for biological denitrification and struvite crystallization. The effects of the reaction variables on the soluble chemical oxygen demand (SCOD) yield were investigated. To obtain the optimal reaction conditions for the SCOD yield, a response surface method was used, and a quadratic regression equation model was established. The optimal reaction conditions were as follows: H_2O_2 dosage: 5.9 g, reaction time: 30 min, reaction temperature: 214°C, and NaOH dosage: 2.7 g. A SCOD yield of 58% was obtained, which is consistent with the predicted value. The results indicate that an alkaline hydrolytic solution can be effectively used as a carbon source for biological denitrification. When the ratio of C/N = 6, the highest denitrification rate of 0.51 mg/(g·h) was obtained. Struvite crystallization was used to recover phosphorus from the alkaline solution. The ratio of Mg/P and pH significantly affected struvite production. The analytical results from scanning electron microscopy, energy-dispersive X-ray spectroscopy, and Fourier-transform infrared spectroscopy indicated that struvite was the main substance in the crystallization production. The results of this study demonstrate the feasibility of reusing sewage sludge as a carbon source and struvite.

Keywords: Municipal sludge; Wet oxidation; Alkali hydrolysis; Carbon source; Struvite crystallization

1. Introduction

The process of urbanization has accelerated as China's socioeconomic status and quality of life have improved; consequently, increasing the annual discharge of domestic wastewater. In 2021, domestic sewage discharge reached 58.96 billion m^3. A large amount of municipal sludge is generated during the treatment of domestic waste [1]. To meet rigorous national drainage standards, advanced treatment is used to reduce the concentration of total nitrogen (TN) in the effluent of the secondary treatment. Due to insufficient biodegradable organic matter in the effluent, glucose, methanol, and sodium acetate have been used as supplementary carbon sources to improve the biological denitrification efficiency [2,3]. However, the use of supplementary carbon sources leads to high wastewater treatment costs [4]. Presently, the annual output of municipal sludge in China has exceeded 72 million tons, and the amount of municipal sludge in China is expected to exceed 90 million tons by 2025 [5]. The cost of sludge treatment and disposal accounts for approximately 50% of the total operating costs of sewage treatment plants [6], which poses severe challenges to their operation.

Municipal sludge is a complex aggregate composed of microbial micelles and a variety of organic and inorganic substances that have been adsorbed on its surface [7],

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including proteins, polysaccharides, carbohydrates, lipids, and nutritional elements (nitrogen and phosphorus) [8,9]. However, these components are trapped in complex networks formed by extracellular polymeric substances (EPS). The cell walls of bacteria are surrounded by highly hydrated EPS structures [10,11], which prevent the natural hydrolysis of sludge.

Many studies have reported sewage sludge treatment using anaerobic digestion [12], ultrasound treatment [13], wet oxidation [14,15], ozone oxidation [16] and alkaline hydrolysis [17,18]. Zhuo et al. [19] studied the effect of temperature on the hydrolysis of sewage sludge and determined that with increasing temperature, sludge hydrolysis significantly improved under alkaline conditions; however, the concentration of volatile fatty acids (VFA) did not increase with an increase in temperature. Xu et al. [20] reported the treatment of municipal sludge using alkaline hydrolysis-coupled ultrasonic treatment. The conditions were as follows: temperature: 73.6°C, alkali dosage: 0.085 g/g·TS, and ultrasonic energy: 9,551 kJ/kg. Under these conditions, 60.41% of sludge was cracked. After this pretreatment, the cost of sludge treatment was greatly reduced. Yang et al. [21] reported the use of ozone and alkaline hydrolysis technologies to treat municipal sludge, wherein 36.16% of sludge was crushed, and 138 mg/L of released polysaccharides was obtained. After 18 h of treatment, the sludge dehydration performance effectively improved. Li et al. [22] also studied the treatment of sludge using thermal alkaline hydrolysis. The results indicated that pH, temperature, and reaction time positively influenced the breaking of sludge cells. Under the optimal conditions of 70°C, pH = 11.0, and 1.0 h, the concentration of soluble chemical oxygen demand (SCOD) was 10,500 mg/L, and 44% of sludge was cracked. Kim et al. [23] used alkali hydrolysis and radiation to treat municipal sludge to recover organic carbon. The experimental results indicated that the chemical oxygen demand (COD) removal efficiency was 84% and TN removal efficiency was 51% under the optimal conditions (pH = 10, γ-ray irradiation: 20 kGy).

In contrast, limitations include high energy consumption, long reaction times, and the independent use of wet oxidation to treat sewage sludge [24]. With the addition of an alkali treatment coupled with wet oxidation, cell hydrolysis was significantly promoted, leading to milder reaction conditions. A better improvement in sludge hydrolysis was obtained with alkaline treatment than with acid treatment [25]. During alkali hydrolysis, alkali reacts with the lipids of microorganisms, resulting in the rupture of microbial cells, and intracellular nutrients are released into the liquid phase [26]. Therefore, the organics in sewage sludge can be reused as a carbon source [27] to compensate for the lack of carbon sources in wastewater plants [28]. Simultaneously, the phosphorus in sludge can be recovered to reduce the global shortage of phosphorus resources [29,30].

Although many studies on the resourceful treatment of municipal sludge have been reported, few have been conducted on the recycling of municipal sludge using wet oxidation combined with alkaline hydrolysis. In this study, wet oxidation coupled with alkaline hydrolysis was used to treat municipal sludge, and the effects of H_2O_2 dosage, reaction time, temperature, and NaOH dosage on SCOD production were investigated. To obtain the optimal conditions for SCOD production, experiments were designed using a response surface methodology (RSM) [31]. An accurate response surface model was obtained, and using glucose ($C_6H_{12}O_6$) and sodium acetate (CH_3COONa) for comparison, the denitrification rate of alkaline hydrolytic solutions for biological denitrification was investigated. Struvite crystallization was used to recover phosphorus from the alkaline solution. Furthermore, the effects of the Mg/P ratio and pH on struvite production were studied.

2. Experimental section

2.1. Experimental materials

The domestic wastewater and sludge used in the experiments were obtained from a domestic sewage treatment plant in Zhengzhou. The wastewater and sludge properties are listed in Tables 1 and 2, respectively. Analytically pure 30% H_2O_2 and NaOH were provided by Tianjin Fuchun Chemical Co., Ltd., (China). The wet oxidation reactor was manufactured by Xi'an Taikang Biotechnology Co., Ltd. (China), and the reactor volume was 200 mL. The maximum temperature and pressure of the reactor are 500°C and 60 MPa, respectively. The reactor was heated by an electric furnace. A schematic of the reactor is shown in Fig. 1.

2.2. Experimental procedures

2.2.1. Wet oxidation-coupled alkaline hydrolysis

For each experiment, 50 g of dewatered sewage sludge was dissolved in distilled water and appropriate amounts of

Table 1
Properties of domestic wastewater

Parameter	Value (mg/L)
COD	285–320
BOD_5	110–165
SS	112–175
TP	3.5–6.0
TN	30–45
NH_3–N	27–35

COD: chemical oxygen demand; BOD_5: biochemical oxygen demand; SS: suspended solids; TP: total phosphorus; TN: total nitrogen; NH_3–N: ammoniacal nitrogen

Table 2
Characteristics of raw sewage sludge sewage sludge sewage sludge

Parameter	Analysis results
Content of water (%)	83.6%
Organic matter (%)	53.37%
pH	6.52
TP (mg/g)	25.52
TCOD (mg/L)	120000

TP: total phosphorus; TCOD: total chemical oxygen demand

H_2O_2 and NaOH were added. The mixture was stirred evenly using an agitator. Next, the reactor was heated by an electric furnace with an average heating rate of 10°C/min, and the pressure in the reactor increased with temperature. When the temperature reached the set reaction conditions, the reaction was performed for the desired time. Simultaneously, the stirrer rotated at a speed of 130 rpm. After the reaction, the cooling device decreased the reactor temperature to normal atmospheric levels. The reaction products were collected and separated via centrifugation. The liquid sample was filtered with a 0.45 μm filter membrane. The SCOD concentration of the liquid phase was analyzed after 48 h.

2.2.2. Denitrification experiment

In this study, an alkaline hydrolytic sludge solution was used as the carbon source for biological denitrification. Denitrification experiments with different carbon sources were conducted based on sludge acclimation. Equal volumes of domestic wastewater were added to each of the three denitrification reactors. All the reactors were aerated for 24 h. After aeration was stopped for 30 min, the concentration of COD, NH_3–N, and TN of the supernatant were analyzed. After 3 h, when the dissolved oxygen concentration in the wastewater decreased, appropriate amounts of glucose ($C_6H_{12}O_6$), sodium acetate (CH_3COONa), and sludge alkaline hydrolytic solutions were added to the wastewater for biological denitrification. The NO_3–N concentration in the wastewater was also analyzed. Each reactor was stirred every 10 min and sampled every 30 min. The NO_3–N concentration was determined for each sample, and the denitrification rate was calculated.

2.2.3. Process of struvite crystallization

Phosphorus in the alkaline hydrolytic sludge solution was recovered to form struvite. Based on the properties of the alkaline hydrolytic solution, appropriate amounts of NH_4Cl and $MgCl_2$ were added to react with the phosphate. The rotation rate of the stirrer was increased to accelerate struvite generation, and a small quantity of NaOH was added to adjust the pH. After the reaction was complete, reaction products were filtrated using a 0.45 μm filter membrane, and total phosphorus (TP) and NH_4^+ concentrations were determined. The characteristics of struvite production were analyzed by scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDX), and Fourier-transform infrared spectroscopy (FTIR).

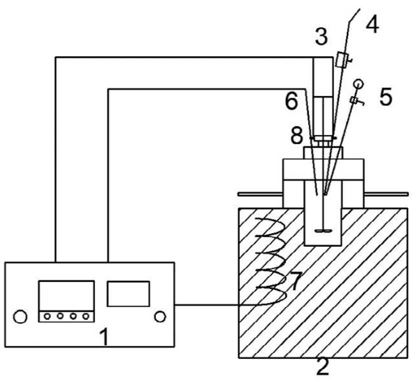

Fig. 1. Schematic diagram of the wet oxidation reactor. 1. Temperature/rotational speed program controller; 2. Reaction kettle; 3. Stirring device; 4. Exhaust port; 5. Pressure gauge; 6. Temperature detection device; 7. Heating device; 8. Cooling device.

2.3. Analytical methods

The total chemical oxygen demand (TCOD), SCOD, NO_3–N, NH_3–N, TN, and TP concentrations in the samples were analyzed according to national standard methods. The SCOD yield was determined using the following equation:

$$\text{SCOD removal}(\%) = \frac{\text{SCOD}_e - \text{TCOD}_0}{\text{TCOD}_0} \times 100\% \quad (1)$$

where SCOD removal (%) is the removal efficiency of SCOD in the sludge. SCOD_e is the SCOD of the liquid product after wet oxidation coupled with alkaline hydrolysis (mg/L), and TCOD_0 is the TCOD concentration in the sludge sample (mg/L).

The rate of denitrification rate was defined as follows:

$$\text{RD} = \frac{R}{\text{MLSS}} \quad (2)$$

where RD is the denitrification rate [mg/(g·h)], R is the slope, and mixed liquor suspended solids (MLSS) is the sludge concentration in the mixed solution (g/L).

The characteristics of struvite production was analyzed by EDX (EDX-8000/8100), SEM (Zeiss EVO LS-15) and FTIR (FTIR-7600).

3. Results and discussion

3.1. Effects of reaction variables on SCOD yield

3.1.1. Effect of H_2O_2 dosage on SCOD yield

The effect of the H_2O_2 dosage on the SCOD yield is shown in Fig. 2a. The SCOD yield increased from 17.92% to 21.67%, then decreased to 17.92% with the addition of H_2O_2. When 7 g of H_2O_2 was added, the maximum SCOD yield obtained was 21.67%.

Municipal sludge contains large quantities of organics, including some refractory organic substances. In this experiment, due to the high total organic carbon concentration (12,000 mg/L) of the sludge, the initial H_2O_2 dosage was relatively low, and the number of OH radicals generated from H_2O_2 was insufficient to decompose complex organic compounds. With an increase in H_2O_2 dosage, the organic matter in the sludge rapidly decomposed, resulting in an increase in the SCOD yield. However, the amount of H_2O_2 was not sufficient to decompose the refractory organic matter, and the newly generated complex organics led to a decrease in the SCOD yield. The values of NH_3–N and NO_3–N in the solution showed the same trend as the SCOD yield, which indicated the decomposition of nitrogenous organic matter with the addition of H_2O_2.

3.1.2. Effect of reaction time on SCOD yield

The effect of the reaction time on the SCOD yield is shown in Fig. 2b. When the reaction time reached 30 min, the maximum SCOD yield obtained was 21.67%. When the reaction time was prolonged, the SCOD yield initially decreased and then plateaued. The NH_3–N and NO_3–N concentrations slowly decreased with increasing reaction time. During sludge wet oxidation, soluble proteins decomposed, resulting in the generation of new organic substances, such as polypeptides and amino acids. Microbial cells also decomposed with reaction time, leading to a gradual increase in TP concentration.

3.1.3. Effect of reaction temperature on SCOD yield

In this study, the reaction temperature range was 170°C–250°C. Fig. 2c shows that the SCOD yield rapidly increases from 21.67% to 30% with a temperature increase from 130°C to 210°C. When reaction temperature reaches 250°C, the SCOD yield decreases to 26.25%. Because the oxidation reaction is endothermic, an increase in the reaction temperature increased the SCOD yield. In addition, at higher temperatures, the molecular thermal movement of the reaction system intensified. The mass transfer resistance between the organic matter and OH radicals generated from the decomposition of H_2O_2 decreased, which led to an acceleration of the reaction rate, resulting in an increased SCOD yield. In addition, the NH_3–N concentration increased rapidly with increasing temperature. However, with a further increase in the reaction temperature, large amounts of hydrothermal carbon, tar, and other by-products were generated, which was not conducive to further oxidation and led to a decrease in the SCOD yield.

3.1.4. Effect of NaOH dosage on SCOD yield

As shown in Fig. 2d, the NaOH dosage had a considerable effect on the SCOD yield. When 1 g NaOH was added to the reaction, the SCOD yield reached 52.08%, which was approximately twice the SCOD yield in the absence of NaOH. When the NaOH dosage was increased to 3 g, the SCOD yield increased slightly. However, when the dosage of NaOH exceeded 3 g, the SCOD yield decreased to 36.25%. The efficiency of alkali treatment depends on the dissolution and destruction of the sludge floc structures and cell walls by hydroxyl groups. In addition, saponification reactions occur via alkali and lipid substances present in the sludge microbial cell walls. When the biofilm ruptured, the intracellular substances dissolved and led to an increased SCOD yield and TP concentration.

3.2. Response surface method

3.2.1. RSM experiment design

The response surface method (RSM) was used to obtain the optimal reaction conditions for the SCOD yield.

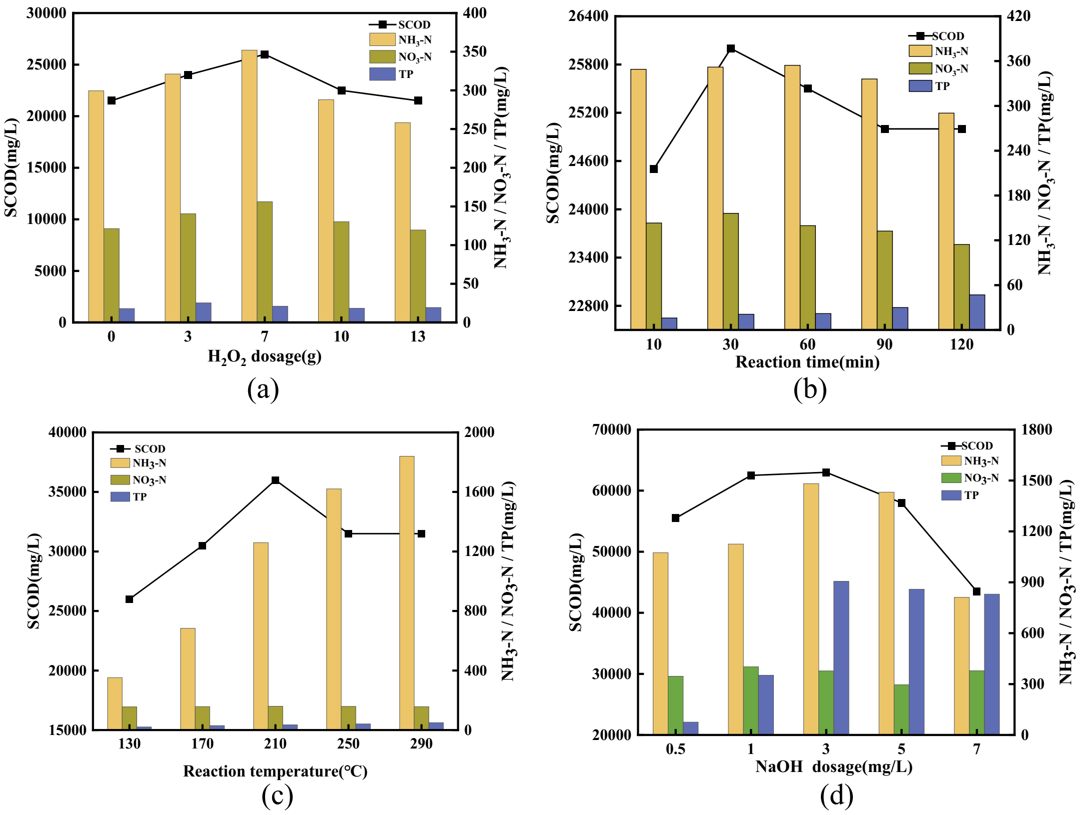

Fig. 2. Effects of (a) H_2O_2 dosage (g), (b) reaction time (min), (c) reaction temperature (°C), and (d) NaOH dosage (mg/L) on SCOD yield.

A central composite module was used to design the experiments, and a quadratic regression equation model was established. The experimental results are listed in Table 3.

The experimental results in Table 2 were analyzed by regression fitting, and a quadratic polynomial regression equation was obtained as follows:

$$Y = \begin{pmatrix} -1058.13 + 59.484A + 2.500B + 12.340C \\ +76.218D - 0.155AB - 0.071AC - 2.488AD \\ +0.015BC + 0.132BD - 0.013CD - 2.826A^2 \\ -0.076B^2 - 0.029C^2 - 11.747D^2 \end{pmatrix} \times 10^{-3} \quad (3)$$

where Y represents the SCOD yield (%), A is the dosage of H_2O_2 (g), B is the reaction time (min), C is the reaction temperature (°C), and D is the NaOH dosage (g).

3.2.2. Variance analysis and the interaction of variables

Using Eq. (3), variance analysis of the fitted model equation was performed. As shown in Table 4, $P < 0.0001$, indicating that the model had a high degree of fit with the experimental results. There were significant effects of H_2O_2 dosage, reaction time, reaction temperature, and NaOH dosage on SCOD yield. The coefficient of variation (CV) value of the model was 1.28%, which indicates a high experimental accuracy. The values of R^2 and R^2_{Adj} also indicate the rationality of the model. The order of the influencing variables is NaOH dosage > reaction temperature > H_2O_2 dosage > reaction time.

The influence of the reaction variable inversions on the SCOD yield is shown in Fig. 3.

As shown in Fig. 3, effects of the variable interactions on the SCOD yield were observed. The order of the variable interactions was as follows: H_2O_2 dosage + NaOH dosage > H_2O_2 dosage + reaction time > reaction time + reaction temperature > H_2O_2 dosage + reaction temperature > reaction time + NaOH dosage > reaction temperature + NaOH dosage.

According to the results of RSM experiments, the optimum conditions for treatment of sewage sludge using wet oxidation coupled with alkaline hydrolysis were as

Table 3
Response surface method experimental results

No.	H_2O_2 dosage (g)	Reaction time (min)	Reaction temperature (°C)	NaOH dosage (g)	SCOD yield (%)
1	6	30	210	5	51.25
2	9	30	210	3	54.66
3	7.5	20	230	2	54.41
4	6	30	210	3	57.91
5	4.5	40	190	2	53.33
6	4.5	20	190	4	52.75
7	7.5	40	230	4	51.25
8	6	30	250	3	53.75
9	4.5	20	190	2	54.12
10	7.5	20	190	4	52.08
11	6	30	210	3	56.91
12	4.5	40	230	4	55.12
13	3	30	210	3	54.56
14	4.5	40	230	2	54.66
15	7.5	40	230	2	54.66
16	6	50	210	3	53.33
17	6	30	170	3	51.42
18	7.5	20	190	2	54.50
19	6	30	210	1	53.66
20	4.5	20	230	4	52.53
21	7.5	20	230	4	52.50
22	6	30	210	3	56.50
23	4.5	20	230	2	55.14
24	4.5	40	190	4	52.58
25	6	10	210	3	54.91
26	6	30	210	3	57.91
27	6	30	210	3	57.08
28	7.5	40	190	4	51.25
29	7.5	40	190	2	53.75
30	6	30	210	3	56.50

Table 4
Variance analysis results of the regression model

Source	Sum of squares	df	Mean square	*F*-value	*P*-value Prob. > *F*	
Model	0.010	14	7.182×10^{-4}	14.87	<0.0001	Significant
A	1.321×10^{-4}	1	1.321×10^{-4}	2.74	0.1189	
B	8.778×10^{-5}	1	8.778×10^{-5}	1.82	0.1976	
C	4.655×10^{-4}	1	4.655×10^{-4}	9.64	0.0072	Significant
D	1.557×10^{-3}	1	1.557×10^{-3}	32.24	<0.0001	Significant
AB	8.696×10^{-5}	1	8.696×10^{-5}	1.80	0.1996	
AC	7.353×10^{-5}	1	7.353×10^{-5}	1.52	0.2362	
AD	2.228×10^{-4}	1	2.228×10^{-4}	4.61	0.0485	Significant
BC	8.327×10^{-5}	1	8.327×10^{-5}	1.72	0.2089	
BD	2.783×10^{-5}	1	2.783×10^{-5}	0.58	0.4595	
CD	1.156×10^{-6}	1	1.156×10^{-6}	0.024	0.8791	
A^2	1.109×10^{-3}	1	1.109×10^{-3}	22.97	0.0002	
B^2	1.578×10^{-3}	1	1.578×10^{-3}	32.68	<0.0001	
C^2	3.578×10^{-3}	1	3.578×10^{-3}	74.11	<0.0001	
D^2	3.785×10^{-3}	1	3.785×10^{-3}	78.38	<0.0001	
Residual	7.243×10^{-4}	15	4.829×10^{-5}			
Lack of fit	5.182×10^{-4}	10	5.182×10^{-5}	1.26	0.4232	Not significant
Pure error	2.061×10^{-4}	5	4.123×10^{-5}			
Cor. total	0.011	29				

follows: H_2O_2 dosage, 5.9 g; reaction time, 30 min; reaction temperature, 214°C; NaOH dosage, 2.7 g. These conditions resulted in an optimal SCOD yield of 57.3%.

Under these conditions, three parallel experiments were conducted; a maximum SCOD yield of 58.0% was obtained, which coincided with the predicted value of 57.3%. Furthermore, the error was 0.012%, which verified accuracy of the model.

3.3. Recycling utilization of liquid solution

3.3.1. Carbon sources for biological denitrification

In this study, a liquid solution of sludge treated by wet oxidation coupled with alkaline hydrolysis was used as a carbon source for biological denitrification. The effect of the liquid solution on denitrification rate was investigated. The characteristics of the liquid solution are listed in Table 5.

To study the efficiency of denitrification, glucose ($C_6H_{12}O_6$), sodium acetate (CH_3COONa), and an alkaline hydrolysis solution were added to the reactor, and biological denitrification was performed. As the reaction time increased, the NO_3–N and COD concentrations in the reactor decreased significantly. The denitrification rate was then measured. As shown in Fig. 4, when glucose and sodium acetate were used as carbon sources, the NO_3–N and COD concentrations in the reactor quickly decreased over 3 h, which indicates that almost all the glucose and sodium acetate decomposed in 3 h. As shown in Table 6, the denitrification rates of 0.54 and 0.78 mg/(g·h) were obtained, respectively. When an alkaline hydrolysis solution was added, the rate of decrease in NO_3–N and COD concentrations was relatively slow. Complete degradation of the alkaline hydrolysis solution took 7.5 h. Nevertheless, the denitrification rate was 0.51 mg/(g·h) in the first 2.5 h. The effect of different COD/TN ratios on denitrification efficiency was also investigated. When the COD/TN ratio changed from 5 to 7, the NO_3–N and COD concentrations rapidly decreased with reaction time. The maximum denitrification rate was obtained with a COD/TN ratio of 6. These results indicate that using an alkaline hydrolysis solution as a carbon source is feasible.

3.3.2. Struvite crystallization for phosphorus recovery

Due to the decomposition of nitrogenous and phosphoric organic substances in the sludge during wet oxidation coupled with alkaline hydrolysis, large quantities of TP and NH_3–N were observed in the reaction liquid.

As a popular way to recover phosphorus from wastewater, struvite crystallization has been reported by lots of literatures. In terms of application, the properties of struvite as an effective source of nutrients for plants and its low solubility in water [32], make it a slow-releasing valuable fertilizer that can reduce economic costs in agriculture [33]. The struvite crystallization method was investigated for recycling phosphorus and nitrogen from the solution. Magnesium chloride ($MgCl_2·6H_2O$) was added to the alkaline solution to generate struvite. The molar ratio of Mg/P and the pH of the solution for the recovery of phosphorus and nitrogen were investigated. As shown in Fig. 5a, TP recovery increased rapidly from 58.8% to 96.2% with an increase in the Mg/P ratio. Meanwhile, the NH_3–N recovery increased slowly from 15% to 35.8% under the same conditions.

In addition, pH significantly influenced struvite production. At a low pH, the generation of struvite was affected because phosphate reacts with heavy metals. However, at high pH, NH_4^+ reacts with OH^- to form $NH_3·6H_2O$. As shown

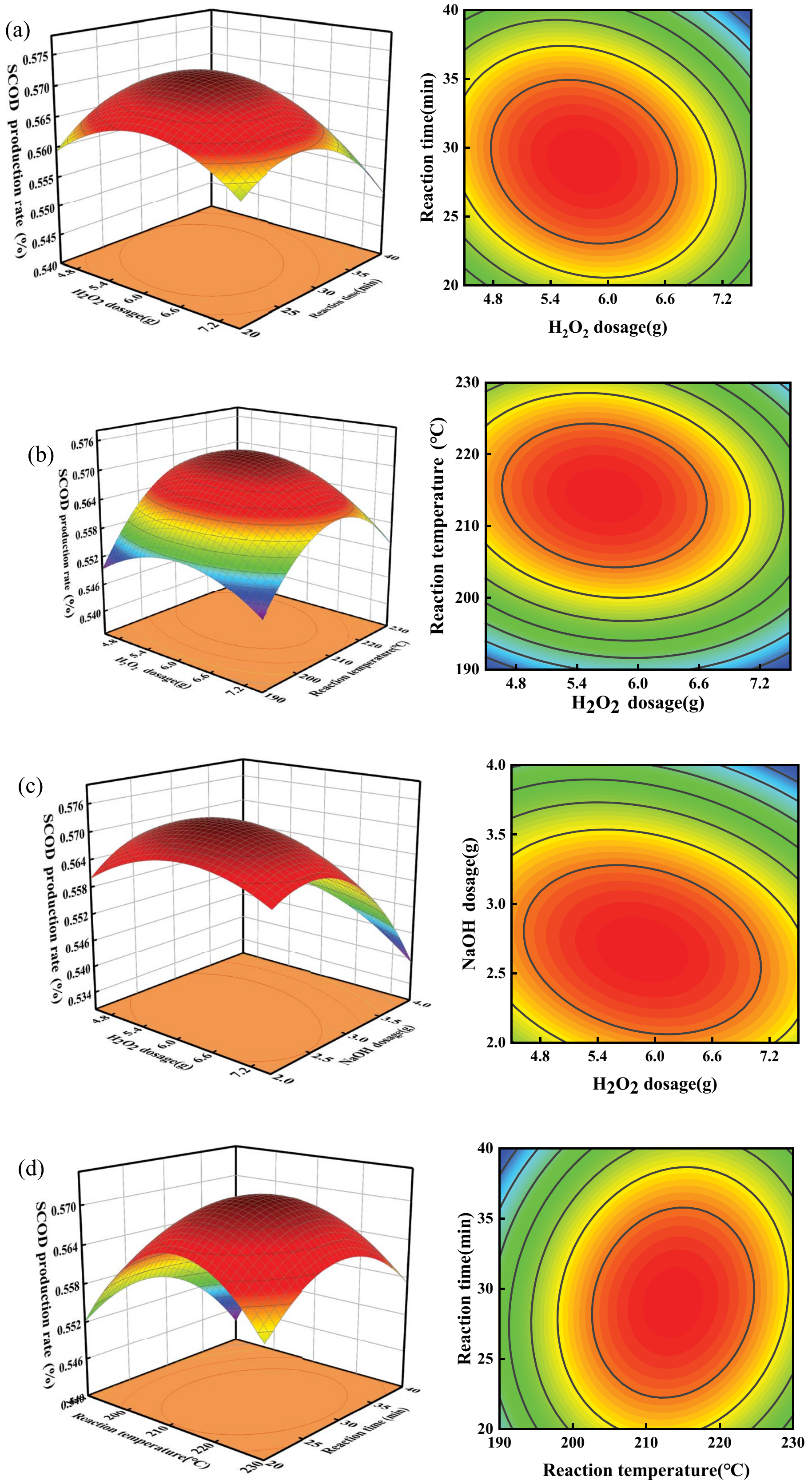

Fig. 3. Effects of interacting reaction variables on SCOD yield. (a) H_2O_2 dosage (g) and reaction time (min), (b) H_2O_2 dosage (g) and reaction temperature (°C), (c) H_2O_2 dosage (g) and NaOH dosage (g), and (d) reaction temperature (°C) and reaction time (min).

in Fig. 5b, when the pH reached 10, maximum TP and NH_3–N recoveries were simultaneously obtained. According to the experimental results, the optimum conditions for struvite production were Mg/P = 6:1 and pH = 10.

Under optimum conditions, struvite production was analyzed using SEM, EDX, and FTIR. As shown in Fig. 6, irregular kidney-shaped crystal particles were observed at a magnification of 500×. At a magnification of 5,000×, the crystalline form is single-phase, orthorhombic, and flat, which corresponds to the struvite crystal form.

The EDX results for struvite production are presented in Table 6. The results show that the main constituents of struvite production are O, Mg, and P, and small amounts of K, Ca, and N are also observed. The theoretical Mg/P molar ratio was 1.0. However, the value of the Mg/P ratio is 0.74, which indicates that some other phosphoric substances besides struvite were generated during production. The small quantities of K and Ca shown in Table 6 also indicate the presence of potassium phosphate and calcium phosphate during production. The EDX results indicate that K^+ and Ca^{2+} in the sludge solution compete with Mg^{2+} to react with PO_4^{3-}, resulting in a decrease in struvite purity. Therefore, a suitable Mg/P ratio must be determined to obtain high-purity struvite.

As shown in Fig. 7, infrared characteristic absorption peaks of PO_4^{3-} were observed at wave numbers of 1,082 and 567 cm^{-1}. This finding indicated the presence of a phosphoric

Table 5
Characteristics of alkaline hydrolysis solution

Parameter	Value
COD (mg/L)	69,500
TP (mg/L)	1,145
TN (mg/L)	2,150
NH_3–N (mg/L)	1,080
NO_3–N (mg/L)	693
pH	11.8

COD: chemical oxygen demand; TP: total phosphorus; TN: total nitrogen; NH_3–N: ammoniacal nitrogen; NO_3–N: nitrate nitrogen

Table 6
Chemical composition of struvite production

Element	Weight percentage (%)	Atomic percentage (%)
N	0.73	1.21
O	32.56	46.51
Mg	21.36	20.08
P	37.42	27.61
K	4.22	2.47
Ca	3.71	2.12

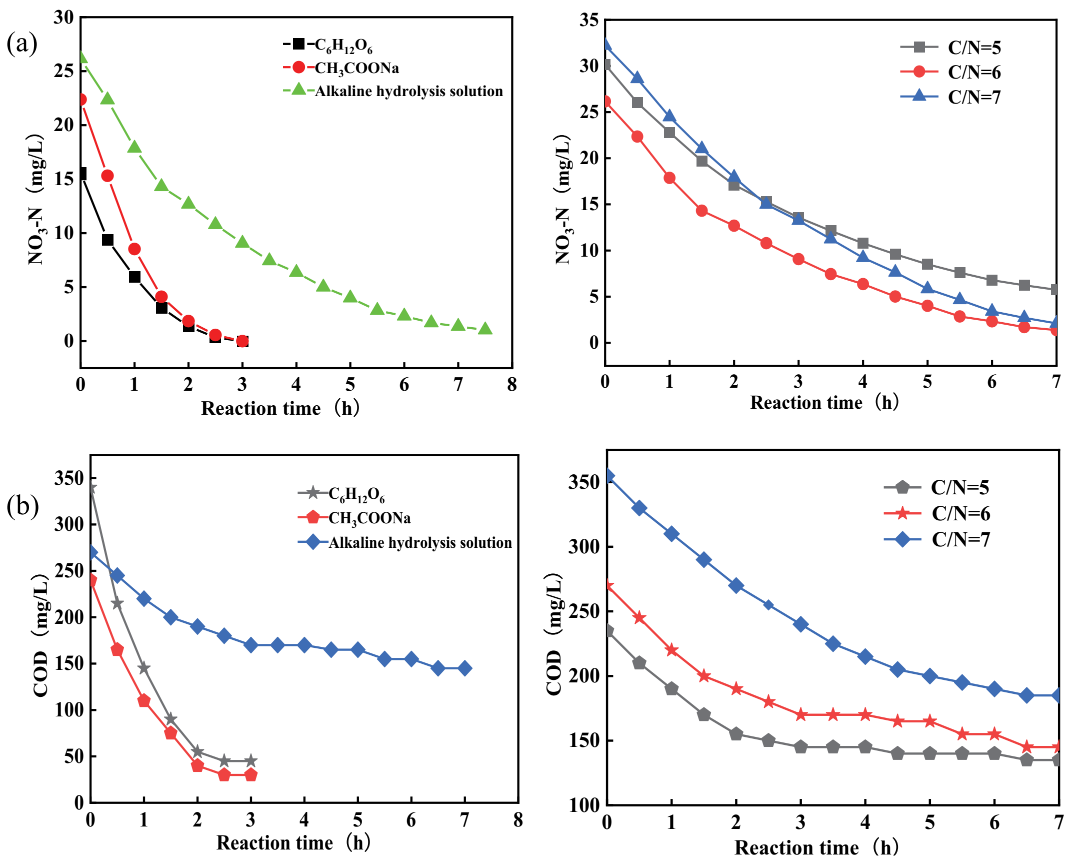

Fig. 4. Comparison of denitrification efficiencies. (a) NO_3–N and (b) chemical oxygen demand concentrations.

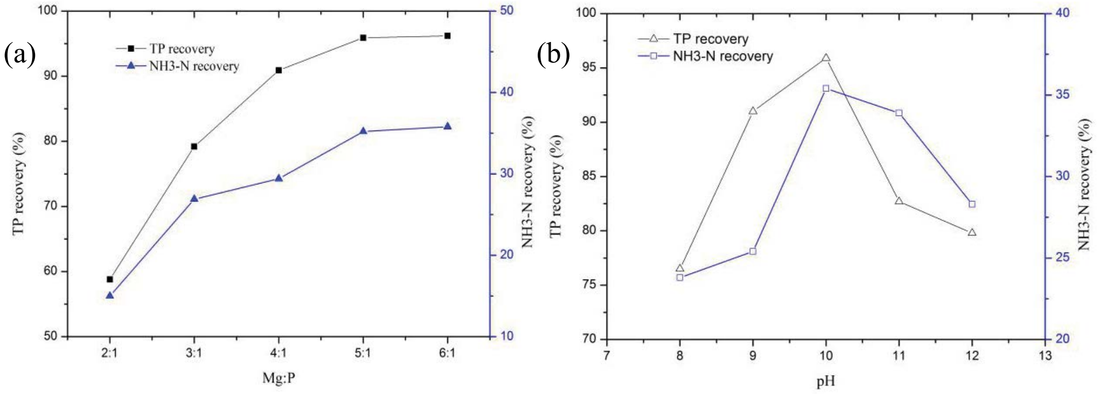

Fig. 5. Effect of molar ratio and pH on phosphorus and nitrogen recovery. (a) Molar ratio of PO_4^{3-}/Mg^{2+} and (b) pH

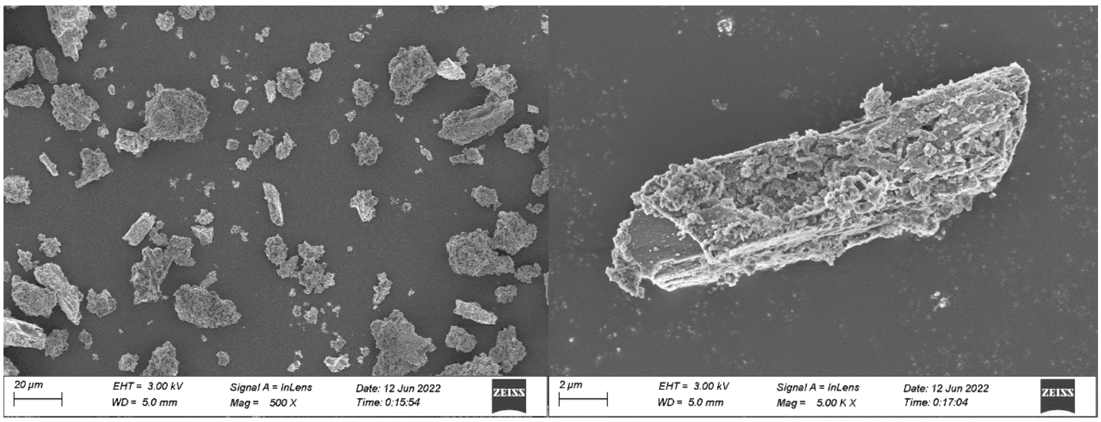

Fig. 6. Scanning electron microscopy of struvite production.

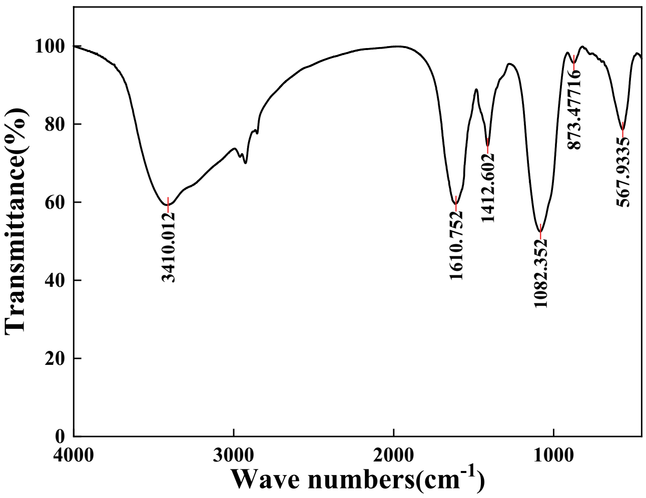

Fig. 7. Analytic Fourier-transform infrared spectroscopy results of struvite production.

substance. In contrast, at wave numbers of 1,412; 870, and 1,610 cm^{-1}, the characteristic absorption peaks of NH_4^+, CO_3^{2-}, and H_2O, respectively, were observed. The FTIR analysis results confirmed the generation of struvite.

4. Conclusions

In this study, wet oxidation coupled with alkali hydrolysis was used to reuse sewage sludge. Based on single-factor experiments, the RSM method was used to determine the reaction conditions for the optimal SCOD yield. Variance analysis expressed a reliable model and reasonable experimental design. Under the optimum conditions, a SCOD yield of 58.0% was obtained, which coincided with the predicted value of the model. The order of variable interactions was also obtained.

In addition, an alkaline hydrolysis solution was used as a carbon source for biological denitrification. Glucose, sodium acetate, and alkaline hydrolysis solutions were added during biological denitrification. The denitrification rate of the alkaline hydrolysis solution was similar to that of the glucose. Almost all the alkaline hydrolysis solutions could be decomposed entirely in 2.5 h. Furthermore, struvite crystallization was used to recover phosphorus from the solution. Significant effects of the Mg/P molar ratio and pH on struvite production were observed. The analytical results of SEM, EDX, and FTIR also indicated the generation of struvite during production. The experimental results of this study show that it is feasible and reasonable to use wet oxidation coupled with alkaline hydrolysis for the reuse of sewage sludge.

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Conflict-of-interest statement

The authors declare that we have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Author contributions

Weijin Gong: methodology and writing—original draft. Lei Huang: supervision, manuscript revision. Yue Ji: investigation. Jingjing Lv: conceptualization. Lina Guo: visualization and investigation. Yang Li: review and editing. Juexiu Li: project administration. Yuanling Ren: investigation. Jingjing Zhang: conceptualization.

References

[1] L.Q. Chu, W. He, F.L. Xu, Y.D. Tong, F.Q. Xu, Ecological risk assessment of toxic metal(loid)s for land application of sewage sludge in China, Sci. Total Environ., 836 (2022) 155549, doi: 10.1016/j.scitotenv.2022.155549.

[2] J.X. Shi, W.L. Huang, N. Wan, J. Wang, Effects of sodium acetate, glucose, and *Chlorella* powder as carbon source on enhanced treatment of phenolic compounds and NO_2^-–N in coal pyrolysis wastewater, Fuel, 339 (2023) 126974, doi: 10.1016/j.fuel.2022.126974.

[3] J. Meng, J.L. Li, J.Z. Li, P. Antwi, K.W. Deng, C. Wang, G. Buelna, Nitrogen removal from low COD/TN ratio manure-free piggery wastewater within an up-flow microaerobic sludge reactor, Bioresour. Technol., 198 (2015) 884–890.

[4] G.J. Yang, D.B. Wang, Q. Yang, J.W. Zhao, Y.W. Liu, Q.L. Wang, G.M. Zeng, X.M. Li, H.L. Li, Effect of acetate to glycerol ratio on enhanced biological phosphorus removal, Chemosphere, 196 (2018) 78–86.

[5] H.Q. Liu, H.Y. Qiao, S.Q. Liu, G.X. Wei, H.L. Zhao, K. Li, F.K. Weng, Energy, environment and economy assessment of sewage sludge incineration technologies in China, Energy, 264 (2023) 126294, doi: 10.1016/j.energy.2022.126294.

[6] K. Hii, S. Baroutian, R. Parthasarathy, D.J. Gapes, N. Eshtiaghi, A review of wet air oxidation and thermal hydrolysis technologies in sludge treatment, Bioresour. Technol., 155 (2014) 289–299.

[7] J. Li, E.R. Xiao, Z.B. Wu, The review of new technology on disposal of excess sludge, Acta Hydrob. Sin., 41 (2017) 1149–1156.

[8] W. Han, P.K. Jin, D.W. Chen, X.K. Liu, H. Jin, R. Wang, Y.J. Liu, Resource reclamation of municipal sewage sludge based on local conditions: a case study in Xi'an, China, J. Cleaner Prod., 316 (2021) 128189, doi: 10.1016/j.jclepro.2021.128189.

[9] S. Baroutian, A.M. Smit, D.J. Gapes, Relative influence of process variables during non-catalytic wet oxidation of municipal sludge, Bioresour. Technol., 148 (2013) 605–610.

[10] J.X. Fu, L.P. Ma, X. Jin, L. Wei, Optimization and reaction kinetics of extracting protein from sludge by thermal alkali hydrolysis, Environ. Sci. Technol., 44 (2021) 103–108.

[11] W. Lin, J.M. Guo, J. Zeng, R.L. Chen, H.H. Ngo, J. Nan, G.B. Li, J. Ma and A. Ding, Enhanced sludge dewaterability by ferrate/ferric chloride: the key role of Fe(IV) on the changes of EPS properties, Sci. Total Environ., 858 (2023) 159562, doi: 10.1016/j.scitotenv.2022.159562.

[12] L. Nazari, Z.S. Yuan, D. Santoro, S. Sarathy, D. Ho, D. Batstone, C.B. (Charles)Xu, M.B. Ray, Low-temperature thermal pre-treatment of municipal wastewater sludge: process optimization and effects on solubilization and anaerobic degradation, Water Res., 113 (2017) 111–123.

[13] H.Y. Jia, B.K. Liu, X.X. Zhang, J. Chen, W.H. Ren, Effects of ultrasonic treatment on the pyrolysis characteristics and kinetics of waste activated sludge, Environ. Res., 183 (2020) 109250, doi: 10.1016/j.envres.2020.109250.

[14] Y.N. Zhao, X.Y. Yan, J.H. Zhou, R. Li, S. Yang, B.F. Wang, R.N. Deng, Treatment of oily sludge by two-stage wet air oxidation, J. Energy Inst., 92 (2019) 1451–1457.

[15] M. Malhotra, A. Garg, Performance of non-catalytic thermal hydrolysis and wet oxidation for sewage sludge degradation under moderate operating conditions, J. Environ. Manage., 238 (2019) 72–83.

[16] D.D. Ge, C. Bian, H.P. Yuan, N.W. Zhu, An in-depth study on the deep-dewatering mechanism of waste activated sludge by ozonation pre-oxidation and chitosan re-flocculation conditioning, Sci. Total Environ., 714 (2020) 136627, doi: 10.1016/j.scitotenv.2020.136627.

[17] J. Liu, X. Zeng, J.F. Zhao, NaOH-enhanced catalytic wet air oxidation of pharmaceutical sludge, Environ. Prot. Chem. Ind., 37 (2017) 106–109.

[18] Y.X. Yan, Y.J. Zhang, J.L. Gao, L. Qin, F. Liu, W. Zeng, J.F. Wan, Intracellular and extracellular sources, transformation process and resource recovery value of proteins extracted from wastewater treatment sludge via alkaline thermal hydrolysis and enzymatic hydrolysis, Sci. Total Environ., 852 (2022) 158512, doi: 10.1016/j.scitotenv.2022.158512.

[19] G.H. Zhuo, Y.Y. Yan, XJ. Tan, X.H. Dai, Q. Zhou, Ultrasonic-pretreated waste activated sludge hydrolysis and volatile fatty acid accumulation under alkaline conditions: effect of temperature, J. Biotechnol., 159 (2012) 27–31.

[20] H.M. Xu, W.H. Qin, G.F. He, X.H. Dai, Optimization of combined ultrasonic and thermo-chemical pretreatment of waste activated sludge for enhanced disintegration, China Environ. Sci., 37 (2017) 3431–3436.

[21] N. Yang, S.C. Yang, X. Zheng, Inhibition of Maillard reaction during alkaline thermal hydrolysis of sludge, Sci. Total Environ., 8 (2022) 152497, doi: 10.1016/j.scitotenv.2021.152497.

[22] Z. Li, J.W. Lin, Y.Y. Hu, The effect of pretreatment of residual sludge with thermal–alkaline combined with hydrolysis process, J. South China Normal Univ., 51 (2019) 42–48.

[23] T.H. Kim, Y.K. Nam, C. Park, M. Lee, Carbon source recovery from waste activated sludge by alkaline hydrolysis and gamma-ray irradiation for biological denitrification, Bioresour. Technol., 100 (2009) 5694–5699.

[24] O. Suárez-Iglesias, J.L. Urrea, P. Oulego, S. Collado, M. Díaz, Valuable compounds from sewage sludge by thermal hydrolysis and wet oxidation. A review, Sci. Total Environ., 584–585 (2017) 921–934.

[25] S.T. Cassini, M.C.E. Andrade, T.A. Abreu, R. Keller, R.F. Gonçalves, Alkaline and acid hydrolytic processes in aerobic and anaerobic sludges: effect on total EPS and fractions, Water Sci. Technol., 53 (2006) 51–58.

[26] W. Fang, P.Y. Zhang, G.M. Zhang, S.G. Jin, D.Y. Li, M.X. Zhang, X.Z. Xu, Effect of alkaline addition on anaerobic sludge digestion with combined pretreatment of alkaline and high pressure homogenization, Bioresour. Technol., 168 (2014) 167–172.

[27] X.Y. Liu, H. Yang, J. Chang, Y.S. Bai, L.Y. Shi, B.J. Su, J. Han, D. Liang, Re-hydrolysis characteristics of alkaline fermentation liquid from waste activated sludge: feasibility as a carbon source for nitrogen removal, Process Saf. Environ. Prot., 165 (2022) 230–240.

[28] Q.S. Shen, F.Y. Ji, J.Z. Wei, L. Jiang, Q. Zhang, Y.X. Mao, Z.C. Liu, Nitrogen removal characteristic of A^2O system with natural corncob supplemented into anoxic zone as carbon source, China Environ. Sci., 42 (2022) 1635–1642.

[29] D. Cordell, J.O. Drangert, S. White, The story of phosphorus: global food security and food for thought, Global Environ. Change, 19 (2009) 292–305.

[30] J.Q. Zhang, Z.J. Chen, Y.W. Liu, W. Wei, B.J. Ni, Phosphorus recovery from wastewater and sewage sludge as vivianite,

J. Cleaner Prod., 370 (2022) 133439, doi: 10.1016/j.jclepro.2022.133439.

[31] A.V. Schenone, L.O. Conte, M.A. Botta, O.M. Alfano, Modeling and optimization of photo-Fenton degradation of 2,4-D using ferrioxalate complex and response surface methodology (RSM), J. Environ. Manage., 155 (2015) 177–183.

[32] X. Li, Q.L. Zhao, Recovery of ammonium-nitrogen from landfill leachate as a multinutrient fertilizer, Ecol. Eng., 20 (2003) 171–181.

[33] V. Arcas-Pilz, M. Rufí-Salís, F. Parada, A. Petit-Boix, X. Gabarrell, G. Villalba, Recovered phosphorus for a more resilient urban agriculture: assessment of the fertilizer potential of struvite in hydroponics, Sci. Total Environ., 799 (2021) 149424, doi: 10.1016/j.scitotenv.2021.149424.