



Nutrient removal from digested swine wastewater by combining ammonia stripping with struvite precipitation

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Abstract

Typical biological processing is often challenging for removing ammonia nitrogen and phosphate from swine wastewater due to inhibition of high ammonia on activity of microorganisms, exhaustion of time, and low efficiency. In this study, a physicochemical process by combining ammonia stripping with struvite precipitation has been tested to simultaneously remove ammonia nitrogen, phosphate, and chemical oxygen demand (COD) from digested swine wastewater (DSW) with high efficiency, low cost, and environmental friendliness. The pH, temperature, and magnesium content of DSW are the key factors for ammonia removal and phosphate recovery through combining stripping with struvite precipitation. MgO was used as the struvite precipitant for NH_4^+ and PO_4^{3-} and as the pH adjusted for air stripping of residual ammonia under the condition of 40 °C and 0.48 $\text{m}^3 \text{h}^{-1} \text{L}^{-1}$ aeration rate for 3 h. The results showed that the removal efficiency of ammonia, total phosphate, and COD from DSW significantly increased with increase of MgO dosage due to synergistic action of ammonia stripping and struvite precipitation. Considering the processing cost and national discharge standard for DSW, 0.75 g L^{-1} MgO dosage was recommended using the combining technology for nutrient removal from DSW. In addition, 88.03% NH_4^+ -N and 96.07% TP could be recovered from DSW by adsorption of phosphoric acid and precipitation of magnesium ammonium phosphate (MAP). The combined technology could effectively remove and recover the nutrients from DSW to achieve environmental protection and sustainable and renewable resource of DSW. An economic analysis showed that the combining technology for nutrient removal from DSW was feasible.

Keywords Digested swine wastewater · Struvite precipitation · Stripping · NH_4^+ -N · Phosphorus recovery · Volatile solid

Highlights

- Combined technology could achieve efficient removal of nutrients from DSW.
- Optimal MgO dosage was 0.75 g L^{-1} according to discharge standard and cost.
- NH_4^+ -N, TP, and COD were below national discharge standard via optimal treatment.
- Recovered efficiency of NH_4^+ -N and TP was 88.03 and 96.07%, respectively.
- A total of 309.4 mg g^{-1} MAP and 601.7 mg g^{-1} volatile solid could be obtained in sediments.

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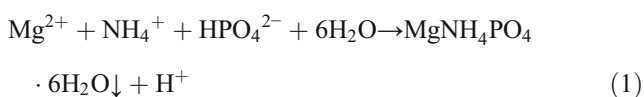
Introduction

With the increase in development of intensive livestock farm, China has become the largest supplier of meat in the world. Meanwhile, the yield of digested swine wastewater (DSW) also drastically increases causing a serious imbalance within the equilibrium of the ecosystem (Huang et al. 2017). Previous studies have reported that DSW contained 5000–20,000 mg L^{-1} chemical oxygen demand (COD), 60–100 mg L^{-1} total phosphorus (TP), 500–1000 mg L^{-1} NH_4^+ -N, and 500–1500 mg L^{-1} total organic carbon (TOC) (Dominic et al. 2018; Zheng et al. 2018; Vanotti et al. 2017), which surpasses the national discharge standard of swine wastewater (SW). Currently, many farms use anaerobic digestion to achieve wastewater treatment goals and utilization of a traditionally wasted resource. This method has the advantage of a green energy generation in production of biogas (Nasir et al. 2012). However, this technology could not achieve effective removal of nutrients from SW, such as nitrogen (N) and phosphorus (P)

sources (Lin et al. 2018; Kizito et al. 2015). These nutrient sources in DSW should be effectively removed/recovered before discharging to prevent costly environmental damage (Kumar and Pal 2015), such as eutrophication, exhaustion of dissolved oxygen, and the red tide phenomena in lakes and rivers caused by excessive N and P substance from DSW (Lin et al. 2018). With the importance of environmental protection, treatment of SW using suitable method has become increasingly urgent for livestock farming in China. Furthermore, the recovery of nutrients (nitrogen, phosphorus, and organic substance) from wastewaters for sustainable utilization has attracted intense attention from researchers worldwide.

Currently, NH_4^+ -N in SW can be removed through biological, physical, and chemical methods, such as nitrification and denitrification (Wang et al. 2010), adsorption of biochar (Sun et al. 2017), and membrane filtration (Li et al. 2018a). Although these methods could show optimistic removal efficiency, they inherently possess many challenges, including time-consuming, high-input cost for treatment of subsequent solid material adjusting pH with chemical material (NaOH and CaO) and even causing secondary pollution (such as increased Na^+ and Ca^{2+} in wastewater) (Limoli et al. 2016; Serna-Maza et al. 2015). In addition, these methods remove only a single substance and do not achieve recycling. The stripping technology could promote the transition of ammonia from NH_4^+ to NH_3 by forcing air into the SW. NH_4^+ -N in SW can be released from the aqueous phase by stripping and absorbed by phosphorus acid to avoid emission into the air causing the greenhouse effect (Shen et al. 2017). Then, the ammonia absorbed by phosphorus acid can be precipitated and recovered by forming struvite with the addition of Mg^{2+} (Li et al. 2017, 2019). However, the stripping method can only be achieved for NH_4^+ -N removal, and it has no significant effect on TP and COD removal from wastewater.

Phosphorus (P), a vital element to fulfill requirements of all living organisms, is a limited and non-renewable resource (Song et al. 2018; Huang et al. 2017). Studies have reported that the phosphate rock would be depleted within the next 50 years due to its low efficiency and non-recycling utilization in agriculture industry (Li et al. 2018b; Manyuchi et al. 2019). Therefore, viewing from the sustainable development of phosphorus and nitrogen sources, recovery of N and P sources from wastewater is very necessary to achieve livestock farming and resource recycling. Magnesium ammonium phosphate (MAP) ($\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$), a white crystalline compound, consists of Mg, NH_4^+ , and P in equal molar concentrations, according to Eq. (1) (Kwon et al. 2018), which can be used as a slow-releasing and long-acting fertilizer to achieve recycling utilization of N and P elements (Qiu et al. 2017).



Struvite precipitation acts as one of the preferred technologies in NH_4^+ -N and phosphorus removal from SW due to its high effectiveness, simplicity, environmental friendliness, and recoverability as a fertilizer additive (Barbosa et al. 2016). Many researchers reported that NH_4^+ -N could be efficiently removed from SW by struvite precipitation using magnesium phosphate (MP) (Song et al. 2018; Huang et al. 2016a). However, excessive addition of MP will also increase the TP concentration in SW. Thus, identifying a low-cost, high-efficient, and environment-friendly treatment technology to recover nutrients from SW is a mandatory requirement. Struvite formation mainly depends on two factors, molar ratio of $\text{Mg}:\text{NH}_4:\text{P}$ and pH value of SW. Many studies have reported that the Mg content is very low in SW. Therefore, a proper Mg source is required to form struvite crystals. Magnesium oxide (MgO), an inexpensive, abundant, and environment-friendly substance, is an important element for all living growth. MgO also has a high alkalinity, which could adjust pH of SW and serve as Mg source in deficient SW (Chimenos et al. 2003). Furthermore, MgO showed high adsorption capacity for removal of organic and polymeric substance, such as polysaccharide, polyphenols, and organic acid (Cai et al. 2017). However, the ratio of NH_4^+ and P was 2–10:1 in SW, which caused most of ammonia (over 50%) to not be removed via struvite precipitation (Cao et al. 2018b; Huang et al. 2017).

Accordingly, this study aims to (1) investigate the effect of MgO in respect of minimal environmental impact, cost on the removal and recovery efficiency of NH_4^+ -N, TP, and TOC in SW by combining stripping and struvite precipitation; (2) analyze the quality of the recovered precipitates, including total solids (TS), volatile solid (VS), and MAP content; and (3) optimize treatment condition according to cost of wastewater treatment and allowable effluent discharge limits in China.

Materials and methods

Materials

Digested swine manure (DSW) was obtained from an anaerobic digestion discharge pool in a pig farm in Pingxiang, Jiangxi Province, China, which is 12 km away from the laboratory. It was stored at 4 °C. Prior to the experiment, the DSW was pretreated by filtering with a 50-mesh filter to remove large solids. The specific characteristics of the filtered wastewater are shown in Table 1. The wastewater was diluted for analysis using ultrapure water.

Design of DSW treatment system

The design of the DSW treatment is shown schematically in Fig. 1. The system consisted of aeration, heating trap, settling

Table 1 Characteristics of the digested swine wastewater used in the experiments

Parameters	Average value plus standard deviation (triplicate)
NH ₄ ⁺ -N (mg L ⁻¹)	297.60 ± 2.39
TN (mg L ⁻¹)	460.20 ± 9.20
COD (mg L ⁻¹)	1602 ± 31.96
TOC (mg L ⁻¹)	780.2 ± 39.01
TP (mg L ⁻¹)	114.9 ± 7.24
TS (g L ⁻¹)	5.14 ± 0.42
VS (g L ⁻¹)	4.61 ± 0.12
Cu (mg L ⁻¹)	2.75 ± 0.10
Zn (mg L ⁻¹)	25 ± 0.35
pH	7.63 ± 0.04

pond, and absorption equipment. The wastewater container with a working volume of 1 L was made of Plexiglas. Air was introduced into the DSW via an aeration pump, and the air flow rate could be adjusted by a flow meter to obtain the required value.

Zhu et al. (2017) have reported the effects of parameters of air stripping (pH, aeration rate, temperature, and stripping time) on ammonia removal from wastewater by a single-factor experiment, in which the mass transfer coefficient (K_{La}) of ammonia stripping was 0.0084 min⁻¹ under the condition of 40 °C, pH 12.0, and 0.5 m³ h⁻¹ L⁻¹ aeration rate. Based on the reported mass transfer coefficient (K_{La}) of

ammonia stripping, characteristic of DSW, and national discharge standard for livestock wastewater in China, the initial pH of DSW could be calculated to be 9–10 under 40 °C, 0.48 m³ h⁻¹ L⁻¹ aeration rate for 3 h according to Eq. (2). The treatment experiments were performed as follows: DSW (1 L) and MgO (0–6 g L⁻¹) were added to the container. The container was buried in a heating trap and maintained at 40 °C. Air was aerated into the bottom of the container by an air pump at 0.48 m³ h⁻¹ L⁻¹ aeration rate for 3 h. After treatment, the DSW was stirred at 150 rpm for 10 min and, then, stored for 12 h to allow struvite accumulation and recovery at ambient temperature. The sediments were separated from the mixed solution through centrifugation and dried at 105 °C, and, then, their composition was analyzed. All experiments were performed in triplicate, and their average data were reported.

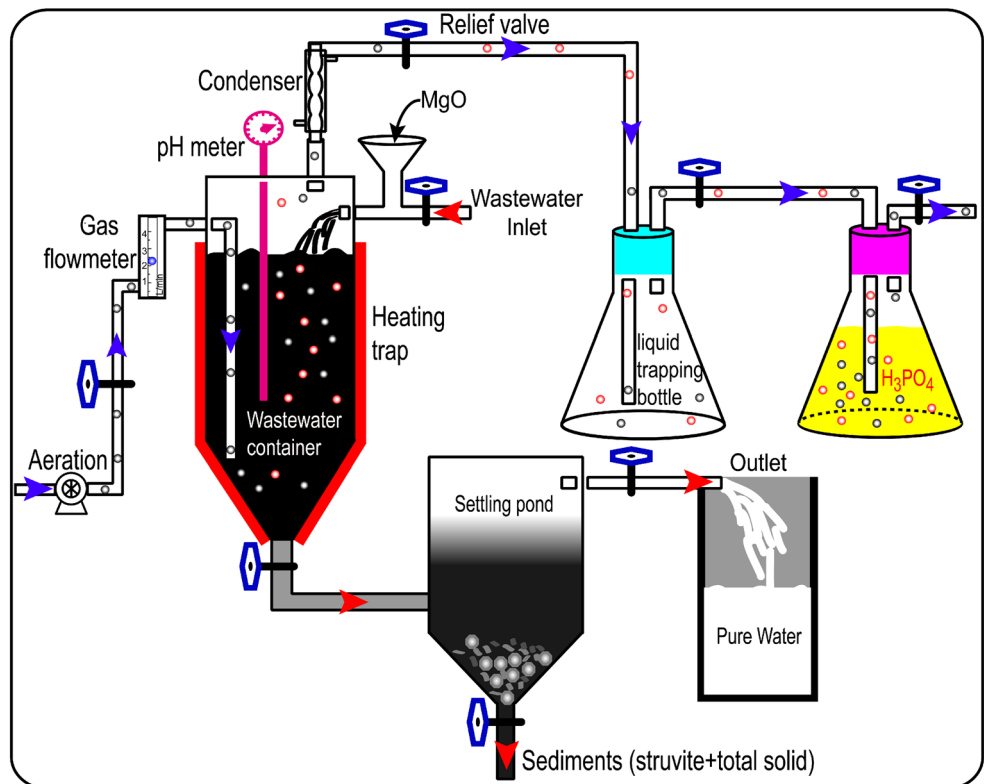
$$-\ln(C_t/C_0) = K_{La} \times t \tag{2}$$

Where C_t and C_0 are the ammonia nitrogen concentration at given time t and initial in DSW (mg L⁻¹), respectively. K_{La} is mass transfer coefficient of NH₃ from liquid phase to gas phase (min⁻¹).

Analysis methods

For the characteristic analysis of DSW, the samples were collected from treatment wastewater, appropriately diluted, and

Fig. 1 Overview of the complete nutrient recovery system in DSW



analyzed with a Lianhua 5B-6C spectrophotometer to determine $\text{NH}_4^+\text{-N}$, COD, and total phosphate (TP) (Cao et al. 2018a). The supernatants were also collected, appropriately diluted, and, then, filtered using 3- μm pore-sized filter paper before analysis. Then, 0.5 mL aqueous solution was placed in the multi N/C3100 Analyzer (Analytik Jena AG, Jena, Germany) to determine the concentration of total carbon (TC), total nitrogen (TN), and inorganic carbon (IC). Total organic carbon (TOC) is the difference between TC and IC. The pH solution was measured with a pH meter (Orion-3 STAR, Orion Corporation, USA). The total solid (TS) and volatile solid (VS) were determined according to Standard Methods (APHA 2009). The recovered precipitate was characterized with an X-ray diffractometer (XRD D8 ADVANCE, Bruker) and a Fourier-transform infrared spectroscopy spectrometer (Thermo Scientific Nicolet IS50, USA). The data was analyzed by IBM SPSS Statistic 23.

Results and discussions

Change in pH value in DSW

The pH value in DSW is a vital condition to ensure a successful stripping process (Gustin and Marinsek-Logar 2011). OH^- could promote the phase equilibrium to shift toward NH_3 and increase the vapor pressure of NH_3 , and, then, the released NH_3 from DSW can be effectively removed with air (Elsayed 2015). In Fig. 2, the pH value increased rapidly with increase to 1.0 g L^{-1} MgO and, then, steadily increased with the increase before treatment, which is mainly due to water diffusion into MgO particles and reaction on the surface. Equation (3) describes the hydroxylation of MgO in aqueous

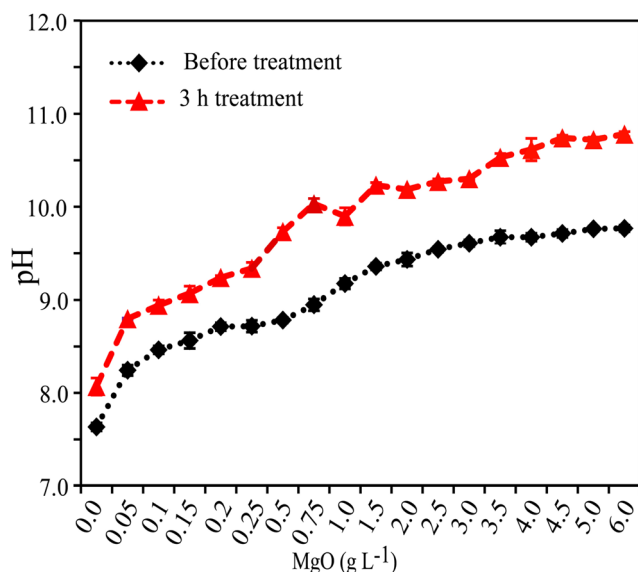
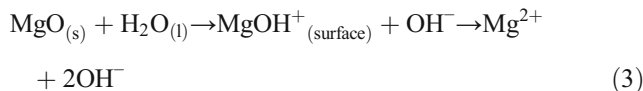


Fig. 2 Effect of MgO on pH before and after treatment

environment. After the reaction, the Mg^{2+} and OH^- could be released to drastically increase pH value in DSW, and, then, the aqueous solution gradually becomes supersaturated with $\text{Mg}(\text{OH})_2$ (Stolzenburg et al. 2015).



The pH over 9.2 in DSW may be attributed to unequilibrium of $\text{Mg}(\text{OH})_2$ ($\text{p}K_{sp} = 11.1$), caused by an excess of MgO (Chimenos et al. 2003). The pH of SW was approximately 7.63, 8.24, 9.17, 9.61, and 9.77 after adding 0, 0.05, 1.0, 3.0, and 6.0 g L^{-1} MgO, respectively. Many studies reported that the pH range for the lowest solubility of magnesium ammonium phosphate (MAP) was 8.0–10.0 (Stolzenburg et al. 2015). Thus, there had no significant effect on solubility of MAP with adding 0.05–6 g L^{-1} MgO to DSW.

After treatment under the condition of 40 °C and 0.48 $\text{m}^3 \text{h}^{-1} \text{L}^{-1}$ aeration rate for 3 h, the pH of DSW had a similar increasing trend as before treatment with increase of MgO. The pH value was higher than that before treatment and increased sharply from 8.07 to 10.23 when MgO dosage ranged from 0 to 1.5 g L^{-1} , which was mainly attributed to the high dissolution of MgO under the treatment temperature (40 °C) in DSW (Liu et al. 2011). Furthermore, phosphorus concentration at the initial reaction also increases the solubility of MgO due to the ion pair formation of Mg^{2+} , NH_4^+ , and PO_4^{3-} (Stolzenburg et al. 2015) and, then, steadily increased the pH to 10.78 at 6 g L^{-1} MgO owing to decrease of organic acids by adsorption precipitation of $\text{Mg}(\text{OH})_2$ in DSW (Cai et al. 2017). Many studies reported that the change in pH was closely related to the release of ammonium, and the maximum reduction of ammonium could be achieved at pH 9.0–10.0 due to ammonia gas formation ($\text{p}K_a = 9.2$) (Song et al. 2018; Gustin et al. 2011). The pH of DSW increased from 9.17 to 9.9 at 1.0 g L^{-1} MgO in DSW after treatment. Therefore, the NH_3 volatilization would reach the maximum value at 1.0 g L^{-1} MgO in DSW according to ammonia gas formation ($\text{p}K_a = 9.2$).

Change of $\text{NH}_4^+\text{-N}$ and TN concentrations in DSW

The concentration and removal efficiency of $\text{NH}_4^+\text{-N}$ and TN in DSW under different MgO dosages is shown in Fig. 3a, b, respectively. Figure 3a shows that the $\text{NH}_4^+\text{-N}$ removal efficiency increased as the MgO dosage increased. The two main reasons for the efficient removal were shown as follows: (1) Abundant OH^- produced by MgO and H_2O could promote the phase equilibrium of ammonia nitrogen toward the gaseous form and increase the rate of mass transfer and vapor pressure of NH_3 . Therefore, the NH_3 can easily enter the bubbles present in the DSW and is then removed by the air (Zhu et al. 2017). (2)

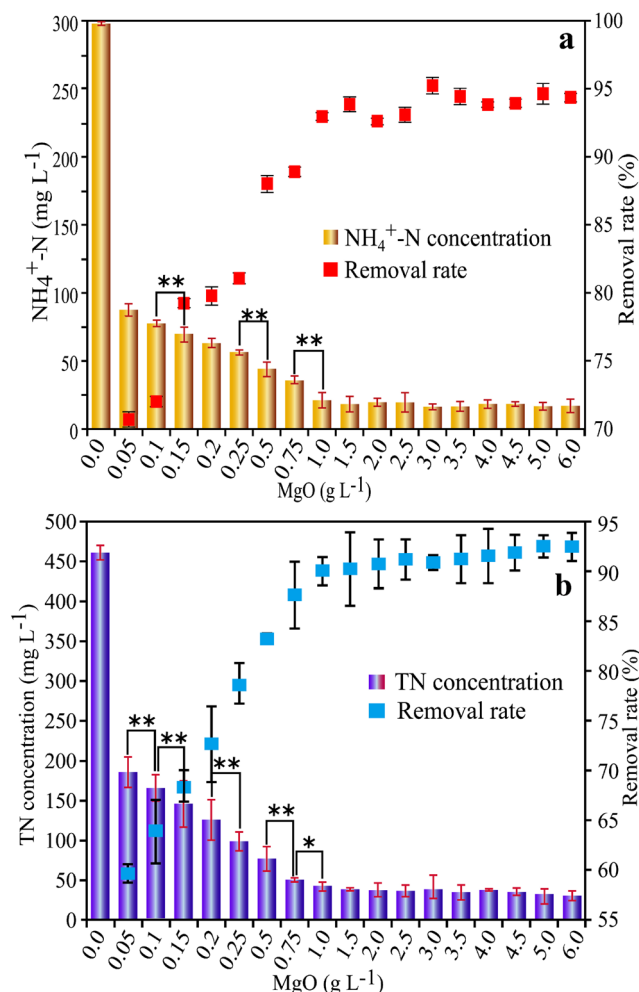


Fig. 3 Change of NH₄⁺-N (a) and TN (b) concentrations with different MgO contents in DSW (**P* < 0.05; ***P* < 0.01)

Formation of struvite precipitation (MgNH₄PO₄·6H₂O) with Mg²⁺ and PO₄³⁻ in DSW (Tansel et al. 2018). The NH₄⁺-N concentration decreased notably from 297.6 to 87.45 mg L⁻¹ (70.61% removal rate) at 40 °C under the condition of 0.48 m³ h⁻¹ L⁻¹ for 3 h stripping with 0.05 g L⁻¹ MgO in DSW. It was observed within the reaction that when 0.15 g L⁻¹ MgO was added, NH₄⁺-N concentration decreased to 67.6 mg L⁻¹ (≤ 80 mg L⁻¹, GB 18596-2001) with a removal rate of 77.28%. The NH₄⁺-N concentration decreased from 297.6 to 21.04 mg L⁻¹ (92.93% removal rate) when 1.0 g L⁻¹ MgO was added. The NH₄⁺-N concentration decreased to 16.90 mg L⁻¹ with a removal efficiency of 94.34% when MgO concentration was further increased to 6 g L⁻¹ MgO in DSW. The NH₃ volatilization rate was extremely high initially between 0.05 and 1.0 g L⁻¹ MgO, and no significant difference was observed between 1.0 and 6.0 g L⁻¹ MgO dosages mainly due to the decrease in the driving force and emission rate caused by the depletion of NH₃ and in DSW (Provolo et al. 2017). The MgO dosage was consistent with predicted dosage according to pH in DSW. In addition, while the MgO dosages increased to 0.15 g L⁻¹, the

NH₄⁺-N concentration in DSW was up to discharge standard (≤ 80 mg L⁻¹), and with removal efficiency of 79.22%.

The effect of MgO on the total nitrogen removal is shown in Fig. 3b. The variation of the curve is similar to the change of ammonium removal owing to NH₄⁺-N being the main component of nitrogen source, which accounts for 64.15% of TN in DSW. In addition, the removal efficiency of TN was lower than NH₄⁺-N. The TN concentration in DSW decreased from 460.2 to 30.61 mg L⁻¹ with 93.3% removal rate at 6.0 g L⁻¹ MgO. TN concentration was 68.27 mg L⁻¹ with addition of 0.15 g L⁻¹ MgO under the condition of 40 °C and 0.48 m³ h⁻¹ L⁻¹ aeration rate for 3 h.

Change in the TOC and COD concentrations in DSW

After anaerobic digestion treatment, the DSW would contain a high amount of organic substance, such as carbohydrates, lipids, and acetic acid, produced from microbial metabolism. In Fig. 4a, the result shows that TOC removal rates significantly increased

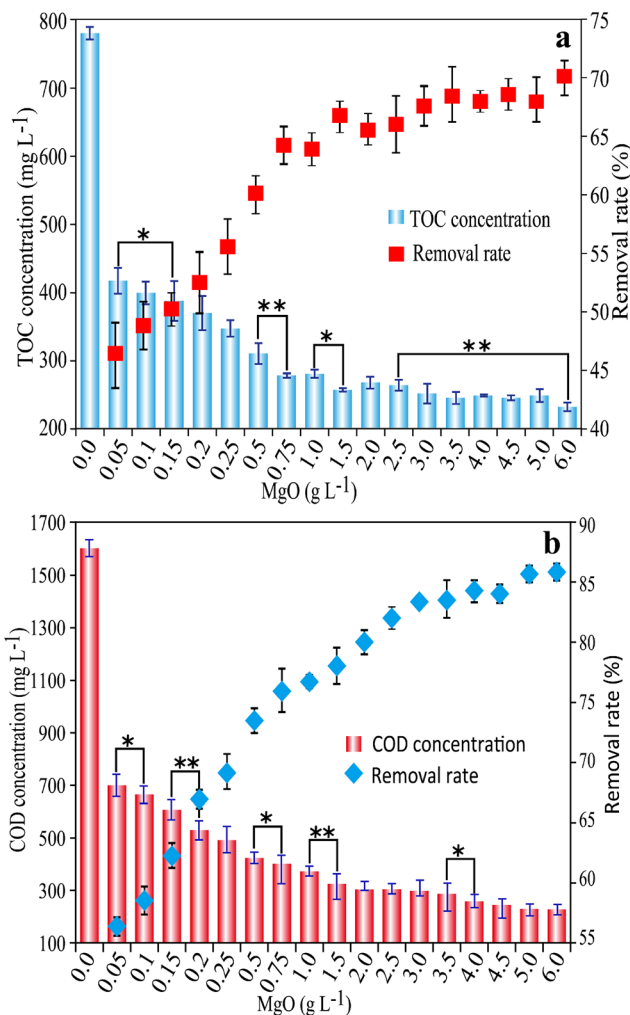


Fig. 4 Change of TOC (a) and COD (b) contents with different MgO concentrations in DSW (**P* < 0.05; ***P* < 0.01)

to 66.90% with the increase to 1.5 g L^{-1} MgO owing to incorporation into the struvite crystal lattice and sorption on the surface of struvite. Furthermore, the presence of carboxyl and hydroxyl groups in the polymeric substances can combine with Mg^{2+} , forming a complex precipitated substance (Liu et al. 2011; Huang et al. 2017), and, then, increase slowly due to depletion of the negative group. TOC removal efficiency was reaching 70.13% at 6 g L^{-1} MgO and TOC concentration in DSW decreased from 682.2 to 244 mg L^{-1} , representing 64.2% reductions at 0.75 g L^{-1} MgO.

COD concentration represents demand of oxygen for degradation of dissolved organic compounds in DSW, which has a positive correlation with TOC concentration. Therefore, a similar trend of change with COD concentration was observed after treatment. In Fig. 4b, the COD concentrations in DSW decreased from 1602.2 to 385.4 mg L^{-1} ($\leq 400 \text{ mg L}^{-1}$, Chinese discharge standards), representing 75.94% reductions at 0.75 g L^{-1} MgO, while TOC decreased from 682.2 to 244 mg L^{-1} with removal efficiency of 64.24%. Considering the treatment cost and discharge standard ($\leq 400 \text{ mg/L}$), 0.75 g L^{-1} MgO was the optimal dosage for COD removal.

Change in the TP concentration

The addition of Mg could increase the formation of struvite crystallization to decrease TP content in DSW (Tansel et al. 2018). Figure 5 reveals the evident effect of MgO on TP concentration in DSW. As seen in Fig. 5, under the condition of $40 \text{ }^\circ\text{C}$, $0.48 \text{ m}^3 \text{ h}^{-1} \text{ L}^{-1}$ for 3 h stripping, the TP concentration significantly decreased from 114.88 to 1.92 mg L^{-1} (98.33% removal rate) with the addition of 1 mg L^{-1} MgO (Mg:P molar ratio = 6.6) in DSW due to the formation of struvite precipitation ($P < 0.01$) and, then, had no significant difference with the increase to 6 g L^{-1} MgO, which indicated

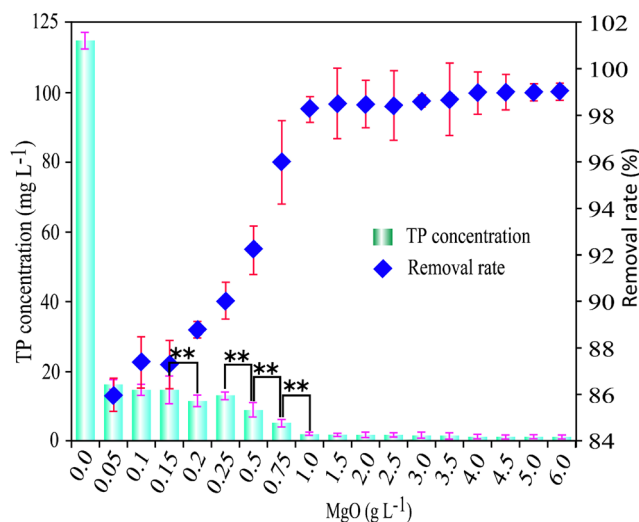


Fig. 5 Effect of MgO concentration on TP in DSW (* $P < 0.05$; ** $P < 0.01$)

that the $\text{PO}_4^{3-}\text{-P}$ was almost exhausted by the formation of struvite precipitation with magnesium and released NH_3 at 1.0 g L^{-1} MgO in DSW. The TP concentration decreased from 114.88 to 4.57 mg L^{-1} ($\leq 8 \text{ mg L}^{-1}$, GB 18596-2001) with an 85.93% removal rate at 0.75 g L^{-1} MgO in DSW.

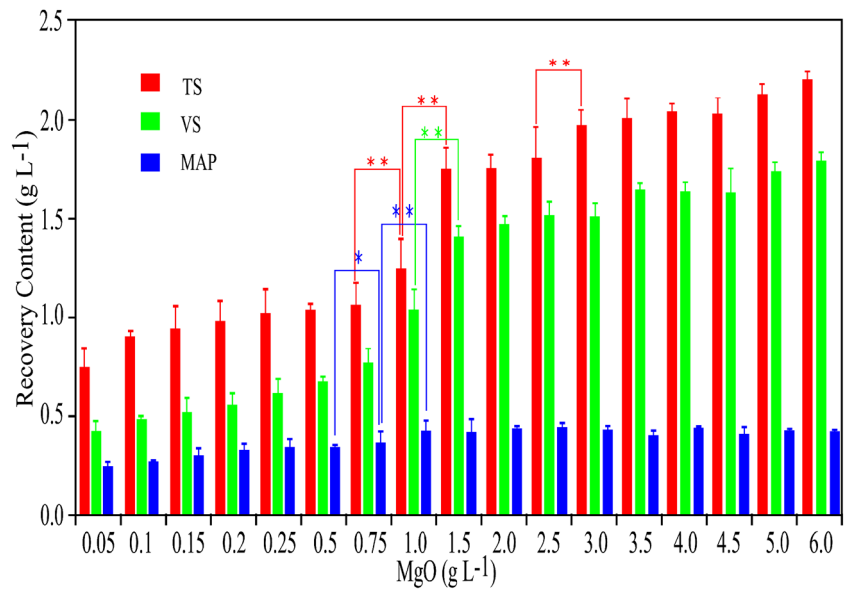
Change and traits of the recovered sediments from DSW

As result of quantities of solids insetting into the sediments during struvite precipitation process, it is unfeasible to obtain pure struvite for analysis. Some studies reported that the calcium concentration in swine manure was about $40\text{--}60 \text{ mg L}^{-1}$ and that calcium has great influence on the purity of struvite in precipitates due to the formation of amorphous calcium phosphate (ACP) (Yan and Shih 2016; Ye et al. 2011). Yan and Shih (2016) reported that there was a positive linear correlation between struvite content in precipitates and Mg/Ca molar ratio in the initial solution. The struvite contents in the precipitates were generally 95% while Mg/Ca molar ratio was 10:1. In this study, Mg/Ca molar ratio will be 10–20:1 after adding 0.75 g L^{-1} MgO, and the struvite content in the precipitates will be over 95%. Therefore, the effect of calcium on the purity of struvite precipitation could not be ignored.

The purification process of struvite mainly included two steps, acid dissolution and alkali precipitation, according to Liu et al. (2011). In Fig. 6, at $0\text{--}1.0 \text{ g L}^{-1}$ MgO, statistical analysis revealed that the MAP formation significantly increased with increased Mg level ($P < 0.01$). The struvite formation gradually increased to 424.65 mg L^{-1} (85.91%) at 1.0 g L^{-1} MgO with pH 9.17–9.9 in DSW and, then, no significant difference with increase in MgO dosage due to depletion of phosphorus sources (Huang et al. 2016b). Furthermore, increasing the pH to over 10 with increase in MgO dosage could promote gasification of ammonia nitrogen in solution converted from NH_4^+ to NH_3 , which cannot be used for struvite crystallization. The results indicated that the 1.0 g L^{-1} MgO was optimal added dosage in DSW for struvite formation, and the corresponding pH values were 9.17–9.90 in wastewater according to Fig. 2. The results were consistent with foregoing reported optimum pH (9.0–10.0) for MAP precipitation in DSW (Song et al. 2018; Lin et al. 2018).

During formation of struvite crystallization, there is settlement of massive solids along with the crystal to the bottom of the reactor due to insert into the crystal lattice or adsorption to the surface of struvite (Liu et al. 2011). As shown in Fig. 6, the recovery VS concentration from DSW significantly increased to 1.42 g L^{-1} with increase to 1.5 g L^{-1} MgO ($P < 0.01$) due to added Mg^{2+} mainly using to struvite formation and limited adsorption capacity of struvite and, then, slowly increased to 1.81 g L^{-1} at 6 g L^{-1} MgO because of adsorption of Mg^{2+} and flocculation precipitation of $\text{Mg}(\text{OH})_2$ with solid in DSW. According to Fig. 4b and Fig. 6, the recovered VS basically

Fig. 6 Change of sediments with different MgO contents in DSW (* $P < 0.05$; ** $P < 0.01$)



corresponded to the removal rate of TOC, which mainly contained organic polymeric substances. In addition, the change in VS showed a similar trend with TS. As shown in Fig. 6, the recovery TS from DSW drastically increased to 1.74 g L⁻¹ at 1.5 MgO g L⁻¹ and, then, slowly increased to 2.14 g L⁻¹ with the addition of 6.0 g L⁻¹ MgO. In addition, the results also exhibited that the VS was the main component in TS, and its content was over 80% depending on the coprecipitation of organic substance with struvite in wastewater.

To determine the mechanism of precipitation during the treatment process, FTIR and XRD characterization of sediments were conducted. The FTIR spectrum (Fig. 7a) demonstrated that the ammonium characteristic bands (1430, 1490, and 1650 nm) of the struvite mixture almost completely appeared after treatment (Huang et al. 2016a), thereby suggesting that the sediment contained ammonium that formed into struvite. Furthermore, the XRD patterns (Fig. 7b) revealed that the characteristic peaks of struvite and brucite appeared in the sediments after treatment (Huang et al. 2016b), whereas no characteristic peaks of struvite were observed in samples without MgO treatment. Thus, the sediments that contained struvite were formed by adding MgO with ammonium and phosphorus in DSW.

Recovery from DSW under optimal treatment condition

Considering the treatment cost and national discharge standard of NH₄⁺-N, TP, and COD for livestock wastewater in China, the optimal MgO concentration was 0.75 g L⁻¹ under the condition of 40 °C and 0.48 m³ h⁻¹ L⁻¹ aeration rate for 3 h, and the NH₄⁺-N, TP, and COD in DSW significantly decreased from 297.6, 114.9, and 1602.2 mg L⁻¹ to 35.6 (≤80), 4.57 (≤8), and 385.4 (≤400) mg L⁻¹, respectively, at 0.75 g L⁻¹ MgO. In addition, 262.0 mg L⁻¹ NH₄⁺-N could be recovered from DSW with

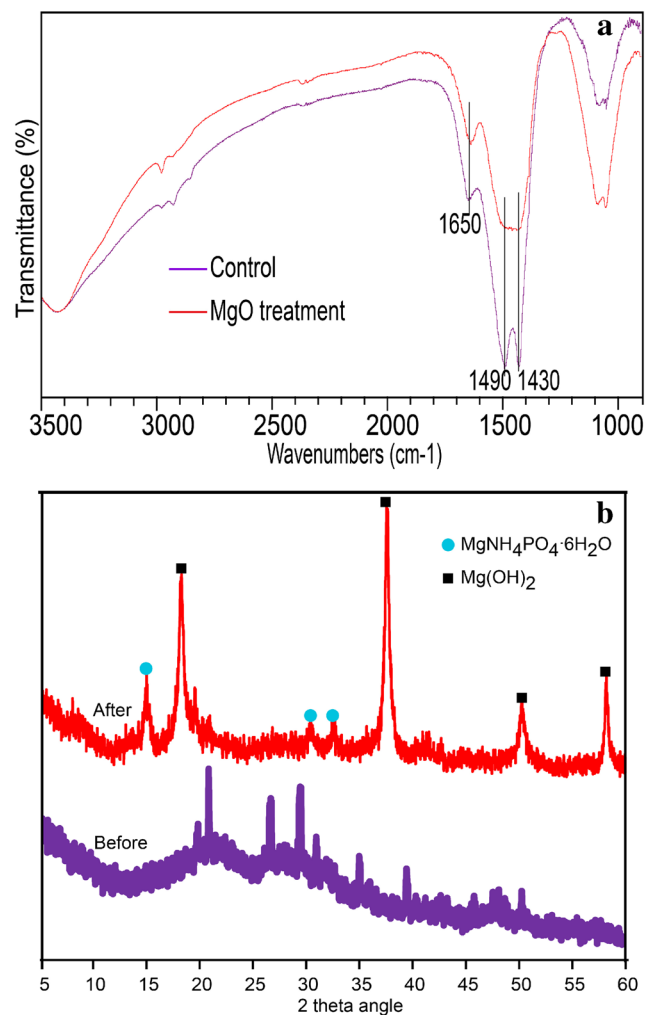
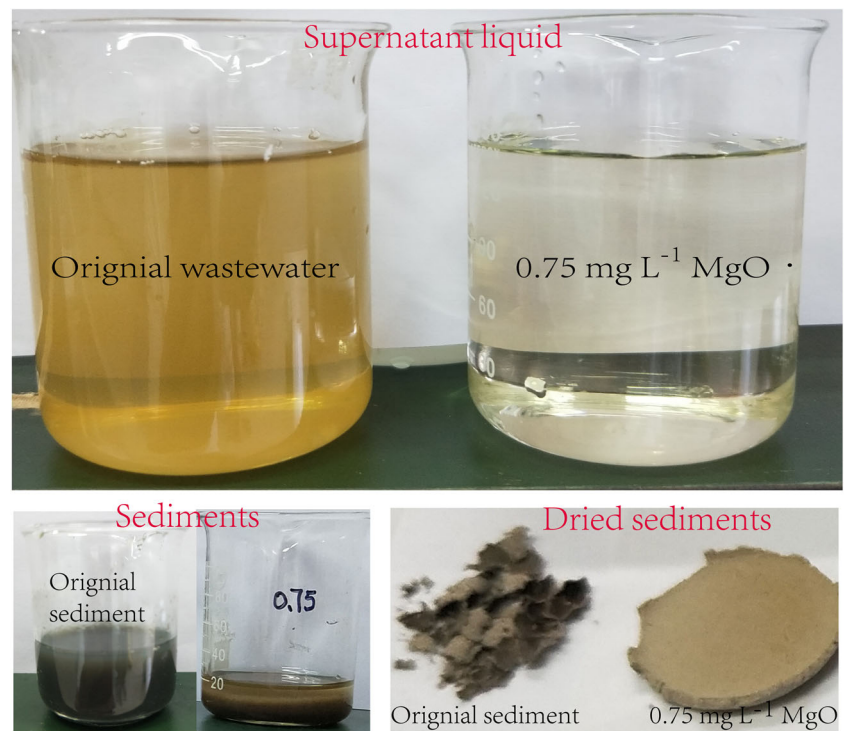


Fig. 7 FTIR patterns (a) and XRD spectra (b) of sediments

Fig. 8 Diagram of phase of DSW under the optimal treatment condition



recovery efficiency of 88.03% by absorption of phosphoric acid (81.2%) and precipitation of MAP (7.83%). A total of 110.33 mg L^{-1} TP could be obtained through precipitation of MAP (365.06 mg L^{-1}) with recovery efficiency of 74.8% and flocculation (21.24%). The TS and VS were 1.18 and 0.71 g L^{-1} with recovery of 23.41 and 16.82%, respectively. The MAP and VS were approximately 308.5 and 600.1 mg g^{-1} in recovery sediments at 0.75 g L^{-1} MgO, respectively.

The characteristics of supernatant solutions, sediments, and dried sediments under the optimal MgO dosages are shown in Fig. 8. After treatment, the supernatant showed greater lucidity than the original solution. The cause of this phenomenon is closely related to TS and VS concentration in DSW. The removal rate of TS and VS in DSW gradually enhanced with the

increase in MgO, as previously described. The MgO suspension in DSW is actually a very effective hydration process, including MgO dissolution and $\text{Mg}(\text{OH})_2$ precipitation step, and more than 90% of the initial MgO is converted into $\text{Mg}(\text{OH})_2$ (Stolzenburg et al. 2015). Therefore, the sediments mainly consisted of $\text{Mg}(\text{OH})_2$, MgNH_4PO_4 , and organic components, according to the abovementioned investigation.

Economic analysis

The economic evaluation of nutrient removal by the combined technology is shown in Table 2. In this preliminary assessment, the values of the recovered product, investment, and labor were not taken into account, and only the costs of chemicals and

Table 2 Economic analysis of the nutrient removal process by the combined technology

Removal nutrients	Chemicals/energy	Requirement amount	Market price	Cost	Total actual cost	References
$\text{NH}_4^+\text{-N}$, TP, COD	MgO	5.49 kg kg^{-1} $\text{NH}_4^+\text{-N}_{\text{removed}}$	$0.12 \text{ \$ kg}^{-1}$	$0.66 \text{ \$ kg}^{-1}$ $\text{NH}_4^+\text{-N}_{\text{removed}}$	$9.44 \text{ \$ kg}^{-1}$ $\text{NH}_4^+\text{-N}_{\text{removed}}$	This study
	H_3PO_4 (85%)	2.14 kg kg^{-1} $\text{NH}_4^+\text{-N}_{\text{removed}}$	$0.4 \text{ \$ kg}^{-1}$	$0.86 \text{ \$ kg}^{-1}$ $\text{NH}_4^+\text{-N}_{\text{removed}}$		
	Energy consumption	$79.2 \text{ kw h}^{-1} \text{ kg}^{-1}$ $\text{NH}_4^+\text{-N}_{\text{removed}}$	$0.1 \text{ \$ kw}^{-1} \text{ h}^{-1}$	$7.92 \text{ \$ kg}^{-1}$ $\text{NH}_4^+\text{-N}_{\text{removed}}$		
$\text{NH}_4^+\text{-N}$	Struvite precipitation				$10.3 \text{ \$ kg}^{-1}$ $\text{NH}_4^+\text{-N}_{\text{removed}}$	Huang et al. (2011)
$\text{NH}_4^+\text{-N}$	Struvite precipitation				$14.9 \text{ \$ kg}^{-1}$ $\text{NH}_4^+\text{-N}_{\text{removed}}$	Webb et al. (1995)
$\text{NH}_4^+\text{-N}$	Biological process				$5.65 \text{ \$ kg}^{-1}$ $\text{NH}_4^+\text{-N}_{\text{removed}}$	Iaconi et al. (2010)

energy (electricity) were considered. Due to energy consumption of heating trap and air pump, the cost of electricity represented approximately 83.8% of the overall costs. It can be calculated that the total cost of chemicals and energy is $9.44 \text{ \$ kg}^{-1} \text{ NH}_4^+ \text{-N}_{\text{removed}}$, which was less than the previously reported costs (Huang et al. 2011; Iaconi et al. 2010). Ueno and Fujii (2001) showed that the market price of the recovered struvite was approximately $4.5 \text{ \$ kg}^{-1} \text{ NH}_4^+ \text{-N}_{\text{removed}}$. If the value of the recovered struvite is considered in the economic analysis, the cost of this technology was only $4.94 \text{ \$ kg}^{-1} \text{ NH}_4^+ \text{-N}_{\text{removed}}$, which is lower than the $5.65 \text{ \$ kg}^{-1} \text{ NH}_4^+ \text{-N}_{\text{removed}}$ cost of the biological process (Iaconi et al. 2010).

Conclusion

The removal of nutrients from DSW was enhanced by employing the stripping method with MgO as an active component. $\text{NH}_4^+ \text{-N}$, TP, and COD in DSW could be effectively removed by using a combined technology. Under the treatment condition of $40 \text{ }^\circ\text{C}$ and $0.48 \text{ m}^3 \text{ h}^{-1} \text{ L}^{-1}$ aeration rate for 3 h, $\text{NH}_4^+ \text{-N}$, TP, and COD significantly decreased to $35.6 (\leq 80)$, $4.57 (\leq 8)$, $385.4 (\leq 400) \text{ mg L}^{-1}$ at $0.75 \text{ g L}^{-1} \text{ MgO}$, respectively, because of the coordinated action of stripping, struvite precipitation, and coagulation/flocculation, thereby satisfying the national discharge standards for DSW. The MAP and VS were approximately 308.5 and 600.1 mg g^{-1} in sediments at $0.75 \text{ g L}^{-1} \text{ MgO}$, respectively. This technology could effectively recover and remove the nutrients from DSW to achieve environmental protection and as a sustainable and renewable resource of nutrients. Finally, the economic evaluation of nutrient removal by the combined technology presented that the process was as effective as and less costly than biological nitrogen removal if the recovered struvite was used as a fertilizer.

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