RESEARCHING THE ABILITY TO TREAT AMMONIUM IN WASTEWATER IN PIG FARM BY MAGNESIUM PRECIPITATION METHOD (MAP)

Vu Thi Thuy Trang
TNU - University of Technology

ARTICLE INFO

Received: 31/3/2023
Revised: 05/5/2023
Published: 05/5/2023

KEYWORDS

Ammonium treatment
Wastewater treatment
Ammonium in wastewater
Properties of ammonium
MAP precipitation

ABSTRACT

This paper studies the ability to treat ammonium in wastewater in pig farm by magnesium precipitation method. The research model includes 1 deposit tank, a reaction tank with dimensions of 30x30x40 cm and a stirring device. Wastewater quality was surveyed for 4 days from November 15, 2022 to November 18, 2022 with a frequency of 3 times/day at 7:00, 13:00 and 19:00. The survey shows that the molar ratio of Mg^{2+}: NH_4^+ : PO_4^{3-} = 1.2 : 1 : 1 was the most optimal. The model was operated with water samples at 19h 16/11/2022 with pH and NH_4^+ concentrations before and after the biogas tank reaching 8.2 and 248; 6.8 and 157mg/l respectively. The model operation results show that the suitable reaction time for pig breeding wastewater treatment by MAP precipitation method was 25 minutes. MAP precipitation method to ammonium treatment in pig breeding wastewater can achieve high treatment efficiency, and MAP precipitation can be used as fertilizer in agriculture.

NGHIÊN CỨU KHẢ NĂNG XỬ LÝ AMONI TRONG NƯỚC THẢI CHĂN NUÔI LỢN BẰNG PHƯƠNG PHÁP KẾT TỦA MAGIE (MAP)

Vũ Thị Thùy Trang
Trường Đại học Kỹ thuật Công nghiệp – ĐH Thái Nguyên

THÔNG TIN BÀI BÁO

Ngày nhận bài: 31/3/2023
Ngày hoàn thiện: 05/5/2023
Ngày đăng: 05/5/2023

TỪ KHÓA

Xử lý amoni
Xử lý nước thải
Amoni trong nước thải
Tính chất của amoni
Kết tủa MAP

TÓM TẮT

Bài báo này nghiên cứu khả năng xử lý amoni trong nước thải chăn nuôi lợn bằng phương pháp kết tủa MAP. Mô hình nghiên cứu bao gồm 1 ngăn lắng, một ngăn phản ứng có kích thước 30x30x40 cm và một thiết bị khuấy. Chất lượng nước thải được khảo sát 4 ngày từ 15/11/2022 đến ngày 18/11/2022 với tần suất 3 lần/ ngày vào 7h, 13h và 19h. Khảo sát cho thấy tỷ lệ mol các chất tham gia phản ứng Mg2+: NH4+ : PO43- = 1,2 : 1 : 1 là tối ưu nhất. Mô hình được vận hành với mẫu nước tại 19h ngày 16/11/2022 với nồng độ pH và NH4+ trước và sau hầm biogas lần lượt là 8,2 và 248; 6,8 và 157 mg/l. Kết quả vận hành mô hình cho thấy thời gian phản ứng phù hợp đối với xử lý nước thải chăn nuôi lợn bằng phương pháp kết tủa MAP là 25 phút. Áp dụng phương pháp kết tủa MAP vào xử lý amoni trong nước thải chăn nuôi lợn có thể đạt hiệu suất xử lý cao, và kết tủa MAP thu được có thể làm phân bón sử dụng trong nông nghiệp.

DOI: https://doi.org/10.34238/tnu-jst.7641

Email: thuytrangcntn@tnut.edu.vn

1. Introduction

Nowadays, water pollution caused by untreated or untreated ammonium-containing wastewater (NH_4^+) is quite common. Ammonium is an essential nutrient for plants and living organisms, but ammonium is harmful to humans and animals when the ammonium concentration is too large. When the concentration of NH_4^+ in wastewater is too large, conventional treatment methods can not solve this problem that will adversely affect the performance of some subsequent treatment works, especially the wastewater treatment by biological methods [1], [2].

At pig farms, the concentration of ammonium in wastewater is about 200-300 mg/l and COD is about 1000-3000 mg/l. With ratio of ammonium and COD, if ammonium is not treated before being put into the biological treatment system, it will reduce the treatment efficiency of this process. However, current pig farms usually only have biogas digesters to treat manure and wastewater, while too large concentrations of NH_4^+ will adversely affect the treatment efficiency of biogas digesters as well as biological treatment system [3] - [5]. Therefore, several commonly used ammonium treatment solutions include raising the pH and blowing air to remove ammonia; chlorination (chlorination with a concentration higher than mutation point on the chlorine absorption curve in water produces chloramines); ion exchange by ion exchanger; precipitating with magnesium; technology anammox, Sharon/anammox; electrodialysis and reverse electrodialysis [6]. Currently, some methods are applied to treat ammonium in wastewater as follows:

Forced blower method

The existence of ammonium and ammonia in wastewater depends on pH. Therefore, for ammonium to be treated, it is necessary to raise the pH of the wastewater about 10 - 12hen NH_4^+ is converted to NH_3 dissolved in water, then aerating into the wastewater or into a cyclone to separate the phase and remove NH_3 from the wastewater.

In addition, the ratio between NH_4^+ and NH_3 depends on temperature. The higher the temperature and pH are, the greater the NH4+ treatment efficiency is. However, raising the wastewater temperature is quite expensive because it requires a large amount of energy [7], [8].

Ion exchange method

The removal of ammonium in wastewater is based on the mechanism of action of cationic ions. Salt or sulfuric acid is used to reconstitute the resin in the ion exchange process. Essentially, zeolites have a fairly high exchange selectivity for ammonium, but their actual active capacity rarely exceeds 50% of the total capacity, usually 1-7 g/kg because ammonium is back-extracted out of solution when it is about to reach the saturation point. Besides, ion exchange capacity is affected by a number of factors such as reaction time, particle size, pH of wastewater and ion exchange resin regeneration mode. In general, ion exchange is a method that requires good operating techniques and high investment costs [6], [7].

Oxidation method

Ammonium can be removed from water by a redox reaction with a number of oxidizing agents. For example, when chlorine or chlorine compounds are added to water, a hydrolysis reaction will occur to create active chlorine according to the equation (1), (2), (3):

$$Cl_2 + H_2O \leftrightarrow HOCl + HCl \quad (1)$$

$$Ca(OCl)_2 + 2H_2O \leftrightarrow Ca(OH)_2 + 2HOCl \quad (2)$$

$$NaOCl + H_2O \leftrightarrow HOCl + NaOH \quad (3)$$

The reaction between ammonia and active chlorine occurs step by step [6], [8]:

$$NH_3 + HOCl \leftrightarrow NH_2Cl + H_2O \quad (4)$$

$$NH_2Cl + HOCl \leftrightarrow NHCl_2 + H_2O \quad (5)$$

$$NHCl_2 + HOCl \leftrightarrow NCl_3 + H_2O \quad (6)$$

MAP precipitation method

MAP (Magnesium Ammonium Phosphate hexahydrated) whichhas the chemical formula $MgNH_4PO_4.6H_2O$ is a white inorganic crystal, insoluble in ammonia but soluble in acid, so we perform the reaction in a basic medium. Precipitated magnesium ammonium phosphate is very easy to phase out at pH > 7 and to wash off, so it is used as a slow release fertilizer because when the pH of the medium is less than 7, it dissolves slowly and can be absorbed by plants [6], [7].

Biological method

Ammonia in wastewater can be removed by a number of processes such as nitrate, nitrification and anammox:

- *The biochemical nitrification process:*

This process consists of two stages: Initially, ammonium is oxidized to nitrite by Nitrosomonas bacteria, then nitrobacteria will convert nitrite to nitrate. This process is described by two reaction equations:

$$NH_4^+ + 1.5O_2 \rightarrow NO_2^- + 2H^+ + H_2O \quad (7)$$

$$NO_2^- + 0.5\ O_2 \rightarrow NO_3^- \quad (8)$$

Equation of the synthesis reaction

$$NH_4^+ + 2O_2 \rightarrow NO_3^- + 2H^+ + H_2O \quad (9)$$

Microorganisms use energy, which is generated from this process, to maintain and grow biomass. The cell fusion reaction is expressed by the reaction equation:

$$4CO_2 + HCO_3^- + NH_4^+ + H_2O \rightarrow C_5H_7O_2N + 5\ O_2 \quad (10)$$

The entire oxidation and synthesis reaction is represented by the following reaction [10]:

$$NH_4^+ + 1{,}83O_2 + 1{,}98\ HCO_3^- \rightarrow 0{,}021C_5H_7O_2N + 0{,}98\ NO_3^- + 1{,}041\ H_2O + 1{,}88\ H_2CO_3 \quad (11)$$

- *The process of denitrification*

Some biodegradable organic compounds such as ethanol, methanol, etc. are often added to wastewater to remove dissolved oxygen in wastewater and achieve high treatment efficiency. This process is represented by two reaction equations [8]:

$$NO_3^- + 1{,}08\ CH_3OH + H^+ \rightarrow 0{,}065\ C_5H_7O_2N + 0{,}47\ N_2 + 0{,}76CO_2 + 2{,}44H_2O \quad (12)$$

$$NO_2^- + 0{,}67\ CH_3OH + H+ \rightarrow 0{,}04\ C_5H_7O_2N + 0{,}48\ N_2 + 0{,}47CO_2 + 1{,}7\ H_2O \quad (13)$$

- *Anammox process:*

The anammox process is an anaerobic oxidation of ammonium in which ammonium and nitrite are oxidized directly to N_2 and to a small extent converted to nitrate. The anammox process is represented by the reaction equation:

$$NH_4^+ + 1{,}3\ NO_2^- + 0{,}066\ HCO_3^- + 0{,}13\ H^+ \rightarrow 1{,}02\ N_2 + 0{,}26\ NO_3^- + 2\ H_2O \quad (14)$$

The advantage of the process is that less oxygen is used and no additional external supply of organic carbon is required, so this process is suitable for low organic carbon wastewater [8].

The treatment of ammonium in swine wastewater requires low treatment costs and environmental friendliness. It cannot be done by methods as forced blower method, ion exchange method and oxidation method. Besides, the time to treat ammonium by biological method is usually quite long. Recognizing this problem, this paper studies the ability to treat and recover ammonium in wastewater of pig farms. The method of treating ammonium with magnesium precipitation produces a precipitate in the form of a slow-release fertilizer called magnesium ammonium phosphate (abbreviated as MAP). This type of precipitate can separate phase when pH > 7 and dissolve slowly when pH < 7 so it can be easily absorbed by plants [9]. In Vietnam, ammonium treatment by MAP precipitation method has been studied to treat some wastewater that has a large concentration of ammonium such as leachate, food technology wastewater, wastewater from the production process, emulsion explosives wastewater… The MAP precipitation method has outstanding advantages such as fast reaction speed, non of stench, and beneficial for agriculture. However, this method requires good techniques, and higher costs than biological methods [8].

2. Methodology

2.1. Experimental model design

The experimental model was designed with 1 tank which has the effect of sedimentation and 1 reaction tank with dimensions of 30x30x40 cm and 1 stirrer. The experimental model is shown in Figure 1.

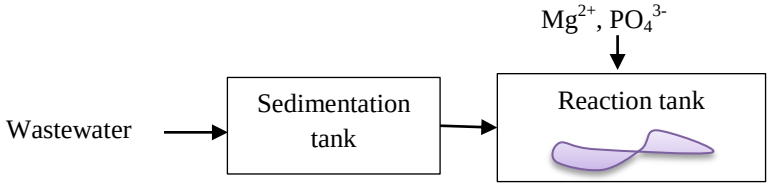

Figure 1. *Experimental model*

Wastewater after being collected was settled for about 1 hour in a sedimentation tank. Then, it was transferred to the reaction tank with dimensions of 30x30x40 cm. At the reaction tank, the wastewater was mixed with Mg^{2+} and PO_4^{3-} with suitable molar ratio by agitator with different reaction time. After the reaction time, the wastewater was removed and analyzed for residual ammonium concentration, and ammonium removal efficiency was determined. Through the ammonium treatment efficiency at different reaction times, the optimal ammonium treatment efficiency would be determined corresponding to the optimal reaction time.

2.2. Model operation

The wastewater for the model was taken from the pig farm of Mr. Truong Tuan Anh, Tich Luong ward with the scale of 50 heads/brood from November 15, 2022 to November 18, 2022. His farm only had a biogas cellar for wastewater treatment. Wastewater was collected at 2 locations, including the sewer before entering the biogas cellar and the wastewater at the discharge end to the stream (output wastewater of the biogas cellar). Wastewater was taken to the laboratory of Thai Nguyen University of Technology to research. It's put into a settling tank to remove solid residue and adjust the pH accordingly, then it was taken to the reaction tank. At the reaction tank, the wastewater was investigated for the optimal molar ratio and reaction time, which was conducted specifically as follows:

- Investigation of the optimal molar ratio:

The experiment was conducted as follows: Take V_1 (ml) NH_4^+ and V_2 (ml) PO_4^{3-} into the beaker and stir well. Then, conduct a pH measurement, this value is recorded as pH_0. Continue to add V_3 (ml) Mg^{2+} and start calculating the reaction time (t). After the end of the reaction time, the precipitate was filtered through filter paper and the solution was measured for post-reaction pH (pHs) and concentration of NH_4^+. The optimum molar ratio of the reaction was determined through determination of ammonium removal efficiency.

- Investigation of the optimal reaction time:

Determination of the optimum reaction time was carried out under the same conditions at the optimum molar ratio for different time periods from 5 mins to 35 mins, then determine ammonium content remaining after the reaction. Based on the survey results of different time periods, the author can choose the best time to conduct the reaction.

2.3. Sampling and analysis

The model was run in batches in the laboratory of Thai Nguyen University of Technology. Wastewater samples were taken from November 15, 2022 to November 18, 2022 with a frequency of 3 times/day at 7 am, 1 pm and 7 pm. Analytical parameters were analyzed for pH and concentration of NH_4^+. The pH was quickly measured by the handheld pH meter of Hana HI 98107 and NH_4^+ was determined according to TCVN 6179:1996.

3. Research results and discussion

3.1. Wastewater quality

Inlet wastewater was collected at 7:00, 13:00, and 19:00 on the days from November 15, 2022 to November 18, 2022. Some wastewater quality parameters are presented in Table 1.

Table 1. *Results of analysis of pH, NH4+ input and output biogas cellar and ammonium treatment efficiency of biogas function during the survey period*

Sign of sample	Sampling time	Input biogas		Output biogas		NH_4^+ treatment efficiency of biogas (%)
		pH	NH_4^+ (mg/l)	pH	NH_4^+ (mg/l)	
NT1	7am/15/11/2022	8.2	247	7.2	151	38.87
NT2	1pm/15/11/2022	8.2	247	7.2	155	37.25
NT3	7pm/15/11/2022	8	241	7	157	34.85
NT4	7am/16/11/2022	8.1	250	7.1	154	38.4
NT5	1pm/16/11/2022	8.3	246	6.3	153	37.8
NT6	7pm/16/11/2022	8.2	248	6.8	157	36.69
NT7	7am/17/11/2022	8	250	7	160	36.0
NT8	1pm/17/11/2022	8	251	6.5	162	35.46
NT9	7pm/17/11/2022	8.2	246	7.1	157	36.18
NT10	7am/18/11/2022	8.3	257	6.3	162	36.96
NT11	1pm/18/11/2022	8	252	6.5	164	34.92
NT12	7pm/18/11/2022	8	245	7	154	37.14
Average		8.1	248.3	6.8	157.2	36.71

The analysis results show that: pH of wastewater input biogas cellar ranges from 8.4 to 9.1; pH of wastewater output biogas cellar ranges from 8 to 8.3. The pH tends to decrease after going through the biogas cellar due to the presence of the acid-forming reaction of the anaerobic microorganisms. Ammonium in wastewater input biogas cellar ranges from 241 mg/l to 257 mg/l, and it ranges from 151 mg/l to 164 mg/l in out put wastewater. The ammonium treatment efficiency is quite low, ranging from 34.85% to 38.87%. Based on the results of such ammonium analysis, it can be said that the total nitrogen in the output wastewater of the biogas digester does not meet the quality standards of pig breeding wastewater according to QCVN 62-MT:2016/BTNMT.

3.2. Investigate the optimal molar ratio of Mg^{2+}: NH_4^+: PO_4^{3-}

Table 2. *Investigated results of the influence of the molar ratio of Mg^{2+}: NH_4^+: PO_4^{3-} on ammonium removal efficiency*

Serial	Ratio	Volume (ml)			Pre-reaction		Post-reaction		NH_4^+ treatment efficiency (%)
		Mg^{2+}	NH_4^+	PO_4^{3-}	pH_0	NH_4^+ (mg/l)	pHs	NH_4^+ (mg/l)	
1	1:01:01	10	10	10	12	249	8	38	84.71
2	1:1:0.6	10	10	6	12	242	7.5	38	84.50
3	1:1:0.8	10	10	8	11.8	248	7.2	40	83.87
4	1:1:1.2	10	10	12	11.5	244	7.8	41	83.20
5	1:1:1.4	10	10	14	11.6	245	8.1	43	82.41
6	1:1:1.6	10	10	16	11.6	245	7.6	45	81.63
7	0.6:1:1	6	10	10	12	250	7.3	48	81.00
8	0.8:1:1	8	10	10	11.5	253	8	47	81.58
9	1.2:1:1	12	10	10	11.6	251	7.5	35	86.06
10	1.4:1:1	14	10	10	11.6	248	7.7	38	84.68
11	1.6:1:1	16	10	10	11.6	251	7.3	40	84.03

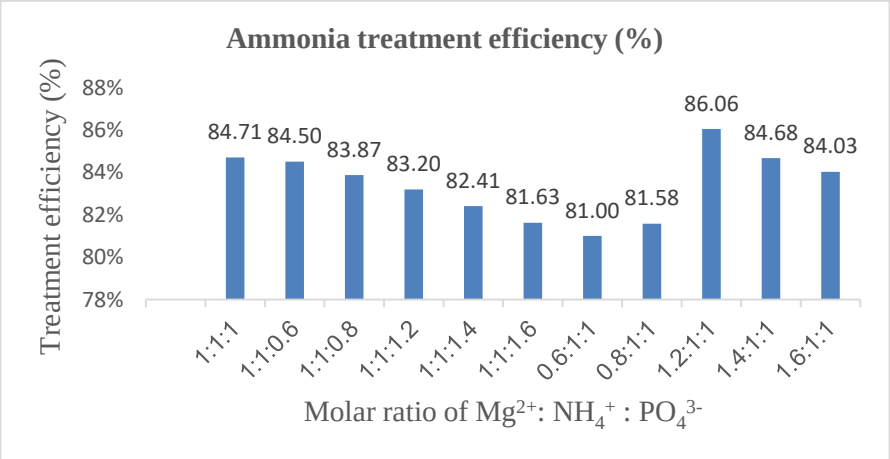

Figure 2. *The influence of the molar ratio of the reactants on the ammonium treatment efficiency*

To investigate the optimal molar ratio of Mg^{2+}: NH_4^+: PO_4^{3-} to ammonium treatment efficiency, the experimental samples were prepared with pure chemicals with a concentration of 0.05M at different ratios. The survey results are shown in Table 2 and Figure 2.

Investigation of the molar concentrations of reactants at different rates shows:

First, the pre-reaction pH ranges from 11.5 to 12, the post-reaction pH ranges from 7.2 to 8.1. Thus, after the MAP precipitation reaction, it is not necessary to adjust the pH when putting into biological treatment.

Second, when the molar ratio of Mg^{2+} is equal or lower than the molar ratio of NH_4^+, the ammonium removal efficiency tends to decrease compared to the theoretical ratio (ratio between Mg^{2+}: NH_4^+: PO_4^3 1:1:1). It may be because some of the Mg^{2+} has been involved in some other chemical reaction. Besides, when the molar ratio of PO_4^{3-} is larger or smaller than the molar ratio of Mg^{2+} and NH_4^+, the ammonium removal efficiency is reduced. This means that the molar ratio of NH_4^+ and PO_4^{3-} = 1 : 1 is suitable. When investigating the molar concentrations of the reactants at different rates, the ammonium treatment efficiency is different. The ammonium removal efficiency is in the range of 81% to 86.06%, in which, the maximum efficiency is at the molar ratio of Mg^{2+}: NH_4^+ : PO_4^{3-} = 1.2 : 1 : 1. This result shows that in survey conditions, the theoretical ratio 1:1:1 did not achieve the greatest efficiency, so the author proceeded to choose the molar ratio Mg^{2+}: NH_4^+ : PO_4^{3-} = 1.2 : 1 : 1 to conduct the survey with wastewater samples NT6 taken at 7pm in 16/11/2022.

3.3. Optimal reaction time survey

Table 3. *Dependence of ammonium treatment efficiency on reaction time*

Serial	Reaction time (min)	Input - biogas			Output - biogas		
		NH_4^+ pre (mg/l)	NH_4^+ post (mg/l)	Efficiency (%)	NH_4^+ pre (mg/l)	NH_4^+ post (mg/l)	Efficiency (%)
1	5	248	95	61.69	157	55	64.97
2	10	248	82	66.94	157	50	68.15
3	15	248	70	71.77	157	43	72.61
4	20	248	61	75.40	157	38	75.80
5	25	248	55	77.82	157	36	77.07
6	30	248	53	78.63	157	35	77.71
7	35	248	51	79.44	157	34	78.34

The surveyed wastewater sample is the NT6 which was collected at 7 pm on 16/11/2022. Conduct the experiment with the molar ratio of Mg^{2+}: NH_4^+ : PO_4^{3-} = 1.2 : 1 : 1 for a period of 5 to 35 minutes. The results showing the variation of ammonium removal efficiency by reaction time are presented in Table 3 and Figure 3.

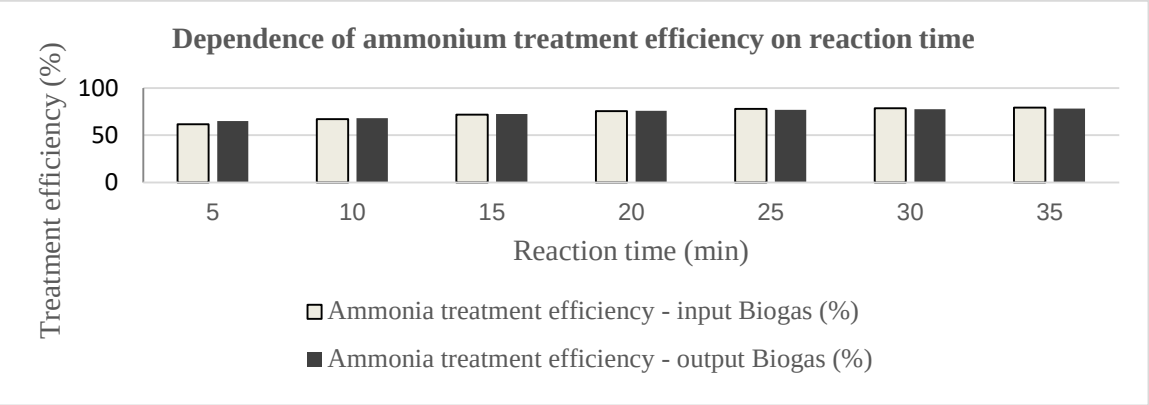

Figure 3. *Effect of reaction time on ammonium removal efficiency*

The analysis results show that treatment of ammonium by MAP precipitation method for two wastewater samples inlet and outlet of biogas cellar are suitable. The ammonium removal efficiency increased with increasing reaction time. After 30 minutes of reaction, ammonium removal efficiency by MAP precipitation method reached 77 - 78%. The ammonium treatment speed increased rapidly from 5to 25 minutes (about 2 to 3%); however, when the reaction time was extended from 25 minutes to 35 minutes, the yield variation tended to decrease (about 0.64 to 0.81%). Therefore, the optimal reaction time for ammonium treatment for NT6 sample at the molar ratio of Mg^{2+}: NH_4^+: PO_4^{3-} = 1.2 : 1 : 1 is 25 minutes.

4. Conclusion

From the survey results cited above, the following conclusions can be drawn: wastewater has the average value of pH and NH_4^+ concentration before and after the biogas cellar, 8.1; 248.3mg/l and 6.8; 157.2 mg/l respectively. Ammonium in pig production wastewater treated by MAP precipitation method can achieve high treatment efficiency. The obtained MAP precipitate can be used as a slow release fertilizer, which is suitable for many crops. The suitable reaction time for pig breeding wastewater treatment by MAP precipitation method with molar ratio of Mg^{2+}: NH_4^+ : PO_4^{3-} = 1.2 : 1 : 1 is 25 minutes.

The MAP precipitation method is a highly efficient method for swine wastewater. The reaction product of the method is a slow release fertilizer that can be used in crops. The wastewater after the MAP precipitation treatment has an ammonium concentration and an environmental pH that meets the conditions for further treatment by biological methods which are safe for the environment.

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