Microwave Irradiation as a Way to Reutilize the Recovered Struvite Slurry and to Enhance System Performance

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회수된 MAP 슬러리의 재이용과 공정효율 향상을 위한 도구로서의 극초단파 조사

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요 약

회분식 반응조를 Mg원 첨가 방법이나 혹은 MAP을 재이용하는 조건이 서로 다른 4가지 상이한 조건하에서 운전하면서 공정으로부터 회수된 magnesium ammonium phosphate (MAP) 혹은 struvite 슬러리의 재이용 수단으로서의 극초단파조사 방법의 이용 가능성을 파악하였다. 또한 극초단파조사 동안의 MAP 용해율과 NH_4-N 소실양상 및 MAP의 물리/화학적 변화를 분석하였다. Mg원을 첨가하지 않은 run A에서의 용해성 인과 암모니아성 질소의 제거율은 각각 33%와 27% 수준이었던 반면 유입수내 용해성 인 기준 동몰비의 Mg원을 첨가한 run B에서는 용해성 인과 암모니아성 질소의 제거율이 각각 87%와 40% 수준으로 증가하였다. 극초단파를 조사한 MAP을 첨가한 run C의 경우, 비록 Mg원을 첨가한 run B에 비해 PO_4-P와 NH_4-N 제거율이 낮았으나, Mg원을 첨가하지 않은 run A에 비해 PO_4-P의 제거율이 2배 정도 높아지는 결과를 보였다. Mg원과 MAP을 각각 1/2씩 첨가한 run D에서의 PO_4-P와 NH_4-N 제거효율은 각각 88%와 35% 수준으로 Mg원만을 1몰비로 첨가한 run B와 거의 유사한 효율을 나타내었다. 이러한 결과에 의거 극초단파로 처리한 후 MAP을 재이용하는 방법은 공정에서의 인과 질소의 제거율을 높임은 물론, Mg원 사용량을 감소시키는 이중효과가 있음을 알 수 있었다. MAP을 극초단파로 조사하면서 NH_4-N 농도변화를 관찰한 결과 극초단파조사 초기단계에서는 NH_4-N 농도가 점차 증가하다가 온도가 45°C 이상으로 상승함에 따라 용액으로부터 NH_4-N가 소실되기 시작하여 감소하였으며 극초단파조사 동안의 PO_4-P 용해율은 초기 MAP 농도에 비례하면서 $0.0091x^{0.6373}$ mg/sec의 상관관계를 갖는 것으로 분석되었다. 또한 주사전자현미경을 이용한 극초단파조사 동안의 MAP 크리스탈 구조변화실험 결과 극초단파 조사시 전자기적 진동력에 의해 단시간내에 MAP 크리스탈 구조가 작은 입방체 과립형태로 부숴지고 극초단파 조사가 지속됨에 따라 점차 용액내로 녹음을 알 수 있었다.

(**Key words :** Microwave, Struvite, MAP ($MgNH_4PO_46H_2O$), Swine wastewater)

Ⅰ. INTRODUCTION

Swine wastewater contains a significant amount of nitrogen and phosphorous which is a great threat to environment if it is not properly treated. Presence of high amount of nitrogen and phosphorus in the water is a cause of eutrophication (Lee et al., 2003) that is hazardous for environment. Some forms of nitrogen (ammonia, nitrite, and nitrate) produce toxicity in the water and affect on aquatic life and public health. Hence, great efforts have been made by researchers for the removal of nitrogen from wastewater through biological nitrification and denitrification (Welander et al., 1998), ammonia stripping (Bonmati and Flotats, 2003), electrochemical conversion (Kim et al., 2006), ion exchange (Jeong et al., 2006) and magnesium ammonium phosphate (MAP) precipitation (Li et al., 1999; Yetilmezsoy and Zengin, 2009; Zhang et al., 2009). Biological nitrification and denitrification are suitable for low ammonia concentrated wastewater and air stripping consumes much energy for nitrogen removal. Digestion, dewater and disposal of wasted sludge through activated sludge process needs a high cost involvement to remove nitrogen (Eskicioglu et al., 2007).

Although chemical precipitation requires a lot of cost involvement due to chemical reagents, MAP or struvite

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recovery from wastewater would be an effective process for the simultaneous removal of nitrogen and phosphorus from wastewater, as well as for the recovery of resources that can be used as a highly valuable slowly releasing fertilizer (Munch and Barr, 2001). Struvite is a crystal of MAP formed in alkaline condition, and its chemical formula is $MgNH_4PO_46H_2O$ and addition of Mg source in the wastewater enhances the struvite formation. Chirmuley (1994) stated that struvite is a white crystalline powder with a specific gravity of 1.7 and it is soluble in acid and insoluble in alkaline condition.

Because of its high levels of NH_4-N and PO_4-P, animal wastewater can be a good source for the recovery of MAP. However, the molar ratio of NH_4-N and PO_4-P in animal wastewater is severely imbalanced (the molar ratio of PO_4-P to NH_4-N is approximately 0.008) and this acts as an obstacle for the simultaneous recovery of nitrogen and phosphorus using struvite crystallization method. For example, if Mg source addition is added based on PO_4-P in influent to form MAP, the NH_4-N removal is much lower since the crystallization of Mg^{2+}, NH_4^+ and PO_4^{3-} occurs in equal molar ratio. In the contrary, if chemicals are added based on NH_4^+ to enhance its removal efficiency, tremendous amount of Mg^{2+} and PO_4^{3-} source must be added resulting to excessively high operational cost. To overcome these problems, a novel process should be developed that can eliminate the NH_4^+ from the recovered MAP and reutilize it as Mg^{2+} and PO_4^{3-} sources.

Microwave irradiation might be a successful strategy for the reduction of nitrogen from the wastewater and elimination of NH_4^+ from MAP. Lin et al. (2009) stated that 3 minutes microwave irradiation could remove more than 96% NH_4-N from a concentrated nitrogenous wasted solution. Recently, the researchers tried to use microwave (Ahn et al., 2004; Liao et al., 2005; Wojciechowska, 2005; Wong et al., 2006; Chan et al., 2007; Qureshi et al., 2008; Lin et al., 2009) to enhance the digestion and for removal of nitrogen from wastewater with a cheaper cost involvement. Microwave is an alternative to conventional heating that dramatically reduce the reaction time by reducing the wavelength and frequency in the electromagnetic spectrum (Eskicioglu et al., 2007). Martin et al. (2005) stated that the frequency of microwave irradiation ranged between 300 MHz (million cycles per second) to 300 GHz (billion cycles per second) which are smaller than ionizing radiation. Quick rise of temperature with microwave irradiation is due to molecular level of heating that leads to homogeneous and quick thermal reactions. Microwave heating saves considerable time and energy for a similar degree of heating compared to conventional ways (Menendez et al., 2002). Ponne and Bartels (1995) stated that chemical structures can be altered by the microwave energies. Instant hydrogen bonded structure requires very low energy for displacement of protons. During microwave irradiation, organic solvents can undergo superheating above their conventional boiling points and creates a significant difference compared to the boiling point (Saillard et al., 1995). Bi et al. (2007) stated that simultaneous microwave irradiation shortened the reaction time and increased the purities of the product.

Microwave irradiation was examined as a way to reutilize the MAP slurry recovered from animal wastewater as Mg source. Physical and chemical changes of MAP by microwave irradiation were also studied in this research.

Ⅱ. MATERIALS AND METHODS

1. System configuration and operational strategies

The schematic diagram of the lab-scale experimental process is shown in Fig. 1. The reactor was made by Plexiglas. Total volume of the reactor was 2 liters and the working volume was 1 liter, and it was operated by batch mode. The sequence of the process was feeding (30 minutes) → aeration (22 hours) → settle (1 hour) → discharge (30 minutes) and the HRT was 3 days. Air was provided by an aerator through an air diffuser placed at the bottom of the reactor. The air flow rate was 1 liter / minute and the rate was controlled by a flow meter. The loading rate of influent, magnesium chloride ($MgCl_2$) and MAP were also controlled by

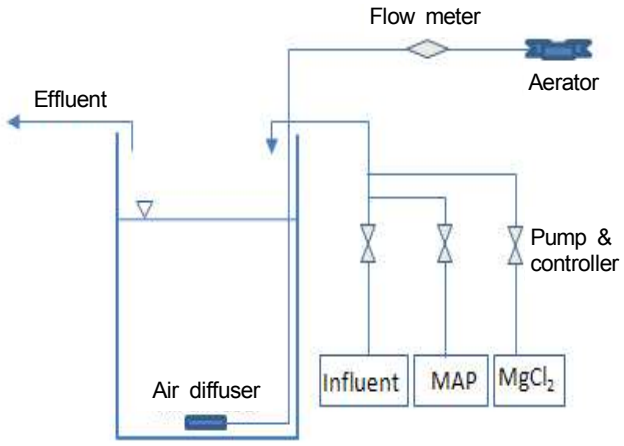


Fig. 1. Schematic diagram of the process.

pumps. The $MgCl_2$ and MAP were loaded into the reactor at the time of feeding according to experimental design.

Four operations were performed in this study as shown in Table 1. In run A, no $MgCl_2$ and MAP were added, while 1 molar ratio of $MgCl_2$ and MAP to PO_4-P of the influent was added in run B and C respectively. In run D, both $MgCl_2$ and MAP were added at the ratio of 0.5 mole to PO_4-P, respectively.

For run C and D, magnesium hydroxide ($Mg(OH)_2$) and potassium hydroxyl phosphate (KH_2PO_4) were added at 1 molar ratio to NH_4-N in swine wastewater supernatant and aerated for 30 minutes to form MAP crystal. Then, the MAP mixture was collected after settling and centrifugation. The concentration of MAP mixture recovered in this manner was analyzed, and predetermined amount of MAP was passed through microwave irradiation for 4 minutes before loading into the reactor. The rate of microwave irradiation was maintained at 7.36 MHz/mL and a commercial microwave (SANYO, 2,450MHz, 10A) was used in this study.

2. Influent wastewater and analytical methods

Throughout the study, fresh swine wastewater was collected from a local farm. Prior to utilization, the swine wastewater was screened using a sieve with 0.5 mm mesh opening and centrifuged at 3000 rpm for 5 minutes to remove solids before feeding into the influent container.

The influent and effluent samples of swine wastewater were taken from the respective bucket on every third day. Parameters routinely assayed included ortho-phosphate (PO_4-P) and ammonium nitrogen (NH_4-N). PO_4-P and NH_4-N were analyzed with an auto analyzer (Quick Chem 8000, LACHAT, USA).

Ⅲ. RESULTS AND DISCUSSION

Table 2 shows the average PO_4-P and NH_4-N levels as well as the treatment efficiencies. Much difference in PO_4-P and NH_4-N removals was found among 4 different runs. Without addition of Mg source in Run A, 38% PO_4-P and 27% NH_4 N removals occurred. Swine wastewater contains low level of Mg^{2+} and Ca^{2+} that can react with NH_4^+ and PO_4^{3-} to form MAP, and this would be a cause of the partial removal of PO_4-P and NH_4-N in that run. Also, ammonia air stripping due to the extended aeration would contribute to the NH_4-N removal.

When one molar ratio of Mg source to PO_4-P in influent was added in run B, the removal efficiency of PO_4-P and NH_4-N was 88% and 40%, respectively. Comparing the PO_4-P and NH_4-N removal efficiencies between run A and B, it was found that an external Mg source should be added in swine wastewater to achieve high removal of nitrogen and phosphorus through MAP crystallization, since struvite crystal is formed by NH_4^+, Mg^{2+} and PO_4^{3-} at 1:1:1 molar ratio in a favorable condition (Jaffer et al., 2002; Suzuki et al., 2005).

When one molar ratio of MAP slurry was added after microwave irradiation for 4 minutes, 67% of PO_4-P and 34% of NH_4-N were removed in Run C. Although the obtained

Table 1. Operational conditions of processes

Condition	RUN			
	A	B	C	D
Mg source	no	yes	no	yes (1/2)
MAP* reuse	no	no	yes	yes (1/2)

* Magnesium Ammonium Phosphate (MAP)

Table 2. Efficiencies in each operation

RUN	PO_4^{3-}					NH_4-N				
	Influent		Effluent		%	Influent		Effluent		%
	AVG	STED	AVG	STED		AVG	STED	AVG	STED	
A	347.9	115.5	215.8	70.4	38.0	2673.3	259.4	1956.9	379.1	26.8
B	323.5	106.6	37.8	22.0	88.3	2632.5	271.1	1593.9	436.1	39.5
C	323.9	110.9	107.3	68.8	66.9	2721.0	269.5	1799.2	436.1	33.9
D	320.3	108.4	32.4	22.0	89.9	2694.2	320.7	1747.3	436.4	35.1

removal efficiencies were lower than run B (PO_4-P:88%, NH_4-N:40%), the removal efficiencies of PO_4-P and NH_4-N were much enhanced when compared with run A. Especially, the PO_4-P removal was almost double in this run by reutilizing the recovered MAP after microwave irradiation. This result might reveal that simple MAP recycling after microwave irradiation would be an effective way to enhance phosphorus and nitrogen removals from swine wastewater.

Removal efficiencies of PO_4-P and NH_4-N in run D, where 0.5 molar ratio of $MgCl_2$ plus 0.5 molar ratio of MAP (microwave irradiated for 4 minutes) were added as Mg source, were 90% and 35%, respectively. The fact that the phosphorus removal was nearly similar to run B might mean that curtailment of chemical Mg usage would be feasible by operating the process as run D.

Track study of NH_4-N concentration during the microwave irradiation of recovered struvite slurry is shown in Fig. 2. During microwave irradiation, gradual increase of NH_4-N occurred up to 90 seconds, and then its level started to decrease gradually as the temperature increased up to 45℃. It might be assumed that rapid dissolution of MAP was occurred with microwave irradiation, resulting in the increase of NH_4-N at initial stage (up to 90 seconds), and this NH_4-N started to emit as ammonia as temperature increased over 45℃. The pattern of NH_4-N change with microwave irradiation in this experiment is very much similar with Eskicioglu et al. (2007). They showed that NH_4-N concentration of wasted activated sludge rapidly increased up to 50℃ and then gradually decreased up to 75℃, followed by a slow decrease up to 96℃. During microwave irradiation, temperature increased gradually up to the end of heating. Initial irradiation up to 50℃ helped to release ammonia from organic N and MAP dissolution, and then ammonia emission occurred at a higher temperature in later stage of irradiation. Electro-magnetic vibration of microwave enhances the hydrolysis and also increases the temperature within a short time that helps to reduce ammonia. Sanz et al. (2003) stated that microwave heating was much higher than that of ordinary heating at the same conditions which enhance the oxidation and rate of reaction. Microwave irradiation reduced the heating time by its molecular vibration and dissociated the complex molecule into simpler form within a short time. Bi et al. (2007) stated that microwave irradiation could shorten the reaction time by 1/18 times, which would greatly reduce the economical costs of catalytic oxidation process. Moreover, Martin et al. (2005) stated that microwave irradiation requires low energy to produce more output.

The relation between initial MAP concentration and dissolution rate of PO_4-P during microwave irradiation are shown in Fig. 3. When initial concentration of MAP was 54 mg/L, the obtained dissolution rate during microwave irradiation was 0.1mg/sec, and when initial MAP concentration was 218 mg/L and 436 mg/L, the dissolution rate was 0.3 mg/sec and 0.45 mg/sec, respectively. It might be stated that dissolution rate of PO_4^{-3} during the microwave irradiation is function of the initial MAP concentration, having $0.0091x^{0.6373}$

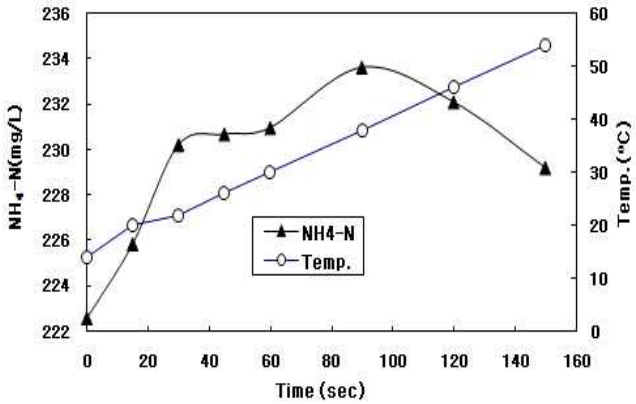


Fig. 2. Tracks of NH_4-N and temperature during microwave irradiation.

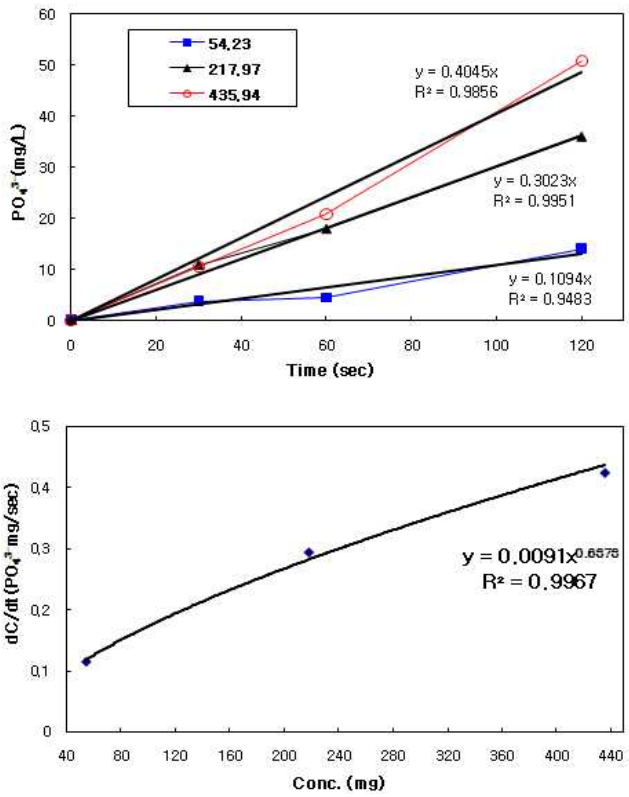
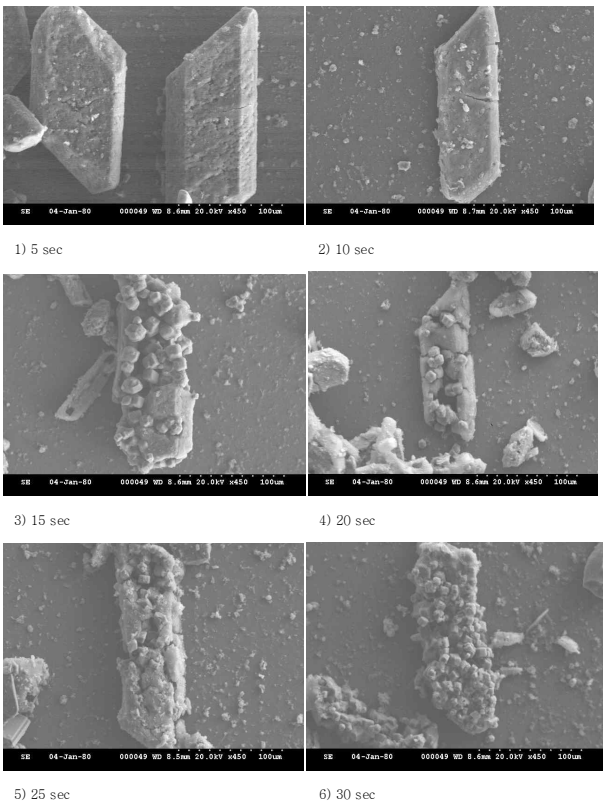


Fig. 3. Dissolution rate of MAP with microwave irradiation.

correlation.

To figure out the physical change of MAP during microwave irradiation, the structure of MAP crystal was observed with SEM (scanning electron microscope) in an interval of 5 sec for 30 seconds (Fig. 4). It was found that the MAP crystal had rhombic structure. Crack was observed at 10 seconds along with the MAP crystal and the crystal structure was broken down by producing lots of cubical granules within 15 seconds. After 25 seconds, the cubical granules started to melt down or started to disappear by electro-magnetic vibration force of microwave. Production of smaller cubical structures due to cracking of MAP crystals during microwave irradiation should increase the practical surface area to contact with liquor, and this would be one reason of higher dissolution rate of MAP during microwave irradiation. High temperature with vibration also could induce the dissolution. Sanz et al. (2003) showed that microwave irradiation dissociates the hydrogen peroxide and generates hydroxyl radicals due to the excitation of the molecule to high vibrational and rotational energy levels. Break down of MAP crystals occurred due to this high vibrational and rotational energy. Dissolution of MAP crystals also might be easy with the microwave irradiation due to presence of hydrogen bond in MAP (Ponne and Bartles, 1995).



1) 5 sec 2) 10 sec

3) 15 sec 4) 20 sec

5) 25 sec 6) 30 sec

Fig. 4. Photographs of MAP (with SEM, x450).

Liao et al. (2005) stated that microwave irradiation acts as a generator agent of oxidizing radicals as well as a heating source in the process of dissolution of phosphate from secondary municipal sludge.

Ⅳ. ABSTRACT

The feasibility of reutilization of magnesium ammonium phosphate (MAP) or struvite slurry recovered from the process through microwave irradiation was studied in this experiment. For this purpose, 4 different operations were performed with or without Mg source addition and different levels of MAP recycled in a batch reactor. Dissolution rate of MAP, NH_4^+ elimination pattern and physicochemical changes of MAP during microwave irradiation were also studied. The result showed that only 33% orthophosphate (PO_4-P) and 27% NH_4-N removal occurred without adding any external Mg source (run A), whereas 87% PO_4-P and 40% NH_4-N removed when 1.0 M ratio of $MgCl_2$ (run B) was added based on PO_4-P in influent. Although the addition of 1.0 molar ratio of microwave irradiated MAP (Run C) removed lower PO_4-P and NH_4-N than 1.0 M $MgCl_2$ (run B), PO_4-P removal was double when compared with no Mg addition (run A). Addition of half MAP and half $MgCl_2$ (run D) showed the similar removal efficiency (88% PO_4-P and 35% NH_4-N) with sole $MgCl_2$ addition (run B). Based on these results, the reutilization of MAP irradiated by microwave would be a feasible way to enhance the removal efficiencies of N and P, as well as curtail the Mg chemical usage. Track study showed that NH_4-N gradually increased at initial stage of microwave irradiation of MAP, and then started eliminating from liquor as temperature increased over 45℃. Dissolution rate of PO_4^{-3} during microwave irradiation was proportional to the initial MAP concentration, having $0.0091x^{0.6373}$ mg/sec. It was found from the scanning electron microscope (SEM) study that physical structure of MAP crystal started breaking down into small cube granules within very short time by electromagnetic vibration force during microwave irradiation and then gradually melted down into solution.

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