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Release and recovery of phosphorus from wastewater treatment sludge via struvite precipitation

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ABSTRACT

The release and the recovery of phosphorus (P) from aerobically digested wastewater, sludge during thermal treatment and the solid–liquid separation by struvite precipitation were investigated. The effects of pH, temperature, and heating time on the liberated phosphate from solid phase to liquid phase were determined. After the wastewater treatment, sludge was thermally treated at a temperature over 100 °C, no microbial activities were observed over a period of 24 h. The maximum total phosphorus release of 48.9 mg/L (93.6%) was observed at pH 2 ± 3 , 170 °C in 80 min. The results showed that the optimum pH values that released phosphate ions from the solid phase to the solution were noted at the range of 2–4. The scanning electron microscopy and energy dispersive X-ray analysis (SEM-EDX) indicated that struvite precipitation is unshaped and nonuniform crystal formed. The surface composition of the precipitates contains high amount of O, P, Mg, and trace of C, Cl. The Fourier transform infrared spectroscopy and X-ray diffraction analysis further indicated that the struvite is evidently the main composition of the precipitates.

Keywords: Wastewater; Phosphorus; Release; Recovery; Struvite

1. Introduction

The major sources of phosphorus in raw wastewater are derived from human, domestic and industrial wastes, especially food processing effluent sand runoff from phosphorus-rich fertilized lands. Human waste usually contains orthophosphate plus phosphorus present in other biological compounds, for example, nucleic acids, phospholipids, and phosphorylated proteins [1]. Phosphorus content in the sewage systems derives from industrial and domestic sources. Main domestic sources are human metabolic waste, detergents, and cleaning products. Human waste loaded to sewage is approximately 0.6 kg/a, and from detergents 0.3 kg/a per capita [2]. Phosphorus (P) is a leading nutrient that stimulates the growth of algae and other photosynthetic micro-organisms and must be removed from wastewater to avoid eutrophication in aquatic water systems [3]. Eutrophication can be defined as the enrichment of waters by nutrients and the consequent deterioration of quality due to the luxuriant growth of plant life, and its repercussions on the ecological balance of the waters affected. The limiting nutrient in most freshwater lakes, reservoirs, and rivers is phosphorus, and inputs of this element from

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anthropogenic sources accelerate the process of eutrophication, which normally proceeds slowly in the lakes' natural ageing process [4]. Eutrophication, in general, is the process during which the formerly deficient nutrients move to the surface water. Looking back through history, eutrophication was a natural process and it took centuries to transform water body into a dry land. This process has several negative impacts these negative consequences are inter connected with one another: (i) the proliferation of bloom-forming species that could be toxic or inedible, (ii) the decrease of water quality (e.g. color, transparency, odor, taste, and water treatment problems), (iii) water plants which die causing the propagation of bacterial decomposers, (iv) bacteria consuming more oxygen, causing its shortage in water body, and thus, killing the fish, (v) loss of biodiversity, (vi) decrease in esthetic and recreational values of the water body. In this case, the phosphorus removal from the wastewater is extremely important, as both saves enormous amount of nonrenewable phosphorus and also prevents water eutrophication and contamination [5]. Many countries around the world including the European Union allow 1-2 mg/L as the limit of total phosphorus (TP) for effluent discharge in wastewater treatment plants. However, some regions follow stringent measures of around 0.5-0.8 mg/L, the aim of controlling eutrophication [6].

Phosphorus recovery from the aqueous phase of biological wastewater treatment plants has reached a maximum value of 40%. From sewage sludge and ashes, up to 90% can be recovered [7]. The treatment and disposal of activated sludge is a major concern of the municipal for reinforcing, more proper wastewater treatment plant facilities due to its hazardous ecological impacts, as well as the handling and disposal costs. Many technical problems can arise from the treating and disposing of the excess sludge, which can easily contribute to secondary environmental pollution. Various physical and chemical methods, such as thermal hydrolysis [8], ultrasonic treatment [9], mechanical disintegration [6], microwave irradiation [10], hydrolysis and acidification [11], have been examined, and their influence on sludge has been examined. Many cases at full-scale plants are based on technologies using crystallization of phosphorus as calcium phosphate [12] or struvite [13–15]. However, these technologies can only reach the recovery efficiency of 50 to 60% of the TP [16] and are often implemented as a solution for the problems caused by the spontaneous precipitation of struvite. Struvite (magnesium ammonium phosphate, MgNH₄PO₄ \cdot 6H₂O) is a crystalline solid which can serve as slow releasing fertilizer

due to its lower solubility. The basic chemical reaction to the formation of struvite can be expressed by Eq. (1) [17]:

$$Mg_{2}^{+} + NH_{4}^{+} + PO_{4}^{3-} + 6H_{2}O \rightarrow MgNH_{4}PO_{4} \cdot 6H_{2}O$$
(1)

The factors that influence the struvite crystallization reaction include pH, temperature, supersaturation of solutes $(NH_4^+, Mg^{2+}, and PO_4^{3-})$, the presence of crystallization nucleus, the type of magnesium source, and impurity ions. Struvite precipitation can be used to remove ammonia, phosphate or both of them. The application of struvite in the agricultural sector would be a profitable investment. Generally, 1kg of struvite per day is enough to fertilize 2.6 ha of arable land by applying phosphorus (as P2O5) at a rate of 40 kg/ hayear [18]. The struvite precipitation technique has been applied to various wastes, such as swine waste [19], animal wastewater [20], dairy manure [17], calf manure [21], landfill leachate [22], semiconductor wastewater [23], slaughterhouse wastewaters [24], and anaerobic digester [25].

Most of the studies in the literature place focus on the removal/recovery of the readily available phosphorus in the wastewaters. However, the release of phosphorus from the solid phase is the only way to recover the highest amount of phosphorus from aerobic digested wastewater. In recent years, phosphorus recovery by phosphate crystallization has become hotly debated and has been extensively studied for the treatment of a variety of phosphorus intensive wastewater treatments. As phosphorus is a nonrenewable element, its recycling is also of great interests to many. A great amount of phosphorus is lost annually for the lack of P recovery. Methods of phosphorus extraction from the wastewater fulfill its recycling, purposes should be developed. Phosphorus is mainly used in agriculture as a fertilizer or as food additive in the animal feed. The other applications of phosphorus include ingredients for human food, pharmaceuticals, detergents, and some exclusive chemicals [26].

The objectives of this work were to investigate the release of phosphorus from the solid phase to liquid phase during the thermal treatment and recovery of phosphorus via struvite crystallization. The effects of the operating conditions for releasing phosphorus from wastewater treatment sludge into the liquid phase were studied. In addition, the struvite precipitation was characterized by (SEM–EDX), Fourier transform infrared spectroscopy (FTIR), and EDX.

2. Materials and methods

2.1. Sampling and analysis

Samples of aerobic wastewater treatment were collected from PTG 122 unit, Indah Water Konsortium Sewage Treatment Plant, Selangor, Malaysia. The sample was stored at 4°C for further use as a substrate and to avoid the change in its physiochemical properties. The characterization of the aerobic wastewater treatment involves the determination of total phosphate (P), chemical oxygen demand (COD) using the HACH DR2500 spectrophotometer, electronic conductivity, turbidity, pH of solution, and total suspended solid. All parameters were analyzed in accordance with the standard methods for the examination of both water and wastewater APHA et al. 2005 [27]. Total phosphate and PO₄-P were determined using the Molybdovanadate Method (4500-P). COD was determined using Colorimetric Method (5220-D). Turbidity and suspended solids were determined using 2130 and 2540 Methods respectively.

2.2. Experimental methods

The procedure where phosphorus was released from the solid phase to solution was achieved in four steps: mixing, heating, duration of heating and solidliquid separation. The range of concentration of TP was 3.7-4.6 mg/L. The samples of the aerobic wastewater treatment (200 mL) were subjected to the convection oven treatment at different temperatures (50, 75, 100, 125, 150, and 175°C) and with varying durations of heating (10, 20, 40, 60, 80, and 100 min). The samples were carried out immediately before and after the heating treatment and also 24 h after the treatment. Throughout the study, the samples were adjusted to pH 2, 4, 6, 8, 10, and 12 (with 0.1 M HCl or NaOH) to determine the effect of pH on TP release. The sludge used for the runs at different temperature and time was stored in the laboratory at room temperature for 24 h, and then, the TP concentration was measured to observe any microbial activities. TP concentration onto the solution was measured by using a HACH DR/ 2500 Spectrophotometer at 425 nm wavelength.

2.3. Struvite precipitation experiments

The struvite precipitation experiments were prepared by mixing measured volumes of 10 g magnesium chloride (MgCl₂·6H₂O) accurately in a set of 250mL Erlenmeyer flasks containing 200 mL of the samples using a magnetic stirrer (MR Hei-Mix L, Heidolph, Schwabach, Germany). During the experiments, the mixing intensity was kept constant at 200 rpm for 30 min at room temperature (25-27°C). In all experimental runs, there was no addition of ammonia nitrogen (NH₄–N). The solution was adjusted to pH 9.0 ± 3 by using 0.1NaOH after the addition of magnesium chloride, to test the effect of the initial pH variation on the struvite precipitation. After the solution's pH became constant at the desired level with a variation of 0.1 pH units, the mixing was done for 30 min and the end of mixing period, the flasks content were allowed to settle for 60 min. After the struvite formation reaction ceased, the samples were collected, centrifuged (KUBOTA, Japan) for 20 min at 4,000 rpm. The struvite formation was completed and filtered through 0.45 mm of filter papers, and the filtrate was analyzed, before the residual phosphorus concentration and the precipitate solid was dried and kept at room temperature until the analyses were fully conducted. The recovery efficiency of phosphate is defined as follows:

P recovered amount $= P_o - P_e$ (2)

Recovery efficiency(%) =
$$\left[1 - \left(\frac{P_e}{P_o}\right)\right] \times 100$$
 (3)

where $P_o (mg/L)$ is the initial concentration of phosphorus and $P_e (mg/L)$ is the concentration of phosphorus at equilibrium.

The struvite precipitate obtained was examined by the scanning electron microscopy with the energy dispersive X-ray analysis (SEM–EDX, S-3400 N, Hitachi, Japan). For the XRD analysis, the step-scanned data were collected between angles (2 h) of 2° and 50° at a rate of 1.8° /min using a computer-automated diffractometer. The FTIR analysis of the catalyst was carried out to determine the active surface functional groups. The spectra were recorded in the range 4,000– 400 cm^{-1} .

3. Results and discussion

3.1. Characteristics of the initial sludge sample

The total phosphorous, chemical oxygen demand, electronic conductivity, turbidity, pH solution, and total suspended solid of the initial sludge sample were 3.7-4.6, 114-139 mg/L, $107.12-111.66 \mu \text{m/cm}$, 8.59 UNT, 9.62-9.64, and 8.96%, respectively.

3.2. Effect of temperature and during heating

The results of phosphorus release the during thermal treatment process at various temperatures are shown in Fig. 1, which shows that the amount of released phosphorus increased with time at high temperature. During the first 10 min, the rate of release was not significant at low temperatures. The amount of released phosphorus increased from 20 to 80 min at elevated temperatures and then leveled off, increasing slowly for the remaining 100 min. Phosphorus release can also be expressed in terms of the fraction of phosphorus that is soluble before and after treatment. The phosphorus concentration in the liquid phase (soluble and suspended) was 3.7-4.6 mg/L. Thus, 38.1 mg/L after 100 min of the phosphorus was released from the solid phase in the solution at 170°C, 20.8 mg/L after 20 min, 27.3 after 60 min, and 37.2% after 80 min. The largest amount of phosphorus released from the liquid phase into the solution was 38.1 mg/L at 175°C for 100 min. The thermal treatment increases the solubilization of organic phosphorus and proteins, as indicated by the release of soluble-P, ortho-P, and ammonium from wastewater treatment sludge. The wastewater treatment sludge is essentially microbial cells, which are relatively easy to release phosphorus when cells are disrupted. Liao et al. [28] found that the higher phosphorus release on the solution wasobtained at higher temperatures when applied to sludge. Tao and Xia [29] found further that the maximum orthophosphate (ortho-P) release of about 90 mg/L was observed at 50°C in 1 h.

The experimental data show that, as the effects of phosphorus release from the solid phase into solution after 24 h, the phosphorus concentrations increase from 18.8 to 23.5, 23.4 to 27.5 and 27.8 to 29.4 mg/L at 50, 75 and 100 °C, respectively. This indicates that micro-organisms remain active and nutrients were also available in fresh wastewater treatment sludge, since both carbon source and active micro-organisms were required for the biological phosphorus release process [30]. In the meantime, the organic substances

are readily broken down into smaller parts, and biodegradable fractions could also be utilized by the active species. For all runs with temperature settings over 100°C, phosphate concentrations in the solutions remained fairly constant over a period of 24 h. This provides an implication that there were no biological activities noted in the sludge solution. When a higher temperature was used for pasteurization, the time period required for destroying pathogens would be greatly reduced. All pathogens could be destroyed when the solid phase was under a high temperature of 91°C [31]. As can be seen for the controls, the phosphate levels remained constant after 24 h indicating that there was either the exhaustion of nutrients or the absence of active microbial activities occurring in the solution.

3.3. Effect of pH

Fig. 2 illustrates the released phosphorus from the solid phase into solution at different pHs. The optimal pH was found to be 2 and 4 which resulted in 48.9 and 48.6 mg/L phosphorus released at 175°C for 80 min. As a result, the acids displayed higher efficiency than the bases. The results indicate that the phosphorus release tends to decrease with the increase in the initial pH of the solution. The predictable reason for this lies in that the main type of phosphorus in sewage sludge is organic-phosphorus, which can be easily released through heating. Stark et al. [32] studied the P released from different sludges (collected from an incineration plant and a wastewater treatment plant located in Sweden) by acid (1.0 M HCl) or base (1.0 M NaOH) and they found that the use of acid gives a higher phosphorus release for all samples. The sulfuric acid has resulted in the release of over 90% of TP and part of heavy metals below pH 1.5 [33]. Montag [16] performs a few



Fig. 1. Phosphorus release during thermal treatment process from wastewater treatment sludge.



Fig. 2. Effect of pH on phosphorus release from wastewater treatment sludge plant at 170 °C within 80 min.



Fig. 3. SEM–EDX of struvite precipitate: (a) scanning electron microscopy analysis and (b) energy dispersive X-ray analysis.

experiments for phosphorus release from ashes with NaOH, H_3PO_3 , H_2SO_4 and HCl discovering the leaching of 25, 50, 80, and 90% of total phosphorus, respectively. It can be seen that the neutral pH 7

dissolves 10% of the total phosphorus. The share of dissolved phosphorus increases linearly as the pH decreases, the pH value 2 eluting 90% of the total phosphorus. A similar phenomenon was observed on the successfully applied acidic treatment for the purpose of the P extraction from poultry litter [34], and also the removal of ammonium and phosphate from the supernatant of the anaerobically digested waste activated sludge [35].

3.4. Struvite precipitation

Magnesium salts are the least used of cations for phosphorus precipitation, apart from the intentional formation of struvite. Phosphorus recovery by MgNH₄PO₄·6H₂O crystallization is one of the most widely recommended technologies for treating sludge digester liquors especially in wastewater treatments plants. Struvite is a white crystalline substance consisting of magnesium, ammonium, and phosphorus in equal molar concentrations. MgCl₂·6H₂O has a very low solubility in the neutral solution. The important factor controlling the crystallization reaction and to be considered in the struvite precipitation is the pH, because it has a crucial effect on the activities of the ions and also on the solubility of struvite [36]. At a pH level above 9.0, struvite becomes more soluble as a result of the decreasing and increasing ion activities of ammonia and phosphate, respectively. Therefore, the solution's pH value influences the crystal nucleation and growth by influencing the saturation of struvite. The present experiments showed that the



Fig. 4. Fourier transforms infrared spectroscopy analysis of struvite precipitate.

optimum pH value for struvite crystallization was above 9. Generally, struvite's solubility decreases with the increasing pH [37]. The removal of ammonia and phosphorus increased concomitantly with the pH as high as 10.5, where 83% of the ammonia and 97% of the phosphorus were removed [38]. Celen and Turker [39] tested the pH range of 8.5–9.0 and found that the crystallization of struvite offers the highest efficiency at the pH of 9.0; Hoffmann et al. [40] also tested the pH range of 7.0–10.0, and also proven the optimum pH to be 9.0. It is appropriate to keep the solution pH at the range of 8.5–9.5, i.e. around 9.0.

3.5. Characteristics of struvite

The SEM–EDX analysis was performed to identify the surface characterization of the precipitates (Fig. 3(a)



Fig. 5. X-ray diffraction analysis of struvite precipitate.

and (b)). Fig. 3(a) illustrates the SEM analysis, where the surface of the unshaped crystal was coarse, and its size irregular. Fig. 3(b) highlights the EDX, which shows that the surface composition of the precipitates contains high amounts of O, P, Mg, and trace of C, Cl. The results from the morphological examination of the precipitates were in agreement with the XRD mineralogical analyses which suggest that increasing magnesium concentrations in the supersaturated solutions, past a threshold value influence the purity of the precipitated struvite.

The FTIR and XRD analysis indicated that the main composition of the precipitates was struvite precipitate (Figs. 4 and 5). The FTIR analysis (Fig. 4) demonstrates that the infrared spectrum of the precipitate was close to that of the struvite as elucidated elsewhere [41,42]. The spectra displayed the following bands:

$3,273\mathrm{cm}^{-1}$	indicated the presence of crystalline hydrate
$2,379{ m cm}^{-1}$	band was attributed to the water-phosphate
	hydrogen bonding
$1,649{ m cm}^{-1}$	band was attributed to the water HOH
	bending region
$1,402{ m cm}^{-1}$	band was the characteristic Mg ²⁺ band
1,235–	corresponding to phosphorous containing
$1,021{ m cm}^{-1}$	groups
$886{ m cm}^{-1}$	band was ascribed to the water-water
	hydrogen bonding
$689 {\rm cm}^{-1}$	band was characteristic of PO ₄ ^{3–}
	•

FTIR analyses demonstrated further that struvite was stands out as the dominant composition of the precip-

Table 1

Comparison of the maximum recovery of phosphorus via struvite precipitation from different wastewater

Type of the waste	Chemicals added	Amount of the chemicals	Optimum pH	Recovery (%)	Ref.
Animal wastewater	MgNH ₄ PO ₄ ·6H ₂ O	1.0 M ratio	8.09-8.43	93 (OP)	[20]
Pharmaceutical wastewater	MgCl ₂ , NH ₄ ClCaCl ₂	Mg/N/P=1.1:1.0:1.0 Ca/P=2.0:1.0	9.0 ± 0.1	99.9	[36]
Anaerobic digester sludge from biological phosphorus removal in WWTP	Na ₂ HPO Mg(OH) ₂	Slurry, 55% (w/w) Mg(OH)	8.5	94 (OP)	[44]
Swine waste	MgCl ₂	Mg:P = 1:1.3 Mg: TP = 1.6:1	9.0	91 (SP)	[45]
Anaerobic supernatant from a civil biological nutrient removal plant	No chemicals added	-	8.78	80	[46]
Wastewater from the cochineal insects processing	Na ₂ HPO ₄ ·2H ₂ O Low grade MgO	24g/L	8.5–9	100	[47]
Anaerobic digestion of sludge from a sewage treatment plant	MgSO ₄ ·7H ₂ O	Mg:P=1.1:1	8.4-8.5	92	[48]
Wastewater treatment sludge	MgCl ₂ ·6H ₂ O	Mg:N:P=1.0:1.0:1.0	9.0 ± 3	93.6	This work

Notes: TP, total phosphorus; SP, soluble phosphorus; OP, orthophosphate; WWTP, wastewater treatment plant.

itate. The FTIR spectra obtained were in agreement with the results reported in the study, which carried out on ammonium nitrogen recovery from the wastewater by means of the chemical precipitation [43].

The XRD patterns of the precipitate obtained from the wastewater sludge using MgCl₂·6H₂O are shown in Fig. 5. The XRD pattern generated from the purified struvite has matched with the database model of the reference (the position and intensity of the peaks), which identified the precipitated crystals as real pure struvite.

Table 1 provides a comparison of the maximum recovery of phosphorus by struvite precipitation from different kinds of wastewater. Compared with previous studies, the sewage treatment sludge plant showed a relatively high recovery of phosphorus as struvite precipitation. The removal and recovery of $PO_4^{3^-}$ ions, by struvite precipitation seem to be possible only for wastewaters containing equal molar concentrations of Mg²⁺, NH₄⁺, and PO₄^{3^-} and the performance of the process can be increased by adding more Mg²⁺ ion. pH was another parameter that control the process. The recycling of the effluent can be beneficial; it does not enable loss of high $PO_4^{3^-}$ content of the effluent in a continuous system.

4. Conclusion

The wastewater treatment plant sludge was a suitable secondary raw material for P fertilizer production. In this study, the effects of a thermal treatment process on wastewater treatment plant sludge for aerobic digestion and the influence of operating parameters of phosphorus released from the solid phase to liquid phase were investigated. The experimental temperature of the range 50-170°C would be released of phosphorus from sludge to liquid phase sludge at higher temperature and lower pH. The maximum total phosphorous release of about 48.9 mg/L was observed at 170°C in 80 min. Sludge can also be stabilized in a thermal process by operating at temperatures above 100°C. No micro-organism activities were observed. Experimental results show that the phosphorus recovery by struvite crystallization efficiency is satisfactory, and the maximum phosphorus recovery at equilibrium and pH 9.0 ± 3 was 93.6%. Both analysis of the FTIR and XRD indicate that struvite precipitate to be the main composition of the precipitate.

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