STRUVITE FORMATION FROM WASTEWATER: AFFECTING FACTORS AND NUTRIENT RECOVERY

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Abstract

Never human being has to face such a serious lack of phosphorus and pollutants from human activities. Nutrient recovery from wastewater is a new trend which attracts the interests of several researchers. Extraction of the nutrients, based on struvite crystal from wastewater as nutritious sources, has been assessed as an urgent solution to tackle the water pollution issue. This review focused on feature characteristics of struvite as a chemical fertilizer for plant, struvite formation process in various wastewaters, which is related to physio-chemical conditions, and potential of applying this idea into practice.

Keywords*:* Struvite; wastewater; nutrient; recovery

1 INTRODUCTION

Nutrient recovery from wastewater is now a new interesting vision for the current situation when the effluent quality requirement becomes stricter in many countries, especially for phosphorus and nitrogen. In fact, human activities are directly discharging the significant amount of nutrients in the form of wastes into the environment, and without any or lack of treatment it can lead to negative problems to ecology called eutrophication. Furthermore, nutrient removal still faces obstacles because of high costs and technical requirements. In such case, after treatment, nutrient compositions in wastewater still remain in sludge which is a kind of hazardous waste. While the shortage of natural phosphorus source is predicted to occur around 2033 [1] due to significantly increasing food demand, phosphorus, which is well-known as an essential compound for life, is a non-renewable source. Moreover, most phosphorus mineral rock concentrates in some places in the world such as Morocco, Iraq, China, Algeria and Syria [1], and it concerns directly to food security in the world. Several researchers have focused on wastewater as a potential nutrient source in the current situation in different ways, for instance, biological, physical, and chemical methods. Especially, the chemical method via crystallization is widely applied for extracting nutrients because of using a simple process which adjusts physio-chemical properties of the solution to convert nutrient composition forms from soluble into particulate. This is more convenient for separating it and using as a nutrient product. Containing both N and P, struvite ($MgNH_4PO_4{\bullet}6H_2O$) attracts many interests from environmentalists as well as agribusiness. Therefore, this review deals with the current situation of nutrient recovery from wastewaters based on struvite crystallization focusing on the mechanism, formation conditions in different types of wastewaters as well as nutrient recovery efficiency.

2 WHAT IS STRUVITE?

2.1 Characteristics of struvite

Basically, struvite is one of orthophosphate forms, which mainly contains magnesium, ammonia, and phosphate. The general molecular formula of struvite is $AMPO_4{\bullet}6H_2O$ where A is potassium (K) or Ammonium (NH_4^+) and M is Cobalt (Co), Magnesium (Mg) or Nickel (Ni) [2].

Normally, the most common struvite, formed in wastewater, is magnesium ammonium phosphate hexahydrates ($MgNH_4PO_4{\bullet}6H_2O$). Struvite precipitation reaction in wastewater solution by the Mg:P:N molar ratio 1:1:1 is as follows:

$$Mg^{2+} + NH_4^+ + HnPO_4^{3-n} \rightarrow MgNH_4PO_4{\bullet}6H_2O + nH+ \ (n = 0, 1, 2)$$

Struvite is formed by two main mechanisms which are nucleation and crystal growth. Firstly, essential ions such as Mg^{2+}, NH_4^+ and PO_4^{3-} existing in a soluble form in wastewater, connect with each other to create a seed or nuclei of struvite in the supersaturated solution. In the next step, after the nuclei of struvite formed, the nuclei are continually grown until the solution reaches a chemical balance that means completed struvite is formed.

During the struvite formation process, a phase change process, converting previously dissolved components into a particulate form, and then with the specific gravity of 1.7 mg/L, struvite can be easily separated from the liquid by gravity settling or by other separation processes. Previous studies determined that struvite crystal which is created from wastewaters is transparent and coffin-shaped crystal [4].

Struvite is assessed as a potential chemical fertilizer for the future because not only it contains high nutrients concentrations, for instance, based on theory, struvite crystal contains approximately 5.7 % nitrogen and 12.6 % phosphorus by weight [5], but also, compared to other crystals, presents several advantages such as nutrients in struvite crystal which are released at a slower rate compared to other fertilizers whose soluble rate of struvite in water is 0.2 g/L [6]. Besides, the impurities in the recovered struvite are lower than that of the commercial phosphate fertilizers [7]. Furthermore, struvite crystal has another characteristic feature such as ease of storage which is preferred to apply for soil nutrition [8].

2.2 Factors impacts on struvite formation in wastewaters

Struvite formation can be affected by many factors such as the initial composition of wastewater – pH, essential ions (Mg^{2+}, NH_4^+, PO_4^{3-}), an appearance of comparative ion (Ca^{2+}) [8], retention time, mixing speed or additional seed crystal, etc. However, three main factors affecting the struvite formation in wastewater are: pH, concentration of essential ions, and Mg source which is used for a low Mg^{2+} stream.

2.2.1 Effect of pH

The pH value is the most important impact factor as for struvite formation because pH affects the product solubility of the struvite crystal, and by the solubility product value, the ability of the precipitate is determined. The results of several researches showed that the favourable pH values for struvite formation is higher than 8 [1], and while pH of the solution reaches 9, the ability of struvite formation declines because the solubility of struvite starts to increase [9]. The optimal pH values for struvite formation are presented in Table 1:

Tab. 1 Optimal pH for struvite formation

Optimal pH	Wastewater	References
≥ 8	-	[1]
9.1	Urine	[10]
9.5	Artificial wastewater	[11]
8 – 11	Municipal landfill leachate	[12]
8.2 – 8.8	Domestic wastewater	[13]

2.2.2 Effect of essential ions

As mentioned above, struvite is formed in the solution which contains PO_4^{3-}, NH_4^+ and Mg^{2+} following a molar ratio of 1:1:1. Mehta et al. (2014) reported that in order to create struvite formation effectively, the minimum concentration of phosphate must be 50 mg/L. By collected struvite, effective nutritional recovery can be achieved over 90% [14]. In fact, in normal types of wastewater, the concentration of ammonium is much higher than the that of phosphate and so the N:P molar ratio in wastewater is usually suitable for struvite formation. Therefore, the efficiency of nutrient recovery or struvite formation mainly depends on the molar ratio of Mg and P. Many studies have suggested that Mg is a limited factor of struvite formation process in most wastewater types such as urine, domestic wastewater or swine wastewater. To reach the goal of maximum nutrient recovery by struvite production, the addition of Mg to wastewater stream is essential. Table 2 shows additional Mg sources and dosages from previous studies.

Tab. 2: Additional Mg sources and dosages for struvite formation from wastewater

Mg sources	Wastewater	Mg/P molar ratio	Reference
Sea water $MgCl_2$ Brine	Urine	1.1	[4]
Tap water	Diluted urine	1.3	[14]
$MgSO_4$	Urine	1.2	[15]
$MgCl_2$	Agro-industry wastewater	1.0 – 1.2	[16]
$MgCl_2$	Artificial wastewater	1.1	[11]
$Mg(OH)_2$	Domestic wastewater	1.0	[13]

There are various magnesium sources which can be used such as the chemicals ($MgCl_2$, $Mg(OH)_2$) whose feature is high purity of formed struvite. However, to focus on economic efficiency, magnesium sources come from waste streams with a high Mg^{2+} concentration, by-product of certain production process (ash) or low-cost Mg^{2+} sources (tap water, seawater) [4, 11, 14].

2.2.3 Effect of other factors

In addition to the three most important factors, pH and Mg/P ratio, there are other factors such as the concentration of the compounds reducing the purity of struvite (Ca^{2+}, SO_4^{2-}, heavy metals, suspended solids). Specifically, the Ca^{2+} concentration is about 250 mg/L [10] in wastewater or in Mg^{2+} sources. It forms $CaCO_3$ precipitate [4], $Ca_4MgAl_4(PO_4)(OH)_4$•$12H_2O$, $Ca_8H_2(PO_4)_6$•$5H_2O$ and other precipitates that cause the struvite crystals to be impure or to lose phosphorus [2]. Kim et al. [17] investigated that stirring intensity and duration time have also an impact on struvite formation. Stirring enhanced the transfer of mass from the solute to the crystals which improved struvite crystallization and growth or the addition of seed materials into the wastewater. The stirring speed had less influence on the phosphorus removal efficiency, but contributed to good quality of crystals [14].

3 POTENTIAL OF NUTRIENTS RECOVERY BASED ON STRUVITE PRODUCTION

Struvite has been produced by a number of countries from wastewater treatment systems and sold at relatively cheap prices. For instance, the market price of struvite (NH_4MgPO_4•$6H_2O$) is approximately $ 2.83 per kg P. A calculation shows that for every kilogram of struvite produced from wastewater, $ 0.86 could be saved because of reduction of sludge generated, which would be $ 2.18- 3.27 for phosphorus removal costs and overall cut per ton of phosphorus costs in a wastewater treatment system can be $ 124.61 [18-21].

Previous studies have assessed the potential for struvite formation, which can be categorized into three main sections: agricultural wastewater, domestic wastewater and industrial effluents [22]. Most of the potential of struvite production from wastewater is assessed in laboratory works. Two types – domestic wastewater and sewage sludge – have been developed by many countries for business systems.

Agricultural wastewater and especially swine wastewater contains high concentrations of phosphate and ammonia which is a favourable condition for the formation of struvite. In fact, many studies in the world have been successful in retrieving struvite from cattle wastewater [23-25]), poultry wastewater [26] and cattle urine [27]. The efficiency of phosphorus recovery from wastewater varies from 75% to 90% depending on the type of effluent [22].

In municipal sewage and urban wastewater, the phosphate concentrations of approximately 21- 270 mg/L and the ammonia concentrations in the range of 168-1400 mg/L [22] are good conditions for spontaneous struvite formation and accumulation on pipelines, pumps and devices, which reduces process effectiveness and increases operation costs. Effluent from anaerobic processes [28-30], leachate [12, 31], or human urine contains high levels of nutrient concentrations and have been investigated for struvite formation in laboratory. In addition, wastewaters in industries such as tannery [32], slaughterhouse and meat packing [33], potato process [15, 34] and yeast production [35] are also good candidates for struvite formation and nutrient recovery. However, for these types of industrial wastewaters, it is necessary to carry out pre-treatment steps for organic removal before the struvite formation.

4 CONCLUSIONS

By creating struvite from wastewater, a useful product can be collected for an agricultural needs. Moreover, this also can be assessed as a treatment step in the wastewater treatment process which reduces the contaminants from wastewater. At present, many experiments have been conducted for several kinds of wastewaters to evaluate struvite formation potential in lab scale and pilot scale. In the future, it is essential to further develop full-scale applications to bring struvite formation technology closer to reality.

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