Estimation of phosphorus recovery by struvite crystallization from animal manure wastewater in China

Intensive farming is main industry which produces large amount of animal manure wastewater with high content of phosphorus. Its discharging to surface water leads to eutrophication. On the other hand, phosphorus is vital for plant growth and its natural reserves are rapidly exhausted. Therefore, recovering phosphorus from animal manure wastewater can achieve two important goals: prevention of eutrophication and recovery of non-renewable phosphorus compounds. The method of struvite precipitation has been presented for phosphorus recovery from animal manure wastewater. Based on scenario study, 8.76 million tons of struvite could be produced from animal manure wastewater in China.

1. INTRODUCTION

The production of biomass, including food, is dependent on the availability of phosphorus, which is necessary for the growth of plants. According to the Mineral Commodity Summaries 2015 from USGS, the amount of global phosphorus reserves is 670 billion tons, while the annual production equals 0.22 billion tons. In China, the reserves of phosphorus compounds account for 3.7 billion tons, whereas the annual production reaches 0.1 billion tons. In the last two years, a total of 45–48% of the world's phosphorus rock mining took place in China [1–4]. It is estimated that the deposits of phosphorus might be exhausted within less than 40 years. Therefore, the future production of
a sufficient amount of food is threatened, whereas the search for other, preferably renewable, sources of phosphorus becomes a necessity [5]. While looking for new sources, attention was drawn to animal manure.

Intensive livestock and poultry farming is very important in China. However, it usually produces large amounts of animal manure wastewater, with high content of phosphorus. If animal manure wastewater is not treated properly, it will not only lead to water eutrophication, but also contribute to the exhaustion of non-renewable resources. According to the First National Sources of Pollution Survey Data 4: the Technical Report about Sources of Pollution in China, non-point source pollution caused by agricultural activity is a major cause of eutrophication, mostly by livestock and poultry farms. Therefore, it would be quite beneficial to combine nutrient recovery with environmental pollution control by recovering phosphates from animal manure wastewater in the form of struvite.

Numerous phosphorus recovery technologies have been developed such as biological phosphates uptake, chemical precipitation, adsorption and crystallization. Recovering phosphorus by crystallization is the most economical and efficient method. As long as the conditions for crystallization are suitable, the struvite crystal can be formed just by adding magnesium (Mg^{2+}) to raw wastewater containing high amounts of H_nPO_{n-3} and NH_4^+-N.

2. MECHANISMS OF STRUVITE PRECIPITATION

Struvite is a white crystal, formed in neutral or mild alkali conditions, slightly soluble in water and well soluble in acid solutions. Highly purified struvite, consisting of regular PO_4^{3-} octahedron, distorted Mg(H_2O)_6^{2+} octahedron and groups of NH_4^+ connected by hydrogen bonding, belongs to orthorhombic crystal, while low-purity one shows rod-like or irregular structure (Fig. 1).

During precipitation, struvite is formed according to the following reactions:

\[
\text{NH}_4^+ + \text{Mg}^{2+} + \text{PO}_4^{3-} + 6\text{H}_2\text{O} \rightarrow \text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}
\]

\[
\text{NH}_4^+ + \text{Mg}^{2+} + \text{HPO}_4^{2-} + 6\text{H}_2\text{O} \rightarrow \text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O} + \text{H}^+
\]

\[
\text{NH}_4^+ + \text{Mg}^{2+} + \text{H}_2\text{PO}_4^{2-} + 6\text{H}_2\text{O} \rightarrow \text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O} + 2\text{H}^+
\]

Rate of formation of struvite crystals depends on pH, mixing energy, saturation index (SI), and other ions existing in solution. pH significantly affects the activity of free ions. The mixing energy could strongly influence the particle size of struvite crys-
Phosphorus recovery by struvite crystallization from animal manure wastewater

The saturation index of solution, which directly determines the crystalline orientation of struvite, is the most important factor. Bonurophoulos et al. [6] have found that for $SI = 1.7$, struvite crystals are heterogeneous, whereas above that value the crystals are homogenous. However, the growth rate of struvite is still very low. Abe et al. [7] showed that even at high phosphorus concentration (greater than 200 mg/dm$^3$), the growth rate of struvite was 0.173 mm/day, and it is only 0.061 mm/day at the low phosphorus concentration (30 to 100 mg/dm$^3$).

Theoretically, the ratio of Mg/P is 1:1, but due to the coexisting ions like OH$^-$ and CO$_3^{2-}$, which co-precipitate with Mg$^{2+}$ and form compounds such as MgCO$_3$, Mg$_3$(PO$_4$)$_2$, MgHPO$_4$, Mg(H$_2$PO$_4$)$_2$, the ratio is always higher than 1 and varies from 1 to 1.5 (Table 1) [8–14]. However, an increase in Mg/P ratio above 1.5 will cause co-precipitation with other compounds, and further decrease of the purity of struvite.

pH of animal manure wastewater is also an important parameter controlling the formation of struvite. Hao et al. [15] stated that the highest purity of struvite was formed at pH = 7.0, and the purity of struvite will decrease with the increase of pH. When pH is higher than 10, the precipitates mainly consist of Mg$_3$(PO$_4$)$_2$ and Mg(OH)$_2$. Therefore, to obtain higher phosphorus recovery ratio and purer struvite, the optimum pH range...
would be 8.0–9.0 (Table 1). As pH of animal manure wastewater is always 7.5–8.5, it is more convenient to recover struvite directly, without adjusting pH.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Initial concentration of phosphorus [mg/dm³]</th>
<th>Molar ratio of Mg/P</th>
<th>pH</th>
<th>Reaction duration</th>
<th>Removal ratio of phosphate [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Animal manure wastewater [8]</td>
<td>60.01</td>
<td>1</td>
<td>8.09</td>
<td>4h</td>
<td>92.82</td>
</tr>
<tr>
<td>Animal manure wastewater [9]</td>
<td>128±13</td>
<td>1.2</td>
<td>9</td>
<td>1h</td>
<td>98</td>
</tr>
<tr>
<td>Animal manure wastewater [10]</td>
<td>96</td>
<td>1.6</td>
<td>9.13</td>
<td>1h</td>
<td>88.5</td>
</tr>
<tr>
<td>Synthetic animal manure wastewater [11]</td>
<td>80</td>
<td>1.4</td>
<td>10.0</td>
<td>2h</td>
<td>97</td>
</tr>
<tr>
<td>Anaerobic digesters animal manure wastewater [12]</td>
<td>51.1</td>
<td>1.4</td>
<td>9.0</td>
<td>1h</td>
<td>84.5</td>
</tr>
<tr>
<td>Anaerobic digesters animal manure wastewater [13]</td>
<td>55.4</td>
<td>1.2</td>
<td>9.0</td>
<td>20min</td>
<td>85</td>
</tr>
<tr>
<td>Anaerobic digester animal manure wastewater [14]</td>
<td>64.2</td>
<td>1</td>
<td>9.0</td>
<td>15h</td>
<td>97.2</td>
</tr>
</tbody>
</table>

Actually, Many coexisting substances interfere in the process of struvite precipitation from animal manure wastewater, such as calcium ions (Ca²⁺) and suspended solids. Ca²⁺ will form Ca₃(PO₄)₂ and CaHPO₄ at pH = 9 with phosphate ions, but the crystals are too small to be separated from effluent [16]. The suspended solids are negatively charged on their surface and may absorb NH₄⁺ and Mg²⁺ ions easily in the alkaline environment, resulting in the decreases of both phosphorus recovery ratio and struvite amount [17].

The addition of crystals seeds can accelerate struvite crystallization and increase the size of crystals. It will also reduce the reaction time and enhance the efficiency of crystals separation from wastewater. Ariyanto et al. [18] showed that the smaller the crystals seeds are, the faster the rate of crystal growth could be reached. On the other hand, excessive amount of crystals seeds would not improve the phosphorus removal efficiency. Hence, adding proper amount of crystals seeds with a proper average size is more efficient.

Struvite, as a slightly soluble crystal, has been successfully used on herbages, vegetables, and grain crops as a fertilizer, especially on the magnesium-fond crops, like sugar beet. It has a lasting positive effect on roots and does not burn the seeding or roots due to its slow releasing character. Besides, compared with other highly soluble fertilizers, struvite is more suitable to be used in the vast areas of forests, which are too large to be fertilized frequently. Struvite can decrease the times of fertilization and reduce the loss of nutrients. However, animal manure wastewater often contains impurities, espe-
cially heavy metal ions. A safety evaluation of struvite made by Ryu et al. [19] confirmed good efficiency of struvite recovery while emphasizing the negative effect of higher concentrations of copper and cadmium in struvite. Therefore, it would be desirable to find a method allowing the removal of heavy metals before precipitations of struvite.

3. ESTIMATION OF THE POSSIBILITY OF PHOSPHORUS RECOVERY FROM ANIMAL MANURE WASTEWATER IN CHINA

In China, the present reserve of phosphate rocks is 3700 million tons (Mt) as P\textsubscript{2}O\textsubscript{5} and nearly 16.7 Mt are used for phosphate fertilizer production every year. Facing the inconsistency between the shortage of resources of natural phosphorus and the growing demand for fertilizer production to produce enough food, recovery of phosphorus from wastewater is extremely urgent.

The annual productions of animal manure and total phosphorus content in China (calculated as P) could be estimated using the data from China Animal Industry Yearbook (2013). In 2012, the production of animal manure was 3037 Mt which contains 3.73 Mt of phosphorous. However, they were not equal to the emissions of phosphorus to the environment. Therefore, an evaluation of phosphorus emission from animal manure wastewater in China is essential.

In this study, the phosphorus emission coefficients (\(\mu_w\)) from animal manure wastewater were used from the First National Pollution Census – the Coefficients Manual of Pollution Production and Emission from Animal Sources in China and the phosphorus emissions from animal manure wastewater could be estimated by the phosphorus emission coefficients, feeding time, and the number of animals. Because the animals in different regions discharge phosphorus compounds of varying quality, the coefficients and number of animals are given according to different regions. The main species of animals in China are pigs, pregnant sows, cows, cattle, hens, chickens, ducks and geese. The feeding time and the number of these animals in different regions are shown in Tables 2 and 3, respectively. The formula for calculation the phosphorus emissions from animal manure wastewater is given by:

\[
Q_w = \sum_{i=1}^{7} \sum_{k=1}^{6} \sum_{j=1}^{t_i} \mu_{wj} n_i
\]  

(4)

where: \(Q_w \times 10^4\) tons) represents the phosphorus emissions from animal manure wastewater in 2012, \(i\) from 1 to 7 stands for seven species of animals (1 – pigs, 2 – pregnant sows, 3 – cows, 4 – cattle, 5 – hens, 6 – chickens, and 7 – ducks and geese), \(k\) from 1 to 6 stands for six regions (1 – North China, 2 – Northeast China, 3 – Eastern China, 4 – Southeast China, 5 – Southwest China, and 6 – Northwest China), \(j\) stands for
different feeding periods (Table 2), \( t \) (d) is the feeding duration, \( n \times 10^4 \) is the number of animals.

<table>
<thead>
<tr>
<th>Species</th>
<th>( t )</th>
<th>Feeding period</th>
<th>( j )</th>
<th>Feeding duration [d]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pigs</td>
<td>1</td>
<td>nursing</td>
<td>1</td>
<td>65</td>
</tr>
<tr>
<td></td>
<td></td>
<td>fattening</td>
<td>2</td>
<td>120</td>
</tr>
<tr>
<td>Pregnant sows</td>
<td>2</td>
<td>pregnant</td>
<td>1</td>
<td>114</td>
</tr>
<tr>
<td>Cows(^a)</td>
<td>3</td>
<td>breeding</td>
<td>1</td>
<td>199</td>
</tr>
<tr>
<td></td>
<td></td>
<td>milk production</td>
<td>2</td>
<td>166</td>
</tr>
<tr>
<td>Cattle(^b)</td>
<td>4</td>
<td>fattening</td>
<td>1</td>
<td>365</td>
</tr>
<tr>
<td>Hens</td>
<td>5</td>
<td>breeding</td>
<td>1</td>
<td>120</td>
</tr>
<tr>
<td></td>
<td></td>
<td>laying</td>
<td>2</td>
<td>245</td>
</tr>
<tr>
<td>Chickens</td>
<td>6</td>
<td>breeding</td>
<td>1</td>
<td>55</td>
</tr>
<tr>
<td>Ducks and geese</td>
<td>7</td>
<td>breeding</td>
<td>1</td>
<td>50</td>
</tr>
</tbody>
</table>

\(^a\)Days of breeding and milk production were prorated for a year (365 days).
\(^b\)The fattening period is 365 days.

As shown in Table 4, the phosphorus emissions in animal manure wastewater were equal to 1.22 Mt, i.e. 32.7% of the total production of phosphorus from animal manure (3.73 Mt). The largest phosphorus emission source from livestock and poultry industry consisted of egg-laying hens, which contributed 38.95%. Pigs took the second place, contributing 23.34%. Because of the large food requirements, especially in regard to eggs and pork, the number of intensive livestock and poultry farms increased thirteen times during last 10 years, which led to an increase in animal manure wastewater production.
Table 4

Phosphorus emissions in 2012 from various animal species

<table>
<thead>
<tr>
<th>Species</th>
<th>Phosphorus emission [10^4 tons]</th>
<th>[%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pigs</td>
<td>28.39</td>
<td>23.34</td>
</tr>
<tr>
<td>Pregnant sows</td>
<td>2.57</td>
<td>2.11</td>
</tr>
<tr>
<td>Cows</td>
<td>12.57</td>
<td>10.33</td>
</tr>
<tr>
<td>Cattle</td>
<td>17.62</td>
<td>14.49</td>
</tr>
<tr>
<td>Hens</td>
<td>47.37</td>
<td>38.95</td>
</tr>
<tr>
<td>Chickens</td>
<td>8</td>
<td>6.58</td>
</tr>
<tr>
<td>Ducks and geese</td>
<td>5.11</td>
<td>4.2</td>
</tr>
<tr>
<td>Total</td>
<td>121.63</td>
<td>100</td>
</tr>
</tbody>
</table>

Struvite crystallization has been recognized one of the most effective methods of recovering phosphorus, and its production determines whether it could substitute the mineral phosphorus fertilizers. Therefore, it will be essential to estimate the production of struvite recovered from animal manure wastewater. According to the law of mass balance:

\[ Q_{\text{influent}} = Q_{\text{solid}} + Q_{\text{effluent}} \]  \hspace{1cm} (5)

where: \( Q_{\text{influent}} \) is the input of total phosphorus, \( Q_{\text{solid}} \) and \( Q_{\text{effluent}} \) are the output contained in struvite and effluent, respectively.

With known input, it is necessary to know the ratio of phosphorus recovery (\( R \)) in crystals. The formula can be expressed as:

\[ Q_{\text{solid}} = R Q_{\text{influent}} \]  \hspace{1cm} (6)

Additionally, as the purity of struvite collected without washing is almost 95% \([17]\) and the molar masses of struvite and phosphorus are 245 g/mol and 31 g/mol, respectively, the struvite production (\( Q_{\text{MAP}} \)) should be modified as:

\[ Q_{\text{MAP}} = \frac{245 R Q_{\text{influent}}}{31 \times 95} = 8.32 R Q_{\text{influent}} \]  \hspace{1cm} (7)

If all the phosphorus in animal manure wastewater was recovered by struvite crystallization, the \( R \) in struvite becomes the key to estimate the production of struvite. However, \( R \) is influenced by many factors such as pH, the initial concentration of phosphorus (\( C_P \)), the molar ratio of magnesium to phosphorus (Mg/P ratio), type of crystallizer, etc. Crystallizers, as the struvite crystallization equipment providing mixing energy and
crystallization zones, are important to determine the phosphorus recovery efficiency. According to the literature data [8–14, 17, 20–30], struvite was mainly recovered by the mechanically stirred reactor or the air agitated fluidized bed reactor. Thus, the two scenarios were set by these two kinds of crystallizers. In scenario 1, struvite was produced using the mechanically stirred reactor, while in scenario 2, it was produced in the air agitated fluidized bed reactor. The formulas could be expressed as:

\[ Q_M = 8.32R_MQ_{\text{influent}} \]  
\[ Q_A = 8.32R_AQ_{\text{influent}} \]

where: \( Q_M \) (Mt) and \( Q_A \) (Mt) represent the productions of struvite using the mechanically stirred reactor and the air agitated fluidized bed reactor, respectively, \( R_M (%) \) and \( R_A (%) \) represent the ratios of phosphorus recovery in these two reactors, respectively.

Based on the literature data, the models of \( R_M \) and \( R_A \) were established on three factors: pH, \( CP \), and Mg/P ratio. The principal component analysis (PCA), the least square method (LSM), and statistical analysis system (SAS) were used to formulate the following:

\[ R_M = -118 + 18.99p + 18.85m + 0.114CP - 9.903(p - 8.9)^2 \\
- 10.42(m - 1.31)^2 - 1.83\times10^4(CP - 101.4)^2 + 2.23(p - 8.9)(m - 1.31) \\
- 0.035(p - 8.9)(CP - 101.4) + 0.0071(m - 1.31)(CP - 101.4) \\
+ 0.033(p - 8.9)^2(m - 1.31) - 20.9(p - 8.9)(m - 1.31)^2 \\
- 0.21(m - 1.31)^2(CP - 101.4), \quad R^2 = 0.776 \]  

\[ R_A = 5.36 + 4.42p + 0.0563CP + 22.84m + 5.39(p - 9.13)^2 \\
+ 0.0051(CP - 100.9)^2 - 18.09(m - 1.35)^2 + 0.15(p - 9.13)(CP - 100.9) \\
- 2.54(p - 9.13)(m - 1.35) - 0.07(CP - 100.9)(m - 1.35) \\
+ 0.42(p - 9.13)^2(CP - 100.9) + 0.0089(CP - 100.9)^2(p - 9.13) \\
- 0.0022(CP - 100.9)^2(m - 1.35), \quad R^2 = 0.775 \]

where: \( p \) is the value of pH, \( m \) is the ratio of magnesium and phosphorus, and \( CP \) is the initial concentration of phosphorus. The models showed that the ratios of phosphorus recovery were related to the monomial, binomial, and interaction terms of three factors. These were consistent with the former study results [8–14] stating that struvite crystallization had its optimum conditions, necessary to obtain higher phosphorus recovery efficiency. The interaction terms of three factors suggested that the ratios of phosphorus
recovery were also influenced by the interaction effect of three factors, not just simple addition of the three effects.

In order to calculate the impacts of three factors, three cases were assumed: (i) base case: the phosphorus emission quantity from animal manure wastewater in 2012 was 1.22 Mt, pH was 9.0, $C_P$ was 65 mg/dm$^3$, and the Mg/P ratio was 1.4, (ii) case 1: each of the three factors was increased by 10%, (iii) case 2: each of the three factors was decreased by 10%. In the base case, the parameters were given in order to carry out two kinds of scenarios at the same base line. Both in the mechanically stirred reactor and the air agitated fluidized bed reactor, 8.76 Mt of struvite could be produced from animal manure wastewater in China, so that the impacts of three factors could be compared.

**Scenario 1.** The results of the case study using the mechanically stirred reactor are given in Table 5 and Fig.2. All the three factors investigated had positive effects on struvite production in the ordering pH > Mg/P ratio > $C_P$. The efficiency of the process could be increased by 9.87%, 2.79%, and 0.91% after a 10% increase of pH, Mg/P ratio and $C_P$, respectively, while it may be decreased by 28.45%, 3.01% and 0.93% after a 10% decrease of the considered parameters. The decrease of pH would have a great negative impact on the struvite production, so controlling the pH during struvite crystallization is essential. The struvite efficiency would be reduced by 2.49 Mt after a 10% decrease of pH.

<table>
<thead>
<tr>
<th>Case</th>
<th>$C_P$</th>
<th>Mg/P</th>
<th>pH</th>
<th>$Q_M$ [%]</th>
<th>$Q_A$ [%]</th>
<th>$Q_M - Q_A$ [Mt]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Base case</td>
<td>65.0</td>
<td>1.40</td>
<td>9.0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Case 1</td>
<td>65.0</td>
<td>1.40</td>
<td>9.9</td>
<td>9.87</td>
<td>4.28</td>
<td>0.49</td>
</tr>
<tr>
<td></td>
<td>65.0</td>
<td>1.54</td>
<td>9.0</td>
<td>2.79</td>
<td>3.04</td>
<td>–0.02</td>
</tr>
<tr>
<td></td>
<td>71.5</td>
<td>1.40</td>
<td>9.0</td>
<td>0.91</td>
<td>–1.59</td>
<td>0.22</td>
</tr>
<tr>
<td>Case 2</td>
<td>65.0</td>
<td>1.40</td>
<td>8.1</td>
<td>–28.45</td>
<td>–22.38</td>
<td>–0.53</td>
</tr>
<tr>
<td></td>
<td>65.0</td>
<td>1.26</td>
<td>9.0</td>
<td>–3.01</td>
<td>–3.87</td>
<td>0.08</td>
</tr>
<tr>
<td></td>
<td>58.5</td>
<td>1.40</td>
<td>9.0</td>
<td>–0.93</td>
<td>1.95</td>
<td>–0.25</td>
</tr>
</tbody>
</table>

**Scenario 2.** The results of case study of the process using the air agitated fluidized bed reactor are shown in Table 5 and Fig. 2. The changes in Mg/P ratio and pH influenced the struvite efficiency more significantly, while those of $C_P$ had a smaller impact. The production would change from –0.27 Mt to 0.34 Mt and from –1.96 Mt to 0.38 Mt, when the Mg/P ratio and pH were increased from –10% to 10%, respectively, while a 10% increase in $C_P$ would decrease the production by 0.13 Mt.
Fig. 2. The impact analysis of various factors to struvite production in 2012:
   a) struvite production ($Q_M$) by the mechanically stirred reactor,
   b) struvite production ($Q_A$) by the air agitated fluidized bed reactor

Comparing the two scenarios, both Mg/P ratio and pH had positive influence on
struvite production, the effect of pH being more significant. The mechanically stirred
reactor could produce more struvite than the air agitated fluidized bed reactor upon similar increase of pH, while the air agitated fluidized bed reactor could produce more upon similar increase of Mg/P ratio. In contrast, the $C_P$ had opposite effect on the mechanically stirred reactor and the air agitated fluidized bed reactor, which meant that the mechanically stirred reactor was suitable for treating animal manure wastewater with higher phosphorus content, while the air agitated fluidized bed reactor was preferred for treating animal manure wastewater with lower phosphorus content.

4. CONCLUSIONS

Crystallization mechanisms, and struvite precipitation ($\text{MgNH}_4\text{PO}_4$) used for phosphorus recovery from animal manure wastewater have been discussed. The phosphorus emissions from animal manure wastewater in China were 1.22 Mt, which corresponds to 32.7% of the total productions of phosphorus from animal manure (3.73 Mt). In the base case of the scenario study, both the mechanically stirred reactor and the air agitated fluidized bed reactor could produce 8.76 Mt struvite from animal manure wastewater. With the mechanically stirred reactor, an increase in the efficiency of struvite could be achieved by increasing any of the three factors such as Mg/P ratio, concentration of phosphorus and pH. Using the air agitated fluidized bed reactor, the increase of pH and Mg/P ratio or decrease of phosphorus concentration could increase the efficiency of struvite. The mechanically stirred reactor was suitable for treating animal manure wastewater with higher phosphorus content, while the air agitated fluidized bed reactor was preferred for treating animal manure wastewater with lower phosphorus content. Struvite could substitute mineral phosphorus fertilizers as a valuable slow-release mineral fertilizer. However, in some cases animal manure wastewater contains heavy metals coming from impurities. Therefore, it is necessary to estimate the potential effects of struvite on the ecosystem before use and to reduce the environmental risk at source.

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