MAP PRECIPITATION FOR RECOVERING NUTRIENTS FROM MANURE

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ABSTRACT

In Germany, the phosphate load of manure is more than three times higher than the phosphate load, that is excreted by the population. Phosphate in manure should be precipitated by adding a surplus of magnesium ions in presence of ammonium, where struvite and some byproducts are formed, called MAP [1]. From this compound, phosphate is easy to recover. Environmental protection also demands to eliminate nitrogen compounds from the manure. Most of the nitrogen of the manure exists as ammonium, especially after anaerobic treatment. The easiest way to eliminate as well phosphate as ammonium is the MAP precipitation. But since the ammonium content is much higher than the content of phosphate, further phosphate has to be added. This procedure is very expensive because of the high costs of phosphate. The solution to this financial problem is to desorb the ammonia from the precipitated MAP by heat and air or vapour (stripping) and to recycle the magnesiumphosphate [1]. This paper reports on laboratory and technical experiences about MAP precipitation from manure in Germany. A combination of anaerobic digestion, separation and MAP precipitation is recommended to treat manure completely, whereas the organic substances are transferred to methane and the nutrients nitrogen and phosphate are recovered. The residual solids may be burnt up. The water may be used for agricultural irrigation.

Keywords: Manure treatment, magnesium ammonium phosphate (struvite), odour control, environmental protection

PHOSPHATE BALANCE IN GERMANY

Within the last years, Germany imported about 150,000 t/a phosphate minerals and phosphate fertilizers, counted as P₂O₅. Further phosphate is imported in the form of animal and vegetable food. On the other hand, a certain amount of phosphate contained in several products is exported. The major amount of phosphate, however, is in a continuous circulation in nature and techniques with animals, plants, industrial products etc [2]. It may be mentioned, that the bodies of 15 million cattle in Germany contain about 300,000 million tonnes P₂O₅ mainly in their bones.
About one billion tonnes $\text{P}_2\text{O}_5$ are fixed in the upper layer of the soil. But most of the phosphate compounds in the soil are insoluble in water and impossible to recover. The phosphates in manure are more reactive and suitable for easy recovering. Table 1 shows a comparison of the amounts of phosphates in cattle, pigs and poultry manure with the phosphates that are excreted by the German population (the phosphates from washing and household agents are not taken into consideration).

<table>
<thead>
<tr>
<th>animals/men</th>
<th>amount</th>
<th>manure/ wastewater</th>
<th>$\text{P}_2\text{O}_5$</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td>cattle</td>
<td>15 millions</td>
<td>220 mt/a</td>
<td>330,000 t/a</td>
<td>500,000 t/a</td>
</tr>
<tr>
<td>pigs</td>
<td>26 millions</td>
<td>50 mt/a</td>
<td>150,000 t/a</td>
<td>190,000 t/a</td>
</tr>
<tr>
<td>poultry</td>
<td>107 millions</td>
<td>10 mt/a</td>
<td>150,000 t/a</td>
<td>210,000 t/a</td>
</tr>
<tr>
<td>sum animals</td>
<td></td>
<td>280 mt/a</td>
<td>630,000 t/a</td>
<td>900,000 t/a</td>
</tr>
<tr>
<td>population</td>
<td>80 millions</td>
<td>5,000 mt/a</td>
<td>180,000 t/a</td>
<td>270,000 t/a</td>
</tr>
</tbody>
</table>

Table 1. Phosphate and nitrogen in the wastes and wastewater by population and livestock in Germany, rough estimation [3]

The greatest recoverable phosphate resources in Germany as well as in other countries are built by the manure from cattle and pigs. The same tendency is valid for nitrogen. The animal excreted phosphate is over three times higher than the human excreted phosphate and exceeds by far the amount of imported phosphate in Germany. This estimation essentially exceeds the figures published by Greaves, UK, [4]. Besides, manure is much more concentrated than domestic wastewater. Therefore recovering of nutrients from manure should be more efficient than from diluted wastewater. If it succeeds to recover a substantial part of the excreted livestock phosphate, the amount of imported phosphates can be diminished and the environment will be relieved.

**PROBLEMS OF LANDSPREADING UNTREATED MANURE**

It is well known that many farmers wish to get rid of the excrements of cattle, pigs, and other domestic animals as soon and as cheap as possible. Storing tanks are expensive and need space. A treatment of the manure would cause additional costs. Therefore fields and meadows are usually irrigated with untreated liquid manure.

By this way nutrients are spread permanently and not according to the requirements of plants at all. Ammonia is stripped into the atmosphere [5] and causes damages of a money level of many billions €/a. Rivers, lakes and ground water are polluted [4]. Moreover, bad odour molest people.

MAP precipitation helps to solve these problems.
MANURE PHOSPHATE - WHAT IS DISSOLVED, WHAT IS UNSOLVED -

It is worth to consider that nearly the entire phosphate in the crude manure is unsolved [4]. By separating the solids (by centrifuges or filtration), the unsolved phosphate compounds get into the separated solid phase (see table 2). The differences between the amounts of the constituents in crude and filtrated manure describe the material, that remains in the filter residue. The individual constituents behave very different:

- Ammonium and potassium are difficult to be eliminated by separation (they remain dissolved)
- The organic nitrogen compounds like urea, uric acid and amino acids are rather difficult to be removed because they are well soluble in water
- Half of the calcium content becomes part of the solid phase, the other half remains in solution
- The organic matter (as COD) including organic phosphorus compounds is rather easy to be eliminated
- The easiest removable substances are orthophosphate and magnesium

The percentages of elimination may vary from manure to manure. But the tendency is similar.

<table>
<thead>
<tr>
<th>constituents</th>
<th>crude manure</th>
<th>manure after filtration</th>
<th>difference</th>
<th>eliminated %</th>
<th>eliminated mM</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dry matter (g/L)</td>
<td>27</td>
<td>15</td>
<td>12</td>
<td></td>
<td></td>
</tr>
<tr>
<td>COD (mg/L)</td>
<td>30,100</td>
<td>21,830</td>
<td>8,270</td>
<td>72%</td>
<td></td>
</tr>
<tr>
<td>total N (mg/L)</td>
<td>3,000</td>
<td>2,630</td>
<td>370</td>
<td>12%</td>
<td></td>
</tr>
<tr>
<td>org. N (mg/L)</td>
<td>820</td>
<td>540</td>
<td>280</td>
<td>34%</td>
<td></td>
</tr>
<tr>
<td>NH₄-N (mg/L)</td>
<td>2,180</td>
<td>2,090</td>
<td>90</td>
<td>4%</td>
<td>6,5</td>
</tr>
<tr>
<td>total P (mg/L)</td>
<td>640</td>
<td>125</td>
<td>515</td>
<td>80%</td>
<td></td>
</tr>
<tr>
<td>org. P (mg/L)</td>
<td>75</td>
<td>10</td>
<td>65</td>
<td>74%</td>
<td></td>
</tr>
<tr>
<td>PO₄-P (mg/L)</td>
<td>565</td>
<td>105</td>
<td>460</td>
<td>81%</td>
<td>14,8</td>
</tr>
<tr>
<td>Mg (mg/L)</td>
<td>200</td>
<td>40</td>
<td>160</td>
<td>80%</td>
<td>6,5</td>
</tr>
<tr>
<td>Ca (mg/L)</td>
<td>570</td>
<td>290</td>
<td>280</td>
<td>49%</td>
<td>7,0</td>
</tr>
<tr>
<td>K (mg/L)</td>
<td>2,100</td>
<td>1,800</td>
<td>300</td>
<td>14%</td>
<td>7,5</td>
</tr>
</tbody>
</table>

Table 2. Composition of crude and separated manure from pigs (example) [6]

The values in the last column of table 2 are the most instructive ones: the amounts of ions (in mM) eliminated by separation. These amounts, seen in relation to each other, illuminate the following facts:
6,5 mM of Mg$^{++}$ and 6,5 mM of NH$_4^+$ apparently form struvite, together with 6,5 mM PO$_4^{3-}$. This is no new experience. Already 175 years ago, struvite crystals have been discovered in old waste pits [7]. And 1 cm long crystals were found in the sediments of manure lagoons in Australia [8].

Nearly the half of the residual 8,3 mM phosphate is bound to calcium, probably as hydroxyl-/ chloro-apatite or as tricalciumphosphate [9]. The rest of phosphate may be bound to iron or to other metals in the manure which are usually not a part of the analysis.

It is unknown how potassium is eliminated by separation. A smaller part of potassium should be bound into the struvite crystals instead of ammonium. Therefore it is likely that a smaller part of the eliminated 6,5 mM ammonium gets lost gaseous into the air as ammonia. But the percentage K : NH$_4$ within struvite doesn´t exceed 5%, as it was proved by analyses of other precipitates [6]. Since all common potassium salts are readily soluble in water the phenomenon of disappearing from the liquid phase during separation can not be explained yet.

METHODS TO APPLICATE MAP PRECIPITATION

There are several methods for treating manure with regard to nutrient recovery and environmental protection.

1) Most simple method

Solid but reactive magnesia is added to the manure in the storage tank (as shown in figure 1) and the manure is mixed up for a short period [10, 11]. This procedure may be performed with fresh or digested manure. The latter has a considerable higher content of dissolved phosphate, caused by hydrolizing effects.

Result:

Nearly the entire phosphate is precipitated as MAP and gets into the sediment of the tank. Considering that the liquid phase is nearly free of phosphate, the farmers may irrigate their fields with the filtrated solution all over the year without phosphate fertilizer problems. The solid phase may be stored and later on spread out as a phosphate and nitrogen fertilizer.

Advantages:

No special equipment is needed besides a transportable mixer or a pump. The chemical costs are very low (about 25 € cent/m$^3$).

Disadvantages:

The majority of ammonium remains in the solution. And the bad odour remains.
In principle, the addition of lime instead of magnesia has the same effect, the binding of phosphate, which gets into the solid phase as calciumphosphate. But this compound is insoluble and therefore has no fertilizer effect when being spread with the solids on the fields.

![Figure 1. Addition of MgO powder and magnesiumphosphate solution (Pollfloc®) into a manure tank](image)

2) **Improved method**

To avoid spreading not only phosphate but also ammonium, the phosphate content of the manure has to be raised to the same molar level as ammonium. Therefore additional phosphate may be given into the manure tank in relation to the ammonium content (molar ratio N : P = 1) and MgO may be added with a molar ratio Mg : P = 1.5. This procedure looks like shown in figure 1. For the purpose to have a component at one’s disposal to adjust easily the required molar relations, the product Pollfloc®-M30 was developed. Pollfloc®-M30 is a liquid product and therefore contains
phosphate and magnesia in the reactive ionic form. Sodium hydroxide has to be added to adjust the wanted pH.

**Results:**
The entire inorganic phosphate and the entire ammonium are precipitated as MAP and get into the sediment. The filtered manure is rather free of phosphate and ammonium and may be spread out all over the year without nutrient problems [12]. Bad odour is decreased by factor 5 or more, as it was proved at a farm at Heiden/Germany during pilot plant experiments.

The solid phase, which contains nearly the entire phosphate and ammonium from the manure, may be stored and later on spread out to meadows and fields as a fertilizer. If it is wanted to recover phosphate and ammonium, the dewatered solid phase may be rinsed by hot water or by diluted acid. The dissolved struvite is crystallized again by cooling and raising the pH with additional MgO.

This method is rather expensive. The costs for chemicals rise up to 15 or 20 €/m³ depending on the concentration of the manure. The purchase of gained MAP may cover a part of this sum [13].

**3) Complete method**

Supposing that a farm has a big housed livestock and not enough land to be fertilized and irrigated with liquid manure other ways have to be found to make the greatest profit as possible by the manure. The valuable components of manure especially are organic substances, phosphate, and nitrogen. Consequently efficient measures are the following:

- Installation of a digester to use the organic substances for methane production. By digestion, organic bound phosphate and organic bound nitrogen are transferred to soluble inorganic substances: phosphate and ammonium which may be precipitated readily.
- Separation of the solids and rinsing them with hot water or acidified effluent to get MAP into solution. The rinsed water is added to the filtrate of the separation process. The solids may be burnt up or used as compost.
- Recovering of the phosphate together with ammonia by MAP precipitation [12].
- Recycling of MP after stripping ammonia out of MAP by heat and air inflation, as it is described in other publications [14,15].

A flow sheet is shown at figure 2.

All the described techniques themselves are well known but not in the mentioned combination. Up to the present, the MAP-process with MP recycling is proved only by pilot plants or experimental plants. But without any doubt the combined process is ready to be put into practice.
4) **Extensive treatment of manure without land spreading**

In 2001, animal epidemics are wide-spread in Europe and elsewhere. Pathogens of the foot-and-mouth disease get transmitted into the excrements and to the manure. The BSE pathogens are also suspected to exist in the manure. On these conditions it surely will be ordered to disinfect the manure completely. In the case of BSE prions a temperature of at least 300°C is needed for disinfection. Burning up the manure should be the safest method. But by this way the valuable components of the manure get destroyed: the organic matter, which can produce methane as well as the nutrients.

A better method is required that saves the energetic value of the organics and recovers the nutrients nitrogen and phosphate. Such an extensive method should involve:

- Anaerobic digestion
- Separation of the solids
- MAP precipitation including recovery of magnesiumphosphate and ammonium
- Burning of the solids; further treatment of the filtrate e.g.
  - by membrane techniques including reverse osmosis
  - by vaporizing and burning up the residue
CONCLUSIONS

MAP precipitation is an efficient process to recover phosphate from manure together with ammonium. A process combination is suggested, which encloses anaerobic digestion, separation, and MAP precipitation. Manure sometimes contains a ten times molar surplus of ammonium. Therefore, it is necessary to add further phosphate and magnesium to adjust the right molar ratio to assure the precipitation of the entire ammonium as struvite. The chemical costs of this procedure are very high. Therefore, it is a better and cheaper way to recycle the magnesiumphosphate and sell MAP or MP than to purchase fresh phosphate.

The technology of anaerobic treatment of manure and the separation of the solid phase are well known. The technology of phosphate recovery by MAP (struvite) precipitation is already practised in other countries, like Japan [16], the Netherlands [10], Italy [17] and others. Recycling of magnesiumphosphate as a precipitation agent is proved within laboratory and pilot plants. But the economic application of this technology on a long-term basis has to be demonstrated yet.

The fear of animal epidemics should not let forget the demands of nutrient saving and environmental protection. In 2001, the burning of cattle, sheep and pig cadavers in the open air to avoid spreading pathogens was a bad example for this. The aim was to kill the pathogens. The question is, whether this succeeds completely or not. But the valuable phosphate and other nutrients were destroyed without benefit. Moreover, open air burning heavily damages the environment by cancerogenic combustion smokes, nitrous gases, dioxine and other harmful substances. The EC decided that four million cattle have to be killed in Europe. If their burning would be carried out in incinerators, about 100,000 tonnes of P₂O₅ could be recovered in a rather pure form as calciumphosphate.

Scientists and technicians should endeaver to solve the nutrient recovery problems of manure as a priority task.

REFERENCES


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