Appendix 1 - Background info

Preventing eutrophication by phosphate adsorption from wastewater

Introduction

What is phosphorus and what is phosphate?

Phosphorus is the chemical element P with atomic number 15. All life on earth depends on phosphorus. Both plants and animals (and therefore also humans) use it to grow and stay alive. In our bodies, for example, you find it as a building material for DNA and our bones. Phosphorus is extremely reactive and therefore occurs in nature almost exclusively as phosphate, a compound between phosphorus and oxygen. Because plants use it to grow, phosphate is one of the nutrients in manure and fertilizer.

What are the challenges related to phosphate?

Environmental damage

Nutrients such as phosphate have a dual nature. On the one hand, we need them, but on the other hand, they can cause a lot of environmental damage. When manure or fertilizer is applied to farmland, it sinks into the soil with rainwater. Some of this washes out into surrounding ditches and then ends up in lakes, canals and the sea. This surplus of nutrients, including phosphate, then causes plants like algae to grow enormously. Because some of the algae block the sunlight for other algae and aquatic plants, the latter die. The plant remains are broken down by bacteria, which requires a lot of oxygen. Because oxygen is poorly soluble in water, a shortage quickly develops for organisms that need oxygen to live. Fish and other aquatic animals die.

High concentrations of nutrients, both in water and on land, also lead to a decrease in biodiversity. This is because plants that benefit from a nutrient-poor environment are driven out by those that benefit from high nutrient levels.

Scarcity

Another challenge we face is the dependence on phosphate mines and the countries where they are located. As is always the case with mines, they slowly become empty. New phosphate never grows. So using the calcium phosphate from these rocks as fertilizer is not future-proof. Moreover, phosphate rocks are found in only a few places on earth. None of these places is in Europe, making us dependent on countries outside Europe for the supply of phosphate rock. About 90 percent of all phosphate rocks are located in the countries of China, Jordan, Morocco, South Africa and America (*figure 1*). When a food crisis threatens in the future, these countries may decide to stop exporting phosphate rock and use it all to provide food for their own populations.

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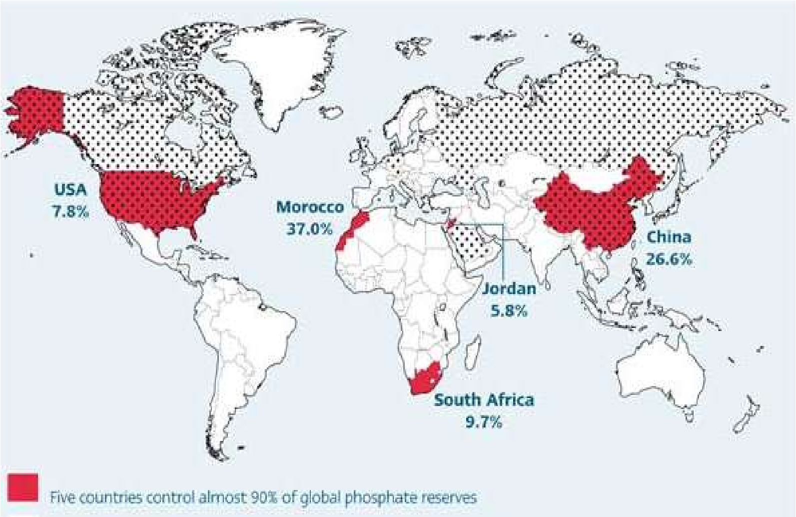

Figure 1: *concentration of phosphate reserves in certain parts of the world*

<u>How are we currently working on solutions to these challenges?</u>

Eutrophication has been an issue for much longer. To reduce it, regulations have been put in place in the past, and water quality has already improved tremendously since then. Because a large proportion of the nutrients that end up in surface water come from agriculture, the rules have been and are still being tightened. Arable farmers are faced with restrictions on the amount of fertilizer or manure they can use to make their crops grow better. Livestock farmers are no longer allowed to use any artificial fertilizer at all, and the amount of animal manure they are allowed to apply to their land is roughly equivalent to the manure yield of one cow per soccer field. In practice, this means that most farmers have a huge manure surplus. They have to pay to have their manure transported to neighboring countries, where there is more farmland in proportion to the livestock population. Despite these strict regulations, there is still a lot of leaching of nutrients from agricultural land into surface water, resulting in eutrophication.

Industrial and human wastewater is now treated in a sewage treatment plant (WWTP) before it is discharged to surface water. A WWTP has to comply with maximum values for, among other things, the phosphate concentration. Currently, they remove the phosphate from the water in two ways (or a combination of both): In the first, they add iron or aluminum salts, which precipitate with the phosphate (chemical method). Another method is with bacteria that, under the right conditions, store the phosphate and thus remove it from the water (biological method). In both methods, the phosphate ends up in the sludge, after which it is burned. The ash containing the phosphorus ends up in, for example, asphalt.

To prevent environmental damage by phosphate as much as possible and not to be dependent on countries outside Europe for its availability, we must move towards a closed phosphorus cycle. To get this done, several studies are running at Wetsus on methods to recover phosphate in a sustainable way.

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The toolkit: preventing eutrophication by phosphate adsorption from wastewater

- Humans consume P and this ends up in the waste water treatment plants (WWTP). This phosphate is removed conventionally by precipitating with metal salts which results in sludge formation. There are technologies that are working on recovering P from this sludge.
- Besides recovering P from sludge, there however is residual P in the range of few mg P/L or even less that can't be removed by conventional treatment. If this is discharged from the WWTP effluent into surface waters, this can trigger the formation of harmful algal blooms due to eutrophication. This would have huge environmental and economic impacts. Thus, there is a need for a technology that can remove P to ultra-low concentrations (less than 0.1 mg P/L) to prevent formation of such algal blooms.
- Adsorption is one such technology which can act as a polishing step and remove P to ultra-low concentrations. Moreover, the adsorbent can be regenerated and reused. Thus, the P adsorbed can then be desorbed and recovered in a more concentrated form.
- In this way, the P can be stopped from causing pollution and the P can thus also be recovered, thus completing the cycle.
- Iron hydroxides and iron oxides, hence forth collectively called as iron oxides show a good binding capacity with phosphate ions. Hence they are suitable candidates for phosphate adsorption.

Mechanism

Adsorption is a phenomenon, where soluble particles (called adsorbate) are removed from a solution using an insoluble material (called adsorbent). There are different types of adsorption, and the one involving interaction of phosphate with iron oxides is called chemisorption. This is because the reaction involves the formation of chemical bonds.

In this case, iron (hydr)oxides have hydroxyl groups (OH groups) on their surface. The phosphate ion binds to the iron oxide, by exchanging with the hydroxyl ions as shown by the reaction below. This involves the formation of a chemical bond between the iron atom and the phosphate.

- **Adsorption**

$$Fe(OH)_3 + PO4^{3-} \rightarrow Fe(PO_4) + 3\ OH^-$$

The reaction is however reversible, when an alkaline solution, i.e. a solution high in concentration of hydroxide ions is brought into contact with the adsorbent. Basically, the higher concentration of hydroxide ion ensures that the phosphate ion is released and the hydroxide ion binds with iron atom. Thus, the phosphate is released and the iron (hydr)oxide is formed again as shown in the reaction below. This is called desorption. This way the phosphate can be recovered as well as the iron oxide adsorbent can be used again.

- **Desorption**

$$Fe(PO_4) + 3\ OH^- \rightarrow Fe(OH)_3 + PO4^{3-}$$

Other projects at Wetsus about phosphate recovery

Recovery of phosphate at high concentrations at the WWTP

Currently, phosphate is already recovered in the form of struvite. This is a mineral (magnesium ammonium phosphate, MgNH4PO4-6H2O) that accumulates in the pipes and pumps of the WWTP. By allowing this to occur in a controlled manner, you can separate the crystals and allow them to settle. These can then be processed into fertilizer. The disadvantage of this technique is that it can only be used at WWTP's that remove the phosphate biologically and the efficiency is maximum 40%.

At Wetsus we do research on the mineral Vivianite (iron(II) phosphate, Fe3(PO4)2-8(H2O)). This is created by adding iron to the sludge (Or do they add it directly to the wastewater?), which is rich in phosphate. After 20 days of anaerobic conditions, this allows 80-90% of the phosphate to be converted to vivianite. The vivianite is paramagnetic and can be removed from the sludge with strong magnets. The phosphate can then be recovered under alkaline conditions. In this way, higher yields can be achieved than in comparison with struvite, up to 60%.

A disadvantage of vivianite is that it cannot be used directly as a fertilizer, because it is difficult to break down. Therefore, it must first be chemically treated before it can be used further. We are still investigating whether it can be used for plants that need a lot of iron, such as olive trees. But you will probably still end up with a large proportion of vivianite. Another disadvantage is that the added iron to form vivianite first binds with sulfur and organic matter before it binds with phosphate. You therefore need a lot of iron to form vivianite.

Recovery of phosphate at high concentrations from cow manure

In the Netherlands there are a lot of cows and therefore also a lot of cow manure. This cow manure is a large source of phosphate, so it would be ideal if we could recover it. At Wetsus we are researching an organic method in which we add calcium to the manure. This creates calcium phosphate, the same mineral that is mined from the mines. With this method (upflow anaerobic sludge bed reactor) 80% of the phosphate can be recovered. The manure pellets that are produced with this method can be applied directly to the land. At this moment there are no parties interested in this. The organic farmers are not allowed to use this, because they are not allowed to use synthetic substances. The other farmers find the concentration of fertilizers in these granules too low. They would have to go out on the land too often to spread manure (in their opinion). The concentration is low because there is also a lot of organic material in the granules.

For them this would become efficient if, because of even stricter rules, they would only be allowed to apply low concentrations on the land.

For example, if the government were to strictly control the leaching of fertilizer into the groundwater. The options that remain are:

1. Spread manure more often;

2. Slow-release fertilizer spreading, where the fertilizers are released slowly and leaching is prevented.

Sources

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