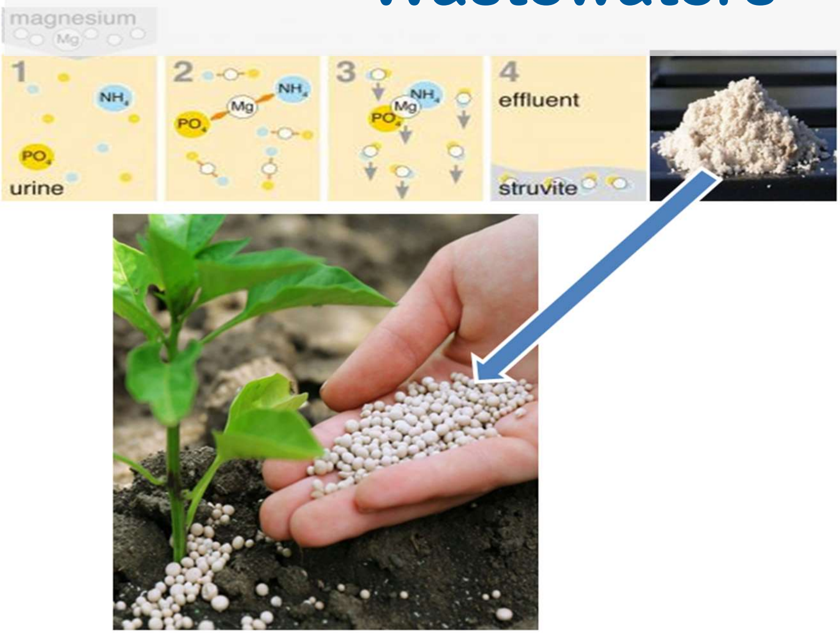
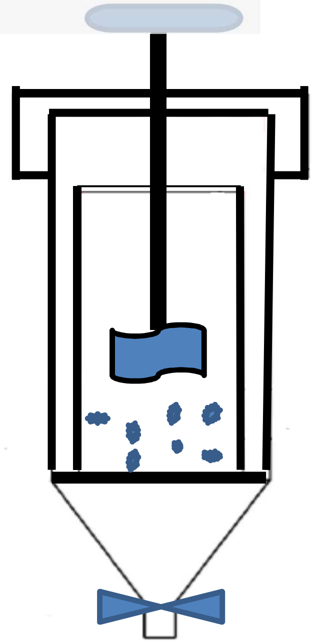
Teachers' Card

Phosphorus Recovery from Wastewaters





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General Introduction

Urine, a product of human excretion, is a component of urban wastewaters. Urine is one of the richest and most accessible sources of **phosphorus** and **nitrogen** to make struvite that can be obtained by a precipitation reaction at basic pH, helped by magnesium dependence.

The laboratory activities in this toolkit are meant for pupils **15-19** years old. The laboratory activity is structured in a theoretical learning phase under the guidance of the trainer and two practical phases. The aim is to obtain the **P recovery as struvite** extracted from wastewaters (synthesised in the lab) by using very common materials. The lab activity is composed by two modules:

Module 1: to make struvite from a synthetic wastewater solution considering the pH effect and the reagents concentration used.

Module 2: to build a simple prototype reactor for the extraction of struvite from synthetic wastewaters and its functioning. The used materials should be available at a DIY store. The aim of this trial is to demonstrate the **P recovery as struvite** extracted from wastewater by using very common materials. This experience will make pupils aware of the P recycling from wastewater to reduce the exploitation of natural resources.

This experience will make pupils aware of the **P recycling from wastewater** to reduce the exploitation of natural resources. In addition, students will be encouraged to learn through laboratory activity how wastewaters are a powerful resource of nutrients for agriculture and environment. Finally, laboratory experience may develop skills in using scientific equipment correctly and safely, making observations, taking measurements, and carrying out well-defined scientific procedures.

Laboratory experience will also promote the student's ability to cooperate effectively with others in performing complex tasks, to participate in project work, to take on different roles at different times and to contribute and respond to ideas.

Link with https://ec.europa.eu/easme/en/horizon-2020-societal-challenge-climate-action-environment-resource-efficiency-and-raw-materials

Key words:

Sustainability; Recycling; Agriculture; Wastewater; Circular Economy

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Extended background information

Phosphorous and Phosphate rocks are **Critical Raw Materials**, raw materials which are economically and strategically important for the European economy, but have a high-risk associated with their supply.

Phosphorus (P) is an essential macronutrient for the growth of all living organisms. The progressive depletion of mineral reserves is based on continuous temporal exploitation of these reserves for anthropogenic use. The main mineral reserves of phosphorus are found in China, Morocco, the United States and Russia (U.S. Geological Survey, 2017). The phosphorites are sedimentary rocks (80-90% of the productive world) and magmatic rocks (10-20% of the productive world) from which P is extracted.

Phosphate rock extraction is constantly growing and, on a global scale, by 2017, phosphate rock extraction should have been 35.7 kg/person. P processed is mainly used for fertilizer production (Stewart et al., 2005) due to the growing global demand for food. Current agriculture, however, depends on phosphorus derived from phosphate rock, which is a non-renewable resource. Only 17% of phosphates comes from renewable sources such as animal sludge and manure, food residues and wastewater Current global P reserves will run out in 50 to 100 years, while demand for P is expected to grow strongly. The global peak of P production is expected around 2030. This effect will produce a higher cost of fertilizers and at the same time phosphate rocks will run out (Cordell et al., 2009).

Without phosphate fertilizers the crop production per surface unit will decrease drastically. 1.2 million tonnes are of phosphate rocks converted to elemental phosphor (evaluated as P_4) devoted to chemical and weapon industries.

Phosphorus can thus be replaced by a resource that we can call "*secondary*", which is recovered from the raw material downstream of the processes that use it. Phosphorus recovery is a practical recycling process and also helps to prevent eutrophication (Joint Research Centre, 2018).

The shift to sustainable use of phosphorus consists of several actions to be applied in anthropic processes. A substantial proportion of the recycling potential comes from the exploitation of the final products of the depuration processes. The European Community considers the agricultural re-use wastewater treatment residues such as "*best practice*" for phosphate matter recovery secondary.

Wastewater treatment plants and animal husbandry facilities are the two most important sources of phosphorus. The release of wastewater into the environment without treatment causes pollution (eutrophication) of the effluent due to high amounts of phosphorus and nitrogen. For these reasons wastewater treatment plants (reactors) play an important role in removing and recovering nutrients (i.e. ammonia and phosphorus).

Phosphorus can be recovered from wastewater in crystal form of magnesium ammonium phosphate (MAP), also known as **struvite** which is also considered an environment-friendly fertilizer.

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Legislation: EU fertilizer regulation recognizes only primary mineral-derived P products, as fertilizer whereas the rest of these recovered P products cannot be labelled as fertilizers yet (EU 2003). Currently, the legislation is under revision to include recovered P residues such as **magnesium ammonium phosphate** (MAP), also known as struvite (European Commission, 2016).

Agriculture: P recovered in the struvite form is highly bioavailable (around 94%) for crops, and therefore, can be used directly as a slow release fertilizer.

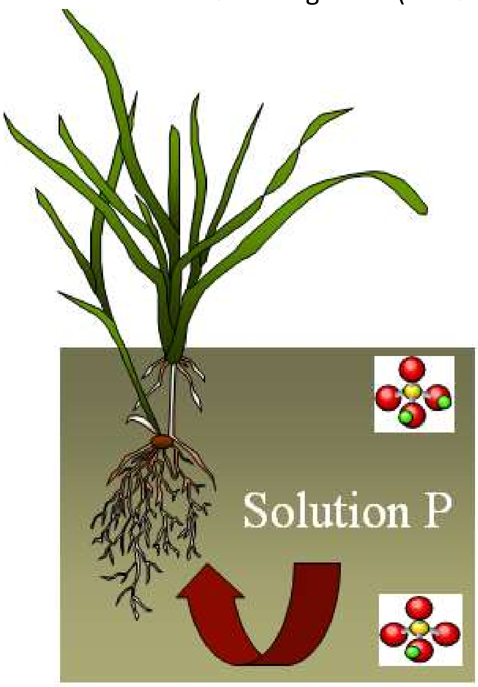
Environment: Struvite is environmentally friendly because reduces eutrophication process and greenhouse gas emissions associated with mineral P fertilizers

Phosphorus in agriculture

Phosphorus is an important element for plants and animal life. Essential component of ATP; DNA, RNA and phospholipids (important in cellular membranes);

Important role for:
Photosynthesis
Nitrogen fixation
Flowering fruiting and seed production
Maturation and crop quality

Not all P in soil is bioavailable to plants and therefore, plays a critical role in agriculture. Total content of P in soil is 0.1-0.2%: inorganic P (≈50 %) and organic P (15-80%). The P solubility is very low and corresponds to ≈ 0.03 mg P/kg.



In soil and water, P exists in soluble form such as orthophosphate ions, $H_2PO_4^{-1}$, HPO_4^{-2} and PO_4^{-3}.

At **acid pH** (less than 7), the **primary orthophosphate** ($H_2PO_4^-$) is prevalent. This molecule has 2 hydrogen atoms (depicted in green) attached to 2 oxygen atoms. More hydrogen atoms reflect the acid environment.

At **alkaline pH** (greater than 7), the **secondary orthophosphate ion** (HPO_4^{2-}) is common. This molecule has 1 hydrogen atom, reflecting the alkaline environment. In a slightly basic soil (pH = 7.2), both are present in equal proportions.

Several soil properties such as abundance of **Ca**, **Al** and **Fe**, **organic matter** content and **pH** influence the solubility and thus, the bioavailability. Among these **pH** is the most **critical factor**.

Reactions that reduce **P availability** occur in all ranges of soil pH but can be very pronounced in **alkaline soils** (pH > 7.3) and in **acid soils** (pH < 5.5) (Figure 1). **Maximum availability** of phosphorus generally occurs in a **pH** range from **6.0 to 7.0** (Figure 1).

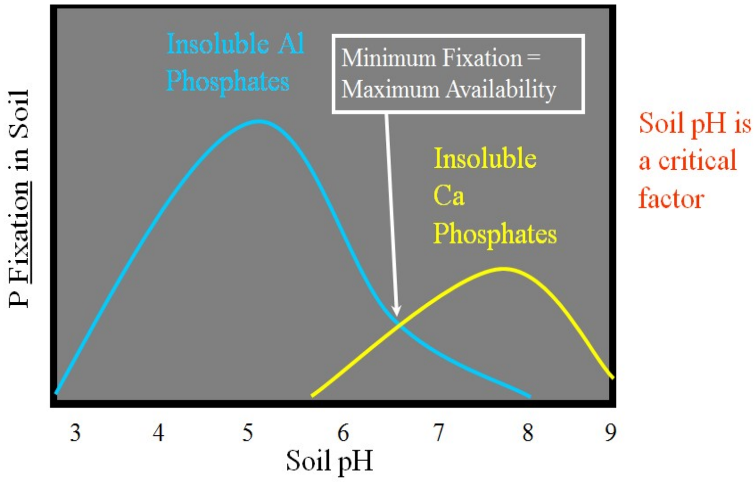


Figure 1. Behaviour of P at different soil pH values. P is only bioavailable at neutral pH.

Source of phosphorus for crops

Nowadays, **phosphorus** is mostly derived from **phosphate rock mining**. The **phosphate rock** were formed in continental **shelf marine** environments or in **igneous deposits** mostly in shield areas and rift zones.

Phosphate rock is converted to phosphoric acid. The majority of P fertilizer is produced by reaction of phosphate rock with acid (H_2SO_4, HNO_3) (Figure 6).

Main source of fertilizer P are:

-Apatite, ($Ca_{10}(PO_4)_6(OH)_2$), is also a component of teeth and bones, is dissolved in acid to make soluble fertilizer P:

$$\textbf{Apatite} + H_3PO_4 \rightarrow Ca(H_2PO_4)\bullet H_2O$$

-**Ammonium phosphate** is produced by reacting 1 mole ammonia with 1 mole of phosphoric acid:

$$NH_3 + H_3PO_4 \rightarrow NH_4H_2PO_4;$$

-Diammonium phosphate (DAP) is produced by reacting 2 moles ammonia with 1 mole of phosphoric acid:

$$2NH_3 + H_3PO_4 \rightarrow (NH_4)_2H_2PO_4$$

However, phosphorus from **phosphate rock mining** is limited and **non-renewable resource**. Due to this, phosphate fertilizers are going to be limited in future.

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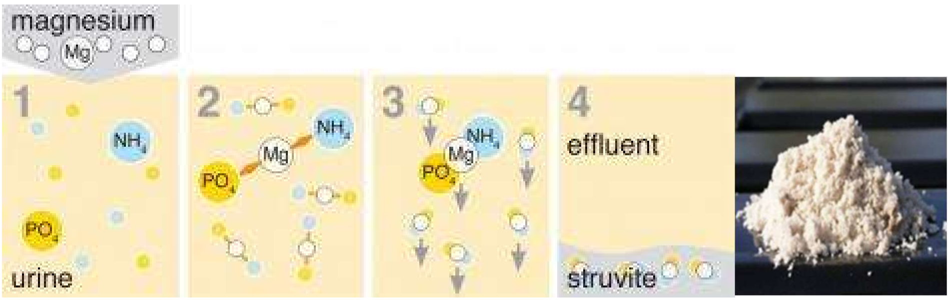
Are there other phosphorus source?

Wastewater treatment plants and **animal husbandry facilities** are the two most important sources of phosphorus. The release of wastewater into the environment without treatment causes pollution (eutrophication) of the effluent due to high amounts of phosphorus and nitrogen. For these reasons wastewater treatment plants (reactors) play an important role in removing and recovering nutrients (i.e. ammonia and phosphorus).

Phosphorus can be recovered from wastewater in crystal form of **magnesium ammonium phosphate** (MAP), also known as **struvite** (MgNH4PO4 6H2O) or a phosphate compound in the form of pellets. Struvite is also considered an environment-friendly fertilizer.

Struvite

Struvite ($MgNH_4PO_4 \cdot 6H_2O$) is a mineral obtained through a basic precipitation reaction of **ammonium**, **phosphate** and **magnesium** in a white powder (Figure below).



Production of struvite from urban wastewaters

Struvite has the following advantages for crops:

- **Bioavailable**: **N**, **P** and **Mg** in struvite can be readily absorbed by the plant.
- **Slow-release**: Due to its **low solubility** guarantees a slow but steady nutrient supply.
- **Highly pure**: pharmaceuticals which may be present in the urine, do not precipitate with the struvite.

Appendix 1 – Phosphorus in Agriculture

Learning Outcomes

By the end of the activity the students will be able to:

- make aware of the importance of Phosphorous (and for what P is important)
- make aware of recycling of P from wastewaters to reduce the exploitation of natural resources
- Know the pH effect on the P solubility and the P form in solution
- Know the sources of phosphorus

Key Competence European Framework

Literacy competence
S1. Ability to understand and interpret concepts, feelings, facts or opinions in oral and written form.
S2. Ability to express concepts, feelings, facts or opinion in written and oral form.
S4. Ability to interact in an appropriate and creative way in any situation.
Multilingual competence
S1. Ability to understand and interpret concepts, feelings, facts or opinions in oral and written
S2. Ability to express concepts, feelings, facts or opinion in oral and written form.
S4. Ability to interact in an appropriate and creative way in any situation.
S5. Knowledge of vocabulary, grammar and language.
S7. Ability to use technical language accordingly to the field of work.
Mathematical competence and competence in science, technology and engineering
S1. Ability to use constructed thinking in order to solve a problem in every situation.
S4. Readiness to address new problems from new areas.
S5. Capacity for quantitative thinking.
S6. Ability to extract qualitative information from quantitative data
S8. Ability to design experimental and observational studies and analyse data resulting from them.
S9. Ability to formulate complex problems of optimisation and decision making and to interpret the solutions in the original contexts of the problems
Digital competence
S1. Critical use of information technology for work
S2. Basic skills in ICT
S3. Understanding the role, opportunity and risks related to ICT in everyday life.
S4. Ability to use and handle technological tools and machines
Personal, social and learning to learn competence
S1. Ability to pursue and persist in different kinds of learning.
S2. Identifying available opportunities.
S3. Ability to gain process and assimilate new knowledge, skills and qualification required for career goals.
Citizen competence
S1. Ability to effective interaction with other people

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S2. Ability to adapt to the changing situation, being flexible and work under pressure
S3. Ability to work effectively and collaborate with other team members
Entrepreneurship competence
S1. Awareness of local, national, European culture heritage and their place in the world
S2. Basic knowledge of contemporary culture
S3. Understanding of cultural diversity
Cultural awareness and expression competence
S1. Ability to turn idea into action
S2. Creativity/innovation
S3. Ability to plan and manage tasks
S4. Independence, Motivation and Determination

United Nations' Sustainable Development Goals

The Sustainable Development Goals are the blueprint to achieve a better and more sustainable future for all. They address the global challenges we face, including those related to poverty, inequality, climate change, environmental degradation, peace and justice. *Goals linked to this activity:*

	1 No poverty, 2 Zero hunger: Enable access to basic services		10 Reduced inequalities: Equal access to global expertise
	3 Good health and well-being: Safe medical devices		11 Sustainable cities and communities: Sustainable urbanization
✓	4 Quality education: Access to education	✓	12 Responsible consumption and production: Responsible consumption and production
	5 Gender equality: Less hardship, more opportunities	✓	13 Climate action: Strengthen resilience, reduce disaster impact
✓	6 Clean water and sanitation: Safe and affordable water		14 Life below water: Reduce marine pollution
	7 Affordable and clean energy: Energy – the golden thread	✓	15 Life on land: Sustainable use of terrestrial ecosystems

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✓	8 DECENT WORK AND ECONOMIC GROWTH — Safety of workers and economic growth	✓	16 PEACE, JUSTICE AND STRONG INSTITUTIONS — Promote peaceful and inclusive societies
	9 INDUSTRY, INNOVATION AND INFRASTRUCTURE — Resilient infrastructure and sustainable industrialization	✓	17 PARTNERSHIPS FOR THE GOALS — Better access to technology and innovation

Contents – Theoretical principles

Urine is a constituent of urban wastewaters having a high content of phosphorus (P) and nitrogen (N) in ionic form ($H_2PO_4^-$, HPO_4^{2-}, PO_4^{3-} and NH_4^+, respectively). These elements arise from the decomposition of biological macromolecules (proteins, nucleic acids, phospholipids) of different origin. In appropriate chemical conditions, P and N react to form a mineral called **struvite**. Struvite is formed at alkaline pH and its precipitation is helped by Magnesium (Mg) addiction (see reaction below):

$$\mathbf{Mg^{2+}\,(aq) + NH_4^+\,(aq) + PO_4^{3-}\,(aq) + 6\,H_2O\,(l) \rightarrow NH_4MgPO_4\,(s).\,6\,H_2O + 2\,H^+}$$

pH adjusted to 8.0

Struvite is formed when $\mathbf{Mg^{2+}}$**,** $\mathbf{NH_4^+}$**,** $\mathbf{PO_4^{3-}}$ are present in **equimolar quantities** (1:1:1).

Appendix 1 – Phosphorus in Agriculture

Lab Procedure

Module 1 - Extraction of struvite

The aim of this experience is to obtain the **P recovery as struvite** extracted from synthetic wastewaters. Three reagents are needed to promote the struvite precipitation at alkaline pH: magnesium (Mg^{2+}), ammonium (NH_4^+) and phosphate (PO^{3-}). The struvite precipitates after about 3 hours in the form of white powder. The struvite yielded can be used to fertilize garden or potted plants. This experience will make pupils conscious of recycling wastewaters in order to reduce the exploitation of natural resources and, as a consequence, a remarkable benefit for the environment.

Module 2 – Reactor

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The aim of this experiment is to build in the laboratory a simple prototype reactor for the extraction of struvite from synthetic wastewaters and its functioning. The used materials should be available at a DIY store. The detailed experimental procedure, the list of the necessary materials, and the safety notes have to be inserted in a Module 2.

Learning Pathway

Step 1 (30 minutes)**:** Teachers introduce the topic and the laboratory experience from Module 1 with a PowerPoint presentation or prepared video.

Step 2 (60 minutes): 60 minutes: Students are divided in groups where each group is formed possibly by 3-4 students. Each team is responsible for completing the work assigned from Module 1 to realize the team's purpose.

Step 3 (15 minutes): Each group has to share with the others the results reached in each phase of the laboratory activity utilizing the video or the laboratory reports.

Step 4 (15 minutes): Teachers briefly give a PowerPoint presentation with the assembly scheme of each single part of the reactor from Module 2.

Step 5 (60 minutes): Students are divided into groups (preferably the number of students in one group is 3-4). Each group has to assemble the singular component of reactor from Module 2.

Evaluation

Write the different forms of P in solution

A: HPO_4^{2-}, $H_2PO_4^-$ and PO_4^{3-} ions are the P forms in the solution.

1. **What ions are involved in the struvite formation**

A: Magnesium (Mg^{2+}), ammonium (NH_4^+), and phosphate (HPO_4^{2-}, $H_2PO_4^-$ and PO_4^{3-}) ions.

2. **Why struvite is formed in the wastewater treatment process**

A: Wastewater contains high amount of ammonium (NH_4^+), phosphate (HPO_4^{2-}, H_2PO^{4-} and $PO_4^{3-)}$ ions and Magnesium (Mg^{2+}) derived from decomposition of microorganisms, macromolecules, detergents and chemicals , that interacting between them form a mineral called struvite.

3. **What is the difference between Organic-P and mineral –P**

A: Organic phosphorus is a product of animal and plant residues like inositol phosphates, nucleic acids and phospholipids. It is mineralized by microorganisms and

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transformed into mineral compounds such as orthophosphates. Mineral phosphorus is derived from sedimentary or igneous rocks.

4. Explain the pH effect on the P solubility?

A: Reactions that reduce P solubility occur in all ranges of pH but can be very pronounced in alkaline (pH > 7.3) and in acid (pH < 5.5) conditions depending also by the presence of some cations.

5. Explain the role of sodium hydroxide used during the lab experience

A: Sodium Hydroxide is used to modify the pH solution in order to reach the ideal pH to favour the struvite precipitation.

6. Which aspect does the precipitate take after the drying?

A: The struvite appears as a white solid.

8. Why is Mg important for phosphorus recovery?

A: Magnesium is a bivalent cation present in the wastewater that interact with phosphate (HPO_4^{2-}, $H_2PO_4^-$ and PO_4^{3-}) ions to form the **struvite.**

9. Why did we use a valve to block the direct passage of the solution through the filter?

A: The struvite precipitation takes several hours, so the solution has to be left in the reactor to complete the reaction.

Description of Student's Cards

Student's Card 1 – Extraction of Struvite

Student's Card 2 – Reactor for Struvite recovery from wastewaters

Sources

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