Lab Guide

Phosphate-Recovery

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Model sewage sludge

To avoid any work with original sewage sludge or original wastewater because of hygienic and safety reasons, it is suggested to use Model-Sewage-Sludge and Model-Waste-Water. The model substances should have a similar texture and the same properties as wastewater and sludge correspondingly relevant for the experiments on phosphate recovery.

Materials/Chemicals	**Equipment**
1 roll of toilet paper	2-L bucket
4-5 sheets of newsprint newspaper (optional)	immersion blender (kitchenware)
1-L hot water	water boiler
potassium dihydrogen phosphate-KDP	colander
(monopotassium phosphate-MKP)	oven
	baking tray

Procedure

Place the paper roll in the bucket, and add 1 L of hot water and let it soak for a while. Remove the inner cardboard roll. Take an immersion blender (kitchenware), and stir the toilet paper well. Then, filter out the pulp from the excess liquid by using a big colander, and put the pulp on a baking tray. Dry it in an oven at 105 °C (i.e., overnight). The pulp dried on the paper can be stored for a long time.

To prepare the model sludge to be used in the phosphate recovery experiments, mix 1 L of water, 1.43 g of potassium dihydrogen phosphate (C = 1g/L PO_4^{3-}) and 5 g dried model sludge. Shake or mix well until the solid particles are dispersed.

Model sewage sludge ash

For the safety reasons, and to avoid any work with original sewage sludge ash, „Model-Sludge-Ash“ is suggested to be used in the experiment. These so-called fly ashes can contain harmful lead, barium, antimony and arsenic compounds. The total P contents (on average) are 73 mg/kg dry weight (DW) in sludge ash, which corresponds to 220 mg/kg PO_4^{3-}. The model substances should have similar properties, appearance, and texture, that increase the success of the phosphate recovery experiments.

Materials/Chemicals	**Equipment**
potting soil (phosphate free)	beaker, 500-mL
water	colander or sieve
potassium dihydrogen phosphate	(for mesh size > 10 mm)
optional: zinc sulfate, iron sulfate, copper sulfate	stirrer

Procedure

A potting soil without phosphate fertilizer is used. Plant remains are removed, and the soil is sieved (mesh size > 10 mm, with a riddle or colander) for homogenization. It should be stored in a dry and dark place. (Optionally, soil contamination can be simulated by adding $ZnSO_4$ (300 g / kg DW), $FeSO_4$ (0.1 g / kg DW), and $CuSO_4$ (0.05 g / kg DW).)

10 g of soil are placed into a beaker for the LEACHPHOS process and suspended with 200 ml of potassium-dihydrogen-phosphate solution (c = 1.43 g / L) by stirring. This suspension can be used as starting solution for the LEACHPHOS process.

Preparing the stock solutions and test solutions

In order to obtain the highest possible concentration of PO_4^{3-} in the stock solution, the salts of disodium hydrogen phosphate and potassium dihydrogen phosphate (monopotassium phosphate) were selected because of their good water solubility.

Materials/Chemicals	**Equipment**
distilled water dry potassium dihydrogen phosphate (CAS 7778-77-0)	1-L volumetric flask stirrer bottles for storage

Procedure:

Fill 1 L of distilled water into a volumetric flask. Add the suitable amount of salt out of the table below for each solution. Stir until all the salt is dissolved.

Solution	**Used for**	**Amount of salt**	**Concentration (phosphate)**
1	MColortest™	0.00143 g	1 mg/L
2	MColortest™	0.00286 g	2 mg/L
3	MColortest™	0.00715 g	5 mg/L
4	MColortest™	0.01073 g	7.5 mg/L
5	All processes	1.43 g	1000 mg/L
6	Dilution	0.143 g	100 mg/L

In case the scales are not precise, solution 6 can be diluted.

Solution	**Used for**	**Amount of 6**	**Concentration (phosphate)**
1	MColortest™	100 µL	1 mg/L
2	MColortest™	250 µL	2 mg/L
3	MColortest™	500 µL	5 mg/L
4	MColortest™	750 µL	7.5 mg/L

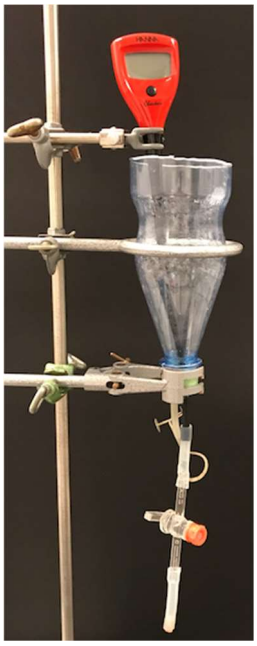
Storage:

The solutions can be stored in the dark; placing them in a fridge is also an option, but it is not necessary.

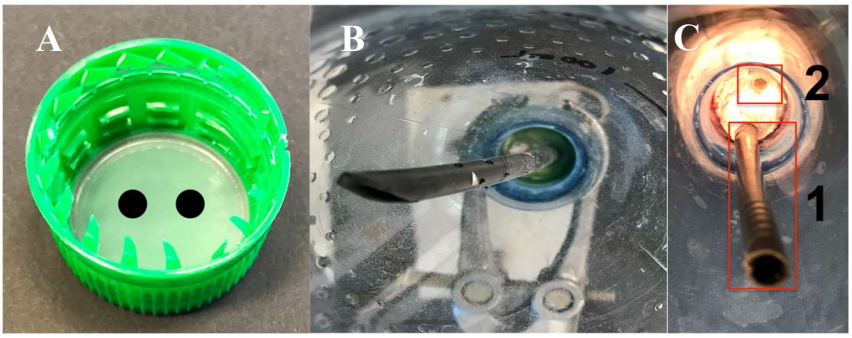
Building a “PEARL reactor”

For the following experiment, a PEARL reactor should be built. The following materials are needed:

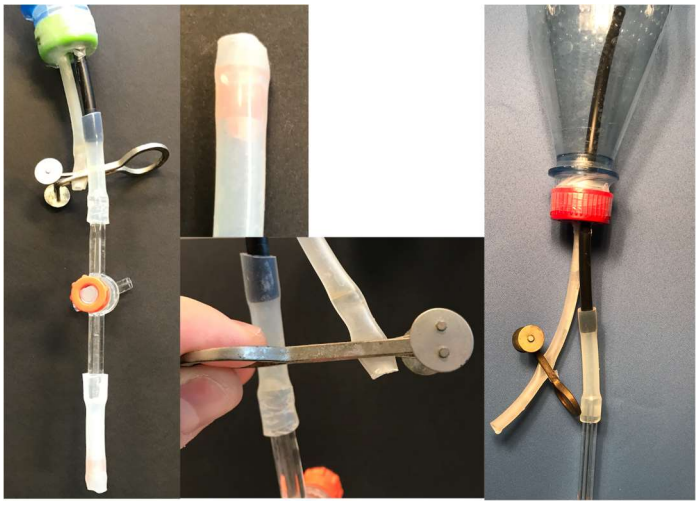
- lab-tripod and fixtures
- an empty water bottle (plastic, PET, quite stable) with a screw cap
- knife, needle, Bunsen burner or lighter
- parafilm
- hot-melt gun
- modeling clay
- 2-way stopcock
- cannula [only the female end is needed, cut the needle with scissors or hold with tongs]
- different flexible and inflexible tubes
- a clip something similar to squeeze or close the release tube. The complete reactor looks like the picture on the left.:



- Take the bottle and cut it in halves using a heated knife. We are using 1-L bottles of mineral water. It is important that they are stable (shown on the right).
- Take the screw cap and make two holes (black dots picture A) into the ground. They should fit the tube.
- Perforate the tube using a hot needle (picture B below). Push the perforated tube through one-hole on the screw cap until it is in about half of the height of the reactor (picture C number 1 below). This is the tube used for the injection of the chemicals. Push a second flexible tube through the second hole for getting chemicals out of the bottle (picture C number 2 below).
- Cap both using the hot-melt glue gun. To close the ends, modeling clay can also be utilized. It is important that they are waterproofed. Another option is to use parafilm after the screwing cap is tightened on the bottle.



- On the perforated tube, a second more flexible tube is added to connect the 2-way stopcock. Below the 2-way stopcock, another tube is added (see the picture on the left).
- At the end of this tube a cannula is added (only the female plastic end is needed; the injection needle should be removed!). The cannula helps the injection of the chemicals with a syringe.
- To control the release, a simple tube clip can be used. It is important that the device is waterproof. Waterproof feature should also be checked after a few days.



Colorimetric analysis of phosphate with MColortest™

Acidic ammonium molybdate solution		H315 H318 H335	P280 P301+P310 P302+P352 P305 P351 P310 P261 P304+P340;

Materials

Equipment

MColortest
The MColortest is delivered from **VWR Merck KGaA,** Darmstadt, Germany (Order-No.: 1.14846.0001; ca. 200 tests; costs €230,-).

4 2-mL pipettes

Chemicals

PO_4–1 solution (acidic ammonia-molybdato-solution, contains sulfuric acid) from MColortest™ kit

PO_4–2 (ascorbic acid powder) from MColortest™ kit
phosphate solutions 1-4 (1; 2.5 mg; 5; 7.5 mg PO_4^{3-}/L)
distilled water

For this measurement, the solutions 1,2,3,4 (see page 3) are needed.

Procedure

- Choose one of the test solutions (1-4).
- Fill six mL of the test solution in a glass vial with screw cap.
- Add five drops of reagent solution PO_4-1, seal the vial and shake well.
- Add one micro spatula of the second reagent PO_4-2 (ascorbic acid powder) into the sample and seal the vial again and shake it well for one minute until the powder is completely dissolved.
- The presence of phosphate becomes evident by a blue colored complex.
- Determine the phosphate content by comparing the colors with the color-disk comparator.
- Note the number and convert the measured phosphate content into the correspondent phosphate content.

Waste disposal: Due to the presence of molybdate, the blue solution has to be collected as heavy metal waste (inorganic).

Hints: The intensity of the blue complex depends on the concentration of phosphate in the solution. The more phosphate is present, the darker the blue color is. Optionally, one has to dilute the solution and test again. The MColortest is working in the concentration range between 0.2 – 3.0 mg/L phosphate.

Recovery process: ExtraPhos®

acidic ammonium molybdate solution		H315 H318 H335	P280 P301+P310 P302+P352 P305 P351 P310 P261 P304+P340;
carbon dioxide, CO_2		H280	P403
sodium hydroxide, 1 M NaOH		H315 H319 H290	P280 P301+P330+P331 P305+P351+P338 P308+P310
lime water, saturated, $Ca(OH)_2$		H315 H318 H335	P280 P301+P310 P302+P352 P305 P351 P310 P261 P304+P340
Calcium phosphate			

Materials:

Equipment

beakers (1x100 mL, 3x250 mL, 1x600 mL)
pH-meter, MColortest
SodaMaxx with bottle
funnel with folded filter/filter (in simple quality)
magnetic stirrer with a magnetic stir bar
graduated flask (100 mL)
several pipettes, spatula, tweezer, glass rod
optional: Büchner flask, filter, and water jet pump
beaker for disposal

Chemicals

lime water (saturated, clear) 50 ml
sodium hydroxide (1 mol/L)
carbon dioxide for the SodaMaxx
chemicals used for MColortest
model-waste-water, 1 L
phosphate solution (c = 1 g/L)
model-sewage-sludge, 5 g/L

Procedure

Leaching

- Shake the model-waste-water and fill 700 mL of the solution into a screw-top SodaMaxx bottle. It is important to ensure that the screw thread is dry and clean.
- Insert the bottle into the SodaMaxx.
- By pressing the upper button, CO_2 is pressed into the bottle (1 stroke every 10 seconds); after every 3-4 strokes, the bottle should be vented. To do this, press the small button at the top right of the SodaMaxx.
- To control the pH, always unscrew the bottle. The pH should be lowered to a value between 5 and 4.5.
- When the pH is 5 or lower (better 4.5), the bottle can be screwed.
- About 150 mL of this sewage sludge solution are needed for the next step.

Filtration

- Approx. 150 mL should be purified from all solids.
- One can choose a funnel with a filter or a vacuum source, Büchner flask with funnel and filter.
- 100 mL of the clear filtrate is needed for the next step.

Crystallization

- On a magnetic stirrer, 100 mL of the solid-free filtrate is stirred in a beaker (600 mL).

- The pH-value is constantly measured.
- Add approximately 0.5-1 mL NaOH (1 mol/L) until the pH reaches at least 7.
- Add lime water ($Ca(OH)_2$; about 9-12 mL) until a pH of 9 or greater is reached.
- If the solution turns cloudy, turn off the stirrer and wait until the crystalline white solid has settled.
- Filter the solution and obtain the product, $Ca_3(PO_4)_2$.

Quantification

- Using the MColortest, the phosphate content of the filtrate is measured. The solution must be diluted by 1:100 before the phosphate content is measured.
- The difference between the starting concentration (1000 mg PO_4^{3-}/L) and this measurement indicates the precipitated phosphate that has been successfully recovered.
- The difference is the yield of recovered $Ca_3(PO_4)_2$.

Waste disposal: The molybdate solution from the MColortest needs to be disposed of as heavy metal waste (inorganic).

Hints: All mentioned pH values are approximate. The pH values can be undercut in the acidic range and exceeded in the alkaline range. In our experience, recovery rates of 40-85% are expected. Note that only 1 g PO_4^{3-} is in one liter of our model-waste water solution.

Some impression:

SodaMaxx (very first generation with separate pressure release can be obtained via eBay)

Recovery process: Stuttgarter Process

acidic ammonium molybdate solution		H315 H318 H335	P280 P301+P310 P302+P352 P305 P351 P310 P261 P304+P340;
ammonium chloride		H314	P280 P301+P330+P331 P305+P351+P338 P309+P310
citric acid		H319	P305+P351+P338
sulfuric acid, 0,5 mol/L		H290	P280 P301+P330+P331 P305+P351+P338
sodium hydroxide, 1 M NaOH		H315 H319 H290	P280 P301+P330+P331 P305+P351+P338 P308+P310
struvite, MAP		H335	P264 P280 P261 P271 P302+P352 P332+P313 P305+P351+P338 P337+P313 P304

Material:

Equipment

beaker (2x600 mL, 1x100 mL)
pH-meter, MColortest
tweezers, spatula
stirring rod (glass)
pipettes (plastic, 3 mL)
magnetic stirrer & magnetic stir bar
graduated flask (100 mL)
funnel with folded filter/filter (simple quality)
optional: Büchner flask, filter, and water jet pump
beaker for disposal

Chemicals

sulfuric acid (0.5 mol/L)
citric acid (0.1 mol/L)
sodium hydroxide (1 mol/L)
precipitant 1: magnesium chloride (2.6g $MgCl_2$/100 mL)
precipitant 2: ammonium chloride (2.5g NH_4Cl/100 mL) + $(NH_4)H_2PO_4$ (0.66 mg/100 mL)
chemicals for the MColortest
model-waste water with phosphate content: c = 1 g PO_4/L
model-sewage-sludge, 5 g/L

Procedure

Leaching

- Take a sewage sludge solution with a phosphate concentration of c = 1000 mg/L that also contains approx. 0.5% solid.
- Shake the sewage sludge solution thoroughly and remove 150 ml of the mixture.
- Sulfuric acid (0.5 mol/L, approx. 2-3 mL) is added to the sewage sludge solution until a pH of 2.5 is reached.
- The solution is stirred with the glass rod for about 2 min.

Filtration

- The solution should be purified.
- Take a funnel with a filter, or a vacuum source, Büchner flask with funnel and filter.
- 100 mL of the clear filtrate are needed for the next step.

Crystallization

- 100 mL of the solid-free filtrate are stirred in a beaker using a magnetic stirrer.
- The pH value is constantly measured.

- For binding heavy metals, add 1 ml of citric acid (0.1 mol/L).
- To prepare the precipitation, add 2.5-5 mL of each of the precipitants (1 and 2).
- A pH greater than 10 is achieved by adding sodium hydroxide solution (1 mol/L, 0.5-1 mL), triggering the crystallization.
- If the solution turns cloudy, turn off the stirrer and wait until the crystalline white solid has settled.
- The product is struvite or MAP ($MgNH_4PO_4$).
- The product can be filtered.

Quantification

- Using the MColortest, the phosphate content of the filtrate is measured. The solution must be diluted by 1:100 before this measurement.
- The difference between the starting concentration (1000 mg PO_4^{3-}/L) and this measurement indicates the precipitated phosphate that has been successfully recovered.
- The difference is the yield of recovered $MgNH_4PO_4$.

Waste Disposal: The molybdate solution from the MColortest needs to be disposed of as heavy metal waste (inorganic).

Hints: All indicated pH values are approximate. The pH values can be undercut in the acidic range and exceeded in the alkaline range. In our experience, recovery rates of 40-85% are expected. Note that only 1 g PO_4^{3-} is in one liter of our model-waste water solution.

Recovery process: OSTARA'S PEARL®

Acidic ammonium molybdate solution		H315 H318 H335	P280 P301+P310 P302+P352 P305 P351 P310 P261 P304+P340;
Ammonium chloride		H314	P280 P301+P330+P331 P305+P351+P338 P309+P310
Sulfuric acid, 0,5 mol/L		H290	P280 P301+P330+P331 P305+P351+P338
Sodium hydroxide, 1 M NaOH		H315 H319 H290	P280 P301+P330+P331 P305+P351+P338 P308+P310
Struvite, MAP		H335	P264 P280 P261 P271 P302+P352 P332+P313 P305+P351+P338 P337+P313 P304

Materials

Equipment

beakers (2x600 mL, 1x100 mL)
pH-meter, MColortest
tweezers, spatula
stirring rod (glass)
reactor (plastic, see p.4)
serv. pipettes (plastic, 3 mL)
graduated flask (100 mL)
funnel with folded filter/filter (in simple quality)
optional: Büchner flask, filter, and water jet pump
beaker for disposal

Chemicals

sulfuric acid (0.5 mol/L)
citric acid (0,1 mol/L)
sodium hydroxide (1mol/L)
precipitant 1: magnesium chloride (2.6g $MgCl_2$/100 mL)
precipitant 2: ammonium chloride (2.5g NH_4Cl/100 mL)
+ $(NH_4)H_2PO_4$ (0.66 mg/100 mL)
chemicals for the MColortests
model-waste-water, 1 L,
PO_4-content: c = 1 g PO_4/L
model-sewage-sludge, 5 g/L (see p. 1&3)

Instruction

Leaching

- Sewage sludge solution is used with a phosphate concentration of c = 1000 mg/L and contains approx. 0.5% solid.
- Shake the sewage sludge solution thoroughly and remove approx. 350 mL of the mixture.
- Sulfuric acid (0.5 mol/L, approx. 2-3 mL) is added to the sewage sludge solution until a pH of 2.5 is reached.
- It should be stirred with the glass rod about 2 min.

Filtration

- Approx. 300 mL should be purified.
- You can use a funnel with a filter or a vacuum source, Büchner flask with funnel and filter.
- 250 mL of clear filtrate are needed in the next step.

Crystallization

- Increase the pH in the solid-free filtrate to approx. 10.5 by adding sodium hydroxide solution (1 M, approx. 2-3 mL).

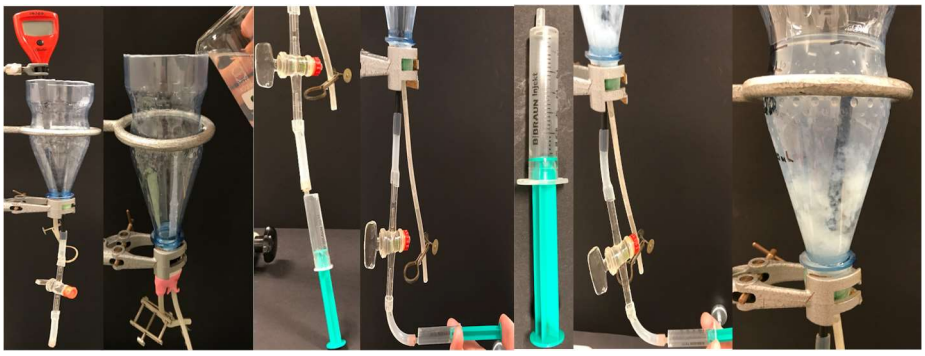
- Fill the solid-free filtrate into the plastic reactor; the reactor has a metering unit with a 2-way stop tap and outlet at the bottom.
- Fill a syringe with each 5 mL of precipitant 1 and 2. Place the first syringe on the dosing unit from below and open the tap and inject precipitant solution 1 into the reactor (from below). Close the tap and repeat the procedure with the syringe with precipitant 2. To clear the pipes, this should also be repeated once with a syringe filled with air.
- The solution becomes cloudy, which indicates the production of struvite (MAP, $MgNH_4PO_4$)).
- Place a funnel with filter paper in a beaker and drain the product through the outlet at the bottom of the dosing unit.

Quantification

- Using the MColortest, the phosphate content of the filtrate is measured. The solution must be diluted by 1:100 before this measurement.
- The difference between the starting concentration (1000 mg PO_4^{3-}/L) and this measurement indicates the precipitated phosphate that has been successfully recovered.
- The difference is the yield of the recovered $MgNH_4PO_4$.

Waste Disposal: The molybdate solution from the MColortest needs to be disposed of as heavy metal waste (inorganic).

Hints: All indicated pH values are approximate. The pH values can be undercut in the acidic range and exceeded in the alkaline range. In our experience, recovery rates of 40-85% are expected. Note that only 1g is in one liter of our model-waste water solution.



Recovery Process: LEACHPHOS©

Acidic ammonium molybdate solution		H315 H318 H335	P280 P301+P310 P302+P352 P305 P351 P310 P261 P304+P340;
Limewater, saturated, $Ca(OH)_2$		H315 H318 H335	P280 P301+P310 P302+P352 P305 P351 P310 P261 P304+P340
Sulfuric acid, 2 mol/L		H290	P280 P301+P330+P331 P305+P351+P338
Sodium hydroxide, 1 M NaOH		H315 H319 H290	P280 P301+P330+P331 P305+P351+P338 P308+P310
Calcium phosphate			

Material

Equipment

beakers (3x400 mL)
magnetic stirrer with a magnetic stir bar
serv. pipettes (plastic, 3 mL)
funnel with folded filter/filter
suction filter and water jet pump
tweezers, big spoon
stirring rod (glass)
measuring cylinder (100 mL)
graduated flask (100 mL)
balance, pH-meter
MColortest

Chemicals

model sewage sludge ash (10 g)
a stock solution I (c =1g PO_4/L; for preparation see p. 2&3)
sulfuric acid (2 mol/L)
lime water (saturated, clear) 50 mL
sodium hydroxide (1 mol/L)
chemicals for the MColortest

Procedure

Leaching

- Start with a sewage sludge ash solution (about 200 mL) containing c= 1000 mg/L phosphate.
- Place the beaker on the magnetic stirrer and add the stir bar.
- Slowly stir and add sulfuric acid (2 M, approx. 3-5 mL) to set a pH of 2.5 or lower.

Filtration

- The mixture is filtered, and the filtrate is collected in a clean beaker. The filtrate must be clear and free of any suspended matter.
- 100 mL are needed to go further.
- Using the MColortest, the phosphate content of the filtrate is measured. The solution must be diluted by 1:100 before the measurement.

Crystallization

- On the magnetic stirrer, 100 mL of the solid-free filtrate is stirred in a large beaker.
- The pH-value is constantly measured.
- Add approximately 0.5-1 mL NaOH (1 mol/L) until the pH reaches at least 7.
- Add limewater, $Ca(OH)_2$ (about 9-12 mL), until a pH greater than 9 is reached.

- If the solution becomes cloudy, turn off the stirrer and wait until the crystalline white solid has settled.
- The product is $Ca_3(PO_4)_2$, and it can be filtered now.

Quantification

- Using the MColortest, the phosphate content of the filtrate is measured. The solution must be diluted by 1:100 before this measurement.
- The difference between the starting concentration (1000 mg PO_4^{3-}/L) and this measurement indicates the precipitated phosphate that has been successfully recovered.
- The difference is the yield of the recovered $Ca_3(PO_4)_2$.

Waste disposal: The molybdate solution from the MColortest needs to be disposed of as heavy metal waste (inorganic).

Hints: All indicated pH values are approximate. The pH values can be undercut in the acidic range and exceeded in the alkaline range. In our experience, recovery rates of 40-85% are expected. Note that only 1g is in one liter of our model-sewage sludge ash slurry.
The acidic solution of the phosphate from the sewage sludge ash does not produce the expected yields. Nearly, 50 % of the total phosphate yield will remain in the ash. However, final precipitation of the dissolved phosphate in the filtrate is almost complete.

Some impressions: