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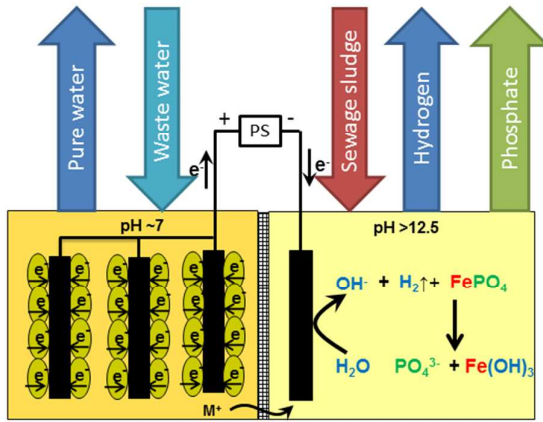
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Graphical abstract



Microbial electrolysis cell accelerates phosphate remobilisation from iron phosphate contained in sewage sludge

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Phosphate was remobilised from iron phosphate contained in digested sewage sludge with a bio-electric cell. A significant acceleration above former results was caused by strongly basic catholytes. For these experiments a dual chambered microbial electrolysis cell with a small cathode (40 mL) and a 80 times larger anode (2.5 L) was equipped with a platinum sputtered reticulated vitreous carbon cathode. Various applied voltages (0.2- 6.0 V) generated moderate to strongly basic catholytes using artificial waste water with pH close to neutral. Phosphate from iron phosphate contained in digested sewage sludge was remobilized most effectively at pH ~13 with up to 95 %. Beside minor electrochemical reduction, hydroxyl substitution was the dominating remobilisation mechanism. Particle-fluid kinetics using “shrinking core” model allowed to determine the reaction controlling step. Reaction rates changed with temperature (15-40°C) and an activation energy of $E_a = 55$ kJ/mol was found. These analyses indicated chemical and physical reaction control, which is of interest for future scale-up work. Phosphate remobilisation rates increased significantly, yields doubled and recovered PO_4^{3-} concentrations increased four times using a task specific bio-electric system. The result is a sustainable process for decentralized phosphate mining and a green chemical base generator useful also for many other sustainable processing needs.

Environmental Impact

Phosphate extraction from daylight mines will peak in 2030 and then decline in the following 50 years to a much lower level. Phosphate contained in waste is probably the most important concentrated phosphate source in the future. Since recently microbial fuel cells are proposed for phosphate recycling as they combine conceptually well with waste water treatment and nutriment extraction. In microbial fuel cells and other bioelectric systems Na^+ , K^+ and other cations migrate from the anode to the cathode. This cation migration allows sustainable chemical base generation, which remobilizes phosphate from insoluble iron-phosphate comprised in digested sewage sludge. This approach is also useful for other industrial processes where chemical base is needed. The integration of this bio-electric system in waste water treatment plants is proposed to mine phosphorous with energy and chemicals contained in waste water.

INTRODUCTION

Low cost phosphorous mining enabled large scale phosphate use in industry and food production over the last hundred years. In the second half of the 19th century, lakes, rivers and sea shores eutrophated due to increasing phosphate use¹. Since then, legislation enforces phosphate removal from waste water. For this end, iron chloride (FeCl_3) is applied as efficient ortho-phosphate removal reagent². In state of the art waste water treatment plants, more than 93% of phosphate is precipitated as insoluble iron phosphate (FePO_4). No other method is considered more convenient and efficient to use in small to large scale waste water treatment plants³. The resulting FePO_4 precipitate is a significant constituent of digested sewage sludge (2-3% elemental phosphorous). Unfortunately, sewage sludge contains toxic metals and other contaminants and therefore a direct use as fertilizer is forbidden in agricultural production, nor is it appreciated by food industry⁴. In consequence digested sewage sludge is incinerated and ashes deposited in landfills⁵.

It is an unpleasant truth that phosphate will deplete in 50-80 years and its availability from daylight mines will peak in ~2030⁶. As a consequence of reduced phosphate availability, agricultural production risks to decline, hunger to rise and the world population to shrink. Resource shortage effects are non-linear and were predicted by Hardin as “The tragedy of the commons”⁷. A way to counteract the looming phosphate shortage is to develop efficient recycling or other extraction processes⁸.

Phosphorus is an abundant element in the earth’s crust but highly dispersed in minerals⁹. Current phosphate use in agriculture, households and industry leads to a total loss to the environment. Once washed away into river, lake and sea sediments, phosphate enters a geological cycle for millions of years. Thus, today’s mined phosphate is magmatic apatit¹⁰, phosphorit sediments¹¹, and from more recent organogenic guano deposits of sea birds¹² and bats¹³. Guano accumulation is faster than the geological cycle, but still takes thousands of years to form relevant deposits. A much faster phosphate accumulation system is human iron phosphate production from waste water treatment including related processes. This technology is a starting point for sustainable phosphate recycling as proposed in this paper.

There are 30 methods to recover phosphate from digested sewage sludge and its ashes³. None of these methods ensure economic plant operation. Current phosphate prices are low. In addition, increasing phosphorus recycling in industrial countries will keep prices steady at current levels, but, will rise at some point rapidly¹⁴. An idea how briskly prices double was experienced in 2008 due to uncertainties in financial markets¹⁵. High fertilizer prices are problematic for sustainable food production. Therefore, recycling systems need to be low-cost to ensure food production at an affordable price. A smooth transition from today’s phosphate rock mining to tomorrows recycling regime is a great challenge.

An emerging phosphorous recycling method is based on microbial fuel cell (MFC) technology using microbial power and chemicals contained in municipal waste water. Bio-electrical systems are an ideal technology to become integrated in waste water treatment plants¹⁶. In preceding work, microbial fuel cell (MFC) power enabled phosphate extraction from digested sewage sludge in up to 82% or 600 mg/L¹⁷. The remobilized phosphate can be transformed into different fertilizers such as superphosphate, triple superphosphate, ammonium phosphate and less traded struvite¹⁸. The MFC approach was also investigated

using swine manure in a single chambered MFC, where phosphate was deposited as struvite in vicinity to an air cathode¹⁹. Microbial electrolysis cell conditions equally caused struvite deposition on hydrogen releasing cathodes²⁰. Also combined nitrogen and phosphate recovery was reported using microbial fuel cell power²¹. There are also non-bioelectric processes such as electrodynamic recovery from packed beds²² and electrochemical phosphate isolation from nanofiltration concentrates²³.

The microbial fuel cell enabled phosphate remobilisation from insoluble FePO_4 is potentially quantitative but slow. To improve reaction rates, an understanding of the remobilisation mechanism is a base to scale-up the process. Earlier results showed that electrochemical reduction occurred under microbial fuel cell conditions, as iron content increased in iron-phosphate particles¹⁷. Another observation concerned a pH increase up to ~ 9 in the abiotic cathode using dual a chambered microbial fuel cell. This is based on the fact that iron and oxygen are reduced in the cathode and a base (OH^-) is formed, which stays there because alkali cations M^{n+} migrate into the cathode. Therefore, a basic iron-phosphate substitution mechanism is a second reaction mechanism.

In this work a supplemental voltage is applied to a dual chambered microbial fuel cell to improve phosphate remobilisation rates (Fig. 1). This transforms the MFC into a microbial electrolysis cell. Particle-fluid kinetics is elaborated to identify the reaction resistance in the phosphate remobilisation process.

Here Fig. 1

EXPERIMENTAL

Material

Escherichia coli K12 DSM 498 was obtained from the “Deutsche Sammlung für Mikroorganismen und Zellkulturen” (DSMZ) [Braunschweig, Germany]. Yeast extract was from Lonza Ltd. [Visp, Switzerland], and enzymatic hydrolysate of soybean meal was purchased from Becton Dickinson AG [Allschwil, Switzerland]. KH_2PO_4 , NaHCO_3 , NaH_2PO_4 , Na_2HPO_4 and glucose were Sigma-Aldrich products [Buchs, Switzerland]. Methylene Blue was from Fluka [Buchs, Switzerland]. Potassium hexacyanoferrat, $\text{K}_3\text{Fe}(\text{CN})_6$

was obtained from Acros Organics [Geel, Belgium]. Ferric phosphate hydrate $\text{FePO}_4 \cdot \text{H}_2\text{O}$ as reference compound was a Riedel-de-Haen product [Seelze, Germany]. Nafion™ proton exchange membranes (PEM) and carbon felt electrodes were from NCBE [Reading, United Kingdom]. Reticulated vitreous carbon foam (RVC), 3% density and 100 ppi, was purchased from ERG aerospace corporation [Emeryville, CA, USA]. Digested sewage sludge was from the waste water treatment plant “Châteauneuf” of the city of Sion Switzerland.

Microbial fuel/electrolysis cell construction

The dual chambered bio-electric cell was constructed to serve as microbial fuel cell as well as microbial electrolysis cell. It consisted of a 2.5 L anode and a 40 mL remobilisation cathode made from polyvinylchloride (PVC)¹⁷ (An important size difference between anode and cathode is strongly recommended). The remobilisation cathode was separated by a Nafion™ proton exchange membrane from the anode. The anode was made from six carbon fibre tissue electrodes of 1150 mm². The cathode contained an electrode made from platinum sputtered reticulated vitreous carbon 25x30x5 mm and was equipped with a mechanical stirrer 60 rpm. The top of the cathode cavity contained a small opening for hydrogen exhaust, liquid handling and sludge particle insertion.

Anodic cultivation

A artificial waste water was made from *Escherichia coli* K12, which was pre-cultivated in medium consisting of 1% yeast extract, 1% enzymatic soybean hydrolysate and 2% D-glucose. Overnight, the mixture was incubated in a 300 ml flask at 30°C and 180 rpm and 50 mL added to the MFC anode. The cultivation medium in the anode contained 5 g/l yeast extract, 8.2 g/l KH_2PO_4 , 10 g/l NaHCO_3 , 20 g/l glucose and 0.2 mM Methylene Blue²⁴. The microbial growth and readiness to provide power was monitored by an integrated MFC-sensor²⁵. The process was started when the electromotive force of this sensor reached 0.7-0.9 V. The anodic cultivation was not protected from contamination and biofilms and

reused repeatedly. To verify results and trends closely, new cultivations with new anodes were employed. In these cases, the anode chamber was cleaned with anti-microbial solution and ethanol and the cultivation medium was sterilized at 120°C.

Generation of basic catholytes

In the MEC cathode with platinized RVC electrode, 30 mL demineralized water was added, and a power supply Voltcraft output 0-30V / 0-2.5A connected between anode and cathode. Current flux was calculated from potentiometric data recorded by a multi metre over an 11Ω resistance. Various applied voltages between 0.2 to 6.0V generated basic solutions reaching high pH values within 24 hours.

Sewage sludge particles

Dewatered digested sewage sludge was lyophilised and milled with a Zentrifugenmühle (Retsch) equipped with a 80 µm sieve. Before milling the dry sewage sludge was cooled with liquid nitrogen to prevent overheating in the mill. Obtained particles were analysed with a Mastersizer 2000 from Malvern Instruments [Worcestershire, England] and elemental composition analysed by a Varian 720-ES ICP-Optical Emission Spectrometer.

Phosphate remobilisation from FePO₄ comprised in sewage sludge

Once the pH of the catholyte reached a steady value, 0.2 - 1.2 g of dried sewage sludge particles (23 µm) were added to the cathode (30 mL). The resulting suspension was mechanically stirred at 60 rpm throughout the remobilization process. In defined intervals (one to 24 hours) 1.5 mL catholyte samples were centrifuged at 10'000 g for 20 minutes at 20 °C (HighCen Zentrifuge Hettich). Then the supernatant solution was decanted off and analysed for phosphor and iron content by ICP-OES.

Kinetics analysis

A semi-artificial reaction system was analysed outside of the microbial electrolysis cell as a well controllable setup. The basic catholyte was replaced by 0.05 M NaOH solution and adjusted to pH 12.6 by hydrochloric acid. 30 mL of the artificial catholyte was added into a 100 mL flask, covered and stirred at 100 rpm at room temperature (24°C) and atmospheric pressure. 0.2 g dry sewage sludge particles were added and samples of 1.5 mL taken in defined intervals and centrifuged at 9300 rpm at 20°C/30 min. The same procedure was applied at 15°C and 40°C to determine the activation energy E_a . Also the pH was varied between 12 and 13 by adapting the method. All experiments were realized in triplicate.

Elemental analysis of catholytes

ICP-OES spectroscopy was used to determine phosphorus and iron content. The supernatant cathode solutions were diluted with 2% HNO₃, for phosphorus 10 times, and iron dosage 100 times, respectively. Also catholytes containing Na⁺, K⁺, Ca²⁺ and others were analysed with this method.

RESULTS AND DISCUSSION

Phosphate remobilisation

Strongly basic abiotic catholytes accelerated phosphate remobilisation from sewage sludge significantly above the state of the art¹⁷ (Table 1, entry 24 and 25). Sludge particles were added into the cathode and a voltage applied, however, foam formation rendered this approach irreproducible with given cathode architecture. Therefore, a step by step protocol was developed. In this improved process, the cathode was turned basic first, and then digested sewage sludge particles (23µm) were added for the remobilisation step. Good to highest remobilisations yields (95%) (Table 1, Entry 22) resulted from strong basic catholytes (pH >12.3). The high reaction rate was verified by using pure FePO₄ as model system, yielding 85% in just one hour (Table 1, entry 20). In comparison to former microbial fuel cell conditions¹⁷, the reaction rate increased significantly and yields doubled.

The basic abiotic catholyte was a none buffered system and remobilisation rates depended on the quantity of added FePO_4 particles (Table 1). Therefore, the power supply was not switched off during the remobilisation process to compensate an eventual pH drop and to use electrical reduction of Fe^{3+} as second mechanism (Table 3). The solubility product of FePO_4 is $K_s = 1.3 \times 10^{-22}$ and as such low and the reason that phosphate can be removed from waste water²⁶. The presence of specific ortho-phosphate forms (H_3PO_4 , H_2PO_4^- , HPO_4^{2-} and PO_4^{3-}) in contrast depends also on the protonation stage and shows that pH needs to be controlled²⁷. In applied strong basic conditions, the remobilised phosphate was entirely deprotonated and a high pH needed to avoid precipitation with iron to ensure solubility. Basicity and remobilisation rates correlated closely as shown by changing the pH gradually between 12 and 13. A pH of at least >12.3 was needed to enter into an effective remobilisation regime. From graphical interpretation, the effective pH was around 12.8 (Fig. 2B). A secondary product was $\text{Fe}(\text{OH})_3$, whose solubility product²⁸ $K_s = 6.3 \times 10^{-38}$ is rather low and enabled a separation of the iron cations from supernatant phosphate solutions (0.5-3%).

The best recovery with 95% was registered after 1 hour and is superior to microbial fuel cell conditions where 82.3% were obtained in 21 days¹⁷. This represents a significant acceleration of the process. Beside enhanced remobilisation rates, also PO_4^{3-} concentrations increased from 600mg/L to 2.23 g/L. The preparation of basic catholytes required in general 24 hours and therefore the acceleration of the whole process including preparation corresponded to a time gain of a factor 20. All in all, the here developed second generation phosphate remobilisation process was much faster than under pure microbial fuel cell conditions and became quantitative.

Here Table 1

Here Fig. 2

Microbial electrolysis to generate a strong base

Microbial electrolysis turned abiotic catholytes strongly basic using a platinized reticulated vitreous carbon (RVC) cathode. A final pH of 10 was possible by only 0.2 V of applied voltage, what corresponds to microbial electrolysis conditions just above the threshold voltage of 0.12 V²⁹. To increase the basicity

further up to pH 11, an applied voltage of 1.0 V was needed. Next higher pH values of 12 and 13 were achieved with applied voltages between 3.0-5.0 V (Fig. 2A). Cation (M^{n+}) migration into cathodes with bioelectric systems is widely observed and increases the pH in the cathode. This is a major problem to scale-up microbial fuel cells for current production³⁰. Conversely, in the here investigated phosphate remobilisation this unwanted cation migration is an advantage and accelerated green chemical base formation strongly³¹ (Figure 1). In a dual chambered microbial electrolysis cell the electron flux into the cathode is ideally accompanied by an equal quantity of protons that migrate through the proton exchange membrane and then combine on a catalytic surface to hydrogen. However, proton supply was highly insufficient, as good quantities of Na^+ , K^+ and Ca^{2+} cations migrated at their place into the cathode according to ICP-OES analysis. As aforementioned, the alkali cation migration was significant as bio-anodic protons were buffered at neutral pH in the cultivation medium. Sodium cations migrated faster than larger calcium or potassium ions (Fig. 3). An electron transfer efficiency analysis showed that 20-80% of alkali cations migrated per delivered electrons, and the registered loss was presumably proton migration and also hydroxide crossover from the cathode into the anode compartment. It has to be mentioned at this point in terms of repeatability that the used microbial fuel cell was strongly asymmetric. The abiotic cathode was 80 times smaller than the bio-anode. This batch type base generator is an alternative to adjust anode and cathode fluxes³¹. The results show that an important industrial chemical base can be produced in a sustainable manner employing a bio-electric batch reactor.

Here Fig. 3

Fluid-particle kinetics in phosphate remobilisation

The non-biological phosphate remobilisation followed fluid-particle kinetics and a theoretical model was searched to find the rate determining step. The microbial electrolysis cell based remobilisation was fast and quantitative, that allowed to design a semi-artificial kinetic experiment. The phosphate remobilisation from sewage sludge particles was adjusted to a 24 hour experiment with close to quantitative $FePO_4$ conversion. A ~0.05 M NaOH solution replaced the catholyte and was set to a pH of 12.6 and 6.67 g/L digested sewage sludge particles were added. Three fluid-particle kinetic models were considered: diffusion through an

ash/sludge layer, diffusion through a liquid film, and chemical reaction control³² (Fig. 4A). Instead of ash as the model theory suggests, here sewage sludge particles were used. They were considered to be a reasonable match to compare the semi-artificial process and identify the reaction resistance in phosphate remobilisation. The base (OH^-) was thought to enter the sewage sludge matrix and to substitute FePO_4 and release ortho-phosphate. The resistance of the reaction was found to be the phosphate substitution and the solid FePO_4 core shrank toward zero over time. The release of ortho-phosphate from the particle was well possible at 12.6 pH. The side product $\text{Fe}(\text{OH})_3$ precipitated most likely in the particle due to its low solubility²⁸ $K_s = 6.3 \times 10^{-38}$. A comparison of the experimental results with the aforementioned models showed a mix of chemical and physical reaction control (Fig. 4B). The degree of chemical reaction control was verified by determining the activation energy $E_a = 55$ kJ/mol using the Arrhenius equation and assuming first order reaction kinetics to calculate reaction constants k_{obs} (Table 3). The activation energy was above a purely diffusion controlled process where an $E_a = 8-25$ kJ/mol is expected, but below an entire chemical reaction control because the activation energy was below 80 kJ/mol. Therefore, physical and chemical reaction control was involved. The physical control increased with time as visible in Fig. 4B. Beside the kinetic particle fluid analysis, the pH was of great importance and changes between 12 and 13 influenced reaction rates very much (Fig. 2B). And in this respect the remobilisation was controlled in first place by the pH and then other factors, such as diffusion and temperature influenced the reaction rate. All in all, the kinetic analysis allowed to determine important reaction parameters and facilitated the following mechanistic discussion.

Here Fig. 4

Here Table 2

Remobilisation mechanisms

An unresolved question in former phosphate remobilisation work using a microbial fuel cell was the reaction mechanism (Table 3). Electrochemical reduction was proposed from qualitative analysis but also a substitution mechanism was not excluded. The hypothesis was that electrochemical reduction of FePO_4

liberates ortho-phosphate in a slow reaction¹⁷ and a vivianite type compound was formed. But it remained unclear why yields varied. Using pure $\text{FePO}_4 \cdot \text{H}_2\text{O}$ particles ($\sim 11 \mu\text{m}$) in a model remobilisation indicated iron accumulation in particles by electron reduction. The alternative substitution mechanism works because OH^- is present that originates from iron and oxygen reduction in the cathode. A pH increase up to 9 was observed with MFC conditions (*Process B*, Table 3) and assumed to be high enough that a slow substitution mechanism competes with the equally slow reduction mechanism that is expected under pure microbial fuel cells conditions (*Process A*)³³. Hydroxyl anions substituted iron phosphate and ortho-phosphate was liberated into the supernatant solution while the side product $\text{Fe}(\text{OH})_3$ precipitated (*Processes B and C*, Table 3). This substitution mechanism removes iron and possibly also toxic cations from reaction mixtures, what is a welcomed purification effect. Alternatively, cations could be galvanized on the cathode. The substitution mechanism was confirmed by using plain chemical base (NaOH) that equally remobilised phosphate and this under none-reductive conditions (Table 1, entry 23)³⁴. The base propelled mechanism is therefore also possible under microbial fuel cell conditions (*Process A*, Table 3) with moderate basic catholytes (pH ~ 9)¹⁷. In other terms, a higher pH increases the solubility of FePO_4 and the substitution rate. The lowest solubility of FePO_4 is around pH 5.5 and is one of the reasons why FeCl_3 and similar reagents are applied to remove phosphate from waste water³⁵.

From above observations basic and electrochemical reduction mechanisms are possible. The electron reduction process is very much limited by low electron density that is difficult to enhance. Conversely, high base concentrations are more easily to establish. In present investigations, the working potential was increased by a power supply initially from 0.3 to 0.5 V. It was assumed that also the electron reduction process would increase electron density and enhance reduction rates; however, higher voltage caused hydrogen formation. This effect was facilitated by using platinised RVC electrodes. It is noteworthy that microbial electrolysis starts at low 0.13 V of applied voltage using Platin cathodes²⁹. Hydrogen formation caused a substantial pH increase in the catholyte as OH^- was formed. The pH increased up to 10 applying 0.2 V of applied voltage only. The basic remobilisation mechanism was then used extensively by producing strong bases at elevated voltages. All in all, there are two remobilisation mechanisms that should be used -if possible combined - to achieve efficient phosphate remobilisation.

Here Table 3

CONCLUSIONS

Quantitative abiotic phosphate remobilisation from iron phosphate was significantly faster using a microbial electrolysis cell than under microbial fuel cell conditions. Applied voltages between 0.2 and 6.0 V generated strong chemical base in a sustainable manner. The application of the base in the remobilisation of orthophosphate from iron phosphate comprised in abiotic digested sewage sludge was optimized to become fast and quantitative.

Five processes were involved in phosphate remobilisation: electron supply by microbes, hydrogen evolution, cation migration, phosphate substitution, and iron precipitation. The focus was set on the phosphate substitution reaction in the abiotic cathode. The substitution was accelerated as much as possible by increasing the pH in the non-biologic catholyte, while the pH in the bio-anode remained unchanged. The base in the cathode was either a result of oxygen intake from air or more efficiently produced by microbial electrolysis. Fluid-particle kinetics showed that the remobilisation was chemically and physically controlled, but dominated by the pH as the solubility products of FePO_4 , PO_4^{3-} and Fe(OH)_3 need to be considered too. The kinetics was also influenced by temperature variation. The related activation energy was 55 kJ/mol, and both analyses confirmed a mix of chemical and physical reaction control. The here reported novel extraction approach enhanced phosphate remobilisation rates significantly, yields doubled and obtained free PO_4^{3-} concentrations quadrupled. In addition, the remobilisation process is thought as an add-on procedure for waste water treatment plants where phosphate is removed with iron chloride or related reagents. In conclusion, four products result from investigated bio-electric system: phosphate, hydrogen, a green chemical base, and certainly purified water.

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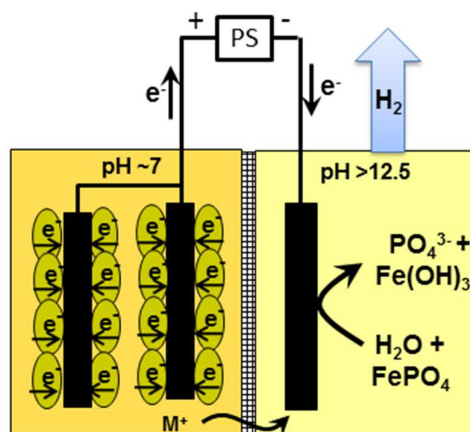


Fig. 1: Microbial electrolysis conditions (*Process C*) caused hydrogen evolution in the abiotic cathode and the formation of a strong chemical base (OH^-), which substituted insoluble iron phosphate (FePO_4) and liberated ortho-phosphate (PO_4^{3-}). The pH in bio-anode was buffered and remained neutral.

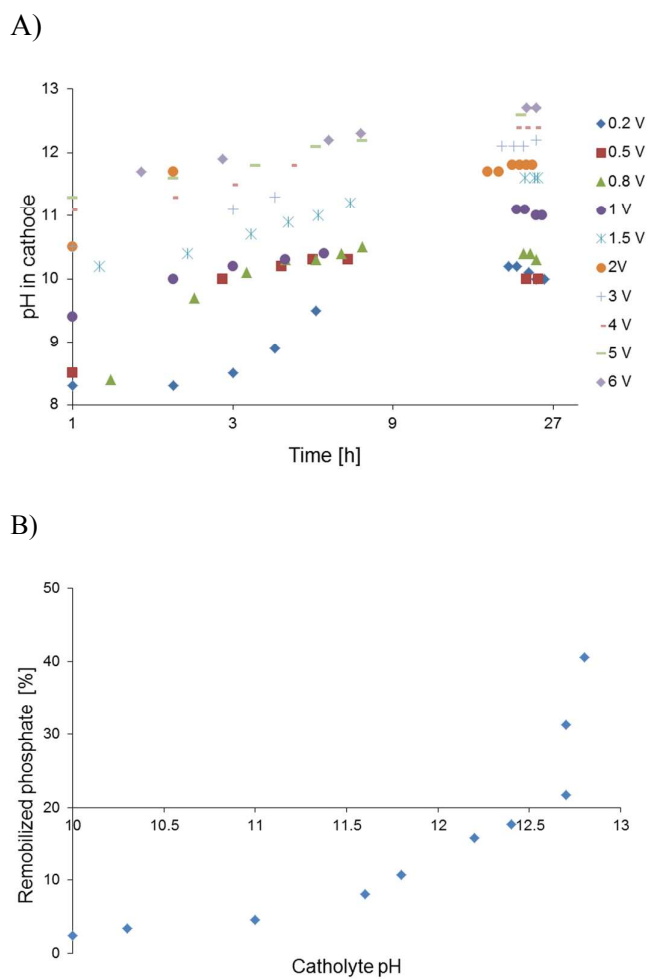


Fig. 2: A) pH evolution in 24 hours by microbial electrolysis in function of applied voltages.

B) pH and phosphate remobilisation efficiency from iron phosphate in digested sewage sludge after one hour at ambient temperature.

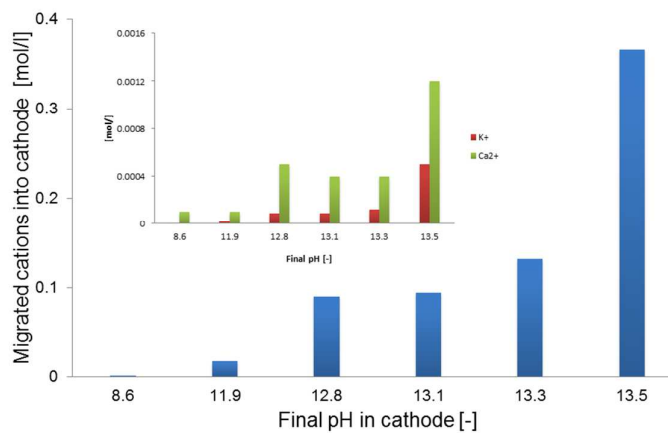
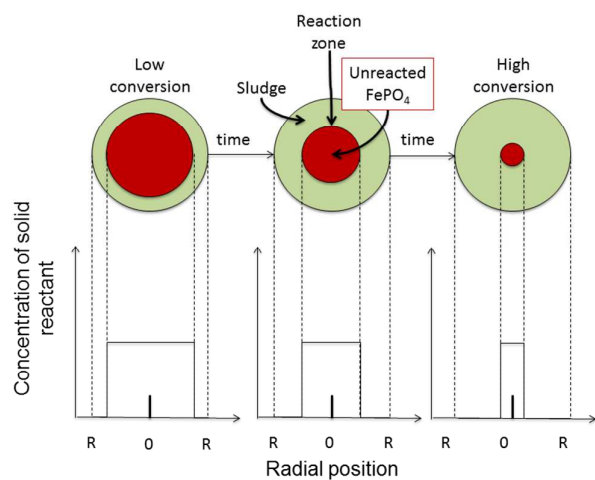


Fig. 3: Migrated Na⁺ cations (blue) from the bioanode into the abiotic catholyte in correlation to achieved pH values.

The small inserted figure shows final K⁺ and Ca²⁺ concentrations.

A)



B)

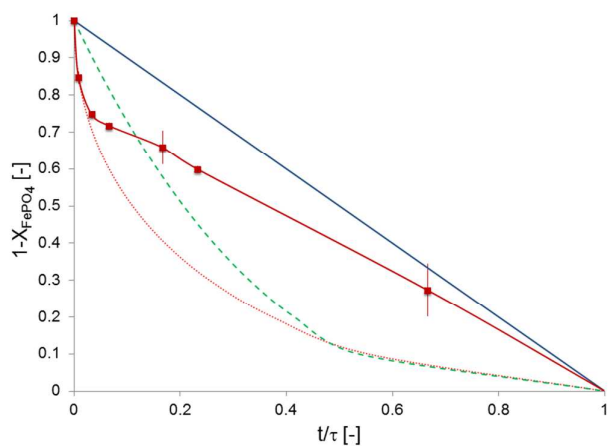


Fig. 4: A) Particle core kinetics adapted to digested sewage sludge to determine the rate controlling step in phosphate remobilisation³⁰. The solid FePO_4 core in sewage sludge particles shrank with time.

B) Particle fluid kinetics models compared to experimental (■) data from a semi-artificial remobilisation system at pH 12.6 at 25°C with 6.67 g/L of sewage sludge particles (*Process C*, Table 3). The model predictions are: diffusion through liquid film (blue), chemical reaction (green), and diffusion through ash layer (red).

Entry	Bio-electric system	pH	Remobilisation Time ^c	Dry Sludge (FePO ₄)	Sludge Mixture	Remobilized PO ₄ ³⁻	Yield PO ₄ ³⁻
		[-]	[min]	[g (mg)]	[g/L]	[mg/L]	[%]
1	Microbial Electrolysis Cell (Process C)	11.9	30	0.2()	8.4	87	11.7
2		12.7	120	0.2(17.7)	9.3	352	42.8
3		13.3	90	0.3(26.6)	10.4	430	46.6
4		13.5	90	0.2(17.7)	6.3	265	47.9
5		13.5	240	0.8(71)	26.7	1228	51.9
6		13	240	0.3(26.6)	10.7	499	52.5
7		13.1	600	0.5(44.4)	25	1632	52.9
8		12.8	240	0.1(8.9)	3.6	175	55.1
9		13.6	360	0.8(71)	13.6	1728	56
10		12.8	75	0.2(17.7)	9.5	478	56.8
11		13.3	360	0.2(17.7)	10	511	57.5
12		13.8	360	1.2(106.5)	42.9	2190	57.6
13		13.8	360	0.2(17.7)	10	534	60.1
14		12.8	1380	0.8(71)	36.4	2231	69.1
15		12.6	1440	0.8(71)	26.7	1730	73
16		12.8	1380	0.2(17.7)	8	540	76.1
17		13.4	600	0.3(26.6)	13.4	1693	76.3
18		13.5	240	0.2(17.7)	6.7	474	80.2
19		12.6	1440	0.2(17.7)	6.7	486	82.3
20		12.5	60	0.0(200) ^a	0	2567	85
21		13.8	60	0.2(17.7)	6.7	549	91.5
22		13.3	60	0.2(17.7)	6.7	570	95
23		12.6 ^b	1200	0.2(17.7)	6.7	580	98
24 ^d	MFC ¹⁷	7-8.5	3*10 ⁴	0.2 (30)	6.7	11.2	82
25 ^d		7-8.5	2.7*10 ⁴	1.9 (270)	67.9	196	14.6

Table 1: Phosphate yields and concentrations from experiments conducted at 22°C/760 Torr

^a) pure FePO₄ particles as model compound

^b) based 0.05 M NaOH base at 40°C

^c) remobilisation time after pH was reached. Preparation time for chemical base one day (Fig. 2A).

^d) former work same MEC reactor operated as microbial fuel cell¹⁷.

Temperature [°C]	Initial Rate Constants k_{obs} [s ⁻¹]
15	$7 \times 10^{-6} \pm 2 \times 10^{-6}$
25	$1.7 \times 10^{-5} \pm 6 \times 10^{-6}$
40	$4.5 \times 10^{-5} \pm 7 \times 10^{-6}$

Table 2: Rate constants k_{obs} at different temperatures in phosphate remobilization.

Phosphate remobilisation under microbial fuel cell conditions		
Bio-anode	Process	Abiotic cathode
Substrate $\xrightarrow{\text{Microbe}} 3e^- + 3H^+_{(aq)} + n CO_{2(g)}$	A	$FePO_{4(s)} + 3e^-/3H^+_{(aq)} \xrightarrow{RVC/mediator} Fe^0_{(s)} + H_3PO_4^{3-}_{(aq)}$
	B	$1.5 O_{2(g)} + 6 e^- \xrightarrow{RVC} 3 OH^-_{(aq)} + 3 Na^+_{(aq)}$ $FePO_{4(s)} + 3OH^-_{(aq)} \rightarrow PO_4^{3-}_{(aq)} + 3 Fe(OH)_{3(s)}$
Phosphate remobilisation under microbial electrolysis cell conditions		
Bio-anode	Process	Abiotic cathode
Substrate $\xrightarrow{\text{Microbe}} 3e^- + 3 H^+_{(aq)} + n CO_{2(g)}$	C	$3 H_2O + 3e^- \xrightarrow{Pt} 3 OH^-_{(aq)} + 3 Na^+ + 1.5 H_{2(g)}$ $FePO_{4(s)} + 3OH^-_{(aq)} \rightarrow PO_4^{3-}_{(aq)} + 3 Fe(OH)_{3(s)}$

Table 3: Remobilisation mechanisms. The electrochemical reduction (*Process A*) and oxygen reduction mechanism (*Process B*) are associated with microbial fuel cell conditions, while the microbial electrolysis cell favours the substitution mechanism (*Process C*) based on H₂ production. H⁺ formed in the anode by microbial activity is exchanged to a good extent by Na⁺, which migrates instead into the cathode to maintain electro neutrality.