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Novel sorbent shows promising financial results on P recovery from sludge water

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Credit Author Statement

JS: financing, management; JM: experiment design, manuscript writing

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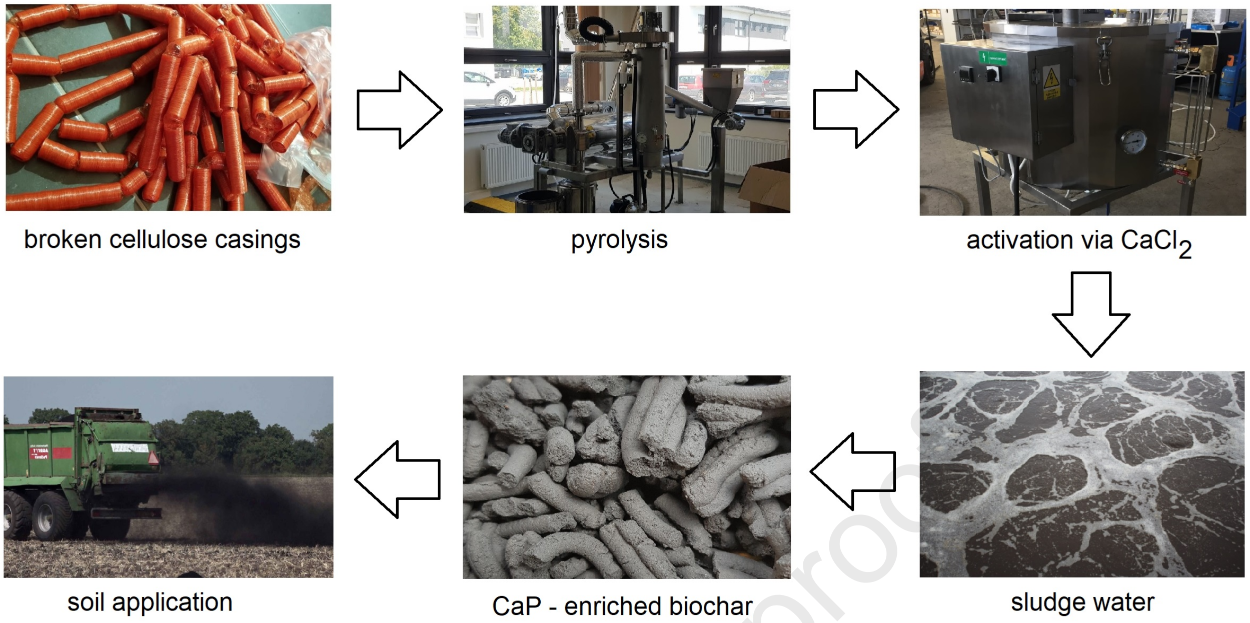

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Title

Novel sorbent shows promising financial results on P recovery from sludge water

Abstract

For several decades, researchers have been struggling to obtain minimum phosphorus (P) capture costs to meet the parameters for discharging wastewater into the watercourse. Findings from ongoing practices suggest that the Modified University of Cape Town process is currently the cheapest P capture method in the USA, whereas struvite precipitation seems to be the most cost effective method in the rest of the developed world. P sorption via biochars is becoming widespread in developing countries because this technique allows for the turning of voluminous biowaste into fertilizer with soil improving properties. Nevertheless, the reliability of this technology fluctuates throughout the year according to biowaste characteristics. For the first time, it has been proposed to use broken cellulose casings, which are readily available in increasing quantities worldwide. The sorbent obtained was subsequently activated by calcium chloride ($CaCl_2$), whose cost is irrelevant as it would be used for agronomical purposes anyway. Pilot scale experiments show that this novel sorbent is capable of capturing 31.8 kg P t^{-1} from sludge water that contains 52.5 mg of extractable P L^{-1}. More importantly, it was reported that the novel sorbent captures P, mostly in calcium phosphates (CaP) forms (191.5 g CaP t^{-1}), which are the most valuable for plant nutrition. Enough evidence was obtained to claim that the ongoing technological race to meet the P discharge standards at the lowest cost possible should also reflect the agronomic value of P to plant nutrition to increase its competitiveness.

Keywords

wastewater management; circular economy; phosphorus; bioeconomy; techno-economic

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assessment

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Nomenclature

AHC_{10-40} = aromatic hydrocarbon compounds containing 10 - 40 hydrocarbon atoms

AlP = aluminum phosphates

ATA = acute toxicity to freshwater algae *Desmodesmus subspicatus*

ATD = acute toxicity to daphnia *Daphnia subspicatus*

ATF = acute toxicity to fish *Poecilla reticulata*

ATS = acute toxicity to seeds *Sinapis alba L.*

BETsa = Brunauere-Emmette-Teller surface area

BOD = biological oxygen demand

CaP = calcium phosphates (CaP1; CaP2 and CaP3)

CE = citizen equivalent

CEC = cation exchange capacity

COD_{Cr} = chemical oxygen demand

DW = dry weight

EC = electric conductivity

EOHs = extractable organic halogens

Esa = external surface area

FeP = ferric phosphates

HV = heating value

LP = labile pool of carbon

Lsa = Langmuir surface area

MPsa = micropore surface area

P_{ext} = extractable P

RP = resistant pool of C

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SPsa = single-point surface area

TSS = total suspended solids

ULD = under limit of detection

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Highlights

- Broken cellulose casings are readily available and undemanding to be charred because of its high heating value
- Activation of charred cellulose casings via calcium chloride is costless provided that the product is used for fertilization purposes anyway
- The sorbent obtained can capture more than 31 kg P t^{-1} which is present in agronomically valuable forms (calcium phosphates)

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- Introduction

1.1 Scarcity of P available to plant nutrition

An adult person produces an average of 1.5 L urine day^{-1}, which contains 3 - 5 g of phosphates (PO_4). Proportionately, an average agglomeration with 1 million inhabitants produces some 1.5 thousand m^3 of urine day^{-1} with some 4 t of PO_4(Dox et al., 2019). It should be noted that this urine is diluted in another 5 to 30 k m^3 wastewater according to local water consumption habits (Guan et al., 2020), which worsens things both technically and economically (Kliestik et al., 2020a). Worldwide wastewater production is growing rapidly, and excessive P discharge into water bodies intensifies eutrophication, leading to a wide range of environmental (Chen et al., 2020) and financial losses (Peters et al., 2020). Increasing P scarcity combined with its uneven geographical distribution is of growing concern since independent projections show economically viable P reserves becoming depleted within a few decades (Law and Pagilla, 2019). The total P content in arable soil ranges from 0.02 to 0.05 % (more in soils rich in organic matter), though ¾ of the world's soils have low P content (less than 0.01) and are therefore not suitable for plant production (Delgadillo-Velasco et al., 2020). Over 90 % of mined P is used for fertilization (Nättorp et al., 2017), whereas ¾ of P rocks are located in Morocco alone (de Boer et al. 2019). Only 1 P mine is currently operated in the EU, making its Member States 92% dependent on P import (over 1.2 M t year^{-1}, Rowland et al., 2019), though purchasing power makes P affordability a limiting factor for agriculture in the developing word (Maroušek et al., 2020). Since there is a wide consensus that the economic importance of P will grow in the future (Stehel et al., 2019), a plethora of P recovery technologies (membrane bioreactors; deep-bed granular media filters; sorption; adsorption; coagulation; magnetically recoverable nanocomposites; ion-exchange resins, leaching of ashes

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etc.) have been designed over previous decades (Peng et al., 2018a). In particular, membrane bioreactors were initially promising (Bai et al., 2016). However, membrane fouling appeared to be a critical obstacle to its widespread implementation as it decreases membrane lifetime and increases energy requirements for sludge water circulation (Bashar et al., 2018). Currently, the most widespread method for P recovery from sludge water is struvite ($MgNH_4PO_4$ x $6H_2O$) precipitation, which can capture up to 90 % of PO_4 which refers to almost 85 % of total amount of P. Calculations by Nättorp et al. (2017) clearly demonstrated that the specific cost per P recovered (4 up to10 € kg^{-1} P, without taking into account its suitability for fertilization) is not nowadays competitive with conventional fertilizer production (1.6 € kg^{-1} P), whereas the precipitation of $PO_4$with Fe^{3+}, Al^{3+}, Fe^{2+} or Ca^{2+} salts into hydroxylapatites; struvite, or vivianite, are currently the least expensive (with struvite precipitation being the less expensive) and are therefore the most commonly used to comply with legal limits (Preisner et al., 2020). Acquisition costs of 1.3 - 2.5 M € 1 M citizen $equivalent^{-1}$ (CE) and rising prices of ferric salts (chlorides, sulfates, or nitrates all above 1 k € t^{-1}) are the main reasons why struvite production currently present cost rather than revenues. To make matters worse, the pH value has to be adjusted for struvite precipitation as well, which results in additional running costs. However, an underestimated economic and environmental threat is the low bioavailability of P that is captured in these complex minerals (Kiilerich et al., 2018). There are initial indications that prevailing precipitation techniques turn PO_4into strong bonds with Al^{3+} and Fe^{3+} ions, which significantly reduces its agrochemical use (Tian et al., 2016). Suppliers consider this disadvantage to be a targeted feature, stating that long-lasting P fertilizers are the aim of the production. However, experienced farmers are no longer buying it. There is an increasing awareness that P in these minerals is mostly present in highly crystalline forms that need to first be broken down by soil microorganisms to become available to plants as nutrition. Low accessibility of struvite P to plant nutrition is associated with the

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complexity of struvite nucleation and crystal morphology during crystal growth (driven by pH, ion speciation, temperature, and concentration of ions) which hinders its subsequent decomposition (Tansel et al., 2018). This process takes decades, and only under conditions under which the soil is optimally irrigated and rich in varied inputs of organic matter. Otherwise, the release of agronomically valuable forms of P takes hundreds of years (Ivanov et al., 2009). Multiple alternatives to improve the availability of nutrients locked in hydroxylapatites, struvite, vivianite, and other mineralization products can be traced in existing literature (Tansel et al., 2018). Nevertheless, all of them require costly chemicals or energy-intensive inputs (Chen et al., 2020). With regards to Fig. 1, it should be remarked that crops can only use calcium-based phosphates (CaP), and to a limited extent, also some aluminum based phosphates (AlP), whereas P present in ferric-based phosphates (FeP) and other forms can be considered inaccessible from the perspective of human life (Kulhánek et al., 2019).

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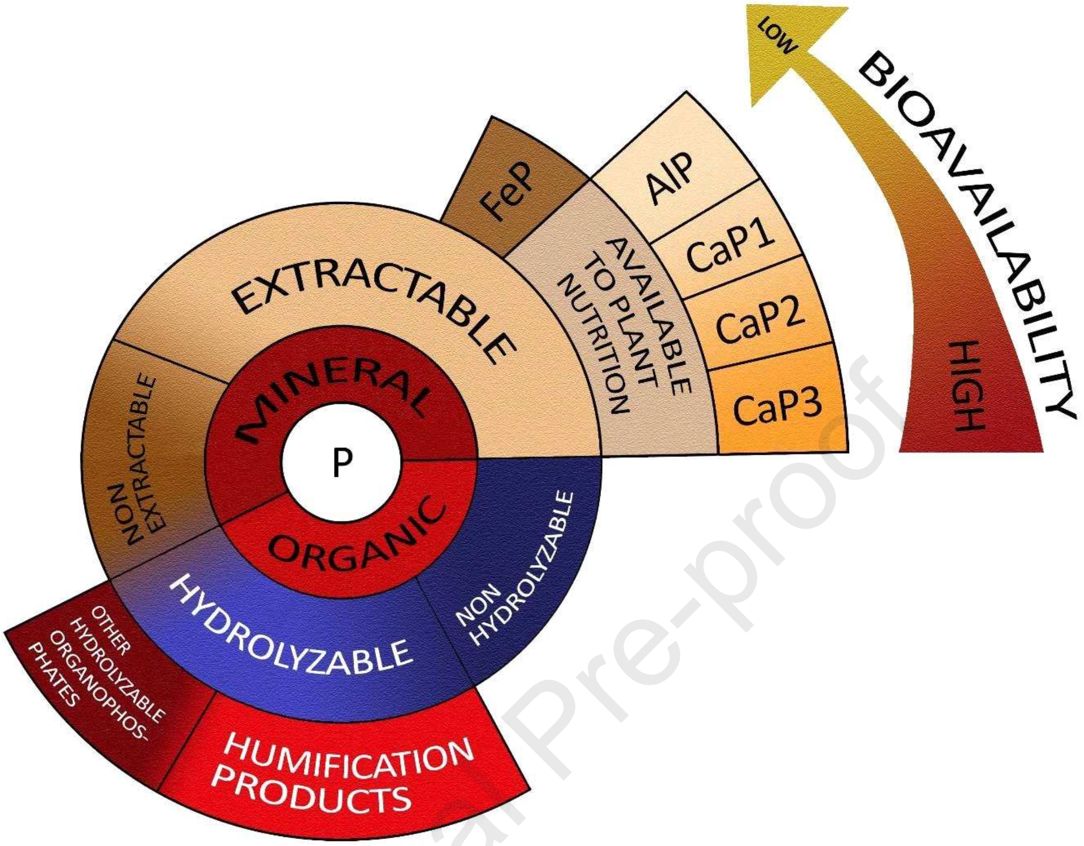

Fig. 1: Classification of soil phosphorus according to the current state of knowledge (source: authors).

1.2 Economics of bio-based sorbent production

Various types of biological waste have already been investigated to serve as P sorbents on a commercial scale (De Gisi et al., 2016). Saha et al. (2019) reported that keratin and chitosan showed some limited sorption properties on their own. Nevertheless, biomass is instead being charred to increase its sorption properties nowadays, prolonging its durability, in particular, in order to increase its economic attractiveness (90 - 230 € t^{-1}) for subsequent use in conventional crop production (Maroušek et al., 2019a). Farmers call these dusty carbonaceous products ‘biochars’

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and value them for reducing soil density, increasing water retention, and promoting nutrient management (Smetanová et al., 2013). Environmentalists point out that biochar application can be understood as one of the few profitable carbon sequestration methods, whereas the planting of trees is the most reasonable one (Luz et al., 2018). It is advantageous if the feedstock is biowaste for the disposal of which processing fees can be obtained (in the EU, the minimum fee for biowaste landfilling is now around 30 € t^{-1}). It is further preferred if the feedstock´s heating value is high enough so that it can pyrolyze itself (Lenhard, et al., 2019), or at least if the energy demands can be obtained from external waste energy source (combustion of methane from landfills, waste heat from industrial combustion engines etc.) to save on costs (Mardoyan and Braun, 2015). Provided that biochar is used as a soil enhancer, it is advantageous if any reactants used are also agronomically valuable so that its cost does not directly affect/increase the cost of P capture.

1.3 Proposal and research hypothesis

No profitable technology to facilitate the capture of P from sludge water is known to wastewater treatment plants (Peng et al., 2018a, b). As a result, developing countries have limited motivation for P capture and are interested only in unassuming methods like biosorments that provide the benefits linked with P recovery for agriculture (Nättorp et al., 2017). Yang et al. (2018) used iron-modified chars made of from wastewater sludge. However, the energy requirements for sludge dewatering and pyrolysis are so high that they make the process economically unfeasible. Micháleková-Richveisová et al. (2017) proposed to hydrolyze biowaste by iron(III) nitrate ($Fe(NO_3)_3$). However, this activation proved too costly and dangerous for adaptation on commercial scale. Ajmal et al. (2020) reported an almost double increase in porosity after magnetization of biobased sorbents. However, similar concepts require robust modifications to current wastewater treatment technologies while the financial point-of-view remains unclear.

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Given that the characteristics of commonly used biomass sorbents vary during the year, artificial casings made of regenerated cellulose are proposed as novel feedstock of constant quality. Since the demand for semi-finished meat products is growing globally, broken cellulose casings have become freely available in large quantities worldwide (Gabiatti et al., 2020a). Cellulose casings are supplied to meat businesses in the form of pleated gags so that they can be used in high-speed automatic filling lines, which are able to produce tens of tons of products per hour. However, once a small crack occurs, the entire roll of casings must be discarded, which represents a large amount of waste. Cellulose casings are made from viscose, which is obtained from plant fibers rich in cellulose. These artificial casings are highly elastic, so they are often reinforced with extra plant fibers to maintain the desired shape (Gabiatti et al., 2020b). A combination of hardly biodegradable regenerated cellulose and complex surface treatments (anti-condensation, against water absorption etc.) does not allow for their use as cattle feed (risk of cattle suffocation) nor for bio-refining (Lazaroiu et al., 2020).

It has been hypothesized that charred cellulose casings that are subsequently activated by calcium chloride ($CaCl_2$) could improve the economy of P recovery from wastewater sludge.

- Materials and Methods

2.1 Sorbent production

Mechanically damaged casings from regenerated cellulose (see the characteristics in Table 1) were obtained from ViskoTeepak, s.r.o. (the Czech Republic) and stored in resealable cartons at 22 °C with 60% relative humidity until their processing. This biowaste was fed into the UHL-07 continuous pyrolysis apparatus (Aivotec, s.r.o., the Czech Republic) and charred at 320 °C (no additional energy source used, the process takes 6 minutes). The carbonaceous dust (see the

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characteristics in Table 2) obtained was placed into the mixing reactor and mixed with 10% $CaCl_2$ (FICHEMA s.r.o., the Czech Republic) for 2 hours.

- Struvite production

Struvite precipitate was obtained by slowly mixing (20 hours at 5 rpm) magnesium chloride hexahydrate ($MgCl_2 \times 6\,H_2O$, PENTA s.r.o., the Czech Republic) with oxygenated sludge water (200 L O_2 minute^{-1} m^{-3}) to obtain Mg : P ratio of 1.3 : 1 (molar weight). Subsequently, the ratio of N : P was adjusted to 3 : 1 (molar weight) by ammonia (NH_3, PENTA s.r.o, the Czech Republic). Precipitate was separated by centrifugation (450 rpm for 1 hour) that was followed by 24 h of drying at 40 °C.

- Sorption experiment

Sorption experiments took place in the sedimentation tank of Strakonice wastewater treatment plant (75 k CE ~ 3.0 M m^{3}y^{-1}, the Czech Republic) according to the schema showed in Fig. 2. Sorbent was filled into bales (3 m * 0.1 m * 1 m) made of permeable fabric to ensure a good reaction surface. The bales filled with sorbent were immersed into the sedimentation tank^{-1}).

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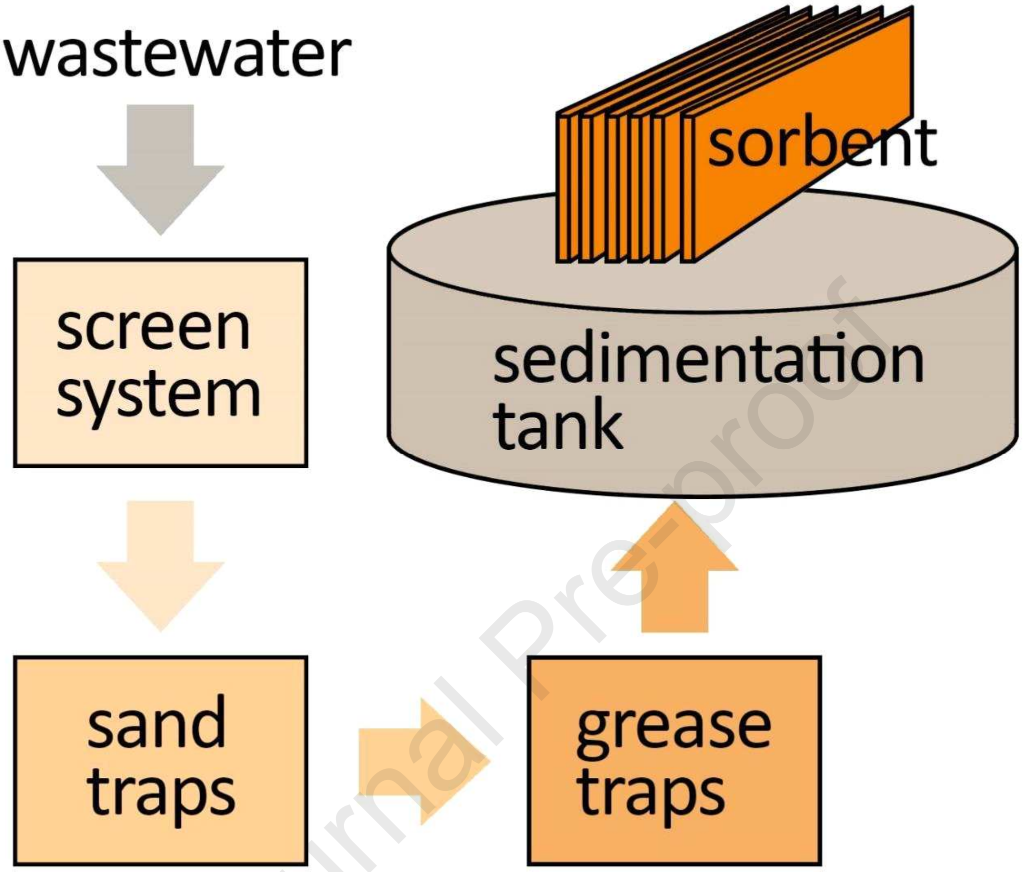

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Fig. 2: Setup of the wastewater treatment plant where the experiment took place.

- Analytical procedures

Dry weight (DW) was analyzed after 3 days at 105 °C in the Goldbrunn1450 vacuum (140 Pa) dryer (Goldbrunn therm, Germany) by the EP 320M weights (Precisa Gravimetrics AG, Switzerland). The thickness of the casings walls was measured using the SBS-CT-123 PRO coating thickness gauge meter (Steinberg systems, Germany). The cellulose content was analyzed using the FIBRETHERM FibreBag technology (C. Gerhardt GmbH & Co. KG, Germany). Oils and fats were quantified using the Soxhlet extractor (Corning Inc., NY, USA) and analytical hexane (99.9 %). Labile (LP) and resistant (RP) pools of carbon (resistance to acid hydrolysis) were analyzed with sulfur acid (H_2SO_4) according to Shirato and Yokozawa (2006), using the EA5100 elemental analysis (Analytik Jena AG, Germany). The heating value (HV) was analyzed using the CAL3K-A bomb calorimeter system (Digital Data Systems Ltd., South Africa). Ash content was determined according to D1762-84 (ASTM). The Seven2GoPro multimeter (Metter-Toledo, Switzerland) was used to analyze pH and electrical conductivity (EC). The cation-exchange-capacity (CEC) was analyzed according to the protocol proposed by Munera-Echeverri et al. (2018). Analyses for lead (Pb), cadmium (Cd), copper (Cu), nickel (Ni), mercury (Hg), zinc (Zn), chromium (Cr), boron (B), manganese (Mn), sulfur (S), naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthrene, pyrene, benzo(a)anthracene, chrysene, benzo(b)fluoranthrene, benzo(k)fluoranthrene, benzo(a)pyrene, indeno(1,2,3–cd)pyrene, dibenzo(a,h)anthracene, benzo(g,h,i)perylene, benzene, toluene, ethylbenzene, m- xylene, p- xylene, o-xylene, naphthalene, extractable organic halogens (EOHs), and aromatic hydrocarbon compounds containing 10 - 40 hydrocarbon atoms ($AHC_{10\text{-}40}$) were carried out as described in Vochozka et al. (2016a). Acute toxicity to fish *Poecilla reticulata* (ATF); daphnia *Daphnia subspicatus* (ATD), freshwater algae *Desmodesmus subspicatus* (ATA), and seeds *Sinapis alba L.* (ATS) was analyzed according to Vochozka et al. (2016b). The Brunauere-Emmette-Teller surface area (BETsa); single-point surface area (partial vapor pressure of helium in equilibrium with the surface)/(saturated pressure of helium) = 0.1 (SPsa); Langmuir surface area (Lsa); micropore surface area (MPsa) and external surface areas (Esa) were analyzed by the 3H-2000PS4 porosimeter (Tmax BE, China) after 48 hours of degassing at 300 °C.

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Extractable P (P_{ext}) and its subsequent fractionation (FeP, AlP, CaP1, CaP2, and CaP3), biological oxygen demand (BOD), chemical oxygen demand (COD_{Cr}), and total suspended solids (TSS) were analyzed as described in Maroušek et al. (2019b). Cost breakdown was carried out as proposed by Hašková (2017), and all the costs are rounded up.

3. Results and Discussion

3.1 Waste cellulose casings characteristics

Analyses on waste cellulose casings (Table 1) showed high proportion of cellulose fiber and high proportion of RP which can be interpreted as a high resistance to H_2SO_4 hydrolysis (Shirato and Yokozawa, 2006). These findings are in accordance with Gabiatti et al. (2020a), who adds that the combination of highly crystalline cellulose and complex surface treatments (esters of glycerol, polyglycerol, sorbitan esters and alcohol ethoxylates are sprayed on the casing's surface or mixed into the matrix of regenerated cellulose) are used to make the fibrous casings resistant microbial attacks. Such a design makes sugar-based biorefining options economically problematic (Gabiatti et al. 2020b). The combination of cellulose, energy-rich oils, and fats makes the HV slightly higher than other cellulose-based feedstock like paper or cardboard (Vochozka et al., 2016c). Provided that pyrolysis is a process of exothermic nature, this allowed to achieve self-sufficient pyrolysis at temperature of 320 °C. Ronsse et al. (2013) reports that such low temperatures are limiting to the formation of good sorption properties. However, an external energy source is not a viable alternative for economic reasons (Jandačka et al., 2017). Provided that cellulose casings made by other manufacturers are made from similar raw materials (Kliestik et al., 2020b), of similar thickness, and via similar procedures (Peters et al., 2020), it is not surprising that they show similar properties (Maroušek et al., 2015). It can be argued that these waste cellulose casings comply with

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globally established commercial standards and allow for valid generalizations of subsequently acquired knowledge.

Table 1: Characteristics of the cellulose casings (n = 12; α = 0.1).

Compounds/Property	Characteristics (unit)
Cellulose	809.3 ± 15.6 (g kg^{-1})
Oils and fats	155.1 ± 10.2(g kg^{-1})
HV	16.9 ± 0.3(MJ kg^{-1})
Casing wall thickness	92.3 ± 44.5(µm)
LP	2 (% cellulose)
RP	98 (% cellulose)

3.2 Sorbent characteristics

In regards to charred cellulose casings, the ash content (Table 2) is as low as it is in chars made of hardly biodegradable phytomass like virgin paper (Vochozka et al., 2016c) or fermentation residues (Mardoyan and Braun, 2015), which consist mainly of cellulose with a high degree of polymerization. Low ash content also indicates that the pyrolytic process did not suffer from defects, since it is probable that only oxygen (O_2) from the air capsules present in the feedstock entered the pyrolysis chamber. The pH level of the char obtained is average compared to pyrolyzed terrestrial phytomass (Ronsse et al., 2013), and this fact confirms that the cellulose casings were not made of terrestrial algae or seaweed. EC is about 50 % lower than found in commercially available chars as reviewed by Saha et al. (2019). Low EC indicates that salt crystals remained

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locked in char aggregates, which is a highly likely to be a consequence of low temperature during pyrolysis (Smetanová et al., 2013). From this, it can be implicitly assumed that it may be useful in the future to investigate whether it would be beneficial to modify this sorbent mechanically, for example, by crushing (Hadzima et al., 2007). One of the latest protocols for biochar CEC analysis (Munera-Echeverri et al., 2018) was applied and looks to be favorably reproducible (as this used to be a problem with earlier methods). However, given that the method by Munera-Echeverri et al. (2018) is quite new, the results reported here are not comparable with prior papers. The levels of extractable Ca, Mg and K are average in comparison with charred sorbents of biowaste origin as reviewed by Li et al. (2017). Data in Table 2 also shows that all crucial heavy metals and other critical substances present are either under limit of detection (ULD) or well below soil hygiene regulations (De Gisi et al., 2016), which reflects the fact that cellulose casing are intended to be in contact with food and must therefore comply with corresponding laws (Gabiatti et al., 2020a). When compared to Luz et al. (2018), only low levels of polycyclic aromatic hydrocarbons could be traced, which was indirectly confirmed by no signs of acute biotoxicity. It follows from the above that charred casings from waste cellulose casings can be used without any obstacles as a soil enhancer. In regard to microporosity, the results are about two-thirds lower than reported by Li et al. (2017). Nevertheless, even a twofold increase in porosity does not guarantee improved results in P capture (Ajmal et al., 2020). In agreement with Ronsse et al. (2013) one can guess that this is due to the low temperatures of the pyrolysis process (Kovacova et al., 2019) which are caused by the effort for minimal cost (no external energy source). Most importantly, CaP is some 82 % of P_{ext}. As far as the sorbent production is concerned, it should be remembered that the technology includes not only the UHL-07 pyrolysis unit but also the tailor-made mixing reactor and a dipping system. The guaranteed lifespan of all devices is 12 years, and the total price is some 0.8 M €. The technology enables the production of 100 kg char $hour^{-1}$ for 8.7 k hours $year^{-1}$ and the overhead is

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about 5 k € year^{-1}. Although the heating value of the feedstock is sufficient for self-pyrolysis, the pyrolysis unit uses natural gas at the very start of the process and to occasionally stabilize the quality of the pyrolytic gas. The cost of natural gas is 1 € char t^{-1} on average. The mixing reactor that activates the sorbent with 10 % $CaCl_2$ needs an electrical supply of some 1.5 € char t^{-1}, the immersion system and other handling requires energy of 0.5 € char t^{-1}. 1 t of char is activated by 160 kg of 10 % $CaCl_2$ (this number seems to be an operationally achievable state of equilibrium; more $CaCl_2$ has never been captured), whereas the wholesale price of 77 % $CaCl_2$ is about 90 € t^{-1}.

Table 2: Characteristics of charred cellulose casings (n = 10; α = 0.1) indicate that low pyrolysis temperature might be limiting for its sorption properties (ULD = under limit of detection, (N/A = not applicable).

Compounds/Property	Sorbent	Sludge water	Struvite
Density (g L^{-1})	631 ± 15.8	1072.6 ± 22.9	1690.3 ± 16.1
Ash (g kg^{-1})	7.8 ± 4.2	N/A	N/A
BOD (mg L^{-1})	N/A	1093.7 ± 64.8	N/A
COD_{Cr} (mg L^{-1})	N/A	2506.4 ± 113.9	N/A
pH	8.1 ± 1.0	8.4 ± 0.5	7.9 ± 0.3
EC (mS cm^{-1})	33.4 ± 7.5	1.8 ± 0.4	N/A
CEC (mol H^+ kg^{-1})	50.7 ± 3.8	N/A	N/A
Pb (ppm)	ULD	ULD	0.2 ± 0.1
Cd (ppm)	ULD	ULD	0.2 ± 0.1
Cu (ppm)	0.2 ± 0.1	0.1 ± 0.1	0.3 ± 0.1

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Ni (ppm)	0.3 ± 0.1	ULD	ULD
Hg (ppm)	ULD	ULD	ULD
Zn (ppm)	4.5 ± 2.2	0.1 ± 2.2	25.7 ± 3.5
Cr (ppm)	ULD	ULD	0.5 ± 0.2
B (ppm)	ULD	ULD	ULD
Mn (ppm)	17.2 ± 3.9	ULD	33.6 ± 15.7
S (ppm)	21.5 ± 6.6	ULD	ULD
Naphthalene (ppm)	ULD	ULD	ULD
Acenaphthylene (ppm)	ULD	ULD	ULD
Acenaphthene (ppm)	ULD	ULD	ULD
Fluorene (ppm)	ULD	ULD	ULD
Phenanthrene (ppm)	ULD	ULD	ULD
Anthracene (ppm)	ULD	ULD	ULD
Fluoranthrene (ppm)	ULD	ULD	ULD
Pyrene (ppm)	1.1 ± 0.4	ULD	ULD
Benzo(a)anthracene (ppm)	0.3 ± 0.3	ULD	ULD
Chrysene (ppm)	ULD	ULD	ULD
Benzo(b)fluoranthrene (ppm)	ULD	ULD	ULD
Benzo(a)pyrene (ppm)	2.6 ± 1.7	ULD	ULD
Indeno(1,2,3-cd)pyrene (ppm)	ULD	ULD	ULD
Dibenzo(a,h)anthracene (ppm)	ULD	ULD	ULD
Benzo(g,h,l)perylene (ppm)	ULD	ULD	ULD
Benzene (ppm)	0.7 ± 0.5	ULD	ULD

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Toluene (ppm)	ULD	ULD	ULD
Ethylbenzene (ppm)	ULD	ULD	ULD
M-xylene (ppm)	ULD	ULD	ULD
P-xylene (ppm)	ULD	ULD	ULD
O-xylene (ppm)	ULD	ULD	ULD
Naphthalene (ppm)	ULD	ULD	ULD
EOHs (ppm)	ULD	ULD	ULD
AHC_{10-40} (ppm)	ULD	ULD	ULD
ATF (%)	ULD	10	N/A
ATD (%)	ULD	5	N/A
ATA (%)	ULD	ULD	N/A
ATS (%)	ULD	ULD	N/A
BETsa ($m^2\ g^{-1}$)	172.8 ± 93.5	N/A	N/A
Lsa ($m^2\ g^{-1}$)	25.7 ± 14.6	N/A	N/A
SPsa ($m^2\ g^{-1}$)	19.0 ± 13.9	N/A	N/A
MPsa ($m^2\ g^{-1}$)	19.8 ± 15.9	N/A	N/A
Esa ($m^2\ g^{-1}$)	16.1 ± 11.3	N/A	N/A
P_{ext} ($mg\ kg^{-1}$)	233.5 ± 40.3	N/A	250.3 ± 31.8
P_{ext} ($mg\ L^{-1}$)	N/A	52.5 ± 6.0	N/A
FeP (% P_{ext})	8	5	25
AlP (% P_{ext})	10	16	36
CaP1 (% P_{ext})	31	13	17
CaP2 (% P_{ext})	22	25	13

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CaP3 (% P_{ext})	29	41	9
Depreciation and overheads (€ t^{-1})	83	N/A	66
Energy cost (€ t^{-1})	3	N/A	13
Reactants (€ t^{-1})	2	N/A	25

3.3 Sludge water characteristics

In terms of sludge water, its density and pH (Table 2) is similar to what was reported by Tansel et al. (2018) and other studies (Preisner et al., 2020; Saha et al., 2019) around the world. BOD, COD_{Cr}, DM, TSS, and EC are also in the usual range (Peng et al., 2018a, b). Crucial heavy metals and other critical pollutants were at almost negligible levels (see Chen et al., 2020) and only mild acute biotoxicity was detected (ATF and ATD). With regards to Vochozka et al. (2016b), it can be argued that the data obtained on acute biotoxicity is a consequence of the combination of BOD and microbial load. Nevertheless, such results do not deviate in any way from the common sludge water values. The level of P is about one seventh higher in comparison with other similarly populated locations (Chen et al., 2020), and it can be concluded that such a high level is probably not solely of urinary origin (Dox et al., 2019). Following that the less accessible forms of P (in particular FeP and AlP) are also represented, it can be assumed that the above-average values of P might originate from local industry or an increased use of detergents containing P (Kiilerich et al., 2018), which may be associated with the ongoing pandemic. Following the above, this sludge water is a sample that shows characteristics similar rather to large agglomerations with higher level of industry. The values of P also prove that sludge water did not undergo any P decrease procedure which are usually required before being discharged into water systems (Guan et al., 2020). It is appropriate to note that only 21 % of P_{ext} is present in forms that are hardly available to plant

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nutrition. All in all, it can be stated that these characteristics of sludge water are in agreement with other literature (Chen et al., 2020) and the lessons learned are potentially widely transferable. The investigated sludge water is by no means being modified; therefore its pricing is slightly negative since getting rid of it means a cost savings for wastewater plants (Kiilerich et al., 2018). However, in many countries, the application of sludge water to soil is subject to various restrictions (it cannot be performed if the fields are under snow, if the soil is frozen, in case of sandy soil, if there are water systems nearby etc.) and in some countries, it is even prohibited (Bashar et al., 2018).

3.4 Struvite characteristics

In terms of the struvite produced, the pH obtained is similar to commercially available products, such as those reviewed by Tansel et al. (2018); therefore, soil acidification should not be expected. The concentration of life-threating heavy metals and other hazardous compounds is generally higher than that of the activated sorbent or wastewater, which corresponds to the method of production and an increased concentration of P. Nevertheless, these figures are similar to those found in commercially available products and meet all the regulations necessary to be used as fertilizer (Nättorp et al., 2017). From a biological point of view, it is important to note that only some 39 % of P_{ext} is present in CaP forms. A struvite reactor, centrifuge, and dryer are mandatory (in total 0.5 M € with guaranteed service life of 6 years) to run struvite production 8.7 k hours year^{-1}. The overhead is some 80 k € year^{-1}. The energy costs of operating the reactor is approximately 4 € struvite t^{-1}, centrifugation 3 € struvite t^{-1} and drying 6 € struvite t^{-1}. $MgCl_2$ x 6 H_2O (21 € t^{-1}), NH_4 (3 € t^{-1}) and O_2 (1 € kg^{-1}) are needed to run the process.

3.5 Economic insights

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Wastewater treatment plants pressingly call for a P capture process that is undemanding in terms of acquisition and running costs and is capable of producing competitive fertilizers which meet all the legal requirements (Peng et al., 2018a). Bashar et al. (2018) identified that the Integrated Fixed-Film Activated Sludge Systems with Enhanced Biological Phosphorus removal (also known as IFAS-EBPR) is the most cost-effective system for P removal in the USA (60 € P kg^{-1}), whereas precipitation of struvite (52 € P kg^{-1}) seems to be of the lowest cost in the EU. The economics of struvite production in this study is similar to other commercial production, provided that the production costs calculated (Table 3) during the pilot testing are only slightly lower than the lowest struvite wholesale prices (Tansel et al., 2018). Low margins are indirectly signaling that there is a little demand for this product. Yang et al. (2018) used iron-activated charred sludge as a sorbent. However, this concept proved unfeasible due to high energy demands since 1/ huge amounts of water needs to be removed from the sludge before it can be pyrolyzed; and 2/ a lot of external energy is needed to pyrolyze sludge. Efforts to activate biowaste sorbents via iron(III) nitrate showed economically unrealistic and dangerous (Micháleková-Richveisová et al., 2017). A closer look at the cost analysis (Table 3) shows that even though struvite production is currently one of the most efficient P capture technologies worldwide, the novel sorbent can be competitive in some aspects. Discussion over the production costs of the sorbent opens wide economic polemics. Cost breakdown indicates that its production cost is somewhere in the neighborhood of 90 € t^{-1}, which is close to the cheapest charcoal produced from fermentation residues (Mardoyan and Braun, 2015). It depends on who (and how) runs the business. Theoretically, the business concept could fulfill all the theoretical concepts of circular economics. Provided that farmers buy biochar, P, and $CaCl_2$ anyway, one can argue that this is a win/win/win/win business where: A/ producers of meat products can get rid of their voluminous waste at lower costs; B/ wastewater treatment plants can capture P at lower costs; C/ farmers can get P at lower costs, and D/ humanity benefits from 1/

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lower wastewater treatment cost; 2/ lower food production cost; 3/ carbon sequestration via biochar; 4/ reduction of landfilling and prevention of greenhouse gas emissions; and 5/ increase in food security due to the reduction of P imports and an increase in the quality of soil and water. Nättorp et al. (2017) demonstrated that P obtained from P rocks is 1.6 € kg^{-1} P. Data in Table 3 indicates that struvite production cost remains at just more than a tenth above this number and is still not competitive with such prices. Nevertheless, the novel sorbent technology may seem attractive, but it is more important to note that similar calculations can be misleading as they do not reflect the biological nature of things (Kulhánek et al., 2019). Analyses on CaP indicate that sorbents are capable of captureing these agronomically valuable P fractions with more than double cost efficiency. Nevertheless, the desire to obtain an agronomically and biologically efficient fertilizer is not a sufficient reason to make such a managerial decision because the cost of the application must also be considered (Valaskova et al., 2020). A calculation-simulating application of 1 kg CaP ha^{-1} at 20 km distance confirms that the application of sludge water is irrational because its P concentration is extremely low and therefore expensive (Skapa, 2012), not taking into account possible legislative restrictions.

Table 3: Cost analysis indicates that conventional methods of capturing P from sludge water are still not competitive with P fertilizers from P rocks. But things can change if the sorbent is produced from biowaste and activated by agrochemicals.

Compounds/Property	Sorbent	Sludge water	Struvite
P (kg t^{-1})	31.8 ± 2.2	0.4 ± 0.1	57.0 ± 4.5
CaP (mg kg^{-1})	191	369	98

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Production cost (€ t^{-1})	88	0	104
Production cost (€ P kg^{-1})	0.4	N/A	1.8
Production cost (€ CaP kg^{-1})	461	N/A	1061
Application cost (€ kg CaP ha^{-1})	128	9 255	305

4. Conclusion

Ignoring economic and legal realities, it can be presumed that the best source of P for plant nutrition is sludge water. Despite this fact, the use of sludge water for plant nutrition is constrained by costly logistics and is often subject to legal regulations. Struvite production is a proven technology, and the cost of such captured P is now closer than ever to meeting the pricing of P from conventional P fertilizers that are made of P rocks. However, one disadvantages of struvite is that less than 40 % of its P_{ext} is present in CaP forms which are the most valuable for plant nutrition. The rest of the P_{ext} in the struvite can become agronomically valuable only over decades, and only if the optimal conditions for high activity of soil microorganisms are created in the soil.

A novel method of sorbent production from waste cellulose casings consisting of pyrolysis and $CaCl_2$ activation was proposed and techno-economically investigated in a pilot scale. It was first reported that this sorbent allows for the capture of 31.8 kg P t^{-1}, whereas more than 80 % of the captured P is present in forms that are easily available as crop nutrition. Due to the fact that numerous cost saving measures and synergies were combined in the production of the sorbent, it can be concluded that the novel sorbent could be financially promising in commercial scales.

Liquid biowaste from agriculture and food production is known for high P levels therefore, further

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research could take this direction.

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6. References

Ajmal, Z., Muhmood, A., Dong, R., Wu, S., 2020. Probing the efficiency of magnetically modified biomass-derived biochar for effective phosphate removal. J. Environ. Manage. 253, 109730.

Bai, Y., Zhang, Y., Quan, X., Chen, S., 2016. Nutrient removal performance and microbial characteristics of a full-scale IFAS-EBPR process treating municipal wastewater. Water. Sci. Technol. 73(6), 1261-1268.

Bashar, R., Gungor, K., Karthikeyan, K.G., Barak, P., 2018. Cost effectiveness of phosphorus removal processes in municipal wastewater treatment. Chemosphere. 197, 280-290.

Chen, J., Tang, S., Yan, F., Zhang, Z., 2020. Efficient recovery of phosphorus in sewage sludge through hydroxylapatite enhancement formation aided by calcium-based additives. Water. Res. 171, 115450.

Journal Pre-proof

de Boer, M. A., Wolzak, L., Slootweg, J.C., 2019. Phosphorus: Reserves, production, and applications. In: Ohtake, H., Tsuneda, S. (Eds.), Phosphorus Recovery and Recycling.
Springer, Singapore, pp. 75-100.

De Gisi, S., Lofrano, G., Grassi, M., Notarnicola, M., 2016. Characteristics and adsorption capacities of low-cost sorbents for wastewater treatment: A review. Sustain. Mater. Technol. 9, 10-40.

Delgadillo-Velasco, L., Hernández-Montoya, V., Montes-Morán, M.A., Gómez, R.T., Cervantes, F.J., 2020. Recovery of different types of hydroxyapatite by precipitation of phosphates of wastewater from anodizing industry. J. Clean. Prod. 242, 118564.

Dox, K., Everaert, M., Merckx, R., Smolders, E., 2019. Optimization of phosphate recovery from urine by layered double hydroxides. Sci. Total. Environ. 682, 437-446.

Gabiatti, Jr, C., Dal Magro, L., Graebin, N.G., Rodrigues, E., Rodrigues, R.C., Prentice, C., 2020a. Combination of Celluclast and Viscozyme improves enzymatic hydrolysis of residual cellulose casings: process optimization and scale-up. Braz. J. Chem. Eng. 37(3), 463-473.

Gabiatti, Jr, C., Neves, I.C., Lim, L.T., Bohrer, B.M., Rodrigues, R.C., Prentice, C., 2020b. Characterization of dietary fiber from residual cellulose sausage casings using a combination of enzymatic treatment and high-speed homogenization. Food Hydrocolloids. 100, 105398.

Guan, T., Li, X., Fang, W., Wu, D., 2020. Efficient removal of phosphate from acidified urine

Journal Pre-proof

Journal Pre-proof

using UiO-66 metal-organic frameworks with varying functional groups. Appl. Surf. Sci. 501, 144074.

Hadzima, B., Janeček, M., Estrin, Y., Kim, H.S., 2007. Microstructure and corrosion properties of ultrafine-grained interstitial free steel. Mater. Sci. Eng. A. 462(1-2), 243-247.

Ivanov, V., Kuang, S., Stabnikov, V., Guo, C., 2009. The removal of phosphorus from reject water in a municipal wastewater treatment plant using iron ore. J. Chem. Technol. Biotechnol. 84(1), 78-82.

Jandačka, J., Mičieta, J., Holubčík, M., Nosek, R., 2017. Experimental Determination of Bed Temperatures during Wood Pellet Combustion. Energ. Fuel. 31(3), 2919-2926.

Hašková, S., 2017. Holistic assessment and ethical disputation on a new trend in solid biofuels. Sci. Eng. Ethics. 23, 509–519.

Kiilerich, B., Nielsen, A.H., Vollertsen, J., 2018. Kinetics of sulfide precipitation with ferrous and ferric iron in wastewater. Water. Sci. Technol. 78(5), 1071-1081.

Kliestik, T., Nica, E., Musa, H., Poliak, M., Mihai, E.A., 2020a. Networked, Smart, and Responsive Devices in Industry 4.0 Manufacturing Systems. Econ. Manage. Financ. Market. 15(3), 23-29.

Kliestik, T., Valaskova, K., Nica, E., Kovacova, M., Lazaroiu, G., 2020b. Advanced methods of

Journal Pre-proof

earnings management: monotonic trends and change-points under spotlight in the Visegrad countries. Oecon. Copernic. 11(2), 371-400.

Kovacova, M., Kliestik, T., Valaskova, K., Durana, P., Juhaszova, Z., 2019. Systematic review of variables applied in bankruptcy prediction models of Visegrad group countries. Oecon. Copernic. 10(4), 743-772.

Kulhánek, M., Černý, J., Balík, J., Sedlář, O., Vašák, F., 2019. Changes of soil bioavailable phosphorus content in the longeterm field fertilizing experiment. Soil. Water. Res. 14, 240-245.

Law, K. P., Pagilla, K. R., 2019. Reclaimed phosphorus commodity reserve from water resource recovery facilities—A strategic regional concept towards phosphorus recovery. Resour. Conserv. Recy. 150, 104429.

Lazaroiu, G., Valaskova, K., Nica, E., Durana, P., Kral, P., Bartoš, P., Maroušková, A., 2020. Techno-Economic Assessment: Food Emulsion Waste Management. Energies. 13(18), 4922.

Lenhard, R., Malcho, M., Jandačka, J., 2019. Modelling of heat transfer in the evaporator and condenser of the working fluid in the heat pipe. Heat Transfer Eng. 40(3-4), 215-226.

Li, H., Dong, X., da Silva, E.B., de Oliveira, L.M., Chen, Y., Ma, L.Q., 2017. Mechanisms of metal sorption by biochars: biochar characteristics and modifications. Chemosphere. 178, 466-478.

Luz, F.C., Cordiner, S., Manni, A., Mulone, V., Rocco, V., 2018. Biochar characteristics and early

Journal Pre-proof

applications in anaerobic digestion-a review. J. Environ. Chem. Eng. 6(2), 2892-2909.

Mardoyan, A., Braun, P., 2015. Analysis of Czech subsidies for solid biofuels. Int. J. Green Energy, 12(4), 405-408.

Maroušek, J., Hašková, S., Zeman, R., Žák, J., Vaníčková, R., Maroušková, A., Váchal, J., Myšková, K., 2015. Techno-economic assessment of processing the cellulose casings waste. Clean. Technol. Envir. 17(8), 2441-2446.

Maroušek, J., Stehel, V., Vochozka, M., Kolář, L., Maroušková, A., Strunecký, O., Peterka, J., Kopecký, M., Shreedhar, S., 2019a. Ferrous sludge from water clarification: Changes in waste management practices advisable. J. Clean. Prod. 218, 459-464.

Maroušek, J., Strunecký, O., Stehel, V., 2019b. Biochar farming: defining economically perspective applications. Clean. Technol. Envir. 21, 1389–1395.

Maroušek, J., Rowland, Z., Valášková, K., Král, P., 2020. Techno-economic assessment of potato waste management in developing economies. Clean. Technol. Envir. 22, 937–944.

Micháleková-Richveisová, B., Frišták, V., Pipíška, M., Ďuriška, L., Moreno-Jimenez, E., Soja, G., 2017. Iron-impregnated biochars as effective phosphate sorption materials. Environ. Sci. Pollut. R. 24(1), 463-475.

Munera-Echeverri, J.L., Martinsen V., Strand L.T., Zivanovic V., Cornelissen G., Mulde, J., 2018.

Journal Pre-proof

Cation Exchange Capacity of Biochar: An urgent method modification. Sci. Total. Environ. 642, 190-197.

Nättorp, A., Remmen, K., Remy, C., 2017. Cost assessment of different routes for phosphorus recovery from wastewater using data from pilot and production plants. Water. Sci. Technol. 76(2), 413-424.

Peng, L., Dai, H., Wu, Y., Peng, Y., Lu, X., 2018a. A comprehensive review of phosphorus recovery from wastewater by crystallization processes. Chemosphere, 197, 768-781.

Peng, L., Dai, H., Wu, Y., Peng, Y., Lu, X., 2018b. A comprehensive review of the available media and approaches for phosphorus recovery from wastewater. Water. Air. Soil. Pollut. 229(4), 115.

Peters, E., Kliestik, T., Musa, H., Durana, P., 2020. Product Decision-Making Information Systems, Real-Time Big Data Analytics, and Deep Learning-enabled Smart Process Planning in Sustainable Industry 4.0. J. Self-Gov. Manage. Econom. 8(3), 16-22.

Preisner, M., Neverova-Dziopak, E., Kowalewski, Z., 2020. An Analytical Review of Different Approaches to Wastewater Discharge Standards with Particular Emphasis on Nutrients. Environ. Manage. 66(4), 694-708.

Ronsse, F., Van Hecke, S., Dickinson, D., Prins, W., 2013. Production and characterization of slow pyrolysis biochar: influence of feedstock type and pyrolysis conditions. GCB Bioenergy. 5(2), 104-115.

Journal Pre-proof

Journal Pre-proof

Rowland, Z., Machová, V., Horák, J., Hejda, J., 2019. Determining the market value of the enterprise using the modified method of capitalized net incomes and Metfessel allocation of input data. Ad Alta: J. Interdiscip. Res. 9, 305–310.

Saha, S., Zubair, M., Khosa, M.A., Song, S., Ullah, A., 2019. Keratin and chitosan biosorbents for wastewater treatment: a review. J. Polym. Environ. 27(7), 1389-1403.

Shirato, Y., Yokozawa, M., 2006. Acid hydrolysis to partition plant material into decomposable and resistant fractions for use in the Rothamsted carbon model. Soil. Biol. Biochemi. 38(4), 812-816.

Skapa, S., 2012. Investment characteristics of natural monopoly companies. J Competitiveness, 4(1), 36-43.

Smetanová, A., Dotterweich, M., Diehl, D., Ulrich, U., Dotterweich, N.F., 2013. Influence of biochar and terra preta substrates on wettability and erodibility of soils. Z. Geomorph. Supp. 57(1), 111-134.

Stehel, V., Horák, J., Vochozka, M., 2019. Prediction of institutional sector development and analysis of enterprises active in agriculture. Business Admin. Manage. 10.15240/tul/001/2019-4-007

Tansel, B., Lunn, G., Monje, O., 2018. Struvite formation and decomposition characteristics for ammonia and phosphorus recovery: A review of magnesium-ammonia-phosphate interactions. Chemosphere. 194, 504-514.

Tian, G., Cox, A.E., Kumar, K., Granato, T.C., O'Connor, G.A., Elliott, H.A., 2016. Assessment of plant availability and environmental risk of biosolids-phosphorus in a US Midwest Corn-Belt Soil. J Environ. Manage. 172, 171-176.

Valaskova, K., Throne, O., Kral, P., Michalkova, L., 2020. Deep Learning-enabled Smart Process Planning in Cyber-Physical System-based Manufacturing. J Self-Governance Manage. Econ., 8(1), 121-127.

Vochozka, M., Maroušková, A., Váchal, J., Straková, J., 2016a. Biochar pricing hampers biochar farming. Clean. Technol. Envir. 18(4), 1225-1231.

Vochozka, M., Maroušková, A., Váchal, J., Straková, J., 2016b. Reengineering the paper mill waste management. Clean. Technol. Envir. 18(1), 323-329.

Vochozka, M., Maroušková, A., Straková, J., Váchal, J., 2016c. Techno-economic analysis of waste paper energy utilization. Energ. Source. Part A. 38(23), 3459-3463.

Yang, Q., Wang, X., Luo, W., Sun, J., Xu, Q., Chen, F., Zhao, J., Wang, S., Yao, F., Wang, D., Li, X., Zeng, G., 2018. Effectiveness and mechanisms of phosphate adsorption on iron-modified biochars derived from waste activated sludge. Bioresource Technol. 247, 537-544.

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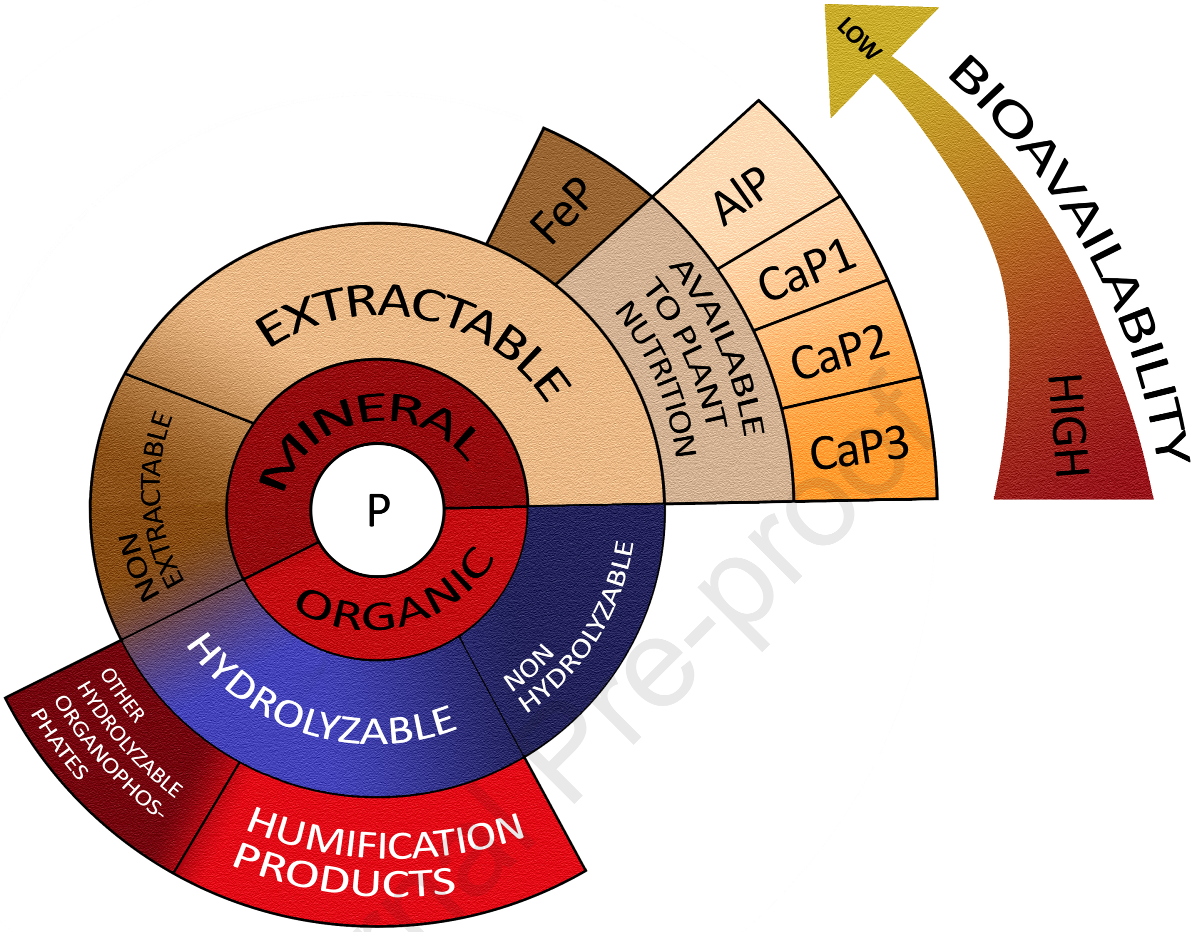

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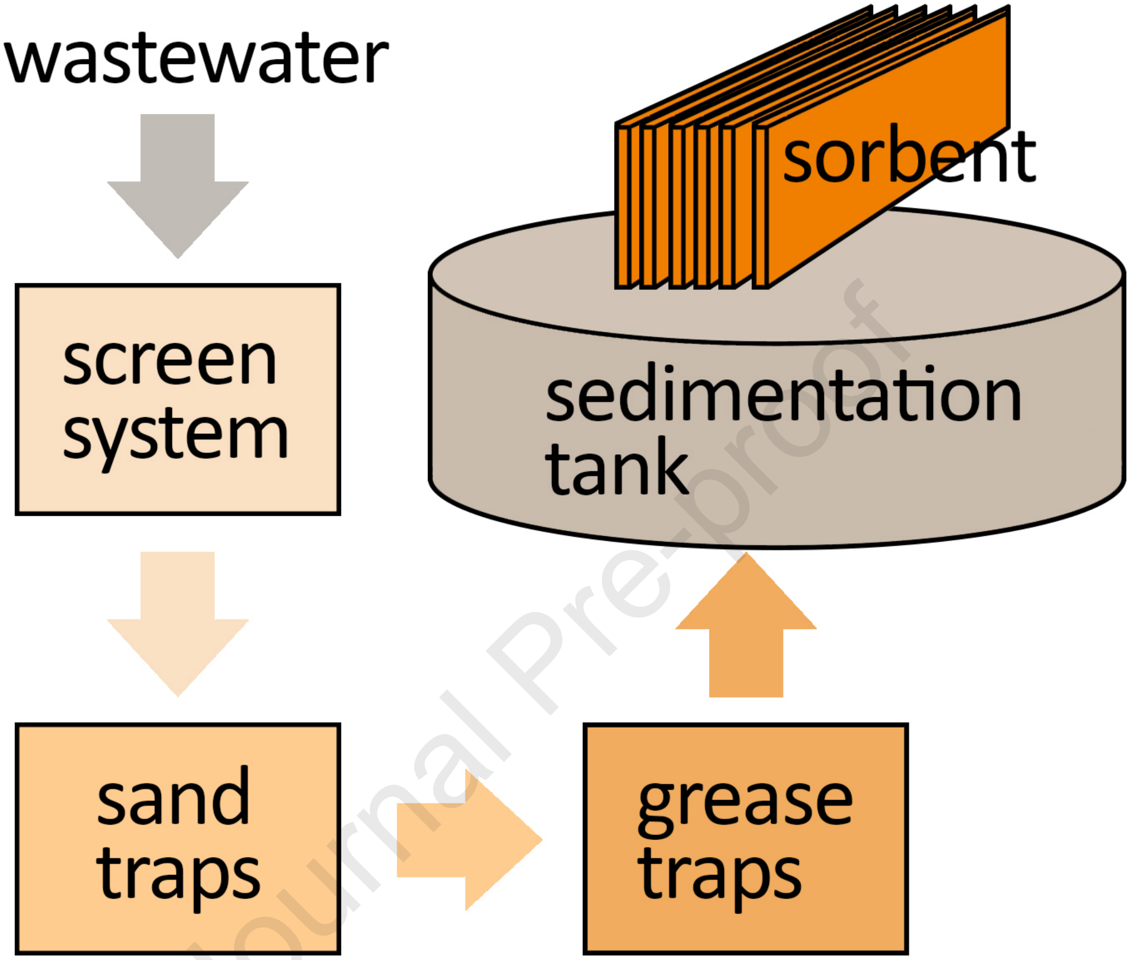

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Highlights

- Charred and calcium chloride-activated broken cellulose casings are used for phosphates sorption
- Technology cost is low since it does not require external energy and reactant cost is irrelevant
- Bioavailability of captured phosphorus is high in comparison with struvite

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Declaration of Interest Statement

Authors declare no conflict of interest.

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