

## UHI Research Database pdf download summary

### **From molecular to large-scale phosphorous recovery from wastewater using cost-effective adsorbents**

Pap, Sabolc; Turk Sekulic, Maja; Bremner, Barbara; Taggart, Mark A.

*Published in:*

Integrated and Hybrid Process Technology for Water and Wastewater Treatment

*Publication date:*

2021

*Publisher rights:*

Copyright © 2021 Elsevier Inc. All rights reserved.

*The re-use license for this item is:*

CC BY-NC-ND

*The Document Version you have downloaded here is:*

Peer reviewed version

*The final published version is available direct from the publisher website at:*  
[10.1016/B978-0-12-823031-2.00025-2](https://doi.org/10.1016/B978-0-12-823031-2.00025-2)

### **[Link to author version on UHI Research Database](#)**

*Citation for published version (APA):*

Pap, S., Turk Sekulic, M., Bremner, B., & Taggart, M. A. (2021). From molecular to large-scale phosphorous recovery from wastewater using cost-effective adsorbents: An integrated approach. In *Integrated and Hybrid Process Technology for Water and Wastewater Treatment* (pp. 61-85). Elsevier. <https://doi.org/10.1016/B978-0-12-823031-2.00025-2>

#### **General rights**

Copyright and moral rights for the publications made accessible in the UHI Research Database are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights:

- 1) Users may download and print one copy of any publication from the UHI Research Database for the purpose of private study or research.
- 2) You may not further distribute the material or use it for any profit-making activity or commercial gain
- 3) You may freely distribute the URL identifying the publication in the UHI Research Database

#### **Take down policy**

If you believe that this document breaches copyright please contact us at [RO@uhi.ac.uk](mailto:RO@uhi.ac.uk) providing details; we will remove access to the work immediately and investigate your claim.

1     **From molecular to large-scale phosphorus recovery from wastewater using**  
2                     **cost-effective adsorbents: an integrated approach**

3             Sabolc Pap<sup>a,b</sup>, Maja Turk Sekulic<sup>b</sup>, Barbara Bremner<sup>a</sup>, Mark A. Taggart<sup>a</sup>

4             <sup>a</sup>*Environmental Research Institute, North Highland College, University of the*  
5                     *Highlands and Islands, Castle Street, Thurso, KW14 7JD, UK*

6             <sup>b</sup>*University of Novi Sad, Faculty of Technical Sciences, Department of Environmental*  
7             *Engineering and Occupational Safety and Health, Trg Dositeja Obradovića 6, 21 000*  
8                     *Novi Sad, Serbia*

9     **Abstract**

10    Phosphorus (P) recovery from wastewater will become increasingly vital in the future  
11    in terms of the protection of valuable freshwater resources (i.e., from eutrophication)  
12    and due to rapidly dwindling terrestrial rock phosphate stocks. Effective management  
13    of P as a critical resource will require new integrated approaches and techniques to  
14    efficiently recover P from wastewater (liquid phase), ideally in a form that can be  
15    readily used in agriculture for fertiliser. This chapter will present a comparative review  
16    of the performance of adsorbents, adsorption mechanisms, desorption and P plant  
17    availability potential regarding cost-effective adsorbents synthesised within the  
18    principles of a more 'circular economy'. In addition, considerations regarding scale-up,  
19    technique costs and legislative perspectives will be explored with respect to large-  
20    scale P recovery systems. Finally, to encourage further applied P-recovery based  
21    research, several adsorption case studies at pilot-, full- and large-scale using  
22    integrated-hybrid P removal systems (e.g., membrane/adsorbent reactors, biological  
23    nutrient removal with tertiary reactive media adsorption, algal hybrid processes) will  
24    be highlighted, while noting key knowledge gaps and future priorities in this field.

## 25 **Keywords**

26 Wastewater treatment; Adsorption; Critical resource management; Secondary P  
27 fertiliser; Circular economy; Nutrient recovery; Integrated P removal; Hybrid  
28 processes.

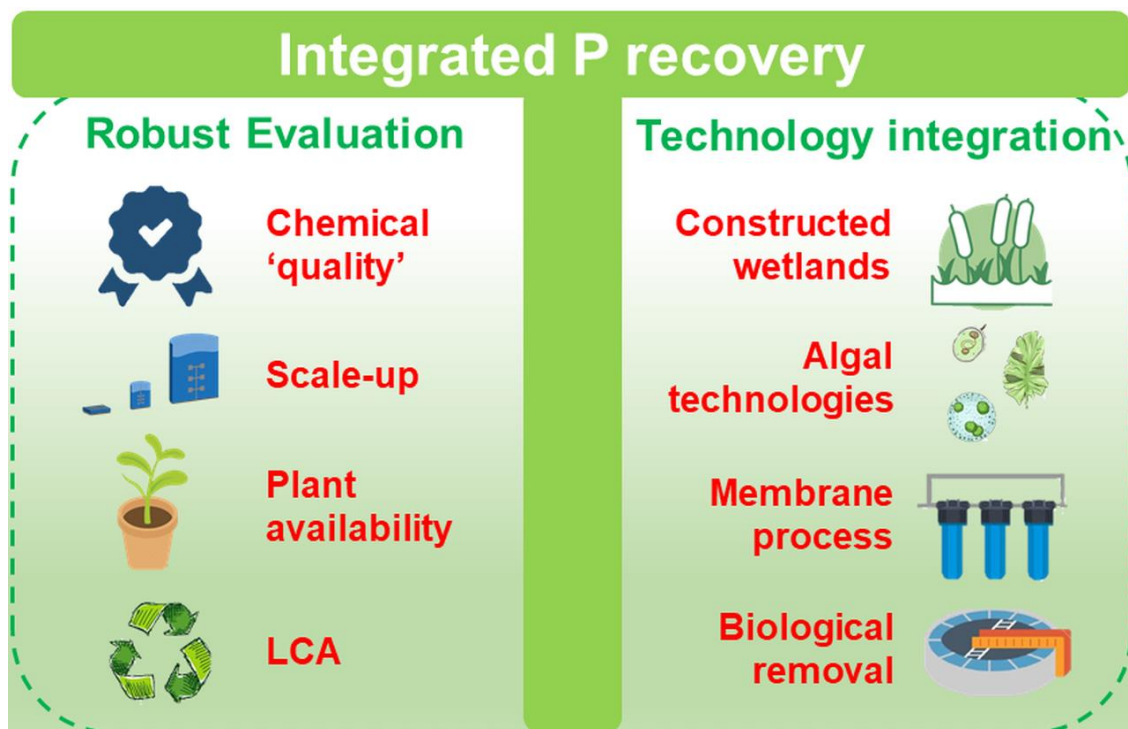
## 29 **Introduction**

30 Phosphorus (P) is an essential element within agriculture (as a key fertiliser  
31 component) and within other industries (i.e., food, metallurgical and chemical). The  
32 dominant source of terrestrial P (i.e., for fertilisers) comes from rapidly dwindling  
33 terrestrial rock phosphate reserves (Ehmann, Bach, Laopeamthong, Bilbao, &  
34 Lewandowski, 2017). Over the last 10 years, the global price of rock phosphate has  
35 fluctuated by ~800% (~\$50/t to ~\$400/t) and is expected to increase exponentially in  
36 the next 20 years (Shepherd, Kleemann, et al., 2016). Schröder et al. (2011) estimated  
37 that by 2035, global P demand will exceed supply. This challenge could be mitigated  
38 (at least in part) by greater use and recovery of P from various waste streams (e.g.,  
39 sewage sludge, solid waste, wastewater), however in many countries (i.e., in  
40 European Union - EU) this practice is restricted by legislation due to potential  
41 environmental risks posed by organic/inorganic pollutants and pathogens which may  
42 be present. Shepherd et al. (2016b) described the paradoxical nature of this problem  
43 whereby both a problematic scarcity and a detrimental profusion of P exists in different  
44 parts of the same system. In other words, P loss exists within all parts of human  
45 society, and finding solutions to better recycle/recover (within the same system) holds  
46 the answer.

47 Municipal wastewater is a promising and viable source of P. Its recovery would help  
48 to re-establish a more 'circular economy'; to extract maximum value from waste and

49 help to enhance resource consumption (Lukas Egle, Rechberger, & Zessner, 2015).  
50 Within this foundation, a new model in wastewater treatment could be established,  
51 with so called '*waste to resource*' or '*waste to crop*' becoming the norm. While the  
52 wastewater solid phase (e.g., sludge and sludge ashes) generally holds much higher  
53 P (which can be extracted through bioleaching, wet-chemical extraction or thermal  
54 hydrolysis), significant recent work has focused on developing novel technologies to  
55 exploit the liquid phase (Chrispim, Scholz, & Nolasco, 2019). This approach would  
56 help address often strict P environmental discharge requirements (i.e., 0.05 and 0.01  
57 mg P/L discharge limits for sensitive lakes, rivers or reservoirs in EU, USA, Canada,  
58 Australia (Solovchenko, Verschoor, Jablonowski, & Nedbal, 2016)) and help address  
59 P scarcity (Loganathan, Vigneswaran, Kandasamy, & Bolan, 2014). Different physico-  
60 chemical and biological methods have been applied to remove aqueous P, but many  
61 have certain limitations: i.e., are effective only at high P concentrations (biological  
62 methods), demonstrate low P selectivity (adsorption), involve large amounts of  
63 additional chemicals (chemical precipitation) or involve high capital, operational and  
64 energy costs (electrodialysis and membrane processes) (Vikrant et al., 2018). Of  
65 these, adsorption is often considered to be a cost-effective and efficient option  
66 because of the ease of process operation, simplicity of design, absence of additional  
67 waste production, economics and the capability to remove P even at low  
68 concentrations (Pap, Kirk, Bremner, Turk Sekulic, et al., 2020). Additionally, recovery  
69 of P through adsorption onto other waste materials or onto their activated forms (e.g.,  
70 biochars, functionalised materials) may provide additional benefits. Ideally, this  
71 process would involve the generation of a value-added P-rich product, low in other  
72 undesirable adsorbed contaminants. In creating such an adsorbent/product, potential  
73 would then exist to use this directly as a secondary P fertiliser and/or soil amendment

74 product. However, adsorption based P recovery needs integrated evaluation which  
75 considers multiple aspects, not least: the feasibility of moving from bench-scale to full  
76 scale implementation; plant availability of recovered P; the chemical/environmental  
77 'quality' (safety) of the saturated adsorbent/product; and the environmental, logistical  
78 and economic reality of transitioning these new products into the market economy (i.e.,  
79 implementation of Life-cycle assessment (LCA) and other tools). Further, adsorption  
80 alone will not be the only process at a wastewater treatment plant (WWTP), and there  
81 will likely need to be integrated connections between technologies. A better  
82 understanding of how to best integrate adsorption processes with other treatment  
83 techniques (to achieve the highest total P recovery/removal and create a clean P-rich  
84 product) is therefore crucial. Fig. 1 shows how an integrated set of treatment options  
85 also needs to be linked to a set of feasibility considerations to achieve integrated P  
86 recovery.



87

88 **Fig. 1.** Integrated P-recovery – schematic expressing how multiple treatment options  
89 potentially need to be linked to a set of key feasibility considerations to achieve  
90 sustainable integrated P recovery.

### 91 **Low-cost adsorbents for P recovery from wastewater**

92 In recent years, numerous adsorbents have been considered for their potential to  
93 remove P from wastewater, including: iron, aluminium, zirconium and rare earth metal  
94 oxides, hydroxides and oxyhydroxides (R. Liu et al., 2018; L. Wang et al., 2019),  
95 zerovalent iron (Bhattacharjee, Darwish, & Shanableh, 2020), calcium and  
96 magnesium carbonates and hydroxides (Loganathan et al., 2014), agricultural and  
97 industrial by-products (Muisa, Nhapi, Ruziwa, & Manyuchi, 2020), functionalised clay  
98 materials (Huang, Zhang, & Li, 2017), layered double hydroxides (LDH) (Bacelo,  
99 Pintor, Santos, Boaventura, & Botelho, 2020; Loganathan et al., 2014), polymers  
100 (Bacelo et al., 2020), anion-exchange resins (Song & Li, 2019), functionalised biochars  
101 and activated carbons (Vikrant et al., 2018; Yang et al., 2020; Yin, Zhang, Wang, &  
102 Zhao, 2017). Some of these showed very high adsorption capacity, relatively high  
103 selectivity, and excellent stability. However, the aforementioned adsorbents still had  
104 limitations in terms of their application – especially in terms of their production and  
105 implementation costs. Suresh Kumar et al. (2019) defined three important factors  
106 which governed the cost of P removal and recovery through adsorption. These were:  
107 (I) the adsorbent cost, (II) the practical loading possible (i.e., adsorption capacity within  
108 real (not ‘idealised’ lab-based) environmental conditions), and (III) the cost of  
109 regeneration. From the P recovery perspective, the final point (the regeneration cost)  
110 can be excluded assuming the P-loaded adsorbent could be simply used directly, i.e.,  
111 as a fertiliser/soil amendment.

112 Among these factors, adsorbent cost can be considered the most important – which  
113 in turn, is governed by the precursors/chemicals used to create the adsorbent and the  
114 number of synthesis steps needed (Suresh Kumar et al., 2018). Three different  
115 categories could be proposed: i.e., *low cost* ( $\leq$ \$1000/t); *intermediate cost* (between  
116 \$3000-6000/t); *high cost* (between \$15000-20000/t) (Suresh Kumar et al., 2019). Of  
117 the afore mentioned adsorbents, only the calcium and magnesium-based waste  
118 materials, agricultural and industrial by-products, layered double hydroxides and  
119 biochars would belong to the low-cost category (based on production price). From  
120 these, biochars and various organic waste/by-products may show the highest potential  
121 for P recovery (see Table 1) with the added benefit of subsequent land utilisation (M.  
122 Zhang et al., 2020). Their physical-chemical properties (often with only minor  
123 modification/functionalisation to improve affinity toward P) would lend them (if low in  
124 other adsorbed contaminants) toward being re-used as P-enriched soil  
125 improver/fertiliser material (Tan, Lin, Ji, & Rainey, 2017; Yu et al., 2019). Recent  
126 studies have reported that converting existing agricultural residues and wastes into  
127 biochar may be a promising approach to sustainable crop management, maintaining  
128 nutrient availability and soil conservation (Y. Dai, Wang, Lu, Yan, & Yu, 2020). By way  
129 of example, Fig. 2 shows how waste brush from tree felling (undertaken in this case  
130 for peatland restoration) in Scotland could be used as a precursor for biochar  
131 production and the subsequent potential creation of a P-enriched fertiliser and/or soil  
132 C stabiliser.



133

134 **Fig. 2.** ‘Circular economy’ based approach – involving the utilisation of waste wood  
 135 brush (created following tree felling during peatland restoration) to create a biochar  
 136 that could then be P-enriched and used as a fertiliser in new forestry (or remain as a  
 137 soil C stabiliser)

138 Adsorption capacity, as the second key important factor in P removal/recovery cost, is  
 139 a function of adsorbent characteristics (i.e., surface chemistry and area), as well as  
 140 the physico-chemical characteristics of the liquid phase/wastewater (i.e., pH,  
 141 concentration of P and presence of other competing ions/molecules) (Bacelo et al.,  
 142 2020). Additionally, interaction mechanisms during adsorption greatly affect  
 143 adsorption performance, and therefore must be taken into consideration. Interaction  
 144 mechanisms between adsorbents and P are typically categorised as: *surface*  
 145 *interactions* which include hydrogen bonding, electrostatic attraction (outer-sphere  
 146 complexation) and ligand exchange (inner-sphere complexation); *surface*  
 147 *precipitation*; and *shape complementarity and pore filling by diffusion* (Bacelo et al.,  
 148 2020; Loganathan et al., 2014; Wu, Wan, Zhang, Pan, & Lo, 2020; Yang et al., 2020).



149 Adsorption performance alongside corresponding P-removal mechanisms for several  
150 low-cost adsorbents (reported in the literature) are listed in Table 1 (an important factor  
151 in creating this Table was consideration of their applicability in real wastewater  
152 treatment systems). The two most utilised wastewater streams for P recovery noted  
153 were various agricultural waste effluents and secondary treated municipal wastewater  
154 (STWW). For example, He et al. (2017) achieved high P recovery from biogas slurry,  
155 with 220 mg of P recovered per g of adsorbent used (220 mg P/g), as a maximum  
156 adsorption capacity onto Fe-doped biochar made from corn straw. The biochar  
157 interacted with  $\text{H}_2\text{PO}_4^-$ ,  $\text{HPO}_4^{2-}$  and  $\text{PO}_4^{3-}$  mainly through the formation of inner-  
158 sphere complexes within the coordination sphere of Fe(III). Moreover, a large number  
159 of hydroxyl groups encouraged surface reactions with P through hydrogen-bonding.  
160 Zheng et al. (2019) used STWW in batch and column adsorption experiments and  
161 results showed that an engineered biochar effectively removed P (8.34 mg P/L) with  
162 relatively fast kinetics (4 h), mainly through formation of outer-sphere complexes with  
163 positively charged functional groups. Successful adsorption of P was also achieved  
164 onto biochar (using an acid-extract from incinerated sewage sludge) which was mainly  
165 due to Ca-P and Mg-P precipitation (Fang et al., 2020). Liu et al. (2020) investigated  
166 a Mg-laden biochar (obtained from wood waste), to recover P from hydrolysed urine  
167 which was controlled by surface interactions and precipitation processes. Table 1 also  
168 highlights the diversity in precursor selection for adsorbent synthesis. Despite a now  
169 growing body of literature on P adsorption and recovery, many of these low-cost  
170 adsorbents would still benefit from further development and improvement (i.e., to  
171 achieve higher P selectivity). Work is also needed to ensure their environmental  
172 safety/low-toxicity (i.e., if they were to be re-used as fertilisers), to quantify P

- 173 availability/desorption (from the saturated adsorbent), and to assess their practical
- 174 efficacy (from a cost analysis perspective).

175 **Table 1**

176 Phosphorus adsorption capacities, wastewater effluents used, and governing adsorption mechanism reported in the literature using various biochars and  
 177 different organic/inorganic waste/by-products.

<b>Adsorbent</b>	<b>Adsorption capacity (mg P/g)</b>	<b>Wastewater type</b>	<b>Adsorption mechanisms</b>	<b>Reference</b>
Biochar from crab shell	11.59	Biogas effluent of swine manure	Ca-P precipitation	(L. Dai et al., 2017)
Biochar from corn straw	220	Biogas slurry water	Inner-sphere complexes through Fe Hydrogen bonding	(He et al., 2017)
Biochars from wood, corncobs, rice husks and sawdust	5.41 - 7.67	Anaerobically digested liquid swine manure	Electrostatically attracted outer-sphere complexes Inner-sphere complexes with cations such as Ca, Mg, Al and Fe	(Kizito, Luo, et al., 2017)
Calcined waste eggshell	10.5	Leached solution form dewatered sludge	Ca-P precipitation	(Panagiotou et al., 2018)
Calcined waste eggshell	22.3	Real wastewater effluent	Ca-P precipitation	(Oliveira et al., 2015)
Thermally treated gastropod shell	3	Aquaculture wastewater	Formation of outer-sphere complexes Ca-P precipitation	(Oladoja, Adelagun, Ahmad, & Ololade, 2015)

Zirconium-loaded soybean residue (okara)	16.43	Real municipal wastewater	Inner-sphere complexes through Zr	(Nguyen et al., 2015)
Ground water treatment plant sludge	41.67	Secondary wastewater	Inner-sphere complexes through Fe and Al Formation of outer-sphere complexes	(Bal Krishna, Aryal, & Jansen, 2016)
Biochar from iron-rich sludge	1.84	Liquid phase of anaerobic digestate	Inner-sphere complexes through Fe Formation of outer-sphere complexes	(H. Wang et al., 2020)
Biochar from hickory wood chips	8.34	Secondary treated municipal wastewater	Formation of outer-sphere complexes	(Zheng et al., 2019)
Fe(III)-doped chitosan	10.2	Secondary treated municipal wastewater	Inner-sphere complexes through Fe Formation of outer-sphere complexes	(B. Zhang, Chen, Feng, & Zhang, 2018)
Black liquor-derived calcium-activated biochar	n.a.	Real wastewater effluent	Ca-P precipitation Inner-sphere complexes with cations	(X. Liu, Shen, Smith, & Qi, 2019)
Biochars from wood waste	180	Hydrolysed urine	Mg-P precipitation	(J. Liu et al., 2020)
Mg/Ca modified biochars from peanut shells	129.79	Acid-extract of incinerated sewage sludge ash	Ca-P and Mg-P precipitation	(L. Fang et al., 2020)
Low-temperature activated crab carapace	21.56	Secondary treated municipal wastewater	Inner- and outer-sphere complexation Ca-P precipitation	(Pap, Kirk, Bremner, Sekulic, et al., 2020)
Ferric oxide hydrate/biochar composite	51.71–56.15	Swine manure	Inner-sphere complexes through Fe Hydrogen bonding	(T. Zhang et al., 2018)

La-doped biochars derived from lignocellulosic wastes	36.06	Secondary treated municipal wastewater	Inner-sphere complexes through La Formation of outer-sphere complexes	(Q. Xu et al., 2019)
Biochar from microwave pyrolysis of rice husk	0.071	Secondary treated municipal wastewater	Hydrogen bonding	(Shukla, Sahoo, & Remya, 2019)
Chinese medicinal herbal residue and spent <i>Pleurotus ostreatus</i> substrate	63.41	Swine wastewater	Inner-sphere complexes Formation of outer-sphere complexes Precipitation	(Feng et al., 2020)
Bauxite residue	0.27	Two agricultural waters of low (forest run-off) and high (dairy soiled water) P content	Inner-sphere complexes through Fe and Al Formation of outer-sphere complexes	(Cusack et al., 2019)
Thermally treated seagrass residues	30.21	Supernatant of anaerobic digester and the liquid extracted from anaerobic dewatered sludge	Inner-sphere complexation Precipitation	(Photiou, Koutsokeras, & Constantinides, 2021)
Sun coral powder	9.59	Secondary treated municipal wastewater	Ca-P precipitation	(Vianna, Marques, & Bertolino, 2016)
Mg modified corn biochar	239	Swine wastewater	Mg-P precipitation	(C. Fang, Zhang, Li, Jiang, & Wang, 2014)
La modified platanus ball fiber biochar	148.11	Real wastewater effluent	Inner-sphere complexes through La Formation of outer-sphere complexes	(Jia, Zeng, Xu, Li, & Peng, 2020)

179 **Desorption from saturated adsorbents and P plant availability**

180 Whilst strong interactions and high affinities for P are vital for P adsorption from  
 181 wastewater, they may not be ideal for subsequent fertiliser re-use. To assess the  
 182 elution of P from saturated adsorbents (and soil-P bioavailability) there are many  
 183 potential test methods available - but no clear consensus on the 'optimal assessment  
 184 method'. In part, this reflects the large number of variables which can influence plant  
 185 availability of P in different soils (Shepherd, Sohi, et al., 2016). P uptake by plants  
 186 depends not only on P speciation, fractionation, and soil/adsorbent P level, but also  
 187 on whether plant roots can efficiently uptake available P.

188 A review of different P desorption and P bioavailability methods that have been applied  
 189 to various low-cost adsorbents is given in Table 2.

190 **Table 2**

191 Desorption and plant availability studies regarding adsorbed P - using biochars and different waste by-  
 192 products.

<b>Adsorbent</b>	<b>Desorption/release solution</b>	<b>P plant availability</b>	<b>Reference</b>
<i>Biochar from waste feedstocks</i>	pH 7 MOPS-buffered deionised (DI) water for 4 days	n/a	(Shepherd, Sohi, et al., 2016)
<i>Biochar from corn straw</i>	DI water, citric acid at pH 4.8, and NaOH at pH 8.8 for 24 h	n/a	(He et al., 2017)
<i>Biochars from sugarcane harvest residue</i>	0.01 M NaCl, Na <sub>2</sub> CO <sub>3</sub> and HCl for 4 days	Soil (type not defined) with 1% by wt. application rate <i>Ryegrass</i> planted for 21 days	(R. Li et al., 2016)
<i>Biochar from tomato leaves</i>	Mehlich 3 method and DI water	Seeds germination assay of grass seeds (first 13 days)	(Yao, Gao, Chen, & Yang, 2013)

<i>Mussel shell</i>	Phosphate fractionation	n/a	(Paradelo et al., 2016)
<i>Biochar from roots of Undaria pinnatifid</i>	n/a	Regular soil with 5% by volume application rate Lettuce planted for 21-30 days	(Jung, Kim, Jeong, & Ahn, 2016)
<i>Biochar from iron-rich sludge</i>	0.25 M NaOH for 6 h	Seed germination assay of grass seeds (first 10 days)	(H. Wang et al., 2020)
<i>Biochar from water hyacinth plants</i>	n/a	Maize ( <i>Zea mays L.</i> ) grown in sandy soil (Typic Torripsamment) 0.5% wt. application rate for 14 days	(Mosa, El-Ghamry, & Tolba, 2018)
<i>Biochar from pre-treated cypress sawdust</i>	DI water at pH 5.2, 7 and 9 for various times between 30 and 3600 min	n/a	(Haddad, Jellali, Jeguirim, Ben Hassen Trabelsi, & Limousy, 2018)
<i>Cerium-modified biochar from straw</i>	n/a	Soils from a rice field with 3%, w/w application rate Biochar effect on soil microbial metabolism	(H. Lu et al., 2019)
<i>Biochar from cow dung</i>	n/a	Seed germination assay of lettuce seeds (first 7 days)	(Chen, Qin, Sun, Cheng, & Shen, 2018)
<i>Biochar from hickory wood chips</i>	n/a	Seed germination assay of Mung bean (first 13 days)	(Zheng et al., 2019)
<i>Biochar from food waste</i>	n/a	Regular soil with 1% by wt. application rate Cabbage seed planted for 45 days	(Alghashm et al., 2018)
<i>Biochar from farm residues</i>	Phosphate fractionation and Olsen extraction	n/a	(Novais, Zenero,

			Tronto, Conz, & Cerri, 2018)
<i>Biochar from iron-sludge</i>	n/a	Seed germination assay of wheat seed (first 10 days)	(Xia et al., 2020)
<i>Biochar from microalgae</i>	n/a	Agricultural soil with 0.2 g/kg application rate Tomato plant planted for 30 days	(Arun, Gopinath, Vigneshwar, & Swetha, 2020)
<i>Calcined sepiolite</i>	Phosphate fractionation	Sandy loam soil with 0.5 g and 1.0 g/kg application rate Rice seeds planted for 35 days	(Hong, Ndingwan, Yoo, Lee, & Park, 2020)
<i>Bentonite modified biochar</i>	n/a	Regular soil with 0.2 g/kg application rate for 20 days	(X. An et al., 2020)
<i>Concrete-waste</i>	Calcium-acetate-lactate-extraction at pH 4 for 56 days	n/a	(dos Reis et al., 2020)
<i>Mg-enriched biochar from manure and sludge</i>	DI water, 2% citric acid and Mehlich-1 test for 4h	Oxisol (Rhodic Hapludox) with 200 mg/kg P application rate Seeds of maize planted for 21 days	(Nardis, Santana Da Silva Carneiro, Souza, Barros, & Azevedo Melo, 2020)

193 Some of the most widely used chemical extraction/desorption methods which seek to  
194 simulate 'availability' in soil environments are: the Olsen extraction, Mehlich-1 and 3  
195 extraction, sequential extraction and extraction with different mineral acids (e.g.,  
196 HNO<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub>, Aqua Regia) (H. Li, Li, Xu, & Lu, 2020). The Mehlich-1 test method was  
197 used by Yao et al. (2013) and Nardis et al. (2020) when looking at biochar. These  
198 studies both determined that ~19-20% of total P in post adsorption biochar was



199 Mehlich-1 extractable, however Mehlich-1 is an acid extractor and its capacity could  
200 be reduced in soils of high buffering capacity. Further, Novais et al. (2018) reported  
201 that the P released by the Olsen extraction (0.5 mol/L NaHCO<sub>3</sub> at pH 8.5) and distilled  
202 water from the biochar was much lower than with an acid based one (0.5 M H<sub>2</sub>SO<sub>4</sub>),  
203 which indicated poor P availability for plants in more alkali soils. Findings from these  
204 studies suggest that P-doped biochars have a high potential to be used as fertiliser in  
205 highly weathered tropical soils (more acidic conditions) where the rich organic matrix  
206 is negatively charged and has limited capacity to adsorb P. Paradelo et al. (2016) and  
207 Jiang et al. (2017) used a P fractionation method (sequential extraction) to determine  
208 which forms of P were desorbed from saturated adsorbents (mussel shell and calcium-  
209 silicate composite), these were: (i) loosely bound-P (desorbed in 0.5 M NaHCO<sub>3</sub>), (ii)  
210 alkali-soluble P (0.1 M NaOH), (iii) acidic-soluble P (0.5 M HCl), (iv) residual P (6 M  
211 HCl). In both studies, approximately 90% of adsorbed P was recovered by the third  
212 step (0.5 M HCl solution) which suggested that predominantly acid-soluble P was  
213 present. Another advantage of the materials with a high P content bonded in their  
214 structure (shells, carapace, certain biochars), is that in acidic environment part of the  
215 bounded P could become available. P release kinetics from pre-loaded biochar was  
216 also investigated by Haddad et al. (2018) using distilled water at different initial pH  
217 values for various contact times (between 30 and 3600 min). Results showed that the  
218 release of P was clearly a time dependent process. Additionally, in continuous  
219 desorption experiments, He et al. (2017) revealed that the P release rate from  
220 saturated biochar was relatively slow , which points to it's potential as *slow release*  
221 fertiliser (which may well be of benefit in certain scenarios).

222 Rather than solely relying on desorption experiments, some studies have utilised seed  
223 germination assays and pot trials to gain further information about P plant availability

224 from saturated adsorbents. Pot trials are clearly more realistic in terms of determining  
225 P availability and solubility in soil – however, results may vary markedly, depending  
226 on the plant species and soil type used (and as such, widely accepted ‘standardised’  
227 methodologies are likely still required). In a study conducted by Zheng et al. (2019),  
228 quartz sand with un-laden biochar and P-laden biochar were used as growth media  
229 for a mung bean seedling growth study. The experiment showed that P-laden biochar  
230 increased seed germination rates from 30% (sand alone) to 46.7% (sand with P-laden  
231 biochar) – indicating that P-laden biochar (created in fixed-bed column through real  
232 wastewater filtration) could be used as a plant fertiliser to improve soil fertility. An  
233 interesting approach was also used by Xia et al. (2020), who pyrolysed P-laden alkali-  
234 treated iron sludge and successfully used this to support wheat growth. Cultivation  
235 experiments consisted of an experimental group (with biochar addition at a 10% by wt.  
236 application rate and two control groups (without biochar addition). The growth of the  
237 wheat dosed with biochar was noticeable in comparison to the control groups, where  
238 P was limited, and stagnant growth was observed. The work demonstrated possible P  
239 recovery potential within the WWTP chain, where not only the produced sludge was  
240 reused, but circulation of surplus P was also achieved. During pot trials conducted by  
241 Li et al. (2016), use of a P-loaded biochar also resulted in much greater plant growth  
242 height when compared to controls (without any supplement). Above-ground biomass  
243 for the P-loaded biochar treatment was 1.124 g/pot (dry weight of ryegrass), which  
244 was significantly larger than for controls (0.367 g/pot). Jung et al. (2016) further  
245 showed that for 21 day pot trials, plant growth rate was faster (with a larger overall  
246 plant yield) in soil mixed with biochar. The limitation of these studies is the lack of more  
247 detailed research on long term field application including the changes in soil chemical  
248 properties, soil microbial activity, and population dynamics with different soil types.

249 More broadly, the influence and benefit of biochar (or other P-enriched secondary  
250 materials) on soil P availability is still a somewhat debated issue. Commonly,  
251 increased soil P availability is documented in acidic soils, however, biochar can  
252 instead reduce P availability in neutral and alkaline soils due to P fixation/ binding (H.  
253 Lu et al., 2019). Ultimately, the net effect of P-enriched secondary materials on P  
254 availability in soil-plant systems will depend on a complex equation based on multiple  
255 sorption mechanisms that are at play - within the soil and the sorbent particles,  
256 alongside differences due to soil type, plant species and root uptake efficiency (among  
257 other factors) (M. Xu et al., 2019).

#### 258 **Scale-up approaches (pilot tests), cost viability and legislative perspectives**

259 Efforts to upscale P recovery processes using adsorption in pilot-scale applications,  
260 with fixed-bed columns and with real wastewaters are increasingly occurring. Full  
261 scale-up of adsorbent production and P-removal is however still in its infancy – and  
262 there is still some way to go before such processes are widely embedded (i.e., in  
263 WWTW's). In support of this, Benafqir et al. (2019) undertook a Process Capability  
264 Study (CPS) which quantified the ability of a process to perform a task with desired  
265 characteristics within well-defined tolerances. The CPS indicated that an adsorption  
266 process with hematite–titaniferous sand adsorbent was capable and stable under  
267 large-scale applications; however, limitation of CPS still exists for large-scale data.  
268 Further, Shepherd et al. (2016b) used bench-scale experimental data and simple  
269 scale-up calculations to estimate adsorber dimensions for a larger WWTP application.  
270 They additionally estimated the agricultural surface area (ha) it would be possible to  
271 fertilise with the produced P enriched material (created at the WWTP). In these  
272 estimates, a large WWTP (PE > 50000) would produce enough P enriched material

273 each year to fertilise >3200 ha of soil with 'Index 0' (a descriptive scale used for  
274 different nutrient concentrations and crop response in soil – lower the index number,  
275 lower the soil quality). Given similarities in different fixed-bed (column) process  
276 parameters such as empty bed contact time (EBCT), mass transfer zone (MTZ) and  
277 hydrodynamic characteristics between lab-scale and either pilot or full-scale systems,  
278 Jung et al. (2017) and Pap et al. (2020a) also calculated the parameters for, and  
279 simulated the performance of, a pilot-scale column system for P removal using the  
280 scale-up approach described by Worch (2012). The methodology showed good  
281 consistence in data between bench- and pilot-scale. However this mathematical tool  
282 does not allow a deeper insight into the mechanisms of the adsorption process  
283 because equilibrium relationships and kinetics are only indirectly considered, therefore  
284 only applicable under restrictive conditions, such as specific similarity criteria (Worch,  
285 2012). Ezzati et al. (2020) used a rapid small-scale column test approach to make  
286 scale-up predictions regarding P retention in large-scale filters, which may include  
287 considerable savings on: time and space required for constructing and operating the  
288 large columns; amount of influent (chemicals and water); procurement/synthesis of the  
289 adsorbent and cost of laboratory analysis of water samples. The developed model  
290 successfully described the pattern of large-scale column performance, but further  
291 model validation is required for more accurate results. An et al. (2019) took forward  
292 laboratory column experiments and theoretical scale-up values to field-scale testing  
293 using hybrid chitosan beads as adsorbents combined with dissolved air flotation  
294 process. The tests showed that the P concentration in treated effluent consistently  
295 satisfied national discharge standards (0.2 mg P/L) within the Republic of Korea.  
296 Okano et al. (2016) developed a mobile pilot-scale plant for *in-situ* examination and  
297 demonstration of P recovery from wastewater. The mobile pilot plant consisted of a

298 1000 L reactor, a self-made filtration system and ancillary equipment. Using this plant,  
299 they evaluated the ability of amorphous calcium silicate hydrates to recover P from  
300 anaerobic sludge digestion liquor. On average, approximately 80% of P was recovered  
301 (during a process involving 20 min mixing, 30 min settling, and 90 min of filtration). In  
302 order to achieve P recovery from secondary WWTP effluent, Kalaitzidou et al. (2016)  
303 investigated adsorption onto several low-cost and commercially available adsorbents  
304 at bench-scale. Based on these experiments, they then successfully constructed and  
305 operated a pilot-plant, utilising iron-manganese oxy-hydroxides (AquAsZero) identified  
306 as the 'best' adsorbent from the laboratory tests. The unit was successfully operated  
307 (for 6 adsorption-regeneration cycles) and the material recovered was considered  
308 promising as a fertiliser, due to its high P content (35.4 wt.%) and near zero content  
309 of other toxic metals. Bolton et al. (2019) developed a pilot-scale wetland to treat  
310 domestic wastewater where functionalised biochar was added to the wetland cells.  
311 During a 7-month study, the cells containing biochar consistently reduced P to lower  
312 levels (than in cells without biochar), with an average inlet P concentration of 15.5  
313 mg/L falling to < 2 mg/L. Despite these studies, most work on P adsorption reports  
314 only on bench/lab scale experiments (mostly in batch mode), and full scale-up work is  
315 still scarce. This is leading to a degree of stagnation in this field – and this 'gap' now  
316 needs to be bridged. This can only be achieved through increased demonstration of  
317 applied large scale research, alongside more support for adsorbent commercialisation  
318 via collaboration with key water quality stakeholders, industrial partners and  
319 regulators.

320 From an economic perspective, P adsorption systems should be designed to attain  
321 maximum recovery from a liquid phase, with low implementation, integration and  
322 maintenance costs. In terms of production and operating costs – systems based on

323 biochars and other low-cost adsorbents have yet to be adequately studied. The cost  
324 of any individual adsorbent reflects several factors, including the availability of the local  
325 biomass precursor, conditions required during pyrolysis/preparation, availability of  
326 reactor filters, processing requirements and lifetime issues (Vikrant et al., 2018). The  
327 production price of any low-cost adsorbent is also highly country specific. Costs will  
328 further depend on whether the adsorbent material is itself a primary product (with  
329 value), or, simply a by-product of different processes (e.g., heat and electricity  
330 production) (Mohan, Sarswat, Ok, & Pittman, 2014). The costs involved in applying a  
331 saturated P-rich adsorbent to soil are additionally important (Mohan et al., 2015).  
332 Ahmed et al. (2016) undertook a detailed review of the economic feasibility of biochar  
333 use and concluded that this depended on a range of factors - from raw material price  
334 to the efficiency of the production technology used - and a detailed (pilot plant-based)  
335 cost equation was proposed. The unit cost (\$/ton) for producing and applying biochars  
336 in North Western Europe includes the following factors: the annualised capital  
337 expenditure of pyrolysis facility (\$/y); the total annual operating expenses of pyrolysis  
338 facility (\$/y); the total annual cost of feedstock harvesting (\$/y); the total annual cost  
339 of feedstock transport (\$/y); the total annual cost of biochar transport (\$/y); the annual  
340 revenue from electricity generation (\$/y); the annual biochar production (ton/y); the  
341 unit cost of biochar application (\$/ton). Additional cost might be required if feedstocks  
342 require intensive cleaning.

343 According to a recent survey of biochar vendors by the International Biochar Initiative  
344 (IBI), global biochar prices range from \$80/t to \$1448/t (Y. Dai et al., 2020). Photiou et  
345 al. (2021) considered this from another angle, whereby they took the cost of collection  
346 and disposal (~€70-80/t) of adsorbent precursors (i.e., seagrass residue) and  
347 calculated the net profit (~€5-20/t) for a company that may switch this around to an

348 investment in P adsorbent production. Ajmal et al. (2020) and Maroušek et al. (2020)  
349 further compared the economics of unmodified vs modified biochars. It was concluded  
350 that modified materials were likely more economical than unmodified ones. While  
351 modification increases production costs, operation costs reduced since much higher  
352 P recovery potential existed with modified biochars. Li et al. (2020) compared the  
353 economics of triple-superphosphate (TS) fertiliser and P-rich biochar. According to  
354 their study, the price of TSP was ~\$2.88/kg, while the cost to create 1 kg of P-laden  
355 biochar using maize stalk and potassium dihydrogen phosphate ( $\text{KH}_2\text{PO}_4$ ) was  
356 comparable at ~\$3.05/kg. Given that less P-laden biochar was needed (than TSP) to  
357 maintain soil P levels, they concluded that P-laden biochar could efficiently act to  
358 reduce soil P fertilisation costs. This was in part because of the slow-release nature of  
359 P laden onto biochar as well as the more homogeneous P distribution that occurred  
360 under P-laden biochar treatments. Bashar et al. (2018) went one step further, and  
361 evaluated several emerging high performance P removal/recovery technologies: i.e.,  
362 the Modified University of Cape Town process (H. Zhang, Wang, Xiao, Yang, & Zhang,  
363 2009), Bardenpho process (Ashrafi, Mehrabani Zeinabad, Borghei, Torresi, & Muñoz  
364 Sierra, 2019), membrane bioreactors (H. Zhang et al., 2009), Integrated Fixed-Film  
365 Activated Sludge Systems with Enhanced Biological Phosphorus Removal (Bai,  
366 Zhang, Quan, & Chen, 2015), struvite recovery and tertiary reactive media filtration.  
367 Their results showed that the Modified University of Cape Town biological nutrient  
368 removal system (with tertiary reactive media filtration/adsorption) was one of the most  
369 cost effective configurations (at ~\$97/kg of P removed). Desmidt et al. (2015) carried  
370 out an economic feasibility study regarding the integrated adsorption/precipitation  
371 (struvite) process. They concluded that the largest operational cost for struvite  
372 precipitation related to the addition of a chemical Mg/Ca source. Therefore, the cost-

373 benefit of P recovery could be significantly improved if waste from a Mg/Ca industry  
374 (or an Mg/Ca rich adsorbent) could be used as a source.

375 In terms of P levels in the environment – and specifically in freshwater receiving P rich  
376 discharges – there is no universal consensus on the concentration of P required to  
377 entirely prevent eutrophication, although most studies consider a concentration > 0.1  
378 mg P/L to be too high (Suresh Kumar et al., 2019). The United States Environmental  
379 Protection Agency (USEPA) suggests a mean total P concentration of 0.01 mg P/L in  
380 its nutrient criteria guidelines for lakes and reservoirs (Rahman, Eckelman, Onnis-  
381 Hayden, & Gu, 2016). USEPA discharge permit limits can typically vary between 0.1  
382 mg P/L up to 2 mg P/L in different states and depending on the sensitivity of the  
383 receiving water body. In the European Union (EU), standards for water quality are set  
384 by the Water Framework Directive (WFD), and the permissible P discharge value from  
385 1 to 0.1 mg P/L was recently tightened (Kong et al., 2019). It must be noted that these  
386 effluent values serve as a guideline, since the risk posed by P discharged into the  
387 environment will not only depend on effluent concentration but also on the  
388 size/sensitivity of the receiving water body. Effluent regulations in individual EU  
389 member states tend to be 1 - 2 mg P/L, often depending on the population served by  
390 a WWTP (population equivalence), with more stringent values set in more sensitive  
391 areas (Suresh Kumar et al., 2019). China has municipal wastewater discharge limits  
392 ranging from 0.5 to 1 mg P/L (W. W. Li, Sheng, Zeng, Liu, & Yu, 2012).

393 Beyond P removal, wastewater discharge operations that recover P also need to  
394 consider market regulations, alongside health and environment protection laws. Often,  
395 lengthy authorisation processes to install systems (e.g., environmental impact  
396 assessment) and then recover P are required. Legislative harmonisation, which  
397 encompasses the inclusion of recycled P into existing fertiliser regulations, and



398 supports new operators in this field, would speed up market penetration of novel  
399 technologies, reduce P losses and safeguard European quality standards (L. Egle,  
400 Rechberger, Krampe, & Zessner, 2016). Hukari et al. (2016) summarised the EU-  
401 legislation governing P recovery processes and market entry. These laws can be  
402 divided into three sections: (i) governing recovery and recycling operations, (ii)  
403 material type and (iii) market placement. Rules regarding the use of fertilisers were  
404 partially harmonised by European Commission (EC) Regulation No 2003/2003, which  
405 covers (almost exclusively), inorganic material-based fertilisers, extracted from mines  
406 or chemically produced (Hidalgo, Corona, & Martín-Marroquín, 2020). However,  
407 following Circular Economy Package (CEP) principles, the new EU Fertilising Products  
408 Regulations (EC No 2019/1009) aim to boost large-scale production of fertiliser from  
409 domestic organic or secondary raw materials. It also seeks to harmonise conditions to  
410 make fertilisers made from recycled or organic materials more available throughout  
411 the internal market (Nedelciu, Ragnarsdóttir, & Stjernquist, 2019). At the same time,  
412 EU-wide limits on contaminants (i.e., heavy metals and organic pollutants) in  
413 fertilisers/secondary products will be imposed (Verbeeck, Salaets, & Smolders, 2020).  
414 Further, in 2016, the EC nominated the STRUBIAS (STRUvite, Blochar, AShes) group  
415 to determine how recycled P fertilisers should become accepted for the fertiliser  
416 market in the EU. The group recently published its final report and various criteria are  
417 now expected to be adopted in the first quarter of 2021, which would be before the  
418 date of entry into application of the new EU Fertilising Products Regulations  
419 (Chojnacka, Moustakas, & Witek-Krowiak, 2020).

#### 420 **Case studies regarding integrated-hybrid P removal systems**

421 Options to recover P occur at multiple points within WWTPs, however, the complexity  
422 of recovery and removal sometimes requires an integrated approach - whereby

423 different technologies are combined to attain much higher efficiency. Egle et al. (2015)  
 424 and Bunce et al. (2018) gave compressive overviews and descriptions of available  
 425 technologies for removing/recovering P from municipal wastewater liquid and solid  
 426 phases. About 50 technologies were identified at various levels of development (be  
 427 that industrial-, full-, pilot- or laboratory-scale). But relatively few integrated P recovery  
 428 technologies involved low-cost adsorbents (see Table 3).

429 **Table 3**

430 Integrated-hybrid P removal systems that have used biochars or different waste/by-products and metal-  
 431 oxides/hydroxides.

<b>Adsorbent</b>	<b>Integrated-hybrid P system description</b>	<b>Reference</b>
Commercial activated carbon	Combination of GAC adsorption and deep-bed filtration with coagulation	(Altmann, Rehfeld, Träder, Sperlich, & Jekel, 2016)
Hydrous ferric oxide coated sand	Modified University of Cape Town biological nutrient removal with tertiary reactive media filtration/adsorption	(Bashar et al., 2018)
Chitosan beads	Adsorber containing chitosan beads following coagulation and DAF processes	(B. An et al., 2019)
Calcium salt	Hybrid precipitation–microfiltration process	(N. C. Lu & Liu, 2010)
Zirconium sulphate surfactant micelle mesostructure	Ultrafiltration membrane (polysulfone) embedded with zirconium sulphate for adsorption	(Furuya et al., 2017)
Iron oxide/hydroxide-based agglomerated adsorbent	Hybrid adsorption–ultrafiltration process	(Zelmanov & Semiat, 2014)
Metal oxide coated beads	Membrane bioreactor filtration and adsorption	(Park, Kwak, Mahardika, Mameda, & Choo, 2017)
Metal-Zr hydroxide	Membrane bioreactor filtration and adsorption	(Johir et al., 2016)

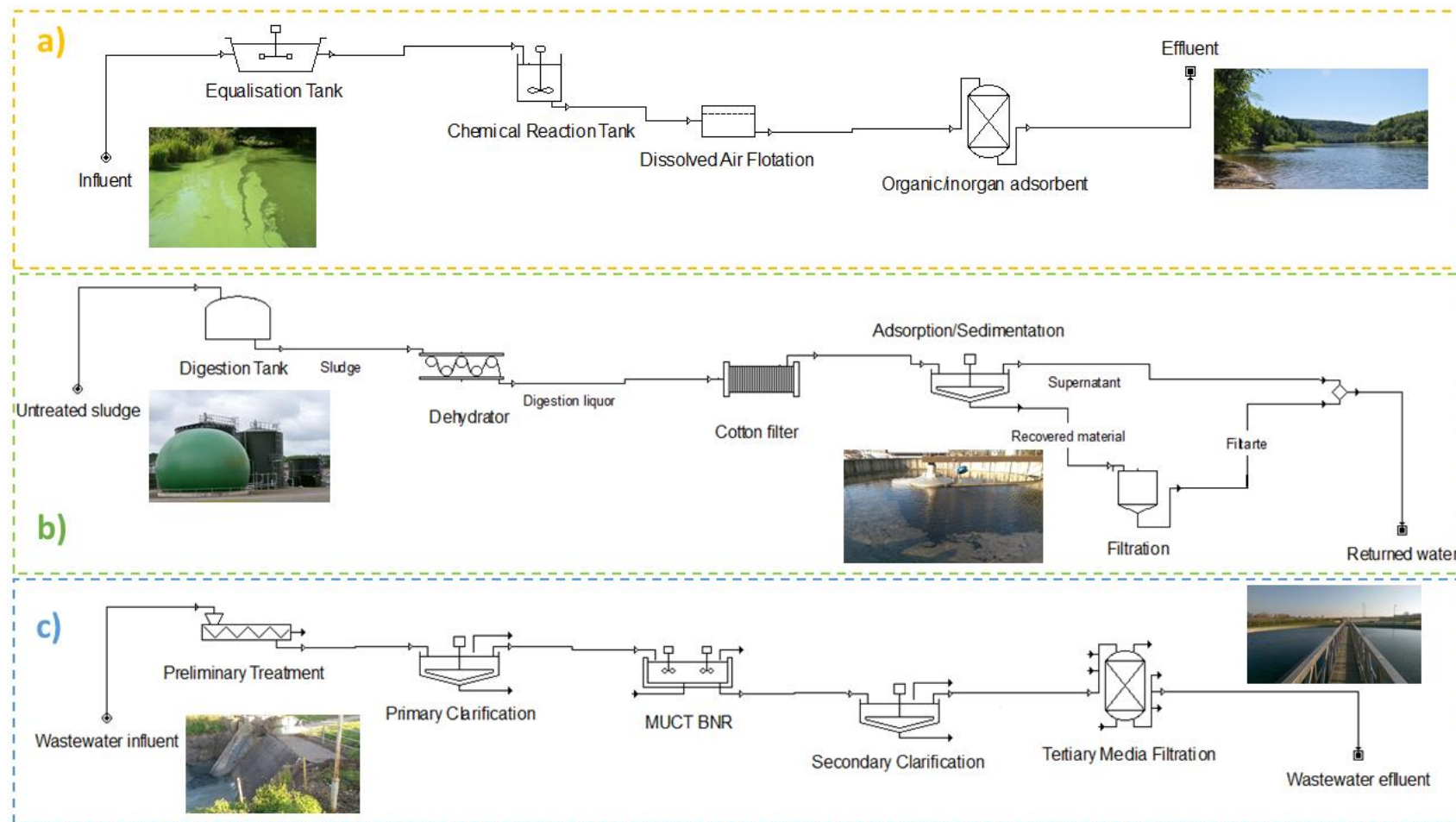
Steel slag	Biologically and chemically mediated simultaneous adsorption and precipitation	(Pratt, Parsons, Soares, & Martin, 2012)
Biochar	Algal based P recovery system with transformation of P-rich algae biomass to biochar	(Cole, Paul, de Nys, & Roberts, 2017)
Biochar	Biotransformation of P to biochar from enhanced biological phosphorus removal	(Qian, Lu, Soh, Webster, & Zhou, 2020; Qian, Wang, Le, & Zhou, 2019)
Biochar from corn cob and wood	Biochar-packed vertical flow constructed wetland columns	(Kizito, Lv, et al., 2017)
Biochar from bamboo	Electrolysis-integrated horizontal subsurface-flow constructed wetland amended with biochar	(Gao et al., 2018; Ju, Wu, Zhang, & Dong, 2014)
White hard clam shells	Horizontal sub-surface flow constructed wetland with adsorption	(Nguyen et al., 2020)
Biochar	Sand media amended with biochar in constructed wetland	(de Rozari, Greenway, & El Hanandeh, 2016)
Biochar from hemp enriched with iron	Iron enriched biochar substrate in constructed wetlands	(Bolton et al., 2019)

---

432

433 Altmann et al. (2016) investigated a combination of granular activated carbon (GAC)  
434 deep-bed filtration (GAC+sand), with coagulation, as an advanced treatment step for  
435 P removal from secondary effluent. GAC adsorption was also assessed as an upper  
436 filter layer in dual-media downflow filtration (sand) and as a mono-media for an up flow  
437 filter. Both filtration concepts effectively removed P, achieving effluent concentrations  
438 of 0.1 mg P/L. Bashar et al. (2018) considered six full-scale hybrid treatment  
439 scenarios. Each configuration consisted of preliminary and primary treatment,  
440 mainstream P removal, solid phase (sludge) line and biogas recovery from the sludge.

441 In one scenario (scenario 6), a reactive media filtration step (with continuous  
442 backwash, up-flow, and a deep-bed granular media filter) was integrated into the  
443 Modified University of Cape Town (MUCT) biological nutrient removal configuration  
444 (consisting of anaerobic, primary anoxic, secondary anoxic and aerobic processes) to  
445 reduce effluent P to 0.05 mg P/L. This configuration proved to be one of the most cost-  
446 effective scenarios, which also resulted in the lowest effluent P concentration. An et  
447 al. (2019) combined adsorption (onto chitosan beads) with coagulation and dissolved  
448 air flotation (DAF) processes. In pilot tests, the resultant P concentration did not always  
449 satisfy the desired regulation limit of 0.2 mg P/L (for Republic of Korea) with  
450 coagulation and DAF use only; however, the addition of adsorption consistently  
451 reduced effluent P to < 0.2 mg P/L. Several schematic diagrams (as examples) of  
452 integrated/hybrid P recovery processes are shown in Fig. 3.



453

454 **Fig. 3.** Schematic diagrams showing integrated/hybrid P recovery processes: (a) organic/inorganic hybrid adsorbent integrated with  
 455 dissolved air flotation (B. An et al., 2019), (b) sludge digestate treatment plant developed by (Okano et al., 2016) and (c) Modified  
 456 University of Cape Towne (MUCT) biological nutrient removal (BNR) process with filtration media (Bashar et al., 2018).

457 Cole et al. (2017) used algal based P recovery (using the freshwater macroalga,  
458 *Oedogonium intermedium*) to recover P from municipal wastewater, then converted  
459 these cultivated algae into a soil ameliorant (a biochar). It has been shown that through  
460 this transformation the P held within the algae was stabilised, enabling it to be stored,  
461 transported and applied to agricultural land. A similar approach was utilised by Qian  
462 et al. (2020), where enhanced biological P removal sludge was used to produce a  
463 biochar as a potential P fertiliser. A low-temperature-steam activation method was  
464 developed to increase P availability in the biochar. This study also observed that  
465 different environmental conditions, i.e., environmental pH, ionic strength of the soil  
466 porewater and the presence of low-molecular-weight acids, had only minor or  
467 negligible effects on P-release from the biochar (Qian et al., 2019).

468 Integration of different low-cost adsorbents into constructed wetland structures is  
469 another promising approach for efficient P recovery. Kizito et al. (2017b) investigated  
470 three types of vertical flow constructed wetland columns, packed with corn cob  
471 biochar, wood biochar or gravel to recover P from anaerobic digested effluent. The  
472 biochar-packed wetland columns provided significantly higher removal of P (compared  
473 to gravel-packed columns). Better removal was explained by the larger surface area  
474 and higher porosity of the biochar, which enabled higher P adsorption and higher  
475 microbial colonisation rates. In the work by Gao et al. (2018), a pilot study using an  
476 electrolysis-integrated, biochar-amended, horizontal, subsurface-flow, constructed  
477 wetland was conducted. The electrolysis combined biochar substrate greatly  
478 enhanced P removal rates through the in-situ formation of ferric ions from a sacrificial  
479 iron anode which caused P chemical sedimentation and physical adsorption onto the  
480 iron modified biochar. Significant microbial diversity within biofilms that formed on the  
481 biochar substrate were also observed.

482 Park et al. (2017) combined membrane bioreactor filtration with adsorption. They  
483 fabricated mixed metal oxide coated beads from sulfonated polymer and tested these  
484 for P removal from membrane bioreactor effluents. The doping with metal oxides  
485 substantially enhanced adsorption rates and capacity, possibly due to increasing  
486 positively charged surfaces. After adsorption, the regenerated beads also showed  
487 higher P recovery performance than when originally used. Similar membrane  
488 adsorption hybrid systems were evaluated by Johir et al. (2016) for the removal of P  
489 from a high rate membrane bioreactor effluent. Due to low P removal by membranes,  
490 two adsorbents (an anion exchange resin and a metal-Zr hydroxide) were used for  
491 further P removal from effluent. It was found that the metal-Zr hydroxide enabled the  
492 elimination of > 85% of P from the effluent.

### 493 **Conclusions, research gaps and future perspectives**

494 At present, a wide variety of low-cost adsorbents have been successfully applied (at  
495 a variety of scales) to the removal and recovery of P from wastewater liquid phases,  
496 generally offering high removal efficiencies and capacities. Typical materials that are  
497 used include biochars (from different plant derivatives), calcium- and magnesium-  
498 based materials, and agricultural and industrial by-products. These will no-doubt  
499 continue to be used as adsorbents because of the advantages they can bring, i.e.,  
500 being low cost materials, which host a diversity of physico-chemical removal  
501 mechanisms, with the additional capacity to be re-utilised as P enriched (adsorbent  
502 based) fertilisers. In exploiting these advantages, the principals of a more circular  
503 economy can be further embedded in future society. Furthermore, nanotechnology  
504 development is now offering new horizons for P removal and recovery. This is opening  
505 up new possibilities to prepare novel, highly tuned and cheap functionalised materials.

506 Adsorbent surfaces with selected metal nanoparticles (e.g., biochars coated with  
507 oxides and hydroxides of Fe, Zr, La, etc.), could offer high P adsorption capacities  
508 alongside high P selectivity – and in turn, help recovered P materials meet future  
509 quality and regulatory standards worldwide. However, environmental and biological  
510 impacts on soil and plants (and potential accumulation within food chains) remains to  
511 be fully investigated.

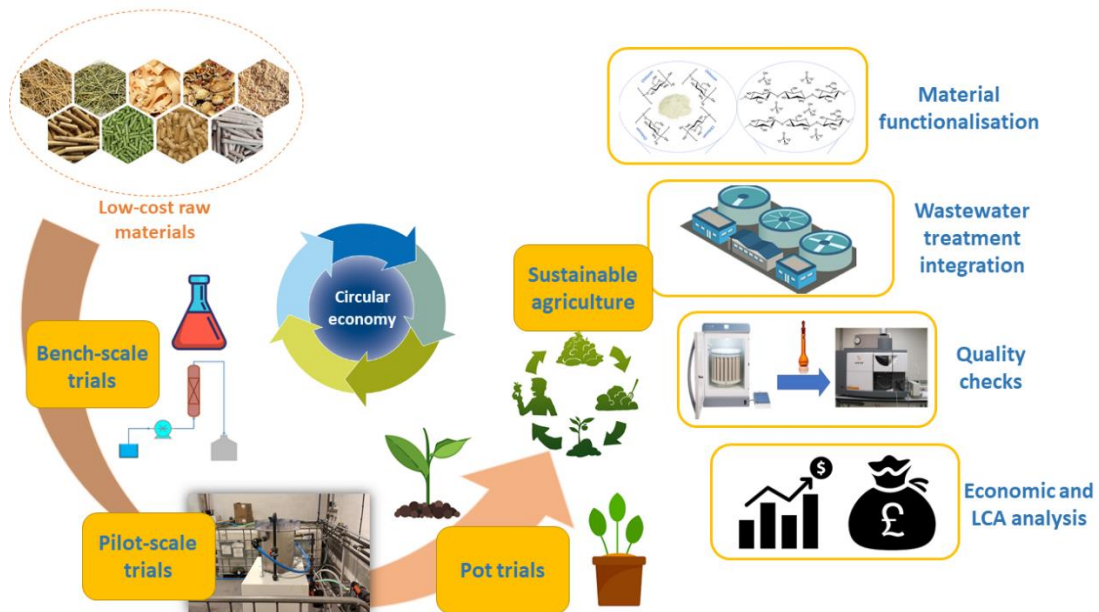
512 As the field of P recovery/removal from wastewater through adsorption is a ‘young’  
513 research area, the progress is very dynamic, therefore, a few critical issues need to  
514 be addressed. As an essential precondition, selection of raw materials with appropriate  
515 compositions and the optimisation of biochars and other adsorbents fabrication  
516 conditions should be improved, as well as activation parameters with desirable  
517 properties for P recovery. In addition, a detailed development of design parameters  
518 with ‘smart’ adsorbent functionalisation would make the product highly efficient for  
519 target applications (e.g. selective P adsorption, future fertiliser product, etc). Extended  
520 research should be carried out on adsorption mechanisms involved during P  
521 adsorption to facilitate the development of effective methods for producing materials  
522 and optimising their efficiency for practical applications (particularly to meet strict P  
523 regulation requirements).

524 Overall, very few studies have actually been carried out in a fully integrated manner,  
525 i.e., to assess the feasibility of full scale implementation (of the tested low-cost  
526 adsorbents); their true potential for integration with other P recovery technologies;  
527 plant P-availability (if to be used as fertiliser); the chemical/microbiological ‘quality’ of  
528 the saturated adsorbent/product (i.e., as a soil amendment and fertiliser); and the  
529 environmental, logistical and economic considerations (through life-cycle



530 assessments and cost-benefit analysis) of transitioning new products into the market  
531 economy.

532 Fig. 4 shows an overview of the steps and considerations needed to move from 'raw  
533 material' to a viable agricultural solution.



534

535 **Fig. 4.** Integrated P recovery - from raw material, through to P recovery from  
536 wastewater, through to sustainable agricultural re-use

537 There will never be a 'one size fits all' technology that works in all situations, however,  
538 the recent 'resource demand' triggered by impending P-rock scarcity is set to drive P  
539 recovery technology using low-cost adsorbents. In turn, this is also set to establish a  
540 more integrated and circular economy with regard to P management, and open up  
541 many new opportunities to fully and sustainably exploit finite P resources.

#### 542 **Acknowledgment**

543 This work was undertaken as part of the 'Phos4You' Project (NWE 292) with financial  
544 support from the INTERREG V B Northwest Europe Programme.

545 **References**

- 546 Ahmed, M. B., Zhou, J. L., Ngo, H. H., & Guo, W. (2016). Insight into biochar properties  
547 and its cost analysis. *Biomass and Bioenergy*, 84, 76–86. Retrieved from  
548 <https://doi.org/10.1016/j.biombioe.2015.11.002>
- 549 Ajmal, Z., Muhmood, A., Dong, R., & Wu, S. (2020). Probing the efficiency of  
550 magnetically modified biomass-derived biochar for effective phosphate removal.  
551 *Journal of Environmental Management*, 253(August 2019), 109730. Retrieved  
552 from <https://doi.org/10.1016/j.jenvman.2019.109730>
- 553 Alghashm, S., Qian, S., Hua, Y., Wu, J., Zhang, H., Chen, W., & Shen, G. (2018).  
554 Properties of biochar from anaerobically digested food waste and its potential use  
555 in phosphorus recovery and soil amendment. *Sustainability (Switzerland)*, 10(12).  
556 Retrieved from <https://doi.org/10.3390/su10124692>
- 557 Altmann, J., Rehfeld, D., Träder, K., Sperlich, A., & Jekel, M. (2016). Combination of  
558 granular activated carbon adsorption and deep-bed filtration as a single advanced  
559 wastewater treatment step for organic micropollutant and phosphorus removal.  
560 *Water Research*, 92, 131–139. Retrieved from  
561 <https://doi.org/10.1016/j.watres.2016.01.051>
- 562 An, B., Lee, S., Kim, H. G., Zhao, D., Park, J. A., & Choi, J. W. (2019).  
563 Organic/inorganic hybrid adsorbent for efficient phosphate removal from a  
564 reservoir affected by algae bloom. *Journal of Industrial and Engineering*  
565 *Chemistry*, 69, 211–216. Retrieved from  
566 <https://doi.org/10.1016/j.jiec.2018.09.029>
- 567 An, X., Wu, Z., Yu, J., Ge, L., Li, T., Liu, X., & Yu, B. (2020). High-Efficiency Reclaiming  
568 Phosphate from an Aqueous Solution by Bentonite Modified Biochars: A Slow  
569 Release Fertilizer with a Precise Rate Regulation. *ACS Sustainable Chemistry*  
570 *and Engineering*, 8(15), 6090–6099. Retrieved from  
571 <https://doi.org/10.1021/acssuschemeng.0c01112>
- 572 Arun, J., Gopinath, K. P., Vigneshwar, S. S., & Swetha, A. (2020). Sustainable and  
573 eco-friendly approach for phosphorus recovery from wastewater by  
574 hydrothermally carbonized microalgae: Study on spent bio-char as fertilizer.  
575 *Journal of Water Process Engineering*, 38(July), 101567. Retrieved from  
576 <https://doi.org/10.1016/j.jwpe.2020.101567>
- 577 Ashrafi, E., Mehrabani Zeinabad, A., Borghei, S. M., Torresi, E., & Muñoz Sierra, J.  
578 (2019). Optimising nutrient removal of a hybrid five-stage Bardenpho and moving  
579 bed biofilm reactor process using response surface methodology. *Journal of*  
580 *Environmental Chemical Engineering*, 7(1). Retrieved from  
581 <https://doi.org/10.1016/j.jece.2018.102861>
- 582 Bacelo, H., Pintor, A. M. A., Santos, S. C. R., Boaventura, R. A. R., & Botelho, C. M.  
583 S. (2020). Performance and prospects of different adsorbents for phosphorus  
584 uptake and recovery from water. *Chemical Engineering Journal*, 381(June 2019),  
585 122566. Retrieved from <https://doi.org/10.1016/j.cej.2019.122566>
- 586 Bai, Y., Zhang, Y., Quan, X., & Chen, S. (2015). Nutrient removal performance and  
587 microbial characteristics of a full-scale IFAS-EBPR process treating municipal

- 588 wastewater. *Water Science and Technology*, 73(6), 1261–1268. Retrieved from  
589 <https://doi.org/10.2166/wst.2015.604>
- 590 Bal Krishna, K. C., Aryal, A., & Jansen, T. (2016). Comparative study of ground water  
591 treatment plants sludges to remove phosphorous from wastewater. *Journal of*  
592 *Environmental Management*, 180, 17–23. Retrieved from  
593 <https://doi.org/10.1016/j.jenvman.2016.05.006>
- 594 Bashar, R., Gungor, K., Karthikeyan, K. G., & Barak, P. (2018). Cost effectiveness of  
595 phosphorus removal processes in municipal wastewater treatment.  
596 *Chemosphere*, 197, 280–290. Retrieved from  
597 <https://doi.org/10.1016/j.chemosphere.2017.12.169>
- 598 Benafqir, M., Anfar, Z., Abbaz, M., El Haouti, R., Lhanafi, S., Azougarh, Y., ... El Alem,  
599 N. (2019). Hematite–titaniferous sand as a new low-cost adsorbent for  
600 orthophosphates removal: Adsorption, mechanism and Process Capability study.  
601 *Environmental Technology and Innovation*, 13, 153–165. Retrieved from  
602 <https://doi.org/10.1016/j.eti.2018.10.009>
- 603 Bhattacharjee, S., Darwish, N., & Shanableh, A. (2020). Phosphate removal using  
604 nanoscale zerovalent iron: Impact of chitosan and humic acid. *Journal of*  
605 *Environmental Chemical Engineering*, 8(5), 104131. Retrieved from  
606 <https://doi.org/10.1016/j.jece.2020.104131>
- 607 Bolton, L., Joseph, S., Greenway, M., Donne, S., Munroe, P., & Marjo, C. E. (2019).  
608 Phosphorus adsorption onto an enriched biochar substrate in constructed  
609 wetlands treating wastewater. *Ecological Engineering: X*, 1(June 2018), 100005.  
610 Retrieved from <https://doi.org/10.1016/j.ecoena.2019.100005>
- 611 Bunce, J. T., Ndam, E., Ofiteru, I. D., Moore, A., & Graham, D. W. (2018). A Review  
612 of Phosphorus Removal Technologies and Their Applicability to Small-Scale  
613 Domestic Wastewater Treatment Systems. *Frontiers in Environmental Science*,  
614 6(8), 0–15. Retrieved from <https://doi.org/10.3389/fenvs.2018.00008>
- 615 Chen, Q., Qin, J., Sun, P., Cheng, Z., & Shen, G. (2018). Cow dung-derived  
616 engineered biochar for reclaiming phosphate from aqueous solution and its  
617 validation as slow-release fertilizer in soil-crop system. *Journal of Cleaner*  
618 *Production*, 172, 2009–2018. Retrieved from  
619 <https://doi.org/10.1016/j.jclepro.2017.11.224>
- 620 Chojnacka, K., Moustakas, K., & Witek-Krowiak, A. (2020). Bio-based fertilizers: A  
621 practical approach towards circular economy. *Bioresource Technology*,  
622 295(September 2019), 122223. Retrieved from  
623 <https://doi.org/10.1016/j.biortech.2019.122223>
- 624 Chrispim, M. C., Scholz, M., & Nolasco, M. A. (2019). Phosphorus recovery from  
625 municipal wastewater treatment: Critical review of challenges and opportunities  
626 for developing countries. *Journal of Environmental Management*, 248(July),  
627 109268. Retrieved from <https://doi.org/10.1016/j.jenvman.2019.109268>
- 628 Cole, A. J., Paul, N. A., de Nys, R., & Roberts, D. A. (2017). Good for sewage  
629 treatment and good for agriculture: Algal based compost and biochar. *Journal of*  
630 *Environmental Management*, 200, 105–113. Retrieved from  
631 <https://doi.org/10.1016/j.jenvman.2017.05.082>

- 632 Cusack, P. B., Callery, O., Courtney, R., Ujaczki, É., O'Donoghue, L. M. T., & Healy,  
633 M. G. (2019). The use of rapid, small-scale column tests to determine the  
634 efficiency of bauxite residue as a low-cost adsorbent in the removal of dissolved  
635 reactive phosphorus from agricultural waters. *Journal of Environmental*  
636 *Management*, 241(April), 273–283. Retrieved from  
637 <https://doi.org/10.1016/j.jenvman.2019.04.042>
- 638 Dai, L., Tan, F., Li, H., Zhu, N., He, M., Zhu, Q., ... Zhao, J. (2017). Calcium-rich  
639 biochar from the pyrolysis of crab shell for phosphorus removal. *Journal of*  
640 *Environmental Management*, 198, 70–74. Retrieved from  
641 <https://doi.org/10.1016/j.jenvman.2017.04.057>
- 642 Dai, Y., Wang, W., Lu, L., Yan, L., & Yu, D. (2020). Utilization of biochar for the removal  
643 of nitrogen and phosphorus. *Journal of Cleaner Production*, 257. Retrieved from  
644 <https://doi.org/10.1016/j.jclepro.2020.120573>
- 645 de Rozari, P., Greenway, M., & El Hanandeh, A. (2016). Phosphorus removal from  
646 secondary sewage and septage using sand media amended with biochar in  
647 constructed wetland mesocosms. *Science of the Total Environment*, 569–570,  
648 123–133. Retrieved from <https://doi.org/10.1016/j.scitotenv.2016.06.096>
- 649 Desmidt, E., Ghyselbrecht, K., Zhang, Y., Pinoy, L., Van Der Bruggen, B., Verstraete,  
650 W., ... Meesschaert, B. (2015). Global phosphorus scarcity and full-scale P-  
651 recovery techniques: A review. *Critical Reviews in Environmental Science and*  
652 *Technology*, 45(4), 336–384. Retrieved from  
653 <https://doi.org/10.1080/10643389.2013.866531>
- 654 dos Reis, G. S., Thue, P. S., Cazacliu, B. G., Lima, E. C., Sampaio, C. H., Quattrone,  
655 M., ... Dotto, G. L. (2020). Effect of concrete carbonation on phosphate removal  
656 through adsorption process and its potential application as fertilizer. *Journal of*  
657 *Cleaner Production*, 256, 120416. Retrieved from  
658 <https://doi.org/10.1016/j.jclepro.2020.120416>
- 659 Egle, L., Rechberger, H., Krampe, J., & Zessner, M. (2016). Phosphorus recovery from  
660 municipal wastewater: An integrated comparative technological, environmental  
661 and economic assessment of P recovery technologies. *Science of the Total*  
662 *Environment*, 571, 522–542. Retrieved from  
663 <https://doi.org/10.1016/j.scitotenv.2016.07.019>
- 664 Egle, Lukas, Rechberger, H., & Zessner, M. (2015). Overview and description of  
665 technologies for recovering phosphorus from municipal wastewater. *Resources,*  
666 *Conservation and Recycling*, 105, 325–346. Retrieved from  
667 <https://doi.org/10.1016/j.resconrec.2015.09.016>
- 668 Ehmann, A., Bach, I. M., Laopeamthong, S., Bilbao, J., & Lewandowski, I. (2017). Can  
669 phosphate salts recovered from manure replace conventional phosphate  
670 fertilizer? *Agriculture (Switzerland)*, 7(1). Retrieved from  
671 <https://doi.org/10.3390/agriculture7010001>
- 672 Ezzati, G., Healy, M. G., Christianson, L., Daly, K., Fenton, O., Feyereisen, G., ...  
673 Callery, O. (2020). Use of rapid small-scale column tests for simultaneous  
674 prediction of phosphorus and nitrogen retention in large-scale filters. *Journal of*  
675 *Water Process Engineering*, 37(February), 101473. Retrieved from  
676 <https://doi.org/10.1016/j.jwpe.2020.101473>

- 677 Fang, C., Zhang, T., Li, P., Jiang, R. F., & Wang, Y. C. (2014). Application of  
678 magnesium modified corn biochar for phosphorus removal and recovery from  
679 swine wastewater. *International Journal of Environmental Research and Public  
680 Health*, 11(9), 9217–9237. Retrieved from  
681 <https://doi.org/10.3390/ijerph110909217>
- 682 Fang, L., Li, J. shan, Donatello, S., Cheeseman, C. R., Poon, C. S., & Tsang, D. C. W.  
683 (2020). Use of Mg/Ca modified biochars to take up phosphorus from acid-extract  
684 of incinerated sewage sludge ash (ISSA) for fertilizer application. *Journal of  
685 Cleaner Production*, 244, 118853. Retrieved from  
686 <https://doi.org/10.1016/j.jclepro.2019.118853>
- 687 Feng, C., Zhang, S., Wang, Y., Wang, G., Pan, X., Zhong, Q., ... Yao, P. (2020).  
688 Synchronous removal of ammonium and phosphate from swine wastewater by  
689 two agricultural waste based adsorbents: Performance and mechanisms.  
690 *Bioresource Technology*, 307(March), 123231. Retrieved from  
691 <https://doi.org/10.1016/j.biortech.2020.123231>
- 692 Furuya, K., Hafuka, A., Kuroiwa, M., Satoh, H., Watanabe, Y., & Yamamura, H. (2017).  
693 Development of novel polysulfone membranes with embedded zirconium sulfate-  
694 surfactant micelle mesostructure for phosphate recovery from water through  
695 membrane filtration. *Water Research*, 124, 521–526. Retrieved from  
696 <https://doi.org/10.1016/j.watres.2017.08.005>
- 697 Gao, Y., Zhang, W., Gao, B., Jia, W., Miao, A., Xiao, L., & Yang, L. (2018). Highly  
698 efficient removal of nitrogen and phosphorus in an electrolysis-integrated  
699 horizontal subsurface-flow constructed wetland amended with biochar. *Water  
700 Research*, 139, 301–310. Retrieved from  
701 <https://doi.org/10.1016/j.watres.2018.04.007>
- 702 Haddad, K., Jellali, S., Jeguirim, M., Ben Hassen Trabelsi, A., & Limousy, L. (2018).  
703 Investigations on phosphorus recovery from aqueous solutions by biochars  
704 derived from magnesium-pretreated cypress sawdust. *Journal of Environmental  
705 Management*, 216, 305–314. Retrieved from  
706 <https://doi.org/10.1016/j.jenvman.2017.06.020>
- 707 He, X., Zhang, T., Ren, H., Li, G., Ding, L., & Pawlowski, L. (2017). Phosphorus  
708 recovery from biogas slurry by ultrasound/H<sub>2</sub>O<sub>2</sub> digestion coupled with  
709 HFO/biochar adsorption process. *Waste Management*, 60, 219–229. Retrieved  
710 from <https://doi.org/10.1016/j.wasman.2016.08.032>
- 711 Hidalgo, D., Corona, F., & Martín-Marroquín, J. M. (2020). Nutrient recycling: from  
712 waste to crop. *Biomass Conversion and Biorefinery*, (4). Retrieved from  
713 <https://doi.org/10.1007/s13399-019-00590-3>
- 714 Hong, S. H., Ndingwan, A. M., Yoo, S. C., Lee, C. G., & Park, S. J. (2020). Use of  
715 calcined sepiolite in removing phosphate from water and returning phosphate to  
716 soil as phosphorus fertilizer. *Journal of Environmental Management*, 270(June),  
717 110817. Retrieved from <https://doi.org/10.1016/j.jenvman.2020.110817>
- 718 Huang, W., Zhang, Y., & Li, D. (2017). Adsorptive removal of phosphate from water  
719 using mesoporous materials: A review. *Journal of Environmental Management*,  
720 193, 470–482. Retrieved from <https://doi.org/10.1016/j.jenvman.2017.02.030>

- 721 Hukari, S., Hermann, L., & Nättorp, A. (2016). From wastewater to fertilisers -  
722 Technical overview and critical review of European legislation governing  
723 phosphorus recycling. *Science of the Total Environment*, 542, 1127–1135.  
724 Retrieved from <https://doi.org/10.1016/j.scitotenv.2015.09.064>
- 725 Jia, Z., Zeng, W., Xu, H., Li, S., & Peng, Y. (2020). Adsorption removal and reuse of  
726 phosphate from wastewater using a novel adsorbent of lanthanum-modified  
727 platanus biochar. *Process Safety and Environmental Protection*, 140, 221–232.  
728 Retrieved from <https://doi.org/10.1016/j.psep.2020.05.017>
- 729 Jiang, D., Amano, Y., & Machida, M. (2017). Removal and recovery of phosphate from  
730 water by a magnetic Fe<sub>3</sub>O<sub>4</sub> @ASC adsorbent. *Journal of Environmental  
731 Chemical Engineering*, 5(5), 4229–4238. Retrieved from  
732 <https://doi.org/10.1016/j.jece.2017.08.007>
- 733 Jahir, M. A. H., Nguyen, T. T., Mahatheva, K., Pradhan, M., Ngo, H. H., Guo, W., &  
734 Vigneswaran, S. (2016). Removal of phosphorus by a high rate membrane  
735 adsorption hybrid system. *Bioresource Technology*, 201, 365–369. Retrieved  
736 from <https://doi.org/10.1016/j.biortech.2015.11.045>
- 737 Ju, X., Wu, S., Zhang, Y., & Dong, R. (2014). Intensified nitrogen and phosphorus  
738 removal in a novel electrolysis-integrated tidal flow constructed wetland system.  
739 *Water Research*, 59, 37–45. Retrieved from  
740 <https://doi.org/10.1016/j.watres.2014.04.004>
- 741 Jung, K. W., Jeong, T. U., Choi, J. W., Ahn, K. H., & Lee, S. H. (2017). Adsorption of  
742 phosphate from aqueous solution using electrochemically modified biochar  
743 calcium-alginate beads: Batch and fixed-bed column performance. *Bioresource  
744 Technology*, 244(July), 23–32. Retrieved from  
745 <https://doi.org/10.1016/j.biortech.2017.07.133>
- 746 Jung, K. W., Kim, K., Jeong, T. U., & Ahn, K. H. (2016). Influence of pyrolysis  
747 temperature on characteristics and phosphate adsorption capability of biochar  
748 derived from waste-marine macroalgae (*Undaria pinnatifida* roots). *Bioresource  
749 Technology*, 200, 1024–1028. Retrieved from  
750 <https://doi.org/10.1016/j.biortech.2015.10.016>
- 751 Kalaitzidou, K., Mitrakas, M., Raptopoulou, C., Tolkou, A., Palasantza, P. A., &  
752 Zouboulis, A. (2016). Pilot-Scale Phosphate Recovery from Secondary  
753 Wastewater Effluents. *Environmental Processes*, 3, 5–22. Retrieved from  
754 <https://doi.org/10.1007/s40710-016-0139-1>
- 755 Kizito, S., Luo, H., Wu, S., Ajmal, Z., Lv, T., & Dong, R. (2017). Phosphate recovery  
756 from liquid fraction of anaerobic digestate using four slow pyrolyzed biochars:  
757 Dynamics of adsorption, desorption and regeneration. *Journal of Environmental  
758 Management*, 201, 260–267. Retrieved from  
759 <https://doi.org/10.1016/j.jenvman.2017.06.057>
- 760 Kizito, S., Lv, T., Wu, S., Ajmal, Z., Luo, H., & Dong, R. (2017). Treatment of anaerobic  
761 digested effluent in biochar-packed vertical flow constructed wetland columns:  
762 Role of media and tidal operation. *Science of the Total Environment*, 592, 197–  
763 205. Retrieved from <https://doi.org/10.1016/j.scitotenv.2017.03.125>
- 764 Kong, L., Tian, Y., Wang, Y., Li, N., Liu, Y., Pang, Z., ... Zuo, W. (2019). Periclase-

- 765 induced generation of flowerlike clay-based layered double hydroxides: A highly  
 766 efficient phosphate scavenger and solid-phase fertilizer. *Chemical Engineering*  
 767 *Journal*, 359(October 2018), 902–913. Retrieved from  
 768 <https://doi.org/10.1016/j.cej.2018.11.007>
- 769 Li, H., Li, Y., Xu, Y., & Lu, X. (2020). Biochar phosphorus fertilizer effects on soil  
 770 phosphorus availability. *Chemosphere*, 244, 125471. Retrieved from  
 771 <https://doi.org/10.1016/j.chemosphere.2019.125471>
- 772 Li, R., Wang, J. J., Zhou, B., Awasthi, M. K., Ali, A., Zhang, Z., ... Mahar, A. (2016).  
 773 Recovery of phosphate from aqueous solution by magnesium oxide decorated  
 774 magnetic biochar and its potential as phosphate-based fertilizer substitute.  
 775 *Bioresource Technology*, 215, 209–214. Retrieved from  
 776 <https://doi.org/10.1016/j.biortech.2016.02.125>
- 777 Li, W. W., Sheng, G. P., Zeng, R. J., Liu, X. W., & Yu, H. Q. (2012). China's wastewater  
 778 discharge standards in urbanization: Evolution, challenges and implications:  
 779 Evolution, challenges and implications. *Environmental Science and Pollution*  
 780 *Research*, 19(5), 1422–1431. Retrieved from [https://doi.org/10.1007/s11356-](https://doi.org/10.1007/s11356-011-0572-7)  
 781 [011-0572-7](https://doi.org/10.1007/s11356-011-0572-7)
- 782 Liu, J., Zheng, M., Wang, C., Liang, C., Shen, Z., & Xu, K. (2020). A green method for  
 783 the simultaneous recovery of phosphate and potassium from hydrolyzed urine as  
 784 value-added fertilizer using wood waste. *Resources, Conservation and Recycling*,  
 785 157(October 2019), 104793. Retrieved from  
 786 <https://doi.org/10.1016/j.resconrec.2020.104793>
- 787 Liu, R., Chi, L., Wang, X., Sui, Y., Wang, Y., & Arandiyan, H. (2018). Review of metal  
 788 (hydr)oxide and other adsorptive materials for phosphate removal from water.  
 789 *Journal of Environmental Chemical Engineering*, 6(4), 5269–5286. Retrieved from  
 790 <https://doi.org/10.1016/j.jece.2018.08.008>
- 791 Liu, X., Shen, F., Smith, R. L., & Qi, X. (2019). Black liquor-derived calcium-activated  
 792 biochar for recovery of phosphate from aqueous solutions. *Bioresource*  
 793 *Technology*, 294(38), 122198. Retrieved from  
 794 <https://doi.org/10.1016/j.biortech.2019.122198>
- 795 Loganathan, P., Vigneswaran, S., Kandasamy, J., & Bolan, N. S. (2014). Removal and  
 796 recovery of phosphate from water using sorption. *Critical Reviews in*  
 797 *Environmental Science and Technology*, 44(8), 847–907. Retrieved from  
 798 <https://doi.org/10.1080/10643389.2012.741311>
- 799 Lu, H., Feng, Y., Feng, Y., Dong, Y., Sun, H., Xing, J., ... Yang, L. (2019). Cerium-  
 800 modified biochar: A recycling biomaterial for regulating phosphorus availability in  
 801 paddy ecosystem from coastal mudflat reclamation. *Geoderma*, 346(50), 43–51.  
 802 Retrieved from <https://doi.org/10.1016/j.geoderma.2019.03.025>
- 803 Lu, N. C., & Liu, J. C. (2010). Removal of phosphate and fluoride from wastewater by  
 804 a hybrid precipitation-microfiltration process. *Separation and Purification*  
 805 *Technology*, 74(3), 329–335. Retrieved from  
 806 <https://doi.org/10.1016/j.seppur.2010.06.023>
- 807 Maroušek, J., Kolář, L., Strunecký, O., Kopecký, M., Bartoš, P., Maroušková, A., ...  
 808 Vrbka, J. (2020). Modified biochars present an economic challenge to phosphate

- 809 management in wastewater treatment plants. *Journal of Cleaner Production*, 272.  
810 Retrieved from <https://doi.org/10.1016/j.jclepro.2020.123015>
- 811 Mohan, D., Sarswat, A., Ok, Y. S., & Pittman, C. U. (2014). Organic and inorganic  
812 contaminants removal from water with biochar, a renewable, low cost and  
813 sustainable adsorbent - A critical review. *Bioresource Technology*, 160, 191–202.  
814 Retrieved from <https://doi.org/10.1016/j.biortech.2014.01.120>
- 815 Mosa, A., El-Ghamry, A., & Tolba, M. (2018). Functionalized biochar derived from  
816 heavy metal rich feedstock: Phosphate recovery and reusing the exhausted  
817 biochar as an enriched soil amendment. *Chemosphere*, 198, 351–363. Retrieved  
818 from <https://doi.org/10.1016/j.chemosphere.2018.01.113>
- 819 Muisa, N., Nhapi, I., Ruziwa, W., & Manyuchi, M. M. (2020). Utilization of alum sludge  
820 as adsorbent for phosphorus removal in municipal wastewater: A review. *Journal*  
821 *of Water Process Engineering*, 35(February), 101187. Retrieved from  
822 <https://doi.org/10.1016/j.jwpe.2020.101187>
- 823 Nardis, B. O., Santana Da Silva Carneiro, J., Souza, I. M. G. De, Barros, R. G. De, &  
824 Azevedo Melo, L. C. (2020). Phosphorus recovery using magnesium-enriched  
825 biochar and its potential use as fertilizer. *Archives of Agronomy and Soil Science*,  
826 00(00), 1–17. Retrieved from <https://doi.org/10.1080/03650340.2020.1771699>
- 827 Nedelciu, C. E., Ragnarsdóttir, K. V., & Stjernquist, I. (2019). From waste to resource:  
828 A systems dynamics and stakeholder analysis of phosphorus recycling from  
829 municipal wastewater in Europe. *Ambio*, 48(7), 741–751. Retrieved from  
830 <https://doi.org/10.1007/s13280-018-1097-9>
- 831 Nguyen, T. A. H., Ngo, H. H., Guo, W. S., Nguyen, T. H. H., Soda, S., Vu, N. D., ...  
832 Pham, T. T. (2020). White hard clam (*Meretrix lyrata*) shells media to improve  
833 phosphorus removal in lab-scale horizontal sub-surface flow constructed  
834 wetlands: Performance, removal pathways, and lifespan. *Bioresource*  
835 *Technology*, 312(April). Retrieved from  
836 <https://doi.org/10.1016/j.biortech.2020.123602>
- 837 Nguyen, T. A. H., Ngo, H. H., Guo, W. S., Pham, T. Q., Li, F. M., Nguyen, T. V., & Bui,  
838 X. T. (2015). Adsorption of phosphate from aqueous solutions and sewage using  
839 zirconium loaded okara (ZLO): Fixed-bed column study. *Science of the Total*  
840 *Environment*, 523, 40–49. Retrieved from  
841 <https://doi.org/10.1016/j.scitotenv.2015.03.126>
- 842 Novais, S. V., Zenero, M. D. O., Tronto, J., Conz, R. F., & Cerri, C. E. P. (2018). Poultry  
843 manure and sugarcane straw biochars modified with MgCl<sub>2</sub> for phosphorus  
844 adsorption. *Journal of Environmental Management*, 214, 36–44. Retrieved from  
845 <https://doi.org/10.1016/j.jenvman.2018.02.088>
- 846 Okano, K., Miyamaru, S., Yamamoto, Y., Kunisada, M., Takano, H., Toda, M., ...  
847 Ohtake, H. (2016). A mobile pilot-scale plant for in situ demonstration of  
848 phosphorus recovery from wastewater using amorphous calcium silicate  
849 hydrates. *Separation and Purification Technology*, 170, 116–121. Retrieved from  
850 <https://doi.org/10.1016/j.seppur.2016.06.040>
- 851 Oladoja, N. A., Adelagun, R. O. A., Ahmad, A. L., & Ololade, I. A. (2015). Phosphorus  
852 recovery from aquaculture wastewater using thermally treated gastropod shell.



- 853 *Process Safety and Environmental Protection*, 98, 296–308. Retrieved from  
854 <https://doi.org/10.1016/j.psep.2015.09.006>
- 855 Oliveira, M., Araújo, A., Azevedo, G., Pereira, M. F. R., Neves, I. C., & Machado, A.  
856 V. (2015). Kinetic and equilibrium studies of phosphorous adsorption: Effect of  
857 physical and chemical properties of adsorption agent. *Ecological Engineering*, 82,  
858 527–530. Retrieved from <https://doi.org/10.1016/j.ecoleng.2015.05.020>
- 859 Panagiotou, E., Kafa, N., Koutsokeras, L., Kouis, P., Nikolaou, P., Constantinides, G.,  
860 & Vyrides, I. (2018). Turning calcined waste egg shells and wastewater to  
861 Brushite: Phosphorus adsorption from aqua media and anaerobic sludge leach  
862 water. *Journal of Cleaner Production*, 178, 419–428. Retrieved from  
863 <https://doi.org/10.1016/j.jclepro.2018.01.014>
- 864 Pap, S., Kirk, C., Bremner, B., Sekulic, M. T., Shearer, L., Gibb, S. W., & Taggart, M.  
865 A. (2020). Low-cost chitosan-calcite adsorbent development for potential  
866 phosphate removal and recovery from wastewater effluent. *Water Research*, 173,  
867 115573. Retrieved from <https://doi.org/10.1016/j.watres.2020.115573>
- 868 Pap, S., Kirk, C., Bremner, B., Turk Sekulic, M., Gibb, S. W., Maletic, S., & Taggart,  
869 M. A. (2020). Synthesis optimisation and characterisation of chitosan-calcite  
870 adsorbent from fishery-food waste for phosphorus removal. *Environmental  
871 Science and Pollution Research*, 27(9), 9790–9802. Retrieved from  
872 <https://doi.org/10.1007/s11356-019-07570-0>
- 873 Paradelo, R., Conde-Cid, M., Cutillas-Barreiro, L., Arias-Estévez, M., Nóvoa-Muñoz,  
874 J. C., Álvarez-Rodríguez, E., ... Núñez-Delgado, A. (2016). Phosphorus removal  
875 from wastewater using mussel shell: Investigation on retention mechanisms.  
876 *Ecological Engineering*, 97, 558–566. Retrieved from  
877 <https://doi.org/10.1016/j.ecoleng.2016.10.066>
- 878 Park, H. S., Kwak, S. H., Mahardika, D., Mamedá, N., & Choo, K. H. (2017). Mixed  
879 metal oxide coated polymer beads for enhanced phosphorus removal from  
880 membrane bioreactor effluents. *Chemical Engineering Journal*, 319, 240–247.  
881 Retrieved from <https://doi.org/10.1016/j.cej.2017.03.017>
- 882 Photiou, P., Koutsokeras, L., & Constantinides, G. (2021). Phosphate removal from  
883 synthetic and real wastewater using thermally treated seagrass residues of  
884 *Posidonia oceanica*. *Journal of Cleaner Production*, 278, 123294. Retrieved from  
885 <https://doi.org/10.1016/j.jclepro.2020.123294>
- 886 Pratt, C., Parsons, S. A., Soares, A., & Martin, B. D. (2012). Biologically and chemically  
887 mediated adsorption and precipitation of phosphorus from wastewater. *Current  
888 Opinion in Biotechnology*, 23(6), 890–896. Retrieved from  
889 <https://doi.org/10.1016/j.copbio.2012.07.003>
- 890 Qian, T., Lu, D., Soh, Y. N. A., Webster, R. D., & Zhou, Y. (2020). Biotransformation  
891 of phosphorus in enhanced biological phosphorus removal sludge biochar. *Water  
892 Research*, 169, 115255. Retrieved from  
893 <https://doi.org/10.1016/j.watres.2019.115255>
- 894 Qian, T., Wang, L., Le, C., & Zhou, Y. (2019). Low-temperature-steam activation of  
895 phosphorus in biochar derived from enhanced biological phosphorus removal  
896 (EBPR) sludge. *Water Research*, 161, 202–210. Retrieved from

- 897 <https://doi.org/10.1016/j.watres.2019.06.008>
- 898 Rahman, S. M., Eckelman, M. J., Onnis-Hayden, A., & Gu, A. Z. (2016). Life-Cycle  
899 Assessment of Advanced Nutrient Removal Technologies for Wastewater  
900 Treatment. *Environmental Science and Technology*, 50(6), 3020–3030. Retrieved  
901 from <https://doi.org/10.1021/acs.est.5b05070>
- 902 Schröder, J. J., Smit, A. L., Cordell, D., & Rosemarin, A. (2011). Improved phosphorus  
903 use efficiency in agriculture: A key requirement for its sustainable use.  
904 *Chemosphere*, 84(6), 822–831. Retrieved from  
905 <https://doi.org/10.1016/j.chemosphere.2011.01.065>
- 906 Shepherd, J. G., Kleemann, R., Bahri-Esfahani, J., Hudek, L., Suriyagoda, L.,  
907 Vandamme, E., & van Dijk, K. C. (2016). The future of phosphorus in our hands.  
908 *Nutrient Cycling in Agroecosystems*, 104(3), 281–287. Retrieved from  
909 <https://doi.org/10.1007/s10705-015-9742-1>
- 910 Shepherd, J. G., Sohi, S. P., & Heal, K. V. (2016). Optimising the recovery and re-use  
911 of phosphorus from wastewater effluent for sustainable fertiliser development.  
912 *Water Research*, 94, 155–165. Retrieved from  
913 <https://doi.org/10.1016/j.watres.2016.02.038>
- 914 Shukla, N., Sahoo, D., & Remya, N. (2019). Biochar from microwave pyrolysis of rice  
915 husk for tertiary wastewater treatment and soil nourishment. *Journal of Cleaner*  
916 *Production*, 235, 1073–1079. Retrieved from  
917 <https://doi.org/10.1016/j.jclepro.2019.07.042>
- 918 Solovchenko, A., Verschoor, A. M., Jablonowski, N. D., & Nedbal, L. (2016).  
919 Phosphorus from wastewater to crops: An alternative path involving microalgae.  
920 *Biotechnology Advances*, 34(5), 550–564. Retrieved from  
921 <https://doi.org/10.1016/j.biotechadv.2016.01.002>
- 922 Song, M., & Li, M. (2019). Adsorption and regeneration characteristics of phosphorus  
923 from sludge dewatering filtrate by magnetic anion exchange resin. *Environmental*  
924 *Science and Pollution Research*, 26(33), 34233–34247. Retrieved from  
925 <https://doi.org/10.1007/s11356-018-4049-9>
- 926 Suresh Kumar, P., Ejerssa, W. W., Wegener, C. C., Korving, L., Dugulan, A. I.,  
927 Temmink, H., ... Witkamp, G. J. (2018). Understanding and improving the  
928 reusability of phosphate adsorbents for wastewater effluent polishing. *Water*  
929 *Research*, 145, 365–374. Retrieved from  
930 <https://doi.org/10.1016/j.watres.2018.08.040>
- 931 Suresh Kumar, P., Korving, L., van Loosdrecht, M. C. M., & Witkamp, G. J. (2019).  
932 Adsorption as a technology to achieve ultra-low concentrations of phosphate:  
933 Research gaps and economic analysis. *Water Research X*, 4, 100029. Retrieved  
934 from <https://doi.org/10.1016/j.wroa.2019.100029>
- 935 Tan, Z., Lin, C. S. K., Ji, X., & Rainey, T. J. (2017). Returning biochar to fields: A  
936 review. *Applied Soil Ecology*, 116(March), 1–11. Retrieved from  
937 <https://doi.org/10.1016/j.apsoil.2017.03.017>
- 938 Verbeeck, M., Salaets, P., & Smolders, E. (2020). Trace element concentrations in  
939 mineral phosphate fertilizers used in Europe: A balanced survey. *Science of the*  
940 *Total Environment*, 712, 136419. Retrieved from

- 941 <https://doi.org/10.1016/j.scitotenv.2019.136419>
- 942 Vianna, M. T. G., Marques, M., & Bertolino, L. C. (2016). Sun coral powder as  
943 adsorbent: Evaluation of phosphorus removal in synthetic and real wastewater.  
944 *Ecological Engineering*, 97, 13–22. Retrieved from  
945 <https://doi.org/10.1016/j.ecoleng.2016.08.004>
- 946 Vikrant, K., Kim, K. H., Ok, Y. S., Tsang, D. C. W., Tsang, Y. F., Giri, B. S., & Singh,  
947 R. S. (2018). Engineered/designer biochar for the removal of phosphate in water  
948 and wastewater. *Science of the Total Environment*, 616–617, 1242–1260.  
949 Retrieved from <https://doi.org/10.1016/j.scitotenv.2017.10.193>
- 950 Wang, H., Xiao, K., Yang, J., Yu, Z., Yu, W., Xu, Q., ... Liu, B. (2020). Phosphorus  
951 recovery from the liquid phase of anaerobic digestate using biochar derived from  
952 iron-rich sludge: A potential phosphorus fertilizer. *Water Research*, 174.  
953 Retrieved from <https://doi.org/10.1016/j.watres.2020.115629>
- 954 Wang, L., Wang, J., He, C., Lyu, W., Zhang, W., Yan, W., & Yang, L. (2019).  
955 Development of rare earth element doped magnetic biochars with enhanced  
956 phosphate adsorption performance. *Colloids and Surfaces A: Physicochemical  
957 and Engineering Aspects*, 561(November 2018), 236–243. Retrieved from  
958 <https://doi.org/10.1016/j.colsurfa.2018.10.082>
- 959 Worch, E. (2012). *Adsorption Technology in Water Treatment: Fundamentals,  
960 Processes, and Modeling*. De Gruyter. Retrieved from  
961 <https://books.google.rs/books?id=xUBhp6r6zwwC>
- 962 Wu, B., Wan, J., Zhang, Y., Pan, B., & Lo, I. M. C. (2020). Selective Phosphate  
963 Removal from Water and Wastewater using Sorption: Process Fundamentals and  
964 Removal Mechanisms. *Environmental Science and Technology*, (852). Retrieved  
965 from <https://doi.org/10.1021/acs.est.9b05569>
- 966 Xia, W. J., Xu, L. Z. J., Yu, L. Q., Zhang, Q., Zhao, Y. H., Xiong, J. R., ... Jin, R. C.  
967 (2020). Conversion of municipal wastewater-derived waste to an adsorbent for  
968 phosphorus recovery from secondary effluent. *Science of the Total Environment*,  
969 705, 135959. Retrieved from <https://doi.org/10.1016/j.scitotenv.2019.135959>
- 970 Xu, M., Gao, P., Yang, Z., Su, L., Wu, J., Yang, G., ... Xiao, Y. (2019). Biochar impacts  
971 on phosphorus cycling in rice ecosystem. *Chemosphere*, 225, 311–319.  
972 Retrieved from <https://doi.org/10.1016/j.chemosphere.2019.03.069>
- 973 Xu, Q., Chen, Z., Wu, Z., Xu, F., Yang, D., He, Q., ... Chen, Y. (2019). Novel  
974 lanthanum doped biochars derived from lignocellulosic wastes for efficient  
975 phosphate removal and regeneration. *Bioresource Technology*, 289(April),  
976 121600. Retrieved from <https://doi.org/10.1016/j.biortech.2019.121600>
- 977 Yang, H., Ye, S., Zeng, Z., Zeng, G., Tan, X., Xiao, R., ... Xu, F. (2020). Utilization of  
978 biochar for resource recovery from water: A review. *Chemical Engineering  
979 Journal*, 397(February). Retrieved from <https://doi.org/10.1016/j.cej.2020.125502>
- 980 Yao, Y., Gao, B., Chen, J., & Yang, L. (2013). Engineered biochar reclaiming  
981 phosphate from aqueous solutions: Mechanisms and potential application as a  
982 slow-release fertilizer. *Environmental Science and Technology*, 47(15), 8700–  
983 8708. Retrieved from <https://doi.org/10.1021/es4012977>

- 984 Yin, Q., Zhang, B., Wang, R., & Zhao, Z. (2017). Biochar as an adsorbent for inorganic  
 985 nitrogen and phosphorus removal from water: a review. *Environmental Science*  
 986 *and Pollution Research*, 24(34), 26297–26309. Retrieved from  
 987 <https://doi.org/10.1007/s11356-017-0338-y>
- 988 Yu, H., Zou, W., Chen, J., Chen, H., Yu, Z., Huang, J., ... Gao, B. (2019). Biochar  
 989 amendment improves crop production in problem soils: A review. *Journal of*  
 990 *Environmental Management*, 232(September 2018), 8–21. Retrieved from  
 991 <https://doi.org/10.1016/j.jenvman.2018.10.117>
- 992 Zelmanov, G., & Semiat, R. (2014). Phosphate removal from aqueous solution by an  
 993 adsorption ultrafiltration system. *Separation and Purification Technology*, 132,  
 994 487–495. Retrieved from <https://doi.org/10.1016/j.seppur.2014.06.008>
- 995 Zhang, B., Chen, N., Feng, C., & Zhang, Z. (2018). Adsorption for phosphate by  
 996 crosslinked/non-crosslinked-chitosan-Fe(III) complex sorbents: Characteristic  
 997 and mechanism. *Chemical Engineering Journal*, 353(May), 361–372. Retrieved  
 998 from <https://doi.org/10.1016/j.cej.2018.07.092>
- 999 Zhang, H., Wang, X., Xiao, J., Yang, F., & Zhang, J. (2009). Enhanced biological  
 1000 nutrient removal using MUCT-MBR system. *Bioresource Technology*, 100(3),  
 1001 1048–1054. Retrieved from <https://doi.org/10.1016/j.biortech.2008.07.045>
- 1002 Zhang, M., Song, G., Gelardi, D. L., Huang, L., Khan, E., Mašek, O., ... Ok, Y. S.  
 1003 (2020). Evaluating biochar and its modifications for the removal of ammonium,  
 1004 nitrate, and phosphate in water. *Water Research*, 186. Retrieved from  
 1005 <https://doi.org/10.1016/j.watres.2020.116303>
- 1006 Zhang, T., Xu, H., Li, H., He, X., Shi, Y., & Kruse, A. (2018). Microwave digestion-  
 1007 assisted HFO/biochar adsorption to recover phosphorus from swine manure.  
 1008 *Science of the Total Environment*, 621, 1512–1526. Retrieved from  
 1009 <https://doi.org/10.1016/j.scitotenv.2017.10.077>
- 1010 Zheng, Y., Wang, B., Wester, A. E., Chen, J., He, F., Chen, H., & Gao, B. (2019).  
 1011 Reclaiming phosphorus from secondary treated municipal wastewater with  
 1012 engineered biochar. *Chemical Engineering Journal*, 362(December 2018), 460–  
 1013 468. Retrieved from <https://doi.org/10.1016/j.cej.2019.01.036>
- 1014