Recycling Phosphorus from Agricultural Streams

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Phosphorus (P) is a crucial element for producing crops and is widely used in both recycled manure and inorganic fertiliser. Its cycle has a high impact on the total environment, interfacing the hydrosphere and the pedosphere, and being heavily dependent on the biosphere and anthroposphere. The grey P adsorbents are based on waste materials from the steel industry, which ensure a high rate of P removal but do not allow for its direct reuse as fertiliser. Green P adsorbents are vegetable wastes; they are abundant, locally available, low-cost, and eco-sustainable, but the challenge is certainly their transport. A limitation to the reuse and recycling of agricultural by-products is seeking reusability at all costs, without evaluating the technical and economic feasibility; extra interventions are frequently proposed (i.e., applying high temperatures or adding expensive synthetic molecules to modify the pH). In general, the most promising feasibility is given by its direct use as a soil conditioner or by composting it as a by-product, as the only pre-treatment.

Keywords: surface water ; agricultural waste ; nutrient recovery ; phosphorus

1. Phosphorus in the Soil Environment

1.1. Overfertilised Soils

The presence of phosphorus (P) is essential for modern agriculture. However, fertiliser efficiency varies between regions, and in general, less than 20% of the P absorbed by the plants is then harvested [1]. Globally, farmers apply about 25 Mt P year^{-1}, and about 14 Mt P year^{-1} is not used by crops, becoming a pollutant. This means that more than half is lost to the environment and can create ecological imbalances in ecosystems and water bodies. Therefore, it is crucial to provide crops with the correct amounts of fertilisers to avoid excesses [2].

1.2. P Losses

As a fundamental element of plant nutrition, P excess does not cause problems for the crop itself but exposes the environment to the risk of P leakage and the consequent eutrophication of water bodies [3][4]. Although people can consider transfer into the oceans a natural process resulting from erosion and runoff, it is nevertheless accelerated by human activities such as arable farming, concentrated animal husbandry, and direct anthropogenic discharges, with losses in the range of 19–31 Mt P year^{-1} [5]. Total P losses to European river basins and sea outlets are estimated to be around 100,000 t P year^{-1} [6].

Losses from agricultural soils occur in both dissolved and particulate forms, and their transport depends on the soil type, the extent of soil P accumulation, erosion vulnerability, and hydrological connectivity to the waterbody [7][8][9][10][11].

Agricultural areas play an important role in P losses, as they are the main areas subject to erosion, which facilitates the loss of significant P flows. Their impacts are obvious not only on a local scale but also on a much larger scale [12][13][14][15]. Thus, the goal of eutrophication control would be more achievable if P concentrations in soils were kept at or below the recommended threshold values for improved fertiliser response [16][14][17][18][19][20][21], including strategies to mitigate the transfer of P by erosion [22].

1.3. Estimated P by Pedotransfer Functions

Pedotransfer functions serve to predictively extrapolate certain unmeasured soil properties using measured data from soil surveys. Pedotransfer functions that use indicators are included in the software developed to be utilised directly at the farm level by farmers, calculating the seasonal need for nutrients that could be used to reduce the use of fertilisers and thus avoid P accumulation in soils. Such software was developed to calculate the seasonal demand for P and the best cost–benefit combination of commercial fertilisers [23]. In this way, farmers should have the information necessary to apply the required doses to increase the yield of their crops, gaining benefits in both economic and environmental terms thanks to the reduction of fertilisers used and consequent P loss. However, even if P concentrations in the soil are reduced to the agronomic optimum, it is not clear whether this would be sufficient to reduce P concentrations in the runoff enough to avoid eutrophication problems [24][25].

On average, each year, about 90% of P flows to rivers, lakes, oceans, or non-agricultural land, so optimising soil management and the efficient use of P would reduce nutrient pollution in intercepting waterways [26]. Overall, livestock production contributes the most to total P releases into water bodies, and the phenomenon is magnified in areas where the soils are naturally submerged or by farming practices [27].

2. Technologies to Remove P from Water

Technologies developed to remove and recover P from P-rich waste streams, such as municipal wastewaters (5–25 mg total P L^{-1}) [28], are basically of two types: physical–chemical, such as membrane filtration, precipitation, adsorption, ion exchange, or crystallisation, and biological processes (**Table 1**). These technologies target different P sources, using different engineering approaches that differ significantly in the P recycling rate, pollutant removal potential, product quality, environmental impact, and cost [29][30][31].

Table 1. Technologies to remove phosphorus from water.

Technologies	Function	Pros	Cons	Constriction	Operative Costs [a] EUR per 10^6 L of Treated Water	Cost of 1 kg of P Recovered [a]
Membrane filtration	Semi-permeable selective separation wall	Low energy cost, low capital investment, high productivity	Membrane fouling	Membrane cleaning	42–744	-
Ion exchange	Functionalised polymeric matrices	Suitable for all ions, high productivity	Economic viability	Pre-treatment	42–330	-
Precipitation	Salt added	Removal of suspended and dissolved solids	Sodium carbonate management or H_2S emissions	Plant maintenance	32–330	1.59
Crystallisation	Ca and/or Mg added	Produce granular hydroxyapatite or struvite	-	-	148–305	0.64
Coagulation/flocculation	Adding polymers or metal ions	-	-	-	32–330	-
Thermochemical treatment of sewage sludge	Mixes the ash with sodium-based salts	Produce P-enrich ash	-	Heavy metal-rich ash	28–180 *	-
Biological treatment	Selected bacteria	Low cost, high productivity	Additional treatment before P recovery	High concentrations of organic substrate	32–330	-
Adsorption	Surface phenomenon of molecular interaction	Low cost, high productivity	Reduced ability to remove organic P	Surface area and selectivity of adsorbent; contact time	42–130	-

[a] The costs expressed in different currencies were converted into EUR and discounted (http://rivaluta.istat.it:8080/Rivaluta/ accessed on 20 November 2022). * Expressed in EUR t^{-1} treated sludge.

The scarcity of raw material coupled with environmental problems related to the overuse of phosphate fertilisers has also been considered. In addition to the point sources of P, such as phosphate rocks, non-point sources containing dissolved P, such as surface water, agricultural runoff channels, or surface rainwater, from which the needed P can be drawn to sustain global needs, are considered [32][33].

2.1. P Adsorption

It is important to recover P from agricultural runoff channels, but because it is not easy to intercept in that context, it is necessary to capture P directly from watercourses, where its concentration is, therefore, low. One of the most suitable techniques to recover these low concentrations of P is physicochemical adsorption, a surface molecular interaction that occurs on contact between a solid phase (the adsorbent) and a fluid (liquid or gaseous) phase (the adsorbate). The adsorption process in a solution–adsorbate system occurs because of two factors: the affinity between a solute and solvent and a higher affinity between a solute and solid. The chemical species of the adsorbates establish chemical – physical interactions through Van der Waals forces or intermolecular chemical bonds with groups of adsorbents. The adsorption process, classified among the more advanced treatments, is suitable for the removal of suspended, dissolved, and colloidal forms still present in wastewater treatment plants. The adsorption of P ions depends on different adsorbent factors, such as the surface area, charge, and physicochemical properties of the solution, P concentration, temperature, pH, and presence of other competing ions or molecules [34][35][36]. The selectivity of an adsorbent, i.e., its ability to remove P preferentially from competing ions, is another factor in adsorption studies and depends on the type of interaction formed by the ions competing directly for the active sites of the adsorbent surface. In general, ions such as chloride and nitrate show little or no competition, while ions such as arsenate and silicate show high competition [37][38][39][40]. Phosphate adsorption usually reaches an optimal level when the pH promotes its electrostatic attraction to the adsorbent, i.e., when the pH of the solution is lower than that of the zero-charge point (ZPC) of the adsorbent, making it electropositive. Since several adsorbents have a ZPC near-neutral pH, optimal P adsorption is often in the acidic range [41][42][43][44][45][46][47].

2.2. P-Adsorbent Industrial Materials: “Grey Removal”

In the beginning, the circular economy and the possibility of recycling fertiliser elements, such as P, was not a research priority given the low cost of the materials. Studies on possible biosorbents started in the 1990s, intending, essentially, to remove metal ions, organic molecules, or dyes from wastewater [48]. Since these experiments also studied the behaviours of different anions, the extension of these findings to the phosphate ion is certainly plausible. Different materials have been used for P removal from waste streams through an adsorption mechanism [49][50].

Another high-volume by-product produced in the steel industry, blast furnace slag, was used to prepare a hydrated calcium silicate adsorbent (CSH) to remove phosphate from aqueous solutions. CSH showed a maximum P adsorption capacity of 53 mg g^{-1} in a solution with an initial P concentration of 13 mg L^{-1}, at pH 7.0 and 25 °C. CSH showed excellent adsorption performance related to abundantly present Fe and Ca ions, even from phosphate solutions with a wide range of initial concentrations (2–26 mg L^{-1}) and pH conditions (pH 3–9) [51].

3. P-Adsorbent Bio-Based Materials: “Green Removal”

Based on the “grey” removal of P using adsorbents derived from by-products or the waste of the industries of steel, aluminium, or other material, or by their modifications, were carried out because of the availability of these materials and their chemical affinity with phosphate ions. Additionally, if often very efficient in P removal, P recovery by the adsorbent is carried out with strong acids or hydroxides. Therefore, many of these adsorbents, also meeting the criteria of a “circular economy” because the adsorbent is fully recovered and reusable several times, do not fit exactly with the concept of a “green treatment” [52]. On the other hand, relatively few works have described typical adsorption processes and the ability of adsorbents derived from agricultural waste to recover important anions such as P, arsenic (As), and chromium (Cr) (VI) anions. The “green removal” agricultural waste products are proposed as bio-based solutions to recover and reuse directly on farmland soils. Indeed, the feasibility of using the recovered materials in agriculture has not received much attention, however, due to their low cost, adsorbents from recovered agricultural materials deserve further study and still need major research. The great advantage in the removal of the P anions consists of the possibility, in the eventuality of a strong bind that does not allow for the recovery of P and reuse of the adsorbent, to use the product obtained as a fertiliser or a substrate. This opportunity, evidently, is not conceivable in the case of Cr or As. **Table 2** lists some agricultural waste materials on which experiments have been conducted to evaluate their Cr(VI) and As(V) removal capabilities. As (V) and Cr (VI) are only considered because, in these oxidation states, they behave as anions, CrO_4^{2-} and AsO_4^{3-}, as well as P (PO_4^{3-}), and thus, these three elements behave similarly in adsorption processes. The adsorption mechanisms of other PTEs (Pb, Fe, Zn, …) were not considered because their behaviours are essentially those of cations.

Biosorbents tested to recover Cr(VI) work under extremely acidic pH conditions (pH 2). Therefore, the development of this solution is a challenge from an economic and chemical point of view because maintaining a pH 2 in an actual plant is far from the concept of a “low-cost and green solution”. The same cannot be said for the biosorbents that have been tested to remove arsenate, which work in a pH range between 4 and 9, ensuring the promising performance of the biosorbent.

Table 2. The adsorption capacity of biosorbents that can remove anions Cr (VI) and As (V), and the conditions under which adsorption processes occur.

Adsorbent	Modification	Pollutant Removed	Adsorption Capacity mg g^{-1}	Removal %	pH	T °C	References
Ficus auriculata leaves	Unmodified	Cr (VI)		94.3	2.0	30	[53]
Milled olive stones	Unmodified	Cr (VI)	2.3		2.0	-	[54]
Olive stone	-	Cr (VI)	53.3		2.0	30	[55]
Date pit	-	Cr (VI)	82.6		2.0	30	[55]
Cellulose derived by rice husk	Treated with alkaline humic acid	Cr (VI)	19.3		5.0	25	[56]
Exhausted coffee waste	Unmodified	Cr (VI)	686		3.0	25	[57]
Raw rice straw	Unmodified	Cr (VI)	8.0		2.0	30	[58]
Date palm trunk	Graft with diethylenetriamine and triethylamine	Cr (VI)	129.8		3.5		[59]
Sludge Biomass	Immobilised with calcium alginate	Cr (VI)	116.1		5.0	25	[60]
Sugarcane bagasse pith	Immobilised with Na-alginate	Cr (VI)	52.8		2.0	25	[61]
Black wattle tannin	Immobilised with nanocellulose	Cr (VI)	104.6		2.0	25	[62]
Cactus mucilage	Unmodified	As (V)	2.8		5.0–9.0	-	[63]
Powder of stem of *Acacia nilotica*	Unmodified	As (V)	50.8		4.0–7.0	-	[64]
Sorghum biomass	Unmodified	As (V)	2.8		5.0		[65]
Opuntia ficus indica fruit powder	Unmodified	As (V)		85–92	6.0–7.0	-	[66]
Mucilage cactus	Unmodified	As (V)		98		30	[67]
Cactus mucilage (non-gelling extract)	Mixed with sodium alginate and $CaCl_2$	As (V)	97.1				[68]
Cactus mucilage (gelling extract)	Mixed with sodium alginate and $CaCl_2$	As (V)	101.6				[[68]]

To take into account the environmental sustainability of the adsorbent and its usefulness and easiness for reintroducing P into the environment, over recent years, researchers have proposed some adsorbents from waste materials of the agricultural sector with good properties that would enable sustainable P recovery, both environmentally and economically. These waste materials or by-products of agricultural processing, with or without further modification, are considered environmentally friendly, low-cost, and highly selective with high adsorption capacities [69][70][71][72][73][74]. The agricultural by-products that can be used to adsorb P, and then used as fertiliser or substrate are various: apple and black currant pulp, tea scraps, banana pith, sugar cane pith, coffee pulp [75][76][77][78], orange peel, potato peel, tangerine peel, onion peel, palm peel, hazelnut peel [79][78][80][81], exhausted coffee, corn cobs, rice hulls, corn straw and sawdust, rice straw and husk, sugarcane bagasse [82][83][84][85], almond shells, palm shell charcoal, hazelnut shells, peanut shells, eggshell or apricot kernels, and sunflower seed shells [86][87][88][89]. Numerous attempts have been made to develop new anion exchangers by grafting positively charged amino groups onto the polymer chains of agricultural residues, such as sugar cane bagasse [90], corn bracts [91][92], raw walnut wooden shells and raw almond wooden shells [93], and wheat straw [94].

These studies have shown that the absorption capacities of the charged materials were significantly increased compared to raw materials. The reuse of agricultural waste in the form of classic fertilisers (pellets, for example) is not yet sustainable, either economically or agronomically. The main problem is the elemental composition: all the elements of plant nutrition should be present and in balanced relative quantities [95][96].

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