

New opportunities for biologically and chemically mediated adsorption and precipitation of phosphorus from wastewater[☆]

Chris Pratt¹ and Ana Soares²



Biologically mediated adsorption and precipitation of phosphorus (P) from waste streams can restrict environmental P discharges. Here, we appraise progress in this field over the past decade. The research discipline has grown considerably in recent years. Industry 'wastes', including steel slags, continue to show promise as adsorbents with exceptionally high P retention capacities ($> 500 \text{ mg P g}^{-1}$). Hydrotalcite, a nanomineral, offers prospects as a P removal technology with imbedded climate change mitigation capacity. Biomineral struvite formation, driven by microbial processes, offers an exciting P removal and recovery approach that can be applied to diverse wastewater types due to its feedstock-independent mechanisms, emerging immobilisation techniques and adaptability to mixed cultures. All of these factors facilitate efficient nutrient recycling and scalable application to the wastewater industry. Adsorbed and precipitated P can be applied to cropland to offset dependence on conventional fertiliser inputs. Therefore, in addition to water treatment, these biologically mediated processes also offer opportunities to support food production. Moreover, as many of the input materials covered in this review are industry byproducts and common organic materials, the removal of P from waste streams by adsorption and precipitation offers strong circularity potential that aligns with the UN's Sustainable Development Goals. We call for future work to focus on long-term full-scale trials involving community, government and industry partners.

Addresses

¹ School of Environment and Science/Australian Rivers Institute, Griffith University, Kessels Road, Nathan, Queensland 4111, Australia

² Cranfield Water Science Institute, Cranfield University, UK

Corresponding author: Pratt, Chris (c.pratt@griffith.edu.au)

Current Opinion in Biotechnology 2025, 92:103261

This review comes from a themed issue on **Phosphate Biotechnology**

Edited by **Lars Blank** and **Chris Pratt**

For complete overview of the section, please refer to the article collection, "[Phosphate Biotechnology \(2025\)](#)"

Available online 22 January 2025

<https://doi.org/10.1016/j.copbio.2025.103261>

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Introduction

Phosphorus (P) is a key element in food production and waste management. It is present in elevated concentrations in almost every waste stream, where it contributes to downstream environmental problems, including eutrophication [1] and toxin production [2]. Hence, concerted efforts are made to remove P from effluent before its discharge into the environment. Although a well-recognised problem, achieving reductions in P discharges is challenging. The concentration and form of P in the effluent, the effluent volume to be treated and the budgetary constraints of effluent managers are all important considerations in identifying and implementing appropriate treatment options.

Conventional methods for phosphorus removal from wastewater include biological removal, chemical dosing and membrane separation [3]. All of these

[☆] Given the role as Guest Editor, Chris Pratt had no involvement in the peer review of the article and has no access to information regarding its peer review. Full responsibility for the editorial process of this article was delegated to Lars Blank

techniques are associated with efficiency and cost challenges. Biologically mediated adsorption and precipitation offer a potentially viable alternative approach to remove P from a range of effluents, thereby helping to abate downstream P accumulation. In a review article published approximately 10 years ago, we synthesised the status of technology opportunities in this field [4•]. Three broad technology approaches were identified: 1) filtration by chemically reactive materials through adsorption and precipitation processes, 2) auto mineralisation (e.g. as struvite), and 3) adsorption onto nanomaterials. The review revealed that each approach can achieve very low P discharge concentrations, with technology implementation costs broadly increasing from 1) to 2) to 3). A key recommendation from the review was the need to focus on recovery and recycling of captured P.

How has this research field progressed more than a decade on? If we examine the drivers for removing P from effluent, scrutiny on P discharge limits remains intense. Further, there has been significant discussion on the scarcity of P fertiliser resources, with some anticipating rapid depletion of this element in the coming decades [5••]. This presents a great opportunity to recycle P from waste streams and incorporate it back into food production systems. The aim of this current review, therefore, is to evaluate the state of biologically mediated adsorption and precipitation technologies for removing P from waste streams. Importantly, the work is conducted from the perspective of not only achieving P removal for downstream environmental gains but also identifying opportunities to harness and reuse captured P to help address food production challenges.

Filtration, including emerging materials

A range of materials have been evaluated for their capacity to remove P from effluent via filtration. These include industry byproducts (e.g. slag from steel-making, coal fly ash), natural materials (e.g. volcanic soils) and synthesised nanomaterials (e.g. hydrotalcite, metal–organic frameworks). Effluent biochemistry is a crucial factor affecting removal mechanisms and effectiveness as it governs physicochemical parameters, such as pH and redox, that directly control P removal.

In our previous review, we summarised the P removal properties for a spectrum of filter materials covering influent P concentrations from 0.5 to 300 mg P L⁻¹ (Table 1). P removal capacities ranged from 0.3 to 12 g P kg⁻¹. There have been many studies on P filtration by various filter substrates in the past decade — how do the results compare with those reported in 2012? In Table 1 we summarise recent performance across a range of materials, highlighting key operating parameters

including influent concentration, which has a substantial impact on adsorption-based processes.

Since 2012, there has been a marked increase in the variety of materials investigated for their P filtration potential, with overall higher P retention capacities reported than a decade ago (Table 1). Reasons for this increase are not clear but may reflect the general pursuit of materials with ever-increasing efficiency as well as technological advances in industrial processing that generate byproducts with higher surface areas.

Based on the studies reported in Table 1, it is evident that there is a great diversity of adsorbent materials with a strong affinity for P removal from waste streams. These materials range from industry byproducts and synthesised nanomaterials to natural/organic compounds (Table 1). Hydrotalcite, which is effectively a silicate-free clay, is an interesting candidate for P removal because, when generated industrially, it draws down atmospheric carbon. Hence, this material could offer climate as well as nutrient control benefits.

Reported P removal efficiencies over the past decade are generally very high (80–100%), and some studies have recorded exceptionally high P retention — reaching over 50% of P content by weight (Table 1). However, despite the promising metrics documented for P adsorption, most studies have been conducted in the lab or at pilot scale in the field, making it difficult to confirm technology efficacy at full scale.

A New Zealand study reported on a field-scale trial involving allophanic soil filters treating effluent from a regional community for 1.5 years [12]. The filters were exceptionally effective in the initial stages, achieving 95% total P removal, but then performance declined as adsorption sites became saturated. Nonetheless, they retained approximately 6.4 mg P g⁻¹ during the trial period, reflecting strong application potential in waste stream treatment [12]. Once saturated, the soil was removed from the filters and applied to agricultural land as a P fertiliser replacement (see the later section on [Regeneration and repurposing](#)).

Phosphorus removal and recovery by biomineral formation processes

Biomineral formation, or biomineralisation, is a widespread natural phenomenon that occurs in soils, sediments, caves and corals, as well as in low- and high-salinity aquatic environments and extreme environments. It has also been found to be associated with pathogens. It refers to a series of processes involving selective extraction, uptake and incorporation of elements from the local environment into functional structures under strict biological control. The application

Table 1

P removal by filter media reported in recent studies, with comparison of filter media performance summarised in 2012.

Recent studies					Comparative summary from 2012		
Filter Substrate/lab or field study	Influent P concentration (mg P L ⁻¹)	Removal rate (%)	Capacity (g P kg ⁻¹)	Ref.			
Industry byproducts					Materials tested	Influent P concentration range (mg P L⁻¹)	Capacity range (g P kg⁻¹)
Copper smelter slag/lab	22.6	30	0.26	[6]	Steel slag, water plant fibres, gels, silicate minerals, polonite, oil shale ash	0.5–300	0.3 to 13
Thermally modified steel slag/ pilot field	5	85	35	[7]			
Magnesite slag/lab	300	98	526	[8]			
Coal slag + ferrasol/lab	10–1000	99	19.4	[9]			
Electric arc furnace slag/lab	15	95	1.6	[10]			
Steel slag/lab	5–700	55–100	20.4	[11]			
Concrete aggregates/lab	5–700	55–100	4.07	[11]			
Natural materials							
Allophanic soil/field	Not described	Not described	8.13	[12]			
Egg shell ash/lab	3	90	120	[13]			
Pyrite with steel slag/field	0.2	80–99	11.6–35.2	[14]			
Attapulgate ^a	5–1000	Not described	0.42–449	[15]			
Peach shell	5–700	55–100	3.68	[11]			
Synthesised/nanomaterials							
Lanthanum carbonate grafted microfibrous composite/lab	100	95	11.80	[16]			
Calcium and magnesium hydrotalcite/lab	600	Not described	150 ^b	[17]			
Hydroxides ^a	0.1–1600	Not described	9–108	[18••]			

^a Average values for range of hydroxide minerals.^b Derived from authors' data.

and knowledge around biomineral formation have grown significantly in the last decade in key areas such as human health (e.g. bone repair, dentin remineralisation, kidney stones formation) [19–21], monument conservation [22], materials science [23] including self-healing cement [24], advancing our understanding of marine environments [25], all the way to carbon capture [26], to name a few. More recently, biominerals have been used as a matrix for the development of synthetic materials through biomimicry approaches [27]. The study of biominerals has significant, multifaceted and interdisciplinary far-reaching contributions to science, the economy and society.

Biominerals have a range of underpinning roles, such as providing protection, gravity and magnetic field sensing, support and amassing of resources. The latter is of particular interest, as biomineral formation can be exploited to remove and recover phosphorus from liquid streams and wastewater. Many studies have been published in the last decade showing the potential of biomineral-forming microorganisms to extract nutrients from synthetic and wastewater solutions, as described in a review by Liang and

Gao [28]. Phosphorus can be removed from aqueous streams and concentrated in rich biominerals such as calcium phosphate (e.g. hydroxyapatite $[\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2]$, HAP], octacalcium phosphate $[\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5 \text{H}_2\text{O}]$, OCP], brushite $[\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}]$, DCPD] and tricalcium phosphate $[\text{Ca}_3(\text{PO}_4)_2]$, TCP], as well as struvite $[\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}]$, bobierite $[\text{Mg}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}]$ and baricite $[(\text{MgFe})_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}]$ [29]. The formation of specific phosphate-rich inorganic salts can be targeted by the application of specific microorganisms. For example, calcium phosphate has been shown to be produced by strains of *Bacillus*, *Serratia*, and *Pseudomonas* [30,31]. Nevertheless, the number of strains documented to be able to produce struvite is increasing, and new strains have been documented: *Pseudomonas calciprecipitans*, *Staphylococcus aureus*, *Myxococcus xanthus*, *Bacillus pumilus*, *Halobacterium salinarum*, *Idiomarina loihiensis*, *Brevibacterium antiquum*, *Leclercia adedecarboxylata* JLS1, *Acinetobacter calcoaceticus* SRB4, *Shewanella oneidensis* MR-1, *Enterobacter* sp. EMB19, *Enterobacter cloacae*, *Proteus mirabilis*, *Microbacterium marinum* sp. nov. H207, *Citrobacter freundii* ZW12, *Streptomyces mirabilis* P16B-1 and *Pseudomonas taiwanensis* R-12–2 [28]. Biomineral-forming microorganisms often

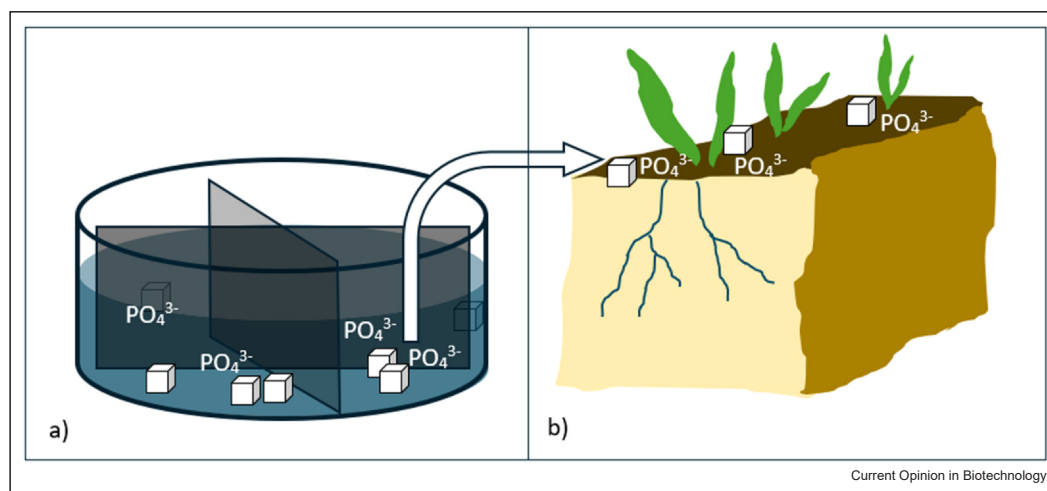
exhibit phenotypes such as exopolysaccharide production, specific metabolic activities, charged cell surfaces and the presence of enzymes like urease or phosphatases that facilitate mineral precipitation. The mechanisms of biomineral formation include biologically induced mineralisation, biologically controlled mineralisation (BCM) and organomineralisation. The mechanisms of struvite biomineral formation in both synthetic media and wastewater seem to be similar, and there is consistency amongst existing literature. BCM is favoured by mildly alkaline pH (8.2–8.8) that is achieved by the metabolism of nitrogen in the aqueous solution. The presence of proteins, urea, ammonia or other nitrogen rich species seems to be very important to obtain struvite precipitation. Local enrichment of ions (i.e. phosphorous, magnesium and ammonia) is required for struvite formation. In a study by Leng and Soares [32], the intracellular concentrations of orthophosphate and magnesium increased to give origin to struvite supersaturation conditions intracellularly, and granular inclusions were also observed inside the cells. The microinclusions can be released from viable cells, but in some cases, it is documented that struvite production is linked with cell autolysis (e.g. *Myxococcus xanthus*) [33]. In most cases, the struvite nucleation points are then released to solution, where crystal growth takes place to form struvite with a size of 0.15–0.4 mm [34]. The assembly of nucleation points has been linked with the presence of molecules such as the siderophore pyoverdine that enable struvite formation to have the lowest energy, resulting in a stable complex in aqueous solution [35]. The most remarkable aspect of these findings is that the biomineral formation mechanisms remain the same in synthetic solutions as in wastewater. The latter is a highly complex feedstock and does not always display the necessary conditions for struvite production using chemical precipitation, such as high orthophosphate concentrations (usually $> 100 \text{ mg P L}^{-1}$). This is a great advantage as the biomineral formation process can be applied to a very wide range of waste streams, with high and low phosphorus concentrations. According to Leng and Soares [36], struvite crystals can be observed when wastewater contains as little as 20 mg P L^{-1} , but phosphorus removal took place even in wastewater with 5 mg P L^{-1} to produce an effluent with $< 1 \text{ mg P L}^{-1}$. The finding that the mechanisms of biomineral struvite formation appear to be universal and not heavily influenced by feedstock composition, unlike other biological processes, is a significant advantage. This allows the process to be reliably predicted for broader application across various wastewater types and situations, de-risking technology development and implementation. To date, there is no model documented for biomineral formation from waste streams, and this is a research gap that needs to be addressed for further advancement in this field. Recent studies also document the ability of microorganisms to be able to tap into a wide range of phosphorus fractions in wastewater [37]. Because of the

hydrolytic properties of the microorganisms to break down organics and other compounds in wastewater, orthophosphate is released from complex molecules and can then be available for struvite formation. The concentration of condensed phosphate has been measured between 276 and 732 mg P L^{-1} in sewage sludge liquors from digestates, and this opens the opportunity to recover more phosphorus fractions that were not available for recovery before. Also, wastewater treatment plants are regulated in relation to total phosphorus. Biomineral formation, tapping into a range of P types, can significantly contribute to achieving regulations and preventing the eutrophication of natural water bodies. On the other hand, the presence of a suitable carbon source (as chemical oxygen demand in wastewater) seems very important for a successful struvite recovery [34,38].

The separation of struvite biominerals from wastewater has primarily been investigated under laboratory conditions using filtration and centrifugation techniques, though large-scale applications remain largely unexplored. Struvite produced through chemical precipitation typically separates by gravity settling in designated tanks, with dense crystals reaching sizes of 1.5–4.5 mm [39]. It is still uncertain whether struvite of a comparable particle size can form through biomineralisation in specialised reactors designed to enhance crystal growth for easier separation, or if alternative separation methods will be required.

Another challenge in scaling up biomineralisation processes lies in the complexity of cultivating and sustaining specific microbial cultures in wastewater. To date, most studies on biomineral formation have been conducted under controlled laboratory conditions with pure cultures; however, for broader application, it is essential for the selected microorganisms to thrive in mixed culture systems, as continuous sterilisation of wastewater or maintenance of axenic conditions is impractical. Although specific microbial cultures have been enriched in wastewater-fed reactor systems by engineering operational conditions that apply selective pressures limiting other competing organisms [40], these approaches often have a high failure rate. Recent developments focus on immobilisation or encapsulation techniques to enhance microbial stability and resilience [28]. For instance, Han and Guo [41] demonstrated that immobilised bacteria achieved more efficient phosphate removal from wastewater, with lower effluent concentrations, than free cells. This approach increased microbial density and improved solid–liquid separation, thereby enhancing the overall recovery process. In support of this, Colston [42] reported comparable results with selected microorganisms encapsulated within biocatalyst matrices in both synthetic media and wastewater, highlighting the potential for scale-up and broader application in the wastewater treatment sector.

Figure 1



Schematic showing how adsorbed and precipitated P can (a) be captured in wastewater treatment systems via biomineralization or adsorption onto industry byproducts/organic compounds and then (b) applied to cropland as P fertiliser.

Regeneration and repurposing

Adsorptive media, including nanomaterials, eventually become saturated with P, and management is needed. It is possible to regenerate the adsorptive potential of many materials, thereby prolonging their P removal lifespan [43–45]. Regeneration is typically achieved via immersing the materials in acid/alkaline or reducing/oxidising solutions. In this regard, commonly occurring and benign reagents are preferable to harsh industrial solutions. Containment of the released P and reuse as a fertiliser or industrial product is desirable.

It makes sense to focus on regeneration techniques for high-tech nanocompounds that are costly to produce but have very effective P removal capacity. For industry byproducts and widely available organic adsorbents, however, it is probably more prudent to pursue a ‘single-use’ approach where the saturated media is removed from the waste stream and applied to agricultural land as a P source. Based on P loading rates in Table 1, many materials are capable of retaining P contents of ca. 10% by weight, which is in the vicinity of many commercial fertilisers. Some studies reported P retention capacities of more than 50% by weight, which is remarkably high. The appropriateness of land application of these P-saturated materials will depend on the chemistry of the adsorptive media — some slag products could contain elevated heavy metal concentrations, which would need to be investigated on a case-by-case basis.

Biomineralized P recovered from wastewater is also typically very P dense (15–20% by weight). Once separated, the struvite produced by bacterial-mediated

processes has been shown to have high purity, minimal antibiotic contamination [46] and low heavy metals, meeting regulations for inorganic fertiliser [47]. The biological mechanisms associated with the struvite formation limit the adsorption of impurities to the recovered product, showing another benefit of the biomineral formation process. The application to land of biominerals such as struvite has not been studied in detail, and this is a research gap that needs addressing. Nevertheless, it is expected that the biomineral will have similar behaviour in the soil as the chemically driven struvite, displaying its potential as a slow-release fertiliser [48••]. The broad concept of recovering adsorbed and precipitated P from wastewater treatment systems and subsequently applying it to agricultural land is depicted in Figure 1.

Conclusions and recommendations

Biologically mediated adsorption and precipitation of P from effluent offers a potentially effective approach to complement wider efforts to regulate P cycling in the environment. Many adsorbents are industry byproducts and common organic compounds. Hence, if they are used to adsorb and precipitate P from effluent and are then applied to agricultural land to supplement conventional P fertiliser inputs, they could present a closed-loop approach to help address nutrient control and food production challenges. Despite promising results reported in this field over the past decade, most studies have been restricted to the laboratory scale. Long-term field tests involving community, government and industry partners are now needed.

Author contributions

Both authors contributed equally to the preparation of the manuscript.

Data Availability

Data will be made available on request.

Declaration of Competing Interest

The authors declare the following financial interests/ personal relationships that may be considered as potential competing interests: Author Chris Pratt is Guest Editor for the Special Issue that this manuscript is being submitted to. If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Pratt, Chris; Soares, Ana

2025-04-01

Elsevier

<https://doi.org/10.1016/j.copbio.2025.103261>

Pratt C, Soares A. (2025) New opportunities for biologically and chemically mediated adsorption and precipitation of phosphorus from wastewater. Current Opinion in Biotechnology, Volume 92, April 2025, Article number 103261