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## Recent developments in polysaccharide-based technologies for phosphorus removal and recovery from wastewater: a review

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Phosphorus (P) is an essential nutrient for the biological function of both animals and plants, as well as a main constituent of industrial products, including crop fertilizers, detergents, chemicals, pharmaceuticals, food and feed, and construction materials. In recent years, the imbalance between P mining and its excessive, inefficient use has led to resource depletion, runoff and water contamination. P contamination predominantly comes from agricultural, industrial, and domestic waste worldwide. The overabundance of P in water bodies has exacerbated eutrophication and related health problems, affecting aquatic life and posing risks to humans. To address global concerns about the depletion of phosphate rock (PR) reserves and alleviate associated environmental and health hazards, various physical, chemical, and biological methods are currently employed to remove and recover P from wastewater. Among these, adsorption, chemical precipitation, membrane filtration, the use of microorganisms, ion exchange, and crystallization are considered the most widely employed techniques. These conventional methods present several drawbacks, including strict control of operation, limited sensitivity to phosphate ions ( $\text{PO}_4^{3-}$ ) at low concentrations, high chemical and energy consumption, poor mechanical and chemical stability, limited scalability, and high costs. Recently, biopolymers, primarily polysaccharide-based technologies, have emerged as sustainable, eco-friendly, low-cost, and innovative alternatives for removing and recovering P from aqueous environments, addressing the prevailing challenges and gaps associated with conventional methods. Polysaccharides and their derivatives exhibit enhanced P removal efficiency, renewability, scalability, high mechanical and chemical strength, and non-toxicity. Although polysaccharides have been widely investigated for wastewater treatment, their involvement and mechanisms in P removal and recovery have not been systematically analyzed. Therefore, this study consolidates recent findings on polysaccharide-based materials, namely cellulose, chitosan, starch, and alginate, for the effective removal and recovery of P, filling an unaddressed area in the literature. The current review also provides a synopsis of current trends and future advancements in polysaccharide-based technologies for the removal and recovery of P. Furthermore, this review serves as a guide to the development of practical and sustainable waste and resource management systems for P, subsequently contributing to the circular bioeconomy.

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### Water impact

Phosphorus (P) is essential for biological processes and commonly found in fertilizers, leading to environmental and health issues. Major P waste sources include agricultural runoff, industrial discharges, and urban wastewater. To reduce the impacts of excess P in water bodies, it is crucial to implement technology-driven solutions and strict regulations for effective P removal and ensure clean water.

## 1 Introduction

Phosphorus (P) is required for the vegetative growth of crop plants and is a primary constituent of cellular membranes,

nucleic acids, proteins, enzymes, and lipids in all living organisms. It plays a pivotal role in numerous cellular processes, including photosynthesis, energy production,

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## Critical review

metabolism, cell growth, cellular signaling and redox homeostasis.<sup>1</sup> P acts as an activator for over 60 enzymes, regulating water content and maintaining salt levels in plants.<sup>1</sup> Albeit the relative abundance of P in topsoil and subsoil is high, in the range of 1200–30 000 kg P ha<sup>-1</sup>, the plant availability of P is low.<sup>2</sup> Moreover, soil P is less mobile and stays intact with the place of origin, making it less available under many soil conditions.<sup>2</sup>

In the context of global industries, P is primarily utilized in agricultural fields, predominantly through synthetic fertilizers and is also critical for producing animal feed additives, thereby ensuring food security for the global

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population. Moreover, P has diverse applications in domestic and industrial products, including detergents, corrosion inhibitors, and food additives, such as those used in beverages.<sup>3,4</sup>

The major natural source of P is PR, which is also a nonrenewable resource with finite reserves. Economic extraction of PR is becoming increasingly challenging, and although predictions vary, experts agree that the supply of extractable phosphate may eventually be exhausted. Apart from the depletion of phosphate, mining for PR and overreliance on P in various industrial, agricultural and domestic applications have resulted in adverse environmental



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effects, including degradation of air, water, and land quality.<sup>5</sup> The most prominent issue is eutrophication, a process in which water bodies like lakes and rivers become enriched with overloaded nutrient content, ultimately triggering the growth of harmful algal blooms (HABs). These HABs act as oxygen scavengers in water bodies, thereby depleting oxygen levels, a condition known as “hypoxia”.<sup>6</sup> This generates dead zones for aquatic species, endangering their lives and consequently leading to a decline in population or the migration of marine organisms to other more favorable environments.<sup>7</sup> The toxins produced and released by these algal blooms can contaminate water bodies and pose a risk of entering human bodies *via* the drinking water supply. These toxins may cause liver damage and neurological problems.<sup>8</sup> Prolonged exposure to low levels of these toxins has also been reported to develop liver tumors (hepatic tumors) with time.<sup>9</sup>

The World Health Organization (WHO) has established guidelines for maximum discharge levels, recommending that P concentrations in lakes or reservoirs should not exceed 0.025 mg L<sup>-1</sup>, and streams draining into them should remain below 0.05 mg L<sup>-1</sup>.<sup>10,11</sup> Streams not flowing into lakes or reservoirs should have P levels below 0.1 mg L<sup>-1</sup>.<sup>11</sup> However, these thresholds can vary regionally depending on local geology, climate, and soil characteristics.

The economic, environmental and health issues related to excessive P levels in water bodies may be resolved by recycling and reusing phosphates discharged into the environment. Additionally, since elemental P cannot be produced in laboratories and there are no known substitutes for phosphates, especially in food production, P recovery from waste is essential to meet present and future demands.<sup>12</sup> Recent studies suggest that waste reduction and

recovery approaches could replace up to 50% of the global mined P content. In addition, compared to other waste types, P recovery is typically easier, as the waste can be collected, treated, and recycled through a well-established and structured management system.<sup>13</sup> Hence, there is a considerable quest for eco-friendly P removal and recovery technologies to maintain ecological equilibrium and advance sustainable resource utilization. Moreover, these technologies need to prioritize achieving a zero-carbon and environmentally benign footprint, aligning with the Sustainable Development Goals (SDGs) and the circular bioeconomy. The use of natural polymers or biopolymers in water treatment technologies has attracted significant attention due to their minimal environmental impact.<sup>14</sup>

Biopolymers are sustainable and eco-friendly materials that have demonstrated significant efficacy in removing pollutants from wastewater. Their biodegradable properties enable them to be decomposed by microorganisms in the environment, thereby reducing waste accumulation and further enhancing their environmental benefits. As non-toxic substances, biopolymers do not pose risks to human health or the ecosystem.<sup>15,16</sup> Being derived from renewable resources, they support sustainability and help to diminish reliance on nonrenewable materials. Three major types of biopolymers include polysaccharides, polypeptides and polynucleotides. Interestingly, these biopolymers, especially polysaccharides, can be tailored to enhance their biological, chemical, and mechanical properties due to the presence of reactive functional groups, including hydroxyl (-OH), carboxyl (-COOH), carbonyl (-C=O), and amine (-NH<sub>2</sub>), which qualify them for application in wastewater treatment, hence making them ideal candidates for P removal and recovery applications.

The current review provides a comprehensive overview of studies on P removal and recovery, primarily reported between 2019 and 2025, which utilize polysaccharides. We provide a comprehensive coverage of current P removal and recovery technologies, including their mechanisms of action, with a particular focus on the most widely used technology, the adsorption process. The implementation of polysaccharide-based materials, primarily cellulose, chitosan, starch, and alginate, and their derivatives in P removal and recovery technologies, along with their efficiencies, and the future perspectives of polysaccharide usage, covering advanced composites, smart and responsive materials, polyphosphate biotechnology, emerging policy frameworks, circular approaches, sustainable resource management, and applications of artificial intelligence (AI) have been explicitly discussed. To the best of our knowledge, this is the first attempt to bridge a research gap by addressing the application of polysaccharide-based materials in the removal and recovery of P. This review highlights the significant potential of polysaccharides in developing eco-benign, low-cost, and efficient P removal and recovery technologies for wastewater treatment, demonstrating promising applications for environmental



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## 2 P removal and recovery technologies

Numerous techniques are employed to remove and recover P from wastewater. The significant difference between P removal and recovery technologies is that the former aims to remove P-free effluents from wastewater, while the latter aims to collect P-containing products and reuse them for other purposes. Generally, these methods can be categorized as chemical, biological, physical and urine source separation. Urine source separation is considered either a chemical or a physical method. Fig. 1 depicts the most widely used technologies for P removal and recovery. Table S1 outlines the benefits and drawbacks of the most widely used physical, chemical and biological methods for comparison purposes.

### 2.1 Adsorption techniques for P removal and recovery

The adsorption process is considered a primary approach for P removal and recovery due to its simplicity of operation, low cost, adaptability in design, reusability, and increased P removal effectiveness without generating hazardous by-products.<sup>17,18</sup> The primary goal of the adsorption process is to concentrate phosphate ions on the surface of the adsorbent. The following section primarily discusses the adsorption process, including examples of adsorbent materials and the mechanisms of adsorption action during P extraction and recovery.

The adsorption process occurs when solute particles, such as molecules, atoms, and ions, in the medium bind to the surface of a solid adsorbent through various chemical interactions, including dispersive and electrostatic interactions.<sup>19</sup> Identifying a suitable and effective adsorbent is the most crucial step in phosphate adsorption. The adsorbent should possess a long lifespan and a high adsorption capacity, and, ideally, be porous, resulting in a wide surface area.<sup>20</sup> Additional parameters, such as metal doping, surface modification, ligand adsorption, and chemical treatments, can contribute to maximizing the adsorption capacity.<sup>20</sup> For successful practical application, large-scale availability, cost-effectiveness, biodegradability,

and biocompatibility are all desirable properties of the adsorbent. The most valuable characteristic of the adsorbent is its selectivity for P over other solutes.<sup>21,22</sup> Table S2 lists the major adsorbent materials reported for phosphate removal in the literature.

### 2.2 Mechanisms of action

The phosphate adsorption mechanism depends heavily on the physical and chemical properties of the adsorbent surface, which determine the reaction rate, adsorption capacity, and energy requirements. The surface interactions of the adsorbent also provide valuable insights into adsorption and the subsequent desorption and regeneration steps. Therefore, understanding these surface interactions can help maximize the effectiveness of adsorption. The following section focuses on the main mechanisms involved in the adsorption process.

**2.2.1 Ion exchange.** A counterion on the surface of the adsorbent is exchanged for a chemically equivalent counterion from the solution in an ion exchange interaction. By replacing the previously attached ion with the adsorbed ion from the solution, this exchange preserves the electroneutrality of the solution. As a result of the retention of exchanged ions of their inner hydration shell and outer coordination shell, this process is also referred to as “outer-sphere surface complexation”. Since electrostatic forces drive this process, interactions are reversible.<sup>23,24</sup>

In phosphate adsorption, the ion exchange mechanism involves phosphate anions physically displacing counter anions, including bicarbonate ( $\text{HCO}_3^-$ ), chloride ( $\text{Cl}^-$ ), and sulfate ( $\text{SO}_4^{2-}$ ) from the outer-sphere surface of the adsorbent. Numerous studies have highlighted ion exchange as a potential pathway for phosphate adsorption in various adsorbents, such as anion exchange resins, polymer-based nanosized hydrated ferric oxides (HFOs), and zirconium-modified chitosan.<sup>25–30</sup> Fig. S1 shows the schematic representation of phosphate adsorption mechanisms *via* ion exchange, where the counter anion,  $\text{Cl}^-$ , is exchanged with  $\text{H}_2\text{PO}_4^-$ .

**2.2.2 Ligand exchange.** Ligand exchange is a rapid, powerful, and often irreversible process that differs from ion exchange, as it involves the formation of chemical bonds between the adsorbent and incoming phosphate ions. This method uses “inner-sphere” complexation to replace –OH groups affixed to a metal surface with phosphate ions. The “inner-sphere” refers to the direct bonding and interaction that occur inside the hydration shell of the metal coordination complex involved in the exchange.<sup>31</sup> The schematic representation of phosphate adsorption mechanisms *via* ligand exchange is depicted in Fig. S2.

This process shifts the point of zero charge (pzc) of the surface toward lower pH values due to the added negative charge from adsorbed phosphate anions. Additionally, the desorption of  $\text{OH}^-$  ions into the solution raises its pH.<sup>32</sup> The typical ligand exchange behavior, commonly explained by



Fig. 1 Commonly used P removal and recovery technologies.

pseudo-second-order kinetics in phosphate adsorption studies, is one indicator of this process. Many different adsorbents are known to utilize this mechanism, including ferric-modified laterites, hydrated aluminum oxide-modified zeolite, lanthanum-modified materials, and polymer ligand exchangers.<sup>33</sup>

**2.2.3 Hydrogen bonding.** Another important type of interaction in adsorption-based phosphate removal is hydrogen bonding (H-bonding). Phosphate adsorption properties are influenced by H-bonding, according to a study by Loganathan *et al.*<sup>32</sup> The strong electronegative oxygen atom of adsorbed phosphate anions interacts with hydrogen atoms of OH<sup>-</sup> groups in metal oxides, forming H-bonds during phosphate adsorption. Since the inner-sphere hydration atoms of metal complexes create H-bonds with previously adsorbed phosphates, this interaction has been suggested as an additional mechanism for ligand exchange. It is a stronger interaction than ion exchange interactions, but weaker than ligand exchange interactions.<sup>32</sup> Fig. S3 illustrates the schematic representation of phosphate adsorption mechanisms involving H-bonding.

**2.2.4 Surface precipitation.** Surface precipitation is the process by which cations from solution deposit onto phosphates that have already been adsorbed, forming metallic phosphate precipitates on the adsorbent surface. It has been proposed that this type of deposition can convert monolayer phosphate ion adsorption into multilayer deposition.<sup>34</sup> Interestingly, surface precipitation can happen even at low phosphate and metallic ion concentrations, where bulk precipitation is not thermodynamically feasible. In such cases, a localized region near the adsorbent surface becomes supersaturated, leading to precipitate formation.<sup>24</sup> Fig. S4 depicts a schematic representation of phosphate adsorption mechanisms through surface precipitation.

However, it is challenging to predict when surface precipitation may start, as surface complexation and surface precipitation often co-occur during phosphate adsorption, and multilayer deposition may begin before monolayer saturation is reached. If the adsorption process correlates with the Freundlich isotherm, which frequently denotes a linear regime, it is ascribed to surface precipitation.<sup>35</sup> Zeta potential variations as a function of adsorbed amounts have recently been identified as a key metric for differentiating surface precipitation and adsorption processes.<sup>36</sup>

**2.2.5 Diffusion.** The process of phosphate adsorption on adsorbents follows a two-phase kinetic model, with diffusion playing a key role in determining the adsorption rate.<sup>32</sup> The two phases are: (i) film diffusion: in this initial phase, phosphate ions rapidly adsorb onto the outer surface of the adsorbent. This stage reaches a state of pseudoequilibrium quickly and is primarily controlled by the rate of mass transfer to the surface, often referred to as mass transfer-controlled adsorption. This fast phase is surface-related and limited by mass transfer.<sup>37</sup> (ii) Intraparticle diffusion: in the

second phase, phosphate ions slowly diffuse into the internal pores, channels, or cavities of the adsorbent. This stage, influenced by the diffusion characteristics of phosphate ions, is referred to as diffusion-controlled adsorption. This process is slower than film diffusion and determines the long-term adsorption capacity of the material.<sup>37</sup>

The distinction between these two phases—film diffusion and intraparticle diffusion—emphasizes the importance of diffusion mechanisms in adsorption kinetics over the adsorption mechanisms themselves. This dual-phase model is particularly relevant for materials, such as hydrous metal oxides and porous adsorbents, where surface and internal diffusion significantly impact performance.<sup>32</sup> This model offers valuable insights for optimizing adsorbent design and enhancing phosphate removal efficiency by considering both surface and intraparticle characteristics.

**2.2.6 Intercalation.** Due to their comparatively weak interlayer bonding, layered double hydroxides (LDHs) are recognized due to their ability to adsorb both organic and inorganic anions through intercalation. LDHs are defined by the general formula  $[M_{1-x}^{2+}M_x^{3+}(\text{OH})_2]^{x+}(A_n)^{x/n}\cdot m\text{H}_2\text{O}$ , in which  $M^{3+}$  is a trivalent cation, such as  $\text{Al}^{3+}$  and  $\text{Fe}^{3+}$ .  $M^{2+}$  is a divalent cation, such as  $\text{Ni}^{2+}$  and  $\text{Mn}^{2+}$ .  $A_n^-$  is the intercalated anions, which can be organic, carboxylates, and oxoanions. Together with water molecules, these anions remain in the interlayer area, guaranteeing charge neutrality and structural integrity.<sup>38</sup>

The replacement of trivalent cations for divalent cations results in the positively charged brucite-like sheets that make up the molecular structure of LDHs.<sup>38</sup> In the hydrated interlayer areas, intercalated anions complement these layers. Because of their high charge density, exchangeable interlayer anions, and wide adsorption surface area, LDHs have an inherent ability to absorb anions. Hence, they have been extensively studied for removing phosphate from contaminated water.<sup>38</sup>

## 2.3 Chemical methods for P removal and recovery

Chemical precipitation is the most widely used chemical method for removing and recovering P. It offers the dual benefits of reducing environmental pollution and recovering P in a form that can be utilized. By mixing cationic salts, such as  $\text{Fe}^{3+}$ ,  $\text{Al}^{3+}$ ,  $\text{Mg}^{2+}$ , or  $\text{Ca}^{2+}$  with phosphate-containing water, this technique forms insoluble phosphate complexes (see eqn (1)–(3)).<sup>39</sup> As precipitates, these complexes subsequently separate from the aqueous phase.<sup>39,40</sup> Despite being the primary chemical for phosphate removal in the past,  $\text{Ca}(\text{OH})_2$  has become less common due to issues with handling, storage, and sludge generation.<sup>39</sup>



Crystallization is a specific type of chemical precipitation method in which dissolved substances undergo a phase transition, forming inorganic precipitates or crystals. This process is accomplished by optimizing experimental parameters, such as temperature, pH, and the addition of exogenous ions, to create supersaturation conditions.<sup>41</sup>

Chemical precipitation techniques based on Mg and Ca are frequently used to recover phosphates, producing reusable phosphate. The crystalline forms of Mg- and Ca-based phosphate precipitates are referred to as hydroxylapatite ( $\text{Ca}_5(\text{PO}_4)_3(\text{OH})$ ) and struvite ( $\text{NH}_4\text{MgPO}_4 \cdot 6\text{H}_2\text{O}$ ), respectively.<sup>42,43</sup>

Struvite, also known as MAP (magnesium ( $\text{Mg}^{2+}$ ), ammonium ( $\text{NH}_4^+$ ), and phosphate), is a crystalline orthophosphate mineral that develops in alkaline environments. Its composition is equimolar quantities of  $\text{Mg}^{2+}$ ,  $\text{NH}_4^+$ , and  $\text{PO}_4^{3-}$  (1:1:1), see eqn (4).<sup>20,44</sup>



Struvite is only marginally soluble in neutral or alkaline environments, but it dissolves readily in acidic ones.<sup>45</sup>  $\text{Mg}[\text{H}_2\text{O}]_6^{2+}$  octahedra and  $\text{PO}_4^{3-}$  and  $\text{NH}_4^+$  tetrahedra comprise its orthorhombic crystal structure.<sup>46</sup> The soluble components of struvite crystallize into a solid precipitate that can be extracted from the liquid solution by a phase change procedure.<sup>46</sup> P can be recovered from a variety of waste products, including swine wastewater, anaerobic supernatant, and human urine, using this technique. Struvite crystallization has been achieved using a variety of crystallization reactor types, including continuous flow reactors, water-agitated fluidized bed reactors, air-agitated fluidized bed reactors, batch reactors, and mechanically stirred reactors.<sup>47–50</sup>

#### 2.4 Biological methods for P removal and recovery

Biological methods utilize microorganisms to collect and store P from wastewater in an environmentally beneficial and economical manner. Due to its environmental advantages, this method is widely used in wastewater treatment facilities and is essential to the enhanced biological phosphorus removal (EBPR) process. Specialized bacteria known as phosphate-accumulating organisms (PAOs) play an imperative role in the biological removal of P. Examples of PAOs include *Candidatus Halomonas phosphatis*, *Candidatus Accumulibacter phosphatis*, *Pseudomonas putida*, species of the genus *Aeromonas*, and the genus *Rhodocyclus*.<sup>51</sup> As the main functional bacterium among PAOs, *Candidatus Accumulibacter phosphatis* is the most effective PAO in EBPR systems.<sup>51</sup>

These microbes store P internally as polyphosphate after absorbing it in excess of their immediate needs. To optimize P uptake, the procedure alternates between anaerobic and aerobic conditions. During the anaerobic phase, PAOs produce energy-rich molecules, such as polyhydroxyalkanoates (PHAs), by metabolizing volatile fatty

acids (VFAs) and releasing P.<sup>52</sup> PAOs grow and take up P from wastewater during the aerobic phase, storing it as intracellular polyphosphate and utilizing the stored PHAs. This cyclical process is essential for the effective removal of P, achieved through the strategic alternation of anaerobic and aerobic conditions.

Certain operating factors must be carefully tuned to achieve the highest level of EBPR efficiency.<sup>53</sup> Low nitrate and COD levels, sufficient oxygen concentration, and an adequate anaerobic retention time are essential because nitrates can prevent PAOs from releasing P. Temperature and pH are additional factors that affect the effectiveness of EBPR. Temperatures between 20 °C and 30 °C, along with a pH range of 7–8, are ideal for PAOs because they promote enzymatic activity, which is essential for PAO metabolism. Hydraulic retention time (HRT) and solids retention time (SRT) are also equally important. To maintain a steady PAO population and balance its growth rates with those of other microbial communities, an SRT of 10–20 days is recommended.

### 3 P removal and recovery using polysaccharides

Increasing concerns about P depletion and the environmental repercussions of P-containing waste have led to heightened interest in polysaccharides for effective P management in both the hydrosphere and the lithosphere.<sup>54,55</sup> In recent decades, polysaccharides have been extensively explored for their potential in removing P from wastewater. These polysaccharides are composed of repeating monosaccharide units ( $\text{C}_n(\text{H}_2\text{O})_n$ ). Polysaccharide-based hydrogels, aerogels, and cryogels, as three-dimensional (3D) solid matrices, allow incorporation of a wide variety of functional groups into their polymeric framework. Functionalizing the surface of these hydrogels *via* crosslinking with metal cations, such as  $\text{Ca}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Al}^{3+}$ , and  $\text{Zr}^{4+}$ , results in a robust 3D network structure, enhancing P-removal and recovery.<sup>55,56</sup> Advanced nanobiopolymer-based adsorbents, such as nanocomposites (NCs), nanofibrillated cellulose (NFC), cellulose nanocrystals (CNCs), carbon, and chitosan nanoparticles (CSNPs), are particularly effective due to their high surface area and porosity, which facilitate phosphate adsorption.<sup>57–60</sup> The following section examines and compares various methods and materials for P removal and recovery, with a focus on the role of four naturally occurring polysaccharides, namely, cellulose, chitosan, starch, and alginate.

#### 3.1 Cellulose and its derivatives for P removal and recovery

Being the most abundant polymer on Earth, cellulose and its derivatives have emerged as promising adsorbents due to their renewable nature, cost-effectiveness, and ability to be functionalized. It is a linear homopolymer of  $\beta$ -D-glucose monomer units covalently linked together *via* 1 → 4 glycosidic linkages. Fig. S5 shows the chemical structure of

cellulose. Cellulose is chemically modified to enhance its adsorption capacity, with common modifications including cationic functionalization, metal ion immobilization, and carboxylation. For example, cationic cellulose derivatives, such as quaternary ammonium cellulose, have demonstrated strong electrostatic interactions with negatively charged ions, including phosphate, thereby significantly enhancing their adsorption efficiency.<sup>61</sup>

Numerous P removal and recovery techniques have been reported utilizing cellulose and its derivatives. For instance, Ma *et al.* developed a novel bioreactor by combining mycelium pellets with tea biochar-cellulose@LDH (TB-CL@LDH), generating composite mycelial pellets (CMPs). These pellets were immobilized with the bacterial strain *Cupriavidus* sp. ZY7 and *Pseudomonas* sp. Y1, forming a synergistic system for pollutant removal.<sup>62</sup> Under optimal conditions, this bioreactor achieved an 80.4% phosphate removal efficiency. The study highlighted how strain Y1 utilized the carbon source produced by strain ZY7 from cellulose breakdown, enhancing the removal of phosphate and Zn<sup>2+</sup> ions through adsorption, co-precipitation, and biomineralization processes. This technology offers a promising approach for wastewater treatment involving Zn and P contaminants.<sup>62</sup>

Similarly, immobilizing metal ions such as La<sup>3+</sup> and Fe<sup>3+</sup> on cellulose introduces active sites for phosphate binding *via* ligand exchange or coordination mechanisms.<sup>63,64</sup> For example, Fe(III)-crosslinked cellulose agar beads (Fe-CLCABs) created through a sol-gel process demonstrated a maximum adsorption capacity of 73.13 mg g<sup>-1</sup> and achieved 94% P removal at pH 5 using 500 beads.<sup>63</sup> The beads could be regenerated with a two-step elution process involving sodium chloride, retaining 42% of their initial efficiency after six cycles, which underscores their robustness and reusability.<sup>63</sup>

Carboxymethyl cellulose (CMC) derivatives further improve P removal by providing additional binding sites. Li *et al.* synthesized a sponge-based nanocomposite adsorbent (MS-CMC@La) using melamine sponge, LaCl<sub>3</sub>, and sodium

CMC.<sup>65</sup> The material achieved a maximum adsorption capacity of 15.28 mg g<sup>-1</sup> and exhibited high selectivity for P in the presence of competing anions, except fluoride. The P removal mechanism was primarily driven by electrostatic attraction, ligand exchange, and inner-sphere complexation, with pH playing a significant role in the process.<sup>65</sup>

A multifunctional nanocellulose/alginate hydrogel (La-NCF/SA-PEI) incorporating nanocellulose fibers, sodium alginate, polyethyleneimine, and lanthanum was designed by Zhang and coworkers to adsorb P effectively.<sup>58</sup> This hydrogel exhibited an exceptional maximum P adsorption capacity of 78.0 mg g<sup>-1</sup>, surpassing most lanthanum-based hydrogels. Its high selectivity for phosphate was attributed to the formation of ammonium phosphate and inner-sphere complexes with La(OH)<sub>3</sub>, making it highly suitable for treating municipal sewage and aquaculture wastewater.<sup>58</sup> Fig. 2 depicts the schematic representation of the synthesis process of the La-NCF/SA-PEI hydrogel and P removal and its recovery mechanisms.

Enhanced P adsorption was reported by incorporating CaCO<sub>3</sub> NPs into microfibrillated cellulose (MFC) and crosslinked CMC hydrogel beads.<sup>59</sup> The *in situ* growth of CaCO<sub>3</sub> *via* CO<sub>2</sub> significantly increased the adsorption capacity, reaching 109.87 mg g<sup>-1</sup>, and further improvement to 132.21 mg g<sup>-1</sup> was achieved by increasing active sites. The process remained stable across a pH range of 3–7, with selectivity primarily driven by chemical interactions. The beads demonstrated excellent reusability, retaining over 80% of their initial capacity after six cycles, highlighting their potential for environmental remediation.<sup>59</sup> Dong *et al.* developed a lanthanum-modified cellulose sponge (LCLM) employing adsorption-electrochemical mediated precipitation (EMP), which enabled *in situ* P recovery as Ca<sub>5</sub>(PO<sub>4</sub>)<sub>3</sub>OH with a capacity of approximately 226 mg P per g La. The process involved electromigration and lattice effects, demonstrating a sustainable approach for P recovery and wastewater dephosphorization.<sup>66</sup> Moreover, Ca<sub>5</sub>(PO<sub>4</sub>)<sub>3</sub>OH was deposited in the cathode chamber (P-CC) instead of the cation exchange membrane (CEM) and cathode, suggesting that the P recovery process was governed by the electromigration effect and the

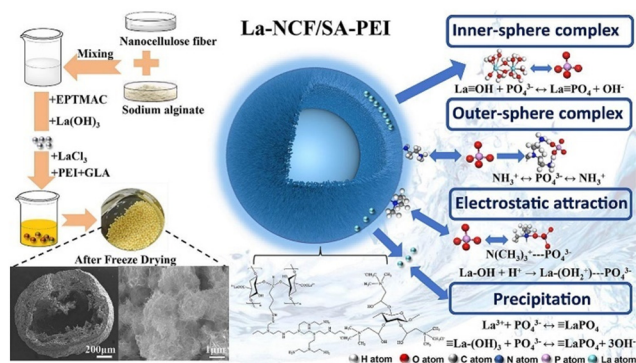


Fig. 2 Schematic representation of the synthesis process of the La-NCF/SA-PEI hydrogel and its morphology and P removal and recovery *via* inner-sphere complex, outer-sphere complex, electrostatic and precipitation mechanisms (reprinted with permission from Zhang *et al.*).<sup>58</sup>



Fig. 3 Schematic diagram of electrochemically mediated P removal and recovery mechanisms of the LCLM sponge filter (reprinted with permission from Zhang *et al.*).<sup>66</sup>

saturation of Ca-P species in the EMP system.<sup>66</sup> Fig. 3 depicts the schematic representation of electrochemically-mediated P removal and recovery mechanisms of the LCLM sponge filter.

Environmentally responsive functional cellulose-based hydrogels that alter their physical and chemical properties in response to environmental stimuli have been developed for the simultaneous removal of P and heavy metal ions. For instance, a novel thermo-responsive polysaccharide-based composite hydrogel containing 2-hydroxy-3-butoxypropyl hydroxyethyl cellulose, sodium alginate and lignin (HBPEC/SA/lignin hydrogel) has been fabricated for P and enhanced Cu<sup>2+</sup> removal.<sup>67</sup> These hydrogels could undergo significant volume changes when exposed to temperatures above or below their volume phase transition temperature (VPTT). Above the VPTT, the hydrogels shrink and release water, while below the VPTT, they expand, allowing small amounts of eluent to penetrate and facilitating effective desorption with minimal eluent consumption. This property enables efficient regeneration and reusability of the hydrogel.<sup>67</sup>

Also, in phosphate remediation processes, mechanically stable pellets were synthesized by blending magnesium carbonate (MgCO<sub>3</sub>) with varying ratios of cellulose, which functioned as a binder.<sup>68</sup> MgCO<sub>3</sub>, known for its extremely low water solubility, served as the primary phosphate adsorbent, while cellulose provided structural integrity. The subsequent burning of the cellulose binder introduced porosity into the pellets, enhancing their adsorption characteristics. The pellets exhibited promising phosphate adsorption performance, with an average adsorption capacity of 96.4 mg g<sup>-1</sup>.<sup>68</sup>

A cellulose-based sponge with pores optimized for supporting magnesium oxide (MgO), specifically with the MgO (100) crystal facet, referred to as C-MgO (100), was fabricated as an efficient phosphate adsorbent.<sup>69</sup> This composite demonstrated an impressive phosphate<sup>-</sup> adsorption capacity of 28.3 mg g<sup>-1</sup>, more than ten times that of pure MgO (100) particles. C-MgO (100) also exhibited strong selectivity for phosphate under wastewater conditions, with phosphate chemically adsorbed through electron transfer from the PO<sub>4</sub><sup>3-</sup> group's p-orbital. A 1% KOH solution in tap water proved effective for regenerating C-MgO (100), achieving a phosphate desorption efficiency of over 82.6% after five reuse cycles.<sup>69</sup> SEM analysis revealed that MgO particles were anchored to the surface of the cellulose sponge, forming blocks, while phosphate adsorption resulted in the deposition of newberyite (MgHPO<sub>4</sub>·3H<sub>2</sub>O) precipitates on the MgO surfaces. Following desorption, the precipitates were significantly reduced, confirming the efficient regeneration of the adsorbent.<sup>69</sup>

### 3.2 Chitosan and its derivatives for P removal and recovery

Chitin (C<sub>8</sub>H<sub>13</sub>O<sub>5</sub>N)<sub>n</sub> is the second most abundant polysaccharide in nature and is found in crustacean shells, insect scales, fungal cell walls, and algae.<sup>70</sup> It is a linear

homopolymer of *N*-acetylglucosamine units linked by β-(1,4)-glycosidic bonds. When chitin is deacetylated by more than 50%, it becomes chitosan, a polycationic polymer with positively charged amino groups (pK<sub>a</sub> ~6.5) that increases its solubility in neutral and acidic solutions [148–151]. Consequently, chitosan is formed by β-(1,4) glycosidic linkages, connecting D-glucosamine and *N*-acetyl-D-glucosamine monomers in an arbitrary sequence. Chitosan exhibits superior properties and broader applications compared to chitin, largely due to the reduced presence (or absence) of acetamido groups. Commercially, chitosan is predominantly produced through the chemical deacetylation of chitin, using raw materials such as crustacean shells and mushrooms. Fig. S6(a and b) depict the chemical structures of chitin and chitosan.

Due to its protonated amino groups, chitosan is soluble in slightly acidic and neutral media, acting as a polycation. Its molecular weight, crystallinity, degree of acetylation, and physical forms, including flakes, powders, and membranes, all influence its physicochemical behavior. The presence of -OH and -NH<sub>2</sub> groups are highly modifiable *via* grafting or crosslinking, making chitosan highly adaptable. Despite its structural similarity to cellulose, the amino group at the C-2 position in chitosan enhances its functionality in a wide range of morphological structures, including hydrogels, films, fibers, NPs, and microspheres. This section explicitly explores how various forms and modifications of chitosan can be used to remove and recover P from aquatic environments.

In natural water systems, where chitosan hydrogels (CSHs) are used to eliminate excess phosphate compounds, the unmodified CSH exhibits a low affinity for phosphate ions at neutral and slightly alkaline pH levels.<sup>71</sup> While CSH exhibits increased adsorption capacity under acidic conditions (pH < 4), such environments risk dissolving the chitosan granules. To address this, various modifications are employed to improve mechanical and physical stability. Crosslinking is one of the earliest methods used to enhance stability, effectively preventing dissolution; however, it often reduces phosphate adsorption efficiency. Common crosslinking agents include glyoxal, formaldehyde, diethyl squarate, epoxy compounds, genipin, polyethylene glycol (PEG), and dialdehyde starch (DAS).<sup>72</sup>

The presence of free -NH<sub>2</sub> groups on chitosan enables it to function as an effective chelating resin for binding transition metal ions, such as Cu<sup>2+</sup>, Ni<sup>2+</sup>, and Zn<sup>2+</sup>. According to Pearson's hard and soft acid-base (HSAB) theory, nitrogen donor atoms, acting as Lewis bases, exhibit exceptionally high selectivity for transition metal ions with moderate Lewis acidity through coordination bonding.<sup>73</sup> Thus, the immobilized transition metal ions on chitosan facilitate both Lewis acid-base interactions and electrostatic interactions with target ligands, such as orthophosphate ions. Consequently, the affinity of the transition metal ion-containing chitosan for various contaminants is determined by the ligand strength. For example, An *et al.* developed a

chitosan-based polymeric ligand exchanger (PLE) by immobilizing  $\text{Cu}^{2+}$  for the removal of P.<sup>74</sup> The authors reported maximum phosphate uptake capacities of 70 and 35  $\text{mg g}^{-1}$  in a single-component system with only phosphate and a binary-component system with phosphate and sulfate, respectively.<sup>74</sup> A cerium(IV)-modified chitosan hydrogel (Ce-CTS) achieved over 98% P removal *via* chemical co-precipitation, which is about four times better than the unmodified CTS.<sup>75</sup> The addition of cerium(IV) significantly improved both chemical and physical adsorption capacities, demonstrating the potential of Ce-CTS for P removal and recovery applications.<sup>75</sup>

Malathion, a synthetic organophosphate insecticide, has contributed to water contamination. To address the removal of pesticides from aqueous solutions, Sabbagh *et al.* developed sponge composites of chitosan and sodium alginate, which proved effective in extracting organophosphate insecticides from water.<sup>76</sup> They produced NCs using five different chitosan-to-sodium alginate ratios. The optimal removal conditions were identified as pH 7, a contact time of 15 minutes, a malathion concentration of 10  $\text{mg L}^{-1}$ , and an adsorbent dosage of 0.15 g. Under these conditions, the composites achieved a maximum removal efficiency of 97.56% and an adsorption capacity of 52.08  $\text{mg g}^{-1}$ .<sup>76</sup>

Chitosan can be effectively blended with other polymeric materials, such as poly(vinyl alcohol) (PVA) and polyethylene glycol (PEG), to enhance its mechanical and chemical properties.<sup>77</sup> The improved properties are attributed to interactions between PVA and chitosan within the blend, which involve hydrophobic side-chain aggregation as well as intra- and intermolecular hydrogen bonding. These hybrid chitosan-based materials have demonstrated significant phosphate removal efficiency.<sup>77</sup> Among the composites, PEG/chitosan exhibited a higher adsorption capacity of 74.85  $\text{mg g}^{-1}$  compared to 46.19  $\text{mg g}^{-1}$  of PVA/chitosan, making PEG/chitosan a more promising candidate for P removal from aqueous solutions.<sup>77</sup>

Montmorillonite/sodium alginate/chitosan beads (CS/SA-FeMT) prepared from the semi-interpenetrating network method were tested for P removal.<sup>78</sup> The study demonstrated an 81.65% P adsorption efficiency after five consecutive adsorption/desorption cycles, with high resistance to interference from common anions, such as  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ , and  $\text{NO}_3^-$ . The over 99% slow release of P from CS/SA-FeMT was achieved within 19, 19, and 20 days in deionized water at pH 5, 7, and 9, respectively.<sup>78</sup>

Jóźwiak *et al.* compared the P removal efficiencies of non-crosslinked CSH granules with those of crosslinked CSH granules (CSHs-ECH) using epichlorohydrin (ECH) as the crosslinking agent.<sup>79</sup> Their study identified pH and contact time as key factors influencing the adsorption process. The optimal pH for orthophosphate adsorption on CSH-ECH was pH 3; however, this led to the dissolution of the granules. The best adsorption on non-crosslinked CSH occurred at pH 4. The results showed that crosslinked CSH-ECH had



Fig. 4 Schematic diagram of the synthesis and mechanism of  $\text{PO}_4^{3-}$ -P and  $\text{NH}_4^+$ -N adsorption on CS-MgCBC *via* electrostatic, precipitation and ligand exchange (reprinted under permission from Li *et al.*).<sup>82</sup>

significantly higher phosphate adsorption capacity than non-crosslinked hydrogels at their respective optimal pH values.<sup>79</sup>

Enhancement of adsorption through carbon-based modifications is another prominent approach. Due to their abundant functional groups, porous structures, and ease of surface modification, carbon materials, such as graphene, carbon nanotubes, and activated carbon are highly effective. These materials are often integrated with chitosan *via* hydrogen bonding between  $-\text{OH}$  and  $-\text{COOH}$  groups of carbon compounds and the amino and  $-\text{OH}$  groups of chitosan. This synergy improves the structure and adsorption performance of the composite.<sup>80,81</sup> For example, Li *et al.* developed a chitosan-modified, magnesium-impregnated corn straw biochar (CS-MgCBC), which showed a remarkable 99.6% phosphate removal at pH 6.<sup>82</sup> The chitosan increased the surface area and introduced functional groups ( $-\text{OH}$ ,  $-\text{CH}_3$ , and  $-\text{NH}_2$ ), facilitating electrostatic attraction, precipitation, and ligand exchange, highlighting CS-MgCBC as a promising material for nutrient removal.<sup>82</sup> Fig. 4 shows the schematic diagram of the synthesis and mechanism of  $\text{PO}_4^{3-}$ -P and  $\text{NH}_4^+$ -N adsorption on CS-MgCBC.

Increasing phosphate adsorption using minerals as fillers in chitosan sorbents is an effective strategy. Because minerals are natural, harmless materials, this approach is beneficial. Because of their ability to adsorb orthophosphate anions, clays, aluminosilicates, and zeolites are among the most widely used mineral-based fillers.<sup>83,84</sup> Using mineral fillers such as clays, aluminosilicates, and zeolites in chitosan adsorbents is another effective method, leveraging their high affinity for orthophosphate anions. For instance, Kong *et al.* created a lanthanum-modified chitosan-attapulgite (La-CTS-ATP) composite that demonstrated excellent phosphate adsorption across pH 4–10, even in the presence of competing ions like  $\text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{HCO}_3^-$ , and  $\text{SO}_4^{2-}$ .<sup>83</sup> Kinetic studies indicated that chemisorption is the main mechanism of adsorption. The composite showed good reusability over five cycles, with phosphate removal and desorption efficiencies of approximately 73% and 77%, respectively, and effectively treated real wastewater samples.<sup>83</sup>

The innovative use of coconut husk biochar pellets modified with chitosan (CHC) was demonstrated by Thongsamer *et al.*, showcasing an effective biofiltration medium for P removal.<sup>85</sup> Compared to conventional activated carbon pellets and gravel, CHC stands out due to its combined adsorption and biodegradation actions. During the initial week, CHC achieved a P removal efficiency of 61.70%, primarily driven by the strong adsorption capacity of the chitosan-modified biochar, which provides abundant active sites for phosphate binding. As the filtration continued, microbial activity further enhanced removal efficiency.<sup>85</sup> The biofilter's microbial community mainly consisted of bacteria involved in nutrient removal pathways, including ammonium oxidation, nitrite oxidation, denitrification, and phosphate accumulation. Notably, polyphosphate-accumulating and denitrifying phosphate-accumulating bacteria played crucial roles in sustaining phosphate removal through biodegradation processes, supplementing the initial adsorption phase.<sup>85</sup>

CSNPs represent a significant advancement in adsorption technology, offering enhanced performance over bulk chitosan. Typically produced through crosslinking with sodium tripolyphosphate (STPP), CSNPs exhibit increased surface area and a higher density of functional groups, such as  $\text{-NH}_2$  and  $\text{-OH}$ .<sup>86</sup> These features facilitate strong interactions with target ions, including phosphates, making CSNPs highly effective in water treatment and environmental remediation processes.<sup>86</sup>

In a notable study, Sasidharan *et al.* investigated polyurethane foam (PUF) impregnated with CSNPs to form PCF (polyurethane foam impregnated with CSNPs) and its silver/silver oxide-enhanced variant (PFCA) as novel sorbents for phosphate removal.<sup>60,87</sup> These composites combine the

structural versatility of polyurethane foam with the functional benefits of CSNPs, offering an innovative solution for greywater treatment. Under optimized conditions, PCF achieved a phosphate removal efficiency of 26.15% within 6 hours when tested with synthetic greywater containing  $155 \text{ mg L}^{-1}$  phosphate.<sup>60</sup> The incorporation of CSNPs into the foam enhances adsorption by introducing amino and  $\text{-OH}$  groups that strongly bind phosphate ions. Further modification with silver (Ag)/silver oxide ( $\text{Ag}_2\text{O}$ ) NPs resulted in PFCA, which demonstrated significantly improved phosphate removal, up to 61.24% from an influent of  $50 \text{ mg P L}^{-1}$ .<sup>87</sup> Reusability assessments showed that PFCA retained a P removal efficiency of 20.58% after seven adsorption/desorption cycles, indicating promising durability for long-term use.<sup>87</sup> Fig. 5 illustrates the schematic representation of the phosphate adsorption mechanism of PFCA through electrostatic attraction between two oppositely charged ions.

Chitosan and its derivatives have also been tested as alternatives to metal-based coagulants. For example, grafting (3-chloro-2-hydroxypropyl)trimethylammonium chloride (CHPTAC) onto carboxymethyl chitosan yields a cationic bioflocculant with remarkable efficiency, achieving up to 97% P removal across a wide pH range.<sup>88</sup> The high performance is primarily due to the enhanced cationic nature conferred by the quaternary ammonium groups of CHPTAC, which facilitate strong electrostatic interactions with negatively charged phosphate ions. Additionally, carboxymethyl modification enhances water solubility and provides more binding sites for pollutants, thereby further increasing removal efficiency.<sup>88</sup>

### 3.3 Starch and its derivatives for P removal and recovery

Starch, the second most abundant carbohydrate in nature, is a homopolymer of D-glucopyranose units with the molecular formula  $(\text{C}_6\text{H}_{10}\text{O}_5)_n$ . It consists of two distinct glucose polymer chains: amylose, a primarily linear  $\alpha$ -(1 → 4)-linked polymer forming helical structures, and amylopectin, a highly branched  $\alpha$ -(1 → 4) and  $\alpha$ -(1 → 6)-linked polymer (see Fig. S7(a and b)). The ratio and structure of these components vary among plant sources, influencing their physicochemical properties and suitability for specific applications.<sup>89,90</sup>

Starch and its derivatives are increasingly recognized as sustainable, biodegradable, and cost-effective materials for removing and recovering phosphate ions from wastewater. Their relative abundance, non-toxicity, and ease of chemical modification make them attractive options for diverse applications. The primary removal mechanisms involve adsorption, ion exchange, and chemical precipitation, relying on interactions such as electrostatic attraction, hydrogen bonding, and chelation. These processes are vital for mitigating eutrophication caused by phosphate-rich effluents from municipal, agricultural, and industrial sources.<sup>91</sup> However, native starch exhibits limitations such as low thermal stability, limited water solubility, and susceptibility to rapid degradation in water, prompting research into



Fig. 5 Schematic illustration of the phosphate adsorption mechanism of PFCA through electrostatic attraction (reprinted with permission from Sasidharan *et al.*).<sup>87</sup>

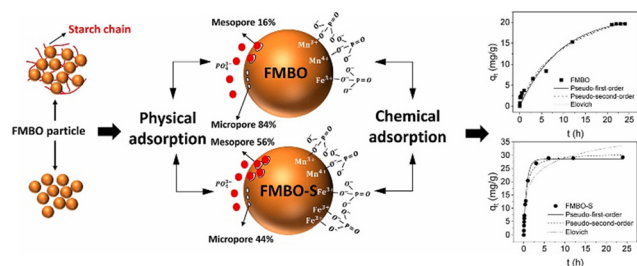


Fig. 6 The adsorption mechanisms and the kinetic plots for the removal of P from FMBO and FMBO-S (reprinted with permission from Yun *et al.*).<sup>94</sup>

various modifications, including grafts, forms, hydrogels, aerogels, films, beads, nanofibers, and NCs.<sup>91–93</sup>

Several studies have been reported on the removal and recovery of P using modified starch. For instance, starch-stabilized ferromanganese binary oxide (FMBO-S) has been synthesized for enhanced phosphate removal applications. Unmodified FMBO has been reported to aggregate in aqueous solutions, thereby reducing its adsorption capacity. To address this limitation, FMBO has been blended with starch to improve its dispersion properties.<sup>94</sup> The incorporation of starch increased the average pore diameter from 14.89 Å to 25.16 Å and significantly enhanced the pore volume within the mesopore region. FMBO-S exhibited a polydispersity index (PDI) value below 0.5, indicating homogeneous size distribution, and demonstrated superior adsorption performance, with a capacity of 61.24 mg g<sup>-1</sup> compared to 28.57 mg g<sup>-1</sup> for unmodified FMBO. Phosphate adsorption by FMBO-S was found to be pH-dependent, with electrostatic attraction identified as the dominant mechanism. These findings highlight the importance of developing adsorbents with high phosphate uptake, particularly under near-neutral pH conditions.<sup>94</sup> Fig. 6 depicts the adsorption mechanisms and the kinetic plots for the removal of P from FMBO and FMBO-S. According to Fig. 6, both FMBO and FMBO-S adsorption data fitted well to the Freundlich isotherm and the pseudo second-order kinetic model, suggesting chemisorption and multilayer adsorption. The phosphate adsorption by FMBO and FMBO occurred *via* ligand exchange and electrostatic attraction.<sup>94</sup>

Starch-based flocculants effectively remove and recover phosphates by promoting charge neutralization and bridging flocculation, which leads to the aggregation and precipitation of P-containing complexes. Ho *et al.* investigated a starch-based flocculant (St-CTA) combined with ferric chloride (FeCl<sub>3</sub>) for removing total P (TP) and turbidity from turbid wastewater.<sup>95</sup> The combined system significantly reduced FeCl<sub>3</sub> dosage, lowered costs, and achieved over 90% TP removal and 95% turbidity reduction.<sup>95</sup> The synergistic effects of charge neutralization and bridging flocculation facilitated efficient sedimentation and P removal.<sup>95</sup>

Modifying starch to introduce cationic groups enhances its affinity for negatively charged phosphate ions. Hu *et al.* evaluated cationic starch-based flocculants (St-CTA and St-

AD) combined with FeCl<sub>3</sub>, observing improved P removal in both simulated and real wastewater.<sup>96</sup> St-AD, with its branched structure and higher positive charge density, demonstrated superior performance in removing organic P forms, especially in complex wastewater matrices. These findings underscore the potential of cationic starch derivatives as biodegradable, sustainable alternatives to synthetic flocculants, such as polyacrylamide (PAM).<sup>96</sup>

Nanocomposite starch materials incorporate nanoscale components to amplify adsorption capacity and functionality. For example, researchers developed a magnetic starch-based Fe<sub>3</sub>O<sub>4</sub> polymer clay nanocomposite (PNC) using glycerol (G) as a plasticizer, combined with activated carbon (AC), nanoclay (NC) and coated iron oxide NPs (CIONPs).<sup>97</sup> NC of the PNC was modified using cetyltrimethylammonium bromide (CTAB) to introduce surface -NH<sub>2</sub> functional groups, whereupon protonation of the -NH<sub>2</sub> group could participate in phosphate through electrostatic attraction at lower pH. At higher pH, the hydrated ions are deprotonated, becoming negatively charged, and hence there is no electrostatic attraction. The major removal mechanism of phosphate ions *via* NH<sub>2</sub> protonation is given by eqn (5)–(7).<sup>97</sup> Physisorption of phosphate ions occurs on the CIONP adsorbent. However, P removal could also occur through inner and surface electrostatic complexations, ligand exchange, and ion exchange mechanisms. Batch adsorption experiments indicated that PNC exhibited phosphate removal efficiencies of 45% to 95% at optimal pH values, primarily driven by electrostatic interactions and ion exchange. The synergistic combination of the starch biopolymer and nanomaterials enhances environmental remediation capabilities.<sup>97</sup> Fig. 7 shows the proposed P removal mechanisms for G-plasticized magnetic starch-based PNCs.



Fig. 7 Schematic representation of the possible P removal mechanisms of the G-plasticized magnetic starch-based PNCs (reprinted with permission from Atnafu *et al.*).<sup>97</sup>

Starch cryogels are emerging as innovative materials for phosphate removal due to their unique structure, high porosity, and environmentally friendly nature. These cryogels are synthesized by freezing and thawing starch solutions, often modified with crosslinking agents or doped with functional materials to enhance their adsorption properties. The resulting porous, sponge-like structure provides a large surface area, facilitating efficient interactions with phosphate ions in wastewater.<sup>98,99</sup> A novel calcium silicate hydrate composite cryogel (Cry-CSH) was successfully developed by Taweekarn *et al.* for the effective removal and recovery of P from wastewater.<sup>100</sup> Cry-CSH was synthesized by mixing calcium silicate hydrate (C-S-H) NPs with a gel precursor prepared from native starch and limewater, using saturated  $\text{Ca}(\text{OH})_2$  as the crosslinker. The mixture underwent three freeze-thaw cycles, resulting in an interconnected macroporous composite with C-S-H NPs immobilized within a monolithic, floatable cryogel matrix. This design not only facilitated easier recovery of the material but also minimized losses associated with the direct use of C-S-H NPs. Cry-CSH exhibited an impressive phosphate adsorption capacity of  $2.50 \text{ mg PO}_4^{3-}$  per g Cry-CSH ( $65.42 \text{ mg PO}_4^{3-}$  per g C-S-H) under optimum conditions, with adsorption reaching equilibrium within 120 minutes. The adsorption process was determined to be endothermic and driven by chemical interactions. Cry-CSH demonstrated excellent P removal efficiency (>98%) when tested on wastewater and effluent samples. In addition to its high performance, the Cry-CSH cryogel offered unique practical advantages. It remained floatable on the water surface for at least 105 days without damage, facilitating easy retrieval. Furthermore, its phosphate-laden form biodegraded within 10 days when buried in soil, highlighting its environmental compatibility. This study highlights the potential of Cry-CSH as an innovative, sustainable, and efficient material for phosphate removal and recovery, offering a practical solution to nutrient pollution and promoting eco-friendly wastewater management.<sup>100</sup>

In a study by Chen *et al.*, a novel approach was developed to remove pesticide residues by integrating adsorption and enzymatic degradation.<sup>101</sup> This method utilized biodegradable microporous starch (MPS) immobilized with laccase (LA-MPS). MPS was derived from maize starch and subjected to enzymatic treatment to enhance its surface area, thereby improving its adsorption capacity. Laccase, a catalytically active enzyme, was immobilized on the MPS surface, forming LA-MPS. The adsorption and degradation efficiency were tested for the removal of triazine herbicides, specifically atrazine and prometryn, from paddy field water samples.<sup>101</sup>

### 3.4 Alginate and its derivatives for P removal and recovery

Alginate, a naturally occurring anionic biopolymer extracted from brown seaweed, has garnered significant attention for its effectiveness in removing and recovering phosphate ions

from water systems. Composed mainly of linear chains of  $\beta$ -D-mannuronic acid (M) and  $\alpha$ -L-guluronic acid (G) residues (see Fig. S8(a-c)), alginate contains numerous  $-\text{COOH}$  groups capable of interacting with metal ions and pollutants, including phosphates. This affinity for anions makes alginate highly suitable for water purification applications, especially in addressing P pollution that contributes to eutrophication in aquatic environments. To enhance its phosphate affinity, researchers increasingly focus on chemical modifications and composite formation, which introduce additional functional groups or metal ions to improve adsorption performance.

Clay minerals such as bentonite, kaolin, and montmorillonite are low-cost, abundant, and environmentally friendly materials with high surface areas, making them ideal for water treatment. A notable study demonstrated the use of iron crosslinked alginate beads infused with kaolin (Alg@K).<sup>102</sup> These beads achieved a maximum phosphate adsorption capacity of  $20.70 \text{ mg g}^{-1}$  at a phosphate concentration of  $150 \text{ mg L}^{-1}$  within 4 hours, with adsorption being pH-dependent and primarily chemisorptive in nature.<sup>102</sup>

Metal-crosslinked alginate hydrogels, such as iron- or lanthanum-modified beads, leverage metal affinity for phosphate. For example, Guan *et al.* developed La-Zr@SA/NIPAM, an alginate-based hydrogel modified with La and Zr, featuring abundant active sites and a mesoporous structure.<sup>103</sup> This composite achieved a maximum adsorption capacity of  $105.3 \text{ mg g}^{-1}$ , maintained 80% efficiency after six regeneration cycles, and operated *via* electrostatic attraction, ligand exchange, and complexation. Its performance in real wastewater confirmed its practical potential for P removal.<sup>103</sup> At lower pH values, the La-Zr@SA/NIPAM hydrogel undergoes protonation, resulting in a positive surface charge. Then, phosphates present in the form  $\text{H}_2\text{PO}_4^-$  and  $\text{HPO}_4^{2-}$  strongly adsorbed onto the surface of the absorbent through electrostatic attraction. However, at higher pH values, due to increased concentrations of  $-\text{OH}$  groups that compete with phosphate ions for adsorption sites, interactions are reduced, and the metal oxides convert into  $-\text{OH}$  groups, leading to exchange between  $-\text{OH}$  groups and P. The complexation

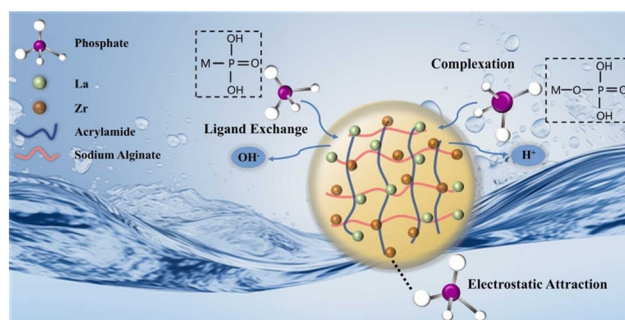


Fig. 8 Schematic representation of the P removal and recovery of the La-Zr@SA/NIPAM hydrogel *via* ligand exchange, electrostatic attraction and complexation mechanisms (reprinted with permission from Guan *et al.*).<sup>103</sup>

mechanism occurs on the La-Zr@SA/NIPAM hydrogel surface, where phosphate replaces the H atom to form M–O–P, which subsequently releases H<sup>+</sup>. Fig. 8 illustrates the schematic representation of the P removal and recovery mechanisms of the La-Zr@SA/NIPAM hydrogel.

Magnetic material-modified alginate hydrogels are another form of adsorbent for P removal, combining the strong binding affinity of alginate with magnetic NPs, such as Fe<sub>3</sub>O<sub>4</sub> and ferrites. This hybrid design enhances both adsorption efficiency and structural stability, allowing for easy recovery *via* magnetic separation. P removal occurs through mechanisms, such as electrostatic attraction, ion exchange, and surface complexation.<sup>104,105</sup> Magnetic modifications facilitate easy separation of adsorbents. Zeng *et al.* synthesized iron-loaded magnetic alginate-chitosan double-gel beads (M-IACBs) from waterworks iron sludge and magnetic NPs.<sup>106</sup> These beads exhibited high selectivity for phosphate, with mechanisms involving ligand exchange and electrostatic attraction. The resourceful use of iron sludge not only enhanced P removal but also contributed to sustainable waste valorization.<sup>106</sup>

Carbon material-modified alginate hydrogels are highly effective adsorbents for P removal and recovery. By incorporating carbon-based materials, such as biochar, activated carbon, graphene oxide, or carbon nanotubes, into alginate matrices, these composites display enhanced adsorption performance. The carbon materials offer a large surface area, abundant active sites, and enhanced mechanical stability, making them highly efficient for phosphate capture.<sup>107–109</sup> For instance, a Fe/La-decorated biochar embedded in sodium alginate beads (SA-KBC-Fe/La) showed a phosphate uptake of 46.65 mg g<sup>-1</sup> at pH 6, with over 80% capacity retention after multiple cycles.<sup>110</sup>

Multivalent metal-based alginate hydrogels are highly efficient adsorbents for phosphate removal and recovery, utilizing the strong binding capabilities of alginate and the high reactivity of multivalent metal ions such as Al<sup>3+</sup>, Fe<sup>3+</sup>, La<sup>3+</sup>, and Zr<sup>4+</sup>. These metal ions form stable crosslinked structures with alginate, providing abundant active sites for phosphate adsorption through mechanisms such as ligand exchange, electrostatic attraction, and surface complexation.<sup>111,112</sup> Lin *et al.* developed an alginate/UiO-66-NH<sub>2</sub> composite hydrogel modified with polyethyleneimine (PEI), achieving a phosphate adsorption capacity of 68.75 mg g<sup>-1</sup> under optimal conditions and demonstrating excellent recyclability over multiple cycles. This approach exhibits the potential for highly efficient, easily separable phosphate adsorbents.<sup>113</sup>

## 4 Future trends of polysaccharides and polysaccharide-based materials in P removal and recovery

The field of biopolymer-based technologies for P removal and recovery is experiencing significant advancements, driven by

the dual imperatives of mitigating water pollution and addressing the global P crisis. As of 2025, emerging trends are reshaping the landscape of phosphate management by integrating innovations in materials science with the principles of the circular economy. Novel polysaccharide-based composites, such as cellulose, chitosan, starch, and alginate, and their derivatives are being engineered to enhance P adsorption efficiency, selectivity, and regeneration potential. Moreover, the incorporation of functional nanomaterials, surface modifications, and hybrid systems is enabling more robust and tunable phosphate capture mechanisms. These novel polysaccharide-based systems offer eco-friendly, cost-effective, and scalable solutions that align with sustainable wastewater treatment and nutrient recovery strategies. Collectively, these developments signal a transformative shift toward closed-loop P cycling, supporting both environmental protection and agricultural resilience.

### 4.1 Advanced functionalized composites

One of the most promising trends in P removal and recovery is the use of functionalized polysaccharides, which exhibit significantly improved affinity for phosphate ions. Researchers are engineering advanced functionalized composites by integrating polysaccharides, including chitosan, alginate, cellulose, and starch, with metal ions such as Fe<sup>3+</sup>, La<sup>3+</sup>, and Zr<sup>4+</sup>, as well as functional groups like –NH<sub>2</sub>, –COOH, –OH, and –SO<sub>2</sub>OH. These modifications increase the surface area, introduce specific binding sites, and promote ion exchange or ligand complexation mechanisms, thereby dramatically enhancing phosphate adsorption capacity. Additionally, these hybrid materials display superior selectivity, stability over a wide pH range, and regeneration potential, making them ideal candidates for practical and scalable wastewater treatment applications. Such innovations not only improve phosphate recovery efficiency, but also contribute to the development of sustainable, circular nutrient management systems.

Guanidine-modified cellulose has emerged as a highly efficient polysaccharide for P removal, demonstrating exceptional adsorption capacities of up to 310 mg g<sup>-1</sup> at a neutral pH (pH 7).<sup>114</sup> The incorporation of guanidinium functional groups (NH<sub>2</sub>–C(=NH<sub>2</sub><sup>+</sup>)–NH<sub>2</sub>) introduces multiple binding sites capable of forming strong electrostatic interactions and H-bonding with phosphate ions, resulting in high affinity and selectivity. Notably, P recovery from these materials can be easily achieved through mild pH adjustment, promoting material reusability and alignment with circular economy principles. In addition to their phosphate-binding performance, guanidine-modified cellulose also exhibits inherent antibacterial properties due to the biocidal activity of guanidinium groups. This dual functionality makes such materials particularly valuable in wastewater treatment applications, where simultaneous nutrient recovery and microbial control are desirable. The convergence of high adsorption efficiency, ease of

regeneration, and antimicrobial action positions guanidine-functionalized cellulose as a leading candidate for next-generation sustainable water treatment technologies.<sup>114</sup>

Mg-functionalized biochars derived from agricultural waste materials, such as rice husks, have shown considerable promise in P removal, achieving adsorption capacities as high as 111.10 mg g<sup>-1</sup>.<sup>115</sup> The incorporation of Mg species onto the biochar surface effectively neutralizes or reverses the inherent negative surface charge of unmodified biochar, which typically limits its interaction with negatively charged phosphate anions. This surface modification enhances electrostatic attraction and facilitates the formation of stable inner-sphere complexes or precipitates, such as Mg<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>, significantly improving both adsorption efficiency and selectivity for phosphate. In addition to their performance, these biochars are derived from low-cost, renewable biomass sources, aligning with the principles of green chemistry and waste valorization. Furthermore, P recovery from Mg-modified biochar can be achieved through desorption techniques or by reusing nutrient-enriched biochar in agriculture, contributing to circular nutrient management systems. This approach offers an eco-friendly and scalable solution for sustainable wastewater treatment and P recovery.<sup>115</sup>

Chitosan-metal oxide NCs, particularly those enhanced with titanium dioxide (TiO<sub>2</sub>) and other metal oxides, such as Fe<sub>3</sub>O<sub>4</sub>, ZnO, and Al<sub>2</sub>O<sub>3</sub>, are emerging as multifunctional materials for advanced wastewater treatment.<sup>116</sup> These hybrid adsorbents combine with the chitosan's naturally cationic nature, facilitating electrostatic attraction of anionic phosphate, with the high surface area and reactivity of metal oxides, which introduce additional coordination and ligand exchange sites for phosphate binding. The inclusion of TiO<sub>2</sub> not only enhances phosphate adsorption capacity, but also imparts photocatalytic and antibacterial properties, enabling the simultaneous removal of nutrients and disinfection of microbes. These synergetic effects arising from each component of the NCs are particularly valuable for treating complex wastewater streams where both phosphate pollution and microbial contamination coexist. Moreover, these composites often exhibit good structural stability, reusability, and performance over a broad pH range, making them attractive candidates for scalable, sustainable applications in water treatment and resource recovery.<sup>116,117</sup>

Polysaccharide-clay mineral composites represent a promising class of materials that synergistically combine the high surface area and ion exchange capacity of natural clays, including montmorillonite, bentonite, and kaolinite, with the functional group versatility of polysaccharides, such as chitosan and cellulose.<sup>118</sup> In these hybrids, the -OH, -NH<sub>2</sub>, and -COOH groups of the biopolymer matrix interact with the layered clay structure, improving dispersion, structural integrity, and accessibility of active sites. The resulting composites exhibit enhanced mechanical stability, reduced swelling, and increased ligand exchange capacity, all of which contribute to superior phosphate adsorption performance.

Additionally, the hybridization process often enhances the thermal and chemical resistance of the composite, making it more durable under various wastewater conditions. These materials can be engineered for high selectivity and reusability, positioning them as sustainable alternatives for phosphate removal in large-scale treatment systems.<sup>117,118</sup>

#### 4.2 Smart and responsive materials

Next-generation polysaccharide-based systems are being engineered with intelligent, multifunctional properties to enhance P removal, recovery, and system sustainability. One key innovation is the development of pH-responsive materials, such as guanidine-modified cellulose, which enable reversible phosphate binding. These materials allow easy regeneration and phosphate release through simple pH adjustments, typically around pH 10, facilitating cyclic reuse and nutrient concentration without the use of harsh chemicals.<sup>114</sup>

Another promising strategy involves magnetic-polysaccharide composites, wherein materials such as chitosan or cellulose are functionalized with Fe<sub>3</sub>O<sub>4</sub>.<sup>117</sup> These composites exhibit strong phosphate adsorption while permitting magnetic separation from treated water, thereby simplifying the recovery process and reducing operational costs.<sup>117</sup>

Additionally, bioactive biopolymer coatings are being explored to combine phosphate capture with antimicrobial functionality. By incorporating biocidal agents or utilizing inherently antimicrobial moieties, such as guanidinium or TiO<sub>2</sub>, these systems can inhibit microbial growth during wastewater treatment and recovery, mitigating biofouling and maintaining system efficiency.<sup>114-116</sup> These intelligent biopolymer innovations represent a crucial step toward realizing smart, sustainable nutrient recovery platforms in wastewater treatment.

#### 4.3 Polyphosphate biotechnology and emerging policy frameworks

Recent research and regulatory shifts highlight a growing global effort to close the anthropogenic P loop by prioritizing recovery and recycling over traditional PR mining. A notable example is the progressive P policy of Germany, which mandates, starting in 2029, the recovery of at least 50% of inorganic P from sewage sludge and 80% from incinerated sludge ash.<sup>119,120</sup>

These recovered materials are intended for repurposing into fertilizers and other agricultural inputs, thereby promoting a circular nutrient economy (PMC). Industrial-scale implementations of these mandates are already taking shape. For instance, two advanced facilities are operational in Germany, producing approximately 20 000 tonnes per year of phosphoric acid and 60 000 tonnes per year of phosphate-based fertilizers through a combination of mono-combustion of sewage sludge and downstream purification technologies (PMC).<sup>120</sup> These developments highlight the intersection of

biotechnology, environmental regulation, and industrial innovation in establishing sustainable practices for managing P.<sup>120</sup>

#### 4.4 Circular approaches to P recovery and sustainable resource management

In the future, there will be a growing focus on holistic P recovery cycles that convert captured P into valuable and marketable products, contributing to sustainable nutrient management and circular economy goals.

One promising avenue is the direct agricultural application of phosphate-loaded biopolymers, which are increasingly recognized for their dual functionality. These materials, such as alginate-based (ALE) biosorbents, serve not only as effective phosphate carriers, but also as hydrogels that enhance soil moisture retention, thereby improving soil health and crop productivity.<sup>121</sup> This dual role positions polysaccharide-based fertilizers as slow-release systems, reducing nutrient runoff and increasing nutrient use efficiency in farming.

Simultaneously, struvite precipitation processes integrated with polysaccharide adsorption are advancing toward commercial viability. In these systems, polysaccharides function as nucleation sites, facilitating the controlled and efficient formation of high-purity struvite crystals directly from wastewater streams. This integration enhances P recovery rates while producing a high-quality and valuable fertilizer product.<sup>117</sup>

Moreover, the emergence of industrial symbiosis models is transforming traditional wastewater treatment plants into hubs for P production. These models enable the valorization of sewage sludge into multiple products, including marketable phosphoric acid and building materials, fostering new economic opportunities within the wastewater sector. Leading conferences, such as the International Water Association (IWA) Resource Recovery 2025, emphasize these transformative technologies and the critical role of P in sustainable urban water management.<sup>117</sup>

#### 4.5 AI in polysaccharide-based P removal and recovery

The integration of AI with biopolymer-based phosphate removal and recovery is revolutionizing wastewater treatment by optimizing material design, process efficiency, and resource recovery. AI-driven approaches, including machine learning (ML) and predictive modeling, are accelerating the development of high-performance polysaccharide composites while reducing experimental costs and improving scalability.

The role of AI in polysaccharide-based P removal and recovery is rapidly transforming the field with enhanced efficiency, precision, and system resilience. AI-powered predictive modeling built on ML and deep learning (DL) enables optimization of adsorption parameters for biopolymers such as chitosan and alginate. Applications of techniques such as Quantitative Structure–Activity Relationship (QSAR) modeling and high-throughput

screening aid in designing novel biopolymer composites with increased P uptake and selectivity. For instance, the potential of ML and computational modeling to accelerate the discovery of polysaccharide-based nanocomposite adsorbents has been highlighted as a promising frontier in recent research.<sup>122</sup>

In operational environments, AI facilitates real-time control and dynamic adjustment, including through reinforcement learning models tailored for wastewater treatment design. A study introducing a deep reinforcement learning (DRL)-based simulator for P removal demonstrated control policy learning with an accuracy above 97%. However, the authors noted challenges arising from error propagation over the long-term simulation horizon.<sup>123</sup> These advancements lay the groundwork for AI-driven, self-optimizing polysaccharide-based adsorption systems capable of reacting swiftly to changing phosphate loads.

Beyond classical ML, hybrid and swarm-based AI methods are also being explored in process control contexts unrelated specifically to phosphate but highly relevant. One such work describes the use of biomimicry-inspired automated ML (AML) embedded in decentralized, sensor-driven wastewater processing systems. This approach delivered up to 14% energy savings and 11% reduction in chemical use, underscoring the effectiveness of AI in real-time system adaptation—insights potentially transferable to polysaccharide-based P removal systems.<sup>124</sup>

Furthermore, AI exhibits strong compatibility with advanced process modeling techniques. One recent application of soft actor-critic reinforcement learning to broader wastewater treatment control (though not exclusively phosphate removal) demonstrated 36% lower P emissions and significant operational cost reductions when accounting for system delays and dynamic responses.<sup>125</sup> Such AI algorithms could optimize regeneration cycles, flow dynamics, and recovery outcomes in polysaccharide-based adsorption systems under real-world conditions.

AI also plays a pivotal role in optimizing biosorbent composition, predicting performance, and automating system control. For example, Nouaa *et al.* developed an Artificial Neural Network (ANN) model to predict phosphate adsorption efficiency in an alginate/iota-carrageenan/natural clay hydrogel system, achieving a high predictive accuracy ( $R^2 = 0.974$ ) and outperforming conventional regression models.<sup>126</sup> Similarly, magnetically responsive chitosan-Fe<sub>3</sub>O<sub>4</sub> NCs optimized using a genetic algorithm combined with support vector regression improved the phosphate recovery efficiency by over 30%.<sup>126</sup>

At an industrial scale, AI is being employed to automate phosphate monitoring and recovery *via* real-time sensors and predictive control algorithms. Sheik *et al.* reviewed ML and explainable AI applications in biological nutrient removal systems, highlighting models like Random Forest and Deep Neural Networks that predict P concentrations, biopolymer performance degradation, and microbial community shifts—

critical factors for maintaining removal efficiency under dynamic influent conditions.<sup>127</sup>

Balasubramanian and coworkers investigated the application of Rough Set Theory (RST), an ML well-suited for handling imprecise or uncertain data, to model P recovery from wastewater.<sup>128</sup> The study analyzed experimental and operational datasets from wastewater treatment processes to identify key influencing variables and predict recovery performance. The RST model showed a strong capability for classifying system behavior and uncovering underlying patterns without requiring prior probabilistic assumptions. Results indicated that RST outperformed conventional statistical methods in identifying decision rules and revealing relationships among critical variables such as pH, adsorbent dosage, and contact time. This approach offers a more transparent and interpretable framework for AI-guided P recovery system designs, particularly in scenarios involving complex parameter interactions.<sup>128</sup>

In another notable study, ML learning models were developed to predict and validate P recovery *via* an electrochemically induced precipitation process.<sup>129</sup> Multiple algorithms, including Linear Regression, Lasso, Ridge, AdaBoost, XGBoost, Random Forest, and SVR, were trained on lab-scale datasets, with key input variables including current density, pH, and electrolysis time. Among these, XGBoost and Random Forest delivered the highest predictive accuracy, achieving  $R^2$  scores above 0.96. The models were further applied to simulate optimal process conditions, accurately forecasting both recovery efficiency and energy consumption trends. By integrating these ML tools, the study enhanced the sustainability and scalability of electrochemical phosphate recovery systems, providing robust decision-support capabilities for real-time optimization of operational parameters.<sup>129</sup>

The use of ML to model nutrient removal efficiency, specifically P and N, in full-scale wastewater treatment plants (WWTPs) developed by Zhang *et al.*<sup>130</sup> The models integrated environmental and operational parameters, such as sludge retention time, dissolved oxygen, and temperature, to elucidate microbial drivers influencing P removal. Gradient Boosting Machines and Random Forest algorithms were employed to identify the most critical factors affecting system performance. The results revealed significant site-specific variability, with temperature and carbon source availability emerging as the primary determinants of P removal efficiency. These findings underscore the potential of ML to enable adaptive, energy-efficient WWTP management, providing insights beyond the capabilities of conventional process control methods.<sup>130</sup>

Wu and coworkers developed trained ML models to predict phosphate adsorption efficiency across six different metal-based adsorbents.<sup>131</sup> Key input variables included solution pH, initial phosphate concentration, adsorbent surface area, and contact time. Random Forest, XGBoost, and Decision Tree algorithms were evaluated, with XGBoost achieving the highest predictive accuracy ( $R^2 = 0.984$ ). The

study demonstrated the potential of ML to screen adsorbents before experimental validation, virtually, significantly accelerating material development. This data-driven strategy offers a sustainable alternative to trial-and-error synthesis, enabling the design of next-generation phosphate adsorbents tailored to specific wastewater treatment conditions.<sup>131</sup>

A novel application of Deep Reinforcement Learning (DRL) has been developed to simulate and control P removal in wastewater treatment plants (WWTPs).<sup>123</sup> Using both synthetic and historical datasets, the authors developed a virtual simulator capable of modeling P concentration dynamics and system responses to control inputs. DRL agents, based on Proximal Policy Optimization and Deep Q-Network (DQN) algorithms, learned optimal control strategies to minimize effluent P levels while reducing operational costs. Simulation results demonstrated that DRL could outperform conventional PID control by dynamically adjusting parameters, such as aeration rates and chemical dosing, in real-time. This work introduces a robust AI-driven control framework for smart WWTPs, offering adaptability to fluctuating environmental and operational conditions.<sup>123</sup>

A recent study by Sbahi *et al.* demonstrated a full-scale ML-driven hybrid multi-soil-layering (MSLHYB) system for efficient removal of P in nature-based treat systems.<sup>132</sup> The authors developed a Random Forest (RF) model to predict total phosphorus (TP) effluent levels by incorporating a three-stage optimization step, including random search, *k*-means clustering, and Bayesian optimization. They also reported a P removal efficiency of up to 84% under real conditions with the ML-driven MSLHYB system.<sup>132</sup>

In summary, AI technologies are driving major improvements in every phase of polysaccharide-based P removal and recovery from adsorbent design and synthesis to real-time process optimization, performance prediction, and system automation. As global policies increasingly mandate P recovery, including countries like Germany, AI-guided biopolymer systems offer a promising path toward sustainable nutrient management and a circular P economy.

## Conclusions

The use of renewable, biodegradable materials for P removal and recovery from wastewater represents a sustainable, environmentally friendly approach to addressing P depletion and water pollution. These materials, including polysaccharides, offer numerous advantages such as cost-effectiveness, mechanical and chemical stability, biocompatibility, and reduced environmental impact. Their renewable nature and biodegradability make them ideal for long-term use in water treatment, while their ability to be modified and tailored enhances adsorption efficiency. This review presents the first systematic evaluation of polysaccharide-based materials, including cellulose, chitosan, starch, and alginate, within the context of P removal and recovery applications and their mechanisms. We have also elaborated on the emerging trends in polysaccharide-based P

removal and recovery, including advanced functionalized composites, innovative and responsive materials, polyphosphate biotechnology, emerging policy frameworks, circular approaches, sustainable resource management, and AI-based applications. Overall, renewable and biodegradable polysaccharides with their distinct characteristics hold significant promise for addressing global P depletion issues, mitigating eutrophication and related health concerns, improving water quality, and contributing to the circular bioeconomy.

## Author contributions

Mohamed M. Farhath: conceptualization, writing original draft – review. Murthi S. Kandanapitiye: writing original draft – review. Danushika C. Manatunga: writing original draft – review. Rohan S. Dassanayake: conceptualization, supervision, writing original draft – review, editing, and proofreading. Meththika Vithanage: supervision, review, editing and proofreading.

## Conflicts of interest

There are no conflicts to declare.

## Data availability

This manuscript is a systematic review of previously published literature. No new primary data were generated in the course of this research. All data supporting the conclusions and analyses presented herein are available within the cited articles and their associated supplementary information (SI) files. Supplementary information: Tables S1 and S2, Pros and cons of P removal and recovery techniques and various adsorbents for P removal and recovery. Fig. S1–S4, schematics of ion exchange, ligand exchange, H-bonding and surface precipitation mechanism. Fig. S5–S8, chemical structures of cellulose, chitosan, starch and alginate. See DOI: <https://doi.org/10.1039/d5ew00812c>.

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