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Integrating 2D nanomaterials with organic acid–mediated rock phosphate solubilization for enhanced phosphorus availability: a review

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Phosphorus (P) is an essential but often limiting macronutrient in agriculture due to the poor solubility of naturally occurring rock phosphate (RP). Organic acids released by plant roots or phosphate-solubilizing microorganisms can enhance RP dissolution; however, their effectiveness is restricted by rapid degradation, soil buffering, and strong adsorption to mineral surfaces. A key limitation arises from the strong adsorption of organic acids onto the soil matrix, particularly in soils rich in 2 : 1 clays and exchangeable calcium, where anions such as citrate become bound to clay surfaces or form Ca–organic-anion complexes instead of dissolving phosphate minerals. This adsorption paradoxically increases phosphate fixation rather than reducing it. To overcome these constraints, two-dimensional (2D) nanomaterials such as graphene oxide (GO), MoS_2, and layered double hydroxides (LDHs) have emerged as potential carriers for both organic acids and phosphate. Their high surface area, tunable functionality, and strong binding affinity enable controlled acid release, sustained proton activity, and reduced P fixation at the RP interface. This review synthesizes recent advances in 2D material-assisted organic acid solubilization of RP and highlights future directions toward hybrid nano-bio systems particularly the integration of biochar-2D material composites as a promising next-generation platform for sustainable phosphorus management in agriculture. This review provides a comprehensive synthesis of molecular mechanisms, highlights emerging nano-enabled smart fertilizer strategies, and identifies key future research directions to bridge laboratory insights and field-scale applications. The work presents a novel interdisciplinary framework for improving P accessibility through hybrid nano-bio interventions.

1 Introduction

Phosphorus (P) is an essential macronutrient that plays a critical role in plant physiological processes such as energy transfer, photosynthesis, and nucleic acid synthesis.[1] However, its availability in soils is often limited due to the predominance of insoluble mineral forms, including calcium phosphate, iron phosphate, and aluminum phosphate, which are not readily accessible to plants.[2] While rock phosphate (RP) serves as the primary mineral source of phosphorus in most commercial fertilizers, direct application of untreated RP to soils is uncommon and typically limited to highly reactive RP applied in strongly acidic conditions. In conventional practice, RP undergoes pre-treatment processes such as acidulation, granulation, or blending to enhance solubility and enable controlled nutrient release in N/P/K fertilizers. Nevertheless, even with these approaches, phosphorus use efficiency remains low, particularly in neutral to alkaline soils, leading to significant nutrient losses.[3]

Organic acids such as citric acid, oxalic acid and acetic acid, have emerged as alternatives to improve RP solubilization through mechanisms such as acidification, chelation, and ligand exchange.[2,4] Despite their potential, the application of organic acids is constrained by factors such as soil pH, the specific organic acid used, and the presence of other soil components, leading to inconsistent results across different soil environments.[5] Moreover, prolonged use of organic acids may lead to soil acidification and adverse effects on soil health and microbial communities.

Recent advances in nanotechnology, particularly two-dimensional (2D) nanomaterials such as graphene oxide (GO), molybdenum disulfide (MoS_2), and layered double hydroxides (LDHs), offer promising opportunities to overcome these limitations.[6] These materials possess exceptionally high surface areas, abundant functional groups, and strong adsorption capacities, enabling them to act as carriers and stabilizers of organic acids while simultaneously mitigating phosphate fixation.[7–9] For instance, 2D materials can adsorb phosphate ions and release them under specific conditions, potentially improving the efficiency of phosphorus uptake by plants.[10] However, research on the synergistic use of 2D nanomaterials with organic acids for RP solubilization remains limited.[11] The mechanistic interactions between these materials and their combined effects on phosphate release kinetics, acid

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stabilization, and environmental fate are not yet fully understood, particularly across diverse soil types.[12]

This review introduces a novel framework that highlights how 2D nanomaterials can enhance the performance of organic acids in solubilizing RP, offering a pathway toward the development of next-generation, slow-release, and environmentally sustainable phosphorus fertilizers. By addressing both scientific and technological gaps, this work lays the foundation for translating nano-enabled organic acid systems into practical, field-relevant agricultural solutions.

A structured literature search was conducted to gather relevant and up-to-date scientific information. Peer-reviewed articles, book chapters, and technical reports were consulted through Google Scholar, Scopus, and ScienceDirect. The search used combinations of keywords such as phosphorus availability, rock phosphate, nanomaterials, 2D nanomaterials, biochar, phosphorus fertilizer, controlled release, and soil amendments. Recent studies published within the last 10–15 years were prioritized, while earlier foundational works were included when appropriate. Sources were selected based on relevance to the research themes and the quality of the evidence presented. Reference lists of key publications were also screened to identify additional supporting literature.

2 Mechanisms of organic acid–mediated rock phosphate solubilization

2.1 Organic acids involved in phosphate solubilization

Organic acids are central mediators of RP dissolution because they combine proton donation, metal-cation chelation and ligand-exchange reactions at mineral surfaces (Fig. 1). Organic acid-mediated phosphate solubilization operates through several interconnected molecular mechanisms that work together to release phosphorus from insoluble forms.[13] The primary mechanism involves acidification, where organic acids are produced in the periplasmic space through direct oxidation pathways and subsequently released into the surrounding environment.[2,14,15] This acidification process results in a significant pH drop that can lower soil pH to as low as 2, facilitating the release of phosphate ions through proton substitution where H^+ replaces cations like Ca^{2+} bound to phosphate minerals.[2,16,17]

Chelation represents another crucial mechanism where the carboxyl and hydroxyl groups present in organic acids bind to and sequester metal cations such as calcium, iron, and aluminum that are associated with phosphate compounds.[1,14,18,19] The effectiveness of this chelation process depends heavily on the molecular structure of the organic acids, particularly the number and position of carboxyl and hydroxyl groups, with tricarboxylic and dicarboxylic acids being more efficient than monobasic acids.[15,19] Ligand exchange reactions constitute a third important mechanism where organic acids directly replace phosphate anions on soil surfaces or form soluble complexes with metal ions linked to insoluble phosphorus.[2,20,21] This process can occur through direct ligand exchange where organic acids replace phosphorus on exchange surfaces, or through complexation of metal ions in the soil matrix holding the phosphorus.[21]

Direct dissolution of mineral phosphates occurs when organic acids act through anion exchange mechanisms, where phosphate anions are directly substituted by organic acid anions.[2,22,23] Additionally, organic acids can compete with phosphate for adsorption sites in the soil, further facilitating phosphate release.[24]

The solubilization process is enhanced by protonation and ion exchange reactions, where the increase in hydrogen ions from microbial organic acid production replaces cations bound to phosphate through H^+-translocation *via* ATPase activity.[15,24] These mechanisms work synergistically, with the efficiency of phosphate solubilization depending on factors such as the type and concentration of organic acids, the stability constant of metal–organic acid complexes formed, and soil pH conditions.[25,26]

Several organic acids have been identified as key agents in phosphate solubilization. Gluconic acid is the most frequent and effective agent for mineral phosphate solubilization, produced *via* direct oxidation of glucose by the membrane-bound quinoprotein glucose dehydrogenase enzyme.[14,15,22,27] 2-Ketogluconic acid, a carboxylic acid derived from gluconic acid oxidation, can chelate calcium ions and dissolve hydroxyapatites.[27] Citric acid, a tricarboxylic acid, exhibits strong binding abilities and has proven competence in soil phosphate solubilization,[2,20,28] while oxalic acid is another highly effective agent due to its strong chelation capacity.[20,29,30] Malic acid is more efficient than succinic acid because of its higher number of hydroxyl groups.[29,31] Other commonly reported acids include lactic, succinic, acetic, tartaric, malonic, fumaric, butyric, formic, propionic, and adipic acids.[22,32–34] Several bacterial species are known to produce distinct organic acids, including itaconic, isobutyric, and isovaleric acids,[28] whereas others excrete isocaproic, isovaleric, and α-ketoglutaric acids, which contribute to phosphate solubilization through acidification and metal chelation mechanisms.[26] Humic acid enhances P availability by complexing with cations such as Ca^{2+}, Fe^{3+} and Al^{3+} that would otherwise bind phosphate, thereby reducing the formation of insoluble phosphate minerals and allowing more P to remain in plant-available forms.[35] The effectiveness of these organic acids largely depends on their molecular structure, with tricarboxylic and dicarboxylic acids generally being more efficient than monobasic acids, and aliphatic acids typically more effective than phenolic or aromatic acids.[15]

Table 1 presents the effectiveness of various organic acids in phosphate solubilization. The table includes the types of organic acids used, mechanisms by which they solubilize phosphate, the reported effectiveness, environmental conditions considered, microorganisms involved, and the experimental approaches adopted. Organic acids such as citric, oxalic, and gluconic acids are frequently highlighted for their efficiency, mainly through chelation and proton donation, which reduce soil pH and enhance phosphorus availability.

2.2 Limitations of organic acids in rock phosphate solubilization

Organic acids rapidly lose effectiveness in neutral/alkaline soils. Calcareous soils (high $CaCO_3$) buffer added acids and keep pH

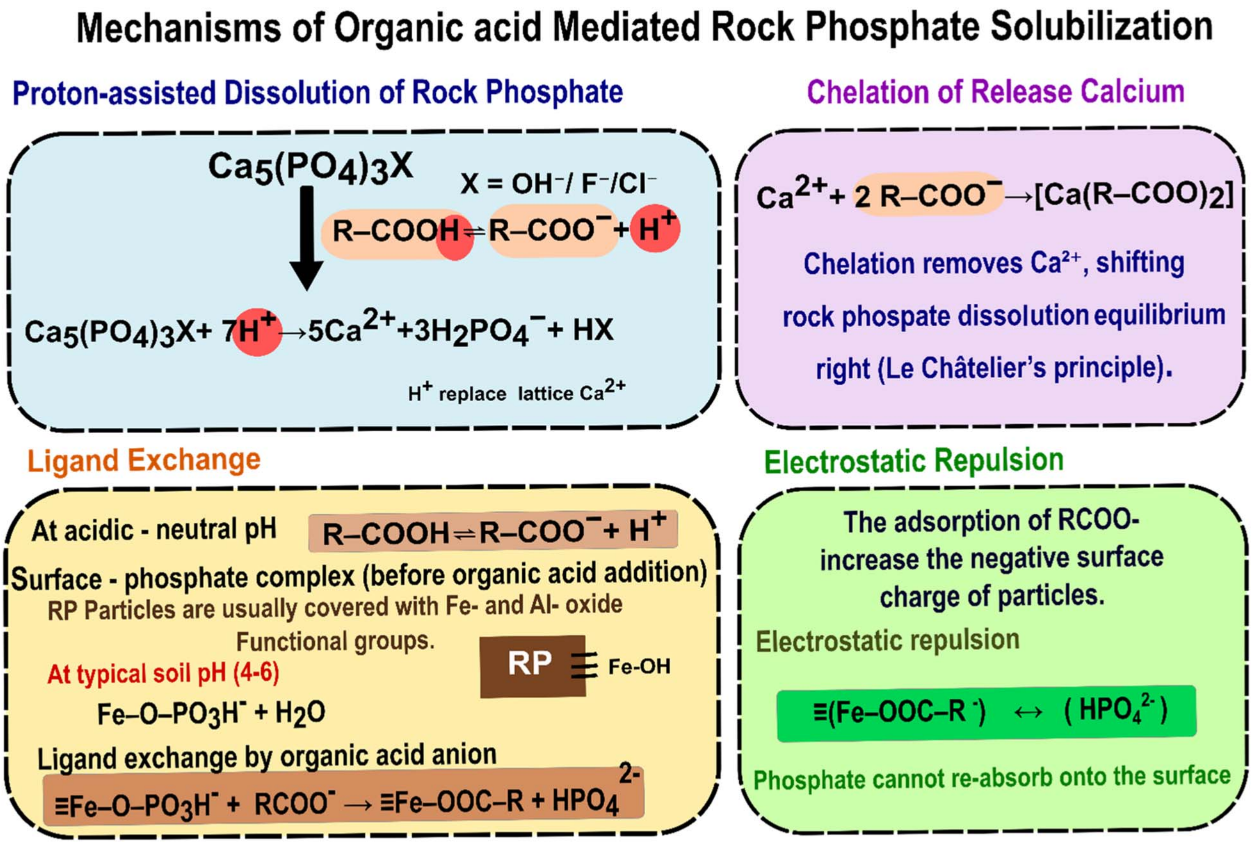

Fig. 1 Mechanisms of organic acid mediated rock phosphate solubilization.

high, so RP remains largely insoluble. For example, RP itself is insoluble especially in soils with high pH.[5] In practice only a small fraction of soil P (~0.1%) is in solution,[2] because up to 75–90% of added P quickly precipitates as insoluble metal phosphates. In neutral-alkaline conditions this means Ca–P forms, in acidic soils Al/Fe–P forms.[2,38] Organic acids can acidify the rhizosphere and chelate Ca^{2+}, but in strongly buffered soils huge doses (high acid : phosphate ratios) are needed to overcome carbonate buffering. Citric acid, for instance, forms poorly soluble calcium salts (*e.g.* calcium citrate), precipitating on rock surfaces and limiting further reaction.[39] Such precipitation is often reversible (Ca^{2+} is freed again when pH rises).[39]

Any phosphate liberated by acids may immediately reprecipitate. In alkaline (Ca-rich) soils P re-forms Ca phosphates; in acidic (Fe/Al-rich) soils it reforms Fe/Al phosphates.[2,38] This fixation limits solubilization efficiency. For example, one study noted that rapidly solubilized P can precipitate with Fe^{3+} and Al^{3+} ions, greatly reducing net P release.[38] Likewise, soil colloids and clays can adsorb organic acids (*e.g.* citrate) or the released P, further reducing availability.

Organic acids diffuse and are consumed rapidly. Soil microbes preferentially metabolize low–molecular-weight acids, so without continuous production the effect is short-lived. In practice organic acids alone can only provide a transient pH drop. Moreover, high microbial degradation of exuded acids means that sustained acid levels are hard to maintain, especially in warm, biologically active soils. Indeed, PSB must constantly produce acids to sustain solubilization.[5]

A key limitation in using organic acids for the solubilization of rock phosphate arises from the strong adsorption of those acids onto the soil matrix, particularly in soils rich in 2 : 1 clays and exchangeable calcium. When organic anions (such as citrate) are introduced, rather than remaining freely in solution to chelate Ca^{2+} and dissolve phosphate minerals, they may become adsorbed onto clay surfaces or form Ca–organic-anion complexes. As shown in modelling and experimental studies, the adsorption of citrate can increase phosphate fixation rather than reduce it, by enhancing the binding of PO_4^{3-} onto mineral surfaces *via* electrostatic interactions with adsorbed Ca^{2+}.[40] Furthermore, in a clay soil dominated by smectite (a 2 : 1 clay), addition of citric and tartaric acids caused a significant decrease in Olsen-P, with increased P sorption capacity ($K(f)$) and sorption intensity. In essence, a portion of the applied acid is mopped up by the soil matrix, reducing the net amount of acid or chelating anion reaching the rock phosphate, thereby limiting the expected enhancement of P solubility.

3 2D nanomaterials for phosphorus delivery in field crops

2D nanomaterials offer ultrahigh surface area and abundant reactive sites, enabling strong adsorption and controlled release of nutrients.[6] For example, graphene oxide (GO) has a π-rich

Table 1 Comparison of major organic acids reported to solubilize phosphate rock, highlighting their chemical nature, microbial or synthetic origin, mechanisms of P solubilization (proton release and chelation), solubilization efficiencies, optimum pH conditions and dominant microbial producers

Organic acid (formula)	Source	Mechanism of solubilization	Solubilization efficiency (quantitative)	Optimum pH (approx.)	Major microbial producers	References
Oxalic acid ($C_2H_2O_4$)	Synthetic & microbial (fungi)	Proton release (strong acid) + strong Ca^{2+} chelation (Ca-oxalate)	*e.g.* 100 mM: ~75% of P solubilized in 1 h; 100% solubilization at stoichiometric dose	~1–3	Fungi (*e.g. Aspergillus niger*, *Penicillium* spp.)	36 and 37
Citric acid ($C_6H_8O_7$)	Synthetic & microbial (fungi, bacteria)	Proton release + strong chelation of Ca/Al/Fe (tricarboxylate)	60 mM: ~153 µmol P (from 1 g medium-reactive RP; ≈4.4% of total P)	~3–5	Fungi (*e.g. Aspergillus niger* produces large citric); some bacteria	5 and 36
Gluconic acid ($C_6H_{12}O_7$)	Microbial (bacteria)	Proton release + chelation *via* multiple –OH/–COOH groups	Production correlates with P release (*e.g. Pseudomonas* sp. produced ~ 11.1 mM; pH ~ 4)	~3–4	*Pseudomonas*, *Bacillus*, *Rhizobium*, *Azospirillum*, *etc.*	27
Malic acid ($C_4H_6O_5$)	Microbial (plants/fungi/bacteria)	Proton release + chelation (dicarboxylate)	60 mM: ~73.5 µmol P (Abu Tartur RP)	~3–5	Fungi (*e.g. Aspergillus niger*), *Pseudomonas*, *Bacillus*, *Paraburkholderia*	27
Tartaric acid ($C_4H_6O_6$)	Microbial (fungi/bacteria)	Proton release + chelation (dicarboxylate)	60 mM: ~117.8 µmol P (Abu Tartur RP)	~2–5	*Bacillus* (*e.g. B. safensis*) and various fungi	36
Succinic acid ($C_4H_6O_4$)	Microbial (bacteria)	Proton release + chelation (dicarboxylate)	(Reported effects modest; <5% P typically)	~3–6	*Pseudomonas*, *Bacillus*, *etc.*	27
Acetic acid ($C_2H_4O_2$)	Microbial (general fermentation)	Proton release (weak monocarboxylic acid)	60 mM: ~42.5 µmol P (Abu Tartur RP)	~4–6	Acetic-acid bacteria, yeasts (common metabolite)	36
Maleic acid ($C_4H_4O_4$)	Synthetic (few microbes)	Strong proton release (dicarboxylic, $pK_{a_1} \approx 1.92$)	60 mM: ~73.5 µmol P (Abu Tartur RP)	~2–4	Few (some fungi)	36
Formic acid (CH_2O_2)	Microbial (general)	Proton release (strong monocarboxylic, $pK_a \approx 3.75$)	—	~3–4	Many bacteria (*e.g. Bacillus*, *Clostridium*)	27
Lactic acid ($C_3H_6O_3$)	Microbial (lactic bacteria, others)	Proton release (monocarboxylic, $pK_a \approx 3.86$)	—	~3–5	*Lactobacillus*, *Bacillus* (few reports)	27

aromatic lattice decorated with oxygen-containing functional groups. These allow cation–π and electrostatic interactions with nutrient ions. GO can therefore act as a nutrient reservoir that captures and gradually releases P (as phosphate) in soil. In one study, GO was combined with Fe^{3+} ("GO–Fe" composite) to bind phosphate: the Fe centers strongly sorbed PO_4^{3-} *via* interactions with GO's oxygen groups and π-system, producing a slow-release P fertilizer.[6,8] Column and pot tests showed that this GO–Fe composite loaded with 15% P maintained wheat yields equal to a soluble fertilizer, indicating improved P efficiency.[8]

3.1 Materials for 2D nanomaterial-based phosphorus delivery

3.1.1 Graphene oxide (GO) and graphene-based carriers. GO and reduced GO (rGO) are the most studied 2D carbon materials for P delivery. Their high surface area and oxygen-functionalization (–OH, –COOH) give them strong affinity for nutrient ions.[6,8] GO can be engineered (*e.g.* folded or crumpled) to further increase its effective surface. In practice, GO is often used as a carrier matrix: phosphate (often as a precipitate with Fe or Ca) is loaded onto GO or rGO sheets, forming a composite that slowly releases P. For example, Andelkovic *et al.* (2018)[41] loaded P onto a GO–Fe composite (15% P by weight, similar to commercial fertilizers). The Fe^{3+} bound phosphate strongly, while the GO sheet matrix slowed its diffusion. Soil column tests confirmed that P diffused more slowly from the GO composite than from soluble fertilizer.[8] When this nano-fertilizer was applied to wheat, grain yield matched that from a high-rate soluble fertilizer,[8] even though P availability was prolonged. Other studies have used GO films or nanoparticles as slow-release coatings for NPK granules, illustrating GO's role as a barrier layer that prevents rapid nutrient loss.[6,42]

3.1.2 Black phosphorus nanosheets (BPNSs). Black phosphorus (BP) is a layered P allotrope whose 2D form (phosphorene) carries ∼25% elemental P by weight. In soils or plant tissue, BPNSs spontaneously oxidize to produce phosphate and related polyphosphates. Thus, BPNSs serve as a built-in P source. In the soybean study mentioned above, TEM imaging showed BPNSs accumulated in the root stele; as they degraded, they released P that boosted root and shoot P levels.[43] The BPNS treatment significantly delayed phosphorus-deficiency symptoms (*e.g.* leaf chlorosis), enabling normal growth without added soluble P.[43] In effect, BPNSs act like an injectable phosphate reservoir. However, bare BPNSs are chemically unstable in air/water (they degrade within days), which is both an asset (for release) and a challenge (requires stabilization). Research is exploring coatings or antioxidant treatments to control BP oxidation so that phosphate release can be tuned.

3.1.3 MXenes (*e.g.* $Ti_3C_2T_x$). MXenes are a family of 2D transition metal carbides/nitrides (general formula $M_{n+1}X_nT_x$, where M = Ti, V, Nb, *etc.*; T = –O, –OH, –F surface groups).[44] They have very high hydrophilicity, large interlayer spacing, and numerous active surface sites.[44] For phosphorus delivery, MXenes can be used as adsorbent carriers. Their surface –OH/–O groups could bind P or Ca/Mg to hold phosphate, analogous to how they trap heavy metals in water treatment. (For example, $Ti_3C_2T_x$ has been shown to adsorb phosphate from wastewater at high capacity when modified with Zr or Fe.) Although field studies on MXene-fertilizers are limited, the principles are promising: MXenes' high cation-binding capacity and tunable composition (different metals can tailor binding strength) suggest they could be loaded with phosphate or P-precursors. In water treatment research, MXenes exhibit massive adsorption capacity for cations,[44] implying that in soil they could similarly sequester nutrients near the root zone. Some studies have noted MXenes' effects on plant growth (*e.g.* mitigating heavy-metal stress in wheat), hinting at biocompatibility. Overall, MXene-based P-fertilizers are an emerging idea – they combine 2D layering (for slow diffusion) with metal oxide chemistry – but more agronomic research is needed to validate their performance and safety.

3.1.4 Biochar as a synergistic carbon carrier. Biochar has become more prominent as a versatile soil enhancer that synergizes with 2D nanomaterials and organic acid-driven rock phosphate (RP) solubilization.[45] It is abundant in aromatic carbon, functional groups containing oxygen, and mineral phases, all of which affect soil pH, organic acid availability, cation exchange capacity, and microbial activity.[46] These characteristics make biochar especially useful for enhancing RP reactivity and maintaining phosphorus release.[47]

Biochar enhances RP dissolution mainly by changing soil chemical properties. Its surface contains –COOH, –OH, and phenolic groups that can chelate Ca^{2+}, Mg^{2+}, and Fe^{3+} ions linked to RP, reducing phosphate precipitation and increasing phosphorus availability. Research indicates that adding biochar raises soil organic acid levels, such as citric and oxalic acids, and stimulates acid-producing microbes, both of which promote RP solubilization.[48] Additionally, biochar improves soil moisture and aeration, aiding the diffusion of organic acids around RP particles.[49]

Biochar helps stabilize 2D nanosheets by reducing aggregation and creating a porous, high-surface-area carbon matrix. Hybrid composites like biochar–GO have shown improved adsorption of phosphate and metal ions, thanks to the synergistic interactions between biochar's aromatic domains and GO's oxygenated groups.[6] These composites can serve as slow-release phosphorus carriers: phosphate released from RP or organic acid breakdown can be captured by the carbon matrix and gradually delivered to plants. Additionally, integrating biochar with MoS_2 or metallic 2D layers introduces redox-active surfaces that influence phosphate sorption and desorption processes.[50]

During pyrolysis or hydrothermal carbonization, biomass emits humic substances and small organic acids that can bind with RP particles. Hydrothermal co-processing of biomass and RP creates carbon–phosphate composites with Ca–P nanoparticles embedded in an oxygen-rich carbon matrix.[49] These hydrochars show much higher phosphorus lability compared to raw RP and function as slow-release fertilizers. The carbon matrix also helps buffer soil pH and shields P from quick fixation.[51]

3.2 Functionalization strategies for 2D nanomaterial-based P fertilizers

P use efficiency can be improved by creating smart fertilizers that combine RP with functional additives. One promising approach is to integrate 2D nanomaterials (graphene oxide or MoS_2), organic acids, and RP in composite formulations.[52] These composites aim to solubilize RP, control P release, and boost crop uptake. Key strategies include: (1) surface functionalization of 2D nanosheets with organic acids and loading of RP-derived P; (2) *in situ* hydrothermal or sol–gel synthesis to form integrated carbon/P composites; and (3) fabrication of layered composites or pellets embedding RP, organic acids, and 2D carriers.

3.2.1 Surface functionalization of 2D nanosheets. In this strategy, 2D nanosheets are chemically modified with acidic groups or co-factors, then used to bind phosphate.[53] For example, Andelkovic *et al.* (2018)[41] synthesized a GO–Fe(III) composite and loaded it with phosphate. They found that ferric ions on GO anchored PO_4^{3-} at ~48 mg P per g of GO–Fe, creating a slow-release P carrier.[41] Likewise, Kabiri *et al.* (2020)[54] prepared a dual-release fertilizer by compacting MAP (monoammonium phosphate) with P-loaded GO (GO–Fe plus P).[54] The GO–Fe nanosheets were formed *in situ* by oxidizing GO in Fe^{2+}/H_2O_2 and then adsorbing P from solution. This MAP + GO–Fe–P composite released P in a biphasic manner (fast + slow release), dramatically reducing P loss in leaching experiments compared to uncoated MAP.[54] These studies demonstrate that functionalized GO nanosheets can carry RP-derived P and retard its release.

Organic acids, citric, oxalic, and humic acids, play two roles. They can be grafted or adsorbed onto 2D surfaces to provide additional binding/chelation sites, and they are themselves P-solubilizers. In separate studies, coating conventional P granules with organic acids (without nanomaterials) slowed P release and improved plant uptake.[55] For instance, Teixeira *et al.* (2016) coated MAP with citric or synthetic organic acids and found a more gradual P release and 3–13% higher agronomic efficiency (AE) compared to uncoated MAP.[56] Over time the organic-acid coatings extended the availability of P in soil and increased apparent P recovery by Maizes.[56] By analogy, attaching organic acids to GO or other 2D carriers should similarly buffer and sustain P release. In practice, functionalizing nanosheets with acid groups or humic residues could anchor RP particles and modulate dissolution.

3.2.2 *In Situ* hydrothermal or sol–gel synthesis. An alternative approach is one-pot synthesis of carbon/P composites under hydrothermal or sol–gel conditions. For example, co-hydrothermal carbonization of biomass (organic acid source) with rock phosphate can yield nutrient-rich hydrochars. Daer *et al.* (2024) co-treated corn straw and RP at 220 °C in water. The straw released humic-acid-like substances and organic acids that activated the RP, dissolving it and reprecipitating mixed Ca–P compounds.[57] The resulting hydrochar contained abundant oxygenated organic matter and new $C–O–PO_3$ and $C–PO_3$ bonds, with up to ~90% of the original P in labile (apatite/$CaHPO_4$) forms. In effect, the hydrothermal process created a carbon-phosphate composite: P from rock phosphate became incorporated into a carbon matrix rich in aromatic and O-containing groups, improving P availability and long-term stability. Such hydrochars are microbially active and slow-release (humic-like) fertilizers.[57]

Sol–gel synthesis is less explored for P fertilizers but offers similar integration. One could, for example, co-condense silica precursors or bio-polymers with RP in the presence of organic acids or 2D fillers. The result would be a hybrid composite (silicate/phosphate/GO) with controlled porosity. While specific sol–gel fertilizer examples are rare, the concept parallels many *in situ* methods in materials science: layered double hydroxides (LDHs) or metal–organic frameworks with P, carbon aerogels loaded with RP, or zeolite/graphene hybrids could be synthesized. These would uniformly distribute RP and organic ligands at the nanoscale.

3.2.3 Layered composites and pellet formulations. This strategy builds structured composites or granules that physically

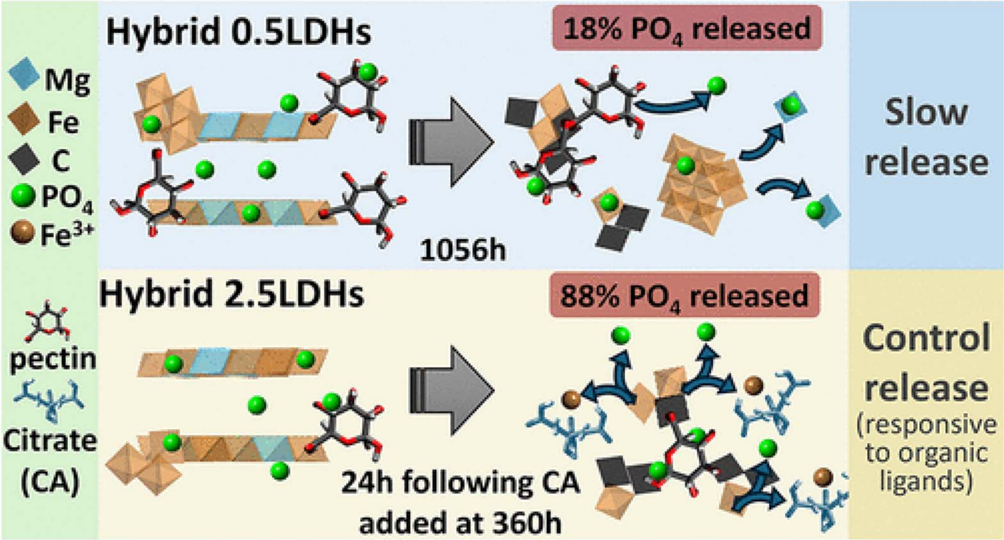

Fig. 2 Organic ligand-responsive phosphate release from pectin–LDH hybrids: structural integration of Mg–Fe layered double hydroxides (LDHs) with apple/citrus-derived pectin enhances phosphate sorption and enables controlled, citrate-triggered PO_4^{3-} release. Synchrotron analysis reveals Fe(III)–P interactions as the release-controlling mechanism, supporting slow- and smart-release fertilization for sustainable agriculture. This figure has been adapted from (Li *et al.*, 2025)[63] with permission from ACS publication, copyright 2025.

embed RP, organic acids, and nanocarriers. For instance, researchers have studied film or shell coatings of fertilizers with GO. Cheng *et al.* (2024) created GO-sheet coatings on commercial NPK granules. The GO shell (50–60 μm thick) dramatically slowed nutrient release: after 4 h, GO-coated pellets had released only ∼43–57% of their NPK, *versus* >80% release from uncoated granules.[58] These GO-shelled granules held back nutrients in the early phase, thus extending delivery. Eventually the GO shells cracked (around 6 h) and release accelerated, but overall, the GO coating gave significant initial retardation of release.

Graphene and GO also reinforce granules mechanically.[59] In wet-granulation processes, adding a small fraction of graphene markedly increases pellet strength. Kabiri *et al.* (2020)[60] reported that adding 0.5% graphene to MAP granules increased crushing strength by ∼1680% (powder processing study). This means granules resist breakage better, reducing fines and dust loss. Such 2D additives could be used to formulate composite fertilizer pellets: blending RP powder with a carbon/binder matrix and GO sheets, then granulating into slow-release pellets. Indeed, Kabiri *et al.* (2020) used a compaction method to combine MAP with slow-P sources (struvite or GO–Fe–P) into one pellet.[54] These dual-release composites behaved like layered fertilizers: an initial soluble P source plus a slower reservoir.

Layered composites can also mean multilayer coatings. For example, one could coat RP granules first with a layer of organic acid to initiate P solubilization and then with a 2D nanofilm to modulate diffusion.[61] Or pellets could be made of layered materials (*e.g.* alginate/Ca-polymer layers containing RP and GO). Although specific studies on such multi-layer RP-2D composites are scarce, analogous systems (*e.g.* polymer/GO coated TSP) have shown improved release and plant growth.[62]

Layered 2D clays like Mg–Al LDH can likewise be loaded with phosphate or organics. A recent example hybridized Mg–Fe LDH with a pectin biopolymer to create an organic-ligand responsive P-fertilizer.[63] In this system, the LDH–pectin sheets strongly sorb phosphate (over 118 mg g^{-1}) and release it slowly. Remarkably, adding a moderate amount of citrate (4 mM) triggered rapid P release: 87.7% of the stored phosphate was released in the presence of citrate (Fig. 2).[63] In plain terms, when an organic acid was present, the LDH gave up its phosphate. This mimics real soil conditions where microbes supply acids: the fertilizer remains locked up until microbial citric/oxalic acids arrive, then it releases P on demand. Similarly, GO can be combined with biopolymers (starch, lignin, *etc.*) to make bio nanocomposites that biodegrade and dispense phosphate over weeks.[41]

4 How 2D nanomaterials enhance organic acid-mediated RP solubilization

4.1 Effect on stability and activity of organic acids

Incorporating organic acids into 2D hosts significantly prolongs their lifetime. For instance, organic acids intercalated in LDH are released slowly rather than immediately dispersing.[64] A recent study on mercaptosuccinic acid (MSA) in LDH showed that the acid-bound LDH resisted dissolution much better than a comparable Ca-based treatment: after acid exposure, Cd bound in MSA–LDH released only ∼2–6% of metal, *versus* >50% for the Ca control.[65] By analogy, an organic acid like citric or oxalic acid held in LDH layers would be far more stable in soil than the free acid. The 2D matrix shelters the acid from rapid microbial degradation and from neutralization by soil minerals.[66,67]

2D materials can concentrate and localize acids near rock phosphate. This means a drop of citric acid could stick onto the GO surface and be delivered directly to an RP particle embedded in the GO. The proximity effect amplifies the acid's action on the mineral. Likewise, LDH can slowly exchange out acid anions, maintaining a low-pH microenvironment. In effect, the acid's proton and chelating groups remain active longer at the dissolution site. The key soil mechanism – protonation and Ca^{2+} chelation – is preserved and extended by 2D supports.[5]

Because 2D carriers can adsorb organic acids, they reduce losses. An organic acid stuck on a GO sheet is less likely to leach away or be rapidly taken up by microbes. It can repeatedly interact with the mineral surface. Embedding organic acids in 2D nanomaterials tends to stabilize them against degradation and spreads out their activity over time, boosting the overall efficiency of rock phosphate solubilization.[68]

4.2 Role in reducing phosphate fixation

4.2.1 Calcareous soils. In high-pH (calcium-rich) soils, added phosphate quickly turns into insoluble Ca-phosphate salts.[2,5] A 2D nanomaterial can mitigate this by either sequestering Ca^{2+} or by locking the phosphate in a form less prone to precipitation. For example, loading P into an LDH structure (*e.g.* as a PO_4^{2-} interlayer) prevents it from immediately encountering Ca^{2+} in solution; the anion exchange must occur slowly as the LDH releases the phosphate. One soil study found that adding graphene decreased nutrient leaching compared to conventional amendments, suggesting improved retention.[69]

4.2.2 Iron/aluminum-rich soils. Acidic soils fix P with Fe and Al, forming highly insoluble Fe/Al phosphate.[2] Layered double hydroxides often contain Fe/Al themselves; for instance, Zn–Fe LDH or Mg–Al LDH.[70] These materials can share the Fe/Al–phosphate fixation problem by incorporating Fe or Al into their lattice and swapping phosphate in a controlled way. In effect, phosphate is bound to the LDH rather than to soil oxides. Graphene oxide can also adsorb Fe from solution, and one theoretical study showed that graphene sheets bind phosphate strongly.[71] Thus, a GO sheet or an Fe-oxide nanocomposite might tie up Fe and simultaneously hold P on its surface. This dual action reduces the amount of free Fe to trap P. In both calcareous and iron-rich soils, 2D carriers act as competitive sorbents: they temporarily take up P or its cations, keeping P bioavailable longer.

4.3 Mechanisms enhancing phosphate release from rock phosphate

In the presence of 2D nanomaterials, several synergistic mechanisms can accelerate solubilization process. First, 2D materials adsorb both the RP surface and the organic acids, bringing them into intimate contact. The vast GO or LDH surface can trap organic acid molecules *via* hydrogen bonding, π–π stacking or electrostatic attraction and hold them near the RP particles.[72] This concentrates the acid near the mineral, increasing local proton activity and sustained dissolution. 2D sheets can adsorb organic acids by electrostatic and hydrogen-bond interactions, then desorb them slowly. For example, GO's –COOH and –OH groups could form hydrogen bonds with citric acid, possesses three carboxylic groups (–COOH) and one hydroxyl group,[73] releasing it gradually as protons are consumed by RP dissolution. Citric acid can deprotonate its carboxylic and hydroxyl groups, forming citrate anions that can engage in hydrogen bonding with GO's functional groups.[74] The hydrogen bonds formed are strong and can be characterized by low-barrier hydrogen bonds, which facilitate proton exchange without significant energy barriers.[75] This contrasts with free acid that diffuses quickly. The high surface area of 2D sheets allows large acid loading per carrier mass.

When considering rock phosphate solubilization, Ca^{2+} complexation plays a key role in enhancing the solubilization of rock phosphate by binding free calcium ions released during mineral dissolution. This reduces the concentration of Ca^{2+} in the solution, shifting the equilibrium toward further dissolution of phosphate minerals. Organic ligands or acids form stable complexes with calcium:

$$\mathrm{Ca}^{2+} + \mathrm{L}^{n-} \rightarrow \mathrm{CaL}^{(2-n)-}$$

where *L* represents a ligand like citrate or oxalate. By removing Ca^{2+} from the system, more phosphate is released into the solution, improving its availability for plant uptake or further reactions. Graphene oxide (GO) membranes demonstrate remarkable calcium ion adsorption capabilities due to several molecular mechanisms. The adsorption process is exothermic and spontaneous, following Lagergren second-order kinetics.[76] The adsorption capacity increases with higher oxygen content and interlayer spacing of GO membranes, reaching up to 0.481 g Ca^{2+}/g GO.[77] This exceptional adsorption is attributed to strong interactions between Ca^{2+} and GO sheets, including ion–π interactions with aromatic graphitic rings and electrostatic interactions with oxygen-containing groups.[77] The selective transport of cations through GO membranes is governed by a balance between cation–π interactions and the desolvation effect of ions.[78] These mechanisms contribute to GO's high affinity for calcium particles, making it useful for water softening and treatment.[76] Additionally, GO membranes exhibit excellent stability and reusability, with easy desorption of Ca^{2+} using water.[77]

Second, 2D nanomaterials create reactive catalytic surfaces. Certain 2D sheets (*e.g.* Fe–graphene[79] mmm, MoS_2, black phosphorus[80] (phosphorene), *etc.*) can facilitate redox reactions or produce reactive radicals under ambient conditions or light. While not yet widely studied in soils, analogous photocatalytic or Fenton-like reactions on 2D surfaces could degrade organic matter into stronger acids or generate additional protons, further promoting phosphate liberation. At minimum, any catalytic breakdown of complex organics by 2D surfaces could regenerate low-molecular-weight acids.

Third, the very structure of 2D materials prevents diffusion losses. Dissolved phosphate or organic acids that adsorb onto a layered nanomaterial are less prone to leach away.[81] In effect, 2D carriers act as phosphate and acid traps, keeping reagents near the site of the rock until plants or microbes can utilize them. Functionalized graphene or MoS_2 can improve wetting of RP and soil, ensuring acid contacts phosphate surfaces. Oxidized graphenes are hydrophilic and can disperse in soil water, potentially carrying attached acids deeper into pores.

5 Agronomic performance and ecological impacts

5.1 Crop yield and phosphorus uptake

Several studies report marked increases in plant P uptake and growth with GO or MoS_2 treatments, compared to controls or conventional fertilizers. In a 60 days greenhouse trial with pepper seedlings, adding a small amount of GO to soil dramatically raised shoot P content. Plants grown with 20 mg L^{-1} GO had ∼4.13 g kg^{-1} P in shoots, *versus* only 2.74 g kg^{-1} in the untreated control – a 2.8-fold increase.[82] Lower GO doses often had stronger effects: the 20 mg L^{-1} treatment boosted P and K uptake much more than higher (50 or 100 mg L^{-1}) doses. Improved nutrient uptake translated into better growth: G20 plants were ≈10% taller than controls. The enhancement is attributed to GO's retention of ions in soil. Leaching tests showed soils with GO lost far less dissolved P, N and K under simulated rain, allowing plants to access more P.[82] Other crop studies echo this: micron-sized graphene or graphite reduced N leaching and increased lettuce growth. In short, GO acts like a soil conditioner that concentrates P near the roots.

MoS_2 itself does not contain phosphate, but it can boost overall nutrient use. In soybean, MoS_2 nanoparticles (500 mg kg^{-1}) increased yield by ∼30% over conventional molybdenum fertilizer sodium molybdate.[83] This dramatic gain was linked to enhanced nitrogen fixation *via* improved nodule health and not directly to P. However, in rice trials MoS_2 showed a clear effect on P: exposure to 10 mg kg^{-1} MoS_2 (both 1T and 2H phases) significantly increased rice P uptake.[84] The mechanism is not fully explained, but may involve MoS_2's influence on root physiology or soil chemistry that makes P more available. Notably, 1T-MoS_2 released far more Mo into the soil solution than 2H, which could affect pH or microbial activity. In the maize study, MoS_2 treatments decreased Ca/Mg in leaves and other nutrients,[85] suggesting altered nutrient balances.

5.2 Environmental safety considerations

5.2.1 Nanoparticle toxicity and soil health. The environmental impact of GO and MoS_2 in soil is a key concern. Both materials exhibit dose-dependent toxicity to plants and microbes.[86] At low concentrations (tens of mg L^{-1}), GO often stimulates plant growth. For example, GO additions (≤100 mg L^{-1}) increased biomass and nutrient content in Arabidopsis, tomato, and grass species. In a controlled pepper study, adding GO to soil raised plant height and dramatically increased phosphorus uptake. However, high GO levels can be phytotoxic: concentrations above ∼200 mg L^{-1} inhibit seed germination and root growth. This toxicity is attributed to oxidative stress and physical interactions with roots that generate reactive oxygen species.[87]

MoS_2 nanosheets also show antimicrobial and plant-toxic effects at high doses. In one greenhouse experiment, maize seedlings grown in soil with 10–100 mg kg^{-1} MoS_2 had significantly stunted growth and disrupted nutrient uptake, even at the lower dose.[85] MoS_2 coated on bacteria or in suspension at 16 mg mL^{-1} killed >99.9% of beneficial soil *Bacillus* and *Pseudomonas*.[88] However, a rice study found that 10 mg kg^{-1} of either MoS_2 polymorph (1T or 2H) did not reduce plant biomass or microbial diversity; in fact it increased P uptake and enriched nitrogen-fixing bacteria.[84] Thus, MoS_2's toxicity depends on dose and form. Generally, low levels of MoS_2 nanoparticles were benign or beneficial, while higher amounts and nanosheets caused stress.

Both nanomaterials can alter microbial communities. GO amendments rapidly changed soil bacterial community composition and temporarily reduced biodiversity.[89] In a polluted soil, GO increased the availability of some metals, such as As, Zn, and, within one week, caused a transient drop in microbial diversity. Similarly, long-term column studies showed that leaching of GO nanosheets through soil altered microbial carbon-use patterns and increased overall species richness.[90] MoS_2 also shifts microbiota: maize with MoS_2 had enriched N-fixing bacteria but overall community disturbance,[89] and the lab study showed MoS_2 nanosheets significantly reduced counts of key soil bacteria (99.998% kill of *Bacillus* at 16 mg mL^{-1}).[88]

5.2.2 Mobility and persistence in soil. The movement and longevity of GO and MoS_2 in soil influence environmental risk. Both materials are chemically stable and can persist for months, but their transport depends on soil properties.[91]

GO sheets tend to adsorb strongly to soil particles but can still migrate under certain conditions. In simulated soil columns, GO leaching depended on porosity and adsorption: highly porous soils allowed more GO to move down the profile, while adsorption onto particles eventually immobilized it.[90] After leaching, GO's physical state changed morphology, functional groups.[90] Thus, in coarse soils or under heavy rainfall, GO could reach deeper layers or groundwater. However, much GO likely remains bound or trapped in soils, especially in fine-textured or metal-rich clays.[92]

Bulk MoS_2 is extremely insoluble in neutral/alkaline environments, but nanosheets release molybdate over time. In the soybean study, MoS_2 nanoparticles dissolved gradually, releasing Mo and S that were taken up by plants.[83] Notably, 1T-phase MoS_2 dissolved much faster than 2H-phase (58.9% *vs.* 4.4% dissolution) under the same conditions.[88] This suggests MoS_2 nanomaterial chemistry (phase, defects) strongly affects release. In soil, released molybdate ($MoO_4{}^{2-}$) is relatively mobile in alkaline conditions and can leach into groundwater. Conversely, under acidic soils common in the tropics, molybdate adsorbs more to Fe/Al oxides and is less mobile.[83] The sulfur component as sulfate also becomes mobile once oxidized. Overall, MoS_2 nanoparticles will persist as particles until oxidized or taken up; transformed Mo and S ions may leach or bind depending on pH.[93]

Because both materials persist, any accumulation over repeated applications is a concern. Long-term studies are limited, but given GO's inert carbon structure and MoS_2's metal content, one should assume multi-year persistence. Their behavior can also be influenced by co-applied organic acids or fertilizer components, acidulation might increase metal solubility.

5.2.3 Water contamination risks. Leaching of nanomaterials or released ions could affect water. Mobile GO sheets might reach subsurface water, potentially carrying adsorbed pollutants.[94] Released molybdate from MoS_2 could contaminate runoff or groundwater; high molybdenum in water is toxic to livestock and can upset aquatic ecosystems.[95] No direct measurements of GO or MoS_2 in field runoff are available, but the mobility data above implies potential for water contamination if applied in excess.[96] Mitigation (*e.g.* buffer strips, controlled-release formulations) would be prudent if these nanomaterials are used at scale.

5.3 Synergistic interactions: microbes, 2D nanomaterials, and organic acids

The ultimate P-release system combines all three actors – microbes, acids, and nanomaterials – to create synergy. Phosphate-solubilizing microorganisms (PSMs) such as *Pseudomonas*, *Bacillus*, *Aspergillus*, naturally secrete organic acids as they grow in the rhizosphere.[97] These acids would solubilize RP on their own, but often plants or microbes run out of acids or the acids diffuse away. Introducing a suitable 2D carrier can keep the process going.[98]

For instance, a GO sheet that initially adsorbs citric or oxalic acid from PSMs will locally intensify the acid on nearby RP, hastening its dissolution.[99] As phosphate is freed, it can adsorb onto the GO or LDH surface instead of being lost, making it more accessible to the microbes or plant roots. In turn, the microbes find more phosphate and continue growing and producing acid. This positive feedback loop means that PSM activity and 2D materials mutually reinforce each other.[99]

Experimental evidence, though still emerging, supports such synergy. Teng *et al.* (2021)[100] reported a soil remediation system where iron nanoparticles loaded with phosphate were combined with a PSB strain. In that case, inoculation with the bacteria became the dominant microflora, improving the utilization rate of phosphate in the nanocomposite and enhancing the remediation outcome.[100] Translating this to RP solubilization: PSB can similarly dominate the micro-ecosystem and draw on the phosphate bound to nanocarriers, effectively mobilizing the P that the carriers provide.

Moreover, 2D nanomaterials often influence the soil microbiome. At low concentrations, GO and related sheets have been shown to stimulate certain bacterial communities (increasing diversity or activity), whereas very high doses can be antimicrobial.[72] Thus, carefully chosen 2D materials could promote beneficial PSM populations. Conversely, PSM themselves can modify 2D surfaces (*via* biofilms or excreted compounds), potentially tuning the carrier's release behavior.

In practice, a fertilizer formulation could include RP, a small amount of organic-acid substrate, and a 2D carrier. PSM in the soil would start producing acids; the 2D carrier would steadily release phosphate in response to the acids; and the microbes would have a sustained P supply for growth. This tripartite synergy maximizes P mobilization: the microbes generate and regenerate acids, the 2D carrier concentrates and slowly dispenses both acids and P, and the rock phosphate serves as the long-term P reservoir.

6 Knowledge gap and future directions

While promising, this field has many open questions. Materials science challenges include scaling up production of functionalized 2D materials in a cost-effective way, and ensuring consistent attachment of organic acids or minerals. The stability of nanocarrier coatings under field conditions (rainfall, temperature, microbial action) is not well understood. Long-term durability and reuse (*e.g.* multiple growing seasons) need study. Therefore, future research work should focused to screen a wide range of 2D nanomaterials (graphene/GO, MXenes like Ti_3C_2, 2D black phosphorus, layered double hydroxides, *etc.*) and organic acids (citric, oxalic, malic, humic) for hybrid designs.[101] Each combination may differ in P affinity and release kinetics.[102]

Soil and environmental interactions of 2D nanomaterials remain largely uncertain, highlighting the need to understand their behavior under realistic conditions. For instance, graphene oxide has been shown to alter soil microbial communities and affect nutrient cycling. However, it is still unclear whether persistent 2D materials in soil could impact earthworms, microbes, or plant roots. Most studies to date have been conducted in sterile or simplified media, underscoring the need for field trials to evaluate crop yields, phosphorus uptake, and potential ecological effects. Additionally, the fate of excess nanomaterials whether they accumulate, degrade, or leach remains a critical safety concern.[103]

Most studies to date have been conducted at the laboratory or greenhouse scale, and there is limited data on how these fertilizers perform under real-world farming conditions, which involve variable soils, crop rotations, and balanced N/P/K fertilizer regimes. The cost–benefit ratio also needs careful evaluation: it is important to determine whether the yield improvements and phosphorus savings justify the additional cost of nanomaterial additives. Moreover, regulatory frameworks for nanofertilizers are still evolving, making comprehensive safety assessments including ecotoxicology and potential human exposure essential before widespread adoption.

Future research opportunities lie in interdisciplinary approaches that integrate nanotechnology with soil science and plant physiology. For example, engineered nanocarriers could be designed to release phosphorus in response to specific soil cues such as pH or moisture. Coupling phosphorus nanocomposites with sensors to monitor soil P levels, or with beneficial microbes that produce organic acids, represents an exciting direction. Advanced characterization techniques, including synchrotron X-ray studies, could provide mechanistic insights into how phosphorus is bound and released at the nanoscale. Finally, integrating these nanocomposites with sustainable practices such as using waste-derived biochars or naturally occurring organic acids could enhance their environmental friendliness and overall agricultural sustainability.

Combining 2D nanomaterials, organic acids, and rock phosphate has shown clear potential to improve phosphorus availability and use efficiency in controlled experiments.[54,56–58] Future work must translate these findings to the field, ensuring that these innovative fertilizers are effective, safe, and economically viable for sustainable agriculture.

Mixing biochar with humic-acid–activated rock phosphate (RP) led to significant gains. In sandy soil experiments with vegetables, a mix of biochar and humic-activated RP increased Ca, Mg, and P uptake by ∼22–136% *versus* control. Spectroscopy showed humic activation chelated P into bioavailable forms, while biochar's adsorption held nutrients near roots. This combination (organic-acid activation + biochar retention) increased soluble P.[104] Additionally, adding biochar to fungal solubilization systems boosted organic acid output, with fungi or PSB providing acids and protons, and biochar removing toxic F^-, enhancing activity.[47] Pot trials with maize found that biochar, P-solubilizing bacteria (*Bacillus megaterium*), and P fertilizer synergistically increased soil P by ∼307% and maize biomass by 90–110% *versus* control. The combined approach significantly improved soil organic matter, K, P, and chlorophyll.[105] Biochar can serve as a habitat for PSB, potentially carrying or slowly releasing organic acids, such as when impregnated with citric acid or plant residues. Developing biochar–organic acid composites is a promising research area. So far, no studies have combined graphene oxide (GO) or MXenes with biochar or organic acids for P solubilization. One approach is GO-coated biochar, leveraging biochar's high adsorption and 2D materials' tunable surfaces, or using nanomaterials with organic amendments to speed phosphate dissolution. These strategies are largely theoretical and need experimental testing.

7 Conclusions

This review has highlighted the transformative potential of integrating two-dimensional (2D) nanomaterials into organic acid–mediated rock phosphate (RP) solubilization strategies. Organic acids, while environmentally preferable, are inherently limited by their short-lived activity and susceptibility to precipitation and microbial degradation. The introduction of 2D nanomaterials, such as graphene oxide, MoS_2, and layered double hydroxides, not only addresses these limitations but also opens new pathways for localized, slow-release, and pH-buffered phosphorus availability.[106]

The novelty of this research lies in conceptualizing 2D nanomaterials as active synergists, rather than inert carriers, in the phosphate solubilization process. These materials offer multifunctional benefits: stabilizing organic acids, preventing phosphate reprecipitation, sequestering interfering cations, and even catalyzing degradation of organic matter into soluble nutrient forms. Despite promising laboratory results, significant gaps persist in understanding how these systems behave in real-world soil environments. Long-term field studies, environmental safety assessments, and cost–benefit analyses are urgently needed to translate this innovation into practice.

In conclusion, the integration of nanomaterials, organic acids, and RP into hybrid formulations represents a novel and underexploited strategy for improving phosphorus use efficiency in agriculture. By bridging the disciplines of nanotechnology, soil microbiology, and plant nutrition, this approach has the potential to revolutionize sustainable phosphorus fertilization in both temperate and tropical cropping systems.

Author contributions

Imalka Munaweera – conceptualization, writing – review & editing, supervision. Sanduni Dabare – writing – original draft, visualization.

Conflicts of interest

All authors have no conflicts of interest.

Data availability

As this is a review paper, no new data was generated or analysed during this study. Data discussed in this review are derived from previously published studies, which are cited appropriately in the manuscript.

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