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Review

Comprehensive review of modified clay minerals for phosphate management and future prospects

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ABSTRACT

Phosphate recovery from water and wastewater serves as a feasible alternative to the exploitation of scarce phosphate rock resources. Currently, phosphate is recovered using adsorption-based techniques due to their desirable features, such as a low running cost, feasible operation, and high efficiency. Clay minerals (CMs), a group of earth-abundant resources, have attracted increasing interest in phosphate management. However, because the surface and crystal lattice of CMs are negatively charged, CMs are inefficient and have been replaced with cost-effective modified CMs (mCMs). This review comprehensively covers the current advances in mCM-mediated phosphate recovery. We first discussed the crystal features of natural CMs and the diverse techniques used for mCMs to enhance their phosphate-removal capacity. Subsequently, we covered the processes of mCM-driven phosphate management, namely, ion exchange, hydrogen bonding, crystallization, Lewis acid-base interactions, electrostatic interactions, precipitation, and electrostatic-ligand exchange. Further assessments revealed that mCMs can efficiently remove phosphate through multiple synergistic mechanisms. This review also discussed the effects of anions, humic acids, and cations on the mCMs management of phosphate and analyzed mCMs applications in various water environments, specifically, phosphate passivation materials in lake sediments and the phosphate management of municipal/seawater wastewater. We examined the reutilization of phosphate-loaded mCMs in agriculture from a circular economy perspective, and finally discussed the commercial application prospects of mCMs in environmental pollution remediation, which may help to avert the global phosphate-resource crisis and improve wastewater management.

1. Introduction

Phosphorus is essential for plant and agricultural growth but when released from natural and human sources, it accumulates as a pollutant in water bodies. In particular, the phosphorous levels discharged in sewage and from agricultural, mining, and industrial activities can exceed the environmental carrying capacity of water bodies. At phosphorous concentrations above 0.02 mg/L, excessive algal growth leads to eutrophication (Loganathan et al., 2014). Phosphorus is a nonmetallic element that primarily exists in nature as phosphate rock, a nonmetallic

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mineral resource with limited regenerative capacity. More than 80% of the extracted phosphate rock is used in the production of phosphate fertilizer, which is largely unused by crops (the proportion of wasted fertilizer usually exceeds 50%). Furthermore, phosphate ore deposits are scarce and natural phosphorus resources will likely be depleted in the next century. As the quality of phosphorus in phosphate rock continues to decline, the cost of phosphorus resources continues to rise. The imminent depletion of phosphate rock reserves necessitates the development and implementation of phosphate recovery strategies from (waste)water (Almanassra et al., 2020, 2021). Among the biological, chemical, and physical methods of phosphate recovery, adsorption can simply and effectively adsorb phosphate at low concentrations. Phosphorus is easily recovered by an adsorbent and a phosphate-saturated adsorbent is easily regenerated in low contents of by-product. However, as the cost of phosphate recovery exceeds that of mining, new phosphate-recovery technologies are needed (Cordell et al., 2011).

Clay minerals (CMs) are highly abundant, nontoxic, inexpensive, and important geological materials with a layered structure and a high Brunauer–Emmett–Teller specific surface area (SSA). Consequently, CMs are widely used in agricultural production and rural ecological construction. With their excellent water retention, fertilizer retention, and soil improvement functionalities, CMs can improve the yield and quality of crops (Murray,). The surfaces, interlayers, and structures of CMs also offer exceptional and variable activity. Interestingly, the unsaturated bonds of CMs can create diverse active centers of both Brønsted and Lewis acids. In addition, the molecular, hydrogen, and ionic bonds in CM structures are notably weak and typically form silicon–oxygen tetrahedrons and aluminum–oxygen octahedrons with structural unsaturation and isomorphism. A promising phosphate absorbent is palygorskite, which crystallizes into silicon–oxygen tetrahedra. The hydrolysis and fracture of Al–O and Si–O bonds in palygorskite simultaneously generate numerous R–OH molecules. At acidic pH, the H^+ ions in solution recombine with R–OH in the palygorskite crystal, generating positive charges on palygorskite and promoting phosphate adsorption (Ezzatahmadi et al., 2017).

More importantly, lattice defects created by vacant negative charges on O_2^- (OH^-) ions within CM layers lead to the formation of permanent negative charges, also known as structural charges. On the CM surface, high-valent cations such as Fe^{3+} or Al^{3+} are replaced with low-valent cations that acquire negative charges. In this scenario, the CM surface efficiently captures metal ions and organic cations. Therefore, modification can largely enhance the adsorption of anions (phosphates, NO_3^-, and Cl^-) by CMs, imbuing modified clay minerals (mCMs) with immense potential for various applications (Ezzatahmadi et al., 2017; Murray,).

Recent reviews on phosphate management have mainly focused on modified biochar (Almanassra et al., 2021) and rare earth elements for phosphate removal (Bacelo et al., 2020; Kunhikrishnan et al., 2022); the use of mCMs in phosphate removal is rarely reported. Several reviews have discussed the uses of biomass-modified CMs (Arif et al., 2021), modified attapulgite (for phosphate removal) (Liu et al., 2023), and CMs loaded with nanoscale zero-valent iron (Ezzatahmadi et al., 2017) for pollutant removal. Although mCMs have been widely applied in recent phosphate treatments (Chen et al., 2016), a comprehensive review and scientific summary covering the different types, modification techniques, mechanisms, and practical applications of mCMs has not been published.

This review covers the various types of CMs and their physical and chemical properties, focusing on the methods, advantages, and disadvantages of mCMs. Additionally, we comprehensively analyze the mechanism of phosphate removal by mCMs and explore the impact of competitive ions on this mechanism. The applications of mCMs are then investigated in various water environments; specifically, we discuss the use of mCMs in passivation eutrophication control of lake sediments, phosphate management of municipal wastewater, seawater, and eutrophication wastewater, and in the recovery and application of phosphate fertilizer. Finally, the review considers the challenges and prospects of mCMs in phosphate management.

2. Different types of phosphate-rich wastewater and their recovery methods

2.1. Sources and concentration of phosphorus in different wastewater

Phosphorus in wastewater exists in the form of organically bound phosphates, orthophosphates, and concentrated phosphates (Almanassra et al., 2020, 2021). Depending on the dissociation constant ($pK_1 = 2.21$, $pK_2 = 7.21$, and $pK_3 = 12.67$) and pH environment, orthophosphates exist in different species forms such as H_3PO_4, $H_2PO_4^-$, HPO_4^{2-}, and PO_4^{3-} (Almanassra et al., 2020, 2021). Biological oxidation processes in nature often convert more complex forms of phosphorus into orthophosphate, which is the main form of recovery. Orthophosphate as a fertilizer can be effectively consumed by most plants and crops for promoting successful growth (Bacelo et al., 2020).

The main source of phosphorus discharge in the environment comes mainly from wastewater treatment plants tasked with treating wastewater containing high levels of phosphorus. Table 1 shows the phosphorus concentration in different liquid streams, including industrial wastewater, municipal wastewater, human excreta wastewater, animal husbandry wastewater, lake water, and food processing industry wastewater. Research has shown that municipal wastewater is the main target and reliable source of phosphorus recovery (Egle et al., 2015). Phosphorus can be directly removed/recovered from urine and wastewater treatment processes, such as anaerobic digestion supernatant, advanced treatment sewage effluent, and sludge dewatering filtrate, with phosphorus concentration of up to 400 mg/L (Drenkova-Tuhtan et al., 2017; Egle et al., 2015; Ye et al., 2016).

The animal husbandry produces a large number of fecal pollutants (Bradford et al., 2008). Lagoon systems are usually used to manage wastewater in animal production facilities. After a series of wastewater treatment processes, including aerobic and anaerobic reactors, the concentration of phosphorus and nitrogen in the solution remains very high. It can be used as a source of agricultural nitrogen and phosphorus fertilizers that promote plant growth. However, its direct use can cause secondary pollution because these wastewaters contain pathogenic microorganisms, hormones, antibiotics, and heavy metals, which could all pose ecological risks (Bradford et al., 2008). Separating and concentrating phosphorus from wastewater to achieve phosphorus removal/recovery is possible. The concentrations of phosphorus in industrial wastewater, municipal wastewater, human excreta wastewater, animal husbandry wastewater, lake water, and food processing industry wastewater are shown in Table .1. Among them, the concentration of phosphorus in industrial wastewater changes the most.

2.2. Review of phosphorus management in wastewater

Biological, physical, and chemical methods are the main methods currently used to remove/recover phosphorus from wastewater (Fig. 1A). The main disadvantages and advantages of removing/recovering phosphorus from wastewater are listed in Table .2. Chemical precipitation can recover phosphorus from wastewater in the form of fertilizers and industrial products, and currently, it is the main method for removing/recovering phosphorus. Calcium and magnesium salts chemically precipitate or crystallize with phosphate to form struvite (MAP, $MgNH_4PO_4{\cdot}6H_2O$) (Fig. 1B) or hydroxyapatite (HAP, $Ca_5(OH)(PO_4)_3$) (Fig. 1C). However, MAP can be formed only when the phosphate concentration is higher than 50 mg/L. In addition, the formation of HAP needs to be between pH levels 7 and 9 (Desmidt et al., 2013). Biological method is used for phosphorus removal/recovery, mainly in the form of vivianite [$Fe_3(PO_4)_2{\cdot}8H_2O$] (Fig. 1D). The natural formation process of vivianite can be summarized into four aspects: ①high concentrations of iron and phosphorus (Fe/P = 2:1) need to exist in wastewater; ②wastewater environmental conditions must exist, with

Table 1

Summary of phosphorus concentration in different types of wastewaters.

Types of phosphorus wastewater	Phosphorus wastewater Sources	Total P (mg-P L^{-1})	References
Lake water	Moses Lake of Washington State of USA	0.15	Welch, 2009
	Laublaken Lake of Netherlands	0.169	Lürling and Oosterhout, 2013
	Poyang Lake, Hong ze Lake, the Taihu Lake and Dongting Lake of China	0.1	Zhou et al. (2022)
	Lakes of Germany (Scharmützelsee, Langer See, Müggelsee, Untere Havel) .	0.03–0.10	Kolzau et al. (2014)
	Lake Mälaren of Sweden (Galten, Björkfjärden, Ekoln)	0.03–0.093	Willén (1987); Willén (2001);
Municipal wastewater	Raw domestic wastewater	5–20	Davis, 2011
	Advanced treatment sewage effluent	5–10	Egle et al., 2015
	Phosphorus-rich digester supernatant	20–400	Vasenko and Qu, 2018
Human metabolism wastewater	Human urine	470–1070	Randall and Naidoo, 2018
Animal husbandry wastewater	Raw swine wastewater	100–987	Cheng et al. (2018)
	Raw poultry wastewater	23–50	Bradford et al. (2008)
	lagoons pre-treatment of swine wastewater	52-78 (32–62)	Vieira (2007)
	Aquaculture wastewater	1–5	Xu et al., 2023a
	Raw slaughterhouse wastewater	25–200	Bustillo-Lecompte and Mehrvar, 2015
Food processing industry Wastewater	Distillery wastewater	3–188	Mosse et al. (2011)
	Dairy industry processing wastewater	350–450	Wang et al. (2009)
	Raw tinned fish wastewater	13–47	Cristovão et al. (2015)
	Wastewater from fruit processing mill (Olive mill wastewater)	182	Ammary, 2004
Industrial wastewater	Fertilizer processing industrial wastewater	24	Anirudhan et al. (2006)
	Dyeing wastewater	0–15	Santos and Boaventura, 2015
	Metal surface treatment Wastewater (Automotive parts coating, steel plate surface treatment, home appliance coating)	100–1000	Jin, 2019.
	Paper mill wastewater	0.6–5.8	Cai et al. (2013)
	Phosphorus containing mineral leachate wastewater (Phosphogypsum leachate wastewater)	5127	Battistoni et al. (2006)
	Anodized industry wastewater	620–5069	Delgadillo-Velasco et al. (2018)
	Wet process of phosphoric acid wastewaters	15–31	Grzmil and Wronkowski, 2006

oxidation–reduction potential < -300 mV; ③organic matter must be relatively abundant (providing carbon sources for heterotrophic microorganisms such as metal reducing bacteria); ④ the wastewater environmental pH must be 6–9. The above analysis shows that the above method for phosphorus removal/recovery has relatively strict conditions.

For low phosphate concentration (<20 mg/L), adsorption is a fast and effective method for phosphorus removal/recovery, and the adsorbent loaded with phosphorus is directly used as a fertilizer (Ye et al., 2016). Developing low-cost, green, and environmentally friendly adsorbents is currently a problem to be solved. Adsorption can decrease the concentration of orthophosphate to below 0.01 mg/L, hence an effective method for controlling eutrophication (Kumar et al., 2019). Over the past two decades, many different types of adsorbents, such as carbonate minerals, porous silica, activated carbon, unmodified/modified biochar, metal oxides/hydroxides, CMs, and polymers, have been used to remove/recover phosphate from wastewater (Almanassra et al., 2021; Bacelo et al., 2020). Among these different types of adsorbents, CMs are widely used in phosphate removal/recovery owing to their abundant resources, high SSA, stability, and porous structure. However, many CMs have structural negative charges, so their phosphate removal ability is extremely low (Almanassra et al., 2021; Bacelo et al., 2020). Therefore, CMs are modified or impregnated with metal ions, providing them increased affinity for phosphate. However, the preparation of a low-cost, green, and environmentally friendly phosphate adsorbent with high adsorption capacity still requires research and exploration by scientists. Table .3 Summarizes the advantages and disadvantages of different types of adsorbents for phosphate removal/recovery.

3. Chemistry of CMs

3.1. 2:1 type layered CMs

2:1 type CMs consist of two silicon oxide tetrahedra and one aluminum oxide hydroxy octahedron sheets. After Al^{3+} and Mg^{2+} substitutions, negative charges are generated on the surface. Different types of 2:1 CMs, including montmorillonite, bentonite, illite, muscovite, laponite, vermiculite, palygorskite, and sepiolite, can be employed in wastewater treatment (Fig. 2) (Murray,).

Montmorillonite belongs to the smectite group of minerals. Bentonite is composed of montmorillonite, which has a lower surface area than the other CM types (Murray,). Illite is classified as a dioctahedral 2:1 structural unit layer with slightly higher amounts of Si^{4+}, Mg^{2+}, Fe^{3+}, and water and slightly lower amounts of tetrahedral Al^{3+} and K^{+} between the neighboring unit layers (Chen et al., 2016). Vermiculite is a member of the phyllosilicates containing octahedral Mg^{2+} sheets and tetrahedral sheets with Si^{4+} to Al^{3+} ratios of 1:2 to 1:3. The excess negative charges in the tetrahedral sheets can be neutralized by substituting Mg^{2+} with Fe^{3+} in the octahedral sheets (Wang et al., 2016a). Sepiolite and palygorskite are characterized by ribbons morphology with a 2:1-layered silicate structure interconnected through inversions of silicon–oxygen tetrahedrons along a series of Si–O–Si bonds (Liu et al., 2023; Sabah and Majdan, 2009). Laponite belongs to the smectite group and contains Li^{+}, Mg^{2+}, and Si^{4+}. It is a synthesized CM with a layered structure. Within each layer, metal ions are sandwiched between two tetrahedral silica sheets, forming a negative octahedral sheet with some positive charges on the external surface and edges, respectively (Fig. 3A). The surfaces and interlayers of laponite can potentially facilitate phosphate adsorption (Jia et al., 2023).

3.2. 1:1 type layered CMs

1:1 type CMs possess a special structure of alternating tetrahedral silica sheets and octahedral alumina sheets linked by hydrogen bonds. These types of CMs, including kaolinite, halloysite, and serpentine, are suitable for remediation of environmental pollution. They are very stable, exhibit high adsorption capacity and ion-exchange performance, and can be produced at low cost (Ezzatahmadi et al., 2017).

Kaolinite, a phyllosilicate mineral, is the most common 1:1 type CM. It has a near-perfect lattice structure with minimal isomorphous substitution, which restricts its expansion in aqueous solutions (Karthikeyan and Meenakshi, 2021). Halloysite is a tubular 1:1 type CM formed by curling kaolinite sheets. Its one-dimensional tubular structure is connected by silicon oxide tetrahedrons and aluminum oxide octahedrons. Typical halloysite tubes are approximately 0.2–2 μm long and

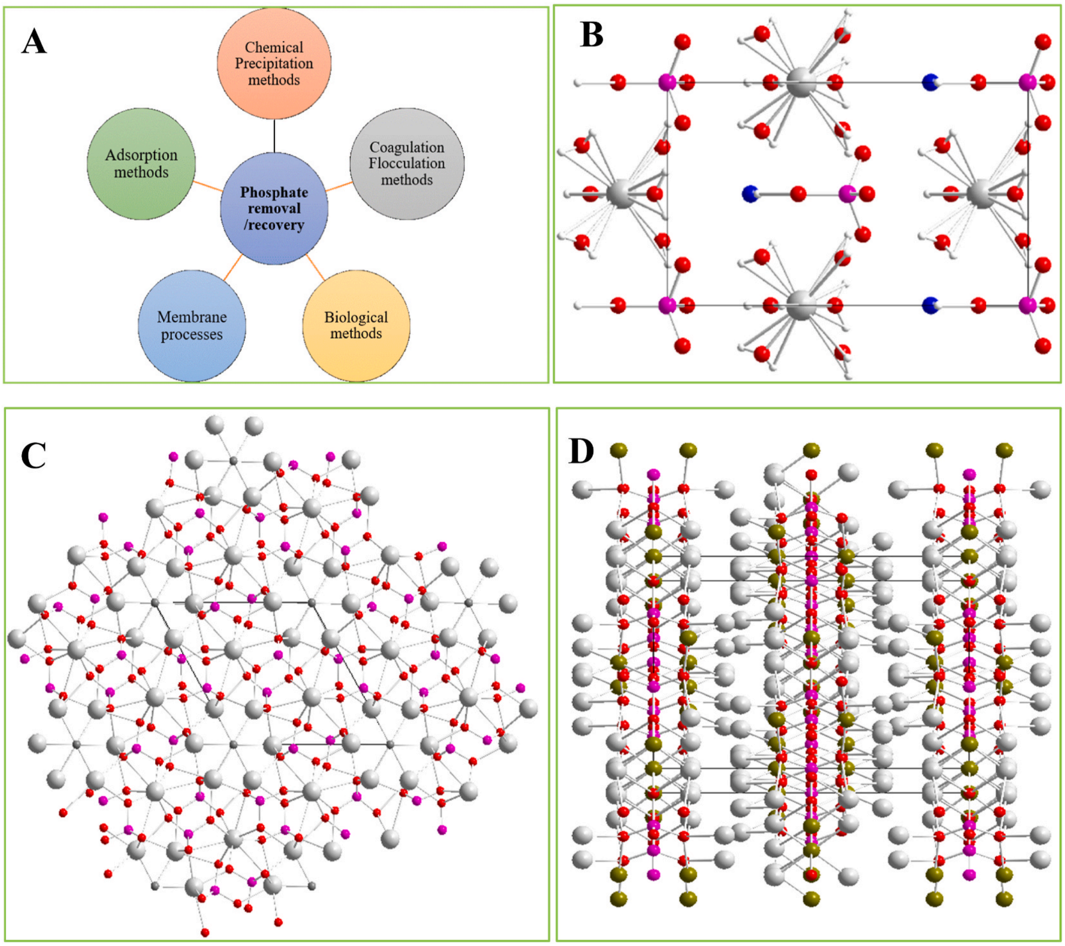

Fig. 1. A-Schematic of the method for recovering phosphate; B-crystal structure of struvite; C-crystal structure of hydroxyapatite; D-crystal structure of vivianite.

Table 2
Review of different wastewater removal and phosphorus recovery technologies.

Methods	Chemical/biological	Phosphate recovery products	Advantages	Disadvantages	References
Chemical precipitation/ Coagulation–flocculation	• Aluminum salts • Iron salts • Lime • Magnesium salt • Calcium salt	• Struvite-MAP • Hydroxyapatite-HAP;	• High efficiency and low cost • Phosphorus removal ratio ≥90% • MAP and HAP as soil fertilizer • HAP recyclability in phosphoric acid industry • Spontaneous formation of precipitates in wastewater by Ca^{2+}, Mg^{2+}, and NH_4^+	• High phosphate concentrations • Required pH of 7–9; • Required control system (variable dose chemicals, pH) • Required addition of several chemicals • Required wastewater neutralization and sludge treatment • Difficult recovery of Fe/Al precipitates and increase in value • Effect of carbonates, organic matter, and suspended solids	Kim et al., 2015
Biological	• Iron salts • Phosphate • Dissimilatory iron-reducing bacteria	• Vivianite	• Low cost • Low usage of chemical agents • Vivianite as soil fertilizer • Synthetic raw materials for lithium batteries;	• Low effectiveness of tracking level • Requirement of strict control (strict aerobic and anaerobic conditions) • Easy to be interfered by its anions and cations such as Mg^{2+}, Ca^{2+}, Al^{3+}, S^{2-}, and CO_3^{2-}	Ye et al. (2016)
Adsorption	• Adsorbent	• Phosphorus-saturated adsorbent	• Low costs and easy operation • Use of low-cost adsorbents • Selectivity and effectiveness for low-concentration phosphorus • High adsorption rate of phosphorus • Adsorbent saturated with adsorbed phosphorus as a phosphate fertilizer	• Pre-treatment of wastewater containing phosphorus • Effect by competitive ions • Downstream processes required for phosphate recovery	Bacelo et al. (2020)

Table 3
Review of different of adsorbents for phosphorus management in wastewater.

Type of adsorbents	Advantages	Disadvantages	References
Clay minerals	• Rich resources • Chemical reactivity • Large specific surface area (SSA)	• Structural charges • Low adsorption capacity	Gan et al. (2009); Chen et al. (2017); Ezzatahmadi et al. (2017)
Modified clay minerals;	• Nontoxicity • Low cost • Stability • Large SSA • Raw functional groups • High adsorption capacity • Large-scale pilot application	–	Xu et al. (2021); Adeyi et al. (2019); Karthikeyan and Meenakshi, 2021
Carbonate minerals	• Rich resources	• Low adsorption capacity • Secondary environmental pollution	Bacelo et al. (2020)
Porous silica	• Large SSA • Controlled pore size and structure • Tunable morphology and mechanical robustness • Nontoxicity • Environmental friendliness	• Low adsorption capacity	
Polymers	• Rich functional groups • High adsorption capacity • High selectivity	• High cost • Secondary environmental pollution	
Activated carbon	• High SSA • High porosity	•Negatively charged functional groups • Low adsorption capacity	Almanassra et al. (2021)
Unmodified biochar	• Availability • High porosity • Low manufacturing cost • Stable carbon structure • Abundant oxygen functional groups • Renewability • Nontoxicity	• Negatively charged functional groups • Low adsorption capacity • Secondary environmental pollution	
Modified biochar	• High SSA • High porosity • Increased adsorption sites • Decreased surface charge	• High adsorption capacity • Secondary environmental pollution	
Metal oxides/ hydroxides	• Tunability • Large SSA • Rich functional groups • High adsorption capacity • Rapid removal performance • High selectivity	•High cost • Secondary environmental pollution	Wang et al. (2021b); Du et al. (2022); Zhang et al. (2022b);

their outer and inner diameters are 50–70 nm and 10–30 nm, respectively. The aspect ratio is 4–30 (Fig. 3B). This hollow structure can be loaded with various objects, such as multifunctional nanoparticles for phosphate removal (Yuan et al., 2015).

The crystal structural characteristics of serpentine with a three-octahedral arrangement resemble those of the 1:1 structural layer of kaolinite. Serpentine contains silicon–oxygen tetrahedron layers and magnesium hydroxide octahedron layers. Adjacent sheets are joined by weak interlayer forces, especially van der Waals forces (Gusmão et al., 2019). Gusmão et al. (2019) identified five categories of active groups in serpentine: unsaturated Si–O–Si bonds, magnesium bonds, hydroxyl bonds, hydrogen bonds, and O–Si–O bonds (Fig. 3C). This categorization highlights the high chemical reactivity of serpentine, which is advantageous for phosphate removal. Phosphates are removed by cation bridges on the edges of kaolinite and the surface of gibbsite. Phosphates (mainly $HPO_4^{2-}$and $H_2PO_4^-$ to a lesser extent) also adsorb to the hydrophilic (001) and (010) facet of kaolinite. More importantly, the adsorption capacity of kaolinite for phosphate is relatively low (Fig. 3D) (García et al., 2021). Significantly, rectorite is a unique interlayer CM composed of alternating dioctahedral mica and montmorillonite layers with a precise 1:1 arrangement. The octahedral sites in both layers are primarily occupied by Al^{3+} ions, which account for two-thirds of the total octahedral sites (Wang et al., 2016a).

Following a comprehensive analysis of the aforementioned information, the surface charges of CMs can be classified into two distinct categories: permanent charges, also known as structural charges, and variable charges, commonly referred to as surface charges. The phosphate-removal capability of CMs is inherently restricted and must be improved by modifications to enable efficient phosphate management.

4. Modification of CMs

CMs can be modified by various elements, such as Zn (Wei et al., 2021b); Ca (Lv et al., 2022); Mg (Bouraie and Masoud, 2017); Al (Pan et al., 2017); Fe (Soliemanzadeh and Fekri, 2017) (Table 5); Ce, Co, Ni, La, and Y (Buzetzky et al., 2017); and Zr (Wan et al., 2021), to improve their phosphate-removal efficiency. Metal elements improve the functional groups, charged nature, SSA, and crystal channel size of CMs (The advantages and disadvantages of different modification methods are listed in Table 4). Metal ions commonly block the pores of CMs, thereby decreasing their SSA and porosity (Almanassra et al., 2021). For example, the porosity and SSA of $La_2O_2CO_3$-modified halloysite decreasing (Wei et al., 2019) (Table .5). Many studies have shown that the increase in SSA and porosity of mCMs can generate rich active sites with in Al- (Pan et al., 2017), La- (Huang et al., 2014), and biochar-(Deng et al., 2021) modified CMs. Regardless of whether the SSA decreases or increases, CM modification can enhance the phosphate-adsorption capacity. Modification with metals ions increases the phosphate-adsorption capacity by reducing the negative charge and increasing the isoelectric point (PZC) of CMs (Bouraie and Masoud, 2017). A comprehensive review of CM modification methods is imminently needed.

4.1. Thermally/mechanically activated CMs

CMs are usually associated with minerals such as dolomite, calcite, gypsum, and apatite (Murray,). CMs also contain different forms of chemical water (crystal water, structural water, surface-adsorbed water, and zeolite water) that evaporates at high temperatures (600 °C–1000 °C), causing destruction and collapse of the CM crystal structures while generating new hydroxyl ligands. Besides increasing the porosity and PZC of CMs, heating leads to the formation of reactive Ca^{2+} ions. For example, Ca–Mg–Si and CaO compounds can release Ca^{2+} ions into wastewater (Gan et al., 2009; Ye et al., 2006; Yin et al., 2017), which chemically combine with PO_4^{3-}, HPO_4^{2-}, or $H_2PO_4^-$ to form lowly soluble Ca–P precipitates. Hong et al. (2020) reported that heating at 600 °C–1000 °C improved the phosphate-adsorption quantity of Ca-rich sepiolite from 42 mg/g to 172.34 mg/g. Song et al. demonstrated that heating at 700 °C destroyed the crystal structure of halloysite and phosphate-maximum adsorption capacity (1.04 mg/g) (Song, 2020). However, thermally modified halloysite has low affinity to phosphate,

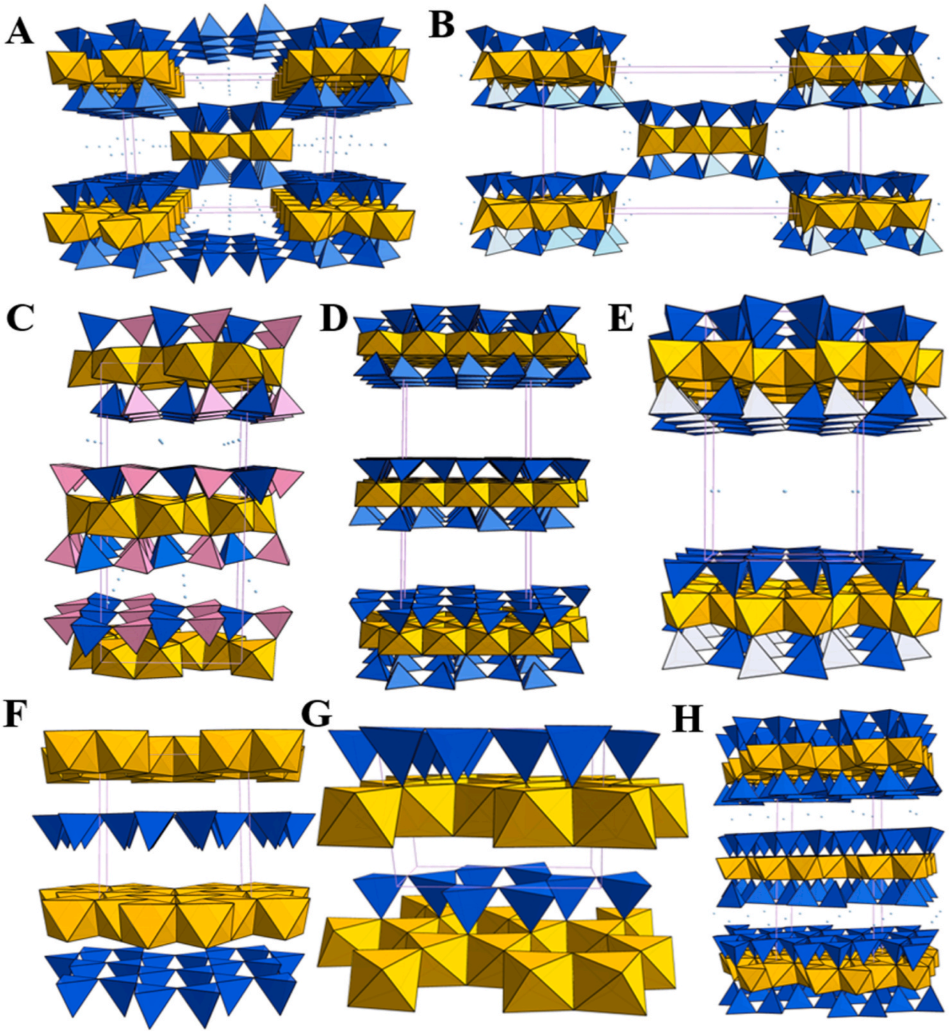

Fig. 2. A schematic representation of illustrating the process of crystal structures of clay minerals employed in wastewater treatment palygorskite (A), sepiolite (B), illite (C), vermiculite (D), montmorillonite (E), halloysite (F), kaolinite (G), and muscovite (H).

resulting in a small phosphate-removal ratio. Thermally modified sepiolite (Hong et al., 2020) showed stronger phosphate-removal ability than thermally modified kaolinite (Song, 2020), bentonite (Wang et al., 2011), and vermiculite (Zheng and Wang, 2010), as shown in Table .5. Attapulgite and sepiolite are often associated with dolomite, calcite, gypsum, and apatite under different formation conditions (Liu et al., 2023).

Mechanically-activated CMs have been rarely reported because mechanical grinding destroys the crystal structure of CMs. However, serpentine has special structural properties and benefits from mechanical grinding, which destroys the crystal structure, increases the SSA, and develops new chemical bonds in serpentine. Mechanical grinding also weakens the Mg–OH bonds, creating unsaturated bonds and active sites that enhance the phosphate-removal capacity (Li et al., 2022) (Fig. 4C). For example, Xin et al. (2022) found that mechanical activation reduces the particle size of serpentine from 41.32 to 12.00 μm and increases its phosphate-adsorption capacity from 51.54 to 126.58 mg/g.

4.2. Acid/alkali-activated modified CMs

Acid treatment can dissolve interlayer metal cations of CMs (such as, Al^{3+}, Mg^{2+}, Ca^{2+}, Na^{+}, and K^{+}), facilitating the opening of interlayer channels. By exchanging the interlayered cations with H^{+}, the interaction forces within the solid layers are weaken (Li et al., 2016), This is favorable of phosphate removal. For instance, Ye et al. (2006) showed that acid modification partially dissolves the octahedral cations and Si^{4+} tetrahedrons in palygorskite, thereby increasing the crystal channel size, channel opening, and SSA (342 m^2/g). After acid modification and subsequent calcination of palygorskite at 320 °C, the phosphate-adsorption quantity reached 9 mg/g. Another study indicated that HCl can replace K^{+} and Na^{+} ions within the palygorskite layers via H^{+}-ion exchange. The resulted acid-modified palygorskite has a zeta potential as high/low as −28.1 mV and a phosphate-removal ratio of 98% (Gan et al., 2010). Acid-modified sepiolite (Sabah and Majdan, 2009) and bentonite (Tanyol et al., 2015) similarly demonstrate higher phosphate-removal capacities than their raw minerals, respectively.

Alkali modification induces a higher dissolution rate of the Si^{4+} tetrahedrons in CMs than Mg^{2+}, Al^{3+}, and Fe^{3+} ions, resulting in the formation of amorphous AlOOH, MgO, and Fe_xO_y aggregates with high affinity to phosphate. For example, NaOH-modified muscovite/phillipsite (NMP) exhibited new functional groups and an SSA of 221 m^2/g. The phosphate-adsorption quantity of NMP was 250 mg/g and the mechanism was electrostatic interaction (Abukhadra and Mostafa, 2019). NaOH-modified palygorskite (Yu et al., 2016) and other alkali-modified CMs have achieved similarly high phosphate-removal capacities.

4.3. Modification of CMs through biomass pyrolysis

Biomass modification of CMs using pyrolysis/co-hydrothermal

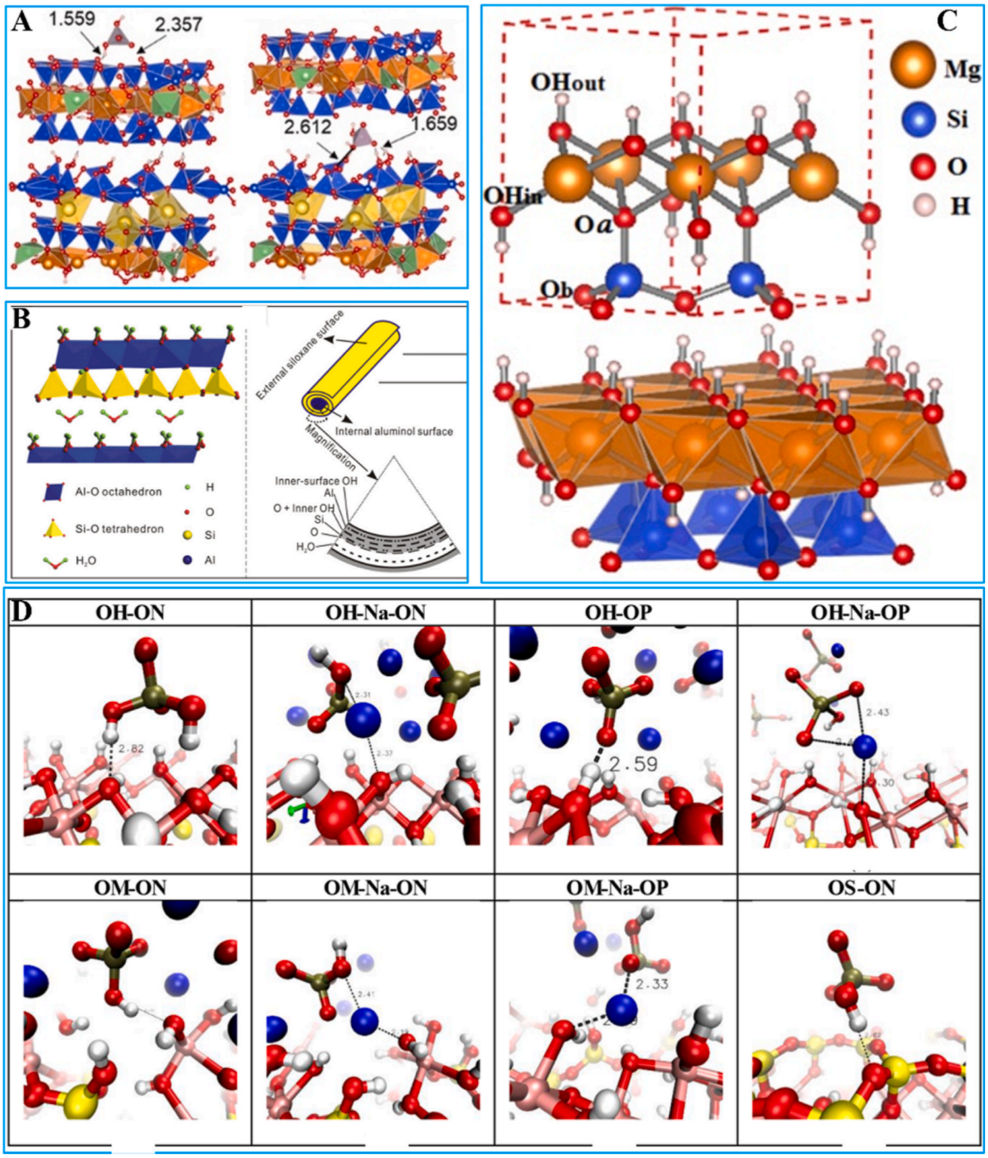

Fig. 3. A schematic representation of crystal structure of modified clay minerals;
(A) laponite (Jia et al., 2023), (B) halloysite (Yuan et al., 2015), and (C) serpentine (Gusmão et al., 2019); (D) interactions between different crystal faces of kaolinite and phosphate (García et al., 2021).

carbonization methods obtains mCMs with higher activities than their parent CMs. Biomass modification of CMs increases the SSA and porosity, forming oxygenated metal functional groups on the CM surfaces that increase their phosphate affinity. Various CMs such as montmorillonite (Chen et al., 2017), sepiolite (Deng et al., 2021), palygorskite (Xu et al., 2021), vermiculite (Huang et al., 2014), and bentonite (An et al., 2020) can be mixed with biomass for CM modification through pyrolysis/co-hydrothermal carbonization methods. For example, researchers have modified palygorskite with spent distillery grains (DG-A15) (Xu et al., 2021), forming new active adsorption sites of amorphous $Mg(OH)_2$. The amorphous sites facilitate phosphate fixation on DG-A15 and enhance its adsorption quantity (97.4 mg/g). Deng et al. (2021) formed biomass-modified sepiolite (Sep-BC800) via the pyrolysis method. The SSA increased from 66.86 m^2/g in biochar (BC800) to 106.67 m^2/g in Sep-BC800. The amount of fixed phosphate on Sep-BC800 was also high (128.21 mg/g) because the Ca^{2+} and Mg^{2+} ions in sepiolite were embedded in biochar, facilitating the formation of porous and rough-structured Sep-BC800. Biomass has been mixed with NaOH-modified bentonite via pyrolysis at 600 °C (An et al., 2020) (Fig. 4D), forming a biomass-modified bentonite with a desirable pore structure, a large SSA (134.06 m^2/g) and a reduced negative charge. The Ca^{2+} and Mg^{2+} ions in bentonite were embedded in the biochar. The phosphate-removal quantity reached 245.56 mg/g.

4.4. Metal-modified CMs

4.4.1. Iron-modified CMs

Magnetic CMs are commonly used in phosphate remediation, as they can be recovered under a magnetic field after adsorption, as shown in Fig. 4C. (Chen et al., 2016). Iron-oxide additive reduces the porosity and SSA of CMs but increases their adsorption capacity for phosphate. Iron elements can be coated onto CMs through various methods such as precipitation (Zamparas et al., 2012; Lin et al., 2020), impregnation (Leite et al., 2020), and liquid phase reduction (Malakootian et al., 2018). For instance, Adeyi et al. (2019) coated kaolinite with iron salts via the precipitation method, forming a magnetically modified kaolinite (MK) with high phosphate-removal ability (52.91 mg/g) conferred by iron-oxide active functional groups formed on the surface or between

Table 4
Modification methods of clay minerals their advantages and disadvantages.

Modification method	Advantages	Disadvantages	References
Thermal/mechanical activation	• Increased zeta • Increased porosity • Increased functional groups • Increased SSA • Generation of defect sites on the facet	• Energy consumption • Increased cost	Gan et al. (2009); Li et al. (2020)
Acid/alkali modification	• Enlarged interlayer spacing • Improved pore structure • Increased SSA • Increased adsorption sites • Change in chargeability and adsorption activity of colloids	• Toxicity • Energy consumption • Increased cost • Severe corrosion • Destruction of crystal structure • Secondary environmental pollution	Gan et al. (2010); Tanyol et al. (2015)
Biomass pyrolysis	• Increased porosity • Low-cost biomass • Increased SSA • Increased adsorption sites • Enlarged layer interval • Generation of carbonyl functional groups	• Energy consumption • Tar and carbon monoxide production • Secondary environmental pollution	Chen et al. (2017); Xu et al. (2021)
Iron modification	• Increased active functional groups • Increased zeta • Increased adsorption sites • Environmental friendliness • Increased recyclability	• Low adsorption capacity	Adeyi et al. (2019); Karthikeyan and Meenakshi, 2021
Calcium/magnesium modification	• Nontoxicity • Increased zeta • Increased SSA • Increased adsorption sites	• Risks to aquatic organisms	Hür and Erken, 2022; Wang et al. (2019)
Lanthanum modification	• Increased adsorption sites • Increased organophilicity • Increased zeta	• Toxicity • Increased cost • Secondary environmental pollution	Tian et al. (2009); Liu et al. (2022)
Aluminum modification	• Increased SSA • Increased zeta • Increased adsorption sites	• Increased dissolved aluminum • Reduction in biodiversity and harm to fish	Yin et al. (2018); Pawar et al. (2016)
Zirconium modification•	• Increased active functional groups	• Radioactivity	Kumar and Viswanathan, 2020; Xi et al. (2021)
LDH modification•		–	Kong et al. (2019); Gan et al. (2011)
Microbial modification	• Pollution-free • Nontoxicity • Safety	–	Xu et al., 2023a

the kaolinite layers. When MK was grafted with active organic functional groups, the phosphate-removal quantity was boosted to 92.05 mg/g. MK chitosan beads can be magnetically separated, enlarging the SSA to 2.12 m^2/g. The chitosan structure contains many amino groups that become protonated in acidic environments. The positive charges allow the adsorption of phosphate in wastewater. Rectorite co-modified with the cationic surfactant cetrimonium bromide (CTAB) and Fe_3O_4 (REC/Fe_3O_4–CTAB) exhibited an SSA of 434.42 m^2/g and a phosphate-adsorption quantity of 174.5 mg/g. Rectorite improved the dispersion of Fe_3O_4 and quaternary ammonium groups (Wang et al., 2016a).

4.4.2. *Magnesium/calcium-modified CMs*

As Ca^{2+} and Mg^{2+} ions are crucial for phosphate capture, the concentrations of soluble Ca^{2+} and Mg^{2+} ions in mCMs plays a vital role in phosphate removal. Furthermore, calcium and magnesium elements are inexpensive and widely used. For these reasons, CMs are commonly impregnated with calcium and magnesium elements (Hao et al., 2019; Lin et al., 2018). Characterization of Mg-modified CMs showed that magnesium elements can be supported on CM surfaces as Mg $(OH)_2$ or MgO compounds. The Mg nanoparticles in Mg-modified CMs shift the PZC to a highly alkaline value (approximately 12.0). MgO-modified palygorskite (MgO–PAL) prepared via impregnation and thermal activation exhibited a phosphate-removal quantity of 69.8 mg/g. MgO–PAL removes phosphate via the electrostatic adsorption mechanism and adsorbs phosphate and ammonia nitrogen by precipitating and crystallizing struvite (Hao et al., 2019; Wang et al., 2017). Notably, Yin et al. (Yin and Kong, 2014) showed that NaCl/$MgCl_2$ co-modified calcined Ca-palygorskite (NCAP–NM) generates new hydroxyl ligands and increases the concentration of soluble Ca^{2+} and Mg^{2+} ions. The PZC increases from 6.53 in palygorskite to 9.30 in NCAP–NM. NCAP–NM removed 97.2% of the phosphate within 5 min.

CaO or $Ca(OH)_2$ nanoparticles have been found on mCMs (Lin et al., 2018). Calcium-modified palygorskite can adsorb phosphate through electrostatic-ligand exchange, electrostatic interactions, and precipitation. Phosphate ions and Ca^{2+} ions precipitate on the calcium/thermally-modified palygorskite (Ca–GAT), promoting the phosphate adsorption to 0.891 mg/g. After calcination and decomposition of Ca–GAT, CaO and Ca–Mg–Si compounds were formed and the SSA decreased because the crystal structure of palygorskite was severely damaged by the thermal treatment and Ca^{2+} ions entered the pores and channels. However, the lowered SSA did not degrade the phosphate-removal ability of Ca–GAT, which was governed mainly by functional groups (OH group, Ca–Mg–Si compounds, and CaO) (Lv et al., 2022). Jang et al. (Jang and Lee, 2019) modified montmorillonite with Ca/chitosan (CMB), where CMB consists of a long chain surfactant, Ca^{2+} ions, and a polymer. The hydrophilic organic modification of the surfactant chitosan increased the interlayer spacing of montmorillonite, allowing Ca^{2+} to enter the interlayer domain of montmorillonite. The SSA and phosphate-adsorption capacity of CMB were 119.76 m^2/g and 76.15 mg/g, respectively, which are considerably larger than those of montmorillonite and La/Al co-modified montmorillonite (Tian et al., 2009).

4.4.3. *Lanthanum-modified CMs*

Lanthanum (La) removes phosphate with remarkable efficiency

Table 5
Comparison of phosphate adsorption effects of different mCMs.

Types of modified clay minerals	Modified clay minerals	Q_m (mg P/g)	Experimental conditions (Initial P concentration range; dosage; temperature; pH)	References
Thermally/mechanically activated CMs	Natural palygorskite	10.9	5–1000 mg/L; 20 g/L; 25 °C; pH of 4.46	Gan et al. (2009)
	700 °C thermally modified palygorskite	42		
	950 °C thermally modified Sepiolite	172.34	5–1000 mg/L; 3.3 g/L; 25 °C; pH of 7	Hong et al. (2020)
	Mechanochemically activated serpentine	126.58	0–30 mg/L; 0.5 g/L; 20 °C; pH of 7;	Xin et al. (2022)
Acid/alkali-activated modified CMs	Acid modified palygorskite	10.5	5–30 mg/L; 2 g/L; 25 °C; pH of 7.5 ± 0.1	Li et al. (2016)
	Acid and thermal palygorskite	9	0–100 mg/L; 1 g/L; 25 °C; pH of 7.0–7.2;	Ye et al. (2006)
	Acid and thermal modified bentonite	20.37	25–150 mg/L; 5 g/L; 45 °C; pH of 3	Tanyol et al. (2015)
	NaOH-modified muscovite/phillipsite	250	100 mg/L; 0.6 g/L; 25 °C; pH of 6	Abukhadra and Mostafa (2019)
Modification of CMs through biomass pyrolysis	SiO$_2$–biochar nanocomposites	159.40	2–100 mg/L; 1 g/L; 25 °C; pH of 5	Wang et al. (2016b)
	Biomass-modified sepiolite	128.21	0–300 mg/L; 0.6 g/L; 25 °C; pH of 8	Deng et al. (2021)
	Montmorillonite-biochar composites	105.28	20–6000 mg/L; 10 g/L; 25 °C; pH of 7.1	Chen et al. (2017)
Metal-modified CMs	Iron oxide modified halloysite	5.46	10 mg/L; 3 g/L; 25 °C; pH of 5	Almasri et al. (2019)
	Nanoscale zero-valent iron modified clay	27.63	10–500 mg/L; 5 g/L; 25 °C; pH of 2–5	Soliemanzadeh and Fekri (2017)
	Lanthanum modified rectorite	147.6	30–400 mg/L; 1.0 g/L; 25 °C; pH of 6	Chen et al. (2020)
	Lanthanum hydroxide modified calcined nano-porous palygorskite	109.63	5–1000 mg/L; 10 g/L; 25 °C; pH of 6.5–7	Kong et al. (2018)
	MgO-modified palygorskite	69.8	50 mg/L; 0.6 g/L; 25 °C; pH of 9;	Hao et al. (2019); Wang et al. (2017)
	Calcination modified alkaline activation palygorskite	126.5	200 mg/L; 0.5 g/L; 25 °C; pH of 7	Wei et al. (2021a)
	Zirconium-modified calcium-montmorillonite	22.37	1–50 mg/L; 0.02 g/L; 25 °C; pH of 7	Zou et al. (2020)
	Lanthanum oxycarbonate modified halloysite	130.4	230–700 mg/L; 2.5 g/L; 25 °C; pH of 4.5	Wei et al. (2019)
	La(NO$_3$)$_3$ and C$_2$H$_5$NO$_2$ co-modification calcination kaolinite	80	300 mg/L; 2.5 g/L; 25 °C; pH of 4.5	Wei et al. (2018)
	La/Al co-modified TCAP	10.6	10–100 mg/L; 20 g/L; 25 °C; pH of 7	Yin et al. (2020)
	ZnO modified Halloysite nanocomposites	97.3	500 mg/L; 2.5 g/L 25 °C; pH of 4.5	Wei et al. (2021b)
	zirconium and alginate co-modified kaolin	37.18	80–140 mg/L; 2 g/L; 30–50 °C; pH of 7	Kumar and Viswanathan, 2020
	mesoporous modified kaolinite	11.85	200 mg/L; 4 g/L; 25 °C; pH of 2.5–9.5	Deng and Shi, 2015
	zirconium and magnetite co-modified bentonite	8.02	5–40 mg/L; 3 g/L; 25 °C; pH of 7	Lin et al. (2020)
	magnetic iron and lanthanum co-modified attapulgite	43.32	2–100 mg/L; 2 g/L; 30 °C; pH of 2–10	Liu et al. (2022)
	lanthanum peroxide modified sepiolite	52.68	5–80 mg/L; 0.2 g/L; 25 °C; pH of 6	Shan et al. (2022)
Layered double hydroxide-modified CMs	layered double hydroxide-coated attapulgite	6.9	2.5–200 mg/L; 4 g/L; 25 °C; pH of 3–9	Gan et al. (2011)
Microbial-modified CMs	silicate bacteria-modified attapulgite	9.54	50 mg/L; 4 g/L; 25 °C; pH of 8.0–8.2	Xu et al. (2023a)
Other metal modified CM	bentonite/zeolite composite material	179.4	25–400 mg/L; 0.2 g/L; 25 °C; pH of 6	Abukhadra et al. (2020b)
	nano-cellulose fibers modified exfoliated bentonite	305	300 mg/L; 0.1 g/L; 25 °C; pH of 6	Abukhadra et al. (2020a)

owing to its strong phosphate selectivity. La can be loaded onto CM surfaces, combined with metallic elements such as Fe (Liu et al., 2022) (Fig. 5A) (Table 5), Mg (Zhang et al., 2022a), Al (Yin et al., 2020), and Fe$_3$O$_4$ (Zhong et al., 2020) to form multi-metallic complexes, or combined with gemini surfactants (Luo et al., 2020), chitosan (Xu et al., 2020a), alginate (Wan et al., 2021a), and Al/biomass through the pyrolysis method (Yin et al., 2022). These modifications can be applied in both powder and granular forms. Several La-modified CMs have been prepared through the precipitation method (Chen et al., 2020; Ye et al., 2022). For example, La-modified rectorite (La–REC) efficiently adsorbs phosphate through complexation, precipitation, electrostatic-ligand exchange, and electrostatic attraction (Chen et al., 2020) (Table 5). Similarly to Ca- and Mg-modified CMs, La-modified CMs are formed when La enters the interlayer or surface of CMs in the form of oxides or hydroxides (Haghseresht et al., 2009; Kong et al., 2018). La modification can increase the PZC, reduce the surface negative charge density, and improve the phosphate affinity of CMs (Mucci et al., 2020). La-modified CMs remove phosphate through complex interactions, electrostatic interactions, surface chemical precipitation, and electrostatic-ligand exchange (Kong et al., 2018). (Table .5) For example, the SSA of calcined LO–HNT was 29.5 m^2/g, versus 64.2 m^2/g in halloysite. The authors concluded that La blocks the inner cavity channels of halloysite, thus decreasing its porosity. Nevertheless, LO–HNT removed 130.4 mg/g of phosphate. The phosphate removal was facilitated by the synergistic effect of active Al and La formed in thermally activated halloysite, which benefited from the unique geometry of halloysite (Wei et al., 2019) (Fig. 5B). Kong et al. (2018) showed that the phosphate-removal quantity of La-modified calcined palygorskite exceeds that of La(OH)$_3$ (109.63 mg/g vs. 69.64 mg/g). Meanwhile, the phosphate-removal quantity of La/chitosan-modified montmorillonite reached 128.5

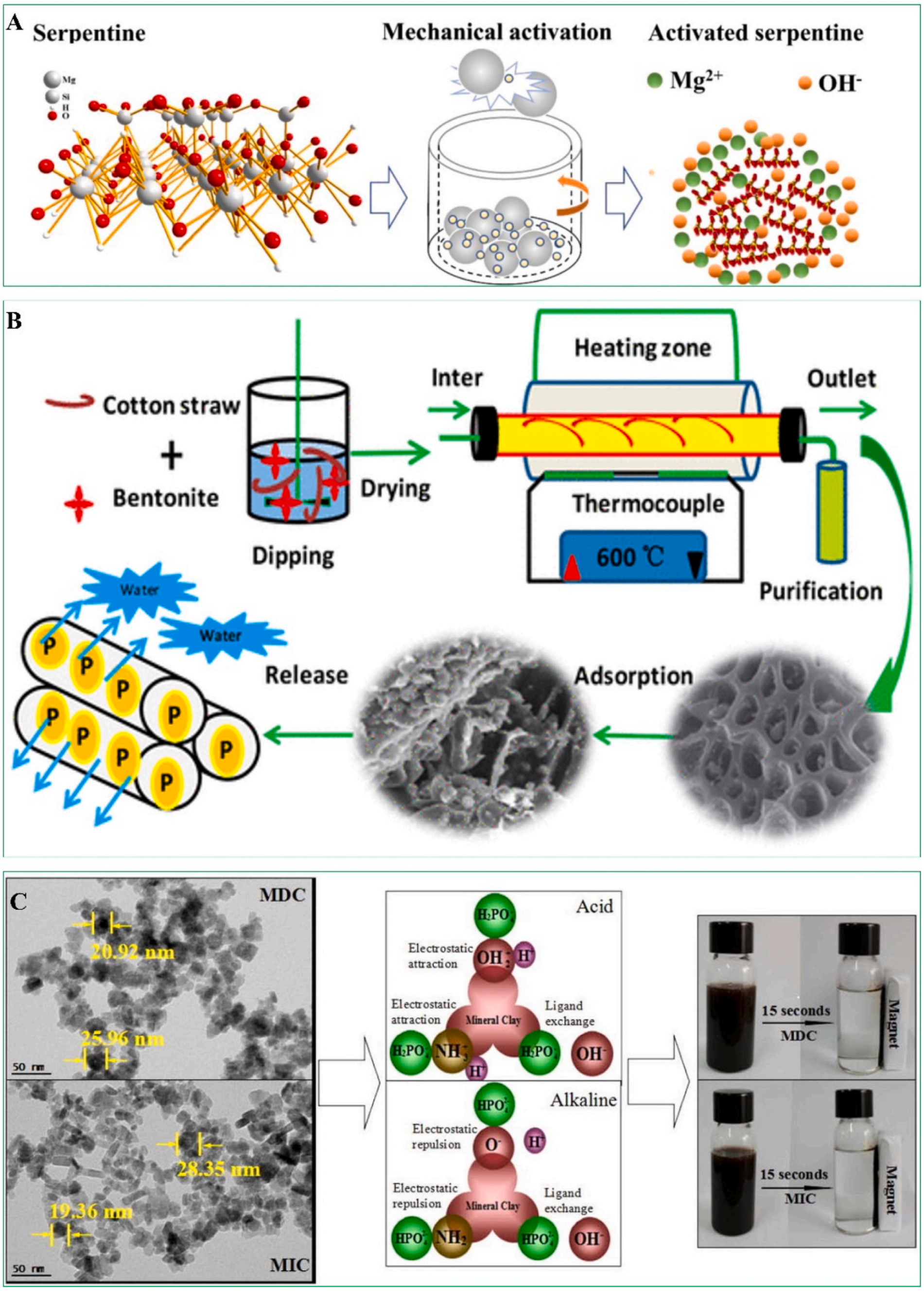

Fig. 4. A schematic representation of morphology and modification process of modified clay minerals;
(A) mechanically-activated modified serpentine (Li et al., 2022); (B) biomass modified bentonite (An et al., 2020); (C) Magnetic separation process of mCMs (Chen et al., 2016).

mg/g. In a study by Huang et al. (2014), the phosphate-adsorption quantity of $La(OH)_3$-modified exfoliated vermiculite (La_5EV) reached 79.6 mg/g and the SSA was 39.1 m^2/g, versus 9.8 m^2/g in unmodified vermiculite. The improved performance of La_5EV could be attributed to the large interlayer domain of exfoliated vermiculite, which increases the La dispersion and number of active sites. Other researchers have proposed La-modified calcined palygorskite (Wei et al., 2021a) (Table 5) and La-modified calcined kaolinite (Fig. 5C) (Wei et al., 2018) for phosphate adsorption (Table 5).

4.4.4. Aluminum-modified CMs

CMs can also be modified with aluminum (Al), another element with high affinity for phosphate. The CMs are modified by immersing them in an Al-containing solution and doping them with Al nanoparticles. The Al is doped in the form of AlOOH. Several studies have reported that Al modification increases the SSA and number of active sites of CMs (Pawar et al., 2016; Mahadevan et al., 2018). For example, amorphous Al compounds have been found on the surfaces of Al-modified palygorskite. The SSA and PZC of pristine palygorskite were 189.389 m^2/g and 6.5, respectively. After modification, the SSA and PZC increased to 212.872 m^2/g and 7.8, respectively, and the phosphate-removal quantity reached 16.86 mg/g (Pawar et al., 2016). Yin et al. (2018) reported a phosphate-removal quantity of 8.79 mg/g in Al-modified thermally treated Ca-palygorskite (TCAP), which they attributed to the high phosphate-binding ability of Al. Phosphate removal on TCAP involves precipitation and electrostatic adsorption (Kumararaja et al., 2019; Yan

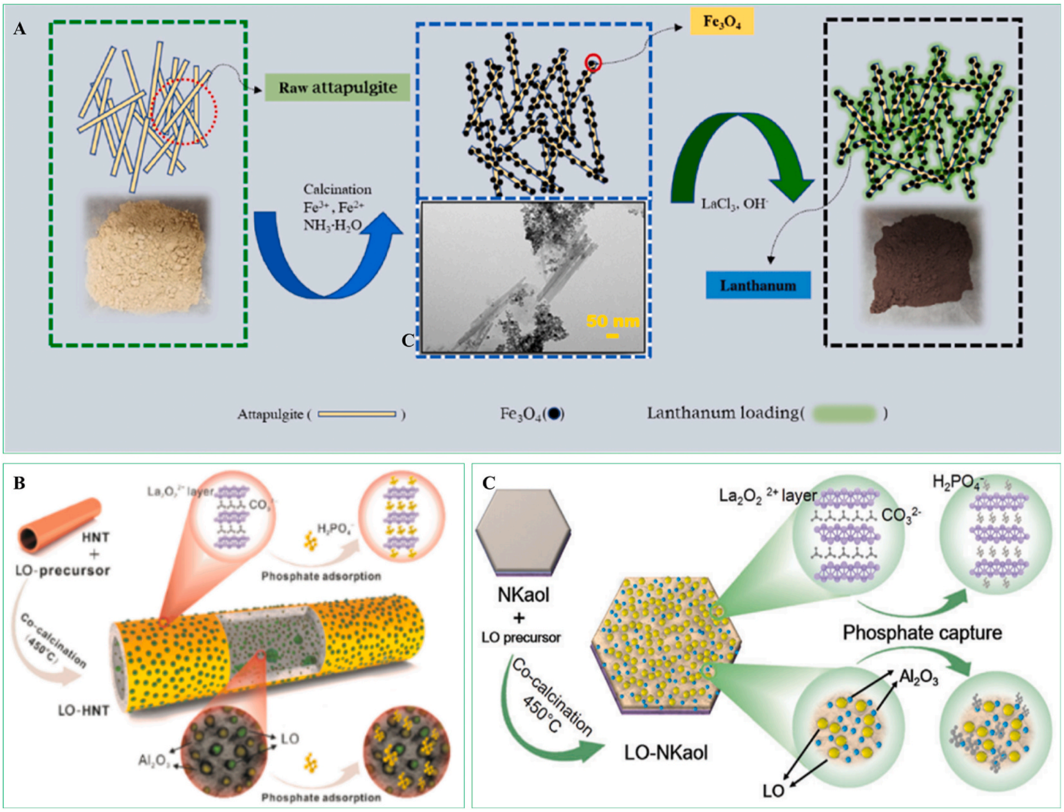

Fig. 5. A schematic representation of illustrating the process of modified clay minerals;
(A) La/Fe_3O_4 co-modified magnetic attapulgite (Liu et al., 2022), (B) La-modified and thermal halloysite nanotubes (Wei et al., 2019), and (C) La-modified and thermal kaolinite (Wei et al., 2018).

et al., 2010). Some studies have co-modified CMs with Al-based bimetallic compounds, using Mg (Deng and Shi, 2015) (Table .5), Zr (Huang et al., 2015), alginate, or Ca (Xu et al., 2020b) as the co-dopant. Among these bimetallic-modified CMs, Zr/Al co-modified montmorillonite achieved an ultra-high phosphate-adsorption quantity of 17.2 mg/g (Huang et al., 2015). Xu et al. (2020b) recommended Ca/alginic acid co-MB (Al–NaBT–CA) for phosphate fixation. They reported an SSA of 17.01 m^2/g, high internal porosity, and a rough external surface of Al–NaBT–CA. The new adsorption sites (Al–OH and Al–H_2O) provided by Al^{3+} and sodium alginate raised the phosphate-adsorption capacity to 15.77 mg/g. More importantly, Al–NaBT–CA is easily recovered from aqueous solutions. Interestingly, Mdlalose et al. (2019) showed that the phosphate-removal capacity is higher in Al-MB than in Fe-MB and Fe/Al co-MB, because the Al-MB surface is enriched with AlOOH and functional groups. The adsorption mechanism of Al-MB is chemical and physical adsorption.

4.4.5. Zirconium-modified CMs

Zirconium (Zr) also exhibits a high chemical affinity for phosphate; accordingly, Zr-modified CMs have been extensively studied for phosphate removal. Phosphate ions can diffuse into the internal pores of amorphous ZrO_2. Zr can be doped as a single element on CMs or combined with materials such as alginate (Kumar and Viswanathan, 2020) (Table .5) or Ca^{2+} (Zou et al., 2020) (Table .5) in powder or granular form. Several studies have reported Zr modification of CMs through precipitation or impregnation methods. An example is Zr-modified Ca–montmorillonite (Zr–CaM) with a phosphate-removal quantity of 22.37 mg/g. The SSA of Zr–CaM is increased by intercalation of Zr into the middle and surface layers of Ca–montmorillonite. Zr–CaM removes phosphate via electrostatic-ligand exchange and electrostatic adsorption (Zou et al., 2020). Lin et al. applied Zr-MB as a passivating agent of phosphate ions in sediments. They showed that the phosphate affinity and structural characteristics of Zr-MB influence the passivation effect (Lin et al., 2020) (Table .5). More specifically, the Zr species are uniformly embedded in the montmorillonite (Zr2.48–MT), increasing the availability of active Zr sites (hydroxyl content) and promoting the removal of phosphate from the inner spherical surface complex. Consequently, the phosphate removal quantity of Zr2.48–MT reached 15.5 mg/g (Wan et al., 2021). Immobilization methods have also yielded alginate/Na_2CO_3+HCl/Zr-MB (NH–SA–ZrBT), in which the interlayer of montmorillonite is partially replaced by Na to form Na-based montmorillonite. Carboxyl groups form on the hydrophobic NH–SA–ZrBT surface. Consequently, the SSA and PZC were determined as 53.8364 m^2/g and 6.19, respectively, and the phosphate-removal quantity was 63.61 mg/g (Xi et al., 2021a,b).

Other metal modified CMs: Less commonly than the above modifications, CM modifications with Zn (Wei et al., 2021b), Co, Ce, Y, or Ni (Buzetzky et al., 2017) have been reported for phosphate removal. For example, ZnO-modified halloysite (ZnO–Hal) with well-dispersed ZnO and active sites has been reported, in which the ZnO nanoparticles are supported on halloysite via non-covalent bonding. The phosphate-removal quantity of ZnO–Hal was 97.3 mg/g and the main phosphate-adsorption mechanism was inferred as surface chemical precipitation in the form of hopeite [$Zn_3(PO_4)_2 \cdot 4H_2O$] (Wei et al., 2021b). Co-, Ce-, Y-, and Ni-modified CMs have been less well studied due to their environmental impact and cost considerations (Buzetzky et al., 2017).

4.5. Microbial-modified CMs

CMs can be biologically modified through the decomposition or metabolic polymerization of biological enzymes produced during the growth and reproduction of microorganisms. Microbial-modified CMs are safe, environmentally friendly, and non-toxic. Silicate microorganisms secrete enzymes and organic acids (such as citric and oxalic acids) and can dissolve CMs. Environmental microorganisms can also utilize the many organic compounds and elements in CMs, realizing facile and natural CM modification (Zhao et al., 2017). For example, the metabolic byproducts of silicate bacteria, such as polysaccharides and proteins, can adsorb on CM surfaces, thereby altering their structural characteristics. In addition, CMs can be encapsulated by silicate bacterial capsule polysaccharides. Within the capsule microenvironment, organic acids can reach sufficiently high concentrations to dissolve CMs. One example includes silicate bacteria-modified attapulgite (AT@SiB-X), with a higher SSA value (316.25 m^2/g) than attapulgite (152.08 m^2/g) and a phosphate-adsorption capacity of 9.54 mg/g. Silicate bacteria was found to accelerate the dissolution and decomposition of metal elements (e.g., Al, Fe, Mg, and Ca) in attapulgite (Fig. 6) (Xu et al., 2023a).

4.6. Layered double hydroxide-modified CMs

Layered double hydroxides (LDHs) consist of two-dimensional nanostructured anionic CMs with a strong anion-exchange ability, making them eminently suitable for the removal and recovery of anions. The functionalization or precipitation of CMs with LDHs will alter the PZC and SSA of CMs, improving their phosphate-removal efficiency (Kong et al., 2019). Fig. 7A presents the three-dimensional structure of periclase-modified palygorskite (PER@PLDO) formed by the hydrothermal method followed by calcination (Kong et al., 2019). The high SSA (238.8 m^2/g) and surface functional groups (Mg–O, Al–O, and Ca–O) can enhance phosphate-removal quantity to a 448.58 mg/g. Modification occurs via anion exchange and internal spherical surface complexation, with calcination-induced defects in the LDH structure enhancing the embedding ability of the anions (Kong et al., 2019). The maximum adsorption capacity of LDH-modified attapulgite prepared via the precipitation method was found to be 6.9 mg/g (Gan et al., 2011).

5. Phosphate-removal mechanisms of mCMs

Phosphate removal from wastewater depends on chemical and physical interactions between phosphate and mCMs. These processes involve various mechanisms encompassing crystallization, ion exchange, hydrogen bonding, precipitation, Lewis acid–base interactions, electrostatic interactions, and electrostatic-ligand exchange.

5.1. Electrostatic interactions

Numerous studies have demonstrated a role for electrostatic interactions during mCM-based phosphate management. CM modification can reduce the negative surface charge, causing pH-dependent dissociation of phosphate ions as follows (Almanassra et al., 2021):

$$H_3PO_4 \Longleftrightarrow (pK_1)\ H_2PO_4^- + H^+ \Longleftrightarrow (pK_2)\ HPO_4^{2-} + 2H^+ \Longleftrightarrow (pK_3)\ PO_4^{3-} + 3H^+,$$

Where $pK_1 = 2.13$, $pK_2 = 7.20$, and $pK_3 = 12.33$.

Electrostatic attraction is affected by the PZC of mCMs and the pH of wastewater. When the PZC of an mCM exceeds the pH of the aqueous solution, the electrostatic force is attractive; conversely, when the PZC is lower than the pH of the aqueous solution, the electrostatic force is repulsive and the water environment will impede the phosphate adsorption of mCMs. Chen et al. (2017) prepared a biomass-modified montmorillonite composite (MBC) via pyrolysis and observed a phosphate-removal quantity of 105.28 mg/g owing to electrostatic attraction between the MBC and phosphate. Similar electrostatic adsorption mechanisms have been reported in other phosphate-adsorbing composite materials, such as bentonite/zeolite–P (BE/ZP) (Abukhadra et al., 2020b) (Table .5). However, studies have shown that phosphate removal is improved when the PZC of an mCM is below the pH of the environment, indicating the presence of mechanisms other than electrostatic interactions. The phosphate-removal mechanism includes Lewis acid–base interactions and electrostatic-ligand exchange. Chen et al. (2016) reported that magnetic illite clay adsorbs phosphate through electrostatic-ligand exchange and electrostatic attraction. Electrostatic interactions between mCMs and phosphate are reversible, simple, and drive other adsorption processes.

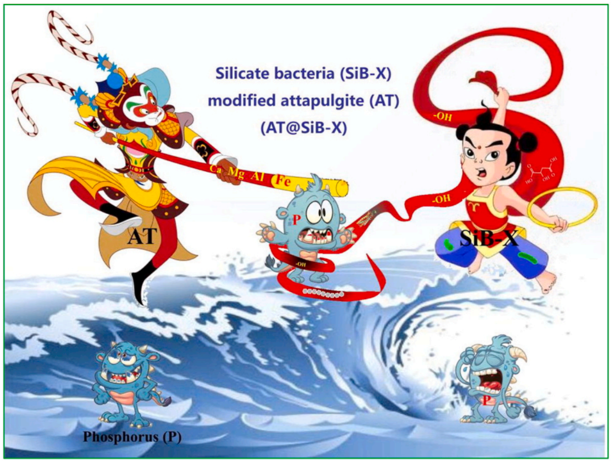

Fig. 6. A schematic representation of microbial modified clay mineral process (Xu et al., 2023a).

5.2. Ion exchange

Ion exchange involves the replacement of ions in mCM structures with phosphate ions. This type of adsorption process is reversible and typically proceeds by outer-layer complexation. The ion-exchange adsorption reaction is a spontaneous endothermic reaction that effectively removes phosphate ions from wastewater (Kumararaja et al., 2019). For example, Al-modified CMs adsorb phosphate via ion exchange in high-salinity aquaculture wastewater at 45 °C. The rich functional groups on mCMs remove phosphate not only through ion exchange, but also through synergistic effects with other mechanisms (Kumararaja et al., 2019). For example, phosphate removal by DG-A15 is a controlled adsorption process governed by electrostatic interaction, ion exchange, complexation, and physical adsorption (Xu et al., 2021). PER@PLDO exhibits a multi-mechanism synergistic phosphorus-removal process dominated by anion exchange (Fig. 7A) (Kong et al., 2019). He et al. (2021) reported that ion exchange mainly coordinates the phosphate-removal process in their proposed akadama clay barrier vegetation drainage system (Fig. 7B).

5.3. Electrostatic-ligand exchange

Adsorption through electrostatic-ligand exchange in mCMs primarily involves ion exchange, especially when hydroxide groups are replaced with phosphate groups. The electrostatic-ligand-exchange process can lead to internal spherical complexes and stronger phosphate–mCM binding than is possible through individual ion exchanges (Almanassra et al., 2021). For example, Lin et al. (2019) demonstrated that Zr-MB (ZrBTs) adsorbs phosphate through electrostatic-ligand exchange between $HPO_4^{2-}/H_2PO_4^-$ and hydroxyl groups. A similar mechanism has been observed in Zr-modified montmorillonite, Zr-modified vermiculite, and Zr-MK (Wan et al., 2021). Electrostatic-ligand exchange can operate synergistically with other mechanisms to achieve efficient phosphate removal. As another example, immobilized SA–MgO@Bt adsorbs phosphate through electrostatic attraction and electrostatic-ligand exchange, forming Mg–P complexes (Xi et al., 2021a,b). Immobilized beads formed from MB powder entrapped in calcium alginate (Al–NaBT–CA) similarly

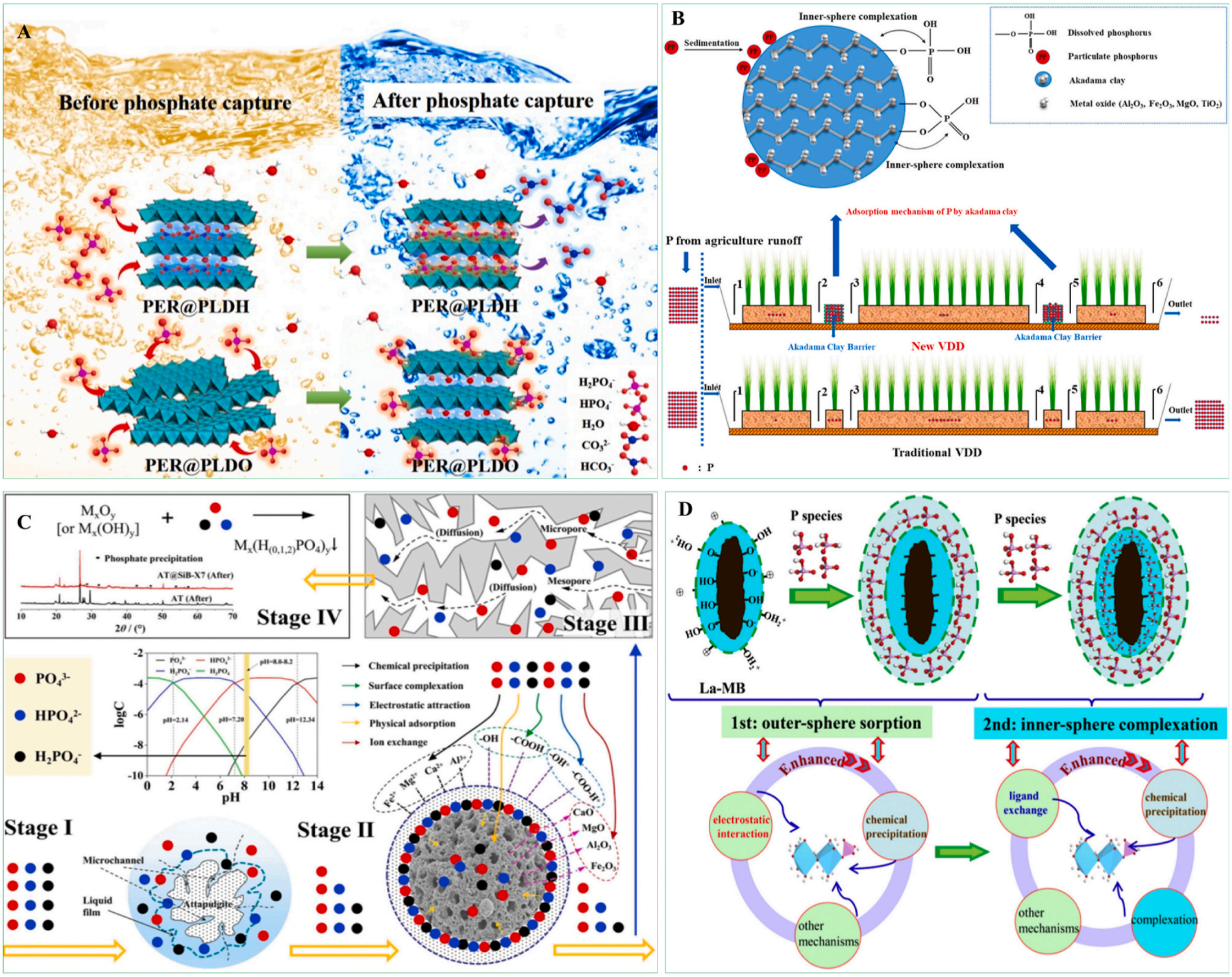

Fig. 7. A schematic representation of mechanisms of phosphate removal by modified clay mineral process;
(A) PER@PLDO (Kong et al., 2019); (B) Akadama clay (He et al., 2021); (C) Silicate-bacteria-modified attapulgite (Xu et al., 2023a); and (D) Millimeter-scale La–MB (Zhong et al., 2020).

adsorb phosphate through the synergistic effect of multiple mechanisms. The pH of wastewater simultaneously affects the morphologies of the phosphate ions and Al–NaBT–CA functional groups (Xu et al., 2020b). Similar synergistic mechanisms have been reported in microbial-modified attapulgite (Xu et al., 2023a) (Fig. 7C) and attapulgite (Xu et al., 2023b) developed for eutrophic seawater treatment.

5.4. Precipitation and crystallization

According to the thermodynamic principles of solubility, a finite volume near the surface of an mCM in a phosphate-supersaturated aqueous environment will become supersaturated with phosphate, causing precipitation of lowly soluble phosphate. Such precipitation has been widely reported on Zn-, Mg-, Al-, Ca-, Fe-, and La -modified CMs. Dithmer et al. (2016) showed that surface chemical precipitation of $LaPO_4$ plays a dominant role in the phosphate-removal process of La-MB. However, advanced characterization techniques have revealed that La-modified CMs mainly adsorbs phosphate via electrostatic-ligand exchange of La–P inner spherical complexes, with electrostatic interactions and surface chemical precipitation playing synergistic roles. Examples include La-modified sepiolite (LPS30) (Shan et al., 2022) (Table .5) and millimetric magnetic La–MB (Fig. 7D) (Zhong et al., 2020). The precipitation process is usually rapid and the precipitated phosphate is not easily recovered. For example, the phosphate-removal mechanism of Sep-BC800 in wastewater involves the formation of a phosphate metal precipitate. Ca(II) and Mg(II) can react with phosphate to form precipitates such as $Ca_5(PO_4)_3OH$ and $Mg_3(PO_4)_2$ (Deng et al., 2021). A similar mechanism has been observed on biomass-modified bentonite (An et al., 2020). MgO–PAL adopts another mechanism, phosphate crystallization, to form struvite. The crystallization of phosphate as struvite is described in the literature (Wang et al., 2017).

5.5. Lewis acid–base interactions

Lewis acid–base theory underlies the main mechanism of phosphate removal by mCMs. Under acidic conditions, abundant H^+ ions will protonate the active adsorption sites on mCMs. The mCMs then become weak acids that accept electrons. Conversely, phosphate ions can act as weak bases that donate electrons. Under alkaline conditions, excessive OH^- deprotonation of the active adsorption sites at the mCM surfaces converts the mCMs to weak bases and the phosphate ions exhibit weak acidity (Almanassra et al., 2021). Consequently, Lewis acid–base interactions between the active sites and phosphate ions on mCMs play a significant role in phosphate removal. Such interactions have been observed in La–PAL (Mi et al., 2022).

5.6. Hydrogen bonding

Hydrogen bonding, by which the hydrogen atoms in $H_2PO_4^-$ and HPO_4^{2-} ions interact with the surfaces and interlayers of mCMs, is also commonly observed in phosphate adsorption by mCMs (Abukhadra et al., 2020a). For example, laponite adsorbs phosphate via hydrogen bonding on its surfaces and interlayers. The interlayer bonding is stronger than the surface bonding (Jia et al., 2023). Complexation reactions and hydrogen bonding are considered as the main phosphate-adsorption mechanisms of Fe-doped CMs (Guaya et al., 2021).

6. Effects of environmental factors on phosphate removal by mCMs

Competitive substances can enhance or inhibit the phosphate-adsorption reaction on mCMs. The influences of different anions (CO_3^{2-}, NO_3^-, F^-, Cl^-, HCO_3^-, and SO_4^{2-}), cations (Ca^{2+}, and Mg^{2+}), and humic acids (HAs) on phosphate removal by mCMs have attracted much interest (Almanassra et al., 2021).

6.1. Anions

Anions compete with phosphate ions for the active sites of mCMs. Divalent anions such as CO_3^{2-} and SO_4^{2-}, with higher charge density than univalent anions such as NO_3^- and Cl^-, exert a larger impact on adsorption phosphate. Several studies have reported that CO_3^{2-} ions can seriously affect phosphate adsorption. In one study, the addition of 0.1 M of CO_3^{2-} reduced the phosphate-removal efficiency of La-modified vermiculite (La_5EV) by 54.3%. This inhibitory effect can be explained as follows. First, CO_3^{2-} inhibits phosphate removal by increasing the pH of wastewater (Huang et al., 2014). The pH effect reduces the phosphate-removal efficiency of Zr/Al co-modified montmorillonite (Zr/Al–Mt) by 25% (Huang et al., 2015). By increasing the pH of wastewater, CO_3^{2-} ions interfere with the balance between PO_4^{3-} and HPO_4^{2-} and compete for phosphate-adsorption sites. Similar inhibitory effects of CO_3^{2-} have been observed in Al-modified acidic bentonite (Al–Abn–AB) (Pawar et al., 2016). Second, CO_3^{2-} ions have high affinity for La_5EV in the reaction system. In the La_5EV adsorption phosphate reaction system, $La_2(CO_3)_3$ was more readily formed than $LaPO_4$, as $LaPO_4$ is more soluble than $La_2(CO_3)_3$ (Huang et al., 2014). In another study, CO_3^{2-} ions inhibited phosphate removal by millimetric magnetic La–MB (Zhong et al., 2020). SO_4^{2-} ions also inhibit the selective removal of phosphate by mCMs by competing with phosphate ions for the active sites. This competition arises from the similar ionic radii of SO_4^{2-} (2.3 Å) and phosphate ions (2.38 Å) (Feng et al., 2017).

F^- ions negatively affect phosphate removal through several mechanisms. First, F^- ions are highly electronegative and easily bind to the surfaces of protonated mCMs. Second, F^- ions can form inner spherical complexes with mCMs, thus inhibiting phosphate adsorption (Huang et al., 2014) as observed in LPAP composite hydrogel beads (Wang et al., 2021). Finally, F^- ions can compete for vacant adsorption sites. Studies have reported similar negative impacts of HCO_3^- ions on phosphate removal (Zou et al., 2020).

The influence of coexisting anions on mCMs depends on the structure and composition of the anions. Some high-performance mCMs exhibit a high affinity for phosphate and selectively remove phosphates from wastewater without interference from coexisting ions. Examples are Mt–OH/Fe (Leite et al., 2020) and Al-modified palygorskite (Pan et al., 2017).

6.2. Humic acids (HAs)

HAs demonstrate high affinity for phosphate in wastewater, and they can compete against the active adsorption sites on modified clay minerals (mCMs), thereby inhibiting phosphate removal by mCMs. Moreover, HAs have high polydispersity, and they block the mCM pores, inhibiting the entry of phosphate ions to the internal mCM channels, thus further reducing the phosphate-removal ability (Mi et al., 2022). Mi et al. (2022) showed that HA reduced the phosphate-adsorption quantity on La–PAL by interfering with its adsorption mechanism. Specifically, La–PAL adsorbs phosphate through electrostatic-ligand exchange and HA chelate with La ion and hinders phosphate ion binding with La, thereby limiting the number of active sites. Phosphate removal in HA environments depends on the HA concentration; low concentrations of HA are less inhibitory than high concentrations. Shan et al. (2022) showed that phosphate removal by LPS30 was inhibited at HA concentrations above 50 mg/L, because HA competes with phosphate ions for the active sites on the adsorbent, forming an La–HA–sepiolite complex. LPS30 can effectively remove phosphate from natural water at HA concentrations of 20 mg/L or lower (Fig. 8A).

Chelation of dissolved organic carbon (DOC) and La further hinders the combination of La and phosphate. Phosphate adsorption by La-modified bentonite (LMB) decreased in wastewaters with C/P molar ratios above 9 (Li et al., 2020) (Fig. 8B). Phosphate adsorption is also affected by natural organic matter (NOM), as demonstrated by the reduced phosphate-ion binding capacity of LMB in the presence of NOM at pH 8.5. NOM promotes the release of La from LMB. The released La binds with NOM and inhibits the La–phosphate binding, thereby decreasing the phosphate-removal efficiency (Zhi et al., 2021) (Fig. 8C).

6.3. Cations

Studies have shown that Ca^{2+} and Mg^{2+} in wastewater promotes phosphate removal by mCMs forming lowly soluble calcium phosphate compounds such as $CaHPO_4$, $Ca_4H(PO_4)_3{\cdot}3H_2O$, $Ca_3(PO_4)_2$, $Ca_5(PO_4)_3OH$, and $Mg(NH_4)PO_4{\cdot}6H_2O$. For example, Ca^{2+} facilitates $Ca_5(PO_4)_3OH$ formation on LPS30, enabling effective phosphate adsorption (Shan et al., 2022). In the ZrCaBT system, Ca^{2+} ions can form tertiary complexes ($Zr(OPO_3H)Ca$) with the adsorbed phosphate (Zou et al., 2020). Furthermore, the coexistence of ammonia ions, OH^-, and Mg^{2+} in urine-containing wastewater promotes phosphate adsorption on the active subgroups of serpentine (Li et al., 2022; Xin et al., 2022). Struvite precipitation in the presence of ammonium ions, OH^-, and Mg^{2+} facilitates the adsorption of phosphate to active serpentine, offering a new approach for recycling phosphate and nitrogen from urine solutions (Fig. 9A) (Li et al., 2022; Xin et al., 2022).

7. Applications of mCMs in diverse water environments

7.1. mCMs for phosphate management in municipal wastewater

Many studies have applied mCMs to the management of municipal wastewater. Phosphate removal through mCMs in these environments is influenced by bacteria and inorganic and organic matters and is more complex than phosphate removal from synthetic wastewater. Interactions between organic matter and phosphate and the clogging potential of mCMs pores by organic pollutants compete with phosphate adsorption (Almanassra et al., 2021).

mCMs have a wide range of sources, making them potential excellent materials for phosphate removal/recovery. However, their treatment targets are mainly the effluent from secondary sedimentation tanks that do not meet the standards in sewage treatment plants. Commonly used CMs for municipal wastewater treatment include palygorskite (Bao et al., 2019), bentonite (Lu et al., 2022), and serpentine (Xin et al., 2022). CMs are usually modified to improve their ability to adsorb phosphate. The commonly used modification methods, such as thermal/mechanical activation (Bao et al., 2019; Xin et al., 2022), acid modification (Liu et al., 2023), biomass pyrolysis (Yin et al., 2022), and metal modification (Lu et al., 2022), have been widely used in municipal wastewater treatment.

In one study of pollutant management in municipal wastewater,

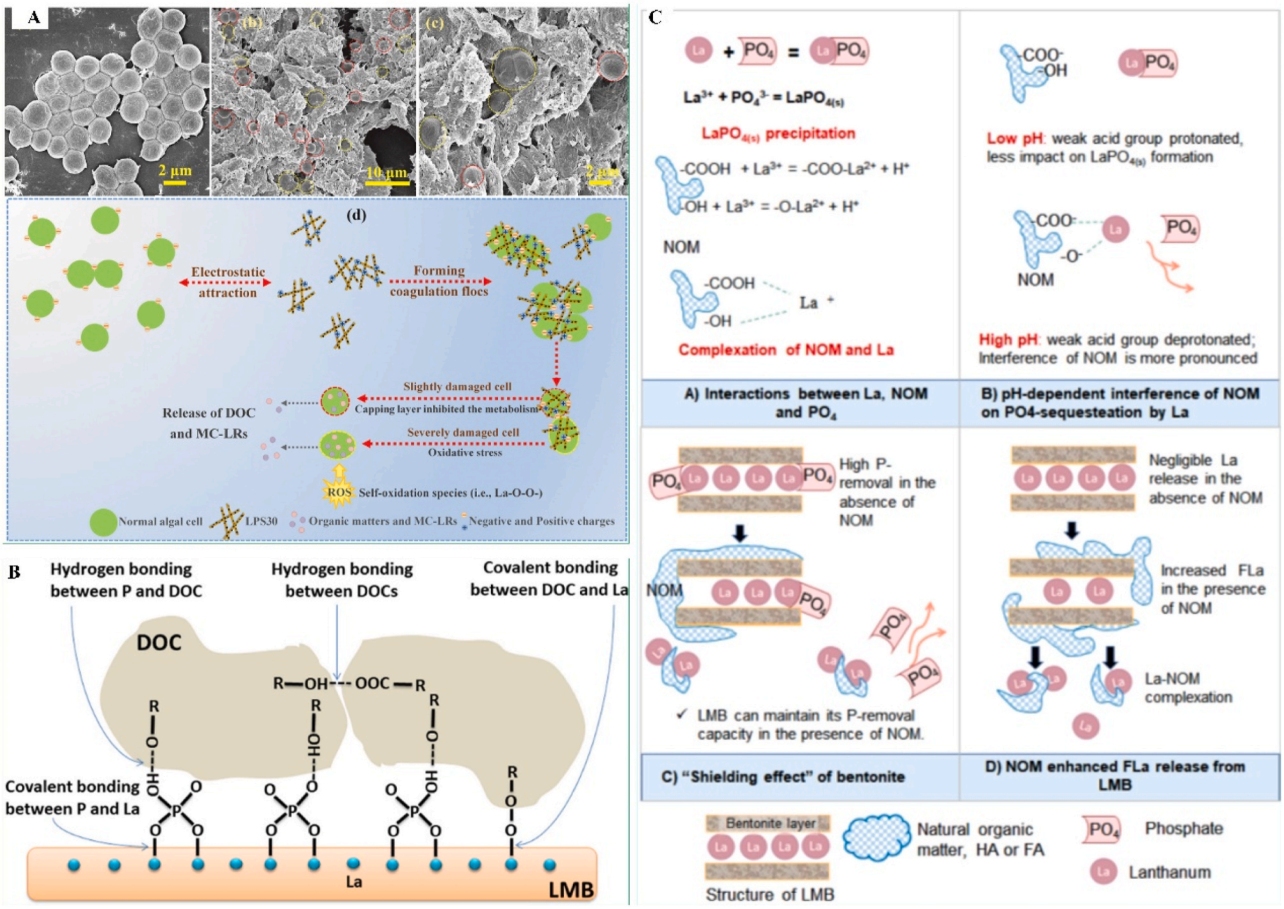

Fig. 8. A schematic representation of competitive adsorption of phosphate on modified clay minerals; (A) LPS30 in competition with competing ions for the active sites (Shan et al., 2022); (B) Interactions of DOC and phosphate with LMB (Li et al., 2020); (C) LMB in competition with natural organic matter (Zhi et al., 2021).

nitrogen and phosphate were simultaneously removed by an Fe_3O_4@-carbon medium in biological aerated filters. The phosphate concentrations were reduced to below 0.01 mg/L (Fig. 9B) (Bao et al., 2019). In another study, Fe_3O_4/La co-modified bentonite (La–Fe–MB) was combined with the anaerobic–anoxic–oxic (A^2/O) process for TP removal from low-carbon-limited municipal wastewater. La–Fe–MB was found to promote TP removal in different regions (anaerobic zone or anoxic zone) of the A^2/O process. This system also removed organic matter and nitrogen species and released trace amounts of iron (Fe^{2+}/Fe^{3+}) to enrich the phosphate accumulating organisms in the wastewater (Lu et al., 2022) (Fig. 9C and D).

In addition, a substrate formed from solidified poly aluminum chloride-amended attapulgate/biochar can remove phosphate from constructed wetlands. At an initial phosphate concentration of 10 mg/L, the average phosphate-removal ratio was 95% (Yin et al., 2022). Ca–GAT has been applied as a phosphate-fixation material in the treatment of membrane bioreactor effluent. After 177 h of Ca–GAT operation, the phosphate concentration in the effluent was below 0.5 mg/L (Lv and Li, 2023). Active serpentine can adsorb nitrogen and phosphate to form struvite (Li et al., 2022; Xin et al., 2022). However, the application of phosphate-decorated active serpentine to crop growth requires further research.

7.2. mCMs for lake phosphorus management

The release of endogenous phosphorus into lake sediments can result in lake eutrophication. Studies have reported that mCMs can manage phosphorus through passivation in situ (Lürling and Oosterhout, 2013; Robb et al., 2003). La with a high affinity toward phosphorus was found to be suitable for phosphorus management in lakes, with the efficacy of phosphorus management by La shown to be considerable improvement on bentonite (Kong et al., 2020) or attapulgite (Mi et al., 2022) supports. Therefore, La-modified CMs can effectively mitigate lake eutrophication.

The La content in Phoslock® (LMB) is approximately 5% ± 0.25%. Phoslock® was originally developed by the Australian Water River Association and the Commonwealth Scientific and Industrial Research Organization for managing phosphorous release from sediment (Lürling and Oosterhout, 2013; Robb et al., 2003). Since its deployment, Phoslock® has successfully managed two estuaries in coastal Western Australia, which experience frequent summer blooms. Phoslock® reduced the phosphate concentration from 50 to 20 μg/L in the lake and has effectively reduced the phosphorus levels in Vasse River, which is dominated by phytoplankton. In contrast, it has delivered poor performance in Canning River, which is dominated by aquatic plants (Márquez-Pacheco et al., 2013). In 2008, Lürling (Lürling and Oosterhout, 2013) combined Phoslock® with polyaluminum chloride to mitigate eutrophication in Lake Rauwbraken (the Netherlands). The average total phosphate (TP) concentration in Lake Rauwbraken decreased from 169 to 14 μg/L over 11 years. Meanwhile, the secondary release concentration of La ranged from 0.02 to 44 μg/L in 2008 but decreased to 0.4 μg/L after 10 years (Lürling, 2020). Aquatic animals and plants are greatly affected by factors in the ecological environment, such as temperature and pH. Sediment analysis showed that 91% of the La is retained in the sediment, with less than 1% present in macrophytes (Oosterhout et al., 2017).

As the temperature increases, the activities of microorganisms and benthic organisms increase accordingly and the organic phosphorus in

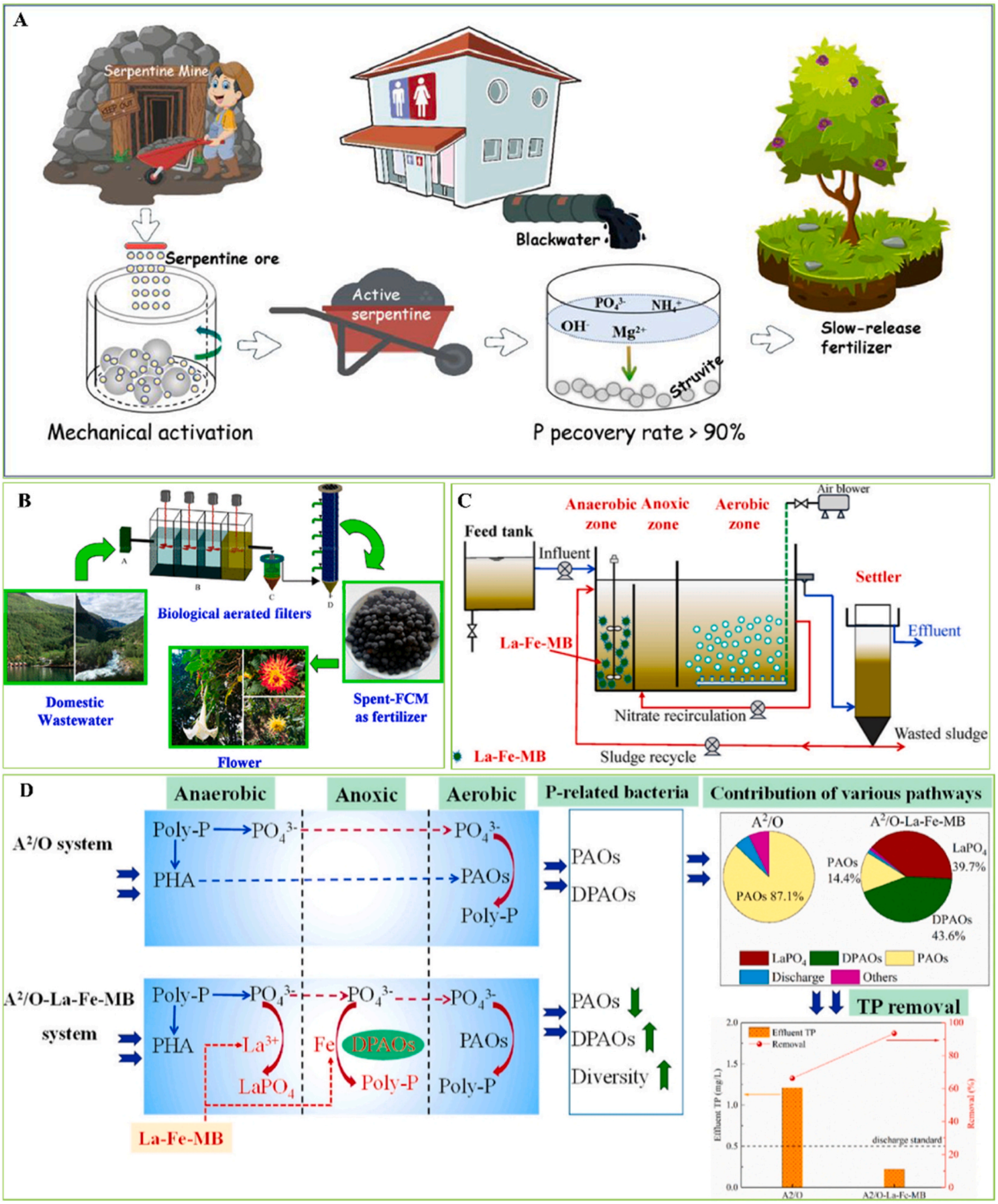

Fig. 9. A schematic representation of application of modified clay minerals in the treatment of diverse wastewater types;
(A) recovery of phosphate from serpentine (Li et al., 2022); (B) biologically aerated filter system with an Fe_3O_4@carbon filter medium (Bao et al., 2019); (C) A^2/O system of La–Fe–MB (Lu et al., 2022); (D) total phosphorous removal mechanism (Lu et al., 2022).

sediments is converted to inorganic phosphate, resulting in endogenous phosphate. Phoslock® can effectively immobilize active phosphorus in overlying water (OW) (Kang et al., 2022). For example, aluminum-modified zeolite (AMZ), Phoslock®, and aluminum salts (Al) can mitigate soluble reactive phosphorus (SRP), although Phoslock® exhibits a higher binding capacity than Al and AMZ at low phosphate concentrations. The ability of Phoslock® to chemically inactivate SRP is strongly temperature dependent and decreases with increasing temperature (Fig. 10A) (Kang et al., 2022).

DOC is an important component of organic carbon in OW. DOC concentrations of 4.45 mg/L inhibit the ability of Phoslock® to mitigate phosphorus release from lake sediments (Dithmer et al., 2016). However, one study reported that after 100 days of Phoslock® administration, the phosphate concentration decreased to 0.35 mg/L. In wastewater containing 51 mg/L DOC, the phosphate-removal ratio was 46.1% and the phosphate concentration decreased to 0.113 mg/L at 400 days after Phoslock® application (a phosphate-removal ratio of 81.5%), indicating that the inhibitory effect of DOC decreases over time. In the early stages of application (up to 100 days), the combination of Phoslock® and phosphate is hindered by surface complexation of DOC with Phoslock®. After prolonged operation (400 days), this inhibitory effect is weakened (Dithmer et al., 2016). In a study comparing the performances of Phoslock® and other phosphate-management methods for controlling sediment phosphorus loading, the long-term application of Phoslock® achieved more effective in situ inactivation than dredging (Yin et al., 2021). More specifically, in situ Phoslock® inactivation and dredging reduced the phosphorus flux by 90% and 82%, respectively, while increasing microbial diversity. Phosphorus management by Phoslock® is mainly mediated by the precipitation of mobile phosphorus as Ca–P and Al–P compounds in sediments (Fig. 10B) (Yin et al.,

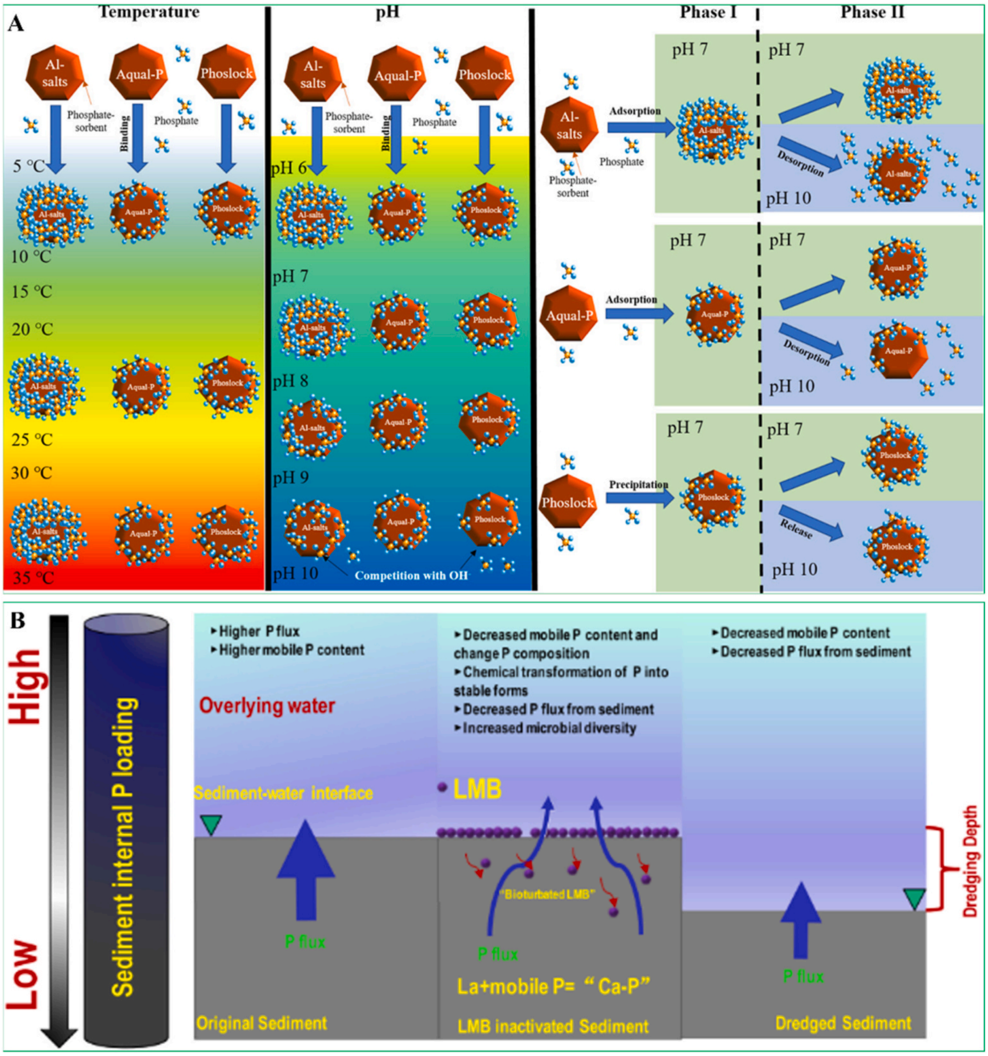

Fig. 10. A schematic representation of exploring the impact of various influencing factors on the application of modified clay minerals as lake passivation agents in eutrophication control;
(A) effects of temperature and pH on lake restoration using different passivation agents (Kang et al., 2022); (B) Phoslock® and dredging (Yin et al., 2021).

2021).

Attapulgite has a viscous, negatively charged surface. Modification can reduce the negative charge and improve the stability of this mineral. Modified Ca–attapulgite can effectively manage phosphorus in lake sediment (Yin et al., 2016a). Thermally-modified attapulgite at 700 °C (NCAP700) has been shown to reduce phosphorus mobility in the upper sediment layer but exerts minimal impact in deeper layers (Yin and Kong, 2015). Yin et al. (2016b) showed that both Phoslock® and NCAP700 can reduce the concentration of flowing phosphorus in surface sediment and alleviate phosphorus flux and wind disturbance. Notably, La/Al co-modified attapulgite (La/Al@ACP) stabilizes reactive phosphorus in eutrophic lakes, lowering the risk of secondary phosphate release into OW (Yin et al., 2020) (Table .5). However, recent research has shown that algal sedimentation can deactivate La/Al@ACP by affecting its passivation effect (Kong et al., 2022).

7.3. mCMs for phosphate management in seawater

Human activity can lead to the eutrophication of marine ecosystems and coastal waters. Phosphate is a nutrient-limiting element that controls the primary marine productivity at atmospheric oxygen levels. Eutrophic seawater can be effectively managed through adsorption methods, and phosphate in seawater can be managed by deploying CMs or mCMs such as attapulgite (Xu et al., 2023a) and bentonite (Xi et al., 2021a,b).

Attapulgite and modified attapulgite are often used as adsorbents in seawater eutrophication. Attapulgite has the characteristics of high SSA, abundant surface silanol groups, high viscosity, and medium layer charge, making it suitable as an in-situ phosphorus passivation material in the sediments of seawater aquaculture ponds (Xu et al., 2023b). However, the adsorption capacity of attapulgite is relatively low (Gan et al., 2009), and attapulgite generally requires modification, including thermal activation (Gan et al., 2009), acid modification (Gan et al., 2010), microbial modification (Xu et al., 2023a). The adsorption capacity of attapulgite can be enhanced by changing the crystal structure.

Attapulgite can manage phosphorus in the sediments of seawater aquaculture ponds (Xu et al., 2023b). One report found that attapulgite reduced the phosphorus flux in sediment by 53.81%, with average SRP in pore water, SRP in OW, and TP reduction rates of 56.32%, 70.83%, and 62.11%, respectively (Xu et al., 2023b). Xu et al. (2022) showed that when attapulgite was modified by calcination at 700 °C (AT700), its adsorption capacity increased to 7.2 mg/g versus 1.5 mg/g in raw attapulgite. The phosphate selectivity of AT700 was found to be 1000–3000 times that of Cl^-, demonstrating that AT700 could effectively manage eutrophication in seawater (Ye et al., 2022). Silicate bacteria can secrete organic acids (e.g., oxalic acid and citric acid) and enzymes that can dissolve CMs. Moreover, CMs can be wrapped by bacterial capsule polysaccharides, and the high concentration of organic acids secreted by silicate bacteria can effectively dissolve CMs. Silicate bacterial metabolic byproducts (such as proteins and polysaccharides) can adhere to the surface of CMs and change their properties (Xu et al., 2023a). Research found that AT@SiB-X can efficiently remove phosphate from seawater (Xu et al., 2023a). Silicate bacteria can quickly dissolve Al, Fe, Ca, and Mg in attapulgite. Thus, the phosphate adsorption capacity of AT@SiB-X was 9.54 mg/g, which is 16.7 times that of the raw attapulgite. Experiments on dynamic purification to remove phosphate from marine aquaculture wastewater showed a removal ratio of 98% and a treatment cost of 7.02 ¥/ton. In addition, the AT@SiB-X production cost was about 2000 ¥/ton, and the application of AT@SiB-X in the treatment of eutrophic seawater has high potential (Xu et al., 2023a).

7.4. Phosphate-loaded mCMs for agricultural applications

The beneficial properties of 2:1 layered CMs such as attapulgite, sepiolite, illite, vermiculite, bentonite, and montmorillonite can be exploited for soil improvement. Attapulgite retains water and fertilizer while sepiolite (with a high Mg content and water-retention and air-permeability characteristics) can regulate soil and improve its permeability (He et al., 2015). Illite contains K and can be applied as a crop fertilizer, whereas vermiculite has elements and properties that can enhance soil structure, retain fertilizer, and improve the air permeability of soil. Both bentonite and montmorillonite have demonstrably improved the structure, increased the fertility, and improved the water-retention capacity of soil (He et al., 2015). Overall, these mCMs are important promoters of crop productivity and soil quality. When mCMs adsorb saturated phosphorus, they can nourish agricultural crops, effectively alleviating the shortage of phosphate mineral resources. For example, phosphate-decorated SA–MgO@Bt can better promote mint growth than commercial chicken manure fertilizer and naked SA–MgO@Bt (Fig. 11A) (Xi et al., 2021a,b). Piash et al. (2022) showed that chicken manure-modified Ca–bentonite (CMB) prepared through the co-pyrolysis method effectively retards the release of P, N, and K by forming slow-release Ca/Mg–phosphates. The K release rate from CMB is 22% lower than that from Ca–bentonite because the K in chicken manure is adsorbed in the interlayers during the co-pyrolysis of Ca–bentonite and crystalline Ca–bentonite. In addition, as Ca–bentonite does not affect N release from the soil, it does not change the decomposable amides (Fig. 11B). Hong et al. (2020) reported that sepiolite calcined at 950 °C (950-SPL) adsorbs phosphate and is an effective fertilizer for crop growth. The stem dry weight, total dry weight, stem height, and tiller number of the crops were significantly higher in the phosphate-decorated 950-SPL group than in the control group (Fig. 11C). Angkawijaya et al. (2020) proposed that acid-MB (Pi@AAB) and half doses of chitosan-MB (Pi@OrB) are effective plant fertilizers that enhance the main root growth of seedlings. However, as plant growth also depends on humidity, pH, and the organic matter, micronutrient, and macronutrient contents, the feasibility of mCMs as agricultural fertilizers for plant growth requires more comprehensive evaluation. Notably, the fertilization effect of phosphate-decorated PER@PLDH matches or betters those of KH_2PO_4 and commercial struvite. Phosphate-decorated PER@PLDH releases Mg and P elements without causing metal toxicity (Fig. 11D) (Kong et al., 2019).

1:1 layered CMs, namely, serpentine and kaolinite, are also applicable as mineral fertilizers in agriculture. Serpentine, which contains Mg and Si, is degraded under acidic soil conditions but its Mg^{2+} ions can still be absorbed by crops. Because it can be used in the smelting of Ca/Mg phosphate fertilizer, serpentine is a promising long-term compound-mineral fertilizer that enhances crop growth. Meanwhile, kaolinite can improve the efficiency of fertilizer by enhancing the retention and release of N, P, K, and organic carbon. Kaolinite saturated with adsorbed phosphate can improve soil quality (He et al., 2015).

8. Challenges and recommendations for future mCM-mediated phosphate management

The existing findings confirm the viability of mCMs for phosphate management. Nevertheless, certain challenges must be addressed. The following recommendations are proposed for future research.

(1) Modification with different elements can affect the SSA, functional groups, and charge of CMs, greatly improving their phosphate-removal efficiency. In addition, mCMs can be released into the environment, where they can harm aquatic ecosystems. For example, Al-modified CMs increase the content of dissolved aluminum in lakes, reducing the lake biodiversity and harming fish. Similarly, Ca-modified CMs can increase the pH, releasing metal oxide-bound phosphates that pose risks to aquatic

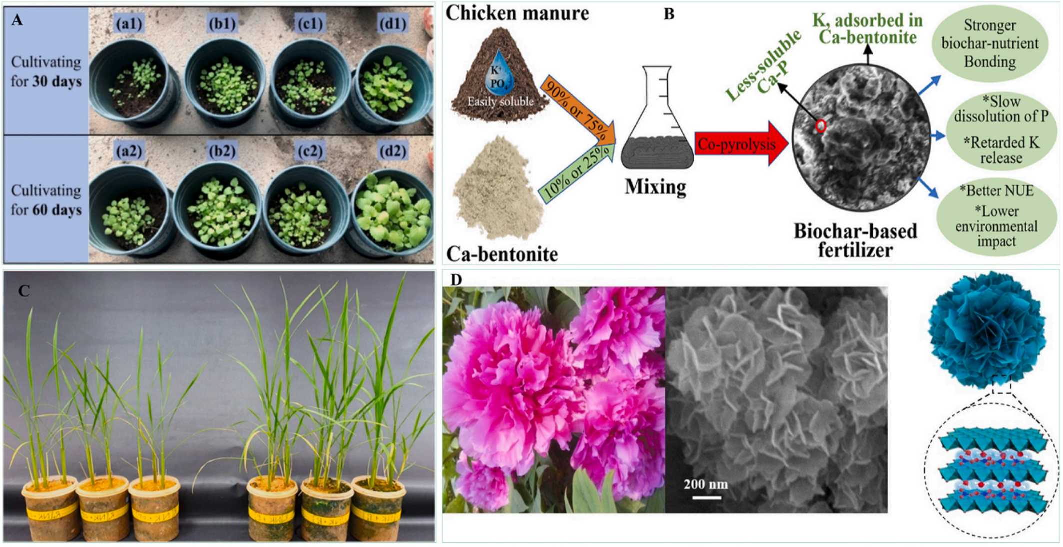

Fig. 11. A schematic representation of applications of phosphate-decorated modified clay minerals as fertilizers:
(A) Sodium alginate/Mg co-modified bentonite (Xi et al., 2021a,b); (B) Chicken manure-modified Ca–bentonite (Piash et al., 2022); (C) 950 °C modified and thermal sepiolite (Hong et al., 2020), and (D) PER@PLDH (Kong et al., 2019).

organisms. Future research should focus on developing environmentally friendly mCMs via physical or microorganism-mediated methods.

(2) Phosphate removal by mCMs involves various mechanisms: ion exchange, electrostatic-ligand exchange, hydrogen bonding, electrostatic interactions, precipitation, Lewis acid–base interactions, and crystallization. Investigating how mCMs and phosphate react is essential for improving the effectiveness of mCMs for wastewater purification. Phosphate adsorption by mCMs is hindered by anions and HAs, which compete with phosphate for a limited number of active sites. Future research should focus on developing highly efficient mCMs-based materials for phosphate management, with particular emphasis on environmentally friendly amorphous nano minerals using CMs.

(3) Rare earth elements are considered harmful to human health because they can accumulate in the body. The application of La-modified CMs is limited by low phosphate-locking capacity, vulnerability to bicarbonate and organic matter interference, and low removal ability for phosphate ions other than orthophosphate. Future research should develop mCMs that could confine layers at the nanoscale to overcome these problems. Such a confined space could block large interfering molecules, such as humus, while allowing the removal of different forms of phosphate. Phoslock® has achieved the removal of phosphate from sediment and overlying water. However, its cost is high (20,000–50,000 ¥ •ton^{-1}), which limits its widespread application on a large scale.

(4) Although mCMs have high phosphate removal efficiency, many problems still exist in their practical applications. Powder can easily cause blockages, and it is susceptible to interference from competing ions in wastewater. So, targeted strategies, such as granulating powder mCMs, which can effectively solve the problem of powder blockage, should be developed, or the adsorption effect of mCMs should be synergistically improved with plants and microorganisms. Finally, waste gas treatment, it can be further promoted on a large scale by combining artificial wetland filtration materials with soil remediation.

(5) Machine learning plays an important role in the research of adsorbent removal/recovery for phosphate. By collecting a large amount of data (properties of CMs, modification methods, modification conditions, and application scenarios), the function and structure of mCMs can be predicted, and the mechanism of phosphate adsorption can be studied, thereby guiding the design of mCMs.

(6) Magnetic separation is considered a feasible method to separate adsorbents from solutions. Magnetically mCMs are considered to be attractive adsorbents. However, their application still has many limitations. The effect of magnetic separation requires further experiments and evaluations. Recent studies have found that smart hydrogel state, volume, or other properties can change remarkable under external stimuli (such as light sensitivity, temperature sensitivity, and pH sensitivity). Smart hydrogels have been widely used in drug delivery, sensing, and tissue engineering applications. Therefore, by controlling the reaction process and conditions of the mCMs phosphate adsorption process, the physical and chemical properties of the mCMs structure can be adjusted, and their automatic descending or floating state can be adjusted, leading to intelligent and efficient recovery of mCMs. The intelligent recovery of mCMs from wastewater could be a key research area in future studies.

(7) Finally, phosphate-decorated modified CMs as agricultural fertilizers have been under-investigated and should be evaluated in future studies. New coated fertilizers have been created on substrates of mCMs saturated with phosphorus, enabling slow/controlled fertilizer release, efficient slow-release biological fertilizer, and enhancement of soil structure. Such a fertilizer has been assessed in a vegetable growth experiment in soils with different pH levels. The biomass, plant height, soluble sugar content, chlorophyll levels, proline concentration, and other relevant factors were monitored throughout the experiment. The study also examined the changes in soil microorganism population, inorganic phosphorus forms, and physical and chemical properties such as organic matter content, oxidation reduction potential, and pH. The results confirmed the feasibility of new coated fertilizers as agricultural phosphate fertilizers.

9. Conclusions

This review offers a thorough analysis and summary of recent research on the use of mCMs to manage phosphate in wastewater, covering the applied methods and providing a comprehensive examination of maximum phosphate adsorption capacities. Furthermore, this review also explores the incorporation of Ca, Mg, Al, La, and Fe into CMs to heighten phosphate adsorption. Additionally, SO_4^{2-}, HCO_3^{2-}, HA, and CO_3^{2-} have the most detrimental effect on phosphate removal. The adsorption mechanism of phosphate, and the application of mCMs as fertilizers in crop growth after adsorption saturation, were also systematically analyzed. Given their phosphate adsorption capacity, mCMs may be effectively applied to enhance crop growth, promote the wastewater management, and solve the shortage of phosphate rock resources.

CRediT authorship contribution statement

Teng Bao: Writing – original draft. **Mekdimu Mezemir Damtie:** Writing – review & editing. **Chu yan Wang:** Project administration. **Zhijie Chen:** Writing – review & editing. **Qi Tao:** Resources. **Wei Wei:** Formal analysis. **Kuk Cho:** Conceptualization. **Peng Yuan:** Methodology. **Ray L. Frost:** Writing – review & editing. **Bing-Jie Ni:** Conceptualization, Funding acquisition, Project administration, Resources, Writing – review & editing.

Declaration of competing interest

We declare that we have no financial and personal relationships with other people or organizations that can inappropriately influence our work, there is no professional or other personal interest of any nature or kind in any product, service and/or company that could be construed as influencing the position presented in, or the review of, the manuscript entitled, "Comprehensive **review of modified clay minerals for phosphate management and future prospects**".

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jclepro.2024.141425.

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