



Existing and emerging technologies for the removal of orthophosphate from wastewater by agricultural waste adsorbents: a review

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Abstract

The presence of orthophosphate in water can lead to eutrophication. Eutrophication has become a global environmental issue due to the increasing discharge of orthophosphate into water bodies as a result of increases in agricultural and industrial activities around the globe. Orthophosphate is among the limiting nutrients governing the growth of algae, and excessive release of phosphorus into the aquatic environment has contributed significantly to the eutrophication process. A rational shift is ongoing in wastewater treatment technology due to the need for cheap adsorbents to reduce wastewater treatment costs. The fact that some agricultural waste adsorbents (AWA) show promise in removing orthophosphate from the wastewater lends support to a hypothesis that they can be of a broad-spectrum for industrial applications. As shown in many studies, the affinity of AWA towards orthophosphate water contaminants can be enhanced through physical and chemical treatment, and few studies were performed on the potential of AWA towards the removal of orthophosphate from waste effluent. This article summarizes progress in transforming diverse agricultural wastage (AW) as potential adsorbent candidates for efficacious orthophosphate removal from wastewater over the last few decades. The production methods and the results obtained were discussed comprehensively. Surface modification through physical and chemical treatment, metal loading, and grafting has been proposed to improve the orthophosphate removal efficiency. The adsorption and desorption options' challenges that need to be considered more in future research include continuous and dynamic mode of adsorption, leaching, and loss of adsorbent material during regeneration and development of suitable models to describe the full range of adsorption with a high concentration of orthophosphate. The AW materials are always available, eco-friendly, and cheap to be used as an adsorbent.

Keywords Adsorption · Eutrophication · Orthophosphate · Surface modification

1 Introduction

Among the many pollutants in wastewater and water bodies, orthophosphate is an influential limiting element, which can lead to eutrophication of water bodies and ultimately leads to

water degradation and death of aquatic plants, animals, and other living microorganisms. Eutrophication has become a global environmental issue due to increases in agricultural and industrial activities around the globe [1]. Agricultural land run-off has manifested itself in excessive algal growth in streams and rivers and most significantly its migration into reservoirs to such an extent that water pipelines and turbines have resulted in blockages [2]. Economic disruption has been caused by the appearance of the dinoflagellates, deadly red algae, in the shore line seawater leading to elimination millions of dollars' worth of fish farming stocks [3]. Adequate availability of clean water has become a global challenge due to environmental issues emerging from heavy discharge of orthophosphate pollutants into surface and underground water around the globe. Therefore, it has been emphasized for decades to recover water from wastewater treatment to reduce the impact of global water shortages [4].

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Various treatment methods have been developed to treat water containing high concentrations of orthophosphate. One of these methods is the use of carbonaceous agricultural wastage (AW) materials to adsorb orthophosphate [1, 5]. In the last two decades, a great deal of research has been initiated in the use of agricultural waste adsorbents (AWA) for orthophosphate adsorption due to their exceptional properties, such as a large surface area, ample pore structure, chemical constancy, the comfort of physical and chemical modifications, ease application for specific application, and ability to remove different pollutants [2, 4, 6, 7].

Several AWA have been proposed for the treatment of orthophosphate and dyes in wastewater, such as rice husks, corn husks, bagasse, rice straw, coconut husks, herbal waste, moringa husk, orange peel, neem leaf, banana peel, palm kernel husk, Albizia fruit, etc. [4, 8]. Alabi et al. [9] reported the treatment of Albizia lebeck seed pod (ALB) with citric acid (CALB) and tartaric acid (TALB) as adsorbents for phosphate removal from wastewater. The maximum capacity was recorded at adsorbent dosage of 0.5 g for ALB and 0.1 g for CALB and TALB. Jung et al. [10] reported biochar produced from oak wood, bamboo wood, maize residue, soybean stover, and peanut shell for phosphate removal in batch mode. After 24 h of intimate contact, peanut shell biochar exhibits the highest capacity of 61.3% (6.79 mg/g) at 30 °C due to its high specific surface of 349 m²/g. Pounce et al. [6] studied the use of alkali-treated sugarcane bagasse, rice husk, and corn husk waste as adsorbents to remove dye at efficiencies of 96%, 99%, and 96%, respectively. They concluded that the alkali treatment of AW provides a good alternative to produce efficient adsorbents. AW has great potential to be used as orthophosphate adsorbent because of plentiful organic constituents with active adsorption sites. The materials are mainly composed of biomass with different classes of biodegradable organic compounds, such as cellulose, hemicellulose, and lignin from plant cell walls [2, 6].

Orthophosphate is a member of phosphate family, and its simplest form is phosphoric acid. It exists as three free ions, namely monovalent $\text{H}_2\text{P O}_4^-$, divalent HP O_4^{2-} , and trivalent H O_4^{3-} , and has the ability to react and make ion pairs with divalent metals such as Ca^{2+} , Mg^{2+} , and Fe^{3+} at neutral pH [11]. It is naturally occurring in seafoods, nuts, and milks and is also being added in some processed foods [12, 13]. In agricultural sector, orthophosphate is often used to increase inorganic nutrient in manure and commercial fertilizer.

Figure 1 shows the chemical structure of organo-phosphate, and Table 1 summarizes the properties of orthophosphate.

Orthophosphate is added into the water pipeline system to delay the corrosion of metal pipes and to prevent metals such as lead from disintegrating into the water [15]. Often, it is added as phosphoric. According to David [16], the

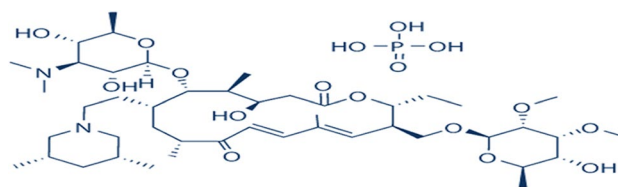


Fig. 1 Organo-phosphate chemical structure [14]

Table 1 Physiochemical properties of orthophosphate

Molecular formula	PO_4^{3-}
IUPAC name	Phosphate
Molecular weight (g/gmol)	95.0
Topological polar surface area (\AA^2)	86.2
Hydrogen bond donor	0
Hydrogen bond acceptor count	4
Rotatable bond count	0
Heavy atom count	5
Formal charge	-3
Complexity	36.8
Isotope atom count	0
Covalently bonded unit count	1

maximum recommended limit of phosphorus in drinking water is no higher than 0.025 mg/L. While phosphorus is usually considered safe for human consumption, however, excessive exposure may cause digestive problems due to toxicity [12]. Vervloet et al. [17] recognized the effect of high phosphate consumption on kidney disease and its relationship with hyperphosphatasemia. Lancaster University and the British Geological reported the negative implications of escalating phosphate concentration in water on aquatic ecosystem. Phosphate in water encourages the growth of algae, hence restricting the penetration of sunlight and depleting the dissolved oxygen in water [18, 19]. This is commonly known as eutrophication that is defined as the enrichment of an ecosystem with chemical nutrients, typically compounds containing nitrogen, phosphorus, or both. The algae, although is not directly toxic, that bloom can be dangerous to marine creatures. When the algae die, the bacteria break it down in a decay process that utilizes dissolved oxygen, thus creating a “dead zone” of limited oxygen supply for the creatures therein to survive [19, 20].

Generally, the phosphate treatment strategies can be classified as physical, chemical, and biological processes with pros and cons [14, 21, 22]. The biological process to degrade phosphate is too sensitive to the system parameters, making the overall efficiency unstable [14, 23, 24]. The chemical process often produces secondary pollution from sedimentation and precipitation that requires additional solid (sludge) storage and disposal [14, 25, 26]. In physical process, some

treatment methods like reverse osmosis and electrodialysis require high capital and maintenance costs [27, 28]. The current commercial technology used to remove orthophosphate is using calcium or magnesium crystals, called hydroxyapatite and ammonium magnesium phosphate. They are used for wastewater containing high concentrations of phosphate and ammonia, which are recovered in the form of crystalline struvite, and are not suitable for wastewater containing low concentrations or trace amounts of phosphate [29, 30]. Among others, adsorption is a preferred method that is low-cost and efficient to remove orthophosphate from wastewater [31, 32]. Adsorption is a technique that utilizes solid (adsorbent) for removing a substance (solute or adsorbate) from a liquid solution [33]. The process involves selective partitioning from the liquid phase onto the adsorbent surface [22, 34, 35]. More than 70% of the cost in adsorption is attributed to the adsorbent [36]. Therefore, the selection and development of low-cost adsorbent is the basis in realizing the cost-competitive adsorption process.

For comparison, the water treatment cost by adsorption is 5.0–200 US\$/m³ treated water as opposed to 10 to 450 US\$/m³ treated water using other physical or chemical methods [37, 38].

Emerging technologies for surface modification of AWA to enhance orthophosphate adsorption capacities include grafting (fixing more of carboxyl groups onto the adsorbent surface), chemical treatment (co-precipitation of acid or alkalis), and metal loading (chemical impregnation of metallic oxides onto adsorbent surface). Wang et al. [8] reported a comparative study of using biomass (*Australis*) loaded with different metal (Al, Ca, Fe, La, and Mg) oxides to remove phosphate from water. The maximum phosphate adsorption capacities are ranging from 38.9 to 220 mg/g, while the time taken to reach equilibrium is between 12 and 72 h. In a related work, Hanna et al. [39] reported that phosphate was adsorbed onto alginate/goethite hydrogel composite with an increase in the removal rate by 50%. Goethite, fine powder element of iron oxyhydroxide (α -FeOOH) is a common, stable crystalline iron. It takes a large specific area (100 m²/g), and it also has tremendous affinity and selectivity towards phosphate ions in water [19, 20]). Unfortunately, the conventional adsorbent is very expensive and has limitation, whereby iron compound is highly susceptible to oxidation–reduction potential and pH. An increase in pH diminishes the selective and affinity of iron compound towards phosphate ion adsorption and increases its solubility with phosphorus. The solubility of iron compound with phosphorus increases in an oxygen-free condition due to the reduction of Fe³⁺ to Fe²⁺. Consequently, the aeration and supplement of coagulants are suggested in the adsorption application. In order to bridge these gaps, Hanna et al. [39] postulated iron oxyhydroxide in the hydrogel form from low-cost biomass such as AW. In their inspiring work, iron

oxyhydroxide adsorbent was prepared using alginate-goethite hydrogel composite by chemical reaction using NaOH and Fe₂(SO₄)₃. The composite hydrogel adsorbent displays a better performance than the raw goethite, but the production is complex and expensive. Hence, the door is still open for further research to fill-up this gap. The purpose of this review is to highlight possible replacement of alginate material with other cellulose materials, which possess chemical surface functional groups similar to algae extract. An example is coconut shell activated carbon that bears surface functional groups rich in –OH and –COOH and has excellent textural properties [22, 34, 35, 40]. Coconut shell is modified by chemical co-precipitation of iron salt. The surface covered with FeOOH allows the crosslinking with polyvalent cations to form iron oxyhydroxide, which is then loaded onto the pores by chemical precipitation. The idea is to minimize the production and so the operating costs by replacing the complex alginate process with a simple one that utilizes low-cost AW to remove orthophosphate from water. Many works explored various AW materials to remove phosphates in wastewater. This review consolidates recent papers aimed at removing orthophosphate from water using carbonaceous AW materials. The current and emerging technologies of AWA and their modification strategies to improve the removal of orthophosphate were discussed. The challenges and way forward were highlighted to shed some light on future applications of AWA to remediate eutrophication at industrial scale.

2 Treatment of AWA for orthophosphate removal

The modification of agricultural waste adsorbents (AWA) usually takes place after sample preparation and activation. The existing modification methods can be divided into physical, chemical, and biological [41]. Metal loading as means to improve the effectiveness of phosphate adsorbent has been widely reported [13, 28]. The widely studied surface modification techniques include cationization (metal loading, quaternization), ionization (sulfate surface coating), and activation (thermal, chemical or steam) [42–47]. Nevertheless, direct exploitation of AWA through carbonization and acid/alkali treatment has also gaining considerable interest due to competitive performance in phosphate adsorption. Table 3 summarizes the AWA for phosphate removal from wastewater.

2.1 Physical treatment

Can et al. [48] reported the use of Chinese medicinal herbal residue and spent *Pleurotus ostreatus* substrate for

phosphate and ammonium removal from swine wastewater. The textural analysis revealed that the pristine samples are mesoporous with many layers, rough spines, and groves. The former recorded a tremendous removal of phosphate of 1632 mg/g, while the latter is 62.6 mg/g. The maximum uptake was attained in 6 h at pH 8. The adsorption varied with pH, and the kinetics obeyed the intraparticle diffusion and pseudo-second-order models. The possible mechanisms governing the phosphate removal are ligand exchange, surface complexation, and precipitation. Similar results of phosphate adsorption were reported elsewhere [14].

Riahi et al. [49] reported the use of date palm fiber to remove phosphate in water. The material was oven-dried and ground to desired size, without any use of chemicals. For a high dosage of 6 g/L, the adsorbent capacity was 4.35 mg/g in 50 mg/L phosphate solution after 120 min. The phosphate adsorption increased with concentration and decreased with solution pH [11, 48, 50, 51]. The mechanism is mainly attributed to surface precipitation.

The application of natural reed (*Arundo donax*) in batch adsorption displays an increase in phosphate removal with concentration, but the trend is opposite for dosage and temperature [52]. The adsorption is exothermic and spontaneous, where the maximum capacity of 16.2 mg/g is reached at neutral pH. The adsorption data fitted well with Langmuir and pseudo-second-order kinetic models, suggesting the chemical-type adsorption. The use of giant reed as phosphate adsorbent was established by Xu et al. [53]. A maximum capacity of 54.7 mg/g was attained at pH range of 5–10. The phosphate removal is pH-dependent and decreased with temperature. Riahi et al. [49] also reported the varying phosphate removal with pH but with endothermic nature by date palm fiber.

Kumar et al. [54] showed an endothermic and spontaneous removal of phosphate from water using coconut shell pith with maximum capacity at 7.74 mg/g in the pH range of 6–10. Yeom and Jung [55] and Kumar et al. [54] reported that the particle size and solution temperature affect the phosphate removal. A maximum phosphate capacity of 100 mg/g was attained with scallop shell size of 45 μm in 3 h. The removal remains constant in the pH range of 2.0–7.5 but is negligible beyond pH 8.0 [55].

Jung et al. [10] showed the removal of phosphate by peanut shell biochar with a capacity of 6.79 mg/g. The high phosphate removal is due to its structural characteristics with specific surface of 349 m^2/g . The equilibrium and kinetics data are well described by Langmuir and pseudo-second-order models, indicating the chemical interactions in adsorption. In a related work, Alabi et al. [9] reported the reverse effect of acid treatment using citric acid and tartaric acid on *Albizia lebbek* seed pod. The maximum capacity is 5.30 mg/g by the untreated residue, which is greater than the treated ones.

2.2 Acid–base treatment

Kumar et al. [54] showed the phosphate capacity of 7.74 mg/g by H_2SO_4 -activated coir pith carbon with considerably high specific surface of 727 m^2/g . In a related work, Mezenner and Bensmaili [56] reported the adsorptive properties of iron hydroxide-eggshell for phosphate removal. The phosphate capacity increased with solution temperature, suggesting the endothermic nature of adsorption. The equilibrium and kinetics data obeyed intraparticle diffusion, and pseudo-second-order models further suggest the chemical interactions between phosphate ions and adsorbent surface. Attempt to use H_3PO_4 to treat eggshell waste was reported by Emma [57]. Unfortunately, the phosphate removal is small at 0.41 mg/g.

2.3 Metal loading

Metal loading through calcination and co-precipitation has been widely employed in phosphate adsorbent preparation, owing to the fact that the divalent metals could bridge the phosphate anions by the sharing of electron pairs. Krishnan and Haridas [58] recognized the improved capacity of iron (III)-loaded coir six times better than the raw coir. Qi et al. [14] prepared metal-loaded sludge activated carbon via co-precipitation of $\text{Fe}^{3+}/\text{Fe}^{2+}$ and single-step FeCl_3 activation. The metal fixation in the latter results in a higher orthophosphate capacity of 111 mg/g. The iron exists to a great degree in amorphous phase as hematite and hydroxide forms, to which the ligand exchange may partly contribute to the uptake of phosphate. The removal varied with pH, and the adsorbent efficiency decreased to 60% after five cycles.

Wu et al. [59] reported the use of iron (II/III)-loaded soil biochar for phosphate adsorption. It shows a 2.5 times greater capacity at 39.2 mg/g than the original soil biochar. The adsorbent is insensitive to solution pH as the iron exists dominantly in an unstructured state as FeOOH which becomes buffer to the surrounding pH and exploits its potential in adsorbing phosphate. Nano-magnetic iron-coated activated carbon was prepared by chemical precipitation of Fe(II) and Fe(III) [11]. Surprisingly, the capacity is small at 1.2 mg/g in 90 min of contact. Similarly, Krishnan and Haridas [58] reported a 4.35 mg/g phosphate removal by iron-loaded coir pith. In both studies, the adsorption is pH-dependent that is preferably at pH 3–4. Pokhrel et al. [13] attributed the effect of pH to the adsorbent point of zero charges (PZC). When the pH is lesser than PZC, the adsorbent surface becomes protonated, providing more sites on top of the exposed divalent metals to accommodate phosphate anions.

Nguyen et al. [46] studied iron-loaded okara (soybean residue) to adsorb phosphate in dynamic mode. The sorption data obeyed Adam-Bohart model with maximum capacity

of 16.7 mg/g at pH 3. The adsorbent regeneration is effective using 0.2 M NaOH. Anirudhan and Senan [60] developed iron-loaded cellulose that yields a 99.1% (24.8 mg/g) removal at pH 6. Similarly, Guzman et al. [61] recorded a 100% (2.0 mg/g) removal of phosphate onto iron-containing quaternized wood nanocomposite within 48 h. In a different study, Junjie et al. [1] showed the phosphate capacity of 89.4 mg/g by Mg–Al oxide bimetallic loaded straw fiber carbon with a specific surface of 42.9 m²/g and an average pore diameter of 2.56 nm. The adsorbent exhibits a good efficiency of phosphorus removal above 72% after five adsorption–desorption cycles.

Attempts to embed other metals onto adsorbent to aid in phosphate adsorption have also been reported. Nguyen et al. [47] reported the phosphate capacity of 44.1 mg/g by zirconium-loaded okara in the pH range of 2–6. The adsorption is rapid, reaching a 95% removal in 30 min. Zhang et al. [62] showed the maximum capacity of phosphate at 29.3 mg/g onto activated carbon fiber loaded with lanthanum oxide. The mechanisms are suggested due to ion exchange, Coulomb interaction, and Lewis's acid–base interaction bonding. Juniper was treated using lanthanum salt for phosphate removal [51]. The phosphate uptake is pH-dependent, where the adsorbent displayed a strong affinity in acidic condition (pH < 4). The capacity of 0.233 mg/g was recorded, by which the driving mechanism is possibly surface precipitation.

2.4 Grafting

Faraji et al. [50] introduced quaternary ammonium groups onto walnut and almond shells that brings about improved capacities of 22.7 mg/g and 14.7 mg/g, respectively. Yet, the effect of pH was not reported. Zhang et al. [63] showed an enhanced anion exchange functionality of bagasse to remove phosphate from water in batch and dynamic modes. The phosphate adsorption capacity is 21.3 mg/g at neutral pH. Anirudhan et al. [64] reported the grafting reaction of banana stem with epichlorohydrin and dimethylamine. The synthesized adsorbent displays a strong affinity towards phosphate with 99% (2.45 mg/g) removal at pH range of 5–7. The removal is endothermic, and the phosphate-loaded adsorbent is restored using 0.1 M NaOH solution.

Tables 2 and 3 summarize the characteristic and orthophosphate adsorptive properties of some common AWA. From Table 2, the values of specific surface of AWA are in the range of 3.01 to 1768 m²/g with pore size ranging from 0.16 to 20.2 nm. The smaller the pore size generally indicates the higher the surface area of adsorbent. From Table 3, the capacities of phosphate adsorption are between 8.35 and 1632 mg/g at solution pH ranging from 3 to 8. At pH 3–9, the monovalent and divalent phosphate ions are dominant in the solution, and due to their high

affinity towards the binding sites, the removal of phosphate increases [13]. The low phosphate removal efficiency as documented using sawdust (2.05 mg/g), hickory wood (8.35 mg/g), orange waste, dairy manure, and sphagnum fuscum peat (< 14 mg/g) can be attributed to the prevalence of negatively charged functional groups, while the number of positively charged functional groups is small [13]. The equilibrium data mostly fitted well with Langmuir model, indicating that the chemical adsorption governs the phosphate removal by AWA. The kinetic data of most AWA could be well described by pseudo-second-order model, signifying that the rate of phosphate adsorption depends solely on the available sites and the time it attains the equilibrium with the adsorbent surface that is also tied-up with chemisorption.

3 Parametric effects on orthophosphate adsorption

Several techniques such as chemical methods (coagulation, filtration with coagulation, precipitation, ozonation, ion exchange, and advanced oxidation), physical methods (reverse osmosis and electrodialysis), biological (use of fungal and bacterial), and adsorption processes have been used for the removal of orthophosphate from wastewater [87]. These techniques are occasional since they are of high capital and operational costs. Adsorption by AWA has shown a potential to be the efficient technique for phosphate water treatment. Adsorption can be categorized as physical adsorption or physisorption (van der Waals adsorption) and chemisorption (activated adsorption). Physical adsorption is a readily reversible phenomenon, which results from the intermolecular forces of attraction between the adsorbent and the adsorbate [2]. On the contrary, chemical adsorption is an irreversible phenomenon, which results from the intermolecular chemical reaction between the adsorbent and the adsorbate. The two common modes of adsorption process are batch (static) and continuous (dynamic) using fixed-bed column. When the throughput is small, batch adsorption is often used to adsorb solutes from solution. As with many other processes, an equilibrium relation such as Freundlich or Langmuir isotherm and material balance are needed. Adsorption in a fixed-bed column can be used continuously under high effluent flow rates, and it has been used in many processes of pollution control and commercial wastewater treatment.

3.1 Solution pH

The adsorption of phosphate from water can be highly dependent on solution pH. As of practical standpoint, effluent should always be assessed at the natural pH that

Table 2 Source, treatment/modification methods, and properties of AWA

Adsorbent material	Treatment /modification methods and conditions	Yield (%)	BET area (m ² /g)	Porosity (nm)	Pore volume (cm ³ /g)	Application	Reference
Rice husk biochar	Hydrothermal carbonization, 180 °C, 70 bar for 20 min	57.9	5.02	20.2	0.025	Wastewater treatment, biofuel production	[4]
Rice husk	Physical treatment, crushed, dried at 105 °C for 24 h	-	3.5	19.6	0.017	Wastewater treatment	[7]
Palm kernel shell	Steam treatment, 300 °C for 30 min, ramped to 800 °C, water injected at 120 mL/h	22	584	0.181	0.26	CO ₂ capture	[65]
Palm kernel shell	ZnCl ₂ activation, 550 °C for 1 h	44	1223	0.221	0.70	CO ₂ capture	[65]
Palm kernel shell	H ₃ PO ₄ treatment, 400 °C, N ₂ for 1 h	48	-	49	0.94	-	[66]
Sugarcane bagasse	Alkali treatment (0.1 M NaOH), 24 h, room temperature	81	4.88	1.60	1.96	MB adsorption	[6]
Rice husk waste	Alkali treatment (0.1 M NaOH), 24 h, room temperature	100	1.64	4.35	1.78	MB adsorption	[6]
Rice straw	KOH activation, 5 °C/min, 280 °C for 2 h, increased to 450 °C for 2 h	-	1305	2.59	-	Carbofuran adsorption	[67]
Corn husk waste	Alkali treatment (0.1 M NaOH), 24 h, room temperature	91	3.01	3.94	0.296	MB adsorption	[6]
Coffee waste	Soaked with polyethyimine, 24 h	-	5.0	2.94	0.022	RB5 adsorption CR adsorption	[68]
Coffee residue	H ₃ PO ₄ activation, 600 °C, anoxic for 1.5 h	41.2	1030	2.13	0.387	Phenol adsorption	[69]
Coffee residue	KOH activation, 600 °C, anoxic for 1.5 h	17.5	399	3.76	0.253	Phenol adsorption	[69]
Agricultural composite Rice husk + groundnut shell + Soya bean shell	KCl activation, 400 °C, N ₂ for 30 min	-	850	6.08	0.497	Wastewater treatment	[70]
Tea fruit peel residue	ZnCl ₂ activation, 500 °C, N ₂ for 40 min	47.4	1024	2.915	0.746	MB adsorption	[71]
Tea fruit peel residue	H ₃ PO ₄ activation, 500 °C, N ₂ for 40 min	46.1	1320	2.380	0.785	MB adsorption	[71]
Cassava (<i>Manihot dulcis</i>) peels	FeCl ₃ activation, 800 °C, N ₂ for 2 h	-	406	2.03	0.11	-	[72]

Table 2 (continued)

Adsorbent material	Treatment /modification methods and conditions	Yield (%)	BET area (m ² /g)	Porosity (nm)	Pore volume (cm ³ /g)	Application	Reference
Desiccated coconut waste (DCW)	Physical treatment, sun-/oven-dried for 72 h		6.63	4.64	0.0077	Cu(II) & Ni(II) adsorption	[73]
<i>Thevetia peruviana</i>	Carbonization, 400 °C for 1 h; H ₃ PO ₄ activation, 800 °C, N ₂ for 10 min	58.6	862	0.544	-	Textile effluent treatment	[31]
Mangosteen peel	H ₃ PO ₄ activation, 850 °C, N ₂ for 20 min	35.1	731	0.35	0.33	-	[74]
Coconut shell	KOH activation via microwave, 600 W for 20 min	-	1769	2.7	-	Capacitance	[35]
Coconut shell	Steam activation, water flowrate 1.35 g/min for 60 min, 900 °C for 120 min	55.2	1500	2.0	0.61	-	[40]
Coconut shell	NaOH activation, 600 °C, N ₂ for 2 h	77	876	2.86	0.414	MB adsorption	[75]
Coconut shell	Steam activation, water flowrate 120 mL/h, 300 °C for 30 min, ramped to 800 °C	24	1011	0.187	0.45	CO ₂ capturing	[65]
Coconut shell	ZnCl ₂ activation, 550 °C for 1 h	45	953	0.181	0.43	CO ₂ capturing	[65]

is left unadjusted [88]. However, if initial isotherm results prove unsatisfactory or a pH response is projected, other pH conditions should be evaluated by pH adjustment using dilute acid or base [88]. The solution pH can also be affected by the presence of adsorbent. Hence, it is always wise to measure the pH of each adsorbent dose, which aids in the interpretation of phosphate adsorption data and characteristics. From Table 2, the pH values of various phosphate adsorbents are ranging between 3 and 8.

Many researchers have worked to establish the optimal pH for phosphate adsorption [89]. Phosphate can exist in three ionic forms in an aqueous solution depending on the solution pH: monovalent H₂PO₄¹⁻, divalent HPO₄²⁻, and PO₄³⁻. According to Biswas et al. [84], monovalent phosphate ions are dominant at pH 2.2, while divalent and trivalent phosphate ions are dominant at pH 7.2 and pH 12.3, respectively.

At the pH range of 3–9, the monovalent and divalent phosphate species are dominant in the solution, and due to their high affinity towards the binding sites, the uptake of phosphate increases [13, 84]. When the pH is less than 4, the monovalent phosphate becomes protonated and converted to trivalent species with low affinity towards the binding

sites, thus decreasing the phosphate removal. Additionally, at solution pH greater than 9, the divalent and trivalent phosphate species are dominant. The low affinity towards the binding sites coupled with strong competition between the hydroxyl ions (OH⁻) and the trivalent phosphate ions (PO₄³⁻) for adsorption sites results in the decrease of phosphate removal [13]. Therefore, a suitable pH environment is required to effectively remove phosphate ions, while a strongly acidic or alkaline medium suppresses the phosphate adsorption process. An optimal pH, ranging from 3 to 9, for phosphate-bearing effluent is suggested [84].

3.2 Temperature

It has been shown in many studies that the phosphate adsorption is endothermic, where the capacity increased with increasing solution temperature [55, 56, 90]. Conversely, Xu et al. [53] reported the exothermic nature of phosphate uptake that decreases with increasing temperature. According to Le-Chatelier's principle, adsorption process is generally exothermic, therefore, at a given concentration, low temperature favors the adsorption. If the temperature increases, adsorbate molecules tend to move faster, the equilibrium is

Table 3 Application of AWA for orthophosphate removal

AWA	Treatment/modification method and condition	Surface area (m ² /g)	Type of wastewater	Adsorption technique	Adsorption conditions (pH & conc. of adsorbate and amount of adsorbent and time)	Phosphate adsorption capacity (mg of P/g)	Adsorption model	Kinetic model	Adsorption mechanism	Reference
Straws of <i>Phragmites australis</i> (BC)	Physical/chemical modification: sun-dried, 7 days; soaked in 0.1 M of AlCl ₃ (Al-BC), CaCl ₂ ·2H ₂ O (Ca-BC), FeCl ₃ ·6H ₂ O (Fe-BC), LaCl ₃ ·6H ₂ O (La-BC), MgCl ₂ ·6H ₂ O (Mg-BC); pyrolysis, 600 °C, N ₂ for 2 h	Al-BC (5.35) Ca-BC (7.96) Fe-BC (14.67) La-BC (73.94) Mg-BC (89.82)	Municipal wastewater	Batch adsorption; spectrophotometer wavelength 880 nm	pH 7.0, 20 mg/L, 2 g	Al-BC (230) Ca-BC (81.5) Fe-BC (46.6) La-BC (38.9) Mg-BC (112.5)	Langmuir, Freundlich intraparticle diffusion (R ² = 0.93)	Pseudo-second-order (R ² > 0.8), Ritchie nth-order (Fe-BC) R ² = 0.93	Electrostatic force, internal bonds	[8]
Rice straw fiber (Al-Mg/SF)	Chemical precipitation: 150 g SF immersed in 200 mL Al(NO ₃) ₃ ·9H ₂ O for 8 h; pyrolysis, 400 °C, N ₂ for 4 h (Al ₂ O ₃ /SF); hydrothermal reaction: 2045 g Mg(NO ₃) ₂ ·6H ₂ O + 0.49 g Al ₂ O ₃ /SF + 0.674 g HMT; autoclave, 120 °C for 12 h	42.88	Aqueous solution	Batch adsorption; 700 nm	pH 6, 100 mg/L, 25 mg	89.37	Freundlich (R ² = 0.99)	Pseudo-second-order (R ² = 0.99)	Chemisorption, precipitation	[1]
Hickory wood (engineered biochar)	Chemical precipitation (metal loading): 10 g of wood immersed in solution of AlCl ₃ for 2 h; dried, 80 °C for 24 h; pyrolysis, 600 °C, N ₂ for 1 h	-	Secondary treated wastewater	Batch adsorption; fixed-bed column (D = 16 mm, H = 50 mm), flowrate 1–1.5 mL/min, adsorbent dose 0.25–1.0 g; ICP-OES	pH 7–8, 40 mL, 0.1 g	8.35	Thomas & Yoon-Nelson (R ² = 0.86)	Pseudo-second-order, N-th-order (R ² = 0.996)	Electrostatic force, internal bonds	[76]
Rice husk ash	Acid treatment; carbonization, 500 °C for 2 h; chemical treatment, 1 N HCl, room temperature for 24 h	-	Synthetic wastewater	Batch adsorption, 150 rpm, 25 °C, 60–240 min; 880 nm	pH 6, 10 ppm, 2 g/L	89%	Langmuir (R ² = 0.99)	Pseudo-second-order (R ² = 0.978)	Electrostatic force, internal bonds	[77]
Sphagnum fuscum peat	Metal loading: 100 g peat + 67.55 g FeCl ₃ ·6H ₂ O + 3 M NaOH for 12 h; air-dried, 60 °C for 4 h	43.8	Synthetic & real wastewater	Batch adsorption; 880 nm	25 mg/L, 140 rpm, 20 °C, 24 h	11.5	Langmuir (R ² = 0.99)	Pseudo-second-order (R ² = 0.99)	Chemisorption	[49]

Table 3 (continued)

AWA	Treatment/modification method and condition	Surface area (m ² /g)	Type of wastewater	Adsorption technique	Adsorption conditions (pH & conc. of adsorbate and amount of adsorbent and time)	Phosphate adsorption capacity (mg of P/g)	Adsorption model	Kinetic model	Adsorption mechanism	Reference
Spent coffee ground (SCG)	Metal loading: 2 g SCG immersed in 160 mL 0.04 M Ca(OH) ₂ for 24 h, dried, 60 °C	-	Wastewater	Batch adsorption; 880 nm	pH 3, 10 mg/L, 0.1 g, 72 h	36.7	Langmuir (R ² = 0.98)	Pseudo-second-order (R ² = 0.98)	-	[78]
Diary manure	Metal loading: CaO impregnation at ambient condition	-	Effluent from dairy farm	Batch adsorption; Hach kit	pH 8.5, 0.02 L, 30 mg/L, 200 rpm, 72 h	13.6	Freundlich (R ² = 0.997)	Pseudo-second-order (R ² = 0.974)	Chemisorption	[79]
Phragmites australis biochar (MPB)	Chemical precipitation: MPB immersed in MgCl ₂ ·6H ₂ O for 2 h; dried, 80 °C for 24 h; pyrolysis, 600 °C for 1 h	-	Synthetic water	Batch adsorption; 880 nm	0.05 mg/L, 0.05 g, 150 rpm, 24 h, 30 °C	100	Langmuir (R ² = 0.97)	Pseudo-second-order (R ² = 0.974)	Chemisorption, ion exchange	[80]
Biochar from corn cobs (BC A), garden wood (BC B), wood chips (BC C)	Metal loading: pyrolysis, 500 °C for 120 min; Fe(NO ₃) ₃ impregnation, 105 °C for 12 h	BC A (16.20) BC B (23.27) BC C (26.42)	Synthetic wastewater	Batch adsorption; 880 nm	pH 3–8, 65 mg/L, 0.5 g, 150 rpm, 26 °C	BC A (1.99) BC B (2.75) BC C (3.20)	Langmuir (R ² = 0.97)	Pseudo-ninth order (R ² = 0.95)	Chemisorption, precipitation	[81]
Orange peel	Chemical co-precipitation: Fe(III)/Fe(II), 250–700 °C for 6 h	501	Synthetic wastewater	Batch adsorption; 284 nm (HPLC)	0–12 mg/L, 6.25 g, 120 rpm, 24 h	43.4	Langmuir (R ² = 0.99)	-	-	[82]
Chinese medical herbal residue (CMHR)	Physical treatment, washed, dried for 72 h	0.918	Swine water	Batch adsorption; 880 nm	pH 8	1632	Langmuir (R ² = 0.96)	Pseudo-ninth order (R ² = 0.95)	Chemisorption, ion exchange	[48]
Spent <i>Pleurotus ostreatus</i> substrate	Physical treatment, washed, dried for 72 h	2.04	Swine water	Batch adsorption; 880 nm	pH 8	62.6	Langmuir (R ² = 0.98)	Pseudo-second-order (R ² = 0.95)	Chemisorption, precipitation	[48]
Date-palm waste and granular date stone	Physical treatment, dried, 110 °C	-	Synthetic wastewater	Batch adsorption; 880 nm	-	26 26.7	Langmuir (R ² = 0.98)	Pseudo-second-order	Chemisorption, precipitation	[83]

Table 3 (continued)

AWA	Treatment/modification method and condition	Surface area (m ² /g)	Type of wastewater	Adsorption technique	Adsorption conditions (pH & conc. of adsorbate and amount of adsorbent and time)	Phosphate adsorption capacity (mg of P/g)	Adsorption model	Kinetic model	Adsorption mechanism	Reference
Orange waste	Grafting: soaked in Ca(OH) ₂ + NaOH + 0.1 M ZrOCl ₂ ·8H ₂ O	-	Synthetic wastewater	Batch adsorption; packed column	pH 3–9, 20 mg/L, 140 rpm, 24 h, 30 °C; column, flowrate 7.0 mL/h	13.9	Langmuir	-	-	[84]
Walnut shell	Grafting: soaked in NaOH/epichlorohydrin/trimethylamine	-	Synthetic wastewater	Batch adsorption; 880 nm		22.7	Langmuir	Pseudo-second-order	Chemisorption, ion exchange	[50]
Almond shell						14.7				
Saw dust	Metal loading, Fe(II) 4% CMC + Fe(II)	-	Synthetic wastewater	Batch adsorption; 880 nm	pH 4.8	2.05	Langmuir	-	-	[85]
Skin split waste	Metal loading, Al(III), Fe(III)	-	Synthetic wastewater	Batch adsorption; 880 nm	pH 7	21.7	Langmuir	Pseudo-second-order	Chemisorption, precipitation	[86]

reached within a short period, and the adsorbent gets saturated with the adsorbate. Further increase in the solution temperature will lead to desorption of phosphate ions from the adsorbent. Thus, adsorption is inversely proportional to temperature. This is true for physical adsorption. In chemical adsorption due to the high energy of activation, the extent of adsorption increases initially and decreases as the temperature increases further, which is the case for many phosphates adsorption studies by metal-loaded AWA.

3.3 Contact time

Adequate contact time between the adsorbent and the fluid is essential for the adsorbent to approach equilibrium with the adsorbate. Each adsorbent particle requires a certain volume of liquid to react. A high adsorbent dosage with less volume to treat per unit weight may reach equilibrium somewhat faster than a low dosage. Sufficient time must be permitted for the low dose to reach equilibrium. Four hours of contact time with vigorous agitation will be sufficient to achieve equilibrium [33, 88]. In phosphate adsorption, the removal has shown to be rapid at the early stage and then continue at a low rate to a point where it subsides with no further increase in phosphate removal as per time growth [44, 54, 62, 90]. The early rapid pace is due to the plentiful, high affinity sites for adsorption. But, as the reaction proceeds and the adsorption of phosphate increases, the overall surface charge decreases and becomes sluggish [9, 10, 52].

3.4 Adsorbent dosage and phosphate concentration

The removal of phosphate from water is affected by the amount of adsorbent. The phosphate ion adsorption has shown to be decreasing with increasing adsorbent dose. The decrease in phosphate adsorption is attributed to the concentration gradient between the phosphate concentration in the bulk solution and the adsorbate concentration on the adsorbent surface. As the mass of the adsorbent increases, the amount of the adsorbate adsorbed per unit weight of the adsorbent (adsorbate/adsorbent) gets reduced. This is consistent with studies by [9, 10, 52, 53, 61–63], etc.

Usually, when the concentration of adsorbate is high, the extent of adsorption is greater at a constant temperature. This is true to a point known as surface saturation of adsorbent. It generally indicates that at the initial stage, the adsorption rate is higher and decreases gradually as the adsorption process progresses more with time. Furthermore, the phosphate removal rate by most AWA has shown to increase with an increasing initial concentration of the adsorbate [53, 61, 63]. An increase in phosphate concentration disrupts the equilibrium condition, so increasing the adsorption driving force

(adsorbate/adsorbent) which is the concentration gradient for higher removal capacities [49, 53, 54, 60]. It indirectly infers that most phosphate adsorbents are effective only at low concentrations [60].

4 Model fittings

4.1 Equilibrium isotherm

Adsorption equilibrium is a relation between the extent of adsorption (quantity of a substance adsorbed per unit mass of an adsorbent) and the equilibrium concentration at a constant temperature [33]. Various isotherm models such as linear, Langmuir, BET, Gibbs, Freundlich, Temkin, and Sips have been employed to describe the equilibrium relationships between the phosphate concentration in the bulk and the concentration of phosphate adsorbed onto adsorbent [54, 60]. The commonly applied models in adsorption studies are Langmuir and Freundlich, which describe the underlying principles of monolayer accumulation of adsorbate molecules onto homogeneous surface and multilayer stacking of adsorbate molecules onto heterogeneous surface, respectively. Both models reduce either directly or indirectly to linear relationships under distinct conditions [88]. The Freundlich isotherm is linear when the power constant, $n = 1.0$, a condition frequently found for adsorption at low adsorbate concentration. The Gibbs and Freundlich models are connected, while the BET isotherm reduces to Langmuir model at low concentration, implying that all isotherm models tend to predict linear phosphate adsorption at low concentrations. However, the linear model is not valid over the full range of concentrations. In other words, it cannot be employed extrapolation beyond the limits of a particular data set [88].

4.2 Adsorption kinetics

The kinetics data determine the rate at which the adsorption reaction is taking place and the possible interaction mechanisms. The kinetic models, such as pseudo-first-order, pseudo-second-order, intraparticle diffusion, and also the dynamic models such as Adam-Bohart and Thomas, have been widely used to describe the rate of phosphate adsorption in water. The kinetics could be described as physical adsorption, wherein the pore diffusion is essential when the curve fitting obeys pseudo-first-order model. In many published reports, however, the kinetics data fitted well into pseudo-second-order model, suggesting a chemically driven adsorption of phosphate. Alabi et al. [9] and Mazenner and Bensmaili [56] reported that the particle diffusion as the rate-limiting step in phosphate adsorption because the kinetics data show the best fit with intraparticle diffusion model. In a different setting of dynamic mode, Nguyen et al. [47]

described the kinetics of phosphate removal in fixed-bed column as chemical adsorption, tied-up to Adam-Bohart model.

4.3 Mechanisms for orthophosphate removal

The removal rate and capacity depend on the physicochemical characteristics of adsorbent and orthophosphate and operating conditions (pH, temperature, co-existing anions, etc.) [13, 28]. The nature of adsorbent, equilibrium, kinetic, and thermodynamic properties are important to explain the mechanisms of phosphate adsorption onto AWA. Generally, the mechanisms of phosphate adsorption can be divided into four main interactions: diffusion, ligand exchange, ion exchange, and electrostatic attraction. Due to the complex nature of adsorbent surface, an interplay of multiple mechanisms can simultaneously exist in a particular adsorption process [43, 91]. Figure 2 illustrates the mechanisms of phosphate removal onto iron-modified adsorbent.

The phosphate removal rate of AWA depends on its internal structure, crystal morphology, and the size of active molecules. Modified AWA has a hierarchical structure with a large specific surface area, exposing more adsorption sites and facilitating the degradation of orthophosphate in water. The co-active effect between metal-loaded elements and AWA plays an important role in orthophosphate adsorption [13, 92]. The loaded metal is amphoteric and therefore exhibits different properties under different conditions. When the iso-electric point between AWA and the loaded metal is less than the pH value of the orthophosphate solution, the AW adsorbent surface is positively charged and alkaline, which can attract and adsorb orthophosphate in water through electrostatic [92, 93]. Then the adsorbed phosphate could be combined with the loaded metal to form chemical

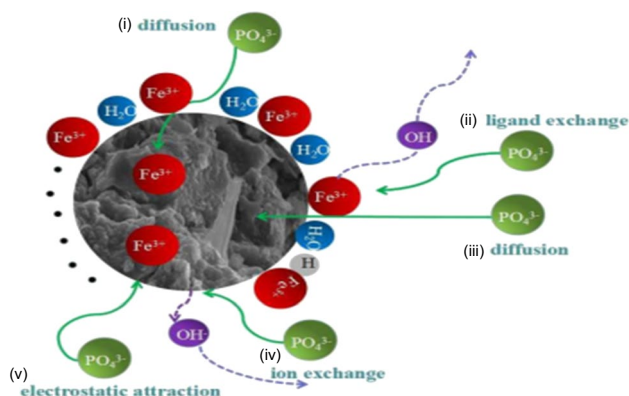


Fig. 2 Orthophosphate adsorption mechanisms: (i) diffusion from high concentration region to low concentration region; (ii) ligand exchanged between Fe^{3+} and PO_4^{2-} ; (iii) diffusion; (iv) ion exchange, i.e., displacement of OH^- by the PO_4^{2-} ; (v) electrostatic attraction between charges

adsorption [8, 92]. In addition, the three-phase synergistic effect among AWA fiber, the enhanced surface area of the adsorbent, and the adsorption site thus improve the proton transfer rate and orthophosphate adsorption rate [13, 94].

5 Regeneration of adsorbent and orthophosphate recovery

Adsorbent regeneration is the ability to restore the adsorbent to its original adsorption capacity after long-term use. A good adsorbent for phosphate removal from wastewater should not only have high adsorption capacity but should also be effortlessly restored for further use [13, 28]. There are several methods to desorb orthophosphate from spent AWA as documented in literature. Typically, the regeneration is accomplished through leaching using warm distilled water, metal salts, alkaline, or acid solutions. In addition to the acid–base regeneration method, heat treatment is also used, that is, a few minutes of heat treatment (hydrothermal or microwave radiation) on the used adsorbent [4]. Table 4 summarizes the desorption efficiency of AWA by different solvents. Often, the adsorption efficiency declines after several adsorption–desorption cycles, attributed to, the loss of adsorbent mass and active sites, and incomplete desorption of adsorbate. From Table 4, the regeneration has conducted using distilled water, NaOH, and HCl, with efficiency of 34.5–97.8%. Solvent NaOH demonstrates the effective strip of phosphate from the spent adsorbent with desorption efficiency > 87%. The use of NaOH is likely to weaken the binding and complexation interactions between phosphate and active sites, which are mainly composed of metal cations. If adsorption is carried out through chemical bonds or ion exchange or a combination of both, the desorption will be affected by stronger desorbents (such as acid or alkaline solutions). If the adsorption is by physical bonding, then the loosely bound metal ion can be easily desorbed with distilled water in most cases [78].

6 Challenges and future research directions

The current progress in valorizing agricultural wastes to remove orthophosphate from water has been deliberated. To bridge the research gaps for successful industrial applications, the challenges for prospects are as follows:

- i) The overall cost associated with the adsorption technology influences the selection in large-scale operation of phosphate removal. The cost of adsorbent itself is around 70% of the total cost. So, the low-cost adsorbent that has been proven effective to anchor phosphate in

Table 4 Desorption efficiency of AWA

Adsorbent	Solvent/heat treatment	Desorption efficiency (%)	Remark	Reference
Spent coffee ground	0.1 NaOH	24.4	Low desorption capacity	[78]
Coconut shell	Microwave irradiation (frequency = 2.45 GHz and 600 W)	77	High desorption capacity	[95]
Coconut waste	Microwave irradiation (frequency of 2.45 GHz and 1500 W)	97	High desorption capacity	[96]
Grafted saw dust	HCl	36.8	Weight loss by NaOH	[97]
	NaCl	34.5		
ZnCl ₂ treated coir pith carbon	Distilled water at pH 2–11	30 (pH 2)	Low desorption capacity	[98]
		50 (pH 11)		
		< 10 (pH 3–11)		
La(III)-loaded saponified orange waste	0.4 M HCl	85	La(III) leaked	[99]
Zr(IV)-loaded saponified orange waste	0.4 M HCl	< 40	Zr(IV) not leaked	[84]
	0.2 M NaOH	95		
Zr(IV)-loaded saponified orange waste	0.2 M NaOH	93	Zr(IV) not leaked	[100]
Zr(IV)-loaded apple peel	Distilled water at pH 12	90	Zr(IV) not leaked	[93]
Fe(III)-loaded okara (soy- bean waste)	Distilled water at pH 12, 0.25 M NaOH	> 94	Fe(III) leaked	[45]
Zr(IV)-loaded okara (soy- bean waste)	0.2 M NaOH	97.8	Zr(IV) not leaked	[47]

laboratory is a sustainable candidate in upscaling the process. It is also imperative for the isotherm and kinetics data to be validated in batch pilot-scale unit operation prior to actual industrial set-up.

- ii) Almost all phosphate adsorption studies in literature dealt with batch process. Only less than 2% of the reports talk about continuous and dynamic mode of adsorption using fixed-bed column. It is sad from the practical standpoint because the continuous process is the key to treat large volume of effluent-containing phosphate. So, more studies are needed to generate the valuable dynamic data of phosphate removal for viable upscaling and development.
- iii) Leaching is frequently encountered in the desorption of phosphate from metal-loaded adsorbent. Leaching and loss of adsorbent material during regeneration signifies the loss of adsorptive power and economic value per unit mass for subsequent adsorption cycles. Most studies are interested with desorption efficiency (recovery of phosphate), while the recovery of spent adsorbent is often ignored. Hence, the effective desorption process must be developed to fulfill both aims, i.e., to recover and reuse the adsorbent and adsorbate.
- iv) In most literature, the equilibrium of phosphate adsorption is described by linear isotherm model, which only obeys when the phosphate concentration is low. The

studies were intentionally carried out at low concentration because of inadequate adsorbent performance. However, this model is not valid for high adsorbate concentration. Thus, suitable models to describe the full range of adsorption with concentration leading to surface saturation are of utmost important to postulate the governing mechanisms of phosphate adsorption and deliver better process design.

- v) The use of some agricultural residues to remove phosphate from water cannot be underestimated. Some studies demonstrate an outstanding removal performance and outweigh that of metal-loading as the commonly perceived method to boost the capacity. This brings insight into fully capitalizing the low-cost adsorption process. However, the inherent properties of these materials which are responsible to immobilize more phosphate anions are yet to be understood, thus providing rooms for dedicated research to unlock their true potentials.

7 Conclusion

Eutrophication revolving around the presence of orthophosphate in water has long become a subject of considerable concern. The review summarizes the literature on phosphate

removal by AWA. The AW materials are always available, eco-friendly, renewable, and cheap to be used as adsorbents. The removal of phosphate by AWA is affected by surface modification strategies such as physical treatment, chemical treatment (acid and base), metal loading, and grafting. These improve the phosphate removal due to the increases in pore characteristics and surface area. The surrounding pH and coexisting ions also play some role in the removal efficiency. In any case, the performance of AWA is still excellent for cost-competitive industrial applications. Mg has been reported as the best modifying element for AWA due to its strong affinity towards phosphate. The orthophosphate adsorption by AWA is pH-dependent with maximum capacities between 8.45 and 1632 mg/g. The extremely acidic and alkaline conditions are favorable for phosphate removal. The regeneration is better performed using NaOH solution. AWA that forms strong binding with phosphate provides useful insight into the recovery of phosphate and reusability of adsorbent for large-scale applications. Research gaps and future development have been acknowledged and outlined considering the positive advancement in the phosphate removal using AWA.

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Declarations

Conflict of interest The authors declare no competing interests.

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