

MDPI

Revieu

## A Review on Lanthanum-Based Materials for Phosphate Removal

Sundarakannan Rajendran <sup>1</sup>, A. V. S. L. Sai Bharadwaj <sup>2,\*</sup>, Praveen Barmavatu <sup>3,\*</sup>, Geetha Palani <sup>1</sup>, Herri Trilaksanna <sup>4</sup>, Karthik Kannan <sup>5</sup> and Nagaraj Meenakshisundaram <sup>1</sup>

- Institute of Agricultural Engineering, Saveetha School of Engineering, Saveetha Institute of Medical and Technical Sciences, Chennai 602105, India; sundarakannan.r.sse@saveetha.com (S.R.)
- Department of Chemical Engineering, MS Ramaiah Institute of Technology, Bengaluru 560054, Karnataka, India
- Department of Mechanical Engineering, Faculty of Engineering, Universidad Tecnológica Metropolitana, Av. José Pedro Alessandri 1242, Santiago 7800003, Chile
- Department of Physics, Faculty of Science and Technology, Airlangga University, Surabaya 60115, Indonesia
- Chemical Sciences Department and the Radical Research Center, Ariel University, Ariel 40700, Israel; karthik@acsdri.com
- \* Correspondence: saibharadwaj@msrit.edu (A.V.S.L.S.B.); pbarmavatu@utem.cl (P.B.)

Abstract: In the past decade, eutrophication and phosphate recovery from surface water have become major issues. Adsorption is an effective method for phosphate removal because of its high efficiency. Even though lanthanum-based compounds are effective at removing phosphate from water, outside factors influence them. Hence, it is vital to develop and employ cost-effective innovations to fulfill ever-tougher requirements and address the issue of water contamination. Adsorption technology is highly effective in phosphate removal at concentrations from wastewater. This work briefly describes the preparation of lanthanum nano-adsorbents for the removal of phosphate efficiently in water, and phosphate adsorption on La-based adsorbents in various La forms. The work presented in this study offers an outline for future phosphate adsorption studies in La-based adsorbents, resulting in La-based materials with substantial adsorption capacity and strong regeneration capability.

Keywords: lanthanum; phosphate removal; adsorption; water treatment; nano-adsorbents



Citation: Rajendran, S.; Sai Bharadwaj, A.V.S.L.; Barmavatu, P.; Palani, G.; Trilaksanna, H.; Kannan, K.; Meenakshisundaram, N. A Review on Lanthanum-Based Materials for Phosphate Removal. *ChemEngineering* 2024, 8, 23. https://doi.org/10.3390/ chemengineering8010023

Academic Editors: Alirio Egidio Rodrigues and George Z. Papageorgiou

Received: 12 October 2023 Revised: 5 January 2024 Accepted: 1 February 2024 Published: 9 February 2024



Copyright: © 2024 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https://creativecommons.org/licenses/by/4.0/).

## 1. Introduction

Several aspects are necessary for organisms, and 93-97% of the biomass in bacteria, animals, fungi, and plants is made up of these five chemical elements. [1]. The phosphate availability in the Earth's atmosphere is unlimited. Around 180 years ago, phosphate-rich sedimentary rocks were mined for agricultural soils and fertilizers were applied [2,3]. Global reserves are expected to be drained in the next 50–100 years, with phosphate rock acting as a non-renewable source [4,5]. Finally, it is difficult to recycle phosphate that is introduced into water bodies for agricultural purposes. Wastewater discharge is rapidly increasing as industries develop. Phosphate is an important function that acts in natural ecosystems organism's growth. Large phosphorus releases into water bodies may begin, resulting in prolonged algae growth, the death of fish and plants, eutrophication, dissolved oxygen depletion, reductions in water quality, and some environmental issues [6]. In the natural environment, with an increase in phosphate content, people begin to suffer from hyperphosphatemia, or it leads to renal osteodystrophy, vitamin D metabolic disorders, and secondary hyperparathyroidism, all of which can affect the deposition of phosphate and calcium. To control water pollution, phosphorus emissions must meet certain criteria [7]. According to a literature review, the phosphate concentration value in streams and rivers must be  $0.03 \text{ mg PL}^{-1}$ . As a result, high-efficiency treatment technologies are urgently needed to alleviate aquatic ecosystem eutrophication for phosphate removal, particularly comparatively low-concentration phosphate removal technology to meet wastewater treatment requirements [8,9].

Excessive phosphate fertilizer consumption, on the other hand, has depleted phosphate stocks while also contaminating fresh water and causing eutrophication [10]. As a result, maintaining adequate phosphate levels, the most common phosphate component found in both pure and salt water, is both an ecological and societal concern [11–13]. Adsorption is a convenient and cost-effective method for elevated phosphate extraction, even at low phosphate values, and it is environmentally friendly due to lower sludge generation [14,15]. Phosphate is a well-known ingredient that is required for the flourishing of every biological species, degrading water precision and destroying the aqua cultural ecology (microalgae blooms, biodiversity disruptions, and enormous seafood deaths) [16]. Figure 1 shows the vector diagram of the phosphorus cycle in the environment.

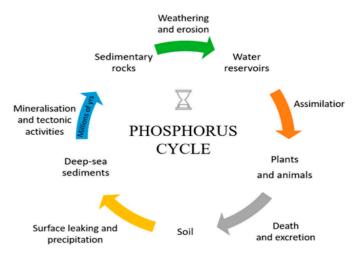


Figure 1. Phosphorus cycle in the environment (reprinted with permission from [17]).

When contrasted to conventional substrate components and La on its own, La-doped or modified adsorbent metals have advantages such as excellent adsorption energy and a broader functioning pH range. The latest breakthroughs in materials production have allowed for the tailoring of characteristics and performance through the production of nanostructured materials. Since mesoporous silicas extract just a small amount of phosphate through water, when La is added to them, they have a high phosphate adsorption capacity. Additional active elements that can be used as host substances for filling La-based adsorbents include zeolites, cellulose fibers, polymers, hydrogels, clays, and carbons [18,19]. Furthermore, lanthanum oxide (La<sub>2</sub>O<sub>3</sub>) and lanthanum hydroxide (La(OH)<sub>3</sub>) in microparticles and nanoparticles were produced and used for phosphate extraction avoiding the use of a substrate element [20]. Because of their substantial La presence and high formalization, they were projected to have enhanced adsorption capabilities than La-doped or incorporated compounds. The phosphate elimination effectiveness of differently formed La<sub>2</sub>O<sub>3</sub> microscopic particles has been observed to be shape-dependent [21]. Phosphate withdrawal was improved in hierarchical La<sub>2</sub>O<sub>3</sub> particles having bigger interfacial regions than in other microscopic particles. Optimizing the porous morphology and improving the surface domain of La<sub>2</sub>O<sub>3</sub> particles has structural and functional limitations.

For phosphate removal, lanthanum (La)-based materials are promising among phosphate metal-based adsorbents because of their chemical stability and strong affinity. Lanthanum reacts with phosphate to form insoluble lanthanum phosphate complexes. These complexes are often in the form of solid precipitates, making it easier to separate the adsorbent from the treated water. This characteristic enhances the efficiency of phosphate removal. Lanthanum-based adsorbents often display selectivity for phosphate ions over other common anions present in water. This selectivity is crucial for targeted phosphate removal without significantly affecting the concentrations of essential ions or other contaminants. Lanthanum-based adsorbents can often be regenerated, allowing for multiple uses [22]. Regeneration involves desorbing the adsorbed phosphate ions from the material,

restoring its adsorption capacity. This characteristic contributes to the economic feasibility of lanthanum-based adsorbents. Lanthanum-based adsorbents have been successfully employed in diverse water sources, including freshwater bodies, industrial effluents, and wastewater. Their versatility makes them suitable for a range of applications where phosphate removal is a priority [23]. In the 3–6 pH range, the La-phosphate complex was found to be stable, with no phosphate release or solubility products detectable. Hence, for different La materials, phosphate adsorption has been synthesized and investigated, like La(OH)<sub>3</sub>, La<sub>2</sub>O<sub>3</sub>, and La-incorporated materials of various types [24]. In reducing the concentration of phosphate to base levels, as these materials are highly efficient, some criteria still have wide use. Under acidic conditions, this exhibits high adsorption capacity, and there will be a great loss of performance in alkaline or neutral conditions when treating sewage. At present, to overcome these disadvantages with enhanced adsorption capabilities over a wider pH range, it is necessary to find new La-based adsorbents [25].

In this review, we discussed La use for the removal of phosphate as well as the current state of knowledge on the overall increase in this area, especially (1) for further research and highlight key environmental concerns that are most useful in better understanding of lanthanum for the potential impacts on ecological systems, and (2) summarizing the reported scientific work on what is known and what is not known on the application of lanthanum for the removal of phosphate. Hopefully, this review may be useful for material developers and other stakeholders who are interested in utilizing La for phosphate removal in wastewater and natural water systems.

#### 1.1. Introduction to Adsorption

For nearly a century, significant adsorption research has been conducted. Adsorption has been studied qualitatively for countless generations. This is not to the field's advantage. Instead, it demonstrates the widespread significance of adsorption as well as the difficulty of attempting to comprehend such a wide range of activities [26].

The increased density of a substance near an interface is known as adsorption. The interface can be gas—liquid, solid—liquid, solid—gas, or liquid—liquid in character, while "absorption", where the absorptive component infiltrates the absorbent, is purely an interfacial phenomenon. Every particle in the adsorbed stage has a lower coefficient compared to the core gaseous form, but due to electrostatic interplay at the boundary, it also has a lower enthalpy. This establishes the fundamental adsorption equivalence: a decrease in entropy relative to the gas phase is counterbalanced by an equal decrease in enthalpy. As a result, adsorption is an exothermic reaction. Most adsorption is enabled by beneficial interrelationships at the contact, which can be molecular or structural in composition [27].

The chemical adsorption process is a phenomenon that occurs once molecular bonds form between the adsorbent and the adsorbate. Physisorption occurs when simply physical interrelationships (such as van der Waals interactions) are involved. The phrase "sorption" is a relatively broad phrase for uncertain situations. Chemical adsorption produces considerably better adsorbent–adsorbate interrelations and is efficient at elevated temperatures, but it necessitates the use of particular adsorbate–adsorbent complexes and is rarely recoverable [28]. Adsorbents are generally employed extensively in commercial activities such as gas extraction and catalysis. Ninety percent of chemicals are used in catalysis and component production in the Universe, and homogeneous or heterogeneous catalysts can be used [29].

# 1.2. Adsorption Process—Parameters Effect pH—Solution

Workaround pH is a significant determinant in the adsorption mechanism, as it has a significant impact on the ability to bind to the adsorbate membrane. Furthermore, the pH of the solvent has a substantial effect on both the adsorbate and the adsorbent, as the substrate charge of the adsorbent changes dramatically with pH. The amount of ionization [30],

ChemEngineering **2024**, *8*, 23 4 of 16

dispersion of operational compounds on reactive regions [31], and chemical composition of the adsorbate, on the other hand, are all pH-dependent.

Furthermore, greater hydrogenation and neutralization of the adsorbent's competing exchangeable cations may promote the rate of diffusion at lower pH, resulting in a larger adsorption propensity. In addition, as pH rises into the alkaline surroundings, the oxidation process happens, prohibiting the molecules from propagating to the surface of the adsorbent [32].

At pH 2, the least metal cations sorption efficiencies were achieved, which could be due to the competing action of hydrogen ions and the occurrence of a comparatively limited number of accessible locations in the surface area of disrupted composition.

The pH of a solution plays a significant role in phosphate adsorption, influencing both the speciation of phosphate ions and the surface charge of adsorbent materials. The adsorption of phosphate is pH-dependent, and the impact of pH can be explained by considering the various forms of phosphate ions present in the solution. Phosphate exists in different chemical forms depending on the pH of the solution [33]. In natural waters, phosphate primarily exists as dihydrogen phosphate ( $H_2PO_4^-$ ) at lower pH values (acidic conditions) and as hydrogen phosphate ( $HPO_4^{2-}$ ) at higher pH values (alkaline conditions). The relative abundance of these two species is pH-dependent, and this affects their adsorption behavior. Generally,  $HPO_4^{2-}$  is more easily adsorbed than  $H_2PO_4^-$ . The electrostatic interactions between phosphate ions and the charged surfaces of adsorbents are influenced by pH. At low pH, when the surfaces of adsorbents are positively charged, there is an enhanced electrostatic attraction between the positively charged surface and the negatively charged phosphate ions ( $H_2PO_4^-$ ). Conversely, at high pH, when the surfaces become negatively charged, there is a stronger electrostatic attraction with the negatively charged phosphate ions ( $HPO_4^{2-}$ ) [34].

The optimal pH for phosphate adsorption varies depending on the specific adsorbent material. For some materials, adsorption may be more efficient under acidic conditions, while for others, it may be more favorable under alkaline conditions. It is common to conduct pH-dependent adsorption studies to identify the pH range where maximum phosphate adsorption occurs. In water treatment applications, adjusting the pH of the solution can be a strategy to optimize phosphate removal [35]. However, it is essential to consider other factors, such as the composition of the water matrix, the characteristics of the adsorbent material, and the overall treatment goals. Researchers and engineers often perform detailed studies to determine the most effective pH range for phosphate adsorption based on the specific conditions of the water being treated.

#### 2. Phosphate and La-NMs Interaction Mechanism

To develop a novel method for making La-NMs and maximize their effectiveness for real-world uses, it is imperative to analyze the interaction mechanism between La-NMs and phosphate. FTIR, XRD, and XPS are all commonly used to investigate the processes of the relationship between phosphate and La-NMs. A phosphorus and La-NM combination could be characterized by five major mechanisms: ion exchange, ligand exchange, surface outer-sphere complexation, surface inner-sphere complexation, and electrostatic attraction. Additionally, for any category of La-NMs, ligand exchange and electrostatic attraction always need to be processed. The attraction of negatively charged phosphate ions by the positively charged surface charge of La-NMs is the primary cause of the electrostatic attraction. Additionally, the phosphate ion establishes a covalent chemical bond with a La cation at the adsorbent surface, leading to the release of other potentially deciding ions like OH ions that were previously linked with the La cation. It is related to the ligand interchange and consequent inner-sphere complexity.

ChemEngineering **2024**, *8*, 23 5 of 16

## 3. Lanthanum Containing Substances for the Removal of Phosphate

#### 3.1. Characteristics for the Removal of Phosphates

Phosphates are common water pollutants, primarily originating from agricultural runoff, industrial discharges, and wastewater. Developing lanthanum composites with enhanced phosphate removal capabilities can contribute to improving water quality by effectively reducing phosphate concentrations, thereby mitigating environmental and ecological impacts. Many regions have strict regulations regarding phosphate levels in wastewater discharges [36]. Developing lanthanum composites that can selectively and efficiently remove phosphates, even at low concentrations, can help industries and municipalities meet regulatory standards for water quality [37].

Lanthanum composites with enhanced properties provide a versatile solution for water treatment applications. They can be applied across a range of water sources, from municipal water treatment plants to industrial effluents, offering a consistent and effective method for phosphate removal. Cost-effective water treatment solutions are crucial for widespread adoption, especially in regions with limited resources [38]. Developing lanthanum composites that efficiently remove phosphates at low concentrations can lead to more affordable and accessible water treatment options [39].

Novel lanthanum composites with improved characteristics may exhibit greater stability over time, ensuring long-term effectiveness in phosphate removal. Additionally, if these composites can be regenerated and reused efficiently, they contribute to the economic viability and sustainability of the water treatment process. Phosphorus is a finite resource, and the efficient removal of phosphates from wastewater allows for the recovery of phosphorus, which can be valuable for various industrial applications, including agriculture [40,41]. Developing novel lanthanum composites ensures a more sustainable and resource-efficient approach to phosphate removal. The importance of developing lanthanum composites with novel properties for selective phosphate removal lies in their potential environmental issues, compliance with regulations, conserving resources, and providing versatile and sustainable solutions for water treatment. These advancements contribute to the broader goal of ensuring clean and safe water resources for communities worldwide [42].

## 3.2. Physico-Chemical Phosphate Removal

The list of factors of physico-chemical nature includes: (i) dissolved oxygen (DO) and chemical oxygen demand (COD); (ii) pH; (iii) nutrients which include nitrate (N-NO<sub>3</sub>) and phosphate (PPO<sub>4</sub>) (added because of its influence on eutrophication); (iv) elements like aluminum ( $Al^{3+}$ ), solvent metal ( $Fe^{2+}$ ), and cadmium ( $Cd^{2+}$ ) are examples of these. A portable multiparameter analysis tool was used to evaluate the pH and DO on the site. Additional chemical characteristics such as metal alloys and micronutrients were analyzed using conventional diagnostic procedures for water and wastewater analysis. Figure 2 shows the concentration of phosphate in the environment.

ChemEngineering **2024**, *8*, 23 6 of 16

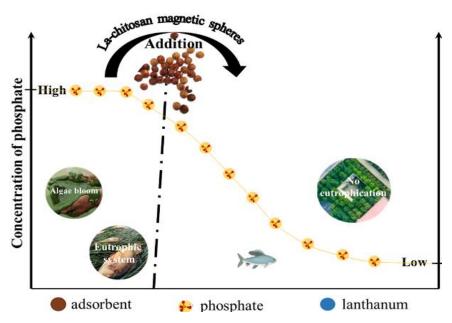


Figure 2. Concentration of phosphate (reprinted with permission from [43]).

Phosphate concentration was tested utilizing phosphate specimens and a procedure based on US norms [44,45]. The methodology has relied on the spectrophotometric determination of orange-yellow molybdo-vanado phosphoric acid formed by the interaction of orthophosphate ionic species in a sulfuric solvent with ammonium heptamolybdate and ammonium vanadate. Spectroscopy was used to detect the absorption intensities of the specimens at 410 nm [46].

All of the findings were evaluated to standardized wastewater purity standards established by the European Council Declaration [47] and Romanian regulation. Phosphate control uses a physico-chemical process for phosphate removal. These techniques are generally reliable and effective, but they are not endless [48].

## 3.3. Phosphate Adsorption Mechanism

The adsorption of phosphate, especially in environmental and water treatment applications, involves the binding of phosphate ions to the surfaces of solid materials. This process is crucial for mitigating eutrophication and controlling phosphate levels in water bodies. Several mechanisms contribute to the adsorption of phosphate onto various substrates [49].

Phosphate ions can form insoluble precipitates with certain metal cations, such as calcium, iron, and aluminum. These metal phosphates are less soluble in water and can be removed through precipitation. Phosphate adsorption can occur through the formation of surface complexes. The surface functional groups of materials, such as oxides, hydroxides, and clay minerals, interact with phosphate ions through chemical bonding, leading to adsorption. Hydrogen bonding between phosphate groups and surface functional groups can contribute to adsorption [50]. This mechanism is common on materials with oxygencontaining groups, such as silica surfaces. Phosphate ions can form complexes with metal ions on the surface of materials. These complexes may enhance adsorption by providing additional binding sites [51].

## 3.3.1. Ion Exchange

Phosphate ions can be adsorbed onto surfaces through ion exchange mechanisms. In this process, other ions on the solid surface, such as hydroxyl (OH $^-$ ) or chloride (Cl $^-$ ), are exchanged with phosphate ions from the water. The electrostatic attraction between negatively charged phosphate ions ( $H_2PO_4^-$  or  $HPO_4^{2-}$ ) and positively charged surfaces facilitates adsorption. This mechanism is particularly relevant for materials with a positive surface charge, such as iron or aluminum oxides [52].

ChemEngineering **2024**, 8, 23 7 of 16

## 3.3.2. Biological Uptake

In natural systems, living organisms, such as plants and microorganisms, can play a role in phosphate adsorption. Plants can uptake phosphate from water, and microorganisms may facilitate adsorption through various metabolic processes [53].

## 3.4. Phosphate Removal Methods

Phosphate removal by deposition involves the precipitation or deposition of phosphate ions from a solution, converting them into insoluble forms that can be separated from the water. This process is crucial for mitigating eutrophication and controlling phosphate levels in water bodies [54]. Figure 3 shows the phosphorus removal from aqueous solutions divisions.

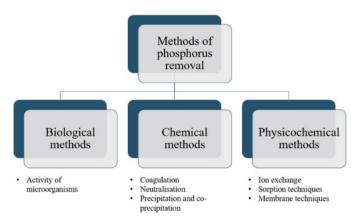


Figure 3. Phosphorus removal from aqueous solutions (reprinted with permission from [17]).

### 3.4.1. Chemical Precipitation

Phosphate ions can undergo chemical reactions with certain metal cations in the water to form insoluble precipitates. Common metal cations involved in phosphate precipitation include calcium ( $Ca^{2+}$ ), iron ( $Fe^{3+}$ ), and aluminum ( $Al^{3+}$ ). The chemical reactions involved in phosphate precipitation include the formation of metal phosphate compounds such as hydroxyapatite, calcium phosphate, iron phosphate, and aluminum phosphate [55]. These compounds are generally less soluble in water and can precipitate out.

#### 3.4.2. Adsorption and Surface Complexation

Surface interactions with solid materials play a role in phosphate deposition. Certain surfaces, such as metal oxides or hydroxides, can adsorb phosphate ions onto their surfaces. Surface complexation involves the formation of chemical complexes between phosphate ions and specific sites on the surface of the precipitating material, contributing to the overall removal mechanism [56].

#### 3.4.3. Co-Precipitation

Co-precipitation involves the simultaneous precipitation of phosphate ions along with other substances that are being precipitated. For example, when metal hydroxides or oxides are formed as precipitates, phosphate ions may co-precipitate with them [57]. This process can enhance phosphate removal efficiency as the presence of other ions or substances may provide additional sites for phosphate precipitation [58].

## 3.4.4. pH Adjustment

The pH of the solution is a critical factor in phosphate removal by deposition. Precipitation reactions are often pH-dependent, and adjusting the pH can optimize the formation of insoluble phosphate compounds [59]. For example, at higher pH values, the solubility of metal hydroxides decreases, leading to the precipitation of metal hydroxides and, in some cases, the co-precipitation of phosphate ions.

#### 3.4.5. Selective Precipitation

In some cases, specific chemicals or additives may be introduced to selectively precipitate phosphate ions. These chemicals enhance the formation of insoluble phosphate compounds while minimizing interference from other ions [60].

## 3.5. Photocatalytic Activity

The ability of lanthanum nano-adsorbents to make use of light energy to initiate chemical processes is usually related to their photocatalytic activity. During the photocatalytic mechanism process, lanthanum nano-adsorbents with photocatalytic properties often involve semiconducting materials. When exposed to light, these materials generate electron–hole pairs, initiating redox reactions on their surfaces. In the case of adsorbents, these reactions can facilitate the degradation or transformation of adsorbed contaminants. Lanthanum nano-adsorbents with photocatalytic activity are employed for the degradation of organic pollutants in water or air [61,62]. Light absorption by the lanthanum composite generates reactive oxygen species (ROS), such as hydroxyl radicals ( $\bullet$ OH), which can oxidize and break down organic compounds into harmless by-products [63].

Lanthanum nano-adsorbents with photocatalytic activity can be applied in water purification processes to remove various contaminants, including organic pollutants, microbes, and even some inorganic species. The photocatalytic reactions contribute to the overall efficacy of the adsorption process [64]. The combination of adsorption and photocatalytic degradation capabilities in lanthanum nano-adsorbents provides a synergistic effect. Adsorption helps concentrate contaminants on the material surface, and subsequent photocatalytic reactions lead to their degradation, resulting in improved overall performance. Lanthanum nano-adsorbents can exhibit selectivity in photocatalysis, targeting specific pollutants based on their chemical structure or properties. This selectivity is advantageous in applications where the removal of specific contaminants is a priority. Depending on the stability and design of the lanthanum nano-adsorbents, they may be reusable in photocatalytic applications. Regeneration processes can be employed to restore or maintain the photocatalytic activity, contributing to the sustainability of the material [65].

Photocatalytic lanthanum nano-adsorbents have potential applications in the environmental remediation of contaminated sites. The combined adsorption and photocatalytic degradation can be tailored to address specific challenges in soil or water remediation projects. Understanding and optimizing the photocatalytic activities of lanthanum nano-adsorbents involves careful consideration of material composition, structure, and synthesis methods to achieve enhanced performance for targeted applications in environmental remediation and water treatment [66].

#### 4. Metal Oxides

Because of its significant attraction among phosphorus-based ions and metal domains, hydroxides and metal oxides have been exploited to extract phosphate from aqueous systems [67]. To modify the unfavorable surface energy of many La-modified substances, a positively charged adsorbent was synthesized using Al with a high pH, pZC (point of zero charge) as the substrate component [68]. The trapped phosphate of Al complexes, which might be dissolved under an alkaline environment, was likewise preserved by this mixture.

The number of adsorptive components varied depending on the methodology of preparation and the species. The adsorption technique benefits metal hydroxides with a high surface-to-volume ratio. Furthermore, the diameter of nanoparticles affects the reactions and absorption coefficients of metals and metal oxides [69]. The pH of metal compounds is anticipated to alter dramatically when their size decreases, particularly when the size is smaller than 5 nm [70].

Titanium dioxide is a suitable semiconductor compound for application as a catalyst support and adsorbent substance because of its moderate toxicity, relatively excellent reaction, and synthetic corrosive endurance [71]. TiO<sub>2</sub> binds phosphate strongly and irreversibly, and the ratio of phosphate adsorption increases as the ion concentration

increases, suggesting a Langmuir adsorption isotherm and the development of surface interactions [72]. Nevertheless, because of the ultrafine dispersion properties of TiO<sub>2</sub> particles, they must be immobilized to facilitate response segregation [73]. For its negatively charged interface in moderate environmental pH conditions, manganese metal oxide has a larger interface region and surface responsiveness, yet it usually incorporates various materials to eliminate phosphate [74]. It was also found that nano-strong Mg(OH)<sub>2</sub> hydraulic impedance hindered its use for the adsorption of hazardous freshwater ions and organic material. Several metal oxides, like hydrous niobium oxide, that have been reported to be robust to changes in atmospheric pH and oxygen, also showed good phosphate extraction discrimination. Metal element doping performance improvement is shown in Figure 4.



Figure 4. Metal element doping performance improvement (reprinted with permission from [75]).

For phosphate adsorption metal oxides like iron oxide, steel slag, hydrous zirconium oxide zinc ferrite, magnesium oxide, and their composites have been developed. Removal capacity highly depends upon the metal oxides and chemical composition properties including number of defects, active sites, and surface area. By changing the synthesis conditions metal oxide properties can also be modified including the amount of precipitating agent, the concentration of the metal salt, the annealing temperature, and changing aging temperature. The zero-valent iron is minimized by various paths of crystal growth. By composite formation, the metal oxide adsorption capacity can be increased. For instance, hydrated zirconium oxide-based composite includes cross-linked hydrous zirconium oxide resin structures where ion and exchange of +ve charge favor the phosphate interaction which generates large adsorption capacity [76]. Each organic acid possesses its role during the adsorption phenomenon by their competing ions, blockage of the active sites at pores, and formation of covalent bonds of ammonium and hydrous zirconium oxide. In the process of good adsorption capacities, the pore structure of the material plays a major role. The mesoporous zirconium obtained from combining the different polymers generates outstanding adsorption for phosphate. The modified copper tailing after the thermal treatment signifies enhanced phosphate removal capacity. Metal oxide separation after adsorption was formerly thought to be a massive undertaking for practical applications; however, magnetic metal oxide substances usage in this area has provided new understanding to an extent, due to their ease of separation. By complex formation, the three-dimensional manganese iron oxide composite adsorbs phosphate [77]. The magnetic composites prepared simply provide efficient phosphate separation in several sectors, for example, agriculture water treatment devices and sewage water. Modified metal-based oxide displays more adsorption capacities. For instance, modified zeolite showed greater adsorption capacity towards phosphate rather than simple calcium hydroxide or zeolite. The zeolite surface becomes heterogeneous after its modification, which leads to phosphate-selective adsorption. The changed Palygorskite was used for the adsorption process of phosphate which

increases adsorption efficiency with the modifications of +ve charge, and the endothermic and spontaneous nature of phosphate uptake. The results indicate that changes in metal oxides are effective for the target pollutant to improve selective adsorption [78]. The resin with anion-exchange capacity was investigated for selective phosphate removal along with the other related pollutants. Generally, phosphate adsorption experiments using metal oxides can be carried out at a pH between 5 and 7, following a pseudo-second-order model like Langmuir in other models with a thermostat temperature of about 25  $^{\circ}$ C.

## 5. La in Phosphate Removal—Application

To summarize the last 10 years (2010–2020), some lanthanum nanomaterials that efficiently utilize water and absorb phosphate from wastewater are presented and studied in a literature review [79].

Metallic Lanthanum-Based Adsorbents—Single Lanthanum

Metallic hydroxide might be injected into multi-wall nanotubes with a patterned structural system and a large exterior area to prevent nanocrystalline particles from aggregating. It has recently been explored if lanthanum hydroxide can be sustained by carboxylated carbon nanotubes [80]. The carboxyl gathering in the nanotubes ensured the adsorbent suspension and offered binding surfaces for La(OH)<sub>3</sub> in the state of La(OH)<sub>2</sub><sup>+</sup> through combination or hydrogen interaction for the sorption of  $H_2PO_4^-$  by generating a monomeric compound [81]. Even though lanthanum immobilization reduced the pore dimension and contact region of the nanotubes, the adsorbent's highest adsorption capability was 48.02 mg P/g. In addition, the phosphate removal rate of adsorbents was strongly impacted by the combination of the metal. Although carbon substances have a significant porosity, metal disintegration and a reduced appropriate adsorption mechanism were generated by the porous type of material enabled by carbon fiber. To aid phosphate accumulation, the electrons of graphene and biochar should be reversed.

## 6. Real Environmental Sample—Application

The adsorption performance of lanthanum nanomaterials in removing phosphate ions from wastewater has proven quite difficult to study, to have the use of La in wastewater treatment and pollution rehabilitation. The adsorption capacity of  $La(OH)_3$ -modified magnetic cobalt ferric nanocomposite on phosphate in wastewater from Xiang Jiang River was studied. The water samples had an initial phosphate concentration of 1.17 mg/L. Within 20 min, the phosphate concentration started to decrease from 1.17 mg/L to 0.05 mg/L. He et al. observed that La-zeolite (La-Z) in polluted water from the lake adsorbs phosphate. This result shows that in wastewater, 2 g/L of La-Z was added, and the phosphate concentration is decreased from 5.34 mg/L to 0.032 mg/L [82].

Lanthanum nano-adsorbents have been studied and utilized for various applications due to their unique properties. Lanthanum nano-adsorbents are effective in heavy metal removal from water, acting as adsorbents to immobilize and capture contaminants such as cadmium, lead, and arsenic.

#### 6.1. Biomedical Applications

Lanthanum nano-adsorbents may be used in drug delivery systems, where their unique biocompatibility and surface properties can be used for the controlled release of medicinal substances [83].

#### 6.2. Wastewater Treatment

Lanthanum nano-adsorbents can be employed in wastewater treatment processes to remove contaminants and pollutants, contributing to the purification of industrial effluents.

## 6.3. Energy Storage—Battery Technology

Lanthanum-based nano-adsorbents may play a role in energy storage applications, like in the development of advanced capacitors and batteries [84].

#### 6.4. Environmental Remediation

Lanthanum nano-adsorbents can be applied for soil remediation, helping to mitigate the impact of heavy metal pollution in industrial and agricultural areas.

## 7. Phosphate Removal in Soil

Phosphate removal in soil and solvent systems involves complex interactions between phosphate ions, soil particles, and solvent constituents. There are two primary mechanisms at play: deposition and interfacial adsorption. Deposition refers to the process of phosphate ions settling or being deposited onto soil particles. This mechanism is influenced by various factors, including the soil composition, pH, and the presence of certain ions. The primary pathways for phosphate deposition in soil solvents include chemical precipitation, co-precipitation, ion exchange, and pH effects. Lanthanum (La) is a rare-earth element that has been studied for its potential use in soil remediation, particularly for phosphate removal [85]. The mechanisms involved in phosphate removal using lanthanum in soil solvents include both deposition and interfacial adsorption. Lanthanum can form insoluble phosphate compounds through chemical precipitation. When lanthanum is added to the soil solution, it reacts with phosphate ions to create lanthanum phosphate precipitates. These precipitates are often highly insoluble and can be removed from the soil matrix. Lanthanum can adsorb onto soil particles, creating a surface with lanthanum ions available for complexation with phosphate. This surface complexation can lead to the adsorption of phosphate ions onto the soil particles, reducing their mobility and bioavailability [86].

Lanthanum can be applied to the soil either in the form of lanthanum salts (e.g., lanthanum chloride or lanthanum nitrate) or lanthanum-containing compounds. The choice of the form depends on factors such as solubility and ease of application. The effectiveness of lanthanum in phosphate removal is often pH-dependent. pH adjustment may be necessary to optimize the precipitation and adsorption processes. Generally, lanthanum phosphate precipitation is favored under slightly alkaline conditions. Regular monitoring of soil and water conditions is essential to assess the progress of phosphate removal and ensure that lanthanum is effectively targeting phosphate ions. Analytical techniques, such as water and soil testing, can be employed to quantify phosphate concentrations. While lanthanum has been studied for its effectiveness in phosphate removal, potential environmental impacts and risks should be considered [87]. Lanthanum is a rare-earth element, and its long-term effects on soil ecosystems need careful evaluation. Compliance with environmental regulations and guidelines is crucial when using lanthanum or any other chemical for soil remediation. Approval from relevant regulatory authorities may be required. The long-term effects of lanthanum application for soil remediation are still an area of active research [88]. Studies have examined its persistence in soils and the potential for leaching into groundwater. Long-term monitoring is essential to understand the fate and transport of lanthanum over time.

#### 8. Future Aspects

The relatively low process costs of adsorption make it a preferred option even when considering much of the recent literature on the topic. To remove and recover La from industrial wastewater, research must be concentrated on using these adsorbent materials. Additionally, the materials produced must be able to extract or eliminate La selectively when common industrial metal impurities including Fe, Al, Na, K, Mg, Ca, and S are present. To selectively separate La from other minerals, research must be carried out to investigate and modify process factors such as temperature and pH.

The loss of adsorption sites caused by La extraction or the change in La species is hypothesized by some researchers to be the reason for a reduction in the adsorption

capacity of regenerated La-based adsorbents. The design of cutting-edge, sustainable green materials with higher selectivity and stability at lower costs is still highly promising and attractive, even if the adsorption technique is commonly utilized and has been established for several decades. In the upcoming years, it will be important to solve the difficulties that arise from converting lab-scale adsorption studies into experimental and industrial-scale operations [89,90]. These challenges include costs, essential adsorbent regeneration, and excessive chemical usage. To be more precise, long-term research is needed to examine La release throughout different applications, especially those with low phosphate levels. It is necessary to provide the removal of La for longer, in addition to aiding researchers in developing high-performance materials for phosphate removal. In conclusion, the selection of the most efficient remediation strategy or methods for phosphate removal in waters may be aided by material developers and water quality managers considering a wide range of societal and ethical parameters, including stakeholder perceptions, in addition to technical performance, cost, and environmental and human health considerations.

## 9. Summary

Phosphate released in large quantities into water bodies from municipal discharge, agricultural activities industrial, and mining leads to eutrophication. In order to reduce the concentration of phosphate, most developing nations have formed rules and regulations relating to the concentration of phosphorous in water. To achieve this, wastewater can be treated with chemical, physical, and biological processes. Generally, sorption is considered as an effective and attractive treatment process because of its capability to reduce phosphate to a very low level, lower waste production, ease of operation, and simplicity of design. In most waste treatment plants, biological and chemical phosphate removal methods are utilized, so sorption is becoming more attractive, with an emphasis on phosphate removal. Despite their low sorption capacities, various organic wastes and industrial wastes are low cost, and the money can be saved for disposal costs. To reduce transport costs, these materials are recommended in the areas where they are locally obtainable for use. It is important to note that the application of lanthanum for soil remediation is an area of ongoing research, and site-specific conditions will influence the effectiveness of this method.

**Author Contributions:** Conceptualization—S.R. and G.P.; methodology, G.P.; software, K.K.; validation, H.T. and P.B.; formal analysis, G.P.; investigation, N.M. and A.V.S.L.S.B.; resources, N.M. and K.K; data curation, S.R. and G.P.; writing—original draft preparation, G.P., K.K. and S.R.; writing—review and editing, H.T.; visualization, P.B.; supervision, H.T.; project administration, N.M., H.T. and P.B.; funding acquisition, P.B. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

**Conflicts of Interest:** The authors declare no conflicts of interest.

## References

1. Zhi, Y.; Zhang, C.; Hjorth, R.; Baun, A.; Duckworth, O.W.; Call, D.F.; Knappe, D.R.U.; Jones, J.L.; Grieger, K. Emerging lanthanum (III)-containing materials for phosphate removal from water: A review towards future developments. *Environ. Int.* 2020, 145, 106115. [CrossRef] [PubMed]

- 2. Behets, G.J.; Mubiana, K.V.; Lamberts, L.; Finsterle, K.; Traill, N.; Blust, R.; D'Haese, P.C. Use of lanthanum for water treatment a matter of concern? *Chemosphere* **2020**, 239, 124780. [CrossRef] [PubMed]
- 3. Wu, Y.; Li, X.; Yang, Q.; Wang, D.; Xu, Q.; Yao, F.; Chen, F.; Tao, Z.; Huang, X. Hydrated lanthanum oxide-modified diatomite as highly efficient adsorbent for low-concentration phosphate removal from secondary effluents. *J. Environ. Manag.* **2019**, 231, 370–379. [CrossRef] [PubMed]
- 4. Bezak-Mazur, E.; Stoińska, R. The importance of phosphorus in the environment—Review article. *Arch. Waste Manag. Environ. Prot.* **2013**, *15*, 33–45.
- 5. Luo, X.; Wang, X.; Bao, S.; Liu, X.; Zhang, W.; Fang, T. Adsorption of phosphate in water using one-step synthesized zirconium-loaded reduced graphene oxide. *Sci. Rep.* **2016**, *6*, 39108. [CrossRef]

6. Yoon, H.-S.; Chung, K.W.; Kim, C.-J.; Kim, J.-H.; Lee, H.-S.; Kim, S.-J.; Lee, S.-I.; Yoo, S.-J.; Lim, B.-C. Characteristics of phosphate adsorption on ferric hydroxide synthesized from a Fe<sub>2</sub>(SO<sub>4</sub>)<sup>3</sup> aqueous solution discharged from a hydrometallurgical process. *Korean J. Chem. Eng.* **2018**, 35, 470–478. [CrossRef]

- 7. Zhao, J.W.; Qi, Y.; Li, X.M.; Wang, D.B.; Luo, K.; Xu, Q.X.; Zeng, G.G. Enhanced production of short-chain fatty acid from food waste stimulated by alkyl polyglycosides and its mechanism. *Waste Manag.* **2015**, *46*, 133–139. [CrossRef]
- 8. Yin, Q.Q.; Zhang, B.D.; Wang, R.K.; Zhao, Z.H. Biochar as an adsorbent for inorganic nitrogen and phosphorus removal from water a review. *Environ. Sci. Pollut. Res.* **2017**, 24, 26297–26309. [CrossRef]
- 9. Almeelbi, T.; Bezbaruah, A. Aqueous phosphate removal using nanoscale zero-valent iron. *J. Nanopart Res.* **2012**, *14*, 197–210. [CrossRef]
- Mekonnen, M.; Hoekstra, Y. Global Anthropogenic Phosphorus Loads to Freshwater and Associated Grey Water Footprints and Water Pollution Levels: A High-Resolution Global Study. Water Resour. Res. 2017, 54, 345–358. [CrossRef]
- 11. Zengin, G.E.; Artan, N.; Orhon, D.; Satoh, H.; Mino, T. Effect of aspartate and glutamate on the fate of enhanced biological phosphorus removal process and microbial community structure. *Bioresour. Technol.* **2011**, *102*, 894–903. [CrossRef]
- 12. Li, J.; Li, B.; Huang, H.M.; Zhao, N.; Zhang, M.G.; Cao, L. Investigation into lanthanum-coated biochar obtained from urban dewatered sewage sludge for enhanced phosphate adsorption. *Sci. Total Environ.* **2020**, *714*, 136839. [CrossRef]
- 13. Angkawijaya, A.E.; Santoso, S.P.; Bundjajac, V.; Soetaredjo, F.E.; Gunarto, C.; Ayucitra, A.; Ju, Y.H.; Go, A.W.; Ismadji, S. Studies on the performance of bentonite and its composite as phosphate adsorbent and phosphate supplementation for plant. *J. Hazard. Mater.* **2020**, 399, 123130. [CrossRef]
- 14. Zou, Y.H.; Zhang, R.Y.; Wang, L.Y.; Xue, K.; Chen, J.G. Strong adsorption of phosphate from aqueous solution by zirconium-loaded Ca-montmorillonite. *Appl. Clay Sci.* **2020**, *192*, 105638. [CrossRef]
- 15. Hatami, H.; Fotovat, A.; Halajnia, A. Comparison of adsorption and desorption of phosphate on synthesized Zn-Al LDH by two methods in a simulated soil solution. *Appl. Clay Sci.* **2018**, *152*, 333–341. [CrossRef]
- 16. Peng, G.F.; Jiang, S.Q.; Wang, Y.X.; Zhang, Q.Y.; Cao, Y.; Sun, Y.Q.; Zhang, W.Q.; Wang, L.P. Synthesis of Mn/Al double oxygen biochar from dewatered sludge for enhancing phosphate removal. *J. Clean. Prod.* **2020**, 251, 119725. [CrossRef]
- 17. Wujcicki, Ł.; Kluczka, J. Recovery of Phosphate(V) Ions from Water and Wastewater Using Chitosan-Based Sorbents Modified—A Literature Review. *Int. J. Mol. Sci.* **2023**, 24, 12060. [CrossRef] [PubMed]
- 18. Huang, W.; Zhang, Y.; Li, D. Adsorptive removal of phosphate from water using mesoporous materials: A review. *J. Environ. Manag.* **2017**, 193, 470–482. [CrossRef] [PubMed]
- 19. Kong, H.; Li, Q.; Zheng, X.; Chen, P.; Zhang, G.; Huang, Z. Lanthanum modified chitosan-attapulgite composite for phosphate removal from water: Performance, mechanisms and applicability. *Int. J. Biol. Macromol.* **2023**, 224, 984–997. [CrossRef] [PubMed]
- 20. Xu, Q.; Chen, Z.; Wu, Z.; Xu, F.; Yang, D.; He, Q.; Li, G.; Chen, Y. Novel lanthanum doped biochars derived from lignocellulosic wastes for efficient phosphate removal and regeneration. *Bioresour. Technol.* **2019**, 289, 121600. [CrossRef] [PubMed]
- 21. Yang, S.; Chen, X.; Zhang, Z.; Jin, P.; Zhang, Q.; Wang, X. The removal of phosphate from aqueous solution through chemical filtration using a sponge filter. *Chem. Lett.* **2018**, *47*, 89–91. [CrossRef]
- 22. Dong, S.; Wang, Y.; Zhao, Y.; Zhou, X.; Zheng, H. La<sub>3</sub>+/La(OH)<sub>3</sub> loaded magnetic cationic hydrogel composites for phosphate removal: Effect of lanthanum species and mechanistic study. *Water Res.* **2017**, *126*, 433–441. [CrossRef]
- 23. Miao, L.; Deng, W.; Chen, X.; Gao, M.; Chen, W.; Ao, T. Selective adsorption of phosphate by carboxyl-modified activated carbon electrodes for capacitive deionization. *Water Sci. Technol.* **2021**, *84*, 1757–1773. [CrossRef] [PubMed]
- 24. Wu, B.; Fang, L.; Fortner, J.D.; Guan, X.; Lo, I.M.C. Highly efficient and selective phosphate removal from wastewater by magnetically recoverable La(OH)<sub>3</sub>/Fe<sub>3</sub>O<sub>4</sub> nanocomposites. *Water Res.* **2017**, *126*, 179–188. [CrossRef] [PubMed]
- 25. Fang, L.; Wu, B.; Chan, J.K.M.; Lo, I.M.C. Lanthanum oxide nanorods for enhanced phosphate removal from sewage: A response surface methodology study. *Chemosphere* **2018**, *192*, 209–216. [CrossRef] [PubMed]
- 26. Zhang, Q.Y.; Du, Y.X.; Luo, C.Y. Advances in researches on phosphorus immobilization by lanthanum modified bentonite in lakes and its ecological risk. *J. Lake Sci.* **2019**, *31*, 1499–1509.
- 27. Liu, J.; Wang, G.; Lu, L.; Guo, Y.; Yang, L. Facile shape-controlled synthesis of lanthanum oxide with different hierarchical micro/nanostructures for antibacterial activity based on phosphate removal. *RSC Adv.* **2017**, 7, 40965–40972. [CrossRef]
- 28. Chen, L.; Zhao, X.; Pan, B.; Zhang, W.; Hua, M.; Lv, L.; Zhang, W. Preferable removal of phosphate from water using hydrous zirconium oxide-based nanocomposite of high stability. *J. Hazard. Mater.* **2015**, *284*, 35–42. [CrossRef]
- 29. Madrakian, T.; Afkhami, A.; Ahmadi, M.; Bagheri, H. Removal of some cationic dyes from aqueous solutions using magnetic-modified multi-walled carbon nanotubes. *J. Hazard. Mater.* **2011**, *196*, 109–114. [CrossRef]
- 30. Liu, B.; Yu, Y.; Han, Q.; Lou, S.; Zhang, L.; Zhang, W. Fast and efficient phosphate removal on lanthanum-chitosan composite synthesized by controlling the amount of cross-linking agent. *Int. J. Biol. Macromol.* **2020**, 157, 247–258. [CrossRef] [PubMed]
- 31. Mittala, A.; Gupta, V.K. Adsorptive removal and recovery of the azo dye eriochrome black T. *Toxicol. Environ. Chem.* **2010**, 92, 1813–1823. [CrossRef]
- 32. Long, F.; Gong, J.-L.; Zheng, G.-M.; Chen, L.; Wang, X.-Y.; Deng, J.-H.; Niu, Q.-Y.; Zheng, H.-Y.; Zhang, X.-R. Removal of phosphate from aqueous solution by magnetic Fe-Zr binary oxide. *Chem. Eng. J.* 2011, 171, 448–455. [CrossRef]
- 33. Koilraj, P.; Sasaki, K. Selective Removal of Phosphate Using La-Porous Carbon Composites from Aqueous Solutions: Batch and Column Studies. *Chem. Eng. J.* **2017**, 317, 1059–1068. [CrossRef]

34. Yue, Q.-Y.; Wang, W.-Y.; Gao, B.-Y.; Xu, X.; Zhang, J.; Li, Q. Phosphate removal from aqueous solution by adsorption on modified giant reed. *Water Environ. Res.* **2010**, *82*, 374–381. [CrossRef]

- 35. Liu, J.; Zhou, Q.; Chen, J.; Zhang, L.; Chang, N. Phosphate adsorption on hydroxyl-iron-lanthanum doped activated carbon fiber. *Chem. Eng. J.* 2013, 215–216, 859–867. [CrossRef]
- Rout, P.R.; Bhunia, P.; Dash, R.R. A Mechanistic Approach to Evaluate the Effectiveness of Red Soil as a Natural Adsorbent for Phosphate Removal from Wastewater. Desalin. Water Treat. 2015, 54, 358–373. [CrossRef]
- 37. Omari, H.; Dehbi, A.; Lammini, A.; Abdallaoui, A. Study of the Phosphorus Adsorption on the Sediments. *J. Chem.* 2019, 2019, 2760204. [CrossRef]
- 38. Alemu, A.; Lemma, B.; Gabbiye, N.; Tadele, M.; Teferi, M. Removal of Chromium (VI) from Aqueous Solution Using Vesicular Basalt: A Potential Low Cost Wastewater Treatment System. *Heliyon* **2018**, *4*, e00682. [CrossRef]
- 39. Asere, T.G.; Mincke, S.; De Clercq, J.; Verbeken, K.; Tessema, D.A.; Fufa, F.; Stevens, C.V.; Du Laing, G. Removal of Arsenic (V) from Aqueous Solutions Using Chitosan Red Scoria and Chitosan Pumice Blends. *Int. J. Environ. Res. Public Health* **2017**, 14, 895. [CrossRef] [PubMed]
- 40. Fan, C.; Zhang, Y. Adsorption Isotherms, Kinetics and Thermodynamics of Nitrate and Phosphate in Binary Systems on a Novel Adsorbent Derived from Corn Stalks. *J. Geochem. Explor.* **2018**, *188*, 95–100. [CrossRef]
- 41. Li, H.; Ru, J.; Yin, W.; Liu, X.; Wang, J.; Zhang, W. Removal of phosphate from polluted water by lanthanum doped vesuvianite. *J. Hazard. Mater.* **2009**, *168*, 326–330. [CrossRef]
- 42. Ahmed, S.; Ashiq, M.N.; Li, D.; Tang, P.; Leroux, F.; Feng, Y. Recent Progress on Adsorption Materials for Phosphate Removal. *Recent Patents Nanotechnol.* **2019**, *13*, 3–16. [CrossRef] [PubMed]
- 43. Cheng, R.; Shen, L.-J.; Zhang, Y.-Y.; Dai, D.-Y.; Zheng, X.; Liao, L.-W.; Wang, L.; Shi, L. Enhanced Phosphate Removal from Water by Honeycomb-Like Microporous Lanthanum-Chitosan Magnetic Spheres. *Water* **2018**, *10*, 1659. [CrossRef]
- 44. Boyer, T.H.; Persaud, A.; Banerjee, P.; Palomino, P. Comparison of low-cost and engineered materials for phosphorus removal from organic-rich surface water. *Water Res.* **2011**, *45*, 4803–4814. [CrossRef] [PubMed]
- 45. Park, Y.; Gorman, C.; Ford, E. Lanthanum carbonate nanofibers for phosphorus removal from water. *J. Mater. Sci.* **2020**, *55*, 5008–5020. [CrossRef]
- 46. Tang, Q. Insight into the synthesis and adsorption mechanism of adsorbents for efficient phosphate removal: Exploration from synthesis to modification. *Chem. Eng. J.* **2022**, 442, 136147.
- 47. Cai, J.; Zhao, X.; Zhang, Y.; Zhang, Q.; Pan, B. Enhanced fluoride removal by La-doped Li/Al layered double hydroxides. *J. Colloid Interface Sci.* 2018, 509, 353–359. [CrossRef] [PubMed]
- 48. Preferable phosphate removal by nano-La(III) hydroxides modified mesoporous rice husk biochars: Role of the host pore structure and point of zero charge. *Sci. Total Environ.* **2019**, *662*, 511–520. [CrossRef] [PubMed]
- 49. Kassem, A.H.; Ayoub, G.M.; Zayyat, A.; Fijul Kabir, S.M. Advances in nanomaterials for phosphates removal from water and wastewater: A review. *Nanotechnol. Environ. Eng.* **2022**, *7*, 609–634. [CrossRef]
- 50. Akter, M.; Abdur Rahman, F.B.; Zainal Abedin, M.; Fijul Kabir, S.M. Adsorption Characteristics of Banana Peel in the Removal of Dyes from Textile Effluent. *Textiles* **2021**, *1*, 361–375. [CrossRef]
- 51. European Commission's. *European Commission Directive 98/15/EC of 27 February 1998*; amending Council Directive 91/271/EEC of May 1991 Concerning Urban Waste Water Treatment; European Commission: Brussels, Belgium, 1998.
- 52. Norms for Establishing Pollutant Load Limits of Industrial and Municipal Wastewater to Discharge into the Natural Receivers; Romanian GD 352 from 21 April 2005, which modify and complete the GD 188/2002—Appendix 3, NTPA-001/2002; Ministry of Justice: Bucharest, Romania, 2005.
- 53. Shwetharani, R.; Poojashree, A.; Balakrishna, G.R.; Jyothi, M. La activated high surface area titania float for adsorption of Pb (II) from aqueous media. *New J. Chem.* **2018**, 42, 1067–1077.
- 54. Wan, S.; Wang, S.; Li, Y.; Gao, B. Functionalizing biochar with Mg–Al and Mg–Fe layered double hydroxides for removal of phosphate from aqueous solutions. *J. Ind. Eng. Chem.* **2017**, 47, 246–253. [CrossRef]
- 55. Liao, T.; Li, T.; Su, X.; Yu, X.; Song, H.; Zhu, Y.; Zhang, Y. La(OH)3-modified magnetic pineapple biochar as novel adsorbents for efficient phosphate removal. *Bioresour. Technol.* **2018**, 263, 207–213. [CrossRef]
- 56. Drissi, R.; Mouats, C. Removal of phosphate by ion exchange resin: Kinetic and thermodynamic study. *Rasayan J. Chem.* **2018**, *3*, 1126–1132. [CrossRef]
- 57. Rezania, S.; Mojiri, A.; Park, J.; Nawrot, N.; Wojciechowska, E.; Marraiki, N.; Zaghloul, N.S.S. Removal of lead ions from wastewater using lanthanum sulfide nanoparticle decorated over magnetic graphene oxide. *Environ. Res.* **2022**, 204, 111959. [CrossRef] [PubMed]
- 58. Zhu, Z.; Huang, C.; Zhu, Y.; Wei, W.; Qin, H. A hierarchical porous adsorbent of nano-α-Fe2O3/Fe3O4 on bamboo biochar (HPA-Fe/C-B) for the removal of phosphate from water. *J. Water Process. Eng.* **2018**, 25, 96–104. [CrossRef]
- 59. Wang, Y.; Cai, F.; Guo, P.; Lei, Y.; Xi, Q.; Wang, F. Short-Time Hydrothermal Synthesis of CuBi2O4 Nanocolumn Arrays for Efficient Visible-Light Photocatalysisnanomaterials. *Nanomaterials* **2019**, *9*, 1257. [CrossRef] [PubMed]
- 60. Thakur, P.; Sharma, R.; Kumar, M.; Katyal, S.C.; Negi, N.S.; Thakur, N.; Sharma, V.; Sharma, P. Superparamagnetic La doped Mn–Zn nano ferrites: Dependence on dopant content and crystallite size Mater. *Res. Express* **2016**, *3*, 075001. [CrossRef]

61. Jiang, D.; Chu, B.; Amano, Y.; Machida, M. Removal and recovery of phosphate from water by Mg-laden biochar: Batch and column studies. *Colloids Surf. A Physicochem. Eng. Asp.* **2018**, *558*, 429–437. [CrossRef]

- 62. Asomaning, S.K. Processes and Factors Affecting Phosphorus Sorption in Soils. In *Sorption in 2020s*; IntechOpen: London, UK, 2020.
- 63. Nobaharan, K.; Novair, S.B.; ALajayer, B.; van Hullebusch, E.D. Phosphorus Removal from Wastewater: The Potential Use of Biochar and the Key Controlling Factors. *Water* **2021**, *13*, 517. [CrossRef]
- 64. Del Campillo, M.C.; van der Zee, S.; Torrent, J. Modelling long-term phosphorus leaching and changes in phosphorus fertility in excessively fertilized acid sandy soils. *Eur. J. Soil Sci.* **1999**, *50*, 391–399. [CrossRef]
- 65. Mocwana, M.L.; Mokoena, P.P.; Mbule, P.S.; Beas, I.N.; Kabongo, G.L.; Ogugua, S.N.; Tshabalala, T.E. Photocatalytic Degradation of Methylene Blue and Ortho-Toluidine Blue: Activity of Lanthanum Composites La<sub>x</sub>MO<sub>y</sub> (M: Fe, Co, Ni). *Catalysts* **2022**, *12*, 1313. [CrossRef]
- 66. Nir, O.; Sengpiel, R.; Wessling, M. Closing the cycle: Phosphorus removal and recovery from diluted effluents using acid resistive membranes. *Chem. Eng. J.* **2018**, *346*, 640–648. [CrossRef]
- 67. Sato, S. Comerford, N.B. Influence of soil pH on inorganic phosphorus sorption and desorption in a humid Brazilian. *Ultisol. Rev. Bras. Ciênc. Solo* **2005**, *29*, 685–694. [CrossRef]
- 68. Jung, K.W.; Ahn, K.H. Fabrication of porosity-enhanced MgO/biochar for removal of phosphate from aqueous solution: Application of a novel combined electrochemical modification method. *Bioresour. Technol.* **2016**, 200, 1029–1032. [CrossRef]
- 69. Yang, F.; Zhang, S.; Sun, Y.; Tsang, D.C.; Cheng, K.; Ok, Y.S. Assembling biochar with various layered double hydroxides for enhancement of phosphorus recovery. *J. Hazard. Mater.* **2019**, *365*, *665–673*. [CrossRef]
- 70. Huang, H.; Liu, J.; Zhang, P.; Zhang, D.; Gao, F. Investigation on the simultaneous removal of fluoride, ammonia nitrogen and phosphate from semiconductor wastewater using chemical precipitation. *Chem. Eng. J.* **2017**, 307, 696–706. [CrossRef]
- 71. Jiang, Y.H.; Li, A.Y.; Deng, H.; Ye, C.H.; Wu, Y.Q.; Linmu, Y.D.; Hang, H.L. Characteristics of nitrogen and phosphorus adsorption by Mg-loaded biochar from different feedstocks. *Bioresour. Technol.* **2019**, 276, 183–189. [CrossRef]
- 72. Kanwar, J.S.; Grewal, J.S. Phosphorus fixation in indian soils: A review. Environ. Sci. 1971, 1–50.
- 73. Zhang, Z.; Yan, L.; Yu, H.; Yan, T.; Li, X. Adsorption of phosphate from aqueous solution by vegetable biochar/layered double oxides: Fast removal and mechanistic studies. *Bioresour. Technol.* **2019**, *284*, 65–71. [CrossRef] [PubMed]
- 74. Antunes, E.; Jacob, M.V.; Brodie, G.; Schneider, P.A. kinetics and mechanism analysis of phosphorus recovery from aqueous solution by calcium-rich biochar produced from biosolids via microwave pyrolysis. *J. Environ. Chem. Eng.* **2018**, *6*, 395–403. [CrossRef]
- 75. Cheng, R.; Xia, J.; Wen, J.; Xu, P.; Zheng, X. Nano Metal-Containing Photocatalysts for the Removal of Volatile Organic Compounds: Doping, Performance, and Mechanisms. *Nanomaterials* **2022**, *12*, 1335. [CrossRef] [PubMed]
- 76. Wang, F.; Zhang, M.; Sha, W.; Wang, Y.; Hao, H.; Dou, Y.; Li, Y. Sorption Behavior and Mechanisms of Organic Contaminants to Nano and Microplastics. *Molecule* **2020**, *25*, 1827. [CrossRef] [PubMed]
- 77. Haddad, K.; Jellali, S.; Jeguirim, M.; Trabelsi, A.B.H.; Limousy, L. Investigations on phosphorus recovery from aqueous solutions by biochars derived from magnesium-pretreated cypress sawdust. *J. Environ. Manag.* **2018**, 216, 305–314. [CrossRef] [PubMed]
- 78. Li, J.; Zhang, K.; Zhang, H. Adsorption of antibiotics on microplastics. Environ. Pollut. 2018, 237, 460–467. [CrossRef] [PubMed]
- 79. Xu, B.; Liu, F.; Brookes, P.C.; Xu, J. Microplastics play a minor role in tetracycline sorption in the presence of dissolved organic matter. *Environ. Pollut.* **2018**, 240, 87–94. [CrossRef]
- 80. Zhang, H.; Wang, J.; Zhou, B.; Zhou, Y.; Dai, Z.; Zhou, Q.; Chriestie, P.; Luo, Y. Enhanced adsorption of oxytetracycline to weathered microplastic polystyrene: Kinetics, isotherms and influencing factors. *Environ. Pollut.* 2018, 243, 1550–1557. [CrossRef]
- 81. Guo, X.; Pang, J.; Chen, S.; Jia, H. Sorption properties of tylosin on four different microplastics. *Chemosphere* **2018**, 209, 240–245. [CrossRef]
- 82. Xu, B.; Liu, F.; Brookes, P.C.; Xu, J. The sorption kinetics and isotherms of sulfamethoxazole with polyethylene microplastics. *Mar. Pollut. Bull.* **2018**, *131*, 191–196. [CrossRef]
- 83. Wu, C.; Zhang, K.; Huang, X.; Liu, J. Sorption of pharmaceuticals and personal care products to polyethylene debris. *Environ. Sci. Pollut. Res.* **2016**, 23, 8819–8826. [CrossRef]
- 84. Razanajatovo, R.; Ding, J.; Zhang, S.; Jiang, H.; Zou, H. Sorption and desorption of selected pharmaceuticals by polyethylene microplastics. *Mar. Pollut. Bull.* **2018**, *136*, 516–523. [CrossRef] [PubMed]
- 85. Wang, W.; Wang, J. Comparative evaluation of sorption kinetics and isotherms of pyrene onto microplastics. *Chemosphere* **2018**, 193, 567–573. [CrossRef] [PubMed]
- 86. Wang, W.; Wang, J. Different partition of polycyclic aromatic hydrocarbon on environmental particulates in freshwater: Microplastics in comparison to natural sediment. *Ecotoxicol. Environ. Saf.* **2018**, *147*, 648–655. [CrossRef] [PubMed]
- 87. Teuten, E.L.; Rowland, S.J.; Galloway, T.S.; Thompson, R.C. Potential for plastics to transport hydrophobic contaminants. *Environ. Sci. Technol.* **2007**, *41*, 7759–7764. [CrossRef]
- 88. Fang, C.; Zhang, T.; Li, P.; Jiang, R.; Wu, S.; Nie, H.; Wang, Y. Phosphorus recovery from biogas fermentation liquid by Ca–Mg loaded biochar. *J. Environ. Sci.* **2015**, 29, 106–114. [CrossRef]

89. Zeytuncu, B.; Akman, S.; Yucel, O.; Kahraman, M. Synthesis and adsorption application of in situ photo-cross-linked electrospun poly(vinyl alcohol)-based nanofiber membranes. *Water Air Soil Pollut*. **2015**, 226, 173. [CrossRef]

90. Liu, F.; Zuo, J.; Chi, T.; Wang, P.; Yang, B. Removing phosphorus from aqueous solutions by using iron-modified corn straw biochar. *Front. Environ. Sci. Eng.* **2015**, *9*, 1066–1075.

**Disclaimer/Publisher's Note:** The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.