

## A review of adsorption techniques for removal of phosphates from wastewater

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### ABSTRACT

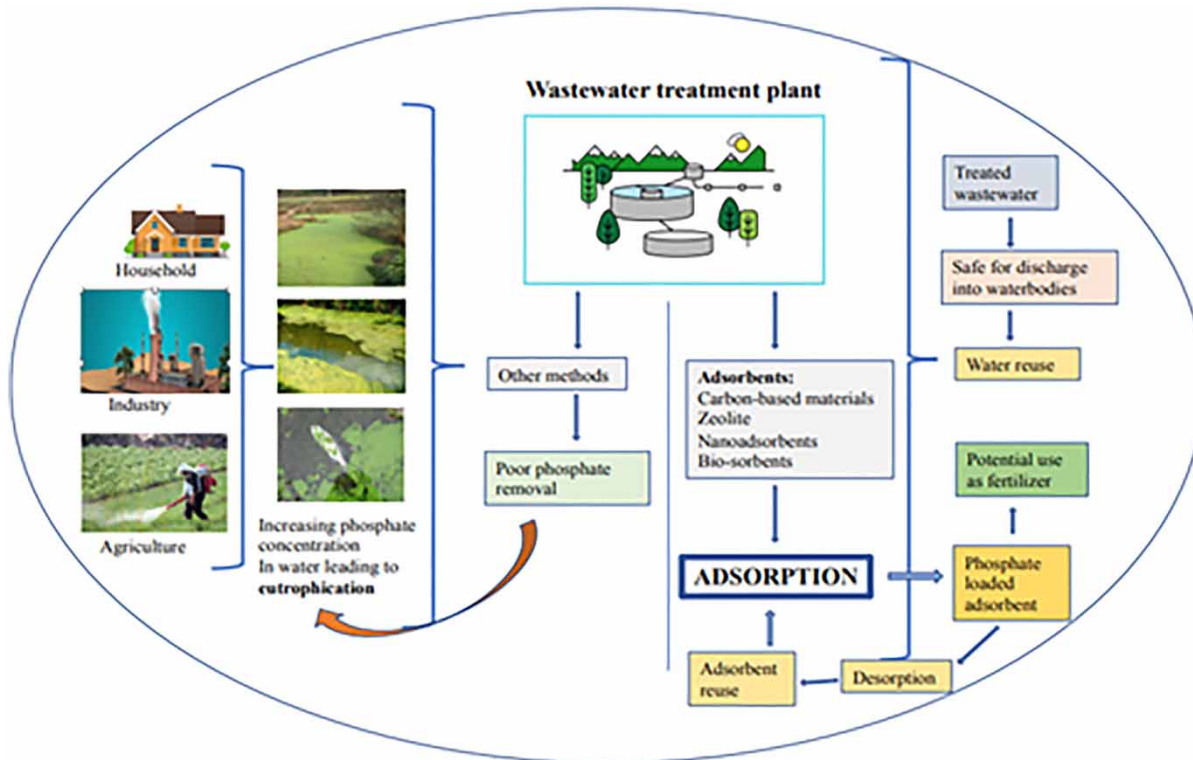
Phosphate is considered the main cause of eutrophication and has received considerable attention recently. Several methods have been used for removal of phosphates in water and these include biological treatment, membrane filtration processes, chemical precipitation, and adsorption. Adsorption technology is highly effective in the removal of phosphate from wastewater even at low phosphate concentrations. Nanomaterials/nanoparticles, carbon-based materials (activated carbon and biochar), and their composites have been widely employed for the adsorptive removal and recovery of phosphate from wastewater due to their exceptional properties such as high surface area and high phosphate adsorption properties. This article is a review of the recently reported literature in the field of nanotechnology and activated carbon for the adsorption of phosphate from wastewater. Highlights of the adsorption mechanisms, adsorption behaviour, experimental parameters, effects of co-existing ions, and adsorbent modifications are also discussed.

**Key words:** activated carbon, adsorption, eutrophication, nanoparticles, phosphates, water treatment

### HIGHLIGHTS

- This review summarizes the removal of phosphate from wastewater using adsorption techniques.
- Removal of phosphates from wastewater using adsorbents and their modification with nanoparticles is described.
- Highlights of parameters affecting the rate of adsorption is given.
- Adsorption mechanisms and reusability of adsorbents is presented.
- Nanotechnology approach in phosphate removal is discussed.

## GRAPHICAL ABSTRACT



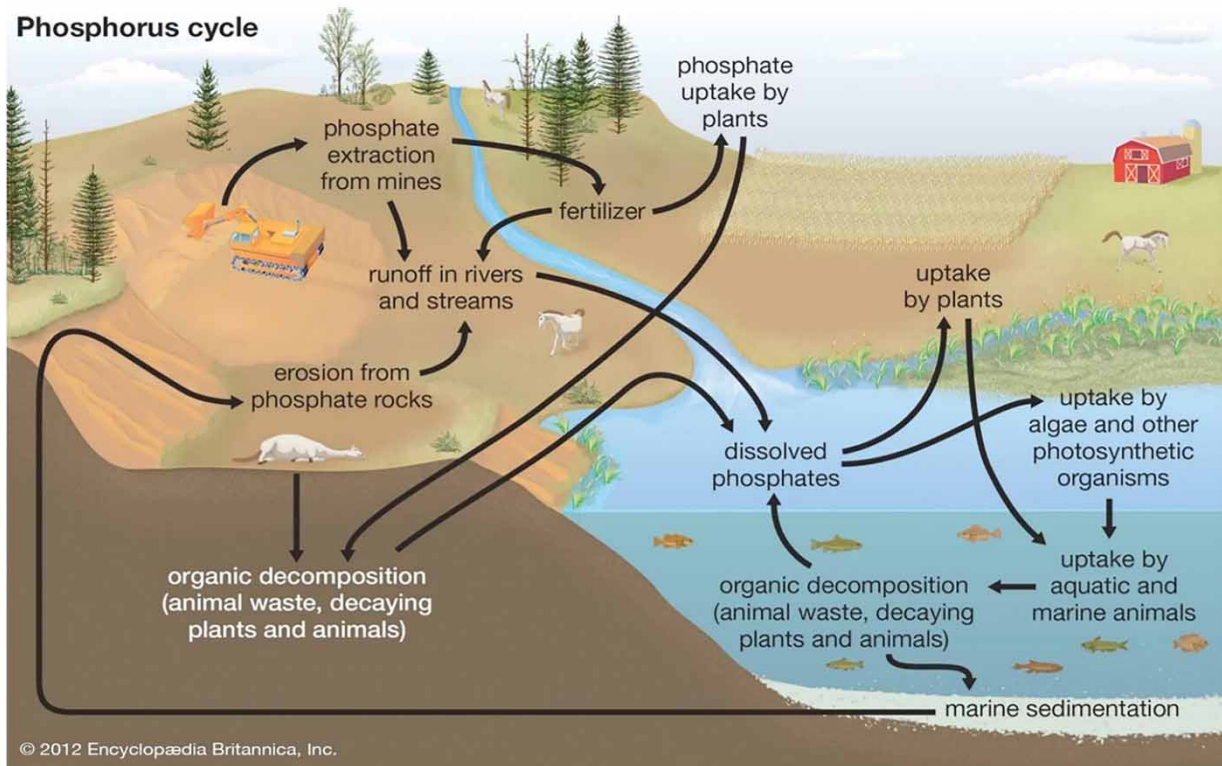
## 1. INTRODUCTION

## 1.1. Phosphorus and the environment

Phosphorus is an essential element for all forms of life, a key supplier to the high-energy compound Adenosine triphosphate (ATP), and a vital component of deoxyribonucleic acid (DNA) (Naushad *et al.* 2018; Alewell *et al.* 2020; Issaian & Reyes 2020). Phosphorus plays a vital role as an essential element for the growth of plants and algae (Khodadadi *et al.* 2017). It exists as phosphate ions in organophosphorus pesticides, rocks and minerals, domestic wastewater, industrial discharge, and run-off from fertilizer in agriculture (Bunce *et al.* 2018; Kumar *et al.* 2018; Samreen & Kausar 2019; Nguyen *et al.* 2020; Reddy *et al.* 2020; Bektaş *et al.* 2021). Once in the environment, phosphate ions find their way into water bodies via soil erosion, weathering of rocks, as well as faecal material from animals and wildlife. The major sources that have increased the presence of phosphate in water resources are agricultural run-off and untreated sewage from households and industries (Curran 2015; Rashid *et al.* 2017; Almanassra *et al.* 2021a; Ownby *et al.* 2021).

## 1.2. The phosphorus cycle

The transport and uptake of phosphorus in the environment have been well documented in the literature and are illustrated in Figure 1. The phosphorus cycle is an important process on earth. Phosphorus occurs naturally in mineral deposits such as rocks. The mining of phosphate rock and the application of commercial fertilizers have increased the loss of phosphorus from terrestrial ecosystems to freshwaters and coastal zones (Yuan *et al.* 2018). During the weathering of rocks, phosphorus is released naturally as phosphate ions which are soluble in water, thus breaking down the mineralized phosphate compounds. The dissolved phosphates either can sink into the soil and be taken up by growing plants or leach into water bodies and be taken up by algae and other photosynthetic organisms. The plants and animals return dissolved phosphate into the cycle through excretion and after death, organic decomposers transform the organic phosphorus compounds into inorganic forms.



**Figure 1** | The phosphorus cycle showing the transport (input and uptake) of phosphorus between the terrestrial and aquatic ecosystems (Source: Encyclopedia Britannica, available from: <https://www.britannica.com/science/phosphorus-cycle> (accessed 5 July 2022).

Phosphorus in wastewater exists in three forms: orthophosphate, polyphosphate and organically bound phosphate which contains phosphorus in different chemical forms. Orthophosphate forms are produced through natural processes, but the major anthropogenic sources include untreated or partially treated sewage, agricultural runoff, and fertilizers applied on farms (Oram 2009). The organically bound phosphate is the phosphate that is tied up in plant tissue, solid wastes, or other organic materials, and they become converted to orthophosphate after decomposition (Oram 2009). In fertilized soils, the phosphates which are not utilized by plants are lost from the soil and enter into waterbodies through leaching and run-off (Filippelli 2009).

The summary of geological processes of the phosphorus cycle involves the weathering of phosphorus minerals or runoff from phosphate mines into rivers. This is then taken up by plants and microbes in the aquatic environment as well as the animals that eat these plants for growth. The phosphorus is returned to the soil through excretion by the animals and by the decomposition of plants. This process repeats itself and over time, some phosphorus is lost to the water where it becomes reincorporated in sedimentary rocks after a long time (Jupp *et al.* 2021). Phosphorus compounds also accumulate in soils and sediments causing the continuous release of phosphorus into the water which has a long-term negative impact on the aquatic environment (Yuan *et al.* 2018). The excessive phosphate loss from land causes eutrophication of waterbodies which manifests in algal blooms and consequently water quality degradation and fish deaths (Yuan *et al.* 2018).

### 1.3. Effects of eutrophication

Excessive discharge of phosphates in the aquatic environment results in the massive growth of algae and other aquatic plants in aquatic ecosystems and may cause eutrophication (Derco *et al.* 2016; Naushad *et al.* 2018; Almanassra *et al.* 2021a; Cegan *et al.* 2021; Verma & Nadagouda 2021). Eutrophication brings about the deterioration of water quality, depletion of dissolved oxygen, and loss of aquatic biodiversity (Hampton *et al.* 2018). According to the United States Environmental Protection Agency (USEPA), phosphate concentration above the limit of 0.025 mg/L can cause algal blooms resulting from eutrophication (Akram *et al.* 2021). The production of harmful algal blooms causes the accumulation of cyanobacteria which forms mats

that cover the water (Watson *et al.* 2015). Increased photosynthesis in the presence of sunlight by these cyanobacteria leads to high production of oxygen which can cause these mats to break and float on the surface of the water posing serious health risks (such as gastrointestinal and dermatological diseases) and aquatic health (fish deaths) (Davis & Shaw 2009; Kudela *et al.* 2015; Naushad *et al.* 2018; Le Moal *et al.* 2019). Cyanobacteria or HAB-causing organisms produce different toxins that have adverse effects on humans and domestic animals such as acute diarrhoea, skin irritation, liver damage, and neurotoxicity (World Health Organization 2020). Other health risks of these toxins are observed by swimming and other activities in water bodies, drinking or consumption of tissues or dietary supplements that have accumulated the toxins (Hwang 2020).

Hepatotoxin microcystin (MCs) is the most commonly reported cyanobacterial toxin produced by freshwater cyanobacteria and is found in higher concentrations than other toxins (Dittmann *et al.* 2013). The consumption of aquatic animals containing MCs poses great risks to humans because they can bioaccumulate in aquatic animals (tissues of some fish) and the toxins are transferred through the food web to higher trophic levels including humans (Semyalo *et al.* 2010). Most of the problems of MCs are worsened because it is concentrated by boiling and is also resistant to chemical hydrolysis or oxidation at near-neutral pH, thus increasing their risk in humans (Lone *et al.* 2015). The most important target organ of MCs is the liver although it affects the heart, kidney, nervous system, and gastrointestinal tract, and sometimes accumulates in the gonads of invertebrates. Intestinal damage is directly linked to MCs because the digestion and absorption of nutrients take place in the intestine and the symptoms are similar to food poisoning. MCs can disrupt gastrointestinal barrier function and also inhibit the secretion of digestive enzymes in the gastrointestinal tract. MCs have also been found to inhibit the release of inflammatory cytokines, which affects the expression of immune related genes that are found in the intestine (Wu *et al.* 2018; Kubickova *et al.* 2019). Higher incidences of colorectal cancers have also been linked to the consumption of water from rivers containing a significant amount of microcystins (Koto *et al.* 2022).

Furthermore, the presence of algae in water reservoirs may lead to the blockage of turbines and water pipes, thus affecting power generation and transportation (Almanassra *et al.* 2021a). The available literature has focused on the removal of phosphorus and other nutrients in the aquatic system to ensure that eutrophication is prevented (Qiu *et al.* 2019; Lin *et al.* 2021), thus the need to develop efficient removal technologies of phosphate ions from wastewater before they are discharged into water bodies. Figure 2 illustrates the impact of phosphates in water on the environment.

#### 1.4. Phosphate removal methods

Wastewater treatment technologies involve the physical, chemical and biological removal of pollutants. In wastewater treatment plants, these processes are organized into some major steps referred to as primary, secondary, and tertiary treatments



**Figure 2** | Algal bloom caused by phosphorus pollution of water (Source: Wikipedia Contributors 2022, The Free Encyclopedia. Available from: <https://en.wikipedia.org/w/index.php?title=Eutrophication&oldid=1094544986> (accessed 4 July 2022).

(Nnaji *et al.* 2018). Conventionally, primary wastewater treatment typically focuses on the physical separation of solid particles which can either float or easily settle out by gravity (sedimentation). The secondary treatment is concerned with the removal of biochemical oxygen demand (BOD) and chemical oxygen demand (COD) through the process of aeration and filtration. This is to further remove residual biodegradable organic matter and suspended solids from the wastewater before passing it to the next stage. These processes are less efficient for the removal of nutrients (nitrogen and phosphorus) leading to the release of high concentrations of phosphorus, nitrates, and other ions into the aquatic environment which leads to eutrophication (Nnaji *et al.* 2018). These methods also result in the excessive accumulation of large amounts of sludge whose further processing results in the high cost of wastewater treatment (Cepan *et al.* 2021). The removal of nutrients and other suspended organics is best achieved by a tertiary treatment which is more advanced.

Phosphorus removal from wastewater can be achieved through enhanced biological uptake (Klein *et al.* 2020), ion exchange (Bektaş *et al.* 2021), chemical precipitation (Rajaniemi *et al.* 2021), and adsorption (Vikrant *et al.* 2018; Sun *et al.* 2020). Biological processes of phosphate removal have been applied in wastewater treatment, yet these methods face some challenges, therefore leaving the phosphorus content of pre-treated water high above standard regulated limits (Ruzhitskaya & Gogina 2017). An example of this process is enhanced biological phosphorus removal (EBPR) which polymerizes phosphate into polyphosphate by utilizing polyphosphate-accumulating organisms (Rizzello & Pompa 2014; Stokholm-Bjerregaard *et al.* 2017). However, several environmental factors and the recovery of micro-organisms from the treated effluents requires high capital investment (Kamika *et al.* 2014).

The ion exchange technologies can selectively remove phosphate from the solution but this technique is difficult to operate at a low concentration of phosphates (Bunce *et al.* 2018). This has attracted attention to the application of chemical precipitation and adsorption methods. However, chemical precipitation methods are costly because large amounts of sludge are generated which must be properly disposed of. The separation of chemically bonded phosphorus can be difficult, thus efficient recovery of phosphates for future use becomes impossible or requires sophisticated separation techniques (Bunce *et al.* 2018). Also, purchasing, transporting, and storage of chemical precipitants can be expensive (Lalley *et al.* 2016). In this regard, researchers have shifted to an effective, reliable, and sustainable alternative known as adsorption technology. A summary of the wastewater treatment technologies used in phosphate removal is presented (Table 1).

**Table 1** | Summary of wastewater treatment technologies used in phosphate removal, advantages, and limitations

Methods of phosphate removal	Advantages	Limitations
Chemical precipitation	Easy technique, Reliable process of phosphate removal Solids residuals are removed by settling under gravity or filtration	Increase the total dissolved constituents of the sludge production Separation of chemically bonded phosphate may be difficult. This reduces the possibility of phosphate recovery Cannot remove phosphate at low concentrations
Ion exchange	Offers simultaneous removal and recovery of phosphate Can selectively remove phosphate in the presence of other ions	Cannot remove a low amount of phosphorus. Requires chemicals that may be expensive for the regeneration of the media
Biological phosphate removal	Cost-effective and environmentally sustainable	Requires skilled operators Fluctuating performance of microorganisms
Algae-based treatments	Algae take up phosphate as orthophosphate and store it as polyphosphate for growth. High level of nutrient removal	Separation of solids from biofilms sloughing requires high-cost processes such as centrifugation or filtration
Adsorption	Fast process Low operational cost Effective removal of phosphate at low concentration Recovery of phosphate and reuse of adsorbent	The phosphate binding capacity of the adsorbent may reach saturation and the adsorbent will need to be replaced Effect of co-existing ions

#### 1.4.1. Adsorption

Owing to the significant drawbacks of existing methods of phosphate removal mentioned above, adsorption is a suitable alternative for phosphate removal from wastewater. Adsorption technology is unique because it offers so many advantages such as low cost, selectivity, effective removal of phosphate from water even at low concentrations, ease of operation, simple design, high capacity, and the prospect of producing low amounts of by-products (Xie *et al.* 2017; Mohammadi *et al.* 2019; Mekonnen *et al.* 2021). The need to remove nutrients (e.g., phosphorus and nitrogen) beyond the capacities of conventional wastewater treatment methods has led to the discovery of more advanced and efficient wastewater treatment processes. Adsorption is a surface phenomenon and it involves the deposition of atoms or molecules on the surface of a material. It is simply the accumulation of adsorbate (pollutants) in the wastewater onto the surface of the adsorbent (Goldberg 2013). This accumulation of the adsorbate on the adsorbent occurs at the interface of the adsorbent thus, forming a two-dimensional structure (Goldberg 2013). This depends on the adsorbent properties like the surface charge, surface area and surface functionality.

Adsorption is also preferred compared to other phosphorus removal methods because of its high efficiency and the possibility of regenerating the adsorbents as well as the recovery of the adsorbate (Almanassra *et al.* 2021a). This makes it suitable for recovering and recycling phosphates from wastewater effluents which can be further used in different applications such as the production of fertilizer for crop improvement in agriculture (Kamika *et al.* 2014; Almanassra *et al.* 2021a). It is very important to highlight that phosphorus is a non-renewable resource and cannot be replaced by other resources. In response to this, several researchers have investigated a low-cost, effective, renewable group of materials (adsorbents) with a large surface area for the removal and recovery of phosphates from wastewater.

#### 1.4.2. Adsorbents used in phosphate removal

Adsorption is the most promising method that employs a wide range of materials (adsorbents) with high efficiency in removing pollutants from wastewater. The suitability of an adsorbent in pollutant removal depends on the properties such as high selectivity, high adsorption capacity, low cost, high stability, and long life (Ghaedi 2021). Different adsorbents have their unique properties which are a function of their active surface, pore diameter, pore distribution, and surface functional group (Ghaedi 2021). Most adsorbents, especially nano-adsorbents, are recyclable thereby making the adsorbed pollutants easily removed from the surface of the nano-adsorbents (Nnaji *et al.* 2018). Nano-adsorbents are a class of nano-sized particles with a strong affinity for contaminants and are synthesized from organic or inorganic materials. Their strong affinity for pollutants is due to their unique characteristics such as small size, catalytic potential, high reactivity and high surface energy (Oghyanous 2022). The use of nano-adsorbents for the removal of phosphates in water has also attracted great attention due to their smaller particle sizes which increase the adsorption capacity of the adsorbents.

Several adsorbents have been used for phosphate removal from water. They include; aluminium-modified biochar (Yin *et al.* 2018), aluminium-doped magnetic nanoparticles (Xu *et al.* 2017), laterite soils, and black cotton soil (Reddy *et al.* 2020). Several materials, e.g. carboxymethyl konjac glucomannan loaded with lanthanum (Zhang *et al.* 2018), silver nanoparticles (AgNPs) (Trinh *et al.* 2020), silver nanoparticles-loaded activated carbon derived from tea residue (AgNP-TAC) (Nguyen *et al.* 2020), Ca-layered double hydroxides (Xu *et al.* 2014), and Mg/Al layered double hydroxides (Novillo *et al.* 2014), have also been studied.

The aluminium-doped magnetic nanoparticles showed an adsorption capacity of 102 mg/g with selectivity for phosphate in the presence of other co-existing ions (Xu *et al.* 2017). Carboxymethyl konjac glucomannan loaded with lanthanum showed an excellent adsorption capacity of 16.06 mg/g at pH 4 for the adsorption of phosphate from slaughterhouse wastewater (Zhang *et al.* 2018). Laterite soils and black cotton soils showed removal efficiency of 86% at the optimum contact time, 66%, and 70% at optimum adsorbent dosages. Gu *et al.* (2018) reported the maximum adsorption capacity for the removal of phosphate from wastewater using immobilized lanthanum (III) onto 1,6-hexamethylenediamine-functionalized copper ferrite as 32.59 mg/g. The authors observed that the adsorbent showed good selectivity for the phosphate ion in the presence of co-existing ions.

In a related study, Khodadadi *et al.* (2017) reported maximum phosphate adsorption efficiency of 100% at pH 2 when iron nanomagnetic particle coated with powder-activated carbon was used for removal. Furthermore, Issaian & Reyes Cuellar (2020) reported phosphate removal efficiencies in synthetic wastewater and river water of 52.7 and 58.7% respectively when Iron/Cobalt chitosan modified nanoparticles were used as adsorbents. Capan *et al.* (2021) carried out comparative research on the adsorption performances of five different adsorbents (magnetite, cobalt ferrite, titanium dioxide, zinc

oxide, zeolite) on phosphate removal from aqueous solution. The result obtained showed that the adsorption efficiency of the materials in ascending order was: zinc oxide 51%, titanium dioxide 71%, cobalt ferrite 80%, magnetite 88%, and mordenite zeolite 96%. This result showed the high efficiency of mordenite-zeolite and magnetic materials in the recovery of phosphate from an aqueous solution. [Jung \*et al.\* \(2017\)](#) reported a maximum adsorption capacity of 163.02 mg/g of phosphate and removal efficiency of 80.4% at pH 3 when magnesium ferrite ( $\text{MgFe}_2\text{O}_4$ )/biochar magnetic composite was used as an adsorbent. This suggests that modification of biochar by the introduction of  $\text{MgFe}_2\text{O}_4$  onto its surface can enhance the removal of phosphate from an aqueous solution. Another study by [Banu \*et al.\* \(2021\)](#) reported phosphate adsorption efficiency of 138.40 and 142.95 mg/g when zirconium-encapsulated chitosan quaternized beads were used for the adsorptive removal of nitrate and phosphate from aqueous solution. [Wu \*et al.\* \(2019\)](#) carried out the simultaneous removal of phosphate and nitrate from wastewater using organic-modified aluminium-manganese bimetal oxide. The authors reported the adsorption capacity of phosphate as 33.16 mg/g. The adsorption capacity of silver nanoparticles on phosphate was investigated by [Trinh \*et al.\* \(2020\)](#), and a maximum removal capacity of 156.12 mg/g was recorded which shows that silver nanoparticles (AgNPs) are a potential adsorbent for the removal of phosphate from aqueous solution. [Mekonnen \*et al.\* \(2021\)](#) carried out an adsorption experiment using waste coal and the maximum removal efficiency was 79% which signifies that waste coal is a possible adsorbent for phosphate removal from wastewater.

Activated carbon is mostly applied in water treatment, solvent recovery, air treatment, and as a decolorizing agent. It can also be used as catalyst support where a catalytic reaction is involved.

Activated carbon is a processed carbon-rich material that has attracted substantial consideration as an adsorbent due to its unique properties such as high surface area, high porosity, availability of functional groups (O – H, C – H, C – O, C = O, C = C,  $\text{COO}^-$ ) that enhance its ability to remove organic and inorganic pollutants from the solution. Activated carbon is prepared in different forms based on the application such as powdered activated carbon, granular activated carbon, and activated carbon fibres. The generation of porosity, surface area, and functional groups depends on the synthesis and activation methods as well as the sources of activated carbon. However, due to the negative surface charge, it shows low adsorption towards negatively charged phosphate ions ([Almanassra \*et al.\* 2021b](#)). The effectiveness of activated carbon in the adsorption of different pollutants depends on the modification which is promising owing to the increased availability of active sites on the activated carbon.

#### 1.4.3. Synthesis and modification of adsorbents used in phosphate removal

Different materials can be used as adsorbents for the removal of phosphate from wastewater. Extensive research is being carried out on the synthesis and characterization of such materials to find adsorbents with the best physical and chemical properties that suit the removal of phosphate from wastewater. Knowledge of this provides researchers with information on the adsorption capacity, removal efficiency and mechanism of phosphate removal by such adsorbents. The methods used in synthesizing and modifying some of the adsorbents used in phosphate removal from wastewater are highlighted below.

In the study of [Zhou \*et al.\* \(2012\)](#), ferric hydroxide was incorporated into activated carbon fibre using the sol-gel method as an effective method for the preparation of nanosized hydrated iron oxide with activated carbon fibre. The surface morphologies of the adsorbent were studied using SEM and FT-IR. The SEM results showed that the activated carbon fibre has a high surface area and the hydrated iron oxides were fixed and well dispersed on the surface of the activated carbon fibre. FT-IR also confirmed the loading of the iron on the surface of the activated carbon fibre as was seen in the SEM images. The maximum adsorption capacity was given as 12.86 mg/g.

Iron oxide nanoparticles (IONP) synthesized by eucalyptus leaf extract in the presence of cetyltrimethylammonium bromide (CTAB) surfactant has also been investigated for the adsorption of phosphates from wastewater by [Cao \*et al.\* \(2016\)](#). In this study, green synthesis of CTAB-modified IONP was employed for the reduction of the iron ions by Eucalyptus leaf extract as a more environmentally friendly synthesis method. The maximum adsorption capacity obtained in this study was 18.7 mg/g. The percentage of phosphate removal also increased from 71 to 97.3%. The improved phosphate removal observed in this study was attributed to the presence of positively charged CTAB layer capping on the surface of IONP and the hydroxyl groups bound to the surface of the iron oxide nanoparticles. This was confirmed by the XPS, FT-IR and SEM/EDS analysis.

Lanthanum-based materials have displayed efficient adsorption capacity for phosphates compared to other transition metals ([Fang \*et al.\* 2018](#)). [Kim \*et al.\* \(2019\)](#) synthesized mesoporous lanthanum hydroxide (MLHO) from ordered

mesoporous silica (KIT-6) using a hard template approach. This method employed the incipient wetness impregnation method to deposit the Lanthanum precursor on the template following the citrate sol-gel process. A series of samples were prepared using two KIT-6 templates and different amounts of lanthanum precursor and were represented as MLHO-35Cs and MLHO-100Cs for KIT-6 formed at 35 and 100 °C. The synthesized lanthanum hydroxide had an ordered structure with nanometer-sized pores as shown by the Transmission Electron Microscope (TEM). The formation of an ordered mesoporous structure was due to the KIT-6 used as the mould. X-ray diffractometer (XRD) showed that the adsorbent contained both amorphous oxide ( $\text{La}_2\text{O}_3$ ) and crystalline  $\text{La}(\text{OH})_3$  phase with well-resolved peaks. Brunauer-Emmett-Teller (BET) showed that MLHO-35C-2 and MLHO-100C-2 gave surface areas of 429.8 and 348.3  $\text{m}^2/\text{g}$  respectively. The total pore volume  $v_t$  of MLHO-35C-2 and MLHO-100C-2 was given as 0.76 and 1.05  $\text{cm}^3/\text{g}$  respectively. The MLHO-100C-2 gave the highest maximum phosphate adsorption capacity of 109.41  $\text{mg}/\text{g}$  due to the presence of large pores of 15–50 nm with large volumes. It was observed that the KIT-6 treated at 35 °C showed less development of micropores among mesopore channels resulting in poor infiltration of lanthanum precursor. These results explained that pore structure is also an important parameter of adsorbents in addition to the surface area of adsorbents.

Iron oxide doped halloysite nanotubes were prepared using the sol-gel method to form a modified material with good adsorption properties. Halloysite nanotubes (HNTs) contain negatively charged functional groups on the exterior and positively charged inner lumen. The presence of the anions on its surface causes electrostatic repulsion with negative phosphate ions. The modification with iron oxide allowed the negative charges to be physically blocked by the iron oxide thereby enhancing the adsorption capacity of the nano-adsorbent for phosphate removal. SEM and high-resolution transmission electron microscope (HRTEM) characterization revealed tubular structures of the nanostructure and showed that the iron oxide was well attached to the surface of the halloysite nanotubes (Almasri *et al.* 2019). BET surface area analysis showed that the specific surface area of iron oxide-modified HNTs increased from 64.4 to 70.5  $\text{m}^2/\text{g}$  due to the contribution of the nano-sized iron oxide particles, hybridized onto HNTs. This is in agreement with the results of XRD and X-ray fluorescence (XRF) which confirmed the presence of iron oxide on the raw and modified HNTs (Almasri *et al.* 2019). The maximum phosphate adsorption capacity of the adsorbent was obtained at 5.46  $\text{mg}/\text{g}$ . The result also showed that the iron oxide-modified HNTs showed a good phosphate removal ability when compared with other adsorbents; iron oxide-coated granular activated carbon (Kumar *et al.* 2017), magnetic iron oxide nanoparticles (Yoon *et al.* 2014), iron hydr(oxide) coated sand (Huang *et al.* 2014) and the raw halloysite used in the same study.

Trinh *et al.* (2020) synthesized AgNPs-TAC using the incipient wetness impregnation method to deposit silver nanoparticles onto tea-activated carbon at different mass ratios. The results confirmed that the AgNPs-TAC had better adsorption capacity than the pristine TAC. An increase in adsorption capacity from 7.38 to 9.87  $\text{mg}/\text{g}$  was observed when the impregnation ratio increased from 0 to 3.0%. The study further confirmed that the presence of AgNPs on the surface of AgNPs-TAC triggered higher adsorption capacity. BET results revealed the specific surface area of 322  $\text{m}^2/\text{g}$  for TAC, after impregnation the surface area increased to 349  $\text{m}^2/\text{g}$ . The average pore volume also increased from 0.0032 to 0.0036  $\text{cm}^3/\text{g}$  for TAC and AgNPs-TAC respectively. This is a confirmation that the presence of AgNPs increased the surface area and pore volume. Scanning Electron Microscope with Energy Dispersive X-ray Spectroscopy (SEM/EDS) also confirmed a good distribution of the AgNPs on the surface of the AgNPs-TAC, similar observations were obtained for XRD and Fourier transform infrared spectroscopy (FT-IR).

In another study by Nuryadin & Imai (2021), a zirconium hydroxide/MgFe layered double hydroxide composite was synthesized by precipitation using sodium hydroxide. The adsorbent was used in phosphate removal in a column adsorption study and the result showed that the adsorbent has high phosphate adsorption capacity and reusability potential. The adsorbent showed a maximum adsorption capacity of 25.15  $\text{mg}/\text{g}$  and 91.7% phosphate recovery when sodium hydroxide was used as a regenerating agent. FT-IR identified peaks indicating the presence of hydroxyl groups and the presence of phosphate-oxygen bonds before and after phosphate adsorption respectively. XRD patterns showed the presence of a layered double hydroxide structure with a halo pattern of amorphous zirconium hydroxide. X-ray Photoelectron Spectrometer (XPS) confirmed the formation of magnesium-oxide-phosphate bond and iron-oxide-phosphate bond through surface complexation. This explained the excellent adsorption of phosphate by the adsorbent.

In a study conducted by Akram *et al.* (2021), pomegranate peel (agricultural waste) was co-doped with ferric chloride and lanthanum hydroxide nanoparticles using a modified solvothermal synthesis method. The iron-lanthanum pomegranate peel (Fe-La/Peel) showed an irregular and rough surface with a specific surface area of 93.18  $\text{m}^2/\text{g}$  and the surface was uniformly covered with iron and lanthanum. The presence of iron and lanthanum on the surface of the pomegranate fibre increased the

adsorption sites for phosphate uptake. The highest adsorption capacity recorded for the Fe-La/Peel was 44.5 mg/g at pH 2 compared to 13.91 and 38.86 mg/g for Fe/Peel and La/Peel respectively. The calculated maximum adsorption capacity from the experiment was 75.09 mg/g. The fabrication of the pomegranate peel with the iron-lanthanum nanocomposite increased the surface area of the adsorbent and also the adsorption of phosphate ions (Akram *et al.* (2021)).

Fly ash is an industrial solid waste with similar chemical components ( $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$ ) as zeolite which makes it suitable for the synthesis of zeolite. Due to the high cation exchange capacity of these materials, their effects on the adsorption of phosphates from wastewater have been studied extensively (Zhang *et al.* 2021). Zeolites synthesized from fly ash have shown higher phosphate adsorption than raw fly ash. Zhang *et al.* (2021) synthesized zeolite from fly ash in the presence of sodium hydroxide as an activator by the hydrothermal method at high temperatures and a certain solid-liquid ratio. SEM and XRD analysis showed the surface of the fly ash transformed from a rough surface with different pores and particle sizes into crystals with various shapes such as plates and rods. The author went further to explain that quartz, amorphous silicon, and aluminium material on the surface of the fly ash particles dissolved in the alkaline solution to form zeolite crystal precursor, and finally zeolite during the hydrothermal synthesis method. The BET results showed that the specific surface area of fly ash increased from 4.4713 to 43.817  $\text{m}^2/\text{g}$  and the average pore volume from 0.019523 to 0.122088  $\text{cm}^3/\text{g}$  after the hydrothermal synthesis to obtain zeolite. The specific surface area and average pore volume increased up to nine and six times the fly ash respectively. The increase in the crystallinity, specific surface area, and pore size when zeolite was formed is the major factor responsible for the excellent phosphate adsorption performance of the synthetic zeolite. (Zhang *et al.* 2021).

Furnace slag has also shown good efficiency in the removal of phosphates from wastewater. Blast furnace slag, a by-product of iron making, contains lime, silica, alumina, and magnesia as its main components. The availability of these components determines the phosphate removal ability of the slag (Yasipourtehrani *et al.* 2019).

## 2. ADSORPTION KINETICS, ISOTHERM, AND MECHANISMS

### 2.1. Adsorption kinetics and isotherm measurement for the removal of phosphate ions

The measurement of kinetics in the adsorption experiment is done to determine the rate of adsorption and proper contact time between the aqueous solution and adsorbents (Akram *et al.* 2021). Kinetics give the rate and mechanism of adsorption which occurs through physical or chemical phenomena (Sabzehmeidani *et al.* 2021). There are two known standard kinetics models which are the pseudo-first-order (Equation (1)) and the pseudo-second-order models (Equation (2)):

$$\log(q_e - q_t) = \log(q_e) - \frac{k_1}{2.303} t \quad (1)$$

where  $q_e$  is the adsorption capacity at equilibrium (mg/g),  $q_t$  is the adsorption capacity at time  $t$  (mg/g),  $k_1$  is the first-order rate constant  $\text{min}^{-1}$ . The plot of  $\log(q_e - q_t)$  versus  $t$  gives a relationship that is linear from which  $k_1$  and  $q_e$  can be determined from the slope and intercept of the plot:

$$q_t = \frac{q_e^2 k_2 t}{1 + q_e^2 k_2 t} \quad (2)$$

where  $q_e$  is the adsorption capacity at equilibrium (mg/g),  $q_t$  is the adsorption capacity at time  $t$  (mg/g),  $k_2$  is the second-order rate constant,  $\text{g}/\text{mg}\cdot\text{min}$ .

There are five basic assumptions of adsorption based on a pseudo-first-order equation and these are:

- i. That adsorption occurs only on localized sites with no consideration for the interaction between adsorbates.
- ii. The energy of adsorption does not depend on surface coverage.
- iii. Maximum adsorption corresponds to a saturated monolayer of adsorbates on the adsorbent surface.
- iv. The concentration of adsorbates is considered to be constant.
- v. The uptake of adsorbate obeys pseudo-first-order (Sabzehmeidani *et al.* 2021).

Some assumptions of the pseudo-second-order include: (a) a linear relationship between energy and surface coverage; (b) keeping the concentration of adsorbate constant, and (c) negligible ion uptake on activated carbons before the exponential

for an energetically heterogeneous surface as described by the Elovich model to support the pseudo-second-order kinetic theory (Sabzehmeidani *et al.* 2021). These assumptions give information about the rate of removal of the adsorbate and ideas about the rate of particle diffusion.

The most common isotherm models used in adsorption studies are Langmuir, Freundlich, Temkin, Redlich-Peterson, and Sips' isotherm models.

The Langmuir model (Equation (3)) allows accumulation only up to a monolayer. This model assumes that monolayer adsorption occurs on a homogenous or heterogeneous surface and energy of adsorption of all the available active sites is at all times comparable:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (3)$$

The linear form of Langmuir isotherm can be represented as shown in Equation (4):

$$\frac{C_e}{q_e} = \frac{1}{k_1 q_{max}} + \frac{1}{q_{max}} C_e \quad (4)$$

where  $q_e$  (mg/g) and  $q_m$  (mg/g) are the adsorption capacity at equilibrium and the maximum saturated adsorption capacity,  $C_e$  (mg/L) is the adsorbate concentration at equilibrium,  $K_L$  (L/mol) is the Langmuir constant. The plot of  $C_e/q_e$  versus  $C_e$  gives a straight line of slope  $1/q_m$  and intercept  $1/K_L q_m$ .

The Freundlich model (Equation (4)) on the other hand presumes the occurrence of multilayer adsorption on a heterogeneous surface, thus describing that all the adsorption locations possess different affinities:

$$q_t = K_F C_e^{\frac{1}{n}} \quad (5)$$

Freundlich isotherm can be used in linear form by obtaining the logarithm of both side of the equation:

$$\log q_t = \log K_F + \frac{1}{n} \log C_e \quad (6)$$

where  $K_F$  (mg/g) is the Freundlich constant, and  $1/n$  is the sorption intensity which indicates the favorability and capacity of the adsorbent/adsorbate system. The plot of  $\ln q_t$  versus  $\ln C_e$  gives a straight line of slope  $1/n$  and intercept  $\log K_F$ .

The Temkin isotherm model (Equation (7)) is based on the assumption that the heat of adsorption ( $\Delta H_{ads}$ ) of all molecules in the layer decreases linearly with the increase in surface coverage of the adsorbent and thus, the adsorption has a uniform distribution of binding energies, up to maximum binding energy:

$$q_e = \frac{RT}{b} \ln K_T + \frac{RT}{b} \ln C_e \quad (7)$$

where  $K_T$  is the equilibrium binding constant (L mol) corresponding to the maximum binding energy,  $b$  is related to the adsorption heat,  $R$  is the universal gas constant (8.314 J/K.mol), and  $T$  is the temperature (K). The plot of  $q_e$  versus  $\ln(C_e)$  gives a straight line of slope  $RT/b$  and intercept  $(RT \ln K_T)/b$ .

The Redlich-Peterson (R-P) isotherm model (Equation (8)) incorporates the elements of both Langmuir and Freundlich isotherms and thus can be applied to both homogeneous and heterogeneous surfaces:

$$\ln \left[ K_R \frac{C_e}{q_e} - 1 \right] = \ln(a_R) + \beta \ln(C_e) \quad (8)$$

where  $K_R$  is the R-P constant (L/g),  $a_R$  is the R-P constant (L/mg), and  $\beta$  is the exponent which lies between 1 and 0. A plot of the left-hand side of Equation (7) against  $\ln C_e$  for finding the isotherm constants is not valid because of the three unknowns ( $a_R$ ,  $K_R$  and  $\beta$ ). Therefore, to obtain the coefficient of correlation ( $R^2$ ), a maximization procedure was adopted for solving

Equation (8) by minimizing the distance between experimental data points and the theoretical model predictions using an add-in function in Microsoft Excel called *solver* (Piccin *et al.* 2011).

The Sips isotherm model (Equation (9)) is a combination of both the Langmuir and Freundlich isotherms. This model fits adsorption on heterogeneous surfaces, thereby circumventing the limitation of increased adsorbate concentration usually associated with the Freundlich model. At low adsorbate concentrations, it predicts the Freundlich model, but at higher adsorbate concentrations, the model predicts the monolayer adsorption (Langmuir model) (Tzabar & Ter Brake 2016; Ayawei *et al.* 2017):

$$q_e = \frac{q_m (bC_e)^{\frac{1}{n}}}{1 + (bC_e)^{\frac{1}{n}}} \quad (9)$$

In studies involving phosphate adsorption from wastewater, it has been shown that both Langmuir and Freundlich isotherms can satisfactorily describe the experimental data with corresponding correlation coefficients ( $r^2$ ) (Cao *et al.* 2016). However, the Langmuir model yields a better fit than the Freundlich model in most adsorption studies (Cao *et al.* 2016; Chen *et al.* 2019; Liu *et al.* 2019; Jia *et al.* 2020; Cegan *et al.* 2021). This explains that most of the adsorption of phosphate is monolayer adsorption (Aljbour *et al.* 2017), the adsorption of each molecule has equal activation energy and the adsorbate-adsorbate interaction can be negligible (Zhou *et al.* 2012; Sabzehmeidani *et al.* 2021).

The result from isotherm and kinetics models of the adsorption of phosphate describes the mechanism of adsorption. Trinh *et al.* (2020) proposed an ion-exchange interaction between  $\text{Ag}^+$  and  $\text{PO}_4^{3-}$  anion which caused precipitation, therefore, reduction of the phosphorus concentration of the solution. The adsorption capacity of AgNPs was higher when compared with other adsorbents like fly ash, iron oxides, activated carbon-loaded iron (III) oxide, and zinc oxide nanorods, indicating AgNPs as a potential adsorbent with a high adsorption capacity (Trinh *et al.* 2020).

## 2.2. Mechanisms of adsorption of phosphate

Studying the mechanism of adsorption is significant in understanding the interaction between phosphate ions and the adsorbent molecules. The mechanisms are also important in controlling the adsorption kinetics, thermodynamics, energy, and capacity (Almanassra *et al.* 2021b). Phosphate adsorption mechanisms can be studied using electron microscopy and other characterization methods to study the morphology of the adsorbents and adsorbate before and after adsorption. FT-IR spectroscopy and other analysis methods are further used to analyze the mechanism of improving the phosphate adsorption performance by studying the functional groups on the surface of the adsorbents. The main mechanism involved in phosphate adsorption is related to the specific surface area (Issaian & Reyes Cuellar), functional groups, and Lewis acid-base concept (Du *et al.* 2022). The mechanisms of adsorption of phosphates by carbon-based adsorbents can be explained by physisorption (physical adsorption and electrostatic adsorption) and chemisorption (surface complexation, ion exchange, precipitation, inner sphere, and outer-sphere complexation, Lewis acid-base interaction) (Almanassra *et al.* 2021a, 2021b; Sabzehmeidani *et al.* 2021).

In the work of Nguyen *et al.* (2020), the mechanism of adsorption of AgNPs-tea activated carbon was found to be ion exchange as confirmed by Brunauer-Emmett-Teller analysis (BET), scanning electron microscope (SEM), X-ray diffractometer (XRD), and Fourier transform infrared spectrometer (FT-IR). The experimental data from adsorption kinetics and isotherm models confirm the reduction of phosphate by the AgNPs-TAC as chemisorption which resulted in the formation of coulombic attraction between phosphate ions and the active sites of AgNPs-TAC. This was shown by the presence of phosphates on the surface of AgNPs-TAC (Nguyen *et al.* 2020).

Chen *et al.* (2015) proposed inner-sphere complexation between phosphate ions and hydrous zirconium oxide-based nanocomposites. This was revealed by spectroscopic techniques like FT-IR and X-ray photoelectron spectroscopy (XPS). Another mechanism of adsorption by activated carbon is the Lewis acid-base interaction. Phosphate ions are weak bases and function as electron donors in acidic conditions. In alkaline media, they are weak acids and accept electrons. This allows electron donor and acceptor interactions to occur between phosphate ions and the elements present in the activated carbon adsorbents (Almanassra *et al.* 2021b). Surface precipitation also occurs where phosphate ions are precipitated as metal phosphate, especially when activated carbon is modified with metals such as calcium, magnesium, and zinc (Almanassra *et al.* 2021b; Cegan *et al.* 2021).

### 2.3. Desorption and reusability of adsorbents

Adsorbent performance can be studied by carrying out a desorption experiment. A good adsorbent for phosphate should possess high adsorption capacity, be cost-effective, and have the ability to be reused for a long time (Almanassra *et al.* 2021b). Desorption of phosphate can be carried out using acid, bases, and salts. Salts are not highly effective when strong interaction between phosphate and the adsorbent is involved. In such cases, acids and bases are more effective. Sodium hydroxide is the most common base used for the desorption of phosphate. After the separation of the adsorbent from the mixed solution by filtration in a batch adsorption experiment, the active sites on the surface of the adsorbent can be regenerated by using sodium hydroxide and the sample is dried before reuse in the next batch study (Trinh *et al.* 2020). Sodium hydroxide is the best regenerating agent because the  $\text{OH}^-$  influences phosphate adsorption to a great extent. Increasing the concentration of sodium hydroxide will increase the regeneration efficiencies. In the study of Jia *et al.* (2020), when the concentration of the base was increased from 0.1 to 1 mol/L, the desorption efficiency was maintained at 100% in three desorption cycles while that of 0.1 mol/L was decreased to 29% using lanthanum-modified platanus biochar as adsorbent. Also, in the study of Xiong *et al.* (2017), the regeneration efficiency increased from 5.18 to 91.4% when the concentration of the base was increased from 0.001 to 0.1 mol/L. The desorption efficiency decreases with the regeneration cycle as a result of the disappearance of functional groups on the adsorbent surface. This is caused by the leaching of metal which reduced the active sites on the adsorbent (Li *et al.* 2020; Akram *et al.* 2021).

## 3. EFFECT OF PHYSICOCHEMICAL PROPERTIES ON PHOSPHATE ADSORPTION

### 3.1. Effect of pH

One of the most important parameters influencing the adsorption process is pH. The pH of a given solution determines the presence of phosphate hydroxyl groups (Nguyen *et al.* 2020). At different pH values, phosphate can exist in various molecular and anionic forms such as  $\text{H}_3\text{PO}_4$ ,  $\text{H}_2\text{PO}_4^-$ ,  $\text{HPO}_4^{2-}$ ,  $\text{PO}_4^{3-}$  (Zhang *et al.* 2018). The main phosphate ions in an acidic solution are  $\text{H}_2\text{PO}_4^-$  and  $\text{HPO}_4^{2-}$  while in alkaline conditions it exists as  $\text{PO}_4^{3-}$  (Trinh *et al.* 2020). The pH of the solution can have a critical effect on the rate of adsorption because the surface charge of the adsorbent is changed by the adsorption of charged phosphate ions (Akram *et al.* 2021).

The pH also determines the species of phosphate present in the solution (Qiu *et al.* 2019). As the pH of the solution increases, the amount of phosphate removed decreases. This is because, at higher pH, more  $\text{OH}^-$  exists in the solution which is likely to compete with phosphates for the adsorption site leading to an obvious decrease. Also, the adsorbent surface becomes more negative at higher pH causing greater repulsion thereby decreasing phosphate removal. A study by Chen *et al.* (2015) reported that as the pH of the solution increased, the fraction of the multi-charged phosphate anions (such as  $\text{HPO}_4^{2-}$  and  $\text{PO}_4^{3-}$ ) also increased. When Nguyen *et al.* (2020) used silver nanoparticles-tea-activated carbon for phosphate adsorption, the adsorption capacity decreased from 10.13 to 5.06 mg/g and the removal efficiency of phosphate dropped from 39.53 to 20.26% as the pH was raised from 3 to 10. This suggested the possibility of competition between  $\text{OH}^-$  and  $\text{PO}_4^{3-}$  in alkaline conditions which caused decreased adsorption of phosphate. At high pH, repulsion of anionic phosphate occurs due to the negative functional groups of  $\text{OH}^-$  at the surface of the adsorbents. Thus, the efficiency of phosphate adsorption by most nanoparticles is reduced. At low pH, on the other hand, the possibility of electrostatic attraction between phosphate and adsorbent increases as well as adsorption efficiency (Khodadadi *et al.* 2017).

### 3.2. Effect of adsorbent dose

Adsorbent dose plays an important role in the adsorption of phosphate. Studies have shown that small doses of adsorbents result in an interaction between the phosphate and the adsorbent which leads to the complete attachment of the anion to the adsorbent (Nguyen *et al.* 2020). The removal efficiency of phosphates is directly proportional to the adsorbent dosage theoretically (Zhang *et al.* 2020). The higher the amount of adsorbent, the higher the rate of adsorption of phosphate. However, in the presence of an excessive amount of adsorbent, aggregation of particles can reduce the active surface area and active site for the adsorption of phosphate from the solution, leading to a reduction in the adsorption (Nguyen *et al.* 2020). This explains the fact that when the dose of the adsorbent increases, the adsorption capacity decreases if the initial phosphate concentration is kept constant. Increased active sites on adsorbents may lead to excessive locations when the phosphate concentration is kept constant and the active site is not fully occupied (Trinh *et al.* 2020).

### 3.3. Effect of contact time

Contact time is an important factor affecting the adsorption of phosphate. The contact time provides information on the adsorption kinetics of the adsorbate for a given dosage or initial concentration of the adsorbent. The determination of contact time is majorly to determine the minimum time required for adsorbents to optimally adsorb the phosphate ions until an equilibrium state is achieved between the adsorbed and desorbed phosphates. This helps to understand the rate of phosphate adsorption onto the surface of the adsorbents as well as the efficiency of the adsorbent (Iftekhhar *et al.* 2018). The contact time should be long enough to enable equilibrium to be reached during adsorption. The equilibrium time mainly depends on the type of adsorbent, initial phosphate concentration, adsorption temperature, and the level of mixing (Zhang *et al.* 2020).

Trinh *et al.* (2020) observed an increase in the phosphate adsorption capacity of AgNPs from 33.33 to 42.38 mg/g at a time of 5–120 minutes. However, as time increased the adsorption capacity remained unchanged. This is because, initially, there were available active sites on the surface of AgNPs so the adsorption process occurred faster and was controlled by the transfer of external volume. After the time increased, the decline in active sites observed was because most of the active sites of the adsorbents are now occupied by phosphate therefore, the adsorption capacity remained constant (Trinh *et al.* 2020). The same effect was observed for AgNPs-TAC on phosphate removal (Nguyen *et al.* 2020). The mechanism for this observation was first, the saturation of adsorption active sites on the surface of AgNPs-TAC, and secondly, gradual reduction in the concentration gradient between the bulk solution and the adsorbent.

### 3.4. Effect of co-existing ions

Adsorption selectivity also influences the effective removal of phosphate from the solution. Real wastewater samples always contain numerous aqueous constituents which may compete for the adsorption sites affecting the phosphate removal ability of adsorbents (Chen *et al.* 2015; Zhang *et al.* 2017). In any adsorption experiment, it is very important to investigate the effect of co-existing ions on the performance of the adsorbent to provide important information about the application and selectivity of the adsorbent towards phosphate ions. Inorganic ions that may be present in real wastewater are sulfates, carbonates, nitrates, chlorides, and fluorides (Zhang *et al.* 2017). The presence of divalent anions such as  $\text{SO}_4^{2-}$ ,  $\text{CO}_3^{2-}$ , poses a higher effect on the adsorption capacity of adsorbents than monovalent anions such as  $\text{Cl}^-$ ,  $\text{NO}_3^-$ . In many studies, the presence of  $\text{CO}_3^{2-}$  was found to decrease the adsorption capacity of phosphates. The  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ , and  $\text{NO}_3^-$  showed no obvious decrease in the removal rate of phosphate. In another study, Rashid *et al.* (2017) reported that the presence of  $\text{CO}_3^{2-}$  changed the overall phosphate solution to alkaline. The increase in pH may be the reason for the decreased phosphate adsorption by the humic acid-coated magnetic nanoparticles. This is because  $\text{CO}_3^{2-}$  possesses a strong affinity towards active adsorption sites. The presence of  $\text{HCO}_3^-$  and  $\text{CO}_3^{2-}$  is also found to increase the pH of the solution and inhibit phosphate removal (Rashid *et al.* 2017; Almanassra *et al.* 2021b). Zhou *et al.* (2012) observed that the effect of coexisting anions on phosphate adsorption by hydrated ferric oxide doped activated carbon fibre decreased in the order  $\text{F}^- > \text{NO}_3^- > \text{Cl}^- > \text{SO}_4^{2-}$ . It was observed that  $\text{F}^-$  had the highest effect on the adsorption of phosphate and the decrease in the adsorption ranged from 12.86 to 5.51 mg/g. This is attributed to the ion exchange reaction between phosphate ions and the hydroxide of Fe (III). The decrease in the adsorption capacity of the adsorbent is ascribed to an ion-exchange mechanism in which the co-existing ions possess the highest affinity for the adsorbent material and compete with phosphate for the adsorption site (Zhou *et al.* 2012).

## 4. NANOTECHNOLOGY IN WASTEWATER TREATMENT

Nanotechnology deals with the design, production, characterization, and application of materials by controlled manipulation of particle structure and size range between 1–100 nm (Remya *et al.* 2017; Abdelghany *et al.* 2018; Salem & Fouda 2021). Nanomaterials can integrate various properties resulting in multifunctional systems such as nanocomposites that enable both particle retention and elimination of contaminants. Owing to their low cost, resource conservation in material synthesis, reusability, and high efficiency in pollutant removal, nanoparticles are regarded as a sustainable and state-of-the-art avenue for improved wastewater treatment (Nnaji *et al.* 2018). They ensure high quality and purity of water by removing metal, organic and inorganic pollutants due to their high surface area to volume ratio, unique size, good adsorption, and absorption feature, better chemical reactivity, diffusion activation energy and strong quantum effect (Zhao *et al.* 2021).

Current developments in nanotechnology demonstrate the applications of nanomaterials such as nano-adsorbents, nano-membranes, metal nanoparticles, and photocatalysts (Ahmad *et al.* 2017; Punia *et al.* 2021). Gold, silver, palladium, and platinum as well as other transition metals nanoparticles such as iron, nickel, and copper have been widely employed in wastewater treatment as antimicrobial agents and removal of toxic ions (Ahmad *et al.* 2017). Khodadadi *et al.* (2017)

synthesized iron nanomagnetic particles coated with powdered activated carbon as an effective adsorbent for phosphate removal from water and sewage. The greatest phosphate adsorption was recorded at a pH of 2 which shows that phosphate adsorption is pH-dependent.

Trinh *et al.* (2020) observed an increase in the phosphate adsorption capacity of AgNPs from 33.33 to 42.38 mg/g between 5 and 120 minutes but as time increased, the adsorption capacity remained unchanged. This is because, initially, there were available active sites on the surface of AgNPs. Thus, the adsorption process occurred faster and was controlled by the transfer of external volume. After the time increased, the decline in the active site observed was because most of the active sites of the adsorbents were occupied by phosphate ions (Trinh *et al.* 2020). Zhang *et al.* (2017) synthesized magnetic zirconium-iron oxide nanoparticles and found a significant decrease in the rate of phosphate adsorption from 93.38 to 78.83% due to strong competition by  $\text{HCO}_3^-$  and the phosphate ions for the adsorption site of the magnetic zirconium-iron oxide nanoparticles.

Dual metal hydroxide nanoparticles have also shown high efficiency in phosphate removal from aqueous solutions. Akram *et al.* (2021) synthesized iron-lanthanum/pomegranate peel nanoparticles for the removal of phosphate at different operating parameters such as temperature, time intervals and pH values. The maximum adsorption capacity obtained was 75.09 mg/g phosphate. It was found that the simultaneous lanthanum doping with iron provided a larger accessible surface and more reactive functional groups for the adsorbent as shown by BET analysis (Akram *et al.* 2021). Iron oxide-synthesized nanoparticles from the leaf extract of eucalyptus plant have also been proven to be effective in the removal of phosphate from an aqueous solution (Cao *et al.* 2016). In this experiment, improved efficiency of 71.0 to 97.3% was observed when cetyltrimethylammonium bromide (CTAB) was used as a stabilizing agent for the nanoparticles.

#### 4.1. Adsorbents modified with nanoparticles

In any adsorption technique the adsorbent must possess properties such as high surface area, pore volume and active surface functional groups to adsorb pollutants from water. Several porous materials such as activated carbon, clays, fly ash, zeolites, metal oxides, graphene oxide, metal-organic frameworks, and carbon nanotubes have been investigated as adsorbents for phosphate removal from wastewater (Verma & Nadagouda 2021). Most nanoparticles have very small sizes (in nanometers) with ultrafine particles that can easily leach into the water during treatment, therefore making separation difficult. The fine nature of these nanoparticles allows them to be immobilized on appropriate support materials to form a nanocomposite, therefore minimizing the problem of leaching. Some carbon-based materials such as activated carbon, graphene, graphene oxides, and carbon nanotubes have been studied as good catalyst support materials for application in water purification. Their efficiency can be improved by modifying them with other materials to form composites.

Composites are materials which consist of two or more different materials combined in a way to achieve the best properties of both materials. Composites are produced in such a way that the characteristics are better than when each of the components exists independently (Pandya *et al.* 2013). A nanocomposite is a composite material with one of the components having at least a nanoscale size range. In every nanocomposite, each component has different properties and is thus blended into a new single substance with a wide-ranging set of properties (Pandya *et al.* 2013). These materials have a great advantage in wastewater treatment because of their ability to combine the properties of the individual materials to achieve better properties (Younas *et al.* 2021). Several kinds of research have focused on the production of such materials with increased adsorption strength and uniform pores to enhance phosphate adsorption. Graphene is a known two-dimensional nanomaterial with excellent thermal and mechanical properties and well-defined pores for the adsorption of pollutants from water (Verma & Nadagouda 2021). Modified graphene-based composites have been studied widely for the removal of phosphates from aqueous solutions. Among these modifications are lanthanum/graphene composites with increased adsorption efficiency. Lanthanum ions have a very high affinity toward phosphate ions, therefore the presence of lanthanum altered the negative surface functional group of graphene and enhanced the nanocomposite's adsorption efficiency. Iron-based nanoparticles immobilized on graphene oxide is an excellent material for the adsorption of phosphate through both electrostatic attraction (physical adsorption) and ion exchange (chemical adsorption). These materials also show advantages such as stability, recyclability due to its magnetic properties and high efficiency (Verma & Nadagouda 2021).

Recently, nano-particles loaded on activated carbon as adsorbents have attracted significant attention in the field of nanotechnology, due to their high surface area to volume ratio and short diffusion route (AbdEl-Salam *et al.* 2017). The nanoparticles loaded onto activated carbon led to an increase in the reactive centre and adsorption capacity thereby leading to the accumulation of various functional groups. Some studies have shown that AgNPs coated with activated carbon can

effectively adsorb pollutants (AbdEl-Salam *et al.* 2017). Nguyen *et al.* (2020) synthesized silver nano-particles loaded tea activated carbon (AgNPs-TAC) with increased surface area as well as pore volume for the adsorption of phosphate from water. The maximum adsorption capacity of AgNPs-TAC was recorded at 13.62 mg/g. In the study of Zhou *et al.* (2012), nanosized hydrated ferric oxide loaded onto mesoporous activated carbon fibre showed high efficiency toward the adsorption of phosphate from water with a maximum phosphate adsorption capacity of 12.86 mg/g. The observed mechanism was governed by electrostatic interaction and ion exchange between the adsorbent surface charge and phosphate ions.

Recent studies have shown that the modification of activated carbon and other nanostructured materials led to an increased removal rate of contaminants (El-Aassar *et al.* 2013; Sabzehmeidani *et al.* 2021). To improve the adsorption capacity of activated carbon, the introduction of cationic species is usually required. Studies have also revealed that activated carbon can be impregnated by some materials which show a high affinity towards phosphate to enhance the phosphate adsorption capacity of the activated carbon (Almanassra *et al.* 2021b).

The introduction of cationic elements, such as calcium, magnesium, aluminium, silver and iron, is the most common method used in enhancing phosphate adsorption performance (Zhang *et al.* 2020; Zhao *et al.* 2021). Several research studies on the modification of activated carbon by nanoparticles to enhance the removal of phosphates include silver nanoparticles-loaded activated carbon (Nguyen *et al.* 2020), iron oxide-coated granular activated carbon (Kumar *et al.* 2017), hydrated ferric oxide-doped activated carbon fibre (Zhou *et al.* 2012), lanthanum-doped activated carbon fibre (Liu *et al.* 2011), calcium oxide-doped biochar (Zhang *et al.* 2020), and calcium hydroxide-coated biochar (Choi *et al.* 2019).

In a study by Nguyen *et al.* (2020), a maximum adsorption capacity of 13.62 mg/g was obtained when silver nanoparticles loaded with activated carbon from tea tree residue (AgNP-TAC) were used for phosphate adsorption. The possible mechanism of phosphate adsorption was the formation of a surface complex silver ion at acidic pH and it was concluded that complex formation and ligand exchange are the main mechanisms of silver nanoparticles-loaded tea-activated carbon (AgNPs-TAC) adsorption of phosphate. This is in agreement with another study that explains anionic coordination exchange adsorption as the main mechanism of phosphate adsorption by modified bentonite granules (Nguyen *et al.* 2020). Hydrated ferric oxide-doped activated carbon fibre (activated carbon fibre-nano hydrated ferric oxide) has also been synthesized by the sol-gel method for the adsorption of phosphates from wastewater and the maximum phosphate adsorption of 12.86 mg/g was obtained within the pH range of 2–6 (Zhou *et al.* 2012). The size of the adsorbent used plays an important role in the removal efficiency of these adsorbents. Therefore, embracing nanotechnology will play an important role in controlling the size of the adsorbent used for the removal of phosphate ions from wastewater.

## 5. CONCLUSIONS

This review summarizes the literature on phosphate removal from aqueous solutions using activated carbons and nano-materials. The adsorption mechanisms, kinetics, and experimental parameters affecting the rate of adsorption are discussed. Generally, phosphate adsorption is affected by the surface chemistry of the synthesized adsorbents. These properties include surface charge, functional groups, surface area, and modifications.

Phosphate can exist in various molecular and anionic forms and thus affect the rate of its adsorption. The interaction between the adsorbent and the adsorbate depends on the dosage of the adsorbent as well as the contact time. Phosphate in real water coexists with other anions and studies have shown that the divalent cation,  $\text{CO}_3^{2-}$  ions have the greatest negative effect on the adsorption of phosphate from an aqueous solution. The highly acidic and basic solutions are found to give low phosphate adsorption, so the optimum pH for phosphate adsorption is between 3–8 for most studies reviewed. The desorption of phosphate is found to be more effective when sodium hydroxide is used even though for adsorbents that form strong bonding with phosphate, the base may not be efficient.

Different adsorbents have been synthesized for the adsorptive removal of phosphate from water. Mostly, the modification of adsorbents such as activated carbon with other nanostructured materials has proven to be very effective in the removal of phosphate and other contaminants from water. The high adsorption capacity and selectivity of nano-adsorbents make them a better approach for the removal of inorganic ions such as phosphate from water. Nanotechnology is a sustainable and innovative approach to enhanced wastewater treatment. Nanomaterials/nano-adsorbents possess several advantages such as increased adsorption capacity and better adsorbate-adsorbent interaction during treatment processes thus increasing their application in phosphate removal.

## 6. KNOWLEDGE GAPS AND RECOMMENDATIONS

Phosphate removal from wastewater by adsorption techniques is a growing area and the number of research in this field is increasing. However, some interesting questions need more investigation and research. Therefore, some of the critical issues are summarized below:

- i. Very little research has been carried out on the desorption of phosphates from the adsorbents. Further research, therefore, should focus on adsorbent regeneration, desorption, and the recovery of both the adsorbent and phosphate. The desorption experiment is very important since it enables the recovery of phosphate as a way to recycle phosphate which is a non-renewable natural resource from wastewater for reuse.
- ii. Most research is carried out on a laboratory scale; research should be carried out on the application of adsorbents for the removal of phosphate from real wastewater samples. This will allow a thorough study of the effects of co-existing ions on the adsorption of phosphate under the usual environmental conditions.
- iii. Studies should not only focus on the removal of orthophosphate from wastewater. The removal of other phosphate species such as polyphosphates, which are a source of phosphorus, should be studied. This is to account for the rest of the phosphorus which may be present in wastewater as organically bound phosphorus.
- iv. The economic feasibility and cost-effective analysis of the adsorbents used for phosphate removal should be considered for large-scale processes and application of adsorbents.
- v. Not much research has been carried out on the comparison of the effective removal of phosphate at high and low concentrations using most adsorbents. The effectiveness of adsorbents is not only assessed by the maximum adsorption capacity. Adsorbents should also be effective at removing phosphate at low concentrations. Adsorption studies at low and high concentrations of phosphate are therefore recommended.

## AUTHORS CONTRIBUTION STATEMENT

All the authors presented in this review made a substantial contribution to the design of the review, revising it critically for important content and structure, and gave their approval for this version of the paper to be published.

## ACKNOWLEDGEMENTS

Great thanks to the African Water Resources Mobility Network (AWaRMN) of the Intra-Africa Academic Mobility Scheme funded by the European Union to Usman. We also acknowledge Makerere University, Uganda, which is part of the partner institutions for all the support in this research.

## FUNDING STATEMENT

This review is part of the research which is supported by the African Water Resources Mobility Network (AWaRMN) of the Intra-Africa Academic Mobility Scheme funded by the European Union to Usman.

## DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

## CONFLICT OF INTEREST

The authors declare there is no conflict.

## REFERENCES

- Abdelghany, T. M., Al-Rajhi, A. M., Al Abboud, M. A., Alawlaqi, M. M., Ganash Magdah, A., Helmy, E. A. & Mabrouk, A. S. 2018 *Recent advances in green synthesis of silver nanoparticles and their applications: about future directions. A review. BioNanoScience* **8**, 5–16.
- AbdEl-Salam, A., Ewais, H. & Basaleh, A. 2017 *Silver nanoparticles immobilised on the activated carbon as efficient adsorbent for removal of crystal violet dye from aqueous solutions. A kinetic study. Journal of Molecular Liquids* **248**, 833–841.
- Ahmad, I. Z., Ahmad, A., Tabassum, H., Kuddus, M., 2017 *Applications of nanoparticles in the treatment of wastewater. In: Handbook of Ecomaterials* (Martínez, L. M. T., Kharissova, O. V. & Kharisov, B. I., eds). Springer, Cham, pp. 275–299.

- Akram, M., Xu, X., Gao, B., Wang, S., Khan, R., Yue, Q., Duan, P., Dan, H. & Pan, J. 2021 Highly efficient removal of phosphate from aqueous media by pomegranate peel co-doping with ferric chloride and lanthanum hydroxide nanoparticles. *Journal of Cleaner Production* **292**, 125311.
- Alewell, C., Ringeval, B., Ballabio, C., Robinson, D. A., Panagos, P. & Borrelli, P. 2020 Global phosphorus shortage will be aggravated by soil erosion. *Nature Communications* **11**, 1–12.
- Aljbour, S. H., Al-Harashsheh, A. M., Aliedeh, M. A., Al-Zboon, K. & Al-Harashsheh, S. 2017 Phosphate removal from aqueous solutions by using natural Jordanian zeolitic tuff. *Adsorption Science & Technology* **35**, 284–299.
- Almanassra, I. W., Kochkodan, V., McKay, G., Atieh, M. A. & Al-Ansari, T. 2021a Review of phosphate removal from water by carbonaceous sorbents. *Journal of Environmental Management* **287**, 112245.
- Almanassra, I. W., McKay, G., Kochkodan, V., Atieh, M. A. & Al-Ansari, T. 2021b A state of the art review on phosphate removal from water by biochars. *Chemical Engineering Journal* **409**, 128211.
- Almasri, D. A., Saleh, N. B., Atieh, M. A., McKay, G. & Ahzi, S. 2019 Adsorption of phosphate on iron oxide doped halloysite nanotubes. *Scientific Reports* **9** (1), 3232. doi:10.1038/s41598-019-39035-2.
- Ayawei, N., Ebelegi, A. N. & Wankasi, D. 2017 Modelling and interpretation of adsorption isotherms. *Journal of Chemistry* **2017**, 3039817.
- Banu, H. A. T., Karthikeyan, P. & Meenakshi, S. 2021 Removal of nitrate and phosphate ions from aqueous solution using zirconium encapsulated chitosan quaternized beads: preparation, characterization and mechanistic performance. *Results in Surfaces and Interfaces* **3**, 100010.
- Bektaş, T. E., Kıvanç Uğurluoğlu, B. & Tan, B. 2021 Phosphate removal by ion exchange in batch mode. *Water Practice & Technology* **16**, 1343–1354.
- Bunce, J. T., Ndam, E., Ofiteru, I. D., Moore, A. & Graham, D. W. 2018 A review of phosphorus removal technologies and their applicability to small-scale domestic wastewater treatment systems. *Frontiers in Environmental Science* **6**, 8.
- Cao, D., Jin, X., Gan, L., Wang, T. & Chen, Z. 2016 Removal of phosphate using iron oxide nanoparticles synthesized by eucalyptus leaf extract in the presence of CTAB surfactant. *Chemosphere* **159**, 23–31.
- Cepan, C., Segneanu, A. E., Grad, O., Mihailescu, M., Cepan, M. & Grozescu, I. 2021 Assessment of the different type of materials used for removing phosphorus from wastewater. *Materials* **14**, 4371.
- Chen, L., Zhao, L., Pan, B., Zhang, W., Hua, M., Lv, L. & Zhang, W. 2015 Preferable removal of phosphate from water using hydrous zirconium oxide-based nanocomposite of high stability. *Journal of Hazardous Materials* **284**, 35–42.
- Chen, L., Li, Y., Sun, Y., Chen, Y. & Qian, J. 2019 La (OH) 3 loaded magnetic mesoporous nanospheres with highly efficient phosphate removal properties and superior pH stability. *Chemical Engineering Journal* **360**, 342–348.
- Choi, Y. K., Jang, H. M., Kan, E., Wallace, A. R. & Sun, W. 2019 Adsorption of phosphate in water on a novel calcium hydroxide-coated dairy manure-derived biochar. *Environmental Engineering Research* **24**, 434–442.
- Curran, D. T. 2015 *Phosphate Removal and Recovery From Wastewater by Natural Materials for Ecologically Engineered Wastewater Treatment Systems*.
- Davis, J. L. & Shaw, G. 2009 Impacts of eutrophication on the safety of drinking and recreational water. In: *Water and Health*, Vol. 2. (W. O. K. Grabow, ed.). EOLSS Publishers Co., Ltd., Oxford, p. 147.
- Derco, J., Kuffa, R., Urminská, B., Dudáš, J. & Kušnierová, J. 2016 Influence of phosphorus precipitation on wastewater treatment processes. In: *Operations Research: the Art of Making Good Decisions* (K. Jian, ed.). InTech, Croatia, p. 103.
- Dittmann, E., Fewer, D. P. & Neilan, B. A. 2013 Cyanobacterial toxins: biosynthetic routes and evolutionary roots. *FEMS Microbiology Reviews* **37** (1), 23–43.
- Du, M., Zhang, Y., Wang, Z., Lv, M., Tang, A., Yu, Y., Qu, X., Chen, Z., Wen, Q. & Li, A. 2022 Insight into the synthesis and adsorption mechanism of adsorbents for efficient phosphate removal: exploration from synthesis to modification. *Chemical Engineering Journal* **442**, 136147.
- El-Aassar, A. H., Said, M. M., Abdel-Gawad, A. M. & Shawky, H. A. 2013 Using silver nanoparticles coated on activated carbon granules in columns for microbiological pollutants water disinfection in Abu Rawash area, Great Cairo, Egypt. *Australian Journal of Basic and Applied Sciences* **7** (1), 422–432.
- Fang, L., Wu, B., Chan, J. K. & Lo, I. M. 2018 Lanthanum oxide nanorods for enhanced phosphate removal from sewage: a response surface methodology study. *Chemosphere* **192**, 209–216.
- Filippelli, G. 2009 Phosphorus Cycle. In: *Encyclopedia of Paleontology and Ancient Environments*. pp. 780–783. doi:10.1007/978-1-4020-4411-3\_186.
- Ghaedi, M. 2021 *Adsorption: Fundamental Processes and Applications*. Academic Press, Cambridge, MA, USA.
- Goldberg, S. 2013 Surface complexation modeling. In: *Reference Module in Earth Systems and Environmental Sciences*, Vol. 10. Elsevier, Amsterdam, The Netherlands.
- Gu, W., Li, X., Xing, M., Fang, W. & Wu, D. 2018 Removal of phosphate from water by amine-functionalized copper ferrite chelated with La (III). *Science of the Total Environment* **619**, 42–48.
- Hampton, S. E., McGowan, S., Ozersky, T., Virdis, S. G., Vu, T. T., Spanbauer, T. L., Kraemer, B. M., Swann, G., Mackay, A. W., Powers, S. M., Meyer, M. F., Labou, S. G., O'Reilly, C. M., DiCarlo, M., Galloway, A. W. & Fritz, S. C. 2018 Recent ecological change in ancient lakes. *Limnology and Oceanography* **63**, 2277–2304.

- Huang, Y., Yang, J. K. & Keller, A. A. 2014 Removal of arsenic and phosphate from aqueous solution by metal (hydr-) oxide coated sand. *ACS Sustainable Chemistry & Engineering* **2** (5), 1128–1138.
- Hwang, S. J. 2020 Eutrophication and the ecological health risk. *International Journal of Environmental Research and Public Health* **17**(17), 6332. doi: 10.3390/ijerph17176332.
- Iftekhhar, S., Ramasamy, D. L., Srivastava, V., Asif, M. B. & Sillanpää, M. 2018 Understanding the factors affecting the adsorption of Lanthanum using different adsorbents: a critical review. *Chemosphere* **204**, 413–430.
- Issaian, T. & Reyes Cuellar, J. C. 2020 Removing phosphate from aquatic environments utilizing Fe-Co/Chitosan modified nanoparticles. *Ciencia en Desarrollo* **11**, 101–110.
- Jia, Z., Zeng, W., Xu, H., Li, S. & Peng, Y. 2020 Adsorption removal and reuse of phosphate from wastewater using a novel adsorbent of lanthanum-modified platanus biochar. *Process Safety and Environmental Protection* **140**, 221–232.
- Jung, K. W., Lee, S. & Lee, Y. J. 2017 Synthesis of novel magnesium ferrite (MgFe<sub>2</sub>O<sub>4</sub>)/biochar magnetic composites and its adsorption behavior for phosphate in aqueous solutions. *Bioresource Technology* **245**, 751–759.
- Jupp, A. R., Beijer, S., Narain, G. C., Schipper, W. & Slootweg, J. C. 2021 Phosphorus recovery and recycling—closing the loop. *Chemical Society Reviews* **50** (1), 87–101.
- Kamika, I., Coetzee, M., Mamba, B. B., Msagati, T. & Momba, M. N. 2014 The impact of microbial ecology and chemical profile on the enhanced biological phosphorus removal (EBPR) process: a case study of Northern Wastewater Treatment Works, Johannesburg. *International Journal of Environmental Research and Public Health* **11**, 2876–2898.
- Khodadadi, M., Hosseinejad, A., Rafati, L., Dorri, H. & Nasseh, N. 2017 Removal of phosphate from aqueous solutions by iron nano-magnetic particle coated with powder activated carbon. *Journal of Health Sciences and Technology* **1**, 17–22.
- Kim, K., Kim, D., Kim, T., Kim, B.-G., Ko, D., Lee, J., Han, J., Jung, J. C. & Na, H. B. 2019 Synthesis of mesoporous lanthanum hydroxide with enhanced adsorption performance for phosphate removal. *RSC Advances* **9** (27), 15257–15264.
- Klein, K., Mandel, A., Lilleoja, H., Salmar, S. & Tenno, T. 2020 Assessment of enhanced biological phosphorus removal process inhibition. *SN Applied Sciences* **2**, 1–10.
- Koto, Y., Kawahara, H., Kurata, K., Yoshikiyo, K., Hashiguchi, A., Okano, K., Sigiura, N., Shimizu, K. & Shimizu, H. 2022 Microcystin-LR incorporated into colonic cells through probenecid-sensitive transporters leads to upregulated MCP-1 expression induced by JNK activation. *Toxicology Reports* **9**, 937–944.
- Kubickova, B., Babica, P., Hilscherová, K. & Šindlerová, L. 2019 Effects of cyanobacterial toxins on the human gastrointestinal tract and the mucosal innate immune system. *Environmental Sciences Europe* **31** (1), 1–27.
- Kudela, R. M., Bickel, A., Carter, M. L., Howard, M. D. & Rosenfeld, L. 2015 The monitoring of harmful algal blooms through ocean observing: the development of the California Harmful Algal Bloom Monitoring and Alert Program. In: *Coastal Ocean Observing Systems* (Y., Liu, H. Kerkering, & R. H. Weisberg, eds.). Elsevier, Amsterdam, The Netherlands, pp. 58–75.
- Kumar, P. S., Prot, T., Korving, L., Keesman, K. J., Dugulan, I., van Loosdrecht, M. C. & Witkamp, G. J. 2017 Effect of pore size distribution on iron oxide coated granular activated carbons for phosphate adsorption—Importance of mesopores. *Chemical Engineering Journal* **326**, 231–239.
- Kumar, S., Kaushik, G., Dar, M. A., Nimesh, S., Lopez-Chuken, U. J. & Villarreal-Chiu, J. F. 2018 Microbial degradation of organophosphate pesticides: a review. *Pedosphere* **28**, 190–208.
- Lalley, J., Han, C., Li, X., Dionysiou, D. D. & Nadagouda, M. N. 2016 Phosphate adsorption using modified iron oxide-based sorbents in lake water: kinetics, equilibrium, and column tests. *Chemical Engineering Journal* **284**, 1386–1396.
- Le Moal, M., Gascuel-Oudou, C., Ménesguen, A., Souchon, Y., Étrillard, C., Levain, A., Moatar, F., Pannard, A., Souchu, P., Lefebvre, A. & Pinay, G. 2019 Eutrophication: a new wine in an old bottle? *Science of the Total Environment* **651**, 1–11.
- Li, X., Xie, Y., Jiang, F., Wang, B., Hu, Q., Tang, Y., Luo, T. & Wu, T. 2020 Enhanced phosphate removal from aqueous solution using resourceable nano-cao<sub>2</sub>/BC composite: behaviors and mechanisms. *Science of the Total Environment* **709**, 136123.
- Lin, Q., Zhang, K., McGowan, S., Capo, C. & Shen, J. 2021 Synergistic impacts of nutrient enrichment and climate change on long-term water quality and ecological dynamics in contrasting shallow-lake zones. *Limnology and Oceanography* **66**, 3271–3286.
- Liu, J., Wan, L., Zhang, L. & Zhou, Q. 2011 Effect of pH, ionic strength, and temperature on the phosphate adsorption onto lanthanum-doped activated carbon fiber. *Journal of Colloid and Interface Science* **364**, 490–496.
- Liu, C., Zhang, M., Pan, G., Lundehøj, L., Nielsen, U. G., Shi, Y. & Hansen, H. C. B. 2019 Phosphate capture by ultrathin MgAl layered double hydroxide nanoparticles. *Applied Clay Science* **177**, 82–90.
- Lone, Y., Koiri, R. K. & Bhide, M. 2015 An overview of the toxic effect of potential human carcinogen Microcystin-LR on testis. *Toxicology Reports* **2**, 289–296.
- Mekonnen, D. T., Alemayehu, E. & Lennartz, B. 2021 Fixed-Bed column technique for the removal of phosphate from water using leftover coal. *Materials* **14**, 5466.
- Mohammadi, E., Daraei, H., Ghanbari, R., Athar, S. D., Zandsalimi, Y., Ziaee, A., Maleki, A. & Yetilmeszo, K. 2019 Synthesis of carboxylated chitosan modified with ferromagnetic nanoparticles for adsorptive removal of fluoride, nitrate, and phosphate anions from aqueous solutions. *Journal of Molecular Liquids* **273**, 116–124.
- Naushad, M., Sharma, G., Kumar, A., Sharma, S., Ghfar, A. A., Bhatnagar, A., Stadler, F. J. & Khan, M. R. 2018 Efficient removal of toxic phosphate anions from aqueous environment using pectin based quaternary amino anion exchanger. *International Journal of Biological Macromolecules* **106**, 1–10.

- Nguyen, T. M. P., Van, H. T., Nguyen, T. V., Ha, L. T., Vu, X. H., Pham, T. T., Nguyen, T. N., Quang, N. V. & Nguyen, X. C. 2020 Phosphate adsorption by silver nanoparticles-loaded activated carbon derived from tea residue. *Scientific Reports* **10**, 1–13.
- Nnaji, C. O., Jeevanandam, J., Chan, Y. S., Danquah, M. K., Pan, S. & Barhoum, A. 2018 Engineered nanomaterials for wastewater treatment: current and future trends. In: *Fundamentals of Nanoparticles* (A. Barhoum, & A. S. H. Maklouf, eds.). Elsevier, Amsterdam, The Netherlands, pp. 129–168.
- Novillo, C., Guaya, D., Avendaño, A. A., Armijos, C., Cortina, J. L. & Cota, I. 2014 Evaluation of phosphate removal capacity of Mg/Al layered double hydroxides from aqueous solutions. *Fuel* **138**, 72–79.
- Nuryadin, A. & Imai, T. 2021 Phosphorus desorption and recovery from aqueous solution using amorphous zirconium hydroxide/MgFe layered double hydroxides composite. In *IOP Conference Series: Earth and Environmental Science*. IOP Publishing, p. 012107.
- Oghyanous, F. A. 2022 Nanoparticles in wastewater treatment. In: *Water Conservation: Inevitable Strategy* (M. Eyvaz, ed.). Intechopen. Available at: <https://www.intechopen.com/books/10976>.
- Oram, B. 2009 *Total Phosphorus and Phosphate Impact on Surface Waters*. Water Research Center, Dalas, USA.
- Ownby, M., Desrosiers, D. A. & Vaneckhaute, C. 2021 Phosphorus removal and recovery from wastewater via hybrid ion exchange nanotechnology: a study on sustainable regeneration chemistries. *npj Clean Water* **4**, 1–8.
- Pandya, S., Jani, S., Chavan, A., Singh, A., Bhatt, S., Patel, D., Bhatt, B., Patel, A., Girma, A. & Naik, K. 2013 Nanocomposites and IT'S application-review. *International Journal of Pharmaceutical Sciences and Research* **4** (1), 19–28.
- Piccin, J., Dotto, G. & Pinto, L. 2011 Adsorption isotherms and thermochemical data of FD&C Red n 40 binding by chitosan. *Brazilian Journal of Chemical Engineering* **28**, 295–304.
- Punia, P., Bharti, M. K., Chalia, S., Dhar, R., Ravelo, B., Thakur, P. & Thakur, A. 2021 Recent advances in synthesis, characterization, and applications of nanoparticles for contaminated water treatment-a review. *Ceramics International* **47**, 1526–1550.
- Qiu, H., Ye, M., Zeng, Q., Li, W., Fortner, J., Liu, L. & Yang, L. 2019 Fabrication of agricultural waste supported UiO-66 nanoparticles with high utilization in phosphate removal from water. *Chemical Engineering Journal* **360**, 621–630.
- Rajaniemi, K., Hu, T., Nurmesniemi, E. T., Tuomikoski, S. & Lassi, U. 2021 Phosphate and ammonium removal from water through electrochemical and chemical precipitation of struvite. *Processes* **9**, 150.
- Rashid, M., Price, N. T., Pinilla, M. Á. G. & O'Shea, K. E. 2017 Effective removal of phosphate from aqueous solution using humic acid coated magnetite nanoparticles. *Water Research* **123**, 353–360.
- Reddy, S., Nagaraddy, N., Ramesh Bashetty, D. & Mise, S. R. 2020 Adsorption of phosphate using laterite soil, black cotton soil and fuller's earth as adsorbents. *International Research Journal of Engineering and Technology (IRJET)* **07** (08), 5091–5095.
- Remya, V. R., Abitha, V. K., Rajput, P. S., Rane, A. V. & Dutta, A. 2017 Silver nanoparticles green synthesis: a mini review. *Chemistry International* **3**, 165–171.
- Rizzello, L. & Pompa, P. P. 2014 Nanosilver-based antibacterial drugs and devices: mechanisms, methodological drawbacks, and guidelines. *Chemical Society Reviews* **43**, 1501–1518.
- Ruzhitskaya, O. & Gogina, E. 2017 Methods for removing of phosphates from wastewater. In: *MATEC Web of Conferences*. EDP Sciences, p. 07006.
- Sabzehmeidani, M. M., Mahnaee, S., Ghaedi, M., Heidari, H. & Roy, V. A. 2021 Carbon based materials: a review of adsorbents for inorganic and organic compounds. *Materials Advances* **2**, 598–627.
- Salem, S. S. & Fouda, A. 2021 Green synthesis of metallic nanoparticles and their prospective biotechnological applications: an overview. *Biological Trace Element Research* **199**, 344–370.
- Samreen, S. & Kausar, S. 2019 Phosphorus fertilizer: the original and commercial sources. In: *Phosphorus-Recovery and Recycling* (H. Ohtake, & S. Tsuneda, eds.). Springer, Singapore, pp. 1–14.
- Semyalo, R., Rohrlack, T., Naggawa, C. & Nyakairu, G. W. 2010 Microcystin concentrations in Nile tilapia (*Oreochromis niloticus*) caught from Murchison Bay, Lake Victoria and Lake Mburo: Uganda. *Hydrobiologia* **638** (1), 235–244.
- Stokholm-Bjerregaard, M., McIlroy, S. J., Nierychlo, M., Karst, S. M., Albertsen, M. & Nielsen, P. H. 2017 A critical assessment of the microorganisms proposed to be important to enhanced biological phosphorus removal in full-scale wastewater treatment systems. *Frontiers in Microbiology* **8**, 718.
- Sun, J., Gao, A., Wang, X., Xu, X. & Song, J. 2020 Removal of phosphorus from wastewater by different morphological alumina. *Molecules* **25**, 3092.
- Trinh, V. T., Pham, T. T. H., Van, H. T., Trinh, M. V., Thang, P. Q., Vu, X. H., Nguyen, V. Q. & Dang, T. T. 2020 Phosphorus removal from aqueous solution by adsorption using silver nanoparticles: batch experiment. *Journal of Hazardous, Toxic, and Radioactive Waste* **24**, 04020038.
- Tzabar, N. & Ter Brake, H. 2016 Adsorption isotherms and Sips models of nitrogen, methane, ethane, and propane on commercial activated carbons and polyvinylidene chloride. *Adsorption* **22** (7), 901–914.
- Verma, S. & Nadagouda, M. N. 2021 Graphene-based composites for phosphate removal. *ACS Omega* **6**, 4119–4125.
- Vikrant, K., Kim, K. H., Ok, Y. S., Tsang, D. C., Tsang, Y. F., Giri, B. S. & Singh, R. S. 2018 Engineered/designer biochar for the removal of phosphate in water and wastewater. *Science of the Total Environment* **616**, 1242–1260.
- Watson, S. B., Whitton, B. A., Higgins, S. N., Paerl, H. W., Brooks, B. W. & Wehr, J. D. 2015 Harmful algal blooms. In: *Freshwater Algae of North America* (J. D., Wehr, R. G. Sheath, & J. P. Kocielek, eds.). Elsevier, Amsterdam, The Netherlands.

- Wikipedia Contributors 2022 Eutrophication. In: *Wikipedia, The Free Encyclopedia*. Available from: <https://en.wikipedia.org/w/index.php?title=Eutrophication&oldid=1094544986> (accessed 4 July 2022).
- World Health Organization. 2020 *Cyanobacterial Toxins: Microcystins. Background Document for Development of WHO Guidelines for Drinking-Water Quality and Guidelines for Safe Recreational Water Environments*. World Health Organization, Geneva, Switzerland.
- Wu, J. X., Huang, H., Yang, L., Zhang, X. F., Zhang, S. S., Liu, H. H., Wang, Y.-Q., Yuan, L., Cheng, X.-M., Zhang, D. G. & Zhang, H. Z. 2018 *Gastrointestinal toxicity induced by microcystins. World Journal of Clinical Cases* **6** (10), 344.
- Wu, K., Li, Y., Liu, T., Huang, Q., Yang, S., Wang, W. & Jin, P. 2019 The simultaneous adsorption of nitrate and phosphate by an organic-modified aluminum-manganese bimetal oxide: adsorption properties and mechanisms. *Applied Surface Science* **478**, 539–551.
- Xie, Q., Li, Y., Lv, Z., Zhou, H., Yang, X., Chen, J. & Guo, H. 2017 Effective adsorption and removal of phosphate from aqueous solutions and eutrophic water by Fe-based MOFs of MIL-101. *Scientific Reports* **7**, 1–15.
- Xiong, W., Tong, J., Yang, Z., Zeng, G., Zhou, Y., Wang, D., Song, P., Xu, R., Zhang, C. & Cheng, M. 2017 Adsorption of phosphate from aqueous solution using iron-zirconium modified activated carbon nanofiber: performance and mechanism. *Journal of Colloid and Interface Science* **493**, 17–23.
- Xu, Y., Lv, H., Qian, G., Zhang, J. & Zhou, J. Z. 2014 Dual removal process of phosphate on Ca-layered double hydroxide with substitution of Fe for Al. *Journal of Hazardous, Toxic, and Radioactive Waste* **18**, A4014001.
- Xu, J., Luu, L. & Tang, Y. 2017 Phosphate removal using aluminum-doped magnetic nanoparticles. *Desalination and Water Treatment* **58**, 239–248.
- Yasipourtehrani, S., Strezov, V. & Evans, T. 2019 Investigation of phosphate removal capability of blast furnace slag in wastewater treatment. *Scientific Reports* **9** (1), 1–9.
- Yin, Q., Ren, H., Wang, R. & Zhao, Z. 2018 Evaluation of nitrate and phosphate adsorption on Al-modified biochar: influence of Al content. *Science of the Total Environment* **631**, 895–903.
- Yoon, S. Y., Lee, C. G., Park, J. A., Kim, J. H., Kim, S. B., Lee, S. H. & Choi, J. W. 2014 Kinetic, equilibrium and thermodynamic studies for phosphate adsorption to magnetic iron oxide nanoparticles. *Chemical Engineering Journal* **236**, 341–347.
- Younas, F., Mustafa, A., Farooqi, Z. U. R., Wang, X., Younas, S., Mohy-Ud-Din, W., Ashir Hameed, M., Mohsin Abrar, M., Maitlo, A. A. & Noreen, S. 2021 Current and emerging adsorbent technologies for wastewater treatment: trends, limitations, and environmental implications. *Water* **13** (2), 215.
- Yuan, Z., Jiang, S., Sheng, H., Liu, X., Hua, H., Liu, X. & Zhang, Y. 2018 Human perturbation of the global phosphorus cycle: changes and consequences. *Environmental Science & Technology* **52** (5), 2438–2450.
- Zhang, C., Li, Y., Wang, F., Yu, Z., Wei, J., Yang, Z., Ma, C., Li, Z., Xu, Z. & Zeng, G. 2017 Performance of magnetic zirconium-iron oxide nanoparticle in the removal of phosphate from aqueous solution. *Applied Surface Science* **396**, 1783–1792.
- Zhang, X., Lin, X., He, Y., Chen, Y., Zhou, J. & Luo, X. 2018 Adsorption of phosphorus from slaughterhouse wastewater by carboxymethyl konjac glucomannan loaded with lanthanum. *International Journal of Biological Macromolecules* **119**, 105–115.
- Zhang, J., Zhang, Y., Zhao, W., Li, Z. & Zang, L. 2020 Facile fabrication of calcium-Doped carbon for efficient phosphorus adsorption. *ACS Omega* **6**, 327–339.
- Zhang, K., Dyk, L. V., He, D., Deng, J., Liu, S. & Zhao, H. 2021 Synthesis of zeolite from fly ash and its adsorption of phosphorus in wastewater. *Green Processing and Synthesis* **10** (1), 349–360. doi:10.1515/gps-2021-0032.
- Zhao, C., Wang, B., Theng, B. K., Wu, P., Liu, F., Wang, S., Lee, X., Chen, M., Li, L. & Zhang, X. 2021 Formation and mechanisms of nano-metal oxide-biochar composites for pollutant removal: a review. *Science of the Total Environment* **767**, 145305.
- Zhou, Q., Wang, X., Liu, J. & Zhang, L. 2012 Phosphorus removal from wastewater using nano-particulates of hydrated ferric oxide doped activated carbon fiber prepared by Sol-Gel method. *Chemical Engineering Journal* **200**, 619–626.

First received 10 August 2022; accepted in revised form 11 November 2022. Available online 24 November 2022