A comprehensive review on nitrate and phosphate removal and recovery from aqueous solutions by adsorption

Alemu Gizaw a,*, Feleke Zewge b, Arun Kumar c, Andualem Mekonnen d andMelaku Tesfaye e

aAfrica Center of Excellence for Water Management, Addis Ababa University, Addis Ababa, Ethiopia
bDepartment of Chemistry, College of Natural and Computational Sciences, Addis Ababa University, Addis Ababa, Ethiopia
cDepartment of Civil Engineering, Indian Institute of Technology, Delhi, India
dCenter for Environmental Sciences, Addis Ababa University, Addis Ababa, Ethiopia
eDepartment of Chemical Engineering, Adama Science and Technology University, Adama, Ethiopia
*Corresponding author. E-mail: alemu.gizaw@aau.edu.et

ABSTRACT

Nitrogen and phosphorus removal and recovery are considered as one of the interventions to control water bodies’ eutrophication by application of various methods. Adsorption is an effective method for phosphate and nitrate removal from wastewater. It is efficient, quick, easy, low-cost and environmentally friendly. Even though different adsorbents have been developed with excellent properties, lack of compilation, lack of consistency in operational conditions, and lack of other important parameters used for direct comparison and practical use selection were observed. The first aim of this review is to provide facts and figures on novel adsorbents used for nitrate, phosphate, and simultaneous nitrate-phosphate removal and recovery. Second, various adsorbents applied for nitrate and phosphate removal have been compared in terms of the number of cycles that the adsorbent used; retained removal capacity (RR); the removal capacity of the adsorbent considering the threshold limit settled by EU and EPA as equilibrium concentration for phosphate (q0.1) and nitrate (q10); and time to reach the equilibrium capacity (t90). Third, based on the afore-mentioned criteria, the best adsorbents is proposed and this is the key novelty of this review work. Moreover, future aspects and challenges regarding nitrate and phosphate removal and recovery are presented.

Key words: adsorption, co-adsorbent, nitrate, phosphate, recovery, removal

HIGHLIGHTS

- Reported novel nitrate, phosphate, and nitrate-phosphate co-adsorbents facts and figures were compiled.
- The reported nitrate and phosphate recovery eluents used were assessed.
- Adsorbents with nitrate and phosphate qm > 50 mg/g were shortlisted for comparison using q0.1/q10 (mg/g), t90 (h), number of cycles (cycles) and retained removal capacity (RR) as comparison parameters.
- Relatively high removal capacity were proposed.
**INTRODUCTION**

Phosphorous and nitrogen are key compounds of fertilizers which can be considered as limiting nutrients for which there is no substitute (Rashidi Nodeh *et al.* 2017). According to the projection made by FAO, the annual demand for phosphorous and nitrogen is expected to increase with the world's population growth. The long-term worldwide nutrients consumption has been forecasted to reach 199.3 million ton (72.2% nitrogen and 27.8% phosphorous) in 2030. Weathering from the rocks by rain, phosphorous mining from rock, other abiotic means such as agriculture, industrial activities, municipal wastewater, etc., are roots through which phosphorus enters water and soil. Once it reaches the water and soil, plants and microorganisms have access to absorb phosphorus for their growth. The absorbed phosphorus will return back to the water and soil after the decomposition of these plants and microorganisms (Meena 2018). In the past, phosphorous mining was able to meet the demands of the ever-increasing fertilizer industry though it resulted in phosphorus depletion. The depletion of phosphorus can be taken as a next-generation equity question since the aforementioned natural inorganic phosphorous cycle takes which takes several million years and it is not a sustainable source (Meena 2018; Chen *et al.* 2019).

About 27 million tons/year of phosphorus is added to agricultural land in the form of fertilizer, while only 3 million tons/year is consumed by humans through diet, and the rest is considered as lost (Kalmykova & Karlfeldt Fedje 2013; Chen *et al.* 2019).

Nitrogen can be fixed by bacteria and blue green algae (nitrogen fixation) and abiotic means such as lightening, ultraviolet radiation, etc., and it can also be converted to ammonia by the Haber–Bosch process. This fixed nitrate and ammonia assimilated by algae and higher plants is further consumed by animals. The remains of these living things are decomposed by microorganism to ammonia (NH₃) and ammonium (NH₄⁺) by the ammonification process. The nitrifying bacterium transforms the soil ammonia to nitrates which plants easily absorb for growth through the nitrification process. Moreover, nitrates metabolized by denitrifying bacteria under anaerobic conditions depletes soil nitrate forming free atmospheric nitrogen (Guignard *et al.* 2017). When urea (the most prominent fertilizer used in the world due to its major nitrogen source) is applied to the soil, urea reacts with water to form ammonia, which makes the nitrogen within the fertilizer available to plants. Nitrate from urea, which is highly mobile in nature, can be easily released in the soil and water through bacterial activities. Approximately more than 50% of nitrogen provided by urea is lost to the surroundings. This makes the agricultural run-off to be considered as one of the common sources of nitrate and phosphate containing wastewater among other potential sources such as sewage, atmospheric deposition, urban run-off and industrial wastewater. Discharge of wastewater containing excess...
nitrate and phosphate is a serious environmental problem worldwide, as these nutrients cause eutrophication of surface water bodies and enhance the growth and proliferation of invasive aquatic plants (Berkessa et al. 2019). Moreover, loads of nitrate containing wastewater shows harmful effects on the water bodies (Berkessa et al. 2019). High concentrations of nitrate and nitrite in drinking water supply sources causes infant methemoglobinemia and teratogenic effects, respectively, and also adversely affects aquatic life such as the growth of algae, fish, and animals. To combat these effects, countries and organizations set nitrate and phosphate discharge limits for water bodies. According to European Union (EU) countries, phosphate discharge to sensitive water bodies such as lakes and rivers is set to be less than 0.01 and 0.07 mg/L, respectively (Guignard et al. 2017; Ruzhitskaya & Gogina 2017; Berkessa et al. 2019; Kim et al. 2019). The US Environmental Protection Agency (EPA) also highly recommends the maximum permissible level of nitrate in drinking water to be 10 mg/L (Bhatnagar & Sillanpää 2011; Rashidi Nodeh et al. 2017). The Bureau of Indian Standards recommended 5 mg/L as the maximum discharge limit for phosphate (Namasivayam & Prathap 2005). Moreover, according to IS 10,500, the maximum allowable concentration of nitrate in drinking water is 15 mg/L (Kumar & Goel 2010). Most African countries, including Ethiopia, tried to adopt their own nitrate and phosphate discharge standard from these established standards. Due to the settled discharge limit, environmental impacts and other driving forces (Figure S1), nitrate and phosphate is highly recommended to be removed and recovered using different conventional and advanced technologies including electrochemical processes, enhanced biological reactors, membrane technologies, wetland, chemical precipitation and crystallization, and adsorption (Namasivayam & Pratham 2005; Kumar & Goel 2010; Monfet et al. 2017). It has been extensively reported by different researchers that adsorption is an effective technology for the removal of nitrate and phosphate ions from wastewater since it is efficient, quick, easy, environmentally friendly, and considered a low-cost method (Liu et al. 2018). Following the nitrate and phosphate removal using appropriate adsorbents, acidic or basic eluents have been commonly used to recover the pollutant in the downstream process (Mayer et al. 2016; Liu et al. 2018).

In this review, previously reported facts and figures are compiled to provide information regarding the removal and recovery of the specified pollutants from the aqueous solution by novel nitrate, phosphate, and nitrate-phosphate co-adsorbents. Different keywords were entered in the Google Scholar database to ensure the consideration of all relevant published papers. The trend indicates that phosphate adsorbents have been exhaustively researched as compared to nitrate adsorbents and nitrate-phosphate co-adsorbents.

The reported adsorbents observed lack of compilation; lack of consistency in the operational conditions; and lack of other important parameters used for direct comparison and practical use selection. This review provides facts and figures on novel adsorbents used for nitrate, phosphate, and simultaneous nitrate-phosphate removal and recovery. Moreover, various adsorbents applied for nitrate and phosphate removal have been compared in terms of the number of cycles that the adsorbent used (Cycles); retained removal capacity (RR); the removal capacity of the adsorbent considering the threshold limit settled by EU and EPA as equilibrium concentration for phosphate ($q_{0.1}$) and nitrate ($q_{10}$); and time to reach this equilibrium capacity ($t_{eq}$). Based on the above-mentioned important criteria this review article proposes the best adsorbents, as shown in Figure 1. This is the key novelty of this review work. Moreover, future aspects and challenges regarding nitrate and phosphate removal and recovery are presented.

**ADSORPTION KINETICS, ISOThERMs AND THERmODYNAMICS**

*Adsorption kinetics*

The kinetic studies for water purification are of utmost importance for speculating the most favorable conditions to perform efficient adsorption of pollutants. The kinetics describes the solute uptake rate that directly controls the residence time of sorbate uptake at the solid-solution interface, which also helps to further understand the adsorption mechanisms. Commonly reported kinetic models are pseudo-first-order, pseudo-second-order, intra-particle diffusion, and inter-particle diffusion. Table S1 provides a summary of kinetic models together with the model equations.

*Adsorption isotherms*

An adsorption isotherm is an equation that relates the equilibrium concentration of a solute on the surface of an adsorbent to the concentration of the solute in the liquid, which can be graphically represented at a particular temperature. There are several models for predicting the equilibrium distribution. However, widely accepted models are Langmuir and Freundlich (Iftekhar et al. 2018). Other adsorption isotherm models used in the adsorption study are summarized in Table S2.
Adsorption thermodynamics

In the adsorbent design and adsorption process study, the thermodynamic parameters are required to understand the effect of temperature on the adsorption behavior of a pollutant on an adsorbent. It also helps to understand the possibility and nature of the adsorption process (Seresheti et al. 2020). Some thermodynamic parameters related to the adsorption process are changes in standard free energy ($\Delta G^o$), enthalpy ($\Delta H^o$), and entropy ($\Delta S^o$), which are calculated using thermodynamic equations. Standard free energy change ($\Delta G^o$) is given as follows:

$$\Delta G^o = -RT \ln K_C$$

(1)

$$K_C = \frac{q_e}{C_e}$$

(2)

where $\Delta G^o$ is in kJ/mol, $T$ is the temperature in K, and $R$ is the universal gas constant (8.314 J/mol/K):

$$\Delta G^o = \Delta H^o - T\Delta S^o$$

(3)

$$\ln K_C = \frac{\Delta S^o}{R} - \frac{\Delta H^o}{RT}$$

(4)

where $\Delta H^o$ is in kJ/mol and $\Delta S^o$ is in kJ/mol/K. The values of $\Delta S^o$ and $\Delta H^o$ will be determined from the slope and intercept of the plot of $\ln K_C$ versus $1/T$. Gibbs free energy change of the sorption ($\Delta G^o$) will be determined using Equation (1). It is reported that the negative value of $\Delta G^o$ indicates spontaneity of adsorption (Shin et al. 2004; Mayer et al. 2016; Monfet et al. 2017; Ruzhitskaya & Gogina 2017; Xiao et al. 2017; Zhang et al. 2017; Liu et al. 2018; Meena 2018; Prashantha Kumar et al. 2018; Berkessa et al. 2019; Kim et al. 2019; Bacelo et al. 2020). The value of $\Delta G^o$, which increases (Deng & Shi 2015; Mor et al. 2016; Aljeboree et al. 2017; Yang et al. 2017; Banu et al. 2019; Gaidoumi et al. 2019; Manhooei...
and decreases with temperature (Chatterjee & Woo 2009; Rezaei Kalantary et al. 2016; Song et al. 2016; Liu et al. 2019a, 2019b; Zhang et al. 2019), indicates that the adsorption process is favorable at low and high temperatures, respectively. A positive $\Delta H^\circ$ value shows that the process of adsorption is endothermic (Rajeswari et al. 2016; Rezaei Kalantary et al. 2016; Song et al. 2016). A negative value of $\Delta H^\circ$ indicates the exothermic nature of the sorption process (Chatterjee & Woo 2009; Deng & Shi 2015). A positive $\Delta S^\circ$ value shows that randomness is enhanced whereas a negative value indicates a decrease in randomness at the solid/liquid interface during the adsorption process (Sereshti et al. 2020). Negative values of $\Delta G^\circ$, $\Delta H^\circ$, and $\Delta S^\circ$ show the exothermic and spontaneous nature of the adsorption process (Esmaeili Bidhendi et al. 2019).

**NITRATE AND PHOSPHATE REMOVAL MECHANISM**

**Electrostatic attraction**

Electrostatic attraction refers to the electrostatic force of long-range interaction occurring between the electrostatic adsorption in aqueous solution with differently charged particles or uncharged particles (Wang et al. 2020a, 2020b). Adsorption creates regions of positive charge that promote electrostatic attraction with negative regions on other particles. The protonated surface of the nitrate and phosphate adsorbents are electrostatically attracted with negatively charged nitrate ion ($\text{NO}_3^-$) and phosphate ions ($\text{H}_2\text{PO}_4^-$, $\text{HPO}_4^{2-}$, $\text{PO}_4^{3-}$). In basic solution, $\text{PO}_4^{3-}$ predominates; in weakly basic conditions $\text{HPO}_4^{2-}$ predominates; and in strong acidic condition, $\text{H}_3\text{PO}_4$ predominates (Jiang et al. 2017a, 2017b; Liu et al. 2019a, 2019b). It has been reported that the presence of positive charges due to different metal ions, $\text{NH}_4^+$, and $\text{OH}_2^-$ at the surface of the adsorbents attracts phosphate ions (Banu et al. 2019).

**Ion exchange**

Ion exchange is a process in which ions are exchanged between a solution and ion exchanging insoluble solid adsorbents. Ion exchanger can be a cation exchanger for the positively charged cations or anion exchanger for the negatively charged anions. Different functional groups such as amine groups (primary, secondary and tertiary), quaternary ammonium functional groups, and chloride ions attached to the surface of the adsorbents through the modification process can play a role in nitrate and phosphate adsorption by the ion-exchange mechanism. The primary amino groups which is available in chitosan resin is reported to have hydrophilic characteristics and removes the nitrate and phosphate (Banu & Meenakshi 2017). The amine group in amine-functionalized epichlorohydrin-grafted cellulose was used as the anion-exchanger to remove $\text{H}_2\text{PO}_4^-$ ion at pH 4.5 (Anirudhan et al. 2012). The highly positive charged quaternary ammonium groups within the host matrix were reported to exchange ions with phosphate ions in Nano-La(III) (hydr)oxides modified wheat straw (Qiu et al. 2017). The $\text{Cl}^-$ ions present in $\text{Zr}^{4+}$ ion embedded chitosan-soya bean husk activated bio-char composite beads (Zr-CS-SAC) were reported to be exchanged by nitrate and phosphate ions (Banu et al. 2019).

**Surface complexation (inner-sphere and outer-sphere)**

Commonly, there are two mechanisms by which surface complexation is formed through electron transfer; the outer-sphere complexation mechanism and inner-sphere complexation mechanism. In the outer-sphere complexation mechanism, electron transfer occurs between complexes that do not undergo substitution and no bonds are broken or formed as a result of the electron transfer. Inner-sphere complexation mechanism electron transfer occurs between complexes via a bridging ligand and at least one of the complexes needs to be liable for the bridge formation. In $\text{La(OH)}_3$ modified magnetic pineapple biochar exchange of $\cdot\text{OH}$ from $\text{La-OH}$ with phosphate to form $\text{La-O-P}$, inner-sphere complexation was one of the removal mechanisms reported (Liao et al. 2018). Reported research indicates that La metal played a key role in the complexation of phosphate (Drenkova-Tuhtan et al. 2017; Rashidi Nodeh et al. 2017; Jiang et al. 2018; Shi et al. 2019). Moreover, in adsorbents such as MgO-modified magnetic biochar (MgO@MBC), surface complexation can be formed between Fe-O/Mg-O and phosphate (Fe-O-P/Mg-O-P) (Liu et al. 2019a, 2019b).

**Ligand exchange**

Ligands are ions or neutral molecules with electron pairs that they can donate to the metal atom to form a coordinate covalent bond. Reports indicated that ligand exchange can be generated by inner-sphere complexes and electrostatic attraction between negatively charged phosphate ions and the positively charged metal and metal oxide surfaces (Jiang et al. 2018). For instance, as reported by Wu et al. (2017), for $\text{La(OH)}_3/\text{Fe}_2\text{O}_3(4:1)$ nanocomposites, ligand exchange reaction between...
OH and phosphate ions can be:

\[ \text{La-OH} + \text{H}_2\text{PO}_4^- \leftrightarrow \text{La-H}_2\text{PO}_4^- + \text{OH}^- \]  
\[ \text{La} = \text{OH} + \text{HPO}_2^2- \leftrightarrow \text{La} = \text{HPO}_2^2- + 2\text{OH}^- \]  
\[ \text{La} = \text{OH} + \text{PO}_3^3- \leftrightarrow \text{La} = \text{PO}_3^3- + 5\text{OH}^- \]  

As indicated in Equations (5)–(7), the release of OH\(^-\) upon ligand exchange resulted in an increase of pH (Wu et al. 2017; Liao et al. 2018).

**Hydrogen bonding**

The hydrogen bond results from an electrostatic attraction between a positively charged hydrogen ion with negatively charged ions such as O\(_2\) or N\(_2\). The hydrogen atom may lose its sole electron to any of its neighbors with equal probability which results in the formation of hydrogen bonding to its neighbors of opposite charges. The hydroxyl ion (OH\(^-\)) is a good example, where one negative charge of O\(_2\) is attracted by the positive charge of hydrogen to form the unit OH\(^-\). This unit, due to its net negative charge, will then form a component of the phosphate crystal structures. The hydrogen bond is not as strong as the ionic and covalent bonds but is stronger than the van der Waals bond (Wang et al. 2020a, 2020b). Reported research indicated that there was a possibility of hydrogen bonding of nitrate with hydroxyl groups present inside chains of adsorbent (NO\(_3\)…OH\(^-\)) (Banu & Meenakshi 2017). Moreover, hydrogen bonding can be formed between nitrate and phosphate ions, and hydroxyl groups present inside chains of chitosan (Banu et al. 2019).

**Physisorption and chemisorption**

Chemisorption occurs when a functional group of an organic chemical interacts with a reactive surface on the adsorbents through the formation of strong chemical bonds, principally covalent bonds (Kong et al. 2019). Physisorption is adsorption by van der Waals force, which is a weak intermolecular attraction that takes place below the critical temperature of the adsorbate and results in the development of a monolayer or multilayer. Since physisorption is caused by intermolecular forces, the binding force is weak with less adsorption heat, and the rate of adsorption and desorption is fast. The adsorbed substance is also easier to desorb, so the physical adsorption is reversible to a certain extent. For example, adsorbed gas on activated carbon is easily extricated without any changes in nature. Chemisorption involves the transfer, exchange, or sharing of electrons between adsorbates and adsorbents (atoms or molecules), and the adsorption of adsorbates on adsorbents is due to the formation of chemical bonds between them. For instance, phosphate ions were adsorbed onto the external surface by external diffusion due to the high concentration of phosphate and a larger number of binding sites in the initial stage. Afterwards, phosphate ions diffused into pores of MgO@MBC and were finally adsorbed in inner pores by the active sites (Liu et al. 2019a, 2019b). In calcium silicate hydrates, reported researches indicated that surface-exposed Ca\(^{2+}\) sites phosphate adsorption rapidly takes place through the pores of the crystal and gradually phosphate-binding affinity decreased as the active sites saturated (Zhang et al. 2019). In magnetic Co\(_3\)O\(_4\)/Fe\(_3\)O\(_4\) doped polyaniline nanocomposite (Esmaeili Bidhendi et al. 2019) and activated carbon-Fe\(_3\)O\(_4\) magnetic nanoparticles (Rezaei Kalantary et al. 2016) formation a single layer of adsorbate at the adsorbent surface followed by the addition of more layers via the electrostatic interaction existing between the negatively charged nitrate ions and the positively charged adsorbent were reported.

**Precipitation**

The precipitation technique is also known as ‘wet precipitation,’ ‘chemical precipitation’ or ‘aqueous precipitation’. Chemical reaction of phosphate with Ca\(^{2+}\) results in precipitation in the form of calcium phosphate complex (Choi et al. 2018; Leng et al. 2019), Mg\(^{2+}\) (Liu et al. 2019a, 2019b; Xu et al. 2019), La\(^{3+}\) (Chen et al. 2018; Liao et al. 2018). Similarly, Leng et al. (2019) reports that Ca\(^{2+}\) ion as a crystal seed was gradually released from the meat and bone meal ash into the solution which further results in precipitation of calcium phosphate complex. The suggested
AQUA – Water Infrastructure, Ecosystems and Society Vol 00 No 0, 7

precipitation reaction mechanism can be written as (Leng et al. 2019):

\[
\begin{align*}
H_2PO_4^- + Ca^{2+} + H_2O & \rightarrow Ca(H_2PO_4)\_2(Ca(H_2PO_4)\_2.H_2O) \quad (8) \\
2HPO_4^{2-} + Ca^{2+} + 2H_2O & \rightarrow CaHPO_4(CaHPO_4\_2.2H_2O) \\
2PO_4^{3-} + 3Ca^{2+} & \rightarrow Ca_3(PO_4)\_2 \\
3PO_4^{3-} + 5Ca^{2+} + OH & \rightarrow Ca_5(PO_4)\_5(OH)
\end{align*}
\]

NITRATE, PHOSPHATE, AND NITRATE-PHOSPHATE REMOVAL

Nitrate removal

Various adsorbents have been developed by different scholars with excellent properties to adsorb nitrates from water. A wide variety of adsorbents have been reported as efficient materials for the nitrate removal from wastewater, such as modified nano adsorbents (Suzaimi et al. 2019), chitosan hydrogel beads (Chatterjee & Woo 2009), chitosan/PEG and chitosan/PVA polymer composites (Rajeswari et al. 2016), cellulose nanocrystal modified with 3-chloropropyl trimethoxysilane (Manhooei et al. 2019), modified steel slag (Yang et al. 2017), amine cross-linked biosorbent (ACB) (Ren et al. 2016), magnetic amine-cross linked biopolymer-based corn stalk (Song et al. 2016), magnetic Co_3O_4/Fe_3O_4 doped polyaniline nanocomposite (Esmaeili Bidhendi et al. 2019), activated carbon magnetic nanoparticles (Rezaei Kalanary et al. 2016), local clay (Battas et al. 2019), zeolites and hollow fiber membrane contactors (Sancho et al. 2017), natural ion exchanger (Taylor et al. 2010), raw aluminosilicate (RAS) and modified aluminosilicate (MAS) (de P. Couto et al. 2016), and valueless waste materials (aluminum building scrap wire, takeout food containers, potato peelings, and bagasse) (El-Nahas et al. 2019).

Nano-adsorbents received special interest in wastewater treatment through the adsorption process due to their high surface area, desired surface charge, and the ability to be specific towards the targeted pollutants in the wastewater (Suzaimi et al. 2019). Chitosan, which is produced from naturally and abundantly available chitin having many free amino and hydroxyl groups, could coordinate with different ions through grafting. A chelation mechanism was used to modify adsorbent for nitrate remediation. Nitrate adsorbents, such as chitosan hydrogel beads (Chatterjee & Woo 2009), chitosan/PEG, and chitosan/PVA polymer composites (Rajeswari et al. 2016) were synthesized through grafting and chelating with chitosan. Chemically modified cellulose nanocrystal (CNC) was investigated for nitrate removal from aqueous solution by Manhooei et al. (2019). According to their experiment, an optimum nitrate removal efficiency of 86.5% was achieved at pH 7, initial nitrate concentration of 20 mg/L, room temperature, and the dose of 3 g/L within 10 minutes, and nitrate adsorption was found to be affected by anions in the order of SO_4^{2-} > HCO_3^- > Cl^- > PO_4^{3-} (Manhooei et al. 2019).

Yang et al. (2017) also synthesized modified steel slag (MSS) by mixing steel slag, aluminum hydroxide, and deionized water using a ratio of 3:0.45:2 followed by aging and thermal activation at 800 °C. They observed that the dipole-dipole bond interaction of Si-O-Si bond and the Al-O-Al bond with nitrate on the surface of the MSS plays a major role in the up-taking of nitrate. The higher adsorption capacity of the MSS was obtained as compared to original steel slag (OSS) which may be due to modification of the steel slag surface (Yang et al. 2017).

Amine cross-linked biosorbent (ACB) studied by Ren et al. (2016) achieved the maximum nitrate adsorption capacity of 118.9 mg/g which was attributed to the effect of the tertiary amine. The amine group was observed to play a major role in the uptake of nitrate by electrostatic attraction (Ren et al. 2016). About 97.3–98.4% removal capacity by ACB was observed after three cycles of adsorption-desorption (Ren et al. 2016). Moreover, according to Song et al. (2016), magnetic amine cross-linked biopolymer-based corn stalk was observed to remove nitrate from simulated wastewater at a lower adsorbent dosage than raw corn stalk (Song et al. 2016). Esmaeili et al. (2019), also reported about 95.24% nitrate removal, over a wide range of pH levels (2–10), dosages (0.25–7.5 g/L), adsorption times (5–150 min), nitrate initial concentrations (1–25 mg/L), and three levels of temperature (20, 25 and 35 °C) for magnetic Co_3O_4/Fe_3O_4 doped polyaniline nanocomposite (Esmaeili Bidhendi et al. 2019). Activated carbon magnetic nanoparticles was another magnetically functioned nitrate adsorbent which showed a retained removal capacity of 90% after ten cycles of adsorption-desorption with an adsorption capacity of 57.1 mg/g (Rezaei Kalantary et al. 2016).

Clay and zeolite have also been explored as adsorbents due to their high surface area. Zeolites can be used at the primary treatment exit as an alternative to the biological removal process in a cost-effective way (Battas et al. 2019). The experiment conducted using natural zeolites and hollow fiber membrane contactors for ammonia removal and recovery showed
efficiency greater than 98% (Sancho et al. 2017). Taylor et al. (2010) used natural zeolite-clinoptilolite to remove ammonium nitrogen from pretreated domestic sewage. For 23 mg/L of total ammonium nitrogen in the down flow column at 3.9-bed volumes (BV) per day, breakthrough was observed to occur after about 560 BV. A natural granular clinoptilolite zeolite was found to have the optimum total ammonium nitrogen removal capacity of 14 g/kg. This study indicated that the use of zeolite materials can be considered as an alternative to subsequent nitrification-denitrification in the downstream processes (Taylor et al. 2010).

Moreover, aluminosilicate clay was used as an alternative adsorbent of ammonia-nitrogen removal with its subsequent utilization as agricultural feedstock after wastewater treatment. Schirmer et al. (2016) used raw aluminosilicate (RAS) and modified aluminosilicate (MAS) for the removal of nitrogen from distilled old landfill leachate. They observed that modification resulted in an increase in the adsorption capacity of aluminosilicates from 1.23 to 7.83 mg/g (de P. Couto et al. 2017).

El-Nahas et al. (2019) examined active acid alumina modified aluminum building wire scraps (AlBWS), aluminum take-out food container waste (AITFC), activated carbon from potato peelings (ACPP), and sugarcane bagasse (ACSB) for nitrate removal from real and synthetic samples. The results of their study reported excellent removal capacity for nitrate removal from groundwater samples (El-Nahas et al. 2019). Double layered hydroxide was also reported to remove nitrate. Zn/Al chloride layered double hydroxide (Zn/Al-DLH) was examined for the nitrate removal exhibited low adsorption and poor regeneration (Islam & Patel 2010).

The reported nitrate adsorbents (Table 1) shows the Langmuir isotherm (assumes monolayer adsorption onto finite and identical surfaces of the adsorbent) (Xiaong et al. 2012) and the Freundlich isotherm (assumes adsorption on uneven surfaces of the adsorbent by monolayer adsorption) (Yang et al. 2017). Moreover, reported nitrate adsorbents were well fitted to the pseudo-second-order kinetic model and predicted a chemisorption process involving ion exchange. Chemisorption occurs when a functional group of an organic chemical interacts with a reactive surface on the adsorbents through the formation of strong chemical bonds, principally covalent bonds (Kong et al. 2019). The adsorption mechanisms of the reported nitrate

| Adsorbent | q_m (mg/g) | Kinetic model | Isothermal model | Optimum conditions of adsorption | Ref. |
|-----------|------------|---------------|-----------------|-------------------------------|------|
| Chitosan hydrogel beads | 92.1 | PSO | 49.02 | Freundlich | 3–6 | 30 | 100 | 10 | 1 | Chatterjee & Woo (2009) |
| Chitosan/PEG | 50.68 | PSO | 4.64 | Freundlich | 3 | 30 | 10 | 1 | 0.3 | Rajeswari et al. (2016) |
| Chitosan/PVA | 35.03 | PSO | 4.26 | Freundlich | 6–9 | 45 | 75 | 1.5 | 1.2 | Ren et al. (2016) |
| CNC | 118.90 | PSO | 6.92 | Freundlich | 4 | 25 | 20 | 3 | 10 | Yang et al. (2017) |
| MSS | 6.165 | PSO | 0.37 | Freundlich | 7 | 25 | 20 | 0.17 | 3 | Manhooei et al. (2019) |
| ACB | 102.00 | PSO | 35.10 | Freundlich | 6–9 | 45 | 75 | 1.5 | 1.2 | Ren et al. (2016) |
| MAB-CS | 102.04 | PSO | 16.00 | Freundlich | 7 | 15 | 100 | 6 | 1 | Song et al. (2016) |
| PANI-Co3O4@MNP | 68.96 | PFO | 14.18 | Freundlich | 6 | 20 | 1–25 | 1 | 3 | Esmaeili Bidhendi et al. (2019) |
| AC-Fe2O3 MNP | 57.1 | PSO | 57.4 | Freundlich | 3 | 30 | 100 | 1 | 1 | Rezaei Kalanary et al. (2016) |
| Local clay | 5.1 | PSO | 0.384 | Freundlich | 2 | 25 | 100 | 2 | 20 | Battas et al. (2019) |
| Natural zeolites | 3.90 | PSO | 0.38 | Freundlich | 8 | 22 | 25 | 0.17 | 10 | Sancho et al. (2017) |
| RAS | 1.23 | PSO | 25.00 | Freundlich | 7 | 25 | 10 | 0.33 | 10 | de P. Couto et al. (2017) |
| MAS | 7.83 | PSO | 20.28 | Freundlich | 7 | 25 | 10 | 0.33 | 10 | de P. Couto et al. (2017) |
| AlBWS | 12.40 | PSO | 5.01 | Freundlich | 4.7 | 25 | 50 | 5 | 6 | El-Nahas et al. (2019) |
| AITFC | 7.50 | PSO | 5.23 | Freundlich | 4.4 | 25 | 50 | 5 | 6 | El-Nahas et al. (2019) |
| ACPP | 8.80 | PSO | 5.77 | Freundlich | 9.8 | 25 | 50 | 5 | 6 | El-Nahas et al. (2019) |
| ACSB | 7.10 | PSO | 4.95 | Freundlich | 7.5 | 25 | 50 | 5 | 6 | El-Nahas et al. (2019) |
adsorbents were mainly electrostatic attraction, ion exchange, chemisorption and physisorption (Chatterjee & Woo 2009; Ren et al. 2016; Rezaei Kalantary et al. 2016; Song et al. 2016; Banu et al. 2019; Alagha et al. 2020). The tertiary amine group through ionic interactions (Rajeswari et al. 2016; Ren et al. 2016), and ligand exchange through replacement of OH group of the adsorbent (Rezaei Kalantary et al. 2016) plays a major role in the adsorption process of nitrate. Table S3 shows the thermodynamic behavior of the reported nitrate adsorbents. Most of the reported nitrate adsorbents had negative value standard free energy ($\Delta G^o$) which indicates spontaneous adsorption (Xiao et al. 2017). The value of $\Delta G^o$ was observed to increase (Banu et al. 2019; Manhooei et al. 2019; Alagha et al. 2020), and decrease (Chatterjee & Woo 2009; Rezaei Kalantary et al. 2016; Song et al. 2016; Manhooei et al. 2019) with a temperature that indicates the adsorption process is favorable at low and high temperature, respectively. Endothermic (Rajeswari et al. 2016; Rezaei Kalantary et al. 2016; Song et al. 2016), and exothermic nature of the adsorption process (Chatterjee & Woo 2009; Deng & Shi 2015) was observed by a positive and negative value of enthalpy ($\Delta H^o$), respectively. A positive and negative value of entropy ($\Delta S^o$) shows that randomness is enhanced while negative values of entropy of $\Delta S^o$ show a decrement of randomness at the solid/liquid interface during the adsorption process (Sereshti et al. 2020). Negative values of $\Delta G^o$, $\Delta H^o$, and $\Delta S^o$ show the exothermic and spontaneous nature of the adsorption process (Esmaili Bidhendi et al. 2019).

Phosphate removal

Calcium silicate hydrate (CSH) adsorbents

CSH is a promising adsorbent for phosphate removal and recovery from wastewater, sludge, and solid waste ashes. In the phosphate adsorption process it acts as the seed crystal and the calcium ion donor and further helps to facilitate pH adjustment. Due to this, phosphate can easily be removed without adding extra chemicals needed for the pH adjustment (Kuwahara & Yamashita 2017; Zhang et al. 2019). CSHs is a well-known material for its biocompatibility and bioactivity (Kuwahara & Yamashita 2017; Zhu 2017). A review conducted on phosphate removal recommended that crystallization of phosphate using CSH can be considered as a feasible and low-cost method (Peng et al. 2018). Novel-CSH (Zhang et al. 2019), blast furnace slag (BF-CSH) (Kuwahara & Yamashita 2017), carbide slag (CS-CSH) (Fang et al. 2018), pure-CSH (Lee et al. 2018), porous CSH (PEG-0.6%) (Guo et al. 2013), waste glass and shells (WGS) (Jiang et al. 2017a, 2017b), Fe3O4@ASC adsorbent (Jiang et al. 2017a, 2017b) and meat and bone meal incineration ash (MBMA) (Leng et al. 2019) were reported for the phosphate removal.

The surface area and pore volume of novel-CSH are estimated to be 27.25 m²/g and 0.121 cm³/g, respectively, with the adsorption capacity of 109.4 mg/g at pH 5 and temperature of 25 °C. The aforementioned adsorbent synthesized using a novel ultrasound-assisted sol-gel method having the phosphate removal efficiency of 86.8% at 1.2 Ca/Si ratios. The adsorbent effectively removes phosphate over a wide range of initial pH. However, its removal efficiency is observed to be slightly inhibited by the presence of carbonate (Zhang et al. 2019).

Kuwahara & Yamashita (2017) have reported phosphate removal from aqueous solution using a blast furnace slag-based calcium silicate hydrate (BF-CSH) adsorbent. Adsorption experiments demonstrated that the slag-made CSH showed a maximum phosphate adsorption capacity of 53.1 mg/g under standard adsorption conditions (pH 7.0 and 25 °C), which was found to be 73 times greater than that of blast furnace slag. BF-CSH showed a strong affinity to phosphate due to $\text{Ca}^{2+}$ species abundant in its structure. It is observed to have a phosphate removal efficiency of 97–99% from simulated water (0.5–0.8 mmol/L). Results indicated that BF-CSH achieved 99% phosphate removal efficiency at 2.5 g/L dose from real wastewater and even 97% phosphate removal efficiency from low phosphate concentrations (0.5 mmol/L) at 1.5 g/L dose (Kuwahara & Yamashita 2017). Similarly, Fang et al. (2018) also examined porous calcium silicate hydrate (CS-CSH) derived from carbide slag with a surface area of 8.802 m²/g and pore volume of 0.024 cm³/g for phosphate removal. In their experiment, the CS-CSH was prepared at 150 °C for 6 h in the autoclave. According to this study, the CS-CSH showed 14.79 mg/g phosphate removal capacity after nine reusing cycles. Calcination of CS-CSH at 700 °C showed an increment in phosphate removal capacity of 5.25 mg/g. This report also showed that the negative effect of $\text{SO}_4^{2-}$ and $\text{HCO}_3^-$ on the phosphate adsorption can be suppressed by controlling the equilibrium pH between 5.3 and 10.2 (Fang et al. 2018). In another study, porous CSH (PEG-0.6%) was synthesized by inserting polyethylene glycol molecules into the void regions of oxygen-silicon tetrahedron chains. The layers of CSH exhibit a 352.96 m²/g surface area and a porous volume of 0.87 cm³/g. The phosphate removal was reported through hydroxyapatite (HAP) formation using porous CSH as a crystal seed (Guo et al. 2013). Calcium-silicate composite (CSC) and alkali-treated calcium silicate composite (ASC) were also examined for phosphate removal. These adsorbents were found to have phosphate adsorption capacity of 120 and 73.0 mg/g, respectively, with a
wide range of pH (3.0–13.0). ASC (surface area 163 m²/g and pore volume 0.33 cm³/g) at a dose of 0.8 g/L could effectively remove phosphate at its initial concentration of 10 mg/L whereas CSC (surface area 25.1 m²/g and pore volume 0.07 cm³/g) at a dose of 4.0 g/L was observed to be inefficient to remove phosphate. Moreover, ASC was shown to reduce the phosphate concentration from 10 to 0.02 mg/L of eutrophic lake water, which indicated the tendency of this adsorbent to control the eutrophication problem. Co-existing ions such as SO₄²⁻, NO₃⁻, Cl⁻, and HCO₃⁻ were observed to have strong effects on phosphate adsorption of CSC whereas it did not show a significant effect on ASC (Jiang et al. 2017a, 2017b).

Magnetic Fe₃O₄ alkali-treated calcium-silicate composite (Fe₃O₄@ASC) was studied by Jiang et al. (2017a, 2017b) as an adsorbent for its phosphate removal from water through column study. The adsorbent was found to achieve 100% removal of 10 mg/L phosphate over a wide pH range (2.5–13) at a breakthrough point of 6,000 mL for 18.02 mg/L initial phosphate concentration (Jiang et al. 2017a, 2017b).

Similarly, a batch experimental study conducted using meat and bone meal ash (MBMA) with a phosphorus content of 13.48% achieves a high phosphate removal capacity of 115 mg/g (removal = 99.5%) from simulated phosphate wastewater within an hour over a wide range of initial pH. According to this study, the phosphate was mainly removed by hydroxyapatite precipitate (HAP) (Leng et al. 2019). CSH can also be used to remove toxic metals such as lead from wastewater. Zhang et al. (2018) showed a lead removal capacity of 543.5 and 946.7 mg/L, respectively on CSH and HAP/CSH at pH 5 and 25 °C. This indicates the dual benefit of the CSH adsorbents for resource recovery and environmental pollution control (Zhang et al. 2018).

Recently, a mobile pilot-scale plant was successfully developed for phosphate recovery from wastewater with a capacity of 1,000 L using amorphous CSH for in-situ demonstration (Okano et al. 2016). About 80% of the phosphate was recovered from the anaerobic sludge liquor of which 20% was found to be soluble P₂O₅. The recovered phosphate fertilizer was confirmed by plant cultivation. Moreover, a simple technology for recycling phosphate from wastewater to agriculture was also reported by Peng et al. (2018). They prepared bi-functional agents through soaking of cement and steel industry-based calcium silicates in HCl. According to their results, the dried calcium silicate phosphate complex was found to contain 19–24% P₂O₅ with additional insignificant toxic materials (Peng et al. 2018).

**Biochar adsorbents**

Biochar is one of the abundantly available resources and it has potential capacity for adsorption after the best means of modification. Salt modified wood waste biochar (Salt-biochar) (Xu et al. 2019), wood waste biochar loaded with magnesium oxides (MgO-biochar) (Xu et al. 2018), MgO-modified magnetic biochar derived from anaerobic digestion residue (MgO@MBC) (Liu et al. 2019a, 2019b), La(OH)₃ modified magnetic pineapple biochar (Lax-MC) (Liao et al. 2018), Mg-laden biochar (Jiang et al. 2018), calcium-flour biochar (Wang et al. 2018), phosphogypsum biochar (PG-biochar) (Wang et al. 2010), calcium hydroxide coated dairy manure (Ca-MB) (Choi et al. 2019), multi-walled carbon nanotubes with chitosan (Chitosan-CNTs) (Huang et al. 2018), chitosan-calcite adsorbent (Pap et al. 2020), agro-waste rice husk ash (RHA) (Mor et al. 2016), amine-functionalized epichlorohydrin-grafted cellulose (Cell-g-E/PEI) (Anirudhan et al. 2012), iron-zirconium modified activated carbon nanofiber (ACF-ZrFe) (Xiong et al. 2017), La-porous carbon composites (La-PCCs) (Koilraj & Sasaki 2017), nano-La(III) (hydr)oxides modified wheat straw (Ws-N-La) (Qiu et al. 2017), and MgFe-LDH modified wheat-straw biochar (MgFe-LDH-Ws-biochar) (Xuo et al. 2016) were considered as sustainable, economic and novel biomass-based adsorbents for phosphate removal and recovery. Besides this, the material was reported as having little removal efficiency loss after three cycles of adsorption-desorption.

Wood waste biochar which is abundantly available biomass was used for sustainable phosphorous removal after applying an appropriate modification. Wood biochar modified in salt solutions of MgCl₂, AlCl₃, CaCl₂, and FeCl₃ were examined to release phosphate from phosphate enriched human urine. According to Xu et al. (2019), among the tested biochar, 2.3 M MgCl₂ modified biochar was found to have a high phosphate removal capacity of 118 mg P/g from the hydrolyzed urine. This study has indicated that the salt-biochar favored hydrolyzed urine rather than fresh at a small pH range of 7–9 (Xu et al. 2019). Similarly, Xu et al. (2018) studied phosphate removal and recovery using magnesium-oxides-modified biochar (MgO-biochar). The synthesized Mg-biochar of this study showed a high phosphate removal capacity of 116.4 mg/g. From the results, one can conclude that the material can be applied for phosphate removal and recovery from urine (Xu et al. 2018).

A novel magnetically recoverable MgO-modified magnetic biochar (MgO@MBC) which was synthesized by chemical co-precipitation of Mg²⁺/Fe³⁺ was used by Liu et al. (2019a, 2019b) to remove phosphate from an aqueous solution. According to the study, the MgO@MBC was exhibiting high removal efficiency of phosphate (149.25 mg P/g at 25 °C). On top of that, the MgO@MBC was easily recovery due to its magnetic properties (Liu et al. 2019a, 2019b).
La(OH)₃ modified magnetic pineapple biochar (Lax-MC) also exhibited excellent magnetic properties for high adsorption capacity up to 101.16 mg P/g and with easy recovery. However, less removal efficiency was observed after three cycles of the adsorption-desorption process. Strong stability of the ions (La³⁺ and Fe³⁺) was observed during the leaching performance investigation. The ions stability in the Lax-MC is very essential to suppress the leaching and enhance reusability during the adsorption–desorption process (Liao et al. 2018).

Mg-laden biochar (surface area 311–399 m²/g) synthesized at different temperatures (400, 500, 600 °C) was used to remove phosphate from aqueous solution using batch and column reactors. Mg-laden biochar synthesized at 400, 500 and 600 °C have shown significant phosphate removal capacities of 344, 357, and 570 mg/g, respectively for batch study; and 60.7, 61.2, and 62.2 mg/g, respectively for column study. Ligand exchange and electrostatic attraction are reported as the main removal mechanisms for this adsorbent (Jiang et al. 2018).

Calcium-decorated biochar (Ca-BC) was synthesized in different Ca(OH)₂ to flour ratios by Wang et al. (2018). Synthesized Ca-BC at the ratio of 2:1 (Ca(OH)₂ to flour) was observed to exhibit a maximum phosphate adsorption capacity of 314.22 mg/g due to the formation of hydroxyapatite (Ca₅(PO₄)₃(OH)) crystals during adsorption (Wang et al. 2018). A novel, adsorbent phospogypsum biochar (PG-biochar) thermally treated at 600 °C was reported to have a phosphate removal capacity of 102.4 mg/g at pH 6 (Wang et al. 2020a, 2020b). Moreover, novel calcium hydroxide-coated dairy manure-derived biochar (Ca-MBC) was examined for phosphate removal from water as a low-cost material (Choi et al. 2018). Similarly, other novel phosphate adsorbent, chitosan modified multi-walled carbon nanotube was synthesized through cross-linking. This study reported that the material achieved a maximum phosphate adsorption capacity of 56.1 mg/g. Interestingly, the material did not lose its removal capacity (94–98%) even after five adsorption-desorption cycles (Huang et al. 2018).

Agricultural waste biomass ash, such as rice husk ash (RHA), was also examined for the removal of phosphate and has shown a maximum removal (up to 89%) at a pH of 6 using a 2 g/L dose for 120 min (Mor et al. 2016). Similarly, amine-functionalized epichlorohydrin-grafted cellulose examined for the phosphate removal from aqueous solution achieved a maximum adsorption capacity of 111.77 mg/g at 30 °C and a pH of 4.5. The reusing capacity of this material (more than six cycles) was also indicated in this work. The impact of co-existing ions on phosphate adsorption reported with the influence magnitude order of HPO₄²⁻ > SO₄²⁻ > Cl⁻ > NO₃⁻ (Anirudhan et al. 2012).

Xiong et al. (2017) reported a novel adsorbent for the removal of phosphate from an aqueous solution which was synthesized by loading zirconium oxide and iron oxide onto activated carbon nanofiber (ACF-ZrFe) simultaneously. La-porous carbon composites (surface area 308.9 m²/g and pore volume 0.56 cm³/g) showed more removal capacity of phosphate from seawater than synthetic wastewater (Koilraj & Sasaki 2017). Nano-La(III) (hydr)oxides modified wheat straw (Ws-N-La) was also reported as a novel adsorbent with the ability of high phosphate removal. This adsorbent was recommended for the soil amendment after phosphate removal (Qiu et al. 2017).

Zeolites and clay adsorbents

Zeolites and clay adsorbents are among the diverse materials that have been tested for phosphate removal and recovery and these include natural clay minerals, kaolin clay, and zeolite, which consist of metal oxides such as Al₂O₃, SiO₂, MgO, and CaO. Especially, kaolin clay is well known for its excellent bonding ability, high whiteness, superior electrical insulating property, and thermal stability.

Thermally treated red mud (at a temperature of 600–1,000 °C) (Lin et al. 2020), and natural zeolite (NZ) and Ca(OH)₂ treated zeolite (CaT-Z) (Mitrogiannis et al. 2018) were also observed as alternative phosphate adsorbents from water and real fresh urine. According to Mitrogiannis et al. (2018), the maximum phosphate removal capacity of 11.11 mg/g from fresh urine with a total phosphate desorption capacity of 10.43 mg/g was exhibited for CaT-Z. Moreover, this study reported that about 84.9 and 72.6% of the adsorbed phosphate was reloaded from CaT-Z and NZ, respectively (Mitrogiannis et al. 2018). Similarly, another report from Mitrogiannis et al. (2017) showed Ca(OH)₂ pretreated natural zeolite (CaPT-Z) removed low concentration phosphate (0.5–10 mg/L) from the simulated solution. This study indicated that natural zeolite pretreatment by 0.25 mM Ca(OH)₂ was able to increase phosphate removal from 1.7 to 97.6% at an initial concentration of 10 mg/L, pH 7, and 25 °C. Moreover, Ca(OH)₂ pretreated natural zeolite was recommended as a promising phosphate adsorbent from a low phosphate residual concentration (81–238 μg/L) tertiary wastewater treatment effluent.

The mesoporous modified kaolin clay (MKC) reported by Deng & Shi (2015) exhibited a strong uptake affinity to phosphate over a wide range of pH (2.5–9.5) with maximum phosphate removal efficiency and adsorption capacity of 98.03% and 11.92 mg/g at 25 °C, respectively. According to this study, phosphate removal was affected by co-existing ions in the
order of $\text{SO}_4^{2-} > \text{NO}_3^- > \text{Cl}^-$ (Deng & Shi 2015). Zeolite beads (ZB) and Lanthanum loaded zeolite beads (La-ZB) were studied by Pham et al. (2019). This study achieved 59.8 and 106.2 mg/g of phosphate adsorption capacity for ZB (surface area 365 m$^2$/g and pore volume 0.22 cm$^3$/g) and La-ZB (surface area 358 m$^2$/g and pore volume 0.19 cm$^3$/g), respectively. Testing this adsorbent for phosphate adsorption using real wastewater containing a high phosphate concentration of 218.6 mg/L revealed 96.8% removal efficiency. This adsorbent was also observed to remove phosphate efficiently from real wastewater (Pham et al. 2017). Lanthanum-incorporated porous zeolite (La-ZP) reported removing 95% phosphate over a wide range of pH (3–7) from 5.34 mg/L real wastewater at a 2 g/L dose. The La-ZP was reported as highly selective to phosphate He et al. (2017). Another novel adsorbent has developed using zeolite loaded with Mg-Al-La ternary (hydr)oxides (MALZ) to remove phosphate over a wide range of pH (4–10) from aqueous solutions using batch and column setups. MALZ (surface area 29.04 m$^2$/g) gained a maximum adsorption capacity of 80.8 mg/g at 25 °C, pH of 6.6, and 12.5 wt% La. Ligand exchange was observed to be the main removal mechanism for the aforementioned adsorbent. Setting the breakthrough point at 0.5 mg/L and initial phosphate concentration at 1 mg/L showed an effective treatment volume of 4,800 and 2,530 BV using a flow rate of 7.5 and 22.5 mL/min, respectively. According to this report $\text{SO}_4^{2-}$, NO$_3^-$ and Cl$^-$ showed an insignificant competitive effect (Shi et al. 2019).

**Iron oxides adsorbents**

Iron-based adsorbents are among the best-commercialized phosphate adsorbents reported so far (Li et al. 2016; Delgado-Velasco et al. 2018). Functionalized diatomite by hydrous iron oxide (HIOMD) was investigated for the removal and recovery of phosphate from wastewater. According to the results of this study, the phosphate adsorption capacity of raw diatomite and hydrous iron oxide modified diatomite was observed to increase from 0.6 to 4.89 and 14.71 to 25.02 mg/g, respectively (Wang et al. 2016). A similar study was conducted by Nakarmi et al. (2018) using the iron oxide nanocomposites (IO-nCs) which were synthesized from modified wood chips. In this study, the phosphate removal capacity at low and high phosphate concentrations was examined. Accordingly, iron oxide nanocomposites achieved a phosphate removal capacity of 33.71 mg/g and 96.41% removal for 500 and 1 mg/L solution at 3 mg/L dosage (Nakarmi et al. 2018). Moreover, Du et al. (2017) used Fe-Mn oxide adsorbent (FMO) (Fe/Mn ratio 5:1) for phosphate removal and the results revealed a maximum adsorption capacity of 18.4 mg/g at 35 °C and pH 7.0. It was also reported that the co-existing anions of nitrate, silicate, sulfate, and carbonate had no negative effect on phosphate adsorption (Du et al. 2017).

Mesoporous Fe$_3$O$_4$@SnTiO$_2$@mLDH composites were reported as a magnetically separable phosphate adsorbent with a capacity of 57.07 mg/g from water at a pH of 7.5. This adsorbent showed a stable retain removal efficiency of 94.0% after five cycles (Li et al. 2020). Mg-Fe-Cl is one among the common LDHs which is reported to reduce phosphate concentrations of 10 mg/L down to 0.1 mg/L at equilibrium. This indicates that the material could be implemented as a tertiary wastewater treatment to meet stringent phosphate discharge regulations (Ashekuzzaman & Jiang 2017b). Amine-functionalized copper ferrite chelated with La(III) (CuFe$_2$O$_4$2N-La) was also studied for the removal and recovery of phosphate. CuFe$_2$O$_4$2N-La with a surface area of 36.15 m$^2$/g and pore volume of 0.16 cm$^3$/g have achieved 32.59 mg/g removal capacity and showed good phosphate selectivity in the presence of common co-existing ions. According to this study, co-existing ions were observed to have a significant impact on the adsorption process in the order of $\text{Cl}^- > \text{NO}_3^- > \text{SO}_4^{2-} > \text{OH}^-$ (Gu et al. 2018). Ferrrihydrite-coated and lanthanum-decorated magnetite (Mag@Fh-La) was reported to achieve 98.8% phosphate removal capacity from real wastewater. For Mag@Fh-La (surface area 85.8 m$^2$/g), the maximum removal capacity was 44.8 mg/g at 15.7% La and 0.2 g/L dose of this material revealed a reduction of phosphate from real wastewater from 1.7 to 0.02 mg/L. This material showed a good separability and reusability using 1 M NaOH as a regeneration agent (Fu et al. 2018). Zero-valent iron (ZVI) (Nagoya et al. 2019) and nanoscale zero-valent iron in the presence of copper chloride (NZVI/CuCl$_2$) (Eljamal et al. 2016) were observed to be another competent adsorbent for phosphate removal. La(OH)$_3$/Fe$_3$O$_4$ nanocomposites (La(OH)$_3$/Fe$_3$O$_4$(4:1)) (Wu et al. 2017), magnetic zirconium-iron oxide nanoparticle (MZION) (Zhang et al. 2017) and iron oxide waste (IOW) (Shahid et al. 2019) was developed as a magnetically recoverable phosphate adsorbents. The study conducted on La(OH)$_3$/Fe$_3$O$_4$(4:1) adsorbent revealed that the phosphate from real wastewater can be reduced from 1.1 to 0.05 mg/L using a 0.5 g/L dose. In addition to this, hydrous lanthanum oxide was loaded onto the surface of Fe$_3$O$_4$@SiO$_2$ core/shell magnetic nanoparticles to develop easily separable adsorbent (Fe-Si-La) after phosphate removal from wastewater (Lai et al. 2016). Similar investigations confirm that magnetite mineral microparticles (Mag-MM) and magnetite nanoparticles (Fe$_3$O$_4$-NPs) produced a quality effluent (<0.1 mg/L) from a low phosphate concentration actual secondary effluent (10 mg/L) (Abo Markeb et al. 2016; Xiao et al. 2017). Pilot-scale phosphate removal using reusable
and magnetically harvested ZnFeZr adsorbent was developed and achieved less than 0.05 mg/L in its effluent using real wastewater (Drenkova-Tuhtan et al. 2017). Another pilot plant was also developed using binary iron-manganese (AquAsZero) oxyhydroxides with a treatment capacity of 200 L/h and phosphate removal capacity of 36.6 mg/L. The regeneration of the pilot plant adsorbent was accomplished by using NaOH at pH 12.6–13 (Kalaitzidou et al. 2016).

**Novel miscellaneous adsorbents**

The layered double hydroxide (LDH) materials have attracted major attention for the removal of phosphate due to their high capacity as compared to the organic anion exchange resins (Seftel et al. 2018). Activated aluminum oxide (AAO) and lanthanum oxide (LO) are well-known, commercially available products for phosphate removal (Xie et al. 2015). The amorphous synthesized lanthanum hydroxide (amorphous (La(OH))3 materials also had a higher specific surface area and showed greater performance for phosphate adsorption than the crystalline commercial lanthanum hydroxide (Xie et al. 2014). Graphene-Lanthanum Composite (3D graphene-La2O3 composite) was tested to remove phosphate from aqueous solution and achieved an adsorption capacity of 82.6 mg/g at pH 6.2 and a dose of 2 g/L within 25 min. This adsorbent showed high co-existing ions tolerance even at 8,000 mg/L concentrations of Cl–, SO42– and NO3– (Chen et al. 2016). Another layered double hydroxide (Zn2Al-LDH) was examined for phosphorus recovery from acidified (pH of 3–6) and non-acidified dewatered sludge. Zn2Al-LDH showed a high affinity toward phosphate and sulfate was the only reported ion with a tendency to reduce the phosphate removal by 25–35%. The optimum removal efficiency reported for this material was 80.2% for acidified sludge with an orthophosphate concentration of 1,157.1 mg/L at pH 3 and 20% for non-acidified acidified sludge with an orthophosphate concentration of 229.3 mg/L at pH 7.79 (Lundehoj et al. 2019). Ashkeuzzaman & Jiang (2017a) studied Ca and Mg incorporated layered double hydroxide (LDH) adsorbents for phosphate removal and this was used to treat real effluent from secondary wastewater treatment plant achieving phosphate effluent of less than 0.1 mg/L successfully. La(OH)3-poly (vinylidene fluoride) composite filtration membrane (La(OH)3-PVDF) was reported as one of the superior phosphate adsorbents with a maximum removal capacity of 256.6 mg/g. The adsorption-desorption results indicated that the material maintained its removal capacity of 90% even after four cycles (Chen et al. 2018). Nanosized hydrated La(III) oxide confined in cross-linked polystyrene networks (nLa(III) oxide-PSN) with the surface area of 24.42 m2/g was studied for phosphate removal enhancement using batch and column setups. At the 0.5 mg/L breakthrough point the material effectively treated 6,500 BV whereas the commercial HFO-201 was treating 550 BV in the presence of 500 mg/L sulfate. Moreover, a novel nanocomposite adsorbent, nHFZO@I402, which had a high capacity and specific affinity towards phosphate under a wide pH range, was synthesized and reported (Zhang et al. 2016). The nHFZO@I402 consisted of nanostructured hydrated ferric oxide and hydrated zirconium oxide loaded on the surface and inside the pores of a polymeric anion exchanger (Zhou et al. 2018). Trimesic acid (benzene-1, 3, 5-tricarboxylic acid, TMA) on a basic alumina surface showed a significant and selective adsorption efficiency for phosphate from aqueous solution (Saha et al. 2009). Alum sludge (DWT-AS) was reported by Nawar et al. (2015) as a low-cost adsorbent for the phosphate removal from liquor within 20 min at pH 5 and 1 g/L dose. Trivalent-metals-based amino-MIL-101 MOF was examined to achieve the removal capacity of 79.41 mg/g at 25 °C irrespective of the solution pH. This adsorbent was easily regenerated using a 1% solution of NaCl (Liu et al. 2019a, 2019b).

Mesoporous zirconia ceramic fibers (MZCF) with a surface area of 293.07 m2/g has been reported as a high-affinity phosphate adsorbent having the removal capacity of 222.79 mg/g. The adsorption-desorption study showed that the material was seen to maintain removal capacity of 92.5% after five subsequent cycles (Dong et al. 2020). In general, one can conclude that the formation of hydroxyapatite especially for CSH (Leng et al. 2019; Zhang et al. 2019); ion-exchange-between phosphate (H3PO4 and HPO42–) and different functional groups such as OH– and amine groups, electrostatic attraction, ligand exchange, and inner and outer-sphere complexation were reported as the removal mechanism for the phosphate uptake. As shown in Table 2, the adsorption data of all phosphate adsorbents best fitted to the pseudo-second-order kinetic model and Langmuir and Freundlich adsorption isotherm model. The reported standard free energy supported that phosphate adsorption occurs spontaneously (Table S4).

**Novel adsorbents for nitrate-phosphate co-removal**

Chitosan/Al2O3/Fe2O3 composite nanofibrous adsorbent with a surface area of 251.7 m2/g was synthesized and its nitrate and phosphate removal capacity compared with chitosan/Al2O3/Fe2O3 commercially available beads. The experimental result revealed that both materials exhibit an insignificant reduction of nitrate and phosphate adsorption capacity after
Table 2 | Adsorption capacity, models (kinetic and isotherm), and adsorption optimum conditions of selective phosphate adsorbents

| Adsorbent                      | q_m  | Model type | q_e  | Model type | pH  | T  (°C) | C_o  (mg/L) | t  (h) | Dose (g/L) | Ref.            |
|--------------------------------|------|------------|------|------------|-----|---------|-------------|------|------------|----------------|
| Calcium silicate hydrate (CSH) adsorbents |      |            |      |            |     |         |             |      |            |                |
| Novel-CSH                       | 109.4| PSO        | 86.25| Langmuir   | 5   | 25      | 60          | 2    | 0.6        | Zhang et al. (2019) |
| BF-CSH                          | 53.10| PSO        | 45.68| Freundlich | 7   | 25      | 4**         | 24   | 0.5        | Kuwahara & Yamashita (2017) |
| CS-CSH                          | 18.02| PSO        | 18.2 | –          | 8.5 | 25      | 20          | 4    | 5-7        | Fang et al. (2018) |
| Pure-CSH                        | –    | –          | –    | –          | 7   | 25      | 123°        | 2    | 15         | Lee et al. (2018) |
| CSC                             | 73   | PSO        | 80.7 | Langmuir   | 3-5 | 25      | 20-500      | 24   | 2          | Jiang et al. (2017a, 2017b) |
| ASC                             | 120  | PSO        | 128  | Langmuir   | 3-5 | 25      | 20-500      | 24   | 2          |                  |
| MBMA                            | 111.1| PSO        | 76.34| Langmuir   | 6.9 | 25      | 0-525       | 1    | 1          | Leng et al. (2019) |
| Biochar adsorbents              |      |            |      |            |     |         |             |      |            |                |
| Salt-biocharu                   | 118  | PSO        | 16.51| Langmuir   | 7-9 | 25      | 318.5       | 24   | 2          | Xu et al. (2019) |
| MgO-biocharu                    | 116.4| PSO        | 107.95| Langmuir  | 8.9 | 25      | 318.5       | 24   | 2          | Xu et al. (2018) |
| MgO@MBC                         | 149.2| PSO        | 104.17| Langmuir | 5-7 | 25      | 200         | 24   | 1          | Liu et al. (2010) |
| Lax-MC                          | 101.2| PSO        | 81.64| Langmuir   | 5   | 30      | 100–400     | 24   | 1          | Liao et al. (2018) |
| Mg-laden biochar                | 344  | PSO        | 330  | Langmuir   | 8   | 25      | 20–498      | 90   | 1          | Jiang et al. (2018) |
| Ca-BC                           | 314.2| PSO        | 302.1| Langmuir   | –   | 25      | 300         | 24   | 1          | Wang et al. (2018) |
| PG-biochar                      | 102.4| PSO        | 59.04| Freundlich | 6   | 25      | 100         | 4    | 1.2        | Wang et al. (2020a, 2020b) |
| Ca-MBC                          | 13.61| PSO        | 4.95 | Langmuir   | 4-8 | 25      | 30          | 72   | 5          | Choi et al. (2018) |
| Chitosan-CNTs                   | 36.1 | PSO        | 20.80| Langmuir   | 3   | 20      | 25–100      | 0.5  | 1          | Huang et al. (2018) |
| RHA                             | 0.74 | PSO        | 1.329| Langmuir   | 6   | 30      | 10          | 2    | 2          | Mor et al. (2016) |
| Cell-g-E/PEI                    | 111.8| PSO        | 97.1 | Freundlich | 4.5 | 30      | 100         | 3    | 1          | Anirudhan et al. (2012) |
| ACF-ZrFe                        | 26.3 | PSO        | 5.54 | Freundlich | 4   | 25      | 10–30       | 12   | 1          | Xiong et al. (2017) |
| La-PCCsaw                       | 13.32| PSO        | 12.48| Langmuir   | 8.2 | 25      | 3.1–6.2     | 24   | 0.5        | Koilraj & Sasaki (2017) |
| La-PCCsw                        | 24.9 | PSO        | –    | Langmuir   | 8.2 | 25      | 6.2         | 24   | 0.5        |                  |
| Ws-N-La                         | 67.1 | PSO        | –    | Langmuir   | 3-7 | 25      | 30          | 24   | 0.5        | Qiu et al. (2017) |
| MgFe-LDH-Ws-biochar             | 24.8 | PSO        | 7.4  | Langmuir   | –   | 22      | 88          | 24   | 2          | Xue et al. (2016) |
| Zeolites and clay adsorbents    |      |            |      |            |     |         |             |      |            |                |
| CaT-Z                           | 15.54| –          | –    | Langmuir   | 5.8 | 25      | 189.5       | 96   | 10         | Mitrogiannis et al. (2018) |
| CaPT-Z                          | 7.57 | PSO        | 1.02 | Langmuir   | 7   | 25      | 25–200      | 120  | 10         | Mitrogiannis et al. (2017) |
| MKC                             | 11.92| PSO        | 2.49 | Langmuir   | 7.5 | 25      | 25          | 7    | 0.4        | Deng & Shi (2015) |
| La-ZB                           | 106.2| PSO        | 85.2 | Langmuir   | 6   | 25      | 200         | 3    | 5          | Pham et al. (2019) |
| ZB                              | 59.8 | PSO        | 42.6 | Langmuir   | 6   | 25      | 200         | 3    | 5          |                  |
| La-ZP                           | 17.2 | PSO        | 2.45 | Langmuir   | 3–7 | 30      | 5–60        | 24   | 2          | He et al. (2017) |
| MALZ                            | 80.8 | PSO        | 5.11 | Freundlich | 6.6 | 25      | 1–5         | 3    | 0.75       | Shi et al. (2019) |
| Iron oxides adsorbents          |      |            |      |            |     |         |             |      |            |                |
| HIOMD                           | 31.2 | –          | –    | Langmuir   | 6   | 25      | 1–600       | 24   | 5          | Wang et al. (2016) |
| IO-nCs                          | 33.3 | PSO        | 15.11| Langmuir   | 7   | 25      | 1–500       | 0.5  | 3          | Nakarmi et al. (2018) |
| FMO                             | 18.4 | PSO        | 10.75| Langmuir   | 7   | 30      | 10–100      | 24   | 2.5        | Du et al. (2017) |

(Continued.)
five adsorption-desorption cycles. According to this study report, the maximum nitrate and phosphate removal capacity of chitosan nanofibrous composite having 2% of Al₂O₃/Fe₃O₄ were reported to be 160.7, 106.5, 135.10, and 61.90 mg/g, respectively (Bozorgpour et al. 2016). A novel Fe₃O₄/ZrO₂/chitosan nanocomposite with a surface area of 212.9 m²/g was synthesized from chitosan and Fe₃O₄/ZrO₂. This adsorbent also showed the maximum adsorption capacity of 89.3 and 26.5 mg/g for nitrate and phosphate, respectively (Jiang et al. 2013). Another Zr⁴⁺ ion embedded chitosan-soya bean husk activated bio-char composite beads (Zr-CS-SAC) was reported with nitrate and phosphate removal capacities of 90.09 and 131.29 mg/g, respectively at 30 °C (Banu et al. 2019). A novel zirconium-based graphene oxide (GO) modified
with strontium nanoparticles (MGO-Sr) had a removal capacity of 238.09 mg/g for phosphate and 357.14 mg/g for nitrate. MGO-Sr was field examined using river water (0.46 mg/L phosphate and 0.06 mg/L nitrate) and sewage wastewater (0.09 mg/L phosphate and 0.56 mg/L nitrate) and showed removal efficiency of 94.6 and 76.7, and 87.4 and 70% for phosphate and nitrate from river water and sewage wastewater, respectively (Sereshti et al. 2020). Nanosized lanthanum hydrous doped on magnetic graphene nanocomposite (MG@La) was synthesized and used for nitrate and phosphate remediation from the sewage water sample. According to this study report, MG@La showed a higher affinity toward nitrate (138.88 mg/g) than phosphate (116.28 mg/g). The common co-existing ions had no significant effect on adsorption and insignificant La leaching from the adsorbent at pH 4, 5, 7, and 10 (Rashidi Nodeh et al. 2017). Biochar-MgAl LDH nanocomposites (surface area 441.04 m²/g and pore volume 0.294 cm³/g) had high affinity and selectivity toward phosphate with a removal capacity of 177.97 and 28.06 mg/g for nitrate. Chloride and phosphate ion were observed to decrease nitrate removal. This adsorbent removed about 84.8% from real wastewater with 3.68 mg/L phosphate and 3.65 mg/L nitrate (Alagha et al. 2020). Chitosan quaternized resin was synthesized for the co-removal of nitrate and phosphate by Banu & Meenakshi (2017). The removal efficiency of nitrate and phosphate for this adsorbent was 78 and 90% at the initial concentration of 100 mg/L, respectively. This adsorbent was reported to retain a nitrate and phosphate adsorption capacity of 25.7 and 30.4 mg/g, respectively after seven regeneration cycles. Abundantly available natural zeolite and solid waste residue from an alum factory were examined and had promising nitrate and phosphate co-removal capacity (Banu & Meenakshi 2017). Natural zeolite revealed the removal efficiency of nitrate and phosphate (94.06 and 98.28%, respectively) (Wan et al. 2017). Clinoptilolite-supported iron hydroxide NPs (Fe(OH)₃/Cp) examined for the simultaneous nitrate and phosphate removal showed 81 and 93% removal efficiency of nitrate and phosphate, respectively (Mikhak et al. 2017). The solid waste residue from the alum factory was reported to potentially remove phosphate but not nitrate wastewater at a pH of 7 and an adsorbent dose of 20 g/L (Berkessa et al. 2019).

Novel layered double hydroxides (LDHs) of the binary composite Zn-Al LDHs enfolded with banana bract activated carbon (BBAC@Zn-Al LDHs) was synthesized. According to the results of this study, BBAC@Zn-Al LDHs composite revealed nitrate and phosphate adsorption capacities of 73.74 and 88.12 mg/g, respectively (Karthikeyan & Meenakshi 2019).

Nanoscale zero-valent iron/nickel supported on zeolite (Z-Fe/Ni) was examined for co-removal of nitrate and phosphate from aqueous solution. The result of this study demonstrated Z-Fe/Ni performed less sensitively to initial solution pH for nitrate and phosphate removal. The synergy study indicated that the removal of either nitrate or phosphate was mutually affected (He et al. 2018). Another nano-scale zero-valent iron supported on treated activated carbon (nZVI-AC) was used to remove nitrate and phosphate from water. The experimental report indicated that this material is highly phosphate selective with a removal efficiency of 100%. However, the same material shows about 50% removal efficiency for nitrate within 2 h (Khalil et al. 2017).

Experimental work reported indicated that commercial ion exchange resin was also used for the removal of nitrate and phosphate. Purolite A500P anion exchange resin and a hydrous ferric oxide (HFO) column (60 cm height, 2 cm diameter, flow rate 1 m/h) in series containing 1–10% (w/w) of these adsorbents and the remainder being anthracite (90–99%) were studied. This study indicated that Purolite showed maximum nitrate and phosphate adsorption capacity of 64 and 7 mg/g, respectively. However, HFO showed a removal capacity of 14 mg/g only for phosphate. Moreover, as the experimental work of this study indicated, passing effluent from the Purolite column through the HFO column removed almost all phosphate and the series column set up removed both nitrate and phosphate from wastewater (Das Gupta et al. 2012). Another commercial 201 × 7 exchange resin column was used for the simultaneous removal of nitrate and phosphate from aqueous solution (Wei et al. 2015). Experimental results indicated a maximum nitrate and phosphate adsorption capacity of 107.59 and 12.47 mg/g, respectively. About 90% of nitrate and 92% of phosphate from secondary wastewater treatment effluent was removed at the optimal flow rate of 50 BV/h within an hour. Similar to the nitrate and phosphate adsorbents, the reported nitrate-phosphate co-adsorbents were observed to follow the Langmuir and Freundlich adsorption model. The majority of the nitrate-phosphate co-adsorbents adsorption data reported also best fitted to the pseudo-second-order kinetic model (Table 3). Moreover, the reported negative value of the standard free energy of the nitrate-phosphate co-adsorbents indicated that the adsorption process was occurring spontaneously (Table S5).

**Nitrate and phosphate recovery**

After the nitrate and phosphate were removed from the enriched aqueous solution using appropriate adsorbents, the downstream process followed will be recovery or reloading of the pre-absorbed nitrate and phosphate by applying the reverse
The common and utmost reported method for the recovery was elution (Suresh et al. 2019; Bacelo et al. 2020). As reported by different authors, the selection of appropriate acid or basic solution, and determining the concentration for optimum leaching of the nitrate or phosphate from the adsorbent, affects the recovery percentage and cost of the process as well (Suresh et al. 2019). The selected eluent needs to be non-interacting with the surface of the adsorbent during the repeated use (the adsorbent should be insoluble and not have surface interaction with the eluent). Different concentrations of HCl (Rezaei Kalantary et al. 2016; Song et al. 2016); H2SO4 (Lee et al. 2018); NaOH (Chatterjee & Woo 2009; Xie et al. 2014; Drenkova-Tuhtan et al. 2017; Rashidi Nodeh et al. 2017; Wu et al. 2017; Jiang et al. 2018; Liao et al. 2018; Pham et al. 2019; Shi et al. 2019; Alagha et al. 2020; Sereshti et al. 2020); NaCl-NaOH binary solution (Zhang et al. 2016; Banu & Meenakshi 2017; Qiu et al. 2017), NaCl (Wei et al. 2015; Liu et al. 2019a, 2019b); citric acid (Jiang et al. 2017a, 2017b), and Na2CO3 (Anirudhan et al. 2012) were used as nitrate and phosphate leaching agent from their adsorbents. Basic solution interferes with the pH driven electrostatic interaction between nitrate and phosphate ions and metal cation (Rashidi Nodeh et al. 2017; Liao et al. 2018; Sereshti et al. 2020). Soaking or backwashing in different concentrations of NaCl recovered the nitrate and phosphate from loaded absorbents (Liu et al. 2019a, 2019b). Due to the higher affinity of the anion Cl\(^-\) than ions of PO_4^{3-} and NO_3\(^-\) in the solution NaCl could be desorbed and regenerate the adsorbent (Wei et al. 2015; Banu & Meenakshi 2017). Moreover, Na_2CO_3 (Anirudhan et al. 2012) and NaCl-NaOH binary solution (Zhang et al. 2016; Qiu et al. 2017) could be used as the nitrate and phosphate eluent considering the economic aspect of desorption and adsorbent regeneration for reuse.

Table 3 | Adsorption capacity, models (kinetic and isotherm), and adsorption optimum conditions of selective nitrate-phosphate co-adsorbents

| Adsorbent | NP | q_m (mg/g) | Kinetic model | Isothermal model | Optimum conditions of adsorption | Ref. |
|-----------|----|------------|---------------|-----------------|-------------------------------|------|
| MG@La MN 139 | P 116 | PSO | 16.33 | Langmuir | 4-8 20 20 1.5 0.01 | Rashidi N | (2017) |
| SWR N 0.07 | P 15.1 | PSO | 0.06 | Freundlich | 7 25 5.14 1.5 20 | Berkessa | et al. (2019) |
| Ch/Al_2O_3/Fe_3O_4 N 160 | P 125 | PSO | 81.3 | Freundlich | 3 20 20 1 0.5 | Bozorgp | gour et al. (2016) |
| Fe_3O_4/ZrO_2/Chnps N 89.3 | P 26.5 | PFO | 29.10 | Langmuir | 3 25 100 24 1 | Jiang | et al. (2013) |
| Zr-CS-SAC N 90.1 | P 131 | PSO | 38.68 | Freundlich | 6.4 30 100 1 2 | Banu | et al. (2019) |
| MGO-Sr N 238 | P 357 | PSO | 135.1 | Langmuir | 5-8 20 10-100 1 0.06 | Seresht | i et al. (2020) |
| Biochar-Mg/Al LDH N 178 | P 28 | PFO | 28.26 | Langmuir | 6 25 10-50 24 2.5 | Alagha | et al. (2020) |
| Chitosan resin N 84.1 | P 181 | PSO | 37.08 | Freundlich | 3-8 30 100 1 2 | Banu & Meenakshi (2017) |
| NPs Fe(OH)_3/Cp N – | P – | PSO | 8.2 | – | – | – | (Mikhak et al. (2017) |
| BBAC@Zn-Al LDHs N 73 | P 87 | PSO | 21.43 | Freundlich | 3.7 30 50 0.7 | 2 | Karthikeyan & Meenakshi (2019) |
| nZVI-AC N 4.6 | P 0.75 | – | – | Langmuir | 4 25 200 1.5 2 | Khalil et al. (2017) |
| Purolite A500P N 64 | P 7 | – | – | Langmuir | 3-7 25 50 6-72 10 | Das Gupta et al. (2012) |
| Commer. 201 × 7 N 108 | P 12.5 | PSO | 117.6 | Langmuir | 7 25 10-750 3 1 | Wei et al. (2015) |

qm, adsorbent removal capacity; t, time; Co, initial concentration; T, temperature.
The second method of nitrate and phosphate recovery reported was as agricultural field application as fertilizer for soil amendment. Two per cent citric acid eluent is a criterion to check nutrient solubility in soil. If the phosphate is desorbed by 2% citric acid, it implies that the recovered phosphate could be used as fertilizer for soil amendment (Jiang et al. 2017a, 2017b; Lee et al. 2018; Xu et al. 2019).

Nitrate recovery

NaOH, HCl, diluted NaCl and citric acid were reported used eluents for nitrate recovery. HCl was used to eluent the nitrate from magnetic amine-cross-linked biopolymer-based corn stalk (Song et al. 2016) and activated carbon magnetic nanoparticles (Rezaei Kalantary et al. 2016). In both of these adsorbents, ion exchange between \( \text{NO}_3^- \) and \( \text{Cl}^- \) was the main adsorption mechanism. In the former, nitrate recovery was high at 0.5 M HCl which in turn negatively affects the magnetic core of the adsorbent by promoting dissolution and surface destruction. Due to this reason, a low concentration of 0.1 M HCl was recommended (Song et al. 2016).

Phosphate recovery

A basic solution such as NaOH with different concentrations was used to desorb phosphate from the adsorbent phosphate complex. The basic solution weakened the electrostatic interaction between the adsorbent and anionic species due to the removal of the \( \text{H}^+ \) ions from the solution and hence favored desorption of anions (Sereshti et al. 2020). Lee et al. (2018) compared the \( \text{H}_2\text{SO}_4 \) and HCl as acid and NaOH as base eluents to release phosphorus from sewage sludge. According to the results of this study, 0.1 M \( \text{H}_2\text{SO}_4 \) was observed to release more than HCl and NaOH at the same concentration. The use of low concentrations of acid (0.1 M \( \text{H}_2\text{SO}_4 \)) as eluent appears to be a more practical and cost-effective phosphate recovery approach from sewage sludge (Lee et al. 2018).

As indicated in Table 4, for most of the trivalent metals modified adsorbents, NaOH was reported as the eluent. Chitosan-based adsorbents were easily regenerated using NaCl or NaCl-NaOH binary solutions.

COMMERCIAL VALUE AND ECONOMICS OF THE RECOVERED NITRATE AND PHOSPHATE PRODUCTS

The recovered nitrate and phosphate from waste has a number of economic values. Nitrate and phosphate products could be used as renewable fertilizers (Mayer et al. 2016). Researchers recommended that the phosphate recovered by 2% citric acid eluent could be directly used as fertilizer for the soil amendment (Jiang et al. 2017a, 2017b; Lee et al. 2018; Xu et al. 2019) or incorporated into sewage sludge and organic wastes (Mayer et al. 2016). This helps to save energy from energy intensive fertilizer production (Haber-Bosch process) and reduces the direct GHG emissions from this process (Mayer et al. 2016). Not only these, but also the recovered nitrate and phosphate could be used as industrial feedstock in the production of chemicals, food and beverages (Mayer et al. 2016). Indirectly, the recovered nitrate and phosphate could help to ensure food security and energy security (biomass energy) (Mayer et al. 2016). Nitrate and phosphate recovery from aqueous solution reduces the eutrophication of lakes and rivers, which is used for fish farming and other economic activities.

COMPARISON OF ADSORBENTS

It is difficult to compare all the reported adsorbents for practical use selection due to the differences in their operational conditions as indicated in Tables 1-4. More convenient parameters for practical use selection are those related to the cost of the adsorption process. Reported work on the cost analysis of phosphate recovery by the adsorption process indicated that about 71% of the total cost is the chemical cost (Suresh et al. 2019). According to this study, practical loading and the number of reuse cycles significantly affect the chemical cost. Practical loading includes parameters of adsorption affinity, adsorption kinetics, selectivity (effect of competing ions), the effect of temperature, and effect of pH. According to scholars, the requirement for phosphate removal by the adsorption process is not only to reduce its concentration, rather it is to eliminate it from the waste stream since a very low concentration (≥0.1 mg/L) can cause eutrophication (Ashekuzzaman & Jiang 2017b). Similarly, the minimum concentration level of nitrate in drinking water or effluent was limited to 10 mg/L (Bhatnagar & Sillanpää 2011). The number of cycles the adsorbent used, retained removal efficiency, the removal capacity at an equilibrium concentration of 10 mg/L (\( q_{10} \)) for nitrate and 0.1 mg/L (\( q_{0.1} \)) for phosphate mainly refers to the affinity of the adsorbent, and time to reach this equilibrium level (\( t_{90} \)) is more reliable than using...
only the maximum adsorption capacities which were observed as a poor parameter to compare adsorbents for practical use (Mouzourakis et al. 2017; Suresh et al. 2019).

Selected nitrate adsorbents among the reported adsorbents were compared using these parameters. Amine cross-linked biosorbent (ACB) (Ren et al. 2016), magnetic amine-cross linked biopolymer-based corn stalk (MAB-CS) (Song et al. 2016), magnetic Co$_3$O$_4$/Fe$_3$O$_4$ doped polyaniline nanocomposite (PANI-Co$_3$O$_4$@MNPs) (Esmaeili Bidhendi et al. 2019), activated

| Adsorbent                          | Ion recovered | Eluent                  | Recovery (%) | Ref.                      |
|------------------------------------|---------------|-------------------------|--------------|---------------------------|
| Chitosan hydrogel beads            | Nitrate       | 0.1 M NaOH              | 75           | Chatterjee & Woo (2009)    |
| MAB-CS                             | Nitrate       | 0.1 M HCl               | 78.67        | Song et al. (2016)         |
| AC-Fe$_3$O$_4$ MNPs                | Nitrate       | 0.1 M HCl               | 98.9         | Rezaei Kalantary et al. (2016) |
| Pure-CSH                           | Phosphate     | 0.1 M H$_2$SO$_4$       | 89.6         | Lee et al. (2018)          |
| CSC                                | Phosphate     | 2% Citric acid          | 97.2         | Jiang et al. (2017a, 2017b) |
| ASC                                | Phosphate     | 2% Citric acid          | 96           |                          |
| MBMAw                              | Phosphate     | 16 mM H + /g ash        | 100          | Leng et al. (2019)         |
| MBMAWs                             | Phosphate     | 16 mM H + /g ash        | 100          |                          |
| Salt-biochar$^a$                   | Phosphate     | Field applied           | 97           | Xu et al. (2019)           |
| Lax-MC                             | Phosphate     | 3 M NaOH                | 65.07        | Liao et al. (2018)         |
| Mg-laden biochar                   | Phosphate     | 3 M NaOH 100 °C         | 96           | Jiang et al. (2018)        |
|                                   | Phosphate     | 3 M NaOH at room        | 55–60        |                          |
| Cell-g-E/PEI                       | Phosphate     | 0.1 M Na$_2$CO$_3$      | 99.6         | Anirudhan et al. (2012)    |
| Ws-N-La                            | Phosphate     | NaOH-NaCl               | NA           | Qiu et al. (2017)          |
| La-ZB                              | Phosphate     | 1 M NaOH                | 100          | Pham et al. (2019)         |
| ZB                                 | Phosphate     | 1 M NaOH                | 100          |                          |
| MALZ                               | Phosphate     | 0.5 M NaOH              | 82.6         | Shi et al. (2019)          |
| La(OH)$_3$/Fe$_3$O$_4$(4:1)        | Phosphate     | 1 M NaOH                | 65           | Wu et al. (2017)           |
| ZnFeZr                             | Phosphate     | 1 M NaOH                | 80           | Drenkova-Tuhtan et al. (2017) |
| Amorphous (La(OH)$_3$)             | Phosphate     | 3 M NaOH 250 °C         | 80           | Xie et al. (2014)          |
| nLa(III) oxide-PSN                 | Phosphate     | Binary NaOH (15 wt %)-NaCl (5 wt %) solution at 60 °C | 95 | Zhang et al. (2016) |
| Amino-MIL-101 MOFs                 | Phosphate     | NaCl, 1% w/v            | NA           | Liu et al. (2019a, 2019b)   |
| MgO-biochar$^a$                    | Nitrate       | –                       | Field        | Xu et al. (2018)           |
| MgO-biochar$^a$                    | Phosphate     | –                       | Field        |                          |
| Chitosan resin                     | Nitrate       | 0.1 M NaCl              | NA           | Banu & Meenakshi (2017)    |
| Chitosan resin                     | Phosphate     | 0.1 M NaCl              | NA           |                          |
| Commer.201 × 7                     | Nitrate       | 5% NaCl                 | 90           | Wei et al. (2015)          |
| Commer.201 × 7                     | Phosphate     | 5% NaCl                 | 96           |                          |
| Biochar-MgAl LDH                    | Nitrate       | 1 M NaOH                | 57           | Alagha et al. (2020)       |
| Biochar-MgAl LDH                    | Phosphate     | 1 M NaOH                | 92           |                          |
| MG@La                              | Nitrate       | 2 M NaOH                | NA           | Rashidi Nodeh et al. (2017) |
| MG@La                              | Phosphate     | 2 M NaOH                | NA           |                          |
| MGO-Sr                             | Nitrate       | 2 M NaOH                | NA           | Sereshti et al. (2020)     |
| MGO-Sr                             | Phosphate     | 2 M NaOH                | NA           |                          |
carbon magnetic nanoparticles (AC-Fe$_3$O$_4$MNPs) (Rezaei Kalantary et al. 2016) showed more than 80% retained removal efficiency in 3–10 adsorption-desorption cycles. Moreover, all adsorbents had the magnetic property so that could be easily separated from the supernatant solution using a magnet after adsorption. Ease of separation also reduces the total time required for the adsorption process which in turn plays its role in the feasibility of using these adsorbents for nitrate removal and recovery. Besides, all these four adsorbents revealed greater nitrate removal affinity ($q_{10}$) of 33.56–97.71 mg/g within 2–90 minutes of adsorption time as indicated in Figure 2. These adsorbents mainly can be applied to remove nitrate from wastewater treatment plant effluents, surface water, and groundwater.

Based on $q_{0.1}$, meat and bone meal incineration ash (MBMA) (Leng et al. 2019), calcium-decorated biochar (Ca-BC) (Wang et al. 2018), Lanthanum loaded zeolite beads (La-ZB) (Pham et al. 2019), Magnetically recoverable La(OH)$_3$/Fe$_3$O$_4$ nanocomposites (La(OH)$_3$/Fe$_3$O$_4$(4:1)) (Wu et al. 2017) and Nanosized hydrated La(III) oxide confined in cross-linked polystyrene networks (nLa(III) oxide-PSN) (Zhang et al. 2016) were among the top five phosphate adsorbents reviewed in this paper. The first two adsorbents mainly removed phosphate due to HAP formation using the calcium in the adsorbent as crystal seed. Moreover, calcium silicate hydrates (CSH) and biochar adsorbents did not require any chemicals for pH adjustment. This, in turn, plays a significant role in the cost reduction of phosphate removal and recovery. They were also reported as biocompatible and mainly originated from biomass.

Figure 2 | Selected nitrate adsorbents: (a) comparison using numbers of cycles adsorbent used and retained removal capacity; (b) comparison using $q_{10}$ and $t_{10}$. 
The third, fourth, and fifth mentioned are modified lanthanum-based adsorbents. Modified lanthanum showed greater phosphate removal capacity among other adsorbents which are modified using metal oxides (Figure 3(b)) since lanthanum provides selective coordination sites for phosphate removal. When it is compared based on the time required to achieve $q_{0.1}$, MBMA (Leng et al. 2019) and (nLa(III) oxide-PSN) (Zhang et al. 2016), it can be considered as one of the fastest (1–10 minutes) among the phosphate adsorbents included in this review (Figure 3(b)). As shown in Figure 3(b), Ca-BC (Wang et al. 2018) adsorbed phosphate slowly. These adsorbents can be applicable to remove and recover phosphate from wastewater treatment plant effluents, surface water, and groundwater.

Most of the adsorbents developed for the repeated phosphate removal and recovery achieved retained removal efficiency greater than 80% and removal capacity at an equilibrium concentration of 0.1 mg/L ($q_{0.1}$) in the range of 0.20–48.23 mg/g for 2–60 adsorption-desorption cycles and within the adsorption time of 1 min to 80 h (Figure 3). These adsorbents are surface modified through different synthesis techniques and their cost of production on a large scale will be considered for practical use. According to Kumar et al. (2019), these adsorbents will be considered as high-cost adsorbent despite no information on their cost (Suresh et al. 2019).

Among the adsorbents reported for simultaneous nitrate and phosphate removal and recovery included in this review, wood waste biochar loaded with magnesium oxides (MgO-biochar) (Xu et al. 2018) and nanosized lanthanum hydroxide doped on magnetic graphene nanocomposite (MG@La) (Rashidi Nodeh et al. 2017) revealed relatively high adsorption capacity (Figure 3(b)).

Chitosan/$\text{Al}_2\text{O}_3$/Fe$_3$O$_4$, Fe$_3$O$_4$/ZrO$_2$/chitosan nanoparticles, chitosan resin, and Zr-CS-SAC observed had a relatively high affinity towards nitrate relatively compared to phosphate removal and recovery. However, as indicated in Figure 3(b), all these adsorbents required a short adsorption time and they can be considered as competitive adsorbents for co-removal of nitrate and phosphate. Moreover, all the adsorbents reported for nitrate and phosphate removal and recovery included in this review showed retained removal efficiency greater than 50% in 5–6 adsorption-desorption cycles (Figure 4(a)). Since

Figure 3 | Selected phosphate adsorbents: (a) comparison using numbers of cycle’s adsorbent used and retained removal capacity; (b) comparison using $q_{0.1}$ and $t_{90}$. 
these adsorbents had shown high affinity toward both nitrate and phosphate, they can be applied to remove and recover nitrate from surface water, groundwater, and mainly from wastewater treatment plant effluents.

**CONCLUSION, CHALLENGES, AND FUTURE RESEARCH**

**Conclusion**

1. Biochar adsorbents modified using magnesium and lanthanum, calcium silicate hydrates, calcium hydroxide pretreated zeolites, and iron oxide nanoparticles discussed in this review showed utmost nitrate and phosphorus removal capacities over a wide range of pH.

2. Wood waste biochar, lanthanum modified graphene, and chitosan-based adsorbents which are modified using trivalent metals showed high removal capacity to both nitrate and phosphate. This is an indication for which future new nitrate and phosphate adsorbent materials will be within this domain.

3. From a review based on the experimental studies it can be concluded that these materials had shown the potential to be used in tertiary wastewater treatment for phosphate and nitrate removal.

4. Mostly HCl and NaOH were used as eluent during nitrate and phosphate recovery. As reported in the literature, the recovered nitrate and phosphate can be used as fertilizer or an additional source of phosphate for fertilizer production.

5. If the removal and recovery potential of phosphate by adsorption technology is fully exploited, it can support world food security efforts which is one of the millennium development goals.

6. Some literature reported on the column study of nitrate and phosphate removal and recovery. The data from the batch experiment is not sufficient for the scale up of the nitrate and phosphate removal and recovery. Therefore, extended column studies are recommended to explore the nitrate and phosphate recovery.
Challenges, and future research

One of the challenges of nutrient removal and recovery by adsorption technology is the release of metals and other chemicals used for the surface modification of the adsorbent. Single, binary, or ternary metal oxides are among the most investigated adsorbents for nitrate and phosphate removal and recovery from water/wastewater. There may be a risk of pollution due to using adsorbents modified with polyvalent metals such as Zr⁴⁺, La³⁺, Al³⁺, or Fe³⁺, irrespective of their role in increasing the nitrate and phosphate adsorption capacities (Mitrogiannis et al. 2017). Moreover, the separation of especially non-magnetic nanomaterial adsorbents required special attention.

Future studies will be conducted under field conditions to exploit the phosphate release from the effluent of a wastewater treatment plant. Extensive research on how to incorporate the nitrate and phosphate adsorption process in wastewater treatment utilities will be required. The cost-benefit analysis of using adsorption as an alternative will need elaboration. Scholars, environmental regulators, and wastewater treatment utility developers will be expected to work closely in this regard. It is important to investigate the amount of acid (MmH⁺/g) or base (mMOH⁻/g) consumed for adsorbent regeneration since this value mainly affects the costs of the operation. Most adsorbents reported had shown 2–5 adsorptions-desorption cycles. It is also important to investigate the number of cycles that the adsorbents used without losing their capacity for repeated usage. This process not only increases the number of times materials can be reused but also makes them more environmentally safe post-disposal (Welsh et al. 2017).

ACKNOWLEDGEMENTS

The authors to appreciate the Africa Center of Excellence for Water Management, Addis Ababa University, Ethiopia; and the Indian Institute of Technology, Delhi, India; for their financial support.

DATA AVAILABILITY STATEMENT

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

REFERENCES

Abo Markeb, A., Alonso, A., Dorado, A. D., Sánchez, A. & Font, X. 2016 Phosphate removal and recovery from water using nanocomposite of immobilized magnetite nanoparticles on cationic polymer. Environ. Technol. (United Kingdom) 37 (16), 2099–2112.

Alagha, O., Manzar, M. S., Zuhair, M., Anil, I., Mu’azu, N. D. & Qureshi, A. 2020 Comparative adsorptive removal of phosphate and nitrate from wastewater using biochar-MgAl LDH nanocomposites: coexisting anions effect and mechanistic studies. Nanomaterials 10 (2), 1–19.

Aljeboree, A. M., Alshirif, A. N. & Alkaim, A. F. 2017 Kinetics and equilibrium study for the adsorption of textile dyes on coconut shell activated carbon. Arab. J. Chem. 10, S3381–S3393.

Anirudhan, T. S., Rauf, T. A. & Rejeena, S. R. 2012 Removal and recovery of phosphate ions from aqueous solutions by amine functionalized epichlorohydrin-grafted cellulose. Desalination 285, 277–284.

Asekuzzaman, S. M. & Jiang, J.-Q. 2017a Improving the removal of phosphate in secondary effluent of domestic wastewater treatment plant. In: 15th International Conference on Environmental Science and Technology Proceedings. In CEST(2017) 00328, pp. 1–6.

Asekuzzaman, S. M. & Jiang, J. Q. 2017b Strategic phosphate removal/recovery by a re-usable Mg–Fe–Cl layered double hydroxide. Process Saf. Environ. Prot. 107, 454–462.

Bacelo, H., Pinto, A. M. A., Santos, S. C. R., Boaventura, R. A. R. & Botelho, C. M. S. 2020 Performance and prospects of different adsorbents for phosphorus uptake and recovery from water. Chem. Eng. J. 381, 1–18.

Banu, H. T. & Meenakshi, S. 2017 One Pot Synthesis of Chitosan Grafted Quaternized Resin for the Removal of Nitrate and Phosphate from Aqueous Solution, Vol. 104. Elsevier B.V., The Netherlands.

Banu, H. T., Karthikeyan, P. & Meenakshi, S. 2019 Zr⁴⁺ ions embedded chitosan-soya bean husk activated bio-char composite beads for the recovery of nitrate and phosphate ions from aqueous solution. Int. J. Biol. Macromol. 130, 573–583.

Battas, A., Gaidoumi, A. E., Kasakas, A. & Kherbeche, A. 2019 Adsorption study for the removal of nitrate from water using local clay. Sci. World J. 2019, 1–10.

Berkessa, Y. W., Mereta, S. T. & Feyisa, F. F. 2019 Simultaneous removal of nitrate and phosphate from wastewater using solid waste from factory. Appl. Water Sci. 9 (2), 1–10.

Bhatnagar, A. & Sillanpää, M. 2011 A review of emerging adsorbents for nitrate removal from water. Chem. Eng. J. 168 (2), 493–504.

Bozorgpour, F., Ramandi, H. F., Jafari, P., Samadi, S., Yazd, S. S. & Aliabadi, M. 2016 Removal of nitrate and phosphate using chitosan/Al₂O₃/Fe₂O₃ composite nanofibrous adsorbent: comparison with chitosan/Al₂O₃/Fe₂O₃ beads. Int. J. Biol. Macromol. 93, 557–565.

Chatterjee, S. & Woo, S. H. 2009 The removal of nitrate from aqueous solutions by chitosan hydrogel beads. J. Hazard. Mater. 164 (2–3), 1012–1018.
Chen, M., Huo, C., Li, Y. & Wang, J. 2016 Selective adsorption and efficient removal of phosphate from aqueous medium with graphene-lanthanum composite. ACS Sustain. Chem. Eng. 4 (3), 1296–1302.

Chen, L., Liu, F., Wu, Y., Zhao, L., Li, Y., Zhang, X. & Qian, J. 2018 In situ formation of La(OH)3-poly(vinylidene fluoride) composite filtration membrane with superior phosphate removal properties. Chem. Eng. J. 347, 695–702.

Chen, H., Zhang, H., Tian, J., Shi, J., Linhardt, R. J., Ye, T. D. X. & Chen, S. 2019 Recovery of high value-added nutrients from fruit and vegetable industrial wastewater. Compr. Rev. Food Sci. Food Saf. 18 (5), 1388–1402.

Choi, Y.-K., Jiang, H. M., Kan, E., Wallace, A. R. & Sun, W. 2018 Adsorption of phosphate in water on a novel calcium hydroxide-coated dairy manure-derived biochar. Environ. Eng. Res. 24 (3), 434–442.

Das Gupta, M., Loganathan, P. & Vigneswaran, S. 2012 Adsorptive removal of nitrate and phosphate from water by a purolite ion exchange resin and hydrous ferric oxide columns in series. Sep. Sci. Technol. 47 (12), 1785–1792.

Delgadillo-Velasco, L., Hernández-Montoya, V., Rangel-Vázquez, N. A., Cervantes, F. J., Montes-Morán, M. A. & del R. Moreno-Virgen, M. 2018 Screening of commercial sorbents for the removal of phosphates from water and modeling by molecular simulation. J. Mol. Liq. 262, 443–450.

Deng, L. & Shi, Z. 2015 Synthesis and characterization of a novel Mg-Al hydrotalcite-loaded kaolin clay and its adsorption properties for phosphate in aqueous solution. J. Alloys Compd. 637, 188–196.

de P. Couto, R. S., Oliveira, A. F., Guarino, A. W. S., Perez, D. V. & da C. Marques, M. R. 2017 Removal of ammonia nitrogen from distilled old landfill leachate by adsorption on raw and modified aluminosilicate. Environ. Technol. (United Kingdom) 38 (7), 816–826.

Dong, Q., Shi, S., Xie, Y., Wang, Y., Zhang, X., Wang, X., Guo, S., Zhu, L., Zhang, G. & Xu, D. 2020 Preparation of mesoporous zirconia ceramic fibers modified by dual surfactants and their phosphate adsorption characteristics. Ceram. Int. 46 (9), 14019–14029.

Drenkova-Tuhtan, A., Schneider, M., Franzreb, M., Gellermann, C., Sextl, G., Mandel, K. & Steinmetz, H. 2017 Pilot-scale removal and recovery of dissolved phosphate from secondary wastewater effluents with reusable ZnFeZr adsorbent @ Fe3O4/SiO2 particles with magnetic harvesting. Water Res. 109, 77–87.

Du, X., Han, Q., Li, J. & Li, H. 2017 The behavior of phosphate adsorbs and its reactions on the surfaces of Fe-Mn oxide adsorbent. J. Taiwan Inst. Chem. Eng. 66, 167–175.

Eljilam, O., Khalil, A. M. E., Sugihara, Y. & Matsunaga, N. 2016 Phosphorus removal from aqueous solution by nanoscale zero valent iron in the presence of copper chloride. Chem. Eng. J. 293, 225–231.

El-Nahas, S., Salman, H. M. & Seleece, W. A. 2019 Aluminum building scrap wire, take-out food container, potato peels and bagasse as adsorbents for removal of nitrate and phosphate: synergistic effect and mechanism. Environ. Prog. Sustain. Energy 34 (1), 1–10.

Esmaeili Bidhendi, M., Asadi, Z., Bozorgian, A., Shahhoseini, A., Gabris, M. A., Shahabuddin, S., Khanam, R. & Saidur, R. 2019 New nanocellulose-based adsorbents for removal of phosphate from wastewater: synthesis, characterization, and mechanism. Appl. Surf. Sci. 476, 995–1004.

He, Y., Feng, L., Fang, Z., Zhang, Q., Shenn, Q., Li, Y., Xu, X. & Ji, F. 2018 Evaluation of porous calcium silicate hydrate derived from carbide slag for removing phosphate from wastewater. Chem. Eng. J. 354, 1–11.

He, Y., Yang, Y., Zhu, R., Liu, J., Usman, M., Chen, Q. & He, H. 2018 Superior adsorption of phosphate by ferrihydrite-coated and lanthanum-decorated magnetic. J. Colloid Interface Sci. 530, 704–713.

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). Sci. Total Environ. 619–620, 42–48.

Guan, W., Ji, F., Chen, Q., Yan, P. & Pei, L. 2013 Synthesis and enhanced phosphate recovery property of porous calcium silicate hydrate using polyethylene glycol as pore-generation agent. Materials (Basel) 6 (7), 2846–2861.

Guignard, M. S., Leitch, A. R., Acquisti, C., Eizaguirre, C., Elser, J. J., Hessen, D. O., Jeyasingh, P. D., Neiman, M., Richardson, A. E., Soltis, P. S. & Soltis, D. E. 2017 Impacts of nitrogen and phosphorus: from genomes to natural ecosystems and agriculture. Front. Ecol. Environ. 5, 1–70.

He, Y., Lin, H., Dong, Y. & Wang, L. 2017 Preferable adsorption of phosphate using lanthanum-incorporated porous zeolite: characteristics and mechanism. Appl. Surf. Sci. 426, 995–1004.

He, Y., Lin, H., Dong, Y., Li, B., Wang, L. & Chu, S. 2018 Zeolite supported Fe/Ni bimetallic nanoparticles for simultaneous removal of nitrate and phosphate: synergistic effect and mechanism. Chem. Eng. J. 347, 669–681.

Huang, J., Kankanamge, N. R., Chow, C., Welsh, D. T., Li, T. & Teasdale, P. R. 2017 Removing ammonium from water and wastewater using cost-effective adsorbents: a review. J. Environ. Sci. 65, 174–197.

Huang, Y., Lee, X., Cristallier, M., Macazo, F. C., Cai, R. & Minteer, S. D. 2018 A sustainable adsorbent for phosphate removal: modifying multi-walled carbon nanotubes with chitosan. J. Mater. Sci. 55 (17), 12641–12649.

Iftikhar, 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.

Islam, M. & Patel, R. 2010 Synthesis and physicochemical characterization of Zn/Al chloride layered double hydroxide and evaluation of its nitrate removal efficiency. Desalination 256 (1–3), 120–128.

Jiang, H., Chen, P., Luo, S., Tu, X., Cao, Q. & Shu, M. 2013 Synthesis of novel nanocomposite Fe3O4/ZrO2/chitosan and its application for removal of nitrate and phosphate. Appl. Surf. Sci. 284, 942–949.

Jiang, D., Amano, Y. & Machida, M. 2017a Removal and recovery of phosphate from water by calcium-silicate composites-novel adsorbents made from waste glass and shells. Environ. Sci. Pollut. Res. 24 (9), 8210–8218.

Jiang, D., Amano, Y. & Machida, M. 2017b Removal and recovery of phosphate from water by a magnetic Fe2O4@ASC adsorbent. J. Environ. Chem. Eng. 5 (5), 4229–4238.
Jiang, D., Chu, B., Amano, Y. & Machida, M. 2018 Removal and recovery of phosphate from water by Mg-laden biochar: batch and column studies. Colloids Surf. A Physicochem. Eng. Asp. 558, 429–437.

Kalaitzidou, K., Mitrakas, M., Raptopoulou, C., Tolkou, A., Palasantz, P. A. & Zouboulis, A. 2016 Pilot-scale phosphate recovery from secondary wastewater effluents. Environ. Process. 3, 5–22.

Kalmykova, Y. & Karlhed Fedje, K. 2013 Phosphorus recovery from municipal solid waste incineration fly ash. Waste Manag. 33 (6), 1403–1410.

Karthikeyan, P. & Meenakshi, S. 2019 Synthesis and characterization of Zn–Al LDHs/activated carbon composite and its desorption properties for phosphate and nitrate ions in aqueous medium. J. Mol. Liquids 296, 1–9.

Khali, A. M. E., Eljamal, O., Amen, T. W. M., Sugihara, Y. & Matsunaga, N. 2017 Optimized nano-scale zero-valent iron supported on treated activated carbon for enhanced nitrate and phosphate removal from water. Chem. Eng. J. 309, 349–365.

Kim, K., Kim, D., Kim, T., Kim, B. G., Ko, D., Lee, J., Han, Y., Jung, J. C. & Na, H. B. 2019 Synthesis of mesoporous lanthanum hydroxide with enhanced adsorption performance for phosphate removal. RSC Adv. 9 (27), 15257–15264.

Koilraj, P. & Sasaki, K. 2017 Selective removal of phosphate using La-porous carbon composites from aqueous solutions: batch and column studies. Chem. Eng. J. 317, 1059–1068.

Kumar, N. S. & Goel, S. 2010 Factors influencing arsenic and nitrate removal from drinking water in a continuous flow electrocoagulation (EC) process. J. Hazard. Mater. 173 (1–3), 528–533.

Kumar, P. S., Korving, L., van Loosdrecht, M. C. & Witkamp, G. J. 2019 Adsorption as a technology to achieve ultra-low concentrations of phosphate: research gaps and economic analysis. Water Res. X 4, 1–17.

Kuwahara, Y. & Yamashita, H. 2017 Phosphate removal from aqueous solutions using calcium silicate hydrate prepared from blast furnace slag. ISIJ Int. 57 (9), 1657–1664.

Lai, L., Xie, Q., Chi, L., Gu, W. & Wu, D. 2016 Adsorption of phosphate from water by easily separable Fe3O4@SiO2 core/shell magnetic nanoparticles functionalized with hydrazine lanthanum phosphate. J. Colloid Interface Sci. 465, 76–82.

Lee, C. G., Alvarez, P. J., Kim, H. G., Jeong, S., Lee, S., Lee, K. B., Lee, S. H. & Choi, J. W. 2018 Phosphorous recovery from sewage sludge using calcium silicate hydrates. Chemosphere 193, 1087–1093.

Leng, L., Zhang, J., Xu, S., Xiong, Q., Xu, X., Li, J. & Huang, H. 2019 Meat & bone meal (MBM) incineration ash for phosphate removal from wastewater and afterward phosphorus recovery. J. Clean. Prod. 238, 1–11.

Li, M., Liu, J., Xu, Y. & Qian, G. 2016 Phosphate adsorption on metal oxides and metal hydroxides: a comparative review. Environ. Rev. 24 (3), 319–332.

Li, T., Su, X., Yu, X., Song, H., Zhu, Y. & Zhang, Y. 2018 La(OH)3-modified magnetic pineapple biochar as novel adsorbents for efficient phosphate removal. Bioresour. Technol. 263, 207–213.

Li, F., Jin, J., Shen, Z., Ji, H., Yang, M. & Yin, Y. 2020 Removal and recovery of phosphate and fluoride from water with reusable mesoporous Fe2O3@mSiO2@mLDH composites as sorbents. J. Hazard. Mater. 388, 1–13.

Lin, J. Y., Kim, M., Li, D., Kim, H. & Huang, C. P. 2020 The removal of phosphate by thermally treated red mud from water: the effect of surface chemistry on phosphate immobilization. Chemosphere 247, 1–11.

Liu, R., Chi, L., Wang, X., Sui, Y., Wang, Y. & Arandiyah, H. 2018 Review of metal (hydr)oxide and other adsorptive materials for phosphate removal from water. J. Environ. Chem. Eng. 6 (4), 5269–5286.

Liu, J., Jiang, J., Alhemaiti, A., Meng, Y., Yang, M., Xu, Y., Gao, Y., Zou, Q. & Chen, X. 2019a Removal of phosphate from aqueous solution using MgO-modified magnetic biochar derived from anaerobic digestion residue. J. Environ. Manage. 250, 1–9.

Liu, R., Chi, L., Wang, X., Wang, Y., Sui, Y., Xie, T. & Arandiyah, H. 2019b Effective and selective adsorption of phosphate from aqueous solution via trivalent-metals-based amino-MIL-101 MOFs. Chem. Eng. J. 357, 139–168.

Lundehøj, L., Jensen, H. C., Wybrandt, L., Nielsen, U. G., Christensen, M. L. & Quist-Jensen, C. A. 2019 Layered double hydroxides for phosphate recovery from acidified and non-acidified wastewater. Water Res. 153, 208–216.

Maeda, H., Yokota, S. & Kasuga, T. 2018 Structural changes in calcium silicate hydrate gel and resulting improvement in phosphate species removal properties after mechanochemical treatment. R. Soc. Open Sci. 5 (12), 1–7.

Manhooei, L., Mehdinejadiani, B. & Amininasab, S. M. 2019 Cellulose nanocrystal modified with 3-chloro propyl trimethoxysilane: a new bio-adsorbent for nitrate removal. Water Environ. J. 34, 50–60.

Mayer, B. K., Baker, L. A., Boyer, T. H., Drechsel, P., Gifford, M., Hanjra, M. A., Parameswaran, P., Stoltzfus, J., Westerhoff, P. & Rittmann, B. E. 2016 Total value of phosphate recovery. Environ. Sci. Technol. 50 (13), 6606–6620.

Meena, V. S. 2018 Role of Rhizospheric Microbes in Soil: Volume 2: Nutrient Management and Crop Improvement. pp. 1–290.

Mikhak, A., Sohrabi, A., Kasaase, M. Z., Feizian, M. & Najafi Disfani, M. 2017 Removal of nitrate and phosphate from water by clinoilolite-supported iron hydroxide nanoparticle. Arab. J. Sci. Eng. 42 (6), 2433–2439.

Mitrogiannis, D., Psychoyou, M., Baziotsi, I., Ingelzakis, V. J., Koukouzas, N., Tsoukalas, N., Palles, D., Kamitsos, E. G. & Markou, G. 2017 Removal of phosphate from aqueous solutions by adsorption onto Ca(OH)2 treated natural clinoilolite. Chem. Eng. J. 320, 510–522.

Mitrogiannis, D., Psychoyou, M., Koukouzas, N., Tsoukalas, N., Palles, D., Kamitsos, E., Pantazidis, A., Oikonomou, G. & Baziotis, I. 2018 Phosphate recovery from real fresh urine by Ca(OH)2 treated natural zeolite. Chem. Eng. J. 347, 618–630.

Monfort, E., Aubry, G. & Ramirez, A. A. 2017 Nutrient removal and recovery from digestate: a review of the technology. Biofuels 9 (2), 247–262.

Mor, S., Chhoden, K. & Ravindra, K. 2016 Application of agro-waste rice husk ash for the removal of phosphate from the wastewater. J. Clean. Prod. 129, 673–680.
Mouzourakis, E., Georgiou, Y., Louloudi, M., Konstantinou, I. & Deligiannakis, Y. 2017 Recycled-tire pyrolytic carbon made functional: a high-arsenite [As(III)] uptake material pyrc350®. *J. Hazard. Mater.* 326, 177–186.

Nagoya, S., Nakamichi, S. & Kawase, Y. 2019 Mechanisms of phosphate removal from aqueous solution by zero-valent iron: a novel kinetic model for electrostatic adsorption, surface complexation and precipitation of phosphate under oxic conditions. *Sep. Purif. Technol.* 218, 120–129.

Nakarmi, A., Kim, J., Toland, A. & Viswanathan, T. 2018 Novel reusable renewable resource-based iron oxides nanocomposites for removal and recovery of phosphate from contaminated waters. *Int. J. Environ. Sci. Technol.* 16 (8), 4293–4302.

Namasiyam, C. & Prathap, K. 2005 Recycling Fe(III)/Cr(III) hydroxide, an industrial solid waste for the removal of phosphate from water. *J. Hazard. Mater.* 123 (1–3), 127–134.

Nawar, N., Ahmad, M. E., El Said, W. M. & Moalla, S. M. N. 2015 Adsorptive removal of phosphorus from wastewater using drinking water treatmentalum sludge (DWTAS) as low cost adsorbent citation. *Am. J. Chem. Appl.* 2 (6), 79–85.

Okano, K., Miyamaru, S., Yamamoto, Y., Kunisada, M., Takano, H., Todai, M., Honda, K. & Ohtake, H. 2016 A mobile pilot-scale plant for in situ demonstration of phosphorus recovery from wastewater using amorphous calcium silicate hydrates. *Separ. Purif. Technol.* 170, 116–121.

Pap, S., Kirk, C., Brenner, B., Sekulic, M. T., Shearer, L., Gibb, S. W. & Taggart, M. A. 2020 Low-cost chitosan-calcite adsorbent development for potential phosphate removal and recovery from wastewater effluent. *Water Res.* 173, 1–14.

Pathania, D., Sharma, S. & Singh, P. 2017 Removal of methylene blue by adsorption onto activated carbon developed from Ficus carica bast. *Arab. J. Chem.* 10, S1445–S1451.

Peng, L., Dai, H., Wu, Y., Peng, Y. & Lu, X. 2018 A comprehensive review of the available media and approaches for phosphorus recovery from wastewater. *Water, Air, Soil Pollut.* 229 (4), 1–28.

Pham, T. H., Lee, K. M., Kim, M. S., Seo, J. & Lee, C. 2019 La-modified ZSM-5 zeolite beads for enhancement in removal and recovery of phosphate. *Microporous Mesoporous Mater.* 279, 37–44.

Piccin, J. S., Dotto, G. L. & Pinto, L. A. A. 2011 Adsorption isotherms and thermochemical data of FD and C RED N° 40 Binding by chitosan. *Brazilian J. Chem. Eng.* 28 (2), 295–304.

Prashantha Kumar, T. K. M., Mandlimath, T. R., Sangeetha, P., Revathi, S. K. & Ashok Kumar, S. K. 2018 Nanoscale materials as sorbents for nitrate and phosphate removal from water. *Environ. Sci. Technol.* 16 (2), 389–400.

Qiu, H., Liang, C., Yu, J., Zhang, Q., Song, M. & Chen, F. 2017 Preferable phosphate sequestration by nano-La (III) (hydr) oxides modified wheat straw with excellent properties in regeneration. *Chem. Eng. J.* 315, 345–354.

Rajeswari, A., Amalraj, A. & Pius, A. 2016 Adsorption studies for the removal of nitrate using chitosan/PEG and chitosan/PVA polymer composites. *J. Water Process Eng.* 9, 123–134.

Rashidi Nodhe, H., Sereshti, H., Zamiri Afsharian, E. & Nouri, N. 2017 Enhanced removal of phosphate and nitrate ions from aqueous media using nanosized lanthanum hydrous doped on magnetic graphene nanocomposite. *J. Environ. Manage.* 197, 265–274.

Ren, Z., Xu, X., Wang, X., Gao, B., Yue, Q., Song, W., Zhang, L. & Wang, H. 2016 FTIR, Raman & XPS analysis during phosphate, nitrate and Cr(VI) removal by amine cross-linking biosorbent. *J. Colloid Interface Sci.* 468, 313–323.

Rezaei Kalantary, R., Dehghanifard, E., Mohseni-Bandpi, A., Rezaei, L., Esrafil, A., Kakavandi, B. & Azari, A. 2016 Nitrate adsorption by synthetic activated carbon magnetic nanoparticles: kinetics, isotherms and thermodynamic studies. *Desalin. Water Treat.* 57 (33), 16445–16455.

Ruzhitskaya, O. & Gogina, E. 2017 Methods for removing of phosphates from wastewater. *MATEC Web Conf.* 106, 1–7.

Saha, B., Chakraborty, S. & Das, G. 2009 A mechanistic insight into enhanced and selective phosphate adsorption on a coated carboxylated surfact. *J. Colloid Interface Sci.* 331 (1), 21–26.

Sancho, I., Licon, E., Valderrama, C., de Arespacochaga, N., López-Palau, S. & Cortina, J. L. 2017 Recovery of ammonia from domestic wastewater effluents as liquid fertilizers by integration of natural zeolites and hollow fibre membrane contactors. *Sci. Total Environ.* 584–585, 244–251.

Seftel, E. M., Ciocarlan, R. G., Michielsen, B., Meynen, V., Mullens, S. & Cool, P. 2018 Insights into phosphate adsorption behavior on structurally modified ZnAl layered double hydroxides. *Appl. Clay Sci.* 165, 234–246.

Sereshti, H., Zamiri Afsharian, E., Esmaeili Bidhendi, M., Rashidi Nodhe, H., Afzal Kamboh, M. & Yilmaz, M. 2020 Removal of phosphate and nitrate ions aqueous using strontium magnetic graphene oxide nanocomposite: isotherms, kinetics & thermodynamics studies. *Environ. Prog. Sustain. Energy* 39 (2), 1–12.

Shahid, M. K., Kim, Y. & Choi, Y. G. 2019 Magnete synthesis using iron oxide waste and its application for phosphate adsorption with column and batch reactors. *Chem. Eng. Res. Des.* 148, 169–179.

Shi, W., Fu, Y., Jiang, W., Ye, Y., Kang, J., Liu, D., Ren, Y., Li, D., Luo, C. & Xu, Z. 2019 Enhanced phosphate removal by zeolite loaded with Mg–Al–La ternary (hydr)oxides from aqueous solutions: performance and mechanism. *Chem. Eng. J.* 357, 33–44.

Shin, E. W., Han, J. S., Jang, M., Min, S. H., Park, J. K. & Rowell, R. M. 2004 Phosphate adsorption on aluminum-impregnated mesoporous silicates: surface structure and behavior of adsorbents. *Environ. Sci. Technol.* 38 (3), 912–917.

Song, W., Gao, B., Xu, X., Wang, F., Xue, N., Sun, S., Song, W. & Jia, R. 2016 Adsorption of nitrate from aqueous solution by magnetic amine-crosslinked biopolymer based corn stalk and its chemical regeneration property. *J. Hazard. Mater.* 304, 280–290.

Suzaimi, N. D., Goh, P. S. & Malek, N. A. N. 2019 Modified-nano-adsorbents for nitrate efficient removal: a review. *J. Appl. Membr. Sci. Technol.* 23 (2), 65–81.

Taylor, S., Aiyuk, H. X. & Van Haandel, A. 2010 Removal of ammonium nitrogen from pretreated domestic sewage using a natural ion exchanger. 37–41.
Wan, C., Ding, S., Zhang, C., Tan, X., Zou, W., Liu, X. & Yang, X. 2017 Simultaneous recovery of nitrogen and phosphorus from sludge fermentation liquid by zeolite adsorption: mechanism and application. *Sep. Purif. Technol.* 180, 1–12.

Wang, Z., Lin, Y., Wu, D. & Kong, H. 2016 Hydrous iron oxide modified diatomite as an active filtration medium for phosphate capture. *Chemosphere* 144, 1290–1298.

Wang, S., Kong, L., Long, J., Su, M., Diao, Z., Chang, X., Chen, D., Song, G. & Shih, K. 2018 Adsorption of phosphorus by calcium-flour biochar: isotherm, kinetic and transformation studies. *Chemosphere* 195, 666–672.

Wang, B., Lian, G., Lee, X., Gao, B., Li, L., Liu, T., Zhang, X. & Zheng, Y. 2020a Phosphogypsum as a novel modifier for distillers grains biochar removal of phosphate from water. *Chemosphere* 238, 1–8.

Wang, L., Chengxiang, S., Lun, P., Xiangwen, Z. & Ji, J. Z. 2020b Rational design, synthesis, adsorption principles and applications of metal oxide adsorbents: a review. *Nanoscale* 12 (8), 4790–4815.

Wei, L. L., Wang, G. Z., Jiang, J. Q., Li, G., Zhang, X. L., Zhao, Q. L. & Cui, F. Y. 2015 Co-removal of phosphorus and nitrogen with commercial 201 × 7 anion exchange resin during tertiary treatment of WWTP effluent and phosphate recovery. *Desalin. Water Treat.* 56 (6), 1633–1647.

Wu, B., Fang, L., Fortner, J. D., Guan, X. & Lo, I. M. C. 2017 Highly efficient and selective phosphate removal from wastewater by magnetically recoverable La(OH)3/Fe3O4 nanocomposites. *Water Res.* 126, 179–188.

Xiao, X., Liu, S., Zhang, X. & Zheng, S. 2017 Phosphorus removal and recovery from secondary effluent in sewage treatment plant by magnetite mineral microparticles. *Powder Technol.* 306, 68–73.

Xie, J., Wang, Z., Lu, S., Wu, D., Zhang, Z. & Kong, H. 2014 Removal and recovery of phosphate from water by lanthanum hydroxide materials. *Chem. Eng. J.* 254, 163–170.

Xie, J., Lin, Y., Li, C., Wu, D. & Kong, H. 2015 Removal and recovery of phosphate from water by activated aluminum oxide and lanthanum oxide. *Powder Technol.* 269, 351–357.

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. *J. Colloid Interface Sci.* 493, 17–23.

Xu, K., Lin, F., Dou, X., Zheng, M., Tan, W. & Wang, C. 2018 Recovery of ammonium and phosphate from urine as value-added fertilizer using wood waste biochar loaded with magnesium oxides. *J. Clean. Prod.* 187, 205–214.

Xu, K., Zhang, C., Dou, X., Ma, W. & Wang, C. 2019 Optimizing the modification of wood waste biochar via metal oxides to remove and recover phosphate from human urine. *Environ. Geochem. Health* 41 (4), 1767–1776.

Xue, L., Gao, B., Wan, Y., Fang, J., Wang, S., Li, Y., Muñoz-Carpena, R. & Yang, L. 2016 High efficiency and selectivity of MgFe-LDH modified wheat-straw biochar in the removal of nitrate from aqueous solutions. *J. Taiwan Inst. Chem. Eng.* 63, 312–317.

Yang, L., Yang, M., Xu, P., Zhao, X., Bai, H. & Li, H. 2017 Characteristics of nitrate removal from aqueous solution by modified steel slag. *Water (Switzerland)* 9 (10), 1–17.

Zhang, Y., Pan, B., Shan, C. & Gao, X. 2016 Enhanced phosphate removal by nanosized hydrated La(III) oxide confined in cross-linked polystyrene networks. *Environ. Sci. Technol.* 50 (3), 1447–1454.

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. *Appl. Surf. Sci.* 396, 1783–1792.

Zhang, Z., Wang, X., Wang, H. & Zhao, J. 2018 Removal of Pb(II) from aqueous solution using hydroxyapatite/calcium silicate hydrate (HAP/C-S-H) composite adsorbent prepared by a phosphate recovery process. *Chem. Eng. J.* 344, 53–61.

Zhang, Z., Wang, X. & Zhao, J. 2019 Phosphate recovery from wastewater using calcium silicate hydrate (C-S-H): sonochemical synthesis and properties. *Environ. Sci. Water Res. Technol.* 5 (1), 131–139.

Zhou, K., Wu, B., Su, L., Xin, W. & Chai, X. 2018 Enhanced phosphate removal using nanostructured hydrated ferric-zirconium binary oxide confined in a polymeric anion exchanger. *Chem. Eng. J.* 345, 640–647.

Zhu, Y. J. 2017 Nanostructured materials of calcium phosphates and calcium silicates: synthesis, properties and applications. *Chinese J. Chem.* 35 (6), 769–790.

First received 23 November 2020; accepted in revised form 28 July 2021. Available online 25 August 2021