



# Guidance on aqueous matrices for evaluating novel precipitants and adsorbents for phosphorus removal and recovery

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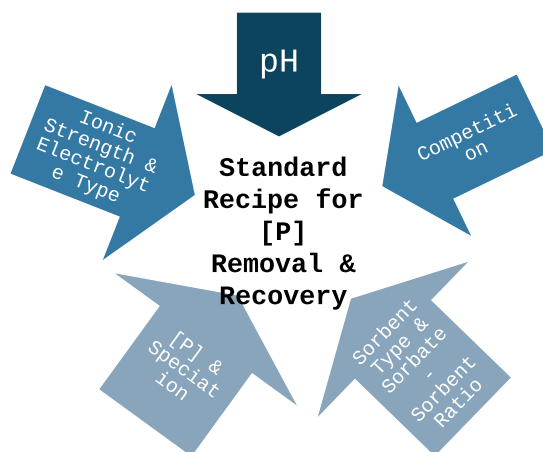
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## HIGHLIGHTS

- Propose systematic approach for testing novel materials for P removal from water.
- Approach identifies aqueous matrices, aqueous components, and standard recipes.
- pH, multivalent metal cations, and dissolved organic matter are key components.
- Recipes developed for groundwater, surface water, anaerobic digestate, and urine.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Phosphorus (P) removal from water and recovery into useable forms is a critical component of creating a sustainable P cycle, although mature technologies for P removal and recovery are still lacking. The goal of this paper

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was to advance the testing of novel materials for P removal and recovery from water by providing guidance on the development of more realistic aqueous matrices used during materials development. Literature reports of “new” materials to remove P from water are often difficult to compare in terms of performance because authors use a myriad of water chemistries containing P concentrations, pH, and competing ions. Moreover, many tests are conducted in simplified matrices that do not reflect conditions in real systems. To address this critical gap, the research herein developed a systematic approach of identifying aqueous matrices relevant to P recovery, including key components in the aqueous matrices having the greatest influence on the mechanisms of P removal with emphasis on phosphate precipitation and phosphate adsorption, and providing guidelines on relevant “recipes” for aqueous solutions for testing novel materials. Key components in the aqueous matrices included hydrogen ion (i.e., pH), multivalent metal cations, and dissolved organic matter due to their influence on phosphate precipitation and adsorption mechanisms. Recipes for buffer solution and synthetic groundwater, surface water, anaerobic digestate, and stored urine are discussed in the context of P removal and recovery processes. Wherein the adoption of standard matrices in other fields have permitted direct comparison of processes or materials, it is anticipated that adoption of relevant aqueous matrix recipes for P removal and recovery will improve the ability to directly compare novel materials and processes.

## 1. Introduction

Phosphorus (P) is an essential nutrient required for plant growth, microbial activity, and human nutrition. Mined P underpins the global food system (Cordell et al., 2009; Jacobs et al., 2017; Zhu et al., 2023), and many socioeconomic and biophysical constraints result in supply vulnerabilities (Baker et al., 2024). Global reliance on mined P has also caused significant ecological problems and has been identified as a high-risk planetary boundary (Steffen et al., 2015). Although food production (agriculture and livestock) represents >90% of the P uses, less than 10% of the mined P ends up in human food because of losses through fertilizer use in soils, industrial-scale animal operations, and food processing. Consequently, sources of P pollution into the aquatic environment result in lower P concentrations at high-water-flow locations (e.g., domestic wastewater effluents, urban and agricultural runoff) or higher P-concentrations at low-water-flow locations (e.g., animal waste lagoons, anaerobic digesters) (Mayer et al., 2016; Rittmann et al., 2011). Reducing society’s reliance upon mined P can be achieved by improving P-removal technologies (Sarvajayakesavalu et al., 2018), but only when P removal is accompanied by recovery in a solution or mineral form suitable for beneficial use, such as in agriculture (Babcock-Jackson et al., 2023). Although many political and societal barriers exist in the P cycle (El Wali et al., 2021; Rahimpour Golroudbary et al., 2020), there is a need to benchmark the performance of existing technologies and develop new technologies for P removal and recovery.

Advanced materials and processes have great potential to improve P sustainability by advancing P removal and recovery (Jones et al., 2020). The two most widely developed removal technologies are selective precipitation and adsorption processes. However, limited viable options exist that are technologically mature for P recovery (Li et al., 2019). For example, struvite, a magnesium ammonium phosphate mineral, precipitation (Guan et al., 2023; Siciliano et al., 2020) is a commercially available process for P recovery from wastewater (Zhu et al., 2023), whereas P adsorption using modified goethite or lanthanum-modified bentonite (Haghseresht et al., 2009; Lalley et al., 2015; Wu et al., 2020) has been used in commercial applications for P removal but not P recovery.

At the laboratory scale, innovations in material science have led to numerous research articles evaluating novel precipitants and adsorbents for P removal from water (Almanassra et al., 2021; Du et al., 2022; Kajjumba and Marti, 2022). One common limitation in material science research on P removal is the lack of testing conditions using environmentally relevant matrices, with the emphasis in this paper on aqueous solutions. Many studies test new materials in deionized or ultrapure water spiked with phosphate (Liu et al., 2019, 2021; Wang et al., 2020), which provides limited information on the performance of a new material in real water situations. For example, solution pH affects phosphate speciation, which affects all aspects of precipitation and

adsorption, and the amount and type of other solutes affects the ion activity product for precipitation and competition for surface binding sites for adsorption. Beyond chemical composition of the test water, other impact factors include the sorbate (i.e., phosphate) to adsorbent (solid phase) mass ratios used during the tests (Hristovski and Markovski, 2017), the morphology and surface area of adsorbents (Luo et al., 2021a, 2021b), and the duration of experiments where there can be phase changes in phosphate-containing minerals (Zhi et al., 2022). Testing new materials in more relevant aqueous matrices would generate more useful results and help identify earlier the limitations of new materials that have the potential to accelerate new P-removal and -recovery technologies.

Despite the pressing societal need for P recovery as part of a more sustainable P cycle, development of technologies for deployment has been slow, in part due to new materials for P removal failing to perform as needed in real situations. Standardization of water chemistries for testing has greatly improved technology development in numerous fields. For example, NSF/ANSI Standards 53 or 61 establish specific drinking-water relevant conditions to test performance of treatment technologies or leaching of chemicals from drinking water contact materials (Kelechava, 2022); the USEPA has soft- or hard-water chemistries recommended for use in aquatic toxicity studies (USEPA, 1986); biomedical testing relies upon specific matrices used to simulate saliva, gastric fluids for various stages of fasting, and synthetic urine (Marques et al., 2011). Accordingly, the goal of this paper was to advance the testing of novel materials for P removal and recovery from water by providing guidance on the development of more realistic aqueous matrices used during materials development. The objectives of this paper were to: (1) develop a framework to systematically evaluate P removal from water by phosphate precipitation and adsorption; (2) identify aqueous matrices relevant to P recovery; (3) identify key components in the aqueous matrices that have the greatest influence on the chemistry of P removal; and (4) provide guidelines on standard recipes for aqueous solutions for testing new materials for P removal and recovery.

## 2. Background

Phosphorus removal, reuse, and recovery are key terms in this paper. Phosphorus removal refers to the capture of P in water and wastewater and includes precipitation and adsorption. Biological uptake of P by aquatic plants and microorganisms is another form of P capture, but not considered in this paper, but phosphate-binding proteins (PBPs) envisioned as adsorbents are within scope (Hussein et al., 2024). As researchers create new precipitants and adsorbents, the results of this study will be useful for screening those materials and evaluating if modifications to their properties can improve P capture. In addition, new materials for P capture can be synthesized considering the key aqueous components identified in this study. Phosphorus reuse refers to

the beneficial use of P that was previously present in water or wastewater. Hence, P recovery is the combination of P capture and P reuse. In this paper, the term “P removal” is used when the emphasis is on the mechanism of P capture in water, whereas “P recovery” is used when the emphasis is on the final product. The most common example of P recovery is precipitation of struvite from wastewater for use as fertilizer or soil amendment (Ferraro et al., 2023; Guan et al., 2023; Mayor et al., 2023), although other P-containing concentrated solutions (e.g., after release from adsorbents), solid-materials, and beneficial uses are also desired.

## 2.1. Phosphorus chemistry

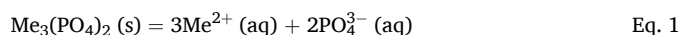
There are many inorganic and organic forms of P as well as dissolved, colloidal, or particulate forms of P, in water, each of which influences the potential for P removal and recovery. Fig. 1 summarizes some of the most common P species in water. The  $pK_a$  of the P species is included in Fig. 1 to illustrate the different forms of P present as a function of pH. Fig. 2 shows operational definitions of P that are used in the literature when considering dissolved or particulate and inorganic or organic. Phosphite, a reduced form of phosphate, is used in some agrochemicals (Havlin and Schlegel, 2021) and is found in wetland soils (Pasek et al., 2014) and a minor component of wastewater (Yu et al., 2015). Pyro- and tri-phosphate are polyphosphate species with numerous oxygen functional groups. DNA, RNA, and phospholipids are major components of algae, bacteria, and other microorganisms. Whereas DNA and RNA degrade rapidly via naturally occurring enzymes in water due to their lability, phospholipids are not very water-soluble. Fig. 1 also shows representative adenosine phosphates, such as adenosine diphosphate (ADP), which is a biologically significant molecule that plays key roles in energy storage and release. Phytic acid, a natural substance found in plant seeds and grain husks, represents one of the most P-rich structures found in nature.

Most waters contain phosphate in the presence of one or more of the other types of P compounds shown in Figs. 1 and 2. There are several methods to measure P in aqueous solutions, including ion chromatography, with the most common and straightforward being

spectrophotometric approaches. The general approach is to directly react a color-responsive reagent with phosphate, sometimes preceded by digesting the sample to release phosphate from organic material or condensed phosphates. The color-responsive reagent is selected based on the expected P concentrations in the samples. The vanadomolybdo-phosphoric acid method is typically used for a P range of 1–20 mg/L and the ascorbic acid method is used for the range of 0.01–6 mg/L. In both methods, the intensity of the color produced after reaction with phosphate is proportional to the P concentration. The reagents come packaged as kits to measure P, and can also be purchased from chemical suppliers. More details on these methods, sample preparation guidance, and limitations can be found in *Standard Methods for the Examination of Water and Wastewater* (Eaton et al., 2005).

## 2.2. Phosphorus precipitation

Phosphorus, in the form of phosphate, can interact with metal cations to form metal phosphate solids. Precipitation occurs when the ion activity product (IAP) exceeds the solubility product ( $K_{s0}$ ) of the solid, as illustrated in Equation (1):



where  $n = 2$  (i.e., the charge on the metal) gives  $IAP = [Me]^3 \times [PO_4^{3-}]^2$  and  $n = 3$  gives  $IAP = [Me] \times [PO_4^{3-}]$ , and the concentration of phosphate species is a function of pH. For  $IAP > K_{s0}$ , the metal phosphate is supersaturated in solution and precipitation is thermodynamically favorable. Table 1 lists metal phosphate solids, with corresponding  $K_{s0}$  values that have the potential for P capture. With  $K_{s0}$  values on the order of  $10^{-40}$  to  $10^{-30}$ , most metal phosphate solids have a low equilibrium phosphate concentration in water. It is worth noting when comparing  $K_{s0}$  values that stoichiometries that differ from Equation (1) are possible for metal phosphate solids with hydroxyapatite ( $Ca_5(PO_4)_3(OH)$ ,  $IAP = [Ca^{2+}]^5[PO_4^{3-}]^3[OH^-]$ ) and struvite ( $MgNH_4PO_4 \cdot 6H_2O$ ),  $IAP = [Mg^{2+}][NH_4^+][PO_4^{3-}]$  being two common examples (Guan et al., 2023; Peng et al., 2018). Finally, the IAP also influences the kinetics of precipitation, albeit in a complex manner depending on crystal nucleation and growth

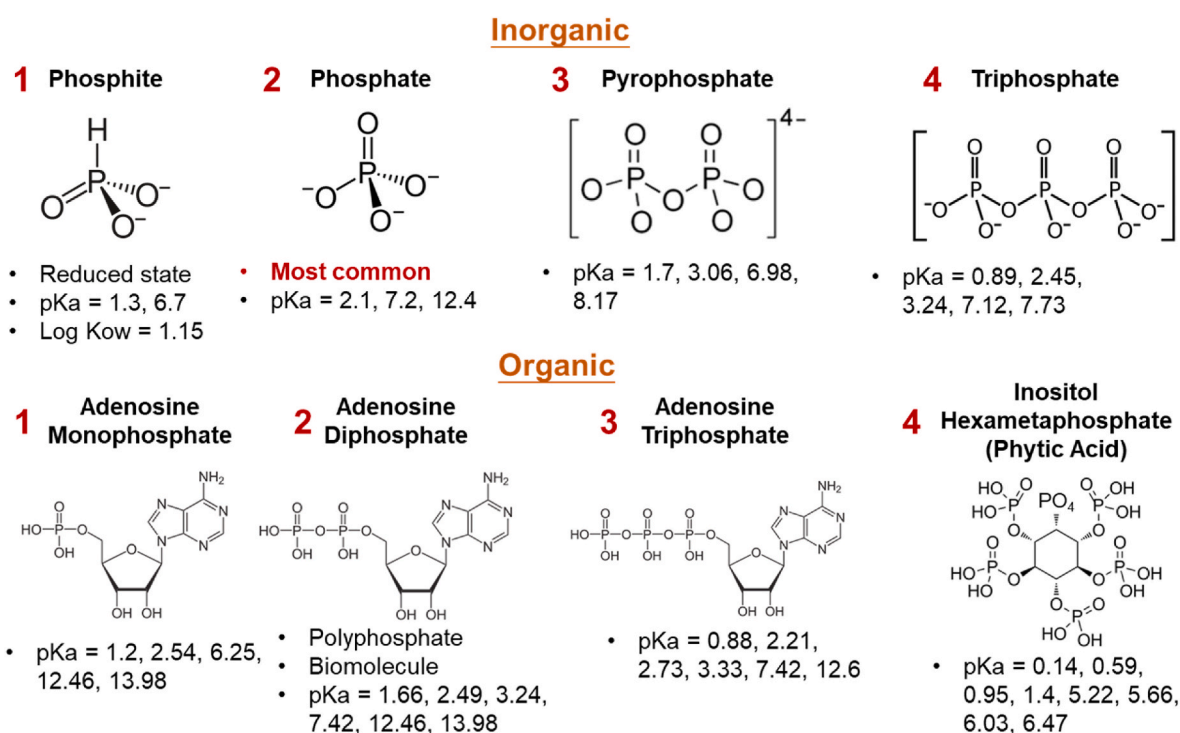


Fig. 1. Common inorganic and organic forms of P in water.

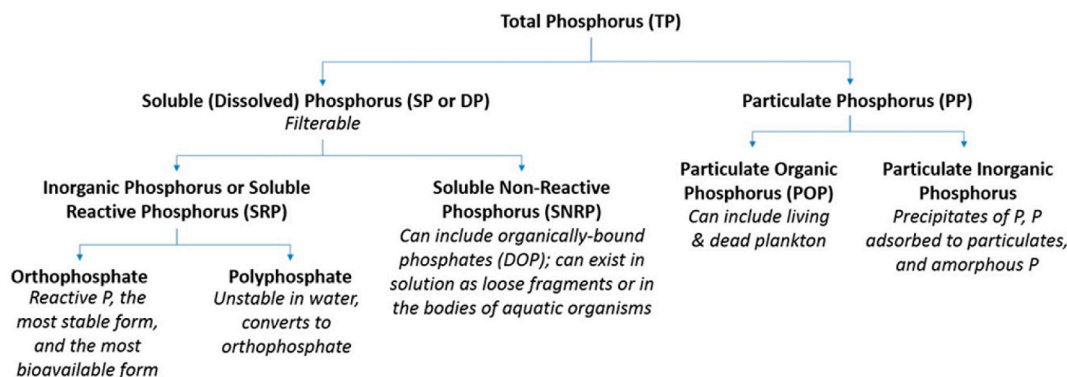


Fig. 2. Phosphorus forms and its characteristics in water. Reprinted with permission from (Macintosh et al., 2018). Copyright 2018 American Chemical Society.

Table 1

Apparent solubility products ( $K_{s0}$ ) of metal phosphates in specific aqueous matrices.

| Metal phosphate  | log $K_{s0}$ | Water matrix tested                                | Reference                |
|--|--------------|--|--------------------------|
| $\text{Ca}_3(\text{PO}_4)_2$                           | −25.5        | Livestock wastewater                               | Cao and Harris (2008)    |
| $\text{Ca}_5(\text{OH})(\text{PO}_4)_3$                | −44.33       | Simple synthetic water, domestic wastewater, urine | Deng and Dhar (2023)     |
| $\text{Cd}_3(\text{PO}_4)_2$                           | −32.60       | Simple synthetic water                             | Matusik et al. (2008)    |
| $\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ | −36          | Groundwater  | Goedhart et al. (2022)   |
| $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$              | −26.4        | Domestic wastewater                                | Thistleton et al. (2002) |
| $\text{LaPO}_4$  | −22.43       | Surface water                                      | Zhi et al. (2020)        |
| $\text{Mg}_3(\text{PO}_4)_2$                           | −23.28       | Synthetic seawater                                 | Golubev et al. (2001)    |
| $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$   | −13.36       | Domestic wastewater, urine, livestock wastewater   | Siciliano et al. (2020)  |
| $\text{Ni}_3(\text{PO}_4)_2$                           | −31.3        | Synthetic industrial wastewater                    | Yu and Jiang (2019)      |
| $\text{Pb}_5(\text{OH})(\text{PO}_4)_3$                | −62.79       | Simple synthetic water                             | Moufih et al. (2005)     |
| $\text{Zn}_3(\text{PO}_4)_2$                           | −32.04       | Simple synthetic water                             | Quimby and McCune (1957) |

mechanisms (Brezonik and Arnold, 2011).

Recent review articles on P capture by metal-phosphate precipitation focus on different metals used to promote precipitation, e.g., rare earth elements (Kajjumba and Marti, 2022; Kunhikrishnan et al., 2022), and producing different forms of phosphate minerals, e.g., struvite, vivianite, and hydroxyapatite (Deng and Dhar, 2023; Yesigat et al., 2022; Zhu et al., 2023). Metal phosphate precipitation is influenced by pH, ionic strength, turbidity, presence of interfering metal cations and anions/ligands, and in some cases redox potential (e.g., vivianite). pH is the most important solution condition to consider because it influences the thermodynamics of metal-phosphate precipitation by shifting the speciation of phosphate, and in some cases, constituent metal cations. Ionic strength influences metal phosphate precipitation by influencing the activity of phosphate and metal cations, and ion interactions with metal mineral surfaces. Together, pH and ionic strength directly influence the IAP, which controls whether metal phosphate precipitation is thermodynamically favorable. Interfering ions and ligands can inhibit precipitation and result in impure products. P recovery requires that metal phosphate solids have a composition, form, and particle size that is amenable to the intended beneficial use.

### 2.3. Phosphorus adsorption

Removal of P as phosphate has been investigated extensively using a variety of adsorbents, including metal (hydr)oxides, organic

functionalized materials, phosphate-binding proteins (PBPs), ion-exchange resin, biochar, and clay-modified materials (Blaney et al., 2007; Haghseresht et al., 2009; Lalley et al., 2015; Wu et al., 2020). Phosphate adsorbs to materials via different mechanisms that include electrostatic/outer-sphere, ligand exchange/inner-sphere, and surface precipitation. For example, a novel lanthanum-modified bentonite (Robb et al., 2003) was found to have a high affinity for dihydrogen phosphate ( $\text{H}_2\text{PO}_4^-$ ) at acidic to neutral pH (5–7) due to surface precipitation (Haghseresht et al., 2009), whereas other materials like metal (hydr)oxides including  $\text{ZrO}_2$  and Fe-based materials (hematite,  $\alpha\text{-Fe}_2\text{O}_3$ ) form inner-sphere complexes of varying structure (e.g., monodentate or bidentate) with phosphate species depending on pH and surface loading (Elzinga and Sparks, 2007). For Fe-based material (goethite,  $\text{FeOOH}$ ), increasing  $\text{pK}_a$  of surface groups was found to be linearly dependent on the binding affinity or strength of these complexes (Liao et al., 2021). Ion exchange resins can remove phosphate by purely electrostatic interactions (Gregory and Dhond, 1972) or more selective inner-sphere complexation for hybrid anion exchange resin containing metal oxides (Blaney et al., 2007).

Table 2 summarizes the phosphate-adsorption capacity on representative adsorbents that have been tested for P capture. The table includes the pH, temperature, and aqueous environment for the adsorption test conditions. The results in Table 2 illustrate the range in phosphate-adsorption capacities documented in the literature. Capacities for commonly used adsorbent materials are ultimately controlled by their surface reactivities, including surface area and surface site density, which constrains the molar amount of ions that can be arranged in a monolayer. The adsorption capacities are also dependent on pH and temperature. Greater adsorption of phosphate typically occurs at acidic pH due to more favorable electrostatic interactions, with pH values lower than the pH point of zero charge ( $\text{pH}_{\text{pzc}}$ ) or isoelectric point ( $\text{pH}_{\text{IEP}}$ ) of the adsorbent surface having more favorable interactions with phosphate anion. The variation in pH and surface charge of the adsorbent results in a large range of adsorbent capacities for various materials, as emphasized in Table 2. Additionally, these capacities depend on other components of the water matrix, as competitive adsorption by other solutes may reduce the number of active adsorbent sites available to phosphate. Common competing ions in water and wastewater include sulfate, bicarbonate, nitrate, and chloride with similar isostructural tetrahedral configurations between sulfate and phosphate, posing a particular challenge for selective removal (Wu et al., 2020). Natural water matrices also include organic acids (e.g., natural organic matter), soluble microbial products, and cations in addition to the previously stated anions, which can inhibit phosphate adsorption.

Phosphate removal via adsorption can be achieved using a variety of materials with subsequent P recovery varying from direct soil application of the phosphate-loaded adsorbent to phosphate recovery from regeneration (i.e., desorption) solutions (O'Neal and Boyer, 2015; Zheng et al., 2023). Previous studies have used desorption methods to recover



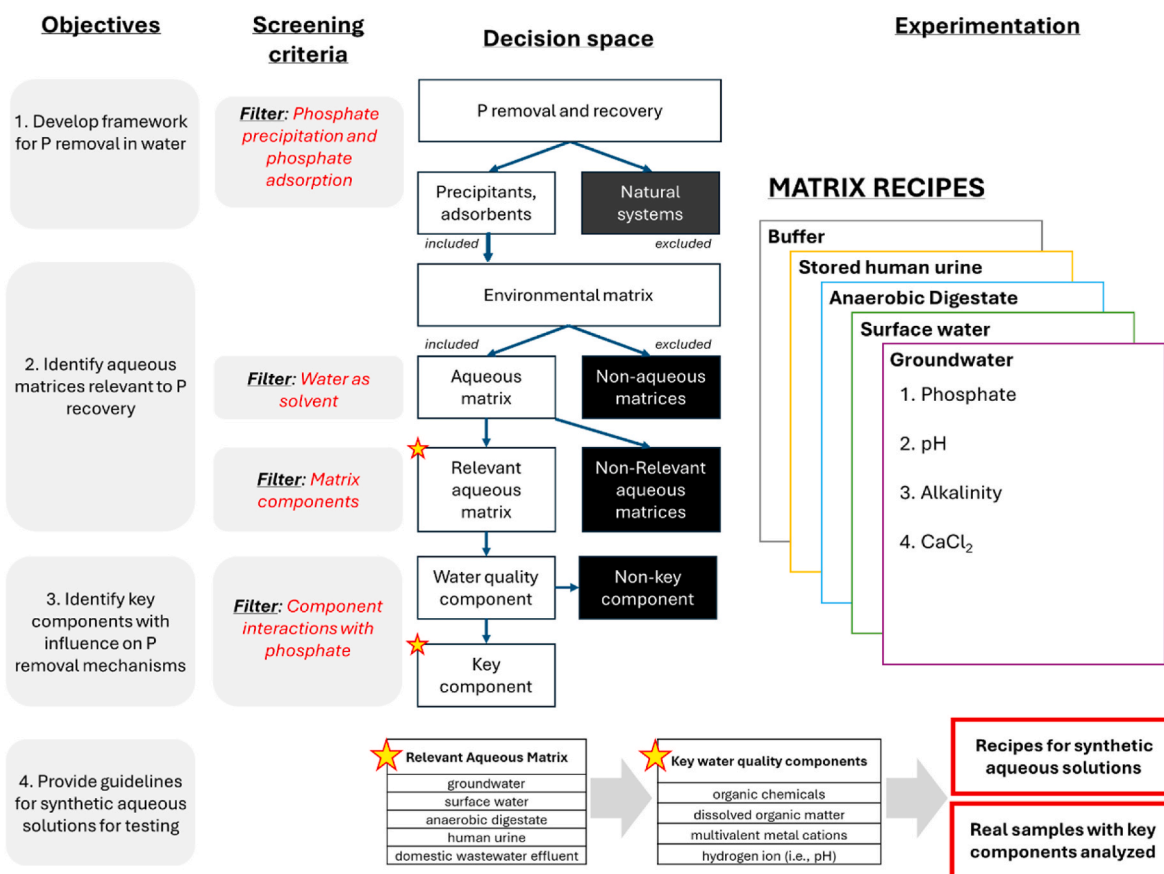
**Table 2**

Phosphate adsorption capacity on representative adsorbents.

| Adsorbent   | pH      | Temperature (°C) | P capacity (mg/g) | Aqueous Environment  | Reference                 |
|---|---------|------------------|-------------------|--|---------------------------|
| E33 Bayoxide  | 7.0     | 21               | 26.8              | NaH <sub>2</sub> PO <sub>4</sub> ·(H <sub>2</sub> O)                         | Lalley et al. (2015)      |
| E33 modified with AgII                                  | 7.0     | 21               | 28.0              | NaH <sub>2</sub> PO <sub>4</sub> ·(H <sub>2</sub> O)                         | Lalley et al. (2015)      |
| Fe-loaded biomass char                                  | 3.0     | 25               | 35.4              | KH <sub>2</sub> PO <sub>4</sub>  | Zhou et al. (2013)        |
| Cerium dioxide  | 4.8–5.6 | 25               | 30–80             | KH <sub>2</sub> PO <sub>4</sub> , NaOH and HCl                               | Wu and Lo (2020)          |
| Fly ash   | 3.0     | 25               | 18.9              | NaH <sub>2</sub> PO <sub>4</sub> , HNO <sub>3</sub> or NaOH                  | Yao et al. (2009)         |
| Metal oxides from manganese ore tailing                 | 6.0     | 25               | 26.3              | NaH <sub>2</sub> PO <sub>4</sub> , 0.01 M NaNO <sub>3</sub> , HCl or NaOH    | Liu et al. (2012)         |
| Magnetic iron oxide nanoparticles                       | 3.0     | 15               | 3.7               | KH <sub>2</sub> PO <sub>4</sub> , NaOH and HCl                               | Yoon et al. (2014)        |
| Naturally occurring bacteriogenic iron (oxyhydr) oxides | 6.0     | 21               | 1.4–22            | KH <sub>2</sub> PO <sub>4</sub> , 0.086 M MES, and 0.01 M NaCl               | Field et al. (2019)       |
| Phoslock (lanthanum-modified bentonite)                 | 5–7     | 10–35            | 9.5–10.5          | KH <sub>2</sub> PO <sub>4</sub> , NaOH or HCl                                | Haghseresht et al. (2009) |
| Red mud   | 4.0     | 25               | 0.5               | NaH <sub>2</sub> PO <sub>4</sub> ·7H <sub>2</sub> O, 0.1 M NaCl, HCl or NaOH | Castaldi et al. (2010)    |
| Steel slag  | 5.5     | 25               | 5.3               | KH <sub>2</sub> PO <sub>4</sub> , 0.01 M KCl, HCl and NaOH                   | Xiong et al. (2008)       |
| Zinc-aluminum layered double hydroxides                 | 9.0     | 25               | 30.0              | Sewage sludge filtrate, HCl or NaOH,   | Cheng et al. (2009)       |

P including salts, acids, bases, or a combination depending on the adsorbent type (Sengupta and Pandit, 2011). After liquid treatment for recovery of P, ammonia-treated Al–Mg layered-double hydroxide and calcite-chitosan-based adsorbent materials have weakened P complexes that can be used as slow-release fertilizer materials (Pap et al., 2020; Yan et al., 2018). Additional studies have quantified desorption and P recovery from waste streams, such as urine and digester filtrate (O'Neal and Boyer, 2015), by comparing phosphate desorption from anion exchange resin followed by precipitation in the regenerant with direct precipitation of phosphate in the original waste stream. In some cases, it

may be necessary to transform organic P species (e.g., RNA, DNA, phospholipids) from algae cells or animal manure using oxidants into inorganic phosphate anions prior adsorption (Molitor et al., 2024; Sindelar et al., 2015b, 2016). Oxidative transformation coupled with ion exchange resin adsorption and slow desorption with KOH was shown as a viable process for P-recovery for intensive algae culturing (Gifford et al., 2015), wherein the concentrated P solution contained potassium which was important in reuse as a nutrient feed solution for the algae biorefinery. Recovery of P from spent adsorbents and liquid concentrates is possible (O'Neal and Boyer, 2015; Sengupta and Pandit, 2011);



**Fig. 3.** Study framework used to identify synthetic aqueous solutions for testing new P removal materials. Study objectives were used to develop screening criteria that were applied to the framework. The result is simulant recipes for synthetic aqueous solutions to be used in experimentation. Common components in synthetic and real samples are highlighted.

however, the processes have limitations as the technologies are still being developed.

### 3. Study framework and approach

Fig. 3 shows the framework that was developed in this paper and was informed by previous work related to environmental indicators (Smeets and Weterings, 1999) and scenario development (Mahmoud et al., 2009). The four study objectives were used to establish boundary conditions for the analysis. Screening criteria were developed for the four study objectives based on review of peer-reviewed literature. Literature review and analysis resulted in the identification relevant aqueous matrices, enumeration of key components in the aqueous matrices, and development of four recipes for aqueous solutions for testing new materials for P removal in water. The framework also indicates the use of real water samples that have been analyzed for the key components included in the synthetic aqueous solutions. Variables excluded from the analysis were noted and may be explored in future meta-analyses (e.g., using the PRISMA framework for metadata curation (Page et al., 2021)).

**Table 3**  
Identification and composition of aqueous matrices relevant to P recovery (See Fig. 2 for definitions of abbreviations for P forms. NR = not reported.).

| Matrix                                     | Total P, mg/L | P forms                              | pH      | Chloride, mg/L         |
|--|---------------|--------------------------------------|---------|------------------------|
| Swine manure effluent <sup>a</sup>         | 1556          | DP = SRP<br>PP=PIP,<br>POP           | 7.1     | NR                     |
| Stored human urine <sup>b</sup>            | 540           | DP = SRP                             | 9.1     | 3800                   |
| Anaerobic digester centrate <sup>c</sup>   | 110           | DP = SRP,<br>DOP<br>PP=PIP,<br>POP   | 7.6     | 580–5,800 <sup>m</sup> |
| Landfill leachate <sup>d</sup>             | 5.42          | DP = SRP,<br>DOP<br>PP=PIP           | 7.0     | 10,000                 |
| Untreated domestic wastewater <sup>e</sup> | 5–20          | DP = SRP,<br>DOP<br>PP=PIP,<br>POP   | 6.5–8.5 | 30–100                 |
| Agricultural surface runoff <sup>f</sup>   | 1.0           | DP = SRP<br>PP=PIP                   | NR      | NR                     |
| Stormwater runoff <sup>g</sup>             | 0.14–2.78     | DP = SRP<br>PP=PIP                   | NR      | NR                     |
| Agricultural tile drainage <sup>h</sup>    | 0.480         | DP = SRP<br>PP=PIP                   | NR      | NR                     |
| Constructed wetland <sup>i</sup>           | 0.11          | DP = SRP,<br>DOP<br>PP=PIP,<br>DOP   | NR      | 60.83                  |
| Surface water <sup>j</sup>                 | 0.111–0.250   | DP = SRP,<br>DOP<br>PP = DIP,<br>POP | 7.3–7.8 | 55–186                 |
| Groundwater <sup>k</sup>                   | 0.66          | DP = SRP                             | NR      | NR                     |
| Seawater <sup>l</sup>                      | 0.09          | DP = SRP                             | NR      | 19,000                 |

<sup>a</sup> Zhang et al. (2020).

<sup>b</sup> Larsen et al. (2021).

<sup>c</sup> Munch and Barr (2001).

<sup>d</sup> Farhangi et al., (2021); Khanzada (2020).

<sup>e</sup> Davis (2020).

<sup>f</sup> He et al. (2006); Tan and Zhang (2011).

<sup>g</sup> Yang and Toor (2017).

<sup>h</sup> Tan and Zhang (2011).

<sup>i</sup> Kohler et al. (2004).

<sup>j</sup> Boyer et al. (2011); Mallin et al. (2009).

<sup>k</sup> Warrack et al. (2022).

<sup>l</sup> Hem (1985).

<sup>m</sup> Chloride estimated from electrical conductivity (McCleskey, 2011).

### 4. Aqueous matrices relevant to P recovery

Table 3 lists aqueous matrices relevant to P recovery and includes P concentration, P form, pH, and chloride concentration as a surrogate for ionic strength, with the forms to total P (TP) illustrated in Fig. 2. As reviewed in section 2, pH and presence of other inorganic ions influence the extent of phosphate capture by precipitation or adsorption; hence, these water quality parameters are included in Table 3. Given the variability inherent to any aqueous matrix, such as seasonal changes or sporadic events (e.g., excessive rainfall), the results in Table 3 are intended to be representative for P concentration and P form, and not an average composition. The aqueous matrices span natural waters and waste streams. The waste streams include point sources, such as urine, wastewater, and anaerobic digester centrate, and nonpoint sources including agricultural surface runoff, tile drainage, and stormwater runoff. It is worth noting that, with the exception of Cheng et al. (2009), the studies listed in Table 2 use simple aqueous matrices in the adsorption experiments, as opposed to those meant to replicate real-world situations.

The concentration of P in aqueous matrices spans five orders of magnitude, from less than 0.1 mg/L to greater than 1000 mg/L. The highest P concentrations are in swine manure effluent, human urine, anaerobic digester centrate, landfill leachate, and untreated wastewater. Natural waters typically have a low P concentration (e.g., <0.5 mg/L in surface water and <0.1 mg/L in seawater); however, surface water can be impacted by point and nonpoint sources resulting in elevated P concentration, and groundwater can have elevated P concentration from its natural mineralogy (geogenic P) and anthropogenic activities.

The TP in aqueous matrices is often separated into dissolved P (DP) and particulate P (PP). The fraction that elutes after filtration with a 0.45 µm membrane filter is DP and the fraction that is retained is PP (Wilde et al., 2014). In many cases, DP is assumed to be equivalent to soluble reactive P (SRP), i.e., phosphate, and PP is not further classified. The fractions of SRP/TP and PP/TP vary considerably within and across aqueous matrices. For example, SRP/TP varied from 0.19 to 1.00 (5<sup>th</sup> to 95<sup>th</sup> percentile) in stormwater runoff from 21 events across six residential catchments (Yang and Toor, 2017). Additionally, median SRP/TP varied from 0.40 in agricultural runoff (He et al., 2006) to 0.63 in stormwater runoff (Yang and Toor, 2017) and approaches 1.0 in stored urine (Griffith et al., 1976). Although PP can account for more than one-half of TP in aqueous matrices, it is often not characterized. When PP is analyzed, it is typically dominated by inorganic fractions including iron phosphate and calcium phosphate minerals (Griffith et al., 1976; Larsen et al., 2021).

Aqueous matrices can also contain dissolved organic P (DOP) and particulate organic P (POP). For example, anaerobic digester centrate and eutrophic surface water can include DOP and POP including bacteria and algae (living and dead), biomolecules (DNA, phospholipids), P-containing synthetic organic chemicals, and P-containing natural organic matter (Ged and Boyer, 2013). In the marine P cycle, dissolved inorganic P (DIP), particulate inorganic P (PIP), and organic P (DOP and POP) are the main P pools (Nausch et al., 2018). For example, DOP concentrations are reported to range between 0.006 and 0.054 mg/L in ocean surface waters (Karl and Björkman, 2015), but can be elevated in coastal waters, as reported by (Lin et al., 2012) for the St. Louis estuary (Gulf of Mexico), where DOP concentrations ranged from 0.016 to 0.067 mg/L. Coastal brackish water can contain greater concentrations of DOP due to interactions with freshwater sources from urban discharge.

### 5. Components of aqueous matrices that influence the chemistry of P removal

Table 4 lists key components in the aqueous matrices that are relevant to P removal via phosphate precipitation and adsorption. Each component is classified as having a minor, moderate, or major impact on

**Table 4**  
Key components in aqueous matrices that influence the chemistry of P removal.

| Component           | Relevant matrix   | Impact on P removal  |
|---------------------|---|--|
| Temperature         | All   | Temperature influences the rate of precipitation, adsorption, and other processes. <b>Moderate impact</b> on precipitation and adsorption.   |
| Turbidity           | Agricultural surface runoff, stormwater runoff, untreated domestic wastewater   | Turbidity can act as seed for precipitation; may foul surfaces and adsorption columns; may contain P associated with solid phases. <b>Moderate impact</b> on precipitation and <b>minor impact</b> on adsorption.  |
| pH                  | All   | pH controls the speciation of phosphate and other weak acids; impacts surface charge, and thus adsorption processes and the aggregation of particles. <b>Major impact</b> on precipitation and adsorption.   |
| Alkalinity          | All   | Alkalinity buffers changes in pH. <b>Moderate impact</b> on precipitation and adsorption.  |
| Monovalent anions   | All   | Chloride ( $\text{Cl}^-$ ) and nitrate ( $\text{NO}_3^-$ ) can compete with phosphate for adsorption sites; adsorption of ions impact surface charge and thus adsorption of other ions; contributes to ionic strength, which impacts precipitation equilibrium. <b>Minor impact</b> on precipitation and adsorption.   |
| Monovalent cations  | All   | Sodium ( $\text{Na}^+$ ) and potassium ( $\text{K}^+$ ) usually have minimal impacts on phosphate precipitation and adsorption; $\text{Na}^+$ and $\text{K}^+$ can precipitate with phosphate under certain conditions; ammonium ( $\text{NH}_4^+$ ) behaves as a monovalent cation and is key species in struvite precipitation. <b>Minor impact</b> on precipitation and adsorption. |
| Multivalent anions  | Groundwater, landfill leachate, stored human urine  | Sulfate ( $\text{SO}_4^{2-}$ ) can compete with phosphate for adsorption sites and precipitate with multivalent cations. <b>Major impact</b> on precipitation and adsorption.  |
| Multivalent cations | Agricultural tile drainage, anaerobic digester centrate, groundwater, landfill leachate, seawater, stored human urine | Calcium ( $\text{Ca}^{2+}$ ), magnesium ( $\text{Mg}^{2+}$ ), iron ( $\text{Fe}^{2+/3+}$ ), and aluminum ( $\text{Al}^{3+}$ ) are common in many aqueous matrices and precipitate with phosphate. Less common metals, such as cerium ( $\text{Ce}^{3+}$ ) and lanthanum ( $\text{La}^{3+}$ ), also precipitate with phosphate. <b>Major impact</b> on                                  |

**Table 4 (continued)**

| Component  | Relevant matrix   | Impact on P removal  |
|--|---|--|
| Nonionic species                                     | Landfill leachate, untreated domestic wastewater, stored human urine  | precipitation and <b>minor impact</b> on adsorption. Ammonia, urea, silica, etc. typically have minimal impact on adsorption and precipitation. <b>Minor impact</b> on precipitation and adsorption.   |
| Ionic strength                                       | Anaerobic digester centrate, groundwater, landfill leachate, seawater, stored human urine   | Ionic strength influences the behavior of charged species in solution; impacts the aggregation of particles. <b>Moderate impact</b> on precipitation and adsorption.   |
| Dissolved organic matter (DOM) and organic chemicals | Agricultural tile drainage, anaerobic digester centrate, constructed wetland, landfill leachate, surface water, untreated domestic wastewater | Dissolved organic matter can complex multivalent ions and inhibit precipitation; can compete with phosphate for adsorption sites; can contain organic P. Organic chemicals can influence phosphate precipitation and adsorption similar to DOM. <b>Major impact</b> on precipitation and adsorption. |

P removal to highlight its importance in the aqueous matrix. A component with a minor impact has <10% change in P removal, whereas a component with a major impact can have >50% change in P removal. Temperature and turbidity represent physical characteristics of water and can be an important consideration if a specific real-world condition is intended to be simulated. Most laboratory experiments on phosphate precipitation or adsorption are conducted at laboratory temperature. For most precipitation and adsorption processes, increasing temperature increases the rate of reaction.

Aqueous matrices such as wastewater, surface water, and runoff can have high turbidity, which include inorganic, organic, and biological particles suspended in the water. These particles can act as seed for heterogeneous nucleation during phosphate precipitation. Turbidity does not have a direct impact on phosphate removal by adsorption but can foul surfaces and disrupt experimental approaches such as packed beds. Including turbidity in test waters can be important for precipitation experiments, especially for mimicking aqueous matrices such as stormwater runoff and agricultural surface runoff for which turbidity is a key component. It is also important to recognize that turbidity can contain P, which can be difficult to recover and potentially impact measurement of P.

pH and alkalinity represent bulk chemical characteristics of water. pH is considered a master variable that controls water chemistry, including protonation/deprotonation of phosphate and other weak acids, and thereby the concentration of species impacting both precipitation and adsorption processes. Typically, the impact of pH can be modeled using chemical equilibrium software, such as PHREEQC (USGS, 2021) or Visual MINTEQ (Gustafsson, 2021). Additionally, pH affects the protonation of surfaces, strongly influencing electrostatic interactions that contribute to adsorption phenomena (Dzombak and Morel, 1991). A related parameter is alkalinity, which in environmentally relevant waters is typically derived from the presence of carbonic acid, dissolved organic matter, or other weak acids, and represents the ability of a water to resist changes in pH. The choice of buffer is important for replicating environmental or biological conditions (see section 6). Controlling pH is critical for testing materials and strategies for P removal. Measuring pH before and after precipitation and adsorption experiments is essential, because P is in equilibrium with

anionic chemical species and surface sites based upon the final solution pH at the end of the experiment.

The presence of ions in solution also influences P removal. Common monovalent ions include sodium, potassium, ammonium, bicarbonate, and chloride, which typically do not compete directly for adsorption sites with phosphate. Some anions (e.g., nitrate, fluoride) can result in competitive adsorption depending on the material. More commonly, multivalent anions such as sulfate, arsenate, selenate, and vanadate may compete with phosphate for binding sites (Blaney et al., 2007). Additionally, the adsorption of monovalent and multivalent ions can influence the charging of surfaces, impacting the electrostatics of adsorption in a manner similar to pH. In situations where the ions are associated with low solubility phases, the ions may also induce precipitation of phosphate. For example, ammonium, which is present in urine and commercial fertilizers, is directly involved in the precipitation of struvite. Multivalent cations, such as calcium, iron, aluminum, and magnesium, may induce precipitation of phosphate as a variety of low solubility phases (cf. Table 1). Potentially toxic ions (e.g.,  $\text{Co}^{2+}$ ,  $\text{CrO}_4^{2-}$ ), even in low concentrations that do not significantly impact P precipitation or adsorption, may restrict the use of recovered P products.

It is worth noting that the presence of monovalent and multivalent ions increases the ionic strength (IS). Except in the most concentrated solutions, ionic strength reduces the activity (effective concentrations) of charged species by relationships that can be calculated or approximated by the Debye-Huckel or Davies equations (Stumm and Morgan, 1996). High ionic strength can also promote the aggregation of particles by screening of the charge between particles and the precipitation of organic compounds, often referred to as “salting out.” Ionic strength of model solutions can be calculated ( $\text{IS} = 0.5 \sum C_i Z_i^2$ ) based upon the molar concentration ( $C_i$ ) and ionic charge ( $Z_i$ ) of each species in solution, while in real samples or complex matrices conductivity (mS/cm) or total dissolved solids (TDS, mg/L) are often measured and used to estimate ionic strength. Various equations and estimates exist for converting among ionic strength, conductivity, TDS, and specific ions such as chloride (McCleskey, 2011).

A final important component of aqueous matrices is natural organic matter (NOM) or dissolved organic matter (DOM), which is the collection of organic molecules found in solution that range from small ionic species to large macromolecules derived from the physical, chemical, and microbiological transformation of organic material (Leenheer and Croue, 2003; Thurman, 1985). DOM is comprised of carbon (~50%), oxygen (40%), hydrogen (5%), nitrogen (4%), sulfur (<1%), phosphorus (<1%) and trace metals, and often analytically measured as dissolved organic carbon (DOC). DOM can complex multivalent ions, thereby inhibiting mineral precipitation (Lin et al., 2005b; Sindelar et al., 2015a). Furthermore, DOM can compete with inorganic anions, such as phosphate, for adsorption sites on sorbent surfaces (Boyer et al., 2008). Additionally, DOM can contain organic P that is typically considered more difficult to remove and can influence measurements of total P (Ged and Boyer, 2013). DOM is a critical component that can affect most capture and recovery strategies for P. It is important to note that the composition and chemistry of DOM changes greatly depending on its source, and thus it is critical to use compounds that match the matrix the experiment is simulating (Chin et al., 1994; Leenheer et al., 2003; Ritchie and Perdue, 2003; Weishaar et al., 2003). For example, DOM in eutrophic surface water or treated wastewater is representative of aquatic DOM that is microbially derived, whereas DOM in landfill leachate or agricultural tile drainage is representative of terrestrial DOM based on lignin. Organic chemicals can be used as a surrogate for DOM (see section 6) and can occur from natural (e.g., microbiological processes, human metabolism) and anthropogenic (e.g., household chemicals, corrosion inhibitors used in industry or drinking water systems) sources. Organic chemicals, such as organic acids and surfactants, can have many of the same impacts on phosphate precipitation and adsorption as DOM.

## 6. Guidelines for developing aqueous matrices for testing new materials for P removal and recovery

Table 5 shows recipes for developing several synthetic aqueous matrices that can be used for testing new materials for P removal and recovery. The recipes follow from the study framework (see section 3 and Fig. 3), which highlights the information that can be obtained from different matrices. Specifically, components were selected from Table 4 that had moderate to major impact on P removal by precipitation or adsorption. The concentration of each component was determined by reviewing the relevant literature and considering aqueous chemistry principles. The following discussion provides additional context for the synthetic aqueous matrices and guidance on how the recipes can be adjusted.

The pH buffer solution is the simplest matrix and useful for screening new materials for P recovery. The pH buffer solution contains a higher phosphate concentration (10 mg/L P) than typically observed in natural waters to allow for easier phosphate measurements. A predetermined buffer (see below) is used to maintain the desired pH. Use of buffer solutions is common when investigating new materials (i.e., precipitants or adsorbents) to evaluate the effects of P concentration and pH. Ideal buffer solutions should be chemically inert with respect to phosphate. Common buffers that may be useful for phosphate precipitation and adsorption studies include acetate (pH 3.6 to 5.6), citrate (pH 3.0 to 6.2), or carbonate (pH 9.2 to 10.6) (Dawson et al., 1989). A limitation of some organic buffers (e.g., acetate, citrate) is that they can be consumed biologically, which decreases the buffer capacity and encourages microbial growth. For more complex mixtures, such as pH-buffered water samples simulating the presence of dissolved biological materials, microorganism(s), or experiments involving biomaterials, it is recommended to utilize one of Good's buffers (Good et al., 1966; Porterfield et al., 2009). A comprehensive list of Good's buffers, including  $\text{pK}_a$  and molecular weight, is shown in electronic Supplementary Material Table S1. These buffers are valid for a pH range of 2.0–11.0 (at 25 °C) and were designed for biochemistry experimentation, with a particular focus on affinity testing of proteins, peptides, nucleotides, and other biomolecules. Some organic molecules (e.g., zwitterionic molecules) are known to interact with ions in solution, including phosphate (Alves et al., 2007). For this reason, zwitterionic buffers shown in Table S1 should be avoided unless the interaction with phosphate and the sorbent has been characterized or data are available.

The synthetic groundwater and surface water solutions offer more realistic matrices than a buffer solution, and the opportunity to probe specific interactions. The synthetic groundwater and surface water contain a realistic phosphate concentration (1 mg/L P), and additional components for pH buffering, ionic composition, and organic composition. For example, the synthetic groundwater contains sodium bicarbonate for alkalinity/pH buffering, sodium chloride for background ionic strength, and calcium chloride for divalent cation interactions. Sodium and chloride ions are not expected to directly impact experiments on phosphate precipitation or adsorption, whereas the calcium may interact with phosphate through precipitation in solution or on adsorbent surfaces. The calcium can be removed from the synthetic groundwater recipe if there is a concern about its interactions, or additional metal cations such as magnesium, iron, or lanthanum can be added to the solution to simulate other aqueous environments. The purpose of the synthetic groundwater is to provide an aqueous matrix that is more relevant than the buffer solution by considering interactions between phosphate and multivalent metal cations such as calcium, which can impact both phosphate precipitation and adsorption mechanisms. To support the relevance of the synthetic groundwater, previous studies show similar phosphate precipitation trends in real groundwater (McCobb et al., 2009) and synthetic groundwater (Baker et al., 1998).

The synthetic surface water includes monovalent and divalent anions and one or more sources of DOM. Sulfate has the potential to interact with metals added for phosphate precipitation and compete with



**Table 5**

Standard recipes for aqueous solutions for testing new materials for P removal and recovery.

| Component   | Buffer   | Groundwater   | Surface water   | Anaerobic Digestate  | Stored human urine   |
|---|--|---|---|--|--|
| Phosphate   | 10.1 mg/L P (0.325 mM)<br>38.994 mg/L NaH <sub>2</sub> PO <sub>4</sub><br>2.0–11.0 | 1 mg/L P (0.0325 mM)<br>3.899 mg/L NaH <sub>2</sub> PO <sub>4</sub><br>8.0  | 1 mg/L P (0.0325 mM)<br>3.899 mg/L NaH <sub>2</sub> PO <sub>4</sub><br>8.0  | 101 mg/L P (3.25 mM)<br>389.94 mg/L NaH <sub>2</sub> PO <sub>4</sub><br>7.5  | 421 mg/L P (13.6 mM)<br>1631.7 mg/L NaH <sub>2</sub> PO <sub>4</sub><br>9.0 <sup>a</sup>   |
| pH  | See Table S1   | 0.1 M HCO <sub>3</sub> <sup>-</sup><br>8.4007 g/L NaHCO <sub>3</sub>  | 0.1 M HCO <sub>3</sub> <sup>-</sup><br>8.4007 g/L NaHCO <sub>3</sub>  | 1 M HCO <sub>3</sub> <sup>-</sup><br>84.007 g/L NaHCO <sub>3</sub>   | 0.25 M HCO <sub>3</sub> <sup>-</sup><br>19.764 g/L NH <sub>4</sub> HCO <sub>3</sub>  |
| Alkalinity  |  | 70.9 mg/L Cl <sup>-</sup> (2 mM)<br>96.1 mg/L SO <sub>4</sub> <sup>2-</sup> (1 mM)<br>116.88 mg/L NaCl<br>142.04 mg/L Na <sub>2</sub> SO <sub>4</sub> | 70.9 mg/L Cl <sup>-</sup> (2 mM)<br>96.1 mg/L SO <sub>4</sub> <sup>2-</sup> (1 mM)<br>116.88 mg/L NaCl<br>142.04 mg/L Na <sub>2</sub> SO <sub>4</sub> | 1595 mg/L Cl <sup>-</sup> (45 mM)<br>96.1 mg/L SO <sub>4</sub> <sup>2-</sup> (1 mM)<br>39.1 mg/L K <sup>+</sup> (1 mM)<br>720 mg/L NH <sub>4</sub> <sup>+</sup> (40 mM)<br>0.2338 g/L NaCl<br>0.142 g/L Na <sub>2</sub> SO <sub>4</sub><br>0.0746 g/L KCl<br>2.1396 g/L NH <sub>4</sub> Cl | 3545 mg/L Cl <sup>-</sup> (100 mM)<br>1441 mg/L SO <sub>4</sub> <sup>2-</sup> (15 mM)<br>1564 mg/L K <sup>+</sup> (40 mM)<br>3.5064 g/L NaCl<br>2.1306 g/L Na <sub>2</sub> SO <sub>4</sub><br>2.9821 g/L KCl |
| Inorganic ions                                    | 11.5 mg/L Cl <sup>-</sup> (0.325 mM)<br>18.993 mg/L NaCl                           | 40.1 mg/L Ca <sup>2+</sup> (1 mM)<br>147.02 mg/L CaCl <sub>2</sub> ·2H <sub>2</sub> O   |   |  |  |
| Dissolved organic matter and/or organic chemicals | None   | None  | DOM isolate <sup>b</sup> :<br>10–20 mg/L DOM to achieve 5–10 mg/L C   | Short-chain volatile fatty acids:<br>93.8 mg/L Acetic acid,<br>331 mg/L Propionic acid,<br>27.5 mg/L Butyric Acid  | Organic metabolites <sup>c</sup> :<br>14.7 mM Creatinine,<br>3.38 mM Hippuric acid,<br>3.0 mM Citric acid,<br>1.56 mM Glycine,<br>1.34 mM Trimethylamine-N-oxide,<br>1.19 mM Taurine,<br>0.97 mM L-Cysteine  |

<sup>a</sup> Add 15.9 mL/L NH<sub>4</sub>OH.<sup>b</sup> See section 5 for discussion of DOM isolates and surrogates.<sup>c</sup> Can be added as 1668 mg/L Creatinine, 604.9 mg/L Hippuric acid, 575.0 mg/L Citric acid anhydrous, 117.3 mg/L Glycine, 149.1 mg/L Trimethylamine-N-oxide dihydrate, 149.4 mg/L Taurine, 117.5 mg/L L-Cysteine.

phosphate for adsorption site (Geelhoed et al., 1997). DOM samples (e.g., Suwannee River NOM) can be obtained from the International Humic Substances Society (IHSS) (IHSS, 2024), which provide samples that have been isolated from environmentally relevant aquatic and terrestrial environments, are well characterized, and are actively used by researchers with decades of published studies (Boyer et al., 2008; McAdams et al., 2022; Ritchie and Perdue, 2003; Yang et al., 2023). Alternative sources of DOM include commercial humic acid extracted from peat (e.g., Fluka humic acid) or tannic acid, which are low-cost and easily available; however, are less preferred because they are not representative of aquatic DOM (Chin et al., 1997; Malcolm and MacCarthy, 1986; Niederer et al., 2007). DOM can also be approximated by organic chemicals containing aromatic hydrocarbons with carboxylic acid and/or phenolic groups and aliphatic hydrocarbons containing carboxylic acid groups (Rahmani and Mohseni, 2017), which can be useful for isolating specific interactions.

The DOM concentration in surface water is typically in the range of 1–20 mg/L C (Obolensky et al., 2007) with DOM isolates containing approximately 50% C by weight (IHSS, 2024). As discussed in section 5, DOM has the potential to inhibit both phosphate precipitation and adsorption, so synthetic surface water is a logical next step in testing new materials after completing experiments with buffer solution and synthetic groundwater. For instance, DOM is known to interact with calcium during calcite precipitation (Lin et al., 2005a) and influence Ca–P precipitation (Sindelar et al., 2015a), so both the synthetic groundwater and synthetic surface water recipes can be altered to investigate specific interactions. To support the relevance of the synthetic surface water, previous studies include calcium phosphate precipitation in organic-rich surface water (Sindelar et al., 2015a), and phosphate precipitation using industrial waste byproducts and phosphate adsorption to anion exchange resin in organic-rich surface water (Boyer et al., 2011).

The synthetic anaerobic digestate and stored human urine solutions are characterized by higher phosphate concentration (100 and 420 mg/L P, respectively) than the synthetic groundwater and surface water, and

they provide challenging matrices for testing new materials for P removal and recovery. The synthetic anaerobic digestate contains additional inorganic and organic compounds relative to the synthetic groundwater and surface water. The additional inorganic compounds include potassium, ammonium, and sulfate. Ammonium, and to a lesser extent potassium, have the potential to promote phosphate precipitation in anaerobic digestate solution to form magnesium ammonium phosphate (i.e., struvite) and magnesium potassium phosphate (i.e., potassium struvite) (Abel-Denee et al., 2018). Magnesium is often the limiting constituent for struvite precipitation in solutions like anaerobic digestate that contain high concentrations of phosphate and ammonium. Precipitation of potassium struvite typically occurs in the absence of ammonium and requires the addition of magnesium. The presence of sulfate has the potential to compete with phosphate for adsorption sites, and sulfate may precipitate with calcium or other cations in solution. Anaerobic digestate contains many organic compounds and is approximated here with low molecular weight organic acids that have the potential to influence phosphate precipitation and adsorption processes (Wei et al., 2019). Additional organic compounds that can be added to the synthetic anaerobic digestate include P-containing biomolecules and microbial biomass and extracellular polymeric substances (Zhou et al., 2019). To support the relevance of the synthetic anaerobic digestate, previous studies show comparable phosphate adsorption to hybrid anion exchange resin using real and synthetic sludge digestates (Bottini and Rizzo, 2012; Guida et al., 2021; O'Neal and Boyer, 2013).

The synthetic stored human urine shares similarities with the synthetic anaerobic digestate with multiple components including monovalent and divalent ions and optional organic metabolites. A key difference between human urine and anaerobic digestate is the higher pH (i.e., pH 9 vs. pH 7.5), which makes phosphate precipitation more thermodynamically favorable, especially with the addition of divalent metal cations (Darn et al., 2006). Human urine also has a higher concentration of ammonium and inorganic ions. The high concentration of ammonium in human urine, in combination with high pH, results in favorable conditions for struvite precipitation (Ronteltap et al., 2007),

although precipitation of other phosphate minerals is possible (Wiltschko et al., 2007; Xu et al., 2011). The high concentrations of chloride and sulfate provide challenging conditions for testing phosphate adsorption due to competitive adsorption. Numerous organic metabolites have been identified in urine (Bouatra et al., 2013; Putnam, 1971), with the most prevalent and highest concentration metabolites included in the recipe for synthetic urine. The inclusion of organic metabolites can be used to evaluate inhibition of phosphate precipitation or competition with adsorption sites (Jagtap and Boyer, 2018). Variations on the composition of stored human urine include fresh human urine where all nitrogen is as urea instead of ammonia/ammonium (Ray et al., 2018) and partially nitrified human urine where 50% of the ammonia is transformed to nitrate (Udert and Wächter, 2012). Given the complexities of anaerobic digestate and stored human urine, their composition can be simplified to eliminate interfering processes and study specific interactions. To support the relevance of the synthetic human urine, previous studies show comparable phosphate precipitation in real and synthetic urine (Jagtap and Boyer, 2018), and comparable phosphate adsorption in real and synthetic urine (Guan et al., 2020).

A complementary approach to preparing synthetic aqueous matrices is to use real waters and waste streams. The challenge, however, is that real solutions are complex and can vary over time and with location, which makes it difficult to understand how each matrix component influences P removal. In the study framework proposed here (see section 3 and Fig. 3), the approach is to test new materials in well-defined matrices, such as those listed in Table 5, and then test new materials in complex, real-world samples such as domestic wastewater effluent, human urine, and swine manure effluent. For example, within the urine research community, it is recognized that both synthetic and real urine solutions are valuable for testing new materials and processes (Simha et al., 2024). When using real solutions, the following methodology can help provide useful insights into P interactions. First, filtering the solution with a 0.45  $\mu\text{m}$  membrane filter can remove most particles. Comparing a filtered to non-filtered solution will reveal possible influence of DP and PP components on P removal. Second, sterilizing the solution (e.g., autoclave), shows P removal in the absence of biological activity; however, the high temperatures during autoclaving can also change solution chemistry (e.g., encourage precipitation). Third, P concentrations in the absence of adsorbents (i.e., negative control) need to be included to determine background P removals that may occur biologically or chemically. Finally, if P concentrations are highly variable, matrix spikes using phosphate salts can be added to provide improved consistency across tests. If real water matrices are used in experiments, it is essential that the components listed in Table 5 be analytically measured to permit benchmarking with other studies. The synthetic aqueous matrices and the complementary real aqueous samples described in this section are expected to provide uniformity in phosphate precipitation and adsorption studies and advance the development and testing of new materials. This is analogous to what happened with arsenic adsorption studies that evaluated new materials using a standard test water (Hristovski et al., 2008; Ilesan et al., 2008; Meddelli et al., 2015).

## 7. Conclusion

Many approaches to P removal and recovery use synthetic aqueous matrices that lack consistency and applicability to real aqueous environments. This paper presents a framework for evaluating new materials for P removal in real-world water via phosphate precipitation and phosphate adsorption. Precipitation and adsorption are the focus of this study because both processes can effectively remove phosphate from water and have the potential to recover phosphate in valuable forms. The performance of phosphate precipitation and phosphate adsorption in laboratory studies often does not translate to real aqueous environments, because the simple aqueous matrices used for testing lack the interactions with P or adsorbent surfaces. Accordingly, this paper

proposes a framework that identifies aqueous matrices relevant to P recovery, key components in the aqueous matrices having the greatest influence on P removal, and recipes for aqueous solutions for testing novel materials.

The framework provides a systematic approach for screening new materials in buffer solutions, followed by synthetic groundwater and synthetic surface water to elucidate interactions between the new material, phosphate, and the aqueous matrix. Additional testing of new materials can be conducted using synthetic anaerobic digestate and synthetic stored human urine, which include monovalent and divalent inorganic compounds and organic compounds that provide for many different interactions with phosphate. At any stage of research, the synthetic aqueous matrices can be modified to probe specific interactions related to phosphate precipitation or adsorption.

As a main concern with using synthetic aqueous matrices is their applicability to real aqueous environments, using real matrices (e.g., domestic wastewater effluent, human urine, swine manure effluent) is essential when evaluating new materials. Characterizing the matrix (e.g., pH, TDS, turbidity, competing anions, DOM) is essential for benchmarking P removal with other studies. The challenge then becomes balancing the benefits of using a known composition and controlled conditions of synthetic aqueous matrices with the applicability of real aqueous samples are difficult to fully characterize.

## CRedit authorship contribution statement

**Treavor H. Boyer:** Writing – original draft, Conceptualization. **Emily Briese:** Writing – original draft. **Lucas Crane:** Writing – original draft. **Jehangir Bhadha:** Writing – review & editing, Conceptualization. **Douglas F. Call:** Writing – original draft, Conceptualization. **Eric S. McLamore:** Writing – original draft, Conceptualization. **Bruce Rittmann:** Writing – original draft, Conceptualization. **Shea Tuberty:** Writing – review & editing, Conceptualization. **Paul Westerhoff:** Writing – original draft, Conceptualization. **Owen W. Duckworth:** Writing – original draft, Conceptualization.

## Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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## Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.chemosphere.2024.143648>.

## Data availability

Data will be made available on request.

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