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Kumar, Prashanth Suresh; Korving, Leon; van Loosdrecht, Mark C.M.; Witkamp, Geert Jan

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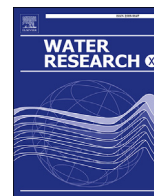
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Review

Adsorption as a technology to achieve ultra-low concentrations of phosphate: Research gaps and economic analysis



Prashanth Suresh Kumar^{a, b, *}, Leon Korving^a, Mark C.M. van Loosdrecht^b,
Geert-Jan Witkamp^{b, c}

^a Wetsus, European Centre of Excellence for Sustainable Water Technology, Oostergoweg 9, 8911 MA, Leeuwarden, the Netherlands

^b Department of Biotechnology, Applied Sciences, Delft University of Technology, Building 58, Van der Maasweg 9, 2629, HZ, Delft, the Netherlands

^c King Abdullah University of Science and Technology (KAUST), Water Desalination and Reuse Center (WDRC), Division of Biological and Environmental Science and Engineering (BESE), Thuwal, 23955-6900, Saudi Arabia

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ABSTRACT

Eutrophication and the resulting formation of harmful algal blooms (HAB) causes huge economic and environmental damages. Phosphorus (P) from sewage effluent and agricultural run-off has been identified as a major cause for eutrophication. Phosphorous concentrations greater than 100 µg P/L are usually considered high enough to cause eutrophication. The strictest regulations however aim to restrict the concentration below 10 µg P/L. Orthophosphate (or phosphate) is the bioavailable form of phosphorus. Adsorption is often suggested as technology to reduce phosphate to concentrations less than 100 and even 10 µg P/L with the advantages of a low-footprint, minimal waste generation and the option to recover the phosphate. Although many studies report on phosphate adsorption, there is insufficient information regarding parameters that are necessary to evaluate its application on a large scale. This review discusses the main parameters that affect the economics of phosphate adsorption and highlights the research gaps. A scenario and sensitivity analysis shows the importance of adsorbent regeneration and reuse. The cost of phosphate adsorption using reusable porous metal oxide is in the range of \$ 100 to 200/Kg P for reducing the phosphate to ultra-low concentrations. Future research needs to focus on adsorption capacity at low phosphate concentrations, regeneration and reuse of both the adsorbent and the regeneration liquid.

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1. Introduction

1.1. Need to achieve very low concentrations of phosphorous

Eutrophication is the process wherein water bodies receive excessive supply of nutrients. In its most excessive form this leads to formation of harmful algal blooms (HABs) (Anderson et al., 2002; Smith et al., 1999). This has been recognized as a global concern for several decades (Nixon, 1995) and has led to huge economic and environmental damages (Dodds et al., 2009; Hoagland et al., 2002; Pretty et al., 2003; Smith et al., 1999). Apart from posing health risks for humans and other organisms in the ecosystem eutrophication

causes economic losses by affecting industries such as fishing, water treatment, housing, recreation and tourism (Ingrid Chorus, 2000; Pretty et al., 2003; USEPA, 2015; Wu, 1999). The annual damage costs due to freshwater eutrophication was estimated to be between \$ 105 to 160 million in England and Wales (Pretty et al., 2003). The overall annual costs incurred as a result of eutrophication in US freshwaters was estimated at \$ 2.2 billion (Dodds et al., 2009). A loss of \$ 6.5 billion was estimated in the lake Tai catchment area in China due to algal bloom (Le et al., 2010). The degradation of water quality due to eutrophication has been acknowledged to cause economic impacts in many countries worldwide (OECD, 2012).

The reduction of phosphorous (P) concentrations in the water bodies has been a dominant theme to combat freshwater eutrophication (L. Correll, 1998; Schindler et al., 2016). Orthophosphate (o-P), also called soluble reactive phosphorous (SRP), is the only form of P that can be assimilated by autotrophs and the microbes present in the water (Correll, 1999). But factors such as varying

* Corresponding author. Department of Biotechnology, Applied Sciences, Delft University of Technology, Building 58, Van der Maasweg 9, 2629, HZ, Delft, the Netherlands.

E-mail address: psureshkumar@tudelft.nl (P.S. Kumar).

redox conditions, mineralization of organic matter, and an equilibrium with dissolved P can cause release of o-P from the settled as well as suspended particulates (Boström et al., 1988; Froelich Philip, 1988; Hupfer and Lewandowski, 2008). This has led to total phosphorous (TP), which includes dissolved and particulate P, to be used as an assessment for controlling eutrophication. There is no clear consensus yet on the concentration of TP that is acceptable for preventing eutrophication, although most studies consider a concentration above 100 µg P/L to be too high (Vollenweider RA, 1980, Dodds et al., 1998; Richardson et al., 2007; Lurling and Oosterhout, 2013; Carvalho et al., 2013). The United States Environmental Protection Agency suggested a mean TP concentration of 10 µg P/L in its nutrient criteria guidelines for lakes and reservoirs (USEPA, 2000). This value has often been promoted as the lowest concentration of TP to be reached to keep clear of eutrophication. This value is however well above the analytical limit of detection for measuring P concentrations in solutions and hence can be monitored (Patey et al., 2008).

Sewage effluent and agricultural run-offs are chief sources for P loading in surface waters (White and Hammond, 2009; Hendriks and Langeveld, 2017). Management of P from diffuse sources like agricultural run-off includes practices that monitor fertilizer usage, livestock numbers and P input from manure (Knowlton et al., 2004; Sharpley, 2016). Regulation of non-point/diffuse sources can nonetheless be difficult since they arise due to activities distributed over wide areas and are more variable over time due to changes in weather (Carpenter et al., 1998). Point sources of P like sewage effluent are easier to monitor and regulate (Dodds and Whiles, 2010). Moreover, P loads from sewage effluent have been shown to have a higher fraction of SRP/bioavailable P compared to nonpoint sources (Gerdes and Kunst, 1998; Maccoux et al., 2016).

Given the risk of P pollution from sewage effluent, regulations regarding the P discharge limits are getting stricter. The National Pollution Discharge Elimination System (NPDES) regulates the discharge of pollutants from point sources in the United States. The NPDES permit limitation for P has already been stringent in different municipalities with required values often ranging from 0.1 to 0.5 mg P/L (USEPA, 2007). In the European Union the standard for quality of water bodies is set by the Water Framework Directive (WFD) and an effluent value of 0.15 mg P/L is sometimes taken to be in line with the WFD (P.M.J. Janssen, 2006). It must be noted that these effluent values serve rather as a guideline, because the total P load discharged into the environment will not only depend on the effluent concentration but also on the size of the receiving water body. The current effluent regulations of individual EU member states need to meet either 1 or 2 mg P/L depending on the population equivalence, with the more stringent value for facilities with higher population equivalence and sensitive areas (Jan Oleszkiewicz, 2015; European Commission, 2017). China has municipal/domestic wastewater discharge limits ranging from 0.5 to 1 mg P/L (Li et al., 2012; Liu, 2005). On the other hand, Brazil does not have discharge standards for phosphorous in every state and the noted effluent concentrations from domestic sewage are generally higher than 4 mg P/L (Sperling, 2016). This shows there is discrepancy between the allowed effluent P discharge levels between different countries. But the rising concern over eutrophication could pose stricter values of 0.1 mg P/L or lower for WWTP effluents in the future (Ashkuzzaman and Jiang, 2017; CanadianWaterNetwork, 2018).

1.2. Technologies to achieve ultra-low P concentrations

The terms ultra-low level/advanced removal of P have often been used to denote achieving very low P concentrations. But they do not refer to an established value yet and can imply P

concentrations lower than those achieved by conventional treatment methods. Such terms usually refer to a concentration range between 0.01 and 0.15 mg P/L (Bolton and Menk, 2016; Genz et al., 2004; Langer et al., 2017; USEPA, 2007; Whalley, 2013).

P removal techniques can broadly be classified as physical, chemical and biological. Physical methods include separation of the P based on size exclusion and include sand filtration or membrane filtration (Erickson et al., 2007; Leo et al., 2011; Wathugala et al., 1987; Yildiz, 2004). Chemical methods that have been used for P removal include precipitation, flocculation or adsorption (Clark et al., 1997; Drenkova-Tuhtan et al., 2017; Langer et al., 2017; Laridi et al., 2005). Precipitation involves the usage of metal salts to react with dissolved P to result in insoluble precipitates (Sedlak, 1991). Flocculation uses metals or organic polymers to destabilize colloidal particles and to result in aggregates (Jiang and Graham, 1998; Ngo and Guo, 2009). Adsorption is the removal of dissolved P via a surface reaction on a solid material called the adsorbent (Loganathan et al., 2014). Biological methods involve P uptake/assimilation by plants, microorganisms. This involves using halophytes in wetlands, polyphosphate accumulating organisms (PAO) for enhanced biological P removal (EBPR) and the use of microalgae (Boelee et al., 2011; Buhmann and Papenbrock, 2013; Oehmen et al., 2007).

The use of a single method is often ineffective to reach ultra-low P concentrations and several studies use a combination of these methods to achieve the desired P concentration (Bolton and Menk, 2016; Kim et al., 2008; Mitchell and Ullman, 2016, P.M.J. Janssen, 2006). For instance, conventional treatments in WWTP's include chemical precipitation with metal salts and can generally achieve P levels between 0.5 and 1 mg P/L in the effluent depending on the salt dosage (Clark et al., 1997; Sedlak, 1991). Reducing the P concentrations further by increasing the salt dosing can lead to significant increase in sludge production (Sedlak, 1991). But a study using a combination of chemical precipitation along with a series of sand filtration and ultra-filtration units was able to achieve TP values of less than 0.015 mg P/L (Mitchell and Ullman, 2016). Another study used a reactive filter where iron salts were dosed along with sands to form a hydrous iron oxide coated sand (Newcombe et al., 2008). The soluble P was removed by co-precipitation with iron or adsorption onto the iron coated sand whereas particulate P was removed by a moving bed sand filter. An average effluent concentration of 0.011 mg P/L was observed.

Phoslock is a lanthanum modified bentonite that removes SRP by forming lanthanum phosphate precipitates (Lürling et al., 2014). Even though Phoslock has been used for P remediation in lakes, a high solid dosage of 200:1 Phoslock:P weight ratio has been shown necessary to bring down concentrations to less than 0.01 mg P/L (Reitzel et al., 2013). Moreover, the presence of humic substances can release the lanthanum from Phoslock which would cause ecotoxicity issues in the surface water (Herrmann et al., 2016; Lürling et al., 2014).

The use of EBPR can lead to effluent P concentrations lower than 0.5 mg P/L depending on the extent of readily biodegradable organics present (Gu et al., 2008). A pilot study used a combination of EBPR with membrane bioreactor to reach average effluent values of 0.3 mg P/L (Smith et al., 2014). It has been suggested that EBPR can reduce effluent TP concentrations to 0.1–0.2 mg P/L under ideal conditions (Blackall et al., 2002). EBPR is however sensitive to several factors like the extent of organics, dosing of metal salts, nitrate, ammonium and heavy metal content that can inhibit the process (Zheng et al., 2014). This makes the ideal conditions rather narrow. Microalgae based biofilm reactors have been used to reach P concentrations less than 0.15 mg P/L (Boelee et al., 2011; Sukačová et al., 2015). The optimal performance of microalgae however depended on parameters like the nutrient loading and illumination

condition. Immobilized thermophilic bacteria grown in a photo-bioreactor decreased phosphate concentrations from 0.75 mg P/L to 0.05 mg P/L (Sawayama et al., 1998). But they required a residence time of 12 h, which caused secondary organic pollution due to excretion of organic compounds from the cyanobacterial cells.

Wetlands offer another way of removing P by using a combination of different processes. Plants and microbes can uptake P whereas some fractions of P can also bind to minerals (Buhmann and Papenbrock, 2013; Lüderitz and Gerlach, 2002; Vohla et al., 2011). The use of submerged aquatic based vegetation wetlands was shown to reduce mean inflow TP concentration of 107 µg P/L to as low as 23 µg P/L (Dierberg et al., 2002). A limitation of wetlands though is the need for very high areas and hence they can be land intensive (R. Kadlec, 1996). Although constructed wetlands can be considered as an alternative solution, their natural capacity to remove P is limited and chemically enriched media have been suggested for improving P binding (Arias, 2005). In such a case adsorption will be the dominant mechanism.

Thus even though certain technologies or combinations can achieve very low P concentrations, each has its own limits. Based on the above observations, this could be a high dependence on physicochemical conditions, the need for membranes which can potentially lead to fouling issues, production of chemical precipitates which might not be recoverable, requirement for large areas. Hence there is a need for technology that can reduce P consistently to ultra-low levels, with less reliance on having ideal conditions, a high throughput without fouling issues, with a low footprint, minimum waste generation and where the P is recoverable.

1.3. Adsorption as a polishing technology

Adsorption is a technology that has often been reported for achieving very low concentrations of o-P. Several studies in literature report on consistently reaching o-P concentrations less than 0.1 mg P/L and even lower than 0.01 mg P/L (Awual et al., 2014; Genz et al., 2004; Luo et al., 2016; Midorikawa et al., 2008; Sengupta and Pandit, 2011; Zhu and Jyo, 2005). One of the limitations of adsorption is its ability to only remove dissolved P. This usually implies o-P (henceforth referred to as phosphate) however studies also show the removal of organic phosphates like phosphonates using adsorption (Boels et al., 2012; Kumar et al., 2010; Rott et al., 2018). Pretreatment by advanced oxidation processes can also be an option to convert organic forms of P into phosphate which can then be targeted by adsorption (Mayer et al., 2013). The limitation of removing only soluble P can further be overcome by combining adsorption with another step that can target particulate P, for instance with flocculation and filtration (Langer et al., 2017).

Apart from removing soluble P to very low concentrations, adsorption also offers the possibility to recover the P by regeneration of the adsorbent (Drenkova-Tuhtan et al., 2017; Kalaitzidou et al., 2016b; Kuzawa et al., 2006; Fitzpatrick et al., 2009). This contributes to a circular economy. Despite several existing literature sources showcasing the potential of adsorption to reach low P concentrations, there is little information regarding their implementation at larger scales. A major reason could be that the process is not economical yet or there is a lack of understanding regarding the parameters affecting the economics. The objective of the following sections is hence to highlight what are the main parameters that affect the economics of phosphate adsorption, the existing research gaps for understanding these parameters, and to give a sensitivity analysis of how these parameters affect the cost. Moreover, the need for adsorbent regeneration is also considered by making a scenario analysis. This analysis includes low cost adsorbents that cannot be regenerated along with more expensive

adsorbents that can be regenerated several times. Although this review primarily focuses on effluent polishing from sewage/municipal wastewater, the findings can be equally relevant for reducing phosphate concentrations in any aqueous stream. For e.g. adsorption can have applications in surface water remediation, treating membrane feed water for biofouling prevention (Vrouwenvelder et al., 2010).

2. Factors governing the chemical costs of phosphate adsorption

The chemical costs of phosphate adsorption are governed by three important parameters, namely, the adsorbent cost, the practical loading and the costs during regeneration (seen in Fig. 1). The following sections will discuss the research gaps for these parameters.

2.1. Adsorbent cost

A wide variety of phosphate adsorbents have been synthesized or studied regularly. These range from using waste materials or byproducts like food residue or slag to using engineered adsorbents based on for instance, metal-organic-frameworks or layered nanosheets (Abbas, 2015; Fang et al., 2015; Sellner et al., 2017; Xie et al., 2017). It is important to note that both waste materials and engineered adsorbents can have inorganic (for e.g. metal oxides) as well as organic components (for e.g. biomass or organic backbone). Therefore, the classification of adsorbents as waste byproducts or engineered adsorbents would be reflected more by their source and cost. However, information on the cost of these adsorbents is seldom provided and is often difficult to deduce. Without providing an estimate on the adsorbent cost it is not possible to have an economic evaluation of these adsorbents.

A way to classify the adsorbents into different cost categories would be to consider the number of steps/chemicals required to produce/modify the adsorbent. For example, despite no information on costs being provided, adsorbents are reported as low-cost due to the usage of waste materials or byproducts with or without further modification (Mezenner and Bensmaili, 2009; Xue et al., 2009; Yuan et al., 2015; Zeng et al., 2004). In a similar way, composite adsorbents having active sites immobilized/impregnated on a backbone involve more chemicals/steps to produce or modify the adsorbent; hence these approaches can be associated with more expensive adsorbents (Fang et al., 2017b; Ge et al., 2016; Huang et al., 2015). Synthesized adsorbents comprising chiefly of metal oxides with no additional backbones can be considered in the intermediate cost category and include granular iron oxide based adsorbents (Genz et al., 2004; Kunaschk et al., 2015).

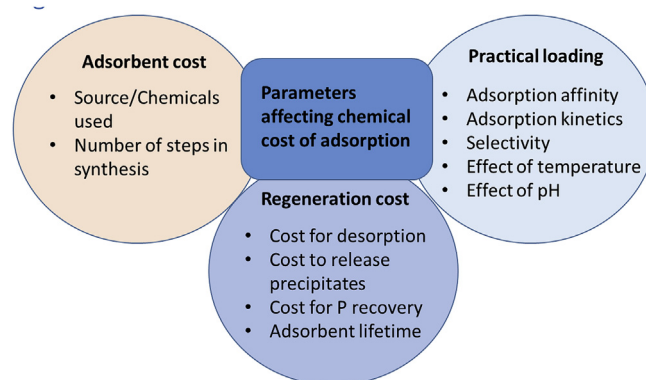


Fig. 1. Summary of factors governing the chemical costs of phosphate adsorption.

Based on the above rationale we classified adsorbents into 3 cost categories. i) Low cost – These include waste biomass and cost significantly lower than 1 \$ per Kg. ii) Intermediate cost – These include granular porous metal oxides which generally cost between \$ 3 to 6 per Kg (based on the information provided for the granular ferric hydroxide GEH and FerroSorp). iii) High cost – These include hybrid ion exchange resins like BioPhree® which cost between \$ 15 to 20 per Kg. Classifying adsorbents into these different categories helps in cost analysis with respect to different scenarios as will be discussed later. Studies reporting synthesis of novel adsorbents must estimate the cost regarding chemicals consumed which would indicate which of these 3 cost categories it will be closer to.

2.2. Practical loading

Adsorption capacity denotes the removal capacity of an adsorbent and is expressed as the amount of phosphate that can be removed per mass of adsorbent. Even though it is the most studied property of adsorbents, it is also the property that is most variable. Phosphate adsorption capacity is a function of the adsorbent properties like the surface area, surface charge, surface functionality as well as the physicochemical properties of the solution like phosphate concentration, temperature, pH, presence of other ions/molecules (Mia et al., 2017; Weng et al., 2012; Zhu et al., 2013). Since different studies are conducted under varying conditions it makes it very difficult to compare the adsorption capacities between different adsorbents.

To simply state adsorption capacity could be confusing and misleading, since it can imply the maximum adsorption capacity or the adsorption capacity at equilibrium. The term practical loading is used here to denote the phosphate adsorption capacity that will be realized in practice for a given set of conditions. For instance, this term can be used to differentiate the adsorption capacity realized at short contact times from the adsorption capacity under equilibrium conditions or at different phosphate concentrations.

2.2.1. Affinity

Phosphate adsorption capacity varies as a function of the equilibrium phosphate concentration and this relationship is given by an adsorption isotherm. The adsorption isotherm is a very valuable characterization because modelling it allows to estimate the adsorption capacity at different concentrations (Foo and Hameed, 2010). Langmuir and Freundlich isotherm models are most commonly used for describing adsorption. The Langmuir adsorption model is based on the assumption of chemisorption which is often the case with phosphate adsorption onto metal (hydr)oxides. Moreover, the Langmuir model allows the comparison of maximum adsorption capacity with adsorption capacity at specific phosphate concentrations. For instance, the Langmuir equation is given by the following expression (Langmuir, 1918):

$$q_e = \frac{q_{\max} K_L C_e}{(1 + K_L C_e)}$$

Where, q_{\max} is the maximum adsorption capacity and K_L is the Langmuir isotherm constant (Foo and Hameed, 2010). In the context of effluent polishing, it is desirable to have a high equilibrium adsorption capacity (q_e) even at lower equilibrium phosphate concentrations (C_e). This property is referred to as the affinity of the adsorbent (Tran et al., 2017; Volesky, 2007). This depends both on the maximum adsorption capacity as well as the Langmuir isotherm constant (Suresh Kumar et al., 2017). However, studies usually focus only on the maximum adsorption capacity of the adsorbent. Such capacities are often observed at equilibrium concentrations much greater than 10 mg P/L, which are rather

unrealistic when applying in the context of effluent polishing.

Fig. 2 uses data of Langmuir modelling from adsorption studies over the past 5 years (references in Table S1 in supporting information) and predicts the q_e at an equilibrium concentration of 0.1 mg P/L, denoted as $q_{0.1}$ (example shown in supporting information). The ratio between q_{\max} and $q_{0.1}$ is shown to point out the wide range of discrepancy between the maximum adsorption capacity and the adsorption capacity that will be achieved at lower phosphate concentrations.

The ratio of $q_{\max}/q_{0.1}$ shows that the maximum phosphate adsorption capacity can decrease even by a factor of more than 100 times at equilibrium concentrations of 0.1 mg P/L. Fig. 2 also shows there is no correlation with the q_{\max} value. This suggests that for the application of effluent polishing the maximum adsorption capacity is irrelevant. Instead it is more important to consider the affinity (for instance expressed as the constant K_L in the Langmuir equation) when developing phosphate adsorbents for this application.

The affinity of adsorbents varies with the type of metal oxides. Lanthanum based adsorbents often show high affinity towards phosphate (Wang et al., 2016; Wu et al., 2007; Zhang et al., 2012). This is attributed to Lanthanum's hard Lewis acidic property which promotes its Lewis acid-base interaction with phosphate. Iron oxides also show good affinity towards phosphate although the adsorption properties vary between the different types of iron oxides (Cornell, 2004; Mc et al., 1981; Parfitt et al., 1975). A study comparing different iron oxides found that ferrihydrite had a higher maximum adsorption capacity per unit area than hematite and goethite (Wang et al., 2013). However, goethite had a much higher value for the affinity constant and this amounted to a higher adsorption capacity at lower phosphate concentrations. This is in line with another study that reports similar trends with ferrihydrite and goethite (Borggaard et al., 2005). This reiterates the need to focus on the adsorption capacity at the relevant concentrations rather than the maximum adsorption capacity.

2.2.2. Kinetics

The phosphate adsorption capacities estimated from adsorption isotherms are based on equilibrium conditions. However, the time taken to reach equilibrium can range from some minutes to several days, with some adsorbents even taking a timescale of weeks (He et al., 2017; J. Torrent, 1992; Wan et al., 2016). The pseudo second order adsorption kinetic model is a commonly used model that has been used in a wide range of adsorbent studies (Ho and McKay, 1999). It is given by the following expression:

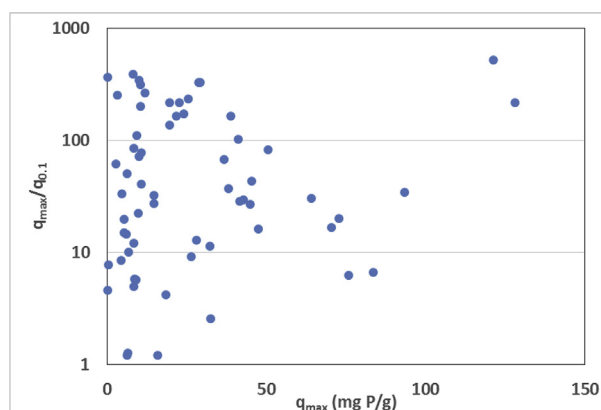


Fig. 2. Ratio of q_{\max} to adsorption capacity at equilibrium concentration of 0.1 mg P/L as a function of q_{\max} (references to the data points shown in Table S1 in supporting information).

$$q_t = \frac{(kq_e^2t)}{(1 + (kq_et))}$$

where, q_t is the adsorption capacity (mg P/g) at time t , k is the rate constant of adsorption (g/mg min) q_e is the adsorption capacity at equilibrium. The value of k and q_e can be estimated by modelling the adsorption kinetic data. This in turn allows to calculate the time taken for q_t to reach a given fraction of the equilibrium adsorption capacity q_e .

Fig. 3 shows the time taken to reach 90% (t_{90}) of equilibrium adsorption capacity based on the pseudo second order model for adsorption studies over the past 5 years (references to the data points shown in Table S2 of supporting information). The value of t_{90} is considered because most of these experiments are also only done for this duration, likely due to the fact that experimentally any change in adsorption is very slow after this time. This can also be understood from the mathematical expression of the pseudo second order model that it takes 11 times longer to reach 99% of equilibrium adsorption capacity (t_{99}) as compared to t_{90} (example shown in supporting information).

Even if t_{90} is considered as the indicator of adsorption kinetics, Fig. 3 shows that in several cases it is in the timescale of several hours to days. From a practical point of view, time is money and hence an adsorbent with superior kinetics is highly preferable. Especially, when run in a column mode, the contact times (measured as empty bed contact time or space velocity) are usually in the order of several minutes to less than an hour (Kalaitzidou et al., 2016a; Midorikawa et al., 2008; Yamashita et al., 2013).

Porous adsorbents offer a high surface area in combination with a particle size big enough to avoid pressure drop problems while using them in column mode. For instance, granular activated carbon provides a very high surface area (in excess of 1000 m²/g) and has been used for coating with iron oxide nanoparticles to enhance phosphate adsorption (Zach-Maor et al., 2011b). However a majority of its surface area comes from micropores (pore width < 2 nm), and phosphate adsorption in such adsorbents via pore diffusion takes place in the order of several days (Suresh Kumar et al., 2017; Zach-Maor et al., 2011b). On the other hand, 96% of phosphate removal was achieved within 30 min in a macroporous (pore size > 50 nm) adsorbent (Yang et al., 2012). In a study comparing phosphate adsorption onto different porous metal oxides, it was determined that pores bigger than 10 nm are required to enhance phosphate adsorption kinetics (Suresh Kumar et al., 2019). This shows the need to characterize the pore structure

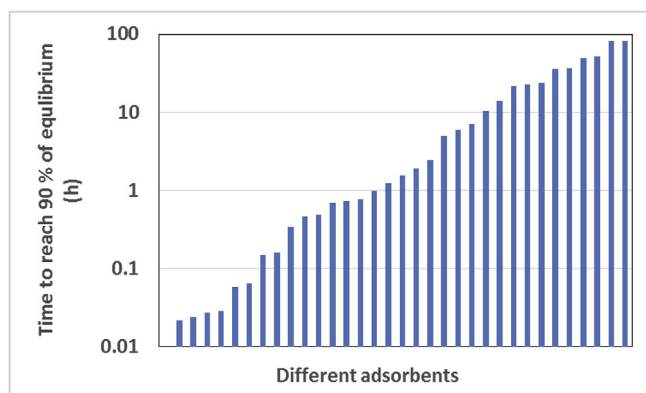


Fig. 3. Estimated time for reaching 90% of equilibrium for different adsorbents based on pseudo second order kinetic model (References shown in Table S2 in supporting information).

of the adsorbents along with their surface area to ensure good phosphate adsorption kinetics.

2.2.3. Selectivity

The ability of an adsorbent to remove phosphate preferentially amidst the competing ions is called its selectivity. The adsorbent selectivity depends on the type of interaction formed by the competing ion with the adsorbent surface. In general, ions like chloride, nitrate show little or no competition whereas ions like arsenate and silicate show high competition (Ge et al., 2016; Lü et al., 2013; Xie et al., 2014a; Zhang et al., 2016). Arsenate, phosphate and silicate are all tetrahedral ions that form inner-sphere complexes with metal (hydr)oxides like iron oxides (Parfitt, 1979; Su and Puls, 2001; Tuutijärvi et al., 2012). Nitrate and chloride form outer-sphere complexes which are weaker interactions (Parfitt, 1979). Sulphate and carbonate on the other hand vary in competing effects although carbonate often has a higher competing effect (Ge et al., 2016; He et al., 2017; Rashid et al., 2017; Xie et al., 2014a). Sulphate can exist as both inner or outer-sphere complexes on metal oxide surfaces (Wijnja and Schulthess, 2000). Carbonate can bind via electrostatic attraction but can also form calcium carbonate surface precipitates (Chitrakar et al., 2006; Kunaschk et al., 2015). Dissolved organic matter like humic acids and fulvic acids can also compete with phosphate adsorption via direct competition with the active sites as well as steric hindrance (Fu et al., 2013; Antelo et al., 2007; Weng et al., 2012).

Apart from ions and molecules that directly compete for active sites, certain cations like calcium and magnesium can also influence phosphate adsorption. The binding of these ions can enhance phosphate adsorption by making the surface more electropositive or by forming intermediate ternary complexes (Antelo et al., 2015; Han et al., 2017; Lin et al., 2017; Talebi Atouei et al., 2016). Thus depending on the type of ions present in the water matrix, the adsorption of phosphate can get enhanced or reduced (Suresh Kumar et al., 2018). Adsorbent selectivity is often tested in the presence of separate competing ions with varying concentrations (Antelo et al., 2007; Gu et al., 2018; Sengupta and Pandit, 2011). But in realistic conditions several competing ions will exist together and can interact to form different complexes or precipitates. To test the selectivity, it is hence ideal to have conditions that are representative of realistic solutions. Alternatively, surface complex models can be used to predict interaction of different components on the adsorbent surface (Rietra et al., 2001).

2.2.4. Effect of temperature

The effect of temperature on an adsorbent's performance is governed by its thermodynamic properties. An endothermic process will lead to improved adsorption at higher temperatures, while an exothermic process will lead vice versa (Huang et al., 2014; Jung et al., 2017). The extent of effect of temperature also varies with adsorbents. Phosphate adsorption on an adsorbent formed by thermal decomposition of alunite and potassium chloride mixture was found to be endothermic (Akar et al., 2010). But the maximum adsorption capacity only increased by 5% when the temperature increased from 20 to 40 °C. On the other hand, a magnesium ferrite biochar composite which also had an endothermic adsorption, showed a 66% increase in maximum adsorption capacity when the temperature increased from 15 to 35 °C (Jung et al., 2017). Similar variations also exist between adsorbents showcasing exothermic property (Huang et al., 2014; Qian et al., 2017). Although some of these studies use temperatures higher than normally encountered in realistic applications, these are used as an example to showcase the possible differences in thermodynamic properties of these adsorbents.

It is also important to consider the effect of temperature on

adsorption kinetics. This is especially relevant for performance in continuous modes where contact times are short. Kinetic constants for different adsorbents mostly increased with an increasing temperature (Table S3 in supporting information). This could be due to improved phosphate diffusion at higher temperatures, indicating practical loading will decrease at lower temperatures for such adsorbents.

2.2.5. Effect of pH

Phosphate has pKa values of 2.15, 7.2 and 12.33, and depending on the solution pH it can thus exist in the form of H_3PO_4 , H_2PO_4^- , HPO_4^{2-} or PO_4^{3-} (Xiong et al., 2017). Phosphate adsorption usually reaches an optimum when the pH favours its electrostatic attraction with the adsorbent. This happens when the pH of the solution is less than the adsorbent PZC so that the adsorbent is electro-positive and the phosphate is in its anionic form. Since several adsorbents have their point of zero charge close to neutral pH, the phosphate adsorption optimum is often in the acidic range (Fang et al., 2017b; He et al., 2017; Wen et al., 2014).

While the effect of pH on phosphate adsorption is well documented, the effect of competing ions must also be considered. For example, it was reported that for similar concentrations of humic acid, phosphate adsorption on goethite reduced by 45% at pH 4.5 compared to a 25% reduction at pH 7 (Antelo et al., 2007). (Sibanda H and Young S 1986) observed similar effects of higher humic acid adsorption on goethite and gibbsite at lower pH. Similarly, even though phosphate adsorption is enhanced at $\text{pH} < \text{PZC}$ of the adsorbent, calcium adsorption happens at $\text{pH} > \text{PZC}$, which would in turn enhance phosphate adsorption (Antelo et al., 2015). observed this while monitoring calcium and phosphate adsorption on ferrihydrite nanoparticles. Even though phosphate adsorption decreased significantly at higher pH in the absence of calcium, increasing the concentrations of calcium increased the phosphate adsorption at the same pH.

2.3. Cost for regeneration

Regeneration is the process by which the molecules bound on the loaded adsorbent are released. This might include phosphate as well as other competing ions. Regeneration is done for two reasons i) To recover the separated molecule of interest, i.e. phosphate. ii) To replenish the active sites of the adsorbent so that the adsorbent can be reused. The reuse of the adsorbent as well as any excess chemicals from the regeneration makes the overall process economic and environmental friendly. The sections below discuss the factors associated with the chemical costs for regeneration.

2.3.1. For replenishing adsorbent active sites

2.3.1.1. Releasing adsorbed complexes.

Phosphate binds to metal (hydr)oxides by a ligand exchange mechanism (innersphere complex) with the surface hydroxyl groups. This includes a range of metal oxides that include metals like aluminium, iron, lanthanum, zirconium, and sometimes even a mixture of different metal oxides (Awual et al., 2011; Fang et al., 2017a; Liu and Hesterberg, 2011; Sibanda H and Young S 1986; Zhang et al., 2009; Schneider et al., 2017). In such a case, desorption of phosphate is done by an alkaline solution like sodium hydroxide (NaOH), since the hydroxide ions acts as a hard Lewis base (Awual et al., 2011). From an economic point of view, it is important to know how much chemical is consumed for the desorption of phosphate. Phosphate adsorption as innersphere complex happens as a monodentate or bidentate complex (Abdala et al., 2015; Connor and McQuillan, 1999; Fang et al., 2017a). This means stoichiometrically, only one or two molecules of hydroxide ion should be consumed for desorption of each phosphate molecule. However, an excess amount of hydroxide ions

are required to provide a driving force. Thus, high concentrations of NaOH solutions are used for phosphate desorption, often ranging from 0.1 to 1 M (Drenkova-Tuhtan et al., 2017; Fang et al., 2017b; Genz et al., 2004; Sun et al., 2014). But the actual amount of hydroxide ions consumed will be less and the excess of the hydroxide ions in the regenerate solution can be reused. For instance, the NaOH solution was replenished and reused for desorption of phosphate for 60 cycles in a pilot study (Drenkova-Tuhtan et al., 2017).

When the adsorbent is used in a water matrix consisting of several competing ions, the actual consumption of hydroxide ion during desorption will also depend on the other ions that bind via the same mechanism. Having a selective adsorbent will decrease the overall consumption of hydroxide ions per mole of phosphate desorbed. However, having a highly selective adsorbent also implies that it will have a high affinity to phosphate and the binding could be too strong to facilitate easy desorption. For example, although lanthanum based adsorbents are known for their strong affinity towards phosphate, the recovery of phosphate from these adsorbents is not always discussed (Wang et al., 2016; Zhang et al., 2012). (Xie et al., 2014c) showed that very high concentrations of up to 12.5 M NaOH along with temperatures in excess of 100 °C are required for optimum desorption of phosphate from lanthanum hydroxide. Similar requirements of high concentrations of NaOH or a combination with thermal steps are reported for desorbing phosphate from other adsorbents based on rare earths like lanthanum and yttrium (Dong et al., 2017; Xie et al., 2014b), (Kim et al., 2017).

2.3.1.2. Releasing surface precipitates.

While NaOH can be used to release molecules adsorbed on the surface, adsorption is not the only interaction that can happen on the adsorbent. Depending on the adsorbent properties and physicochemical properties of the solution, sometimes surface precipitation might also occur. Surface precipitation leads to formation of multilayered structures (/three dimensional molecular arrangement) as opposed to the monolayer coverage during chemisorption (Sparks, 2003; Sposito, 1987). In such a case the precipitate can bury the adsorbed phosphate and hence prevent it from getting desorbed (Li and Stanforth, 2000). Surface precipitation can form either from the dissolution and re precipitation of ions from the adsorbent or due to the binding of competing ions from the solution. For instance, the dissolution of iron from goethite has been reported to contribute to surface precipitation (Li and Stanforth, 2000). (Kunaschk et al., 2015) studied phosphate adsorption from a drinking water matrix, where calcium based surface precipitates were reported to block effective desorption of phosphate. In such a case, an acid treatment with a HCl solution of pH 2.5 was recommended to release the surface precipitates and effectively regenerate the adsorbent. Similarly, calcium carbonate precipitation was observed while using adsorbents in a wastewater matrix and an acidic treatment was required to improve the adsorbent reusability (Suresh Kumar et al., 2018). The chemical consumption of acid needs to be monitored in such scenarios.

2.3.1.3. Neutralization of excess NaOH in the adsorbent.

In the case of porous adsorbents, some of the NaOH used during desorption will be retained in the pores. The removal of such NaOH will be necessary prior to a subsequent reuse cycle to allow for efficient adsorption and to prevent unwanted precipitation inside the pores during the next adsorption cycle. While the excess NaOH can be rinsed by water, an acid neutralization step can be used to speed up the process (Suresh Kumar et al., 2018; Zach-Maor et al., 2011a). Neutralizing such columns purely with water could result in high consumption of water and result in large amounts of waste stream

(Suresh Kumar et al., 2018). In case of using an acid neutralization step, the acid consumption needs to be considered.

2.3.2. For phosphate recovery

Phosphate concentrated in the regenerate stream (NaOH) can be recovered as a form of calcium phosphate or magnesium ammonium phosphate/struvite (Drenkova-Tuhtan et al., 2017; Kalaitzidou et al., 2016b; Kuzawa et al., 2006; Midorikawa et al., 2008). Recovery as struvite needs addition of magnesium and ammonium and a pH around 9 was suggested as the optimum pH for obtaining compact structures and maximum yield (Drenkova-Tuhtan et al., 2017; Ye et al., 2014). Recovery as calcium phosphate only needs the addition of a calcium source and has been suggested as the better choice due to the high pH of the regenerate solution (Kuzawa et al., 2006).

The composition of the regenerate stream will affect the consumption of the chemicals used for precipitation of phosphate. For example, after phosphate adsorption from secondary wastewater effluent, the molar ratio of magnesium:ammonium:phosphate required to form struvite in the regenerate stream was 1.5:1.5:1 (Drenkova-Tuhtan et al., 2017). This was higher than the stoichiometric ratio of 1:1:1 and was attributed due to competing parallel reactions. Similarly, a molar ratio of Ca to P between 2 and 2.5 was required for optimum calcium phosphate formation (Kuzawa et al., 2006; Kalaitzidou et al., 2016b; Midorikawa et al., 2008). This is higher than the stoichiometric molar ratio of 1.5 and 1.67, required for forming tricalcium phosphate and hydroxyapatite, respectively (Song et al., 2002b). Excess requirement of calcium could be due to the presence of carbonates in the regenerate solution which will lead to the formation of calcium carbonate (Song et al., 2002a). A pilot study recovering calcium phosphate from the regenerate found that about 40% of their recovered product consisted of calcium carbonate (Kalaitzidou et al., 2016b). This was attributed to CO₂ adsorption from the atmosphere since the regeneration solution was maintained in an open tank.

Thus the amount of chemicals consumed for phosphate recovery will be dependent on the conditions during regeneration as well as the selectivity of the adsorbent. Moreover, more studies are needed to show the potential for reusing the regenerate solution, especially the effect on desorption due to the accumulation of phosphate in the regenerate. This will give essential information on when and how often the phosphate needs to be recovered to enable effective reuse of the regenerate solution.

2.4. Adsorbent lifetime

The adsorbent lifetime is increased by reusing it multiple times. Many studies test the adsorbent reusability between 5 and 10 cycles (Fang et al., 2017b; Ju et al., 2016; Jung et al., 2017; Kim et al., 2017; Luo et al., 2017; Wan et al., 2016). Adsorbent attrition during the adsorption or regeneration process is the common reason for reusability getting affected. For example, zirconium oxide particles confined in mesoporous carbon showed a drop in adsorption capacity from 17 to 13 mg P/g over the first 4 cycles whereas the capacity remained stable over the next 3 cycles (Ju et al., 2016). This was attributed to the leaching of zirconium oxide particles located on the external surface or pore mouth region of the adsorbent composite. Adsorption capacity of calcined LDH decreased by about 50% over 5 cycles which was attributed to destruction of the layered structure (Sun et al., 2014). The structure or active sites of amino-functionalized clay adsorbent composites was considered damaged during regeneration with NaOH (Unuabonah et al., 2017). This led to a decrease in adsorption performance over every consecutive adsorption cycle (Drenkova-Tuhtan et al., 2017). tested nanocomposite magnetic particles in wastewater effluent over 20

adsorption-desorption cycles. Effluent concentrations less than 0.05 mg P/L could only be achieved for the first few runs after which the adsorption efficiency decreased. This was attributed to a consistent loss of adsorbent particles at a rate of about 5% per cycle. Furthermore, attrition of adsorbent can form very small particles/fines which can get released into the effluent. If such particles are loaded with phosphate they can be an additional source of pollution.

Incomplete desorption of phosphate has also been found to decrease the reusability. For instance (Kunaschk et al., 2015), reasoned that calcium based surface precipitation blocked adsorbed phosphate. This would lead to a decrease in available active sites during the next adsorption cycle and thus affect the reusability. Presence of phosphate into micropores of iron oxides has also been reported to affect desorption (Cabrera et al., 1981). Additionally, the adsorbent crystallinity or type of metal oxides can change during regeneration which would affect their surface functional groups. For instance the crystallinity of goethite was observed to increase after regeneration with NaOH and was correlated to a decrease in adsorption capacity after the very first cycle (Chitrakar et al., 2006). In contrast the crystallinity of akaganeite did not change even after 10 cycles and the reusability was also intact (Suresh Kumar et al., 2018). monitored the adsorbent characteristics such as change in surface area, crystallinity, as well mass balance of competing ions for 3 adsorption - regeneration cycles in a real wastewater effluent. Amongst all the other parameters, calcium based surface precipitation was shown to have the highest influence on adsorbent reusability. However, the surface precipitates were not found to affect phosphate desorption, but rather affect calcium adsorption which in turn affects phosphate adsorption. Understanding the mechanism of surface precipitation was suggested as important step to enhance adsorbent reusability.

There are also studies where the reusability is intact for the studied duration (Fang et al., 2017b; Wan et al., 2016; Wu et al., 2017; Zong et al., 2013). This could be related to the stability of the adsorbent but it could also be due to the fact that not enough regeneration cycles were done. For instance, nanocomposites based on lanthanum hydroxide and iron oxide showed stable adsorption capacities during 5 adsorption cycles (Wu et al., 2017). However the phosphate desorption efficiency varied between 70 and 80% during each regeneration cycle. This incomplete desorption could affect the reusability on the long run.

From a practical viewpoint, the adsorbent lifetime needs to be much higher than 5 to 10 reuse times. But rather than performing endless regeneration cycles, studies should focus on developing a better understanding of the parameters that affect reusability. In that way optimal regeneration methods can be developed. If with such methods it can be shown that the adsorbent characteristics do not change over a certain number of reuse cycles, then the adsorbent lifetime can be extrapolated to longer reuse cycles with more certainty.

3. Economic analysis for phosphate adsorption

The economics of the adsorption process can be divided in the operating costs and the capital costs. The operating costs mainly include the chemical costs as well as the costs due to energy consumption. The following sections describe the sensitivity and scenario analysis for the chemical costs, followed by a brief overview on the energy and capital costs.

3.1. Scenario and sensitivity analysis for chemical costs

The chemical costs are the costs that can be addressed by phosphate adsorption studies. A simple schematic of the

adsorption process applied in a column mode is shown below (Fig. 4). However, the evaluation used for these chemical costs will also apply for a batch mode.

Based on the scheme shown in Fig. 4, the chemical cost for phosphate adsorption can be expressed as follows:

$$\text{Chemical cost of adsorption} \left(\frac{\$}{\text{mole P}} \right) = \frac{[A + (B \cdot n)]}{(n + 1)}$$

Where, A = Cost for 1st adsorption cycle (\$/mole P), B = Cost per regeneration cycle (\$/mole P/cycle), n = Number of regeneration cycles. The denominator in the formula denotes the total number of cycles and is n+1 since the regeneration begins after the 1st cycle. The term A is a function of the adsorbent cost and adsorption capacity. It can be expressed as:

$$A = a_1/a_2$$

Where, a₁ = adsorbent cost (\$/Kg adsorbent), a₂ = Practical loading (moles P/Kg adsorbent).

The cost per regeneration cycle can be further split as:

$$B = (C + D + E)/a_2$$

Where, C = Cost per cycle of desorption (\$/Kg adsorbent/cycle), D = Cost per cycle of acid wash (\$/Kg adsorbent/cycle), E = Cost per cycle of P recovery (\$/Kg adsorbent/cycle). Table 1 shows the split up of the variables used in calculating cost of each of these steps.

Certain assumptions have been made to arrive at these derivations. The following points discuss these assumptions and their limitations:

- The adsorption capacity stays same throughout the n regeneration/reuse cycles. In reality, the adsorption capacity will vary depending on the change in the physicochemical characteristics of the incoming solution as well as the amount of wear and tear the adsorbent undergoes.
- The excess of chemicals used during regeneration can be reused. Hence, only the cost for the chemicals actually consumed per cycle is considered. Studies show the possibility to reuse the regenerate solution by replenishing only the spent chemicals (Kalaitzidou et al., 2016a; Kuzawa et al., 2006). The phosphate recovery from the regenerate stream allows to reuse the regenerate stream effectively.
- Complete desorption of phosphate is achieved using NaOH solution. This assumption was necessary to relate the OH consumption to the phosphate adsorption capacity. Complete

desorption might not be achieved in the first couple of cycles for porous adsorbents due to phosphate diffusion into inner pores. But once such sites are saturated near complete desorption can be expected (Zach-Maor et al., 2011a). Moreover, the extent of desorption also depends on the affinity of the adsorbent.

- Surface precipitation happens primarily via calcium binding. This allows to establish a relationship between calcium binding and amount of acid required to remove surface precipitates. Calcium based surface precipitation has been reported before on phosphate adsorbents (Kunaschk et al., 2015; Suresh Kumar et al., 2018). Given its ubiquitous nature in surface and wastewaters it can be the chief component to cause a precipitate. However, precipitates based on adsorbent dissolution are also possible (Li and Stanforth, 2000).

The overall formula for calculating the chemical cost can be used to show the importance of reusing the adsorbent several times. Fig. 5 shows the variation in chemical cost as a function of the regeneration cycles. The figure is plotted varying parameter 'n' in the equation for chemical cost of adsorption as shown in Table 1. To express the chemical cost in percentage, the value of term A is taken as 100 and value of term B is varied to give rise to different ratios of B/A, i.e. the cost per regeneration cycle as compared to the cost of 1st adsorption cycle.

The chemical cost is both a function of the number of regeneration cycles as well as the ratio of cost per regeneration cycle to the cost of 1st adsorption cycle. For scenarios where the cost per regeneration cycle is at least 5 times cheaper than the cost of 1st adsorption cycle, about 80% or more of the reduction in chemical costs is reached by 30 regeneration cycles. However, the number of regeneration cycles that can be implemented relates to the adsorbent lifetime which in turn depends on the composition of the adsorbent. This includes how stable the adsorbent material is to abrasion and structural modification over the adsorption and the regeneration cycles. There are several studies which specify low cost phosphate adsorbent alternatives which are natural or modified products of industrial waste or biomass (Biswas et al., 2008; Ismail, 2012; Karthikeyan et al., 2004; Namasivayam and Sangeetha, 2004; Mortula et al., 2007; Nawar et al., 2015). However most of these adsorbents are either not resistant to the conditions used in regeneration (alkaline or acidic pH) or are suggested as direct application as fertilizers (Nguyen et al., 2014).

To compare how their adsorption costs fare with reversible adsorption (i.e. reusable adsorbents), we consider a scenario analysis for 3 different categories of adsorbent: Waste biomass based adsorbents, porous metal oxides, hybrid ion exchange resins. The

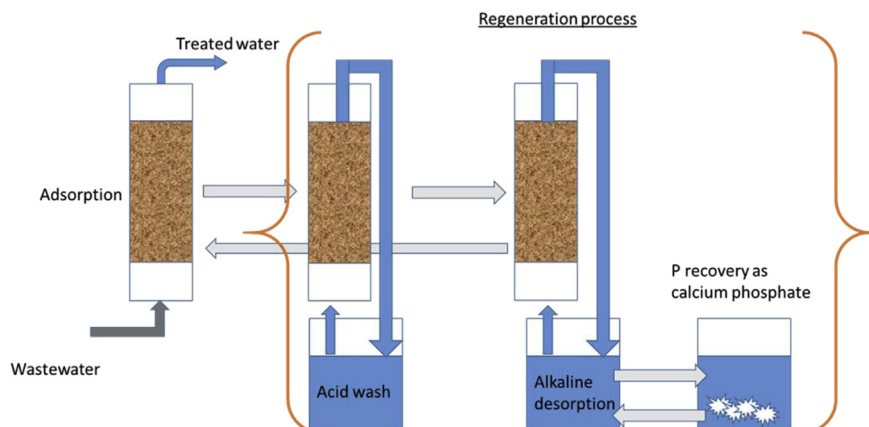


Fig. 4. Scheme of adsorption process. The acid wash step serves to remove surface precipitates.

Table 1
Parameters and formulas used for calculating the chemical costs of phosphate adsorption.

Variables involved	Steps with formulas
For adsorption step: a_1 = Adsorbent cost (\$/Kg) a_2 = Practical loading (Moles P/Kg)	$A = a_1/a_2$
For desorption step: c_1 = OH consumed to desorb (Moles OH/mole P) c_2 = Adsorbent pore volume (L/Kg) c_3 = Concentration of NaOH (Moles OH/L) c_4 = Cost of NaOH (\$/mole NaOH)	$B = (C + D + E)/a_2$ $C = ((c_1 * a_2) + (c_2 * c_3)) * c_4$
For acid wash step: d_1 = Acid consumption to release surface precipitate (Moles H/mole Ca) d_2 = Practical loading for calcium (Moles Ca/Kg adsorbent) d_3 = Cost of HCl (\$/mole HCl)	$D = ((d_1 * d_2) + (c_2 * c_3)) * d_3$
For recovery step: e_1 = Calcium consumed for calcium phosphate precipitation (Moles Ca/mole P) e_2 = Cost of calcium (\$/mole $CaCl_2$) e_3 = Hydroxide consumed during calcium phosphate precipitation (Moles OH/mole calcium phosphate) e_4 = Cost of calcium phosphate (\$/mole calcium phosphate)	$E = (e_1 * a_2 * e_2) + (e_3 * a_2 * c_4) - (a_2 * e_4)$
For reusability: n = Number of reuse cycles	Chemical cost of adsorption $\left(\frac{\$}{\text{mole P}} \right) = \frac{[A + (B * n)]}{(n + 1)}$

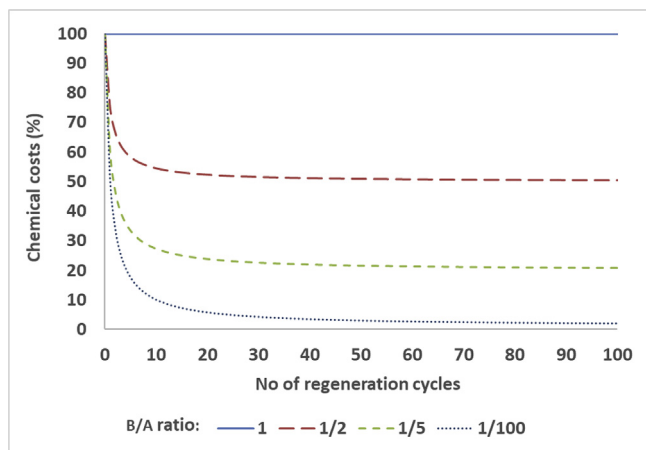


Fig. 5. The variation in chemical cost of adsorption as a function of the number of regeneration cycles. The legends show the ratio of the terms B/A, i.e. the cost per regeneration cycle as compared to the cost of 1st adsorption cycle.

main criteria for categorizing this way is based on the adsorbent cost as discussed in section 2.1, but the other important differences to consider include the adsorption capacity, and the lifetime of the adsorbents. Table 2 summarizes these aspects.

A Monte Carlo simulation was used to account for the uncertainty in calculating the chemical costs for the 3 categories of adsorbents. A lower and upper range was provided for each parameter used in estimating the chemical cost and 10,000 random variables were generated using a uniform distribution. The range for the main parameters used for calculating the chemical costs are shown in Table 3 (values for complete parameters shown in Table S4 in supporting information). These parameter values will of course depend on the operating conditions and the type of water matrix being treated. But at least in the case of porous metal oxides and the ion exchange resin they have been estimated from adsorption in a wastewater effluent matrix (Suresh Kumar et al., 2018). Hence these provide a more realistic value than phosphate solutions prepared using clean water.

The main assumption made is the lifetime/number of

regeneration cycles for porous metal oxides and the hybrid ion exchange resin. Rice husk was considered as the waste biomass and the adsorbent was considered for a one time use. Hence for this adsorbent regeneration costs were not considered. For porous metal oxide, FerroSorp (FSP) which is a granular iron oxide was used as the example. The average lifetime was considered as 30 regeneration cycles since around 80% reduction in chemical costs is achieved by this lifetime in line with explanation provided by Fig. 5. For the hybrid ion exchange resin, BioPhree[®] which is an ion exchange resin impregnated with iron oxide was used as the example. The lifetime of ion exchange resins depends on the process conditions and can vary between 7 and 15 years. In our case, we considered an average lifetime of 100 regeneration cycles. The lower and upper range for the FSP and BioPhree[®] were thus taken as $\pm 10\%$ of 30 and 100 cycles, respectively.

Fig. 6 shows the box plot for the chemical costs of these 3 categories of adsorbents as estimated by the Monte-Carlo simulation. The error bar shows the spread of possible chemical costs as per the range provided for the different parameters.

It can be seen from Fig. 6 that despite considering a very low cost for the waste biomass based adsorbents, reversible adsorption with porous metal oxides and hybrid ion exchange resins are more cost effective due to their higher adsorption capacity and longer lifetime. The median value for the chemical cost was around \$ 100/Kg P for both the porous metal oxide and the hybrid ion exchange resin. Some studies also suggest the use of naturally occurring calcium carbonate minerals like calcite and dolomite for phosphate adsorption (Karaca et al., 2004; Karageorgiou et al., 2007; Sørensen et al., 2011; Xu et al., 2014). These adsorbents facilitate formation of calcium phosphate products and are suggested for direct application as fertilizers. However, the solubility of calcium phosphate and its subsequent application as fertilizer depends on the pH of the soil (Cabeza et al., 2011). More information is also needed on the selectivity and practical binding capacity of these adsorbents at very low phosphate concentrations. Just like in the comparison with biomass, engineered adsorbents with higher practical loading and lifetime can be more economical than one time use adsorbents.

Fig. 7 shows the sensitivity for different parameters towards the chemical cost for the porous metal oxide. Fig. S2 in supporting info shows a similar graph for the ion exchange resin.

Fig. 7 shows that amongst all parameters, the adsorbent cost,

Table 2
Differences in adsorbent categories.

	Low cost	Intermediate cost	High cost
Example	Waste biomass (Nguyen et al., 2014)	Porous metal oxide (Genz et al., 2004)	Hybrid ion exchange resins (Sengupta and Pandit, 2011)
Composition	Waste biomass which can be used as such, but often modified with metal salts to increase selectivity towards phosphate adsorption	Bulk metal oxides like iron or aluminium oxides with high specific surface area due to the porous structure	Include ion exchange resins that are impregnated with metal oxides like iron oxide to increase selectivity towards phosphate adsorption
Phosphate adsorption	Low adsorption capacity due to low specificity and surface area	Higher adsorption capacity due to high surface area, but adsorption kinetics is limited by diffusion into the pores and hence practical loading depends on contact time in continuous mode	Lower surface area than the porous metal oxides but adsorption kinetics is faster and hence displays high adsorption capacity with relatively low contact times
Lifetime	One time useable	Reusable but mechanically less stable than resins. Hence might undergo breakdown during regeneration which would result in development of very fine particles. These fines can lead to increase in pressure drop or can also escape into the effluent carrying the adsorbed phosphate onto them.	High lifetime due to mechanically superior/abrasion resistant properties.

Table 3
Main parameters used for simulating the chemical cost for reaching 0.1 mg P/L.

Parameters/Adsorbent type	Waste biomass	Porous metal oxide	Hybrid ion exchange resin
Example used	Ricehusk	FerroSorp (FSP)	BioPhree®
Adsorbent cost (\$/Kg)	Minimum = 0.1 Maximum = 0.2	3 to 6	15 to 20
Practical loading (moles P/Kg adsorbent)	0.01 to 0.02	0.05 to 0.1	0.04 to 0.08
Reuse cycles	None	27 to 33	90 to 110

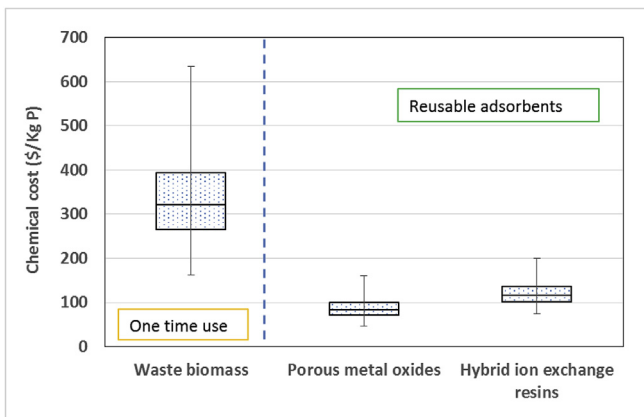


Fig. 6. Scenario analysis for the chemical costs of 3 types of phosphate adsorbents.

the practical loading and number of regeneration cycles had the most significant effect. An increase in practical loading and regeneration cycles reduced the chemical cost non-linearly, whereas a decrease in adsorbent cost reduced the chemical cost linearly at a higher slope than the other parameters. Thus optimization of these parameters would be essential for making the process economically feasible.

The chemical costs calculated here are for an effluent concentration of 0.1 mg P/L. For an effluent concentration of 0.01 mg P/L, these costs will be higher depending on how the adsorption capacity decreases corresponding to that concentration. If an adsorbent has a high affinity, this decrease in adsorption capacity will be minimal. For the example for the porous metal oxide used, the practical loading at an effluent concentration of 0.016 mg P/L capacity was 60% of the loading observed at 0.1 mg P/L. Assuming all other parameters to be constant, the change in chemical cost can be

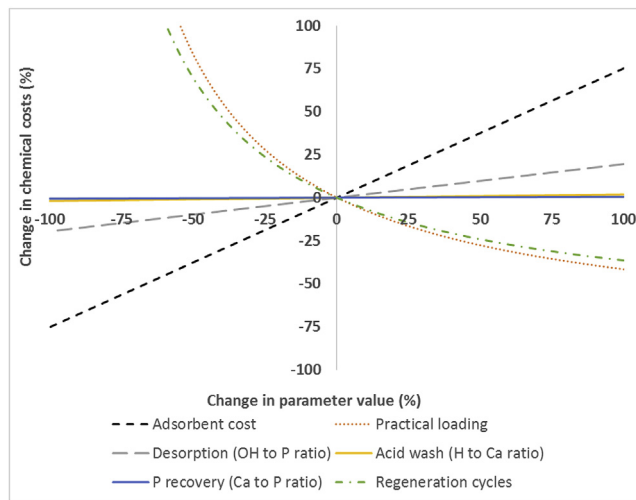


Fig. 7. Sensitivity of different parameters to chemical costs of porous metal oxide.

deduced from the sensitivity analysis as shown in Fig. 7. In this case, the chemical cost increased only by 50% even though the effluent concentration was reduced by a factor 6. Moreover, the practical loadings used in this analysis are based on a relatively short empty bed contact time (EBCT) of 5 min. Depending on the adsorption kinetics increasing the EBCT can significantly increase the practical loading. This will hence lower the chemical costs.

3.2. Energy and capital costs

Energy consumption costs will vary based on the mode of operation. Stirred tank batch systems will consume energy primarily due to the stirring, whereas fixed bed column studies will

consume energy primarily due to pumping. Similarly, adsorbents with magnetic properties would need a magnetic separator to facilitate their recovery (Drenkova-Tuhtan et al., 2017). For the current scenario, the energy and capital costs are based on fixed bed continuous mode of operation. The regeneration would be simpler for the fixed adsorbent bed compared to a stirred tank reactor where the adsorbent needs to be first recovered after the adsorption process. A continuous mode can also lead to a more efficient use of the adsorption capacity because the adsorbent is always exposed to the same influent concentration rather than the decreasing concentrations in batch mode (Loganathan et al., 2014). The energy cost in terms of P removed can be given by the following formula:

$$\text{Energy cost (\$/Kg P)} = \frac{(F * G)}{(Q * (C_{in} - C_{out}) * 10^{-3})}$$

Where, F = Hourly power consumption (kWh/h), G = Electricity cost (\$/kWh), Q = Volumetric flow rate (m³/h), C_{in} = Phosphate concentration at inlet (mg P/L), C_{out} = Phosphate concentration at outlet (mg P/L).

The power consumption is related to the pressure drop over the adsorbent column as follows:

$$F = (Q * \Delta P) / 36 \eta$$

Where, ΔP = Pressure drop (bar), η = Pump efficiency (%). The pressure drop can be calculated by the Ergun equation (supporting information).

The capital costs will chiefly include the cost of the adsorbent column(s), the regeneration tanks (one for desorption with alkaline solution and other for acid washing), and a crystallizer for recovering the desorbed phosphate as calcium phosphate. The process can use two adsorbent columns in series so that when one is getting regenerated the other adsorbent column can still be in operation. An assumption is that any fouling of the adsorber bed will be cleaned during the regeneration process. For instance, inorganic fouling such as surface precipitation will be removed during acid wash (Suresh Kumar 2017). Phosphate limitation will control bio-fouling (Vrouwenvelder et al., 2010) but any biofouling formed will also be cleaned during the alkaline desorption step due to the high pH (Goode et al., 2013). Thus, no separate operational or capital costs are considered for handling fouling of the adsorber bed.

A simplified way to estimate the capital cost would be to assume that the equipment will operate effectively for a fixed lifetime, in which case the capital cost in terms of P will be:

$$\text{Capital cost (\$/Kg P)} = \frac{(H)}{I * Q * (C_{in} - C_{out}) * 10^{-3}}$$

Where, H = Total investment cost (\$), I = Lifetime of equipment (h)

It is difficult to establish the capital costs since the cost of equipment will vary with scale and the specific costs will usually reduce at bigger scales due to economy of scale. In this case, the costs were based on pilot scale experiments at a scale of 1.5 m³/h (Fig. S1 and Table S5 in supporting information show). However, these were scaled up to determine the costs for treating at a full scale flowrate of 500 m³/h. This was done by using the scaling coefficient which relates the capacity increase (in this case denoted by the increase in volumetric flowrate) to the increase in equipment cost (Tribe and Alpine, 1986). A scaling coefficient value of 0.6 was used in this case, which is in line with common practice (Tribe and

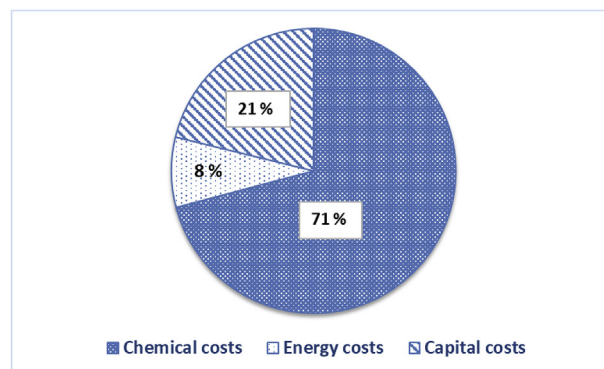


Fig. 8. Overall cost distribution for phosphate adsorption on porous metal oxide.

Alpine, 1986). Moreover, to consider the installation charges, the Lang factor was considered in the calculation (Wain, 2014). Since adsorption is used for treating liquids, a Lang factor of 4.8 was used and multiplied with the full scale equipment cost (Wain, 2014). Thus the total investment cost, denoted by the term H, includes the installation cost as well. The calculated value for the total investment cost for a capacity of handling 500 m³/h amounted to \$ 970,000. Considering the equipment has a lifetime of 10 years, an influent concentration (C_{in}) of 1 mg P/L, and the desired effluent concentration (C_{out}) of 0.1 mg P/L, the capital cost expressed in terms of P amounts to about \$ 25/Kg P. The energy cost for these conditions (parameters used are listed in Table S6 of supporting information) amounts to about \$ 10/Kg P. Thus the overall cost including capital, energy and chemical costs for reducing phosphate from 1 to 0.1 mg P/L using reversible adsorption on porous iron oxides is about \$ 120/Kg P. Fig. 8 shows the distribution of the different costs.

As can be seen from Fig. 8, chemical costs, which includes the cost of the adsorbent, contributed to more than 70% of the overall costs. A similar cost distribution was obtained for the hybrid ion exchange resins, although the percentage of chemical costs was slightly higher (Fig. S3 in supporting information). Once the process is in operation, the process does not require much manual maintenance, except in the case of checking for the breakthrough (once the effluent P concentration exceeds the required level) and regenerating the adsorbent. Thus the labor costs for the process should ideally be minimal.

The other costs that are not considered in this calculation include the cost for waste generation. One time use biomass based adsorbents can ideally be used directly as fertilizers provided they did not bind toxic materials like heavy metals and there is indeed a fertilizer value. For reusable adsorbents, although the excess chemicals in the regenerate stream are assumed to be completely reused, there could be accumulation of other ions in this stream. The accumulation of other ions depends on the adsorbent selectivity and could happen both in streams used for alkaline desorption as well as acid wash. In that case, occasionally a part of the regenerate stream would need to be bled. This stream might need to be neutralized and further treated before being discarded. Studies are needed on understanding the composition of the regenerate stream after multiple reuse. Additionally, even if highly selective engineered adsorbents are designed, some of these adsorbents contain elements which can cause toxicity issues if released into the environment (Table S1 in supporting information). Hence it is necessary to thoroughly investigate the chemical leakage from such adsorbents before they can be applied.

3.3. Comparison with other technologies and defining the ideal conditions for adsorption

The ideal conditions for adsorption can be underlined by comparison with chemical precipitation. Chemical precipitation with iron salts is a commonly used technique to lower the phosphate concentrations in municipal wastewater (Sedlak, 1991). Iron salts can be added near or slightly higher than stoichiometric Fe:P molar ratios to reduce phosphate concentrations to around 1 mg P/L. In practice, a Fe:P molar ratio between 1 and 2 is generally used in wastewater plants to achieve phosphate concentrations around 1 mg P/L (Paul et al., 2001). But reducing the phosphate concentrations below 1 mg P/L using chemical precipitation requires significant increase in metal salt dosing due to the limitation by solubility product, which in turn leads to high sludge production, as well as due to the formation of metal hydroxides (Neethling, 2013; Sedlak, 1991). Fig. 9 (a) shows the relation between required Fe:P molar ratio and the residual phosphate concentration based on data from a wastewater plant (Sedlak, 1991). At residual phosphate concentration around 1 mg P/L, the ratio is near the stoichiometric region and the majority of the P removal is via precipitation. However, as the residual phosphate concentration decreases, the required ratio goes very high. In this zone, phosphate removal is mainly due to adsorption onto iron (hydr)oxide complexes (Sedlak, 1991). To quantify the effects of this in terms of cost, Fig. 9(b) shows a comparison of P removal costs via reversible adsorption and chemical precipitation with iron at 3 different concentrations: 10 to

1 mg P/L, 1 to 0.1 mg P/L and 1 to 0.016 mg P/L. A lowest concentration of 0.016 mg P/L was chosen since this allows us to use the adsorption capacity for porous iron oxides estimated at this concentration (Suresh Kumar, 2018 #6). This does not include the capital costs, but the chemical costs for adsorption and the chemical as well as disposal costs due to sludge formation via chemical precipitation. For chemical precipitation with iron, a Fe:P molar ratio of 2, 20 and 100 are assumed for the concentration ranges of 10 to 1, 1 to 0.1 and 1 to 0.016 mg P/L (Table S7 in supporting information shows parameters used for the calculation). The chemical cost for chemical precipitation to bring phosphate concentration from 10 to 1 mg P/L was around \$ 8/Kg P. This is in the same order of magnitude as estimated elsewhere (Paul et al., 2001). For adsorption, the chemical costs were calculated for porous metal oxide assuming that it is reused successfully for 30 cycles. Even if the equilibrium adsorption capacity for this adsorbent (FSP) at 1 mg P/L is considered as the practical loading value (Suresh Kumar et al., 2019), the cost to reduce phosphate concentrations from 10 to 1 mg P/L is around \$ 35/Kg P. However, as the phosphate concentration goes lower, the costs for adsorption compete and eventually better those of precipitation (see Fig. 9 (b)). This shows that adsorption is better suited for treating lower concentrations of phosphate.

The overall costs for reversible adsorption estimated in this review was compared with the costs of other technologies that achieve ultra-low P concentrations (≤ 0.15 mg P/L). The technologies compared here are as follows:

- i) Reversible adsorption (RAD) – This includes the estimates made in this review for overall costs to reduce phosphate from 1 to 0.1 mg P/L (denoted RAD-0.1) and from 1 to 0.016 mg P/L (denoted RAD-0.016) using porous metal oxide.
- ii) Acti-Flo – In this approach, soluble phosphorus is first removed by dosing iron salts. The resulting flocs are ballasted with microsand in the presence of a polymer. After providing sufficient time in a mixing tank, the water is passed onto a clarifier which removes the microsand along with flocs (Bolton and Menk, 2016). An effluent concentration of 0.17 mg P/L could be achieved by treatment using Acti-Flo.
- iii) Phoslock – Phoslock is a lanthanum modified bentonite that removes SRP by forming lanthanum phosphate precipitates. Cost estimation for Phoslock was based on the price of Phoslock (2750 €/ton) (Mackay et al., 2014) and on an average adsorption capacity of 9 mg P/g to reduce P concentrations to ≤ 0.05 mg P/L in surface water (Reitzel et al., 2013). This however does not include costs that might be incurred for dosing.
- iv) Microalgae - Cost for P removal by microalgae was based on the P uptake by microalgae and reported cost for microalgae production in Netherlands (Boelee, 2013; de Vree, 2016). The estimated cost is to reduce P concentrations upto 0.15 mg P/L.

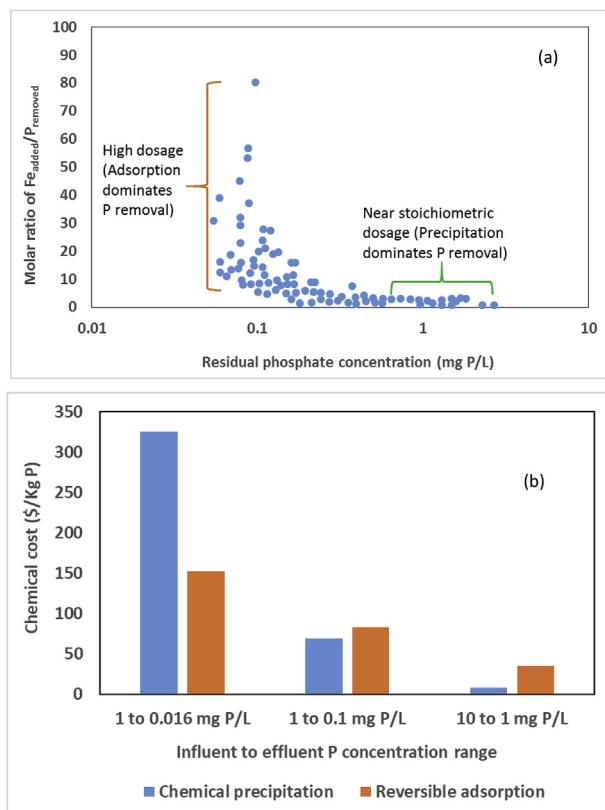


Fig. 9. (a) Increment in Iron dosing as a function of residual phosphate concentration. The plot has been made using data extracted from (Sedlak, 1991) using WebPlotDigitizer. (b) Comparison of chemical costs of reversible adsorption on porous metal oxides versus the cost related to chemical precipitation via iron dosing which includes cost for chemical consumption and sludge disposal. Note that chemical precipitation is the term used to denote P removal by dosing iron salts, although the actual removal can happen via multiple mechanisms.

Fig. 10 shows the cost comparison for P removal by these different methods. This includes the operational as well as capital costs wherever provided.

As can be seen from Fig. 10, RAD-0.1 along with Acti-Flo provide the least expensive options. There are other types of technologies like Acti-Flo, which include precipitation with metal salts aided by separation with sand (Newcombe et al., 2008; STOWA, 2009). The metal salts dosed result in soluble phosphorus removal by precipitation as well as by forming metal (hydr)oxide complexes which adsorb the phosphorus (Newcombe et al., 2008). However, as discussed earlier in reference to Fig. 9, P removal to concentrations lower than 0.1 mg P/L would require rather high dosing of these metal salts. Alternatively, the use of adsorption will be more suited

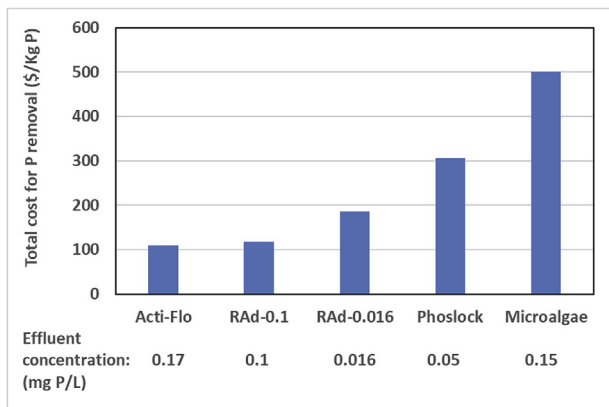


Fig. 10. Total cost for P removal via different treatment methods that can reach ultra-low concentrations of P. Final effluent concentrations corresponding to each method are listed under their names in the x-axis.

for reducing phosphate to even lower concentrations. As can be seen from Fig. 10, the cost of using reversible adsorption to reach a concentration of 0.1 mg P/L is about \$ 120/Kg P. But a further reduction to a concentration 6 times lower, i.e. 0.016 mg P/L, increases the overall cost only by a factor 1.6, i.e. about \$ 190 kg/P. This is rather due to the high affinity of adsorbents which will imply a high adsorption capacity at lower P concentrations. Thus reversible adsorption has the potential to give better economics compared to other methods when it is required to reduce the P concentrations further lower.

There is no consensus currently in literature as to a decisive cost for preventing eutrophication. However, a report on restoring the grand lake St. Mary in Ohio, estimated the loss due to excess P loading to \$ 102 million. Based on the amount of excess P loaded annually in this lake, the loss was estimated as \$ 708/lb P (Grand.Lake.St.Marys.Restoration.Commission, 2011). Thus, the cost of phosphate adsorption would be an economically viable option as per this estimate. However, a concrete assessment needs to be done by stakeholders and responsible organizations to establish a widely acceptable value to prevent eutrophication.

4. Conclusion

P removal to ultra-low concentrations is necessary to prevent

eutrophication. Adsorption studies show a possibility to consistently reach such low concentrations of phosphate. However, despite an increasing interest in scientific literature, a wide spread implementation of adsorption on commercial scale has not yet taken place. This may indicate that there are still important economic aspects that are not yet being addressed by the scientific community.

Therefore, this study performed an economic analysis for different types of adsorbents. A Monte Carlo simulation based scenario analysis showed that reusable adsorbents are more cost effective than one time use low cost adsorbents. Sensitivity analysis also showed that the most important parameters that govern chemical costs of adsorption are the adsorbent cost, practical loading and the adsorbent reusability. An expensive adsorbent can still be part of a cost effective process provided it has a high lifetime. For e.g. the cost of adsorption by hybrid ion exchange resins is comparable with that of porous metal oxides even though the adsorbent cost was 3–5 times higher for the resins. This was possible due to the assumption that the hybrid ion exchange resins could be reused about 100 times compared to the 30 times by the porous metal oxides.

Literature review also showed the research gaps involved in determining the parameters that govern the economics. Fig. 11 shows the key findings as well as future research potential in this direction. For instance, studies from the past 5 years show a big discrepancy between the adsorption capacity at 0.1 mg P/L ($q_{0.1}$) and the maximum adsorption capacity (q_{max}). Since adsorption is considered as a polishing step, it is necessary to have a high $q_{0.1}$. Practical loading is also governed by the adsorbent kinetics. Adsorption studies in general need to be done in realistic conditions since competing ions can either increase or decrease the adsorbent performance. Studies should focus on understanding the factors affecting adsorbent reusability so that a better estimation can be made regarding the adsorbent lifetime. Additionally, reusing the regenerate solution also needs more attention. Reusing the chemicals in the adsorption process is of economic and environmental significance.

Declaration of interests

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.

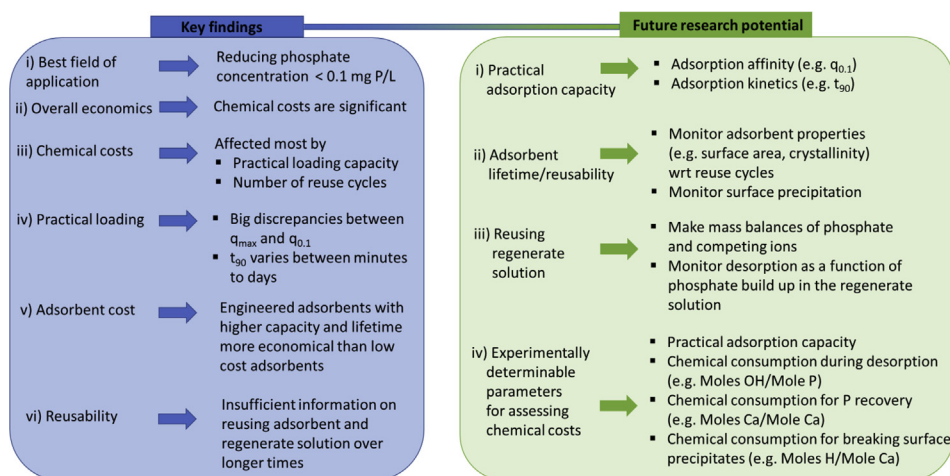


Fig. 11. Key findings and future research potential in the field of phosphate adsorption based on this review.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.wroa.2019.100029>.

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