CRANFIELD UNIVERSITY

Benjamin David Martin

Removal and Recovery of Phosphorus from Municipal Wastewaters using a Ferric Nanoparticle Adsorbent

School of Applied Sciences
Department of Sustainable Systems
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PhD
Academic Year: 2007 - 2010

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ABSTRACT

Phosphorus is removed from wastewater streams to prevent the ecologically harmful effects of eutrophication in receiving natural systems. Current chemical and biological techniques for removing phosphorus from wastewater are not able to practicably achieve the new discharge limit expected under the Water Framework Directive of 0.1 mg phosphorus L^{-1}. In addition, they do not represent an economically viable route for the recovery and reuse of the phosphorus they remove.

The use of a hybrid ferric nanoparticle adsorbent / ion exchange media is reported in this thesis that utilises the ligand strength of phosphorus to selectively remove it from wastewater, resulting in an effluent stream of less than 0.1 mg phosphorus L^{-1}, with a saturation capacity of 6.27 mg phosphorus g_{media}^{-1}. The removal behaviour fits adsorption models such as Langmuir, Freundlich, and Temkin. The limiting mechanism on phosphorus uptake is a mix of film and intraparticle diffusion, with a Biot number of 175, implying that intraparticle diffusion plays a more significant role. 90 % of the media's capacity for phosphate resides on the ferric nanoparticles, and competing ions such as sulphate only impact the remaining 10 % represented by the ion exchange component. The process can represent the sole removal technique at a treatment works, or be placed downstream of chemical or biological processes as a polishing step.

The media can be regenerated and reused for many fixed bed cycles, and a concentrated stream of 1000 mg phosphorus L^{-1} can be produced from the regeneration process using a single bed volume of 1 M sodium hydroxide, which recovers 80 % of the total phosphorus adsorbed onto the media from a service run. This partial regeneration scheme has no significant disadvantage in subsequent service runs, and maximises the concentration of the recovered phosphorus whilst minimising chemical use.

The ferric nanoparticle adsorbent addresses the twin aims of removal and recovery of phosphorus from wastewater via selective adsorption and desorption. It will allow the water industry to comply with new legislation, and help to ensure the sustainable use of phosphorus - a valuable and finite resource.

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1. Introduction

1.1 Background to the project

Phosphorus enters municipal wastewater treatment works from both domestic and industrial sources, with typical concentrations between 4 and 12 mg L^{-1} (Metcalf & Eddy, 2003). Under the Urban Wastewater Treatment Directive (EC, 1991), the levels of phosphorus in municipal wastewater streams must be reduced before discharge to the environment. The directive sets limits for discharge from sewage treatment works, and is typically 2 mg phosphorus L^{-1} for a 10,000 – 100,000 population equivalent, and 1 mg phosphorus L^{-1} for treatment works serving populations greater than 100,000 (EC, 1991).

Carbon, nitrogen and phosphorus regulate biological activity, and when their composition approaches a ratio of C:N:P = 106:16:1, optimum productivity occurs (Redfield, 1958; Redfield *et al.,*1963). Phosphorus has no atmospheric pool, unlike carbon and nitrogen, and this makes it the limiting nutrient for terrestrial and freshwater environments (Valsami-Jones, 2004). Phosphorus is therefore the key element that can lead to eutrophication (the excessive nutrient enrichment of waters), which can cause algal blooms that lead to a decrease in the quality of waters and a number of associated problems. During an algal bloom, microbial biomass also increases, taking up available oxygen in the water, decreasing the amount other organisms are able to use. This impacts on the biodiversity of the water system as fish and macrophyte ecologies are compromised. Specific blue-green algae species represent an additional impact due to their toxicity, which in bloom conditions can have serious consequences for wildlife and livestock (Herath, 1997).

In response to this continuing environmental challenge, the Urban Wastewater Treatment Directive is due to be updated with The Water Framework Directive (EC, 2000), which seeks to further improve surface waters to “good” ecological quality. Phosphorus is of particular concern in this context because of its potential for ecological damage. Although there is no widely accepted standard for the background concentration of phosphorus in river waters, a mean of 0.1 mg L^{-1} has been proposed (EA, 2000). This level refers to the concentration of soluble reactive phosphorus (the portion that is most available to biota). In a survey of 98 UK rivers, 80 % failed this target (Muscutt and Withers, 1996), and point (sewage effluent) rather than diffuse (agricultural) sources of phosphorus pose the most significant risk for river eutrophication because of the greater bioavailability of the phosphorus in sewage effluent (Jarvie *et al.,* 2006). The Water Framework Directive is expected to impose a reduction in consent limits to bring the phosphorus concentration of wastewater treatment works' final effluent in line with the 0.1 mg phosphorus L^{-1} found in natural waters.

1.2 Project development

Current treatment approaches are based on converting the soluble phosphorus in wastewater streams to insoluble forms, either by incorporating it into biological biomass or by using metal based coagulants to precipitate it. Traditional biological phosphorus removal is incapable of achieving an effluent stream of 0.1 mg phosphorus L^{-1} (Blaney *et al.,* 2007). Further, whilst it is possible to increase chemical dosing to attain this concentration, the additional cost, sludge production, and the water industry's drive towards chemical free treatment make it an undesirable option. An investigation into new techniques is therefore required, to enable the water industry to comply with the tighter consent limits and so protect the ecology of surface waters. Additionally, estimates of phosphate resources predict that they may be exhausted in as little as several decades (Kotabe, 1987). The dramatic rise in the price of phosphorus based fertiliser in 2008 (Figure 1.1), which saw diammonium phosphate prices almost double during the first quarter to nearly $1000 material ton^{-1} (Coons, 2008), means that sustainable use of this valuable and finite resource is becoming increasingly important.

Part of the reason for the 2008 increase was political, and has since stabilised somewhat (United States Geological Survey, 2010), but there is still increasing concern over the availability and quality of phosphorus rock resources. Because of this, the likelihood is that the value of phosphorus commodities will continue to increase.

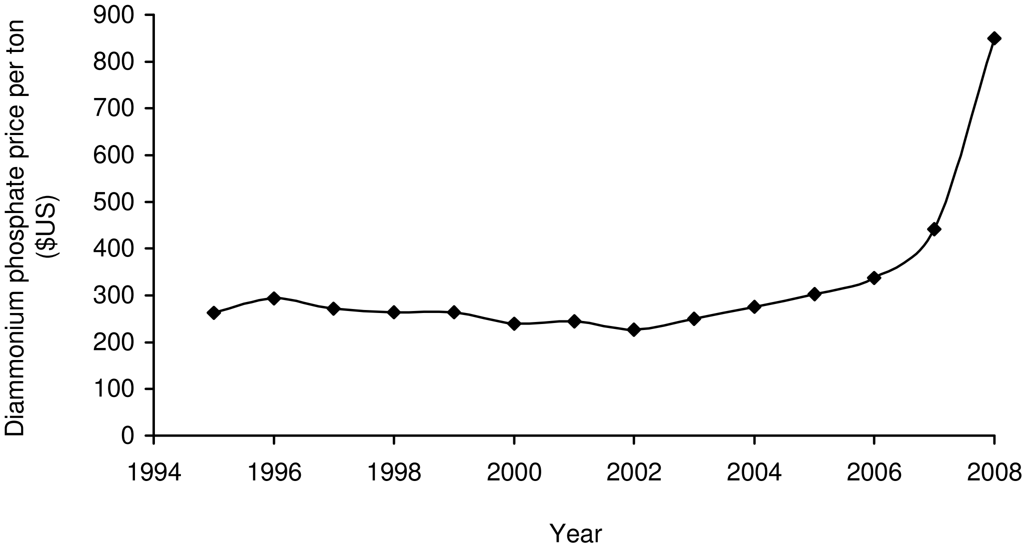

Figure 1.1: Price trend for the common fertiliser product diammonium phosphate (source: United States Department of Agriculture Economic Research Centre).

The most valuable phosphorus product that could be produced by the water industry is the crystalline solid struvite ($(NH_4)MgPO_4{\cdot}6H_2O$), which can be used as a fertiliser. The value of struvite is likely to be tied to the price of phosphate rock, and current fertiliser prices. Struvite is considered to be a better fertiliser than current commercially available products such as diammonium phosphate and monocalcium phosphate (superphosphate), because it has a much lower level of contamination from heavy metals, and the presence of magnesium means it is taken up more readily by plants than the commercial competition (Ricardo *et al.*, 2009). This means that struvite is likely to command a higher price, estimated at somewhere between £0.13 and £1.26 per kg (Jaffer *et al.*, 2002). Previous illustration of this is reported by Ueno and Fujii (2001), who sold struvite to fertiliser companies for £0.20 per kg.

Since phosphorus occurs in final effluent wastewater streams predominantly as phosphate anions (Snoeyink & Jenkins, 1980), an ion exchange process could be used. An initial literature review focused on the potential of adsorbent and ion exchange materials to achieve the dual aims of removal and recovery. Of the many natural and synthesised materials capable of removing phosphorus from wastewater, one newly developed product held the most potential. This material, a hybrid anion exchanger

(Blaney *et al.*, 2007), displayed a high capacity for removing phosphate. The process is also reversible and so the phosphate can be recovered. Additionally, the material can be used for many years without degrading. Based on work by Morel and Hering, (1993), and Zhao and Sengupta, (1998), immobilising particles of a transition metal cation onto a polymer base will enable it to act as an anion exchanger with a high affinity towards anions with strong ligand characteristics such as phosphate. The hybrid anion exchanger was made using such a process. The parent material is a standard polymeric strong base anion exchanger, into which hydrated ferric oxide nanoparticles have been dispersed (Figure 1.2).

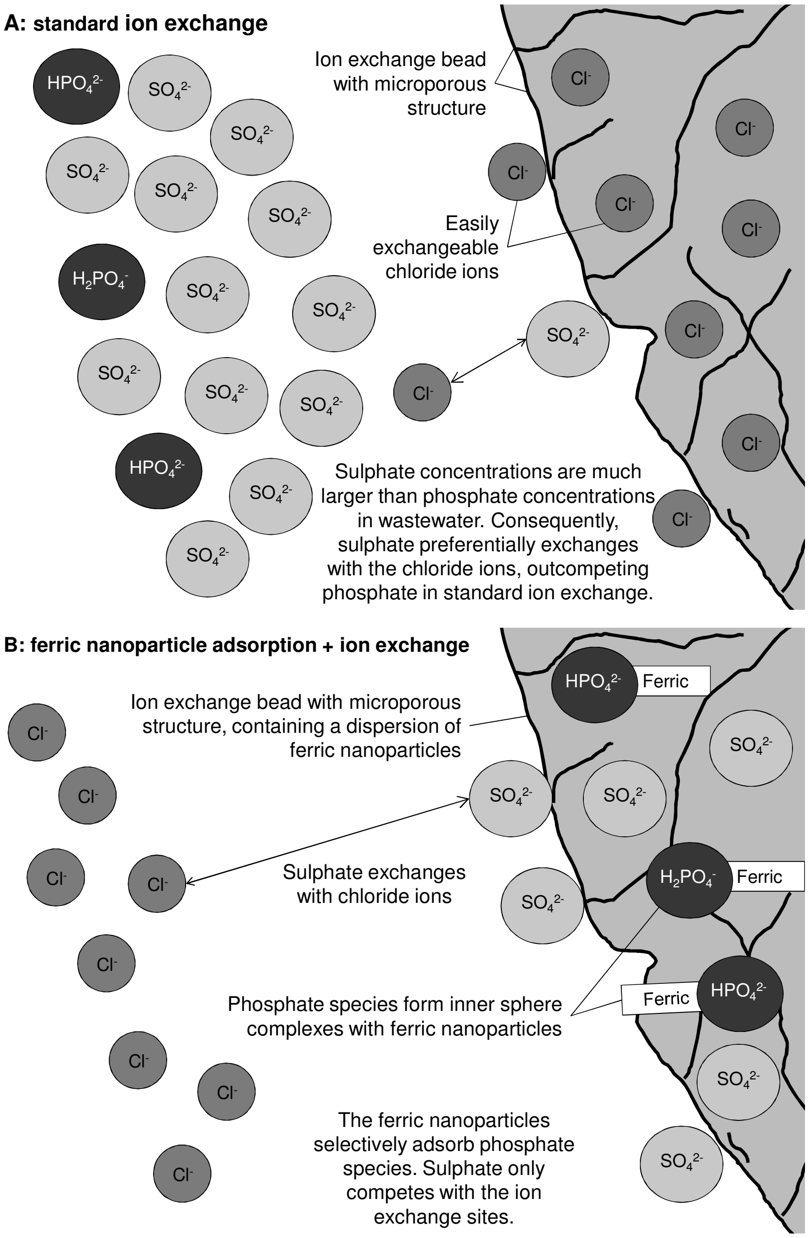

Figure 1.2: Mechanistic schematic of ion exchange (A), and ferric nanoparticle adsorption (B)

At above neutral pH the phosphate in wastewater streams exists primarily as the divalent anion HPO_4^{2-} (Zhao & Sengupta, 1998), and its intermediate, the monovalent $H_2PO_4^-$ (Blaney *et al.*, 2007). HPO_4^{2-} is a fairly strong bidentate ligand containing two oxygen donor atoms. Likewise, $H_2PO_4^-$ is a fairly strong monodentate ligand with one oxygen donor atom. The ligand strength of both forms (i.e. their ability to form inner sphere complexes with transition metals - for e.g. ferric iron) is much greater than the other inorganic anions commonly present in wastewater (Zhao & Sengupta, 1998). This enables the ferric nanoparticle adsorbent media to act as a phosphate selective ion exchanger, and because it can be regenerated in a similar manner as a conventional exchange resin, the phosphate can be desorbed and recovered.

1.3 Hypothesis

Based on the twin aims of enhancing removal and enabling efficient recovery of phosphorus from wastewater, and the promise shown by previous studies using a hybrid adsorbent, the following hypothesis was developed: *if adsorption can be phosphorus selective and reversible, then greater removal and efficient recovery will be achievable in wastewater treatment.*

1.4 Aims and objectives

The thesis aims to demonstrate the effectiveness of a ferric nanoparticle adsorbent to selectively remove phosphorus to produce an effluent quality of < 0.1 mg L^{-1}, in addition to providing a sustainable and economically sound method of recovering phosphorus from wastewater streams. The following objectives were developed to meet these aims:

- To elucidate the challenges of increasing removal rates and phosphorus recovery in terms of current practices, emerging techniques and the character of phosphorus in wastewater streams.
- To classify adsorption or ion exchange as the optimum phosphorus removal technique.

- To model the limitation mechanism of phosphorus uptake onto the adsorbent.
- To quantify the effect of competing ionic species on the adsorbent's phosphorus removal capacity.
- To quantify the levels of phosphorus recovery and regeneration efficiency.
- To confirm the operational applicability and economic validity of implementing such a process at full operational scale.

1.5 Thesis structure

The thesis is presented as a collection of discrete chapters, all contributing to the research objectives (Figure 1.3). To clarify the challenges of meeting a final effluent quality of 0.1 mg phosphorus L^{-1}, with viable phosphorus recovery, Chapter 2 is a "state of the art" review investigating the mechanisms underlying chemical and biological

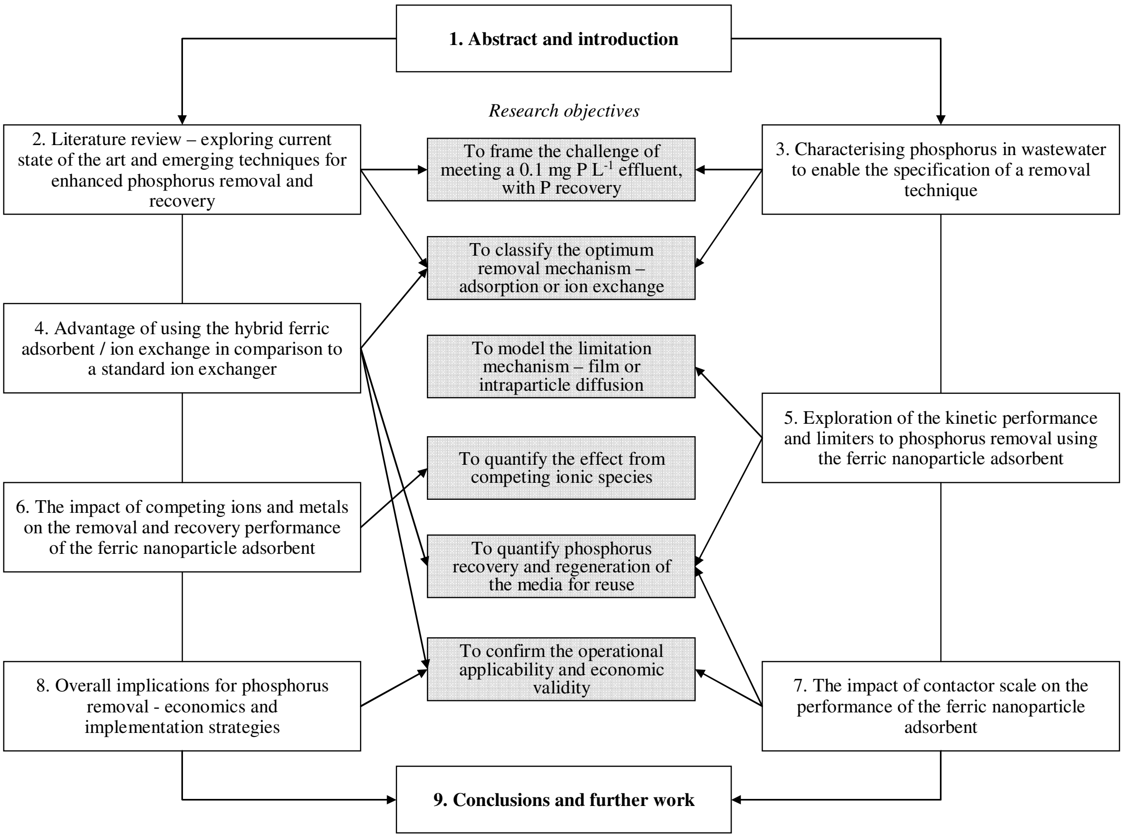

Figure 1.3: Thesis plan.

phosphorus removal, with a view to enhancing them and recovering the phosphorus in a usable form. Where this is not possible, alternative techniques using adsorption and ion exchange materials are explored, which have superior removal capabilities and recovery methodologies. This leads to the identification of the ferric nanoparticle adsorbent that becomes the main focus of the thesis.

Chapter 3 investigates the character of phosphorus in wastewater streams entering and leaving five UK treatment works in terms of speciation and molecular weight distribution. The work identifies that the majority of the phosphorus is inorganic, and dissolved, and that chemical and biological treatments do not adequately remove the dissolved fractions. The challenge for future techniques is therefore to be able to target the dissolved phosphorus, and it is shown that the ferric nanoparticle adsorbent is able to significantly reduce this fraction.

Chapter 4 details experimental work with the ferric nanoparticle adsorbent in relation to its performance when compared to a standard ion exchange resin, and when contacted with differing real wastewaters and model solutions. The adsorbent outperforms the ion exchange media, suggesting that adsorption is a more appropriate technique than ion exchange. The work also investigates repeat performance of the media after partial regeneration (to minimise chemical use), and finds that capacity and removal performance are unaffected, improving the economic potential of implementing the media at full scale.

Chapter 5 reports the findings of experimental trials with the ferric nanoparticle adsorbent to investigate its kinetic and equilibrium performance and the limiting mechanisms to phosphorus uptake. Additionally, the optimisation of the regeneration and recovery operation is explored.

Chapter 6 quantifies the effect of competing ions such as sulphate on the overall removal capacity of the ferric nanoparticle adsorbent, finding that competition only affects the ion exchange component of the media, leaving all of the adsorbent sites available for phosphorus.

Chapter 7 scales up the experimental work to much larger contact vessels than have been used with the media previously, and reports favourable increases in mass transfer and capacity with larger scales. It validates the technical feasibility of applying the ferric nanoparticle adsorbent at full scale, and also investigates the possible economics of the regeneration step.

Chapter 8 is an overall discussion of the findings presented in the previous Chapters, coupled with an economic analysis projecting costs and values for recovered phosphorus over a 20 year life cycle for placing the adsorbent at different treatment works, in comparison with the net present value of attaining a final discharge of 0.1 mg phosphorus L^{-1} using chemical dosing.

1.6 References

Blaney, L.M., Cinar, S., SenGupta, A.K., (2007). Hybrid anion exchanger for trace phosphate removal from water and wastewater. *Water Research* 41, pp. 1603-1613.

Coons, R., (2008). Prices soar in the first quarter on tight agricultural markets. *Chemical Week* **170** (13).

EC, (1991). Urban Wastewater Treatment Directive: http://eur-lex.europa.eu/smartapi/cgi/sga_doc?smartapi!celexapi!prod!CELEXnumdoc&lg=en&numdoc=31991L0271&model=guichett (Accessed November 2010).

EC, (2000). EC. Directive 2000/60/EC of the European Parliament and of the Council establishing a framework for the Community action in the field of water policy. Official Journal L 327, P. 0001-0073 (22/12/2000); 2000. http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=CELEX:32000L0060:EN:NOT (Accessed November 2010).

Forrest, A.L., Fattah, K.P., Mavinic, D.S., Koch, F.A., (2008). Optimizing Struvite Production for Phosphate Recovery in WWTP. *Journal of Environmental Engineering* **134** (5), pp. 395-402.

Herath, G., (1997). Freshwater Algal Blooms and Their Control: Comparison of the European and Australian Experience. *Journal of Environmental Management* **51**, pp. 217-227.

Jaffer, Y., Clark, T. A., Pearce, P., and Parsons, S. A. (2002). Potential phosphorus recovery by struvite formation. *Water Research* **36** (7), pp. 1834–1842.

Jarvie., H.P., Neal, C., Withers, P.J.A., (2006). Sewage-effluent phosphorus: A greater risk to river eutrophication than agricultural phosphorus? *Science of the Total Environment* **360,** (1-3), pp. 246-253.

Kotabe, H., (1987). Present situation and future of phosphate resources. *Gypsum Lime* 210, pp. 307-316.

Metcalf & Eddy, (2003). *Wastewater Engineering. Treatment and Reuse*. McGraw-Hill, New York.

Morel, F.M.M., Hering, J.G., (1993). *Principles and Applications of Aquatic Chemistry.* John Wiley and Sons, Inc., New York, NY.

Muscutt, A.D., Withers, P.J.A., (1996). The phosphorus content of rivers in England and Wales, *Water Research* **30**, pp. 1258–1268.

Redfield, A.C., (1958). The biological control of chemical factors in the environment. *American Scientist.* **46**, pp. 205-221.

Redfield, A.C., Ketchum, B.H. and Richards, F.A., (1963). The influence of organisms on the composition of sea water. In *The Sea, II* (ed. Hill, M.N.), Interscience, New York, pp. 26-77.

Ricardo, G-P., Lopez-de-Sa. E.G., Plaza, C., (2009). Lettuce response to phosphorus fertilization with struvite recovered from municipal wastewater. *Hortscience* **44** (2), pp. 426-430.

Snoeyink, V.L., and Jenkins, D., (1980). *Water Chemistry.* John Wiley and Sons, New York, NY.

Ueno, Y., and Fujii, M., (2001). Three years experience of operating and selling recovered struvite from full-scale plant. *Environmental Technology* **22** (11), pp. 1373–1381.

United States Department of Agriculture Economic Research Service, (2008). http://www.ers.usda.gov/Data/FertilizerUse/Tables/Table7.xls Accessed November 2010.

United States Geological Survey, (2010). Minerals information: phosphate. http://minerals.usgs.gov/minerals/pubs/commodity/phosphate_rock/mcs-2010-phosp.pdf. Accessed November 2010.

Valsami-Jones, E., (2004). The Geochemistry and mineralogy of phosphorus. In *Phosphorus in Environmental Technologies* (ed. Valsami-Jones, E.), IWA Publishing, London, pp. 20-50.

Zhao, D., Sengupta, A.K., (1998). Ultimate removal of phosphate from wastewater using a new class of polymeric ion exchangers. *Water Research,* **32** (5), pp. 1613-1625.

2. Towards a final effluent phosphorus concentration of 0.1 mg L^{-1} in municipal wastewater: a review of the available techniques

2.1 Introduction

Phosphorus is an essential nutrient for all living things. It is a component of both DNA and RNA, is present in animal skeletons, and used in metabolism. In plants it has a role in numerous biochemical reactions, and transports energy as the nucleotide adenosine triphosphate. In addition to phosphorus, carbon and nitrogen comprise the main elements that regulate biological activity. When their composition approaches a ratio of C:N:P = 106:16:1, optimum productivity occurs (Redfield, 1958; Redfield *et al.,* 1963). Carbon and nitrogen are available from the atmosphere, but phosphorus is not, and this makes it the limiting nutrient for terrestrial and freshwater environments (Valsami-Jones, 2004).

2.1.1 Phosphorus as a pollutant

Because phosphorus is the main limiting nutrient in natural systems, it is the key to eutrophication (the excessive nutrient enrichment of waters), which can lead to algal and bacterial blooms that decrease the quality of freshwater systems. During a bloom, algal biomass can form a thick, floating mat which prevents light from reaching plants under the surface. When algal organisms die, they sink to the bottom where they are digested by bacteria living on the sediment. It is this mechanism that causes a bacterial bloom in conjunction with an algal bloom, and the increased bacterial activity consumes dissolved oxygen. This has an adverse impact on the biodiversity of the water system as both fish and macrophyte ecologies are compromised. Additionally, certain blue-green algae species are toxic and in bloom conditions, can have serious consequences for wildlife and livestock (Herath, 1997). Values for phosphorus concentrations that might tip the balance towards eutrophication are not well defined, as the characteristics of each water body will influence the response to an enrichment event. But what is known is that phosphorus pollution significantly increases the risk of eutrophication, and that point (sewage effluent) rather than diffuse (agricultural) sources of phosphorus pose the most significant risk for river eutrophication (Jarvie *et al.,* 2006). In 1991, the Urban Wastewater Treatment Directive (EC, 1991) sought to protect natural waters from the harmful effects of sewage discharges. Limits were set to restrict the release of phosphorus based on the size of the population each treatment works served. Currently, typical limits for discharge from sewage treatment works are 2 mg phosphorus L^{-1} for a 10,000 – 100,000 population equivalent, and 1 mg phosphorus L^{-1} for treatment works with a population equivalent larger than 100,000 (EC, 1998). Smaller works (i.e. those serving a population less than 10,000) may still have consents in place if they discharge to an ecologically sensitive zone, but the strictest limit remains at 1 mg L^{-1} phosphorus in the United Kingdom.

The Urban Wastewater Treatment Directive is being replaced by the Water Framework Directive (EC, 2000), which seeks to improve surface waters to “good” ecological and chemical quality. Programmes of measures to achieve these aims are due by 2012, and the deadline for meeting the environmental objectives is 2015. In terms of the phosphorus objective, it is expected to tighten the concentrations permitted to be released into the environment by the water industry. This may go as far as legislating that final effluents from treatment works have an equal phosphorus concentration to the natural waters they are discharged to. Although there is no widely accepted standard for the background concentration of phosphorus in river waters, a mean of 0.1 mg of phosphorus L^{-1} has been proposed (EA, 2000). This level refers to the concentration of soluble reactive phosphorus – the portion that is most available to biota. In a survey of 98 UK rivers, 80 % failed this target (Muscutt & Withers, 1996). More recently, the UK Environment Agency, in their assessment of current ecological status, have found occasions where phosphorus standards are not being met, but there is no impact on the biological community. In other natural systems, they found pronounced detriment to biological systems where phosphorus standards are not being met, and generally consider the weight of evidence to indicate that phosphorus elevation has an adverse impact (EA, 2011).

In the main, there are two techniques currently employed by the UK water industry to remove phosphorus from wastewater: chemical and biological. The chemical removal method works by dosing iron or alum salts, which cause phosphorus to precipitate out of solution, settle, and be removed as sludge. Biological removal uses bacteria to incorporate phosphorus from solution into biomass, which is also settled and removed as sludge. Both of these techniques are successful at removing sufficient concentrations of phosphorus to meet the stipulations of the Urban Wastewater Treatment Directive. However, traditional chemical precipitation and biological nutrient removal processes are unable to practicably reduce phosphate concentrations below 0.1 mg of phosphorus L^{-1} (Blaney *et al.,* 2007). Enhanced techniques will therefore need to be employed by the water industry to enable the necessary improvements in phosphorus removal to comply with the new legislation.

2.1.2 Phosphorus as a resource

To sustain crop yields for food production, phosphate fertiliser must be applied to agricultural land. At the present time, this phosphate is derived from non-renewable natural resources of rock. Whilst it is acknowledged that energy and water issues must be addressed for meeting the future nutritional demands of a growing population, the need for securing phosphorus supply for fertiliser production has not been widely recognised (Cordell *et al.*, 2009). Based on the most extreme predictions, phosphate rock reserves could be exhausted in the next 50 - 100 years (Kotabe, 1987; Steen, 1998). Political and business interests conspire to make accurate predictions impossible. For example, the United States Geological Survey (USGS) relies on information from foreign governments and cannot communicate directly with the producers of phosphate commodities. Their data is based on second and third hand information which changes constantly (Gilbert, 2009). Whilst quantifying the amount of phosphate resources available for the future remains uncertain, the effects of scarcity are already becoming apparent. In 2008, fertiliser prices rose dramatically and acute shortages caused social unrest in many developing countries. "Fertiliser riots," hoarding, black marketing, and violence were reported in India, Pakistan, Ethiopia, The Philippines, Taiwan, Nigeria, Vietnam, Kenya, Nepal, and Egypt (IFDC, 2008). The need for sustainable use of this valuable and finite resource is evidently becoming increasingly important.

The global population excretes about 3 million tonnes of phosphorus annually, and about 20 million tonnes of phosphorus is used each year in fertiliser (Cordell *et al.*, 2009). The recovery of wastewater phosphorus for use as fertiliser could play a key role in securing future supply. The water industry is now changing its perception of phosphorus as a pollutant, to seeing it as a resource. The priority will always be the removal of phosphorus (as oppose to the recovery of it) from wastewater plants to prevent eutrophication, but an opportunity for sustainability exists in the removal techniques chosen. As infrastructure and operator experience is already in place for chemical and biological techniques, it would be economically preferable to stay as close to these methods as possible. The aim of this review is to investigate recent studies that have attempted to enhance phosphorus removal and recovery using modifications and additions to biological and chemical techniques, or that have trialled alternative solutions such as adsorbents and ion exchangers.

2.2 Biological phosphorus removal

For hundreds of years, bacteria have increased the efficiency of wastewater treatment systems, despite the lack of a detailed understanding of their role (Weismann *et al.*, 2007). Only in the last century, when what became known as the *activated sludge* process was studied, did a better understanding begin to develop. Arden and Lockett (1914) optimised conditions for the degradation of organics by increasing the concentration of aerobic bacteria using sludge sedimentation and recycling. This is achieved by bubbling atmospheric air or pure oxygen through primary treated (screened and settled) wastewater. Bacteria thrive in these conditions and take in nutrients, and degrade organic material. This combination of wastewater and biomass (mixed liquor), after sufficient contact time has passed, is transferred to a settling tank. The supernatant is decanted off for further treatment (for e.g. settlement / filtration before discharge), and a portion of the settled sludge is returned to the aeration tank to re-seed the process.

The problem with a conventional activated sludge plant is that the bacteria only use enough phosphorus to satisfy their basic metabolic requirements, which only results in removal rates between 20 and 40 % (Brett *et al.*, 1997). Typical influent concentrations of total phosphorus to UK wastewater treatment works are between 5 and 10 mg L^{-1} (see Chapter 3). An activated sludge plant would therefore be expected to result in effluent phosphorus concentrations of 2 - 4 mg L^{-1} if it removes 40 % of the influent concentration. This is only just efficient enough to meet the loosest discharge consent of 2 mg L^{-1}, provided the influent concentration never exceeds 5 mg L^{-1}. However, this can be remedied relatively easily. A class of bacteria, known as polyphosphate accumulating organisms (PAOs) can, in the right conditions, take up phosphorus in excess of that needed for normal metabolism, a phenomenon termed *luxury uptake*. To create these conditions, an anaerobic tank is placed in front of the aerobic stage (Figure 2.1).

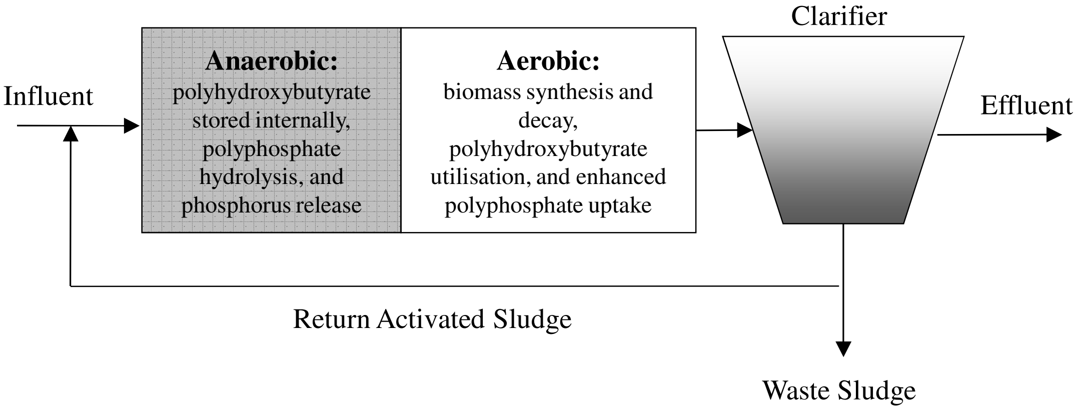

Figure 2.1: The Activated Sludge process, with anaerobic zone (adapted from Metcalf & Eddy, 2003).

The return activated sludge is transferred from the clarifier and contacted with primary treated wastewater here. When subjected to anaerobic conditions in the absence of nitrates and oxygen, PAOs are able to take up short chain fatty acids, such as acetates, as a feed stock. The stored polyphosphates are used as an energy source, and phosphate is released into the reactor liquor. Acetates are stored as polyhydroxybutyrate inside the cells until they reach the aerobic zone of the reactor, at which point it is metabolised, providing energy within the cell for uptake of all available orthophosphate, including that in solution (Brett *et al.*, 1997).

A complicating factor is the nitrate found in wastewater. If present in the anaerobic zone, it has an adverse effect on the competitive advantage PAOs have over other bacteria. In these conditions, heterotrophic bacteria will use nitrate to consume readily biodegradable chemical oxygen demand (rbCOD) in the anaerobic zone, leaving less for PAOs, resulting in an overall decrease in phosphorus removal efficiency (Metcalf & Eddy, 2003). If the influent stream to a works has a high nitrate concentration, or if a discharge limit has been placed on nitrate leaving the works, an anoxic zone must be added to the plant. In an anoxic environment, biological denitrification is achieved by both NH_4-N oxidation and NO_3-N and NO_2-N reduction to nitrogen gas (Metcalf & Eddy, 2003). In this configuration, the return activated sludge is passed to the anoxic zone from the final clarifier, and the mixed liquor recycle to the anaerobic zone is drawn following the anoxic zone (Figure 2.2) where the nitrate concentration is minimal (Metcalf & Eddy, 2003).

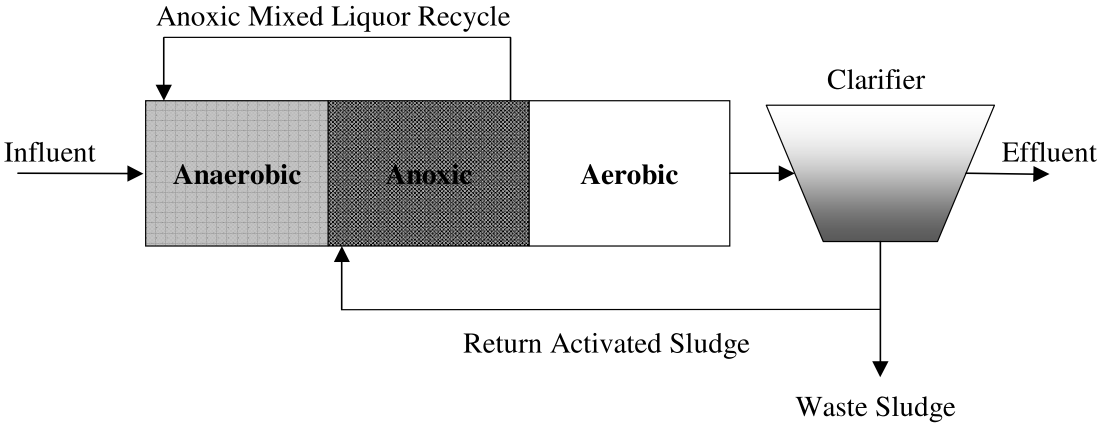

Figure 2.2: The Activated Sludge process, with anaerobic and anoxic zones to facilitate phosphorus removal (adapted from Metcalf & Eddy, 2003).

Many configurations are in use which follow the basic processes outlined above, and are determined by the character of the wastewater flowing into the works, and the discharge limits imposed. These consist of the modified activated sludge process, discussed above and shown in Figure 2.2, and the Bardenpho, Phoredox, Rotanox, sequencing batch reactor and A/O processes (Table 2.1). For brevity, they will not be explored in detail here, but key general observations across all configurations are discussed.

Biological phosphorus removal, as described above, is capable of reducing the effluent phosphorus concentration to below 1 mg L^{-1} (see Chapter 3). However, the performance of a biological phosphorus removal system depends on a variety of factors. There needs to be a constant and readily biodegradable supply of chemical oxygen demand (COD) in the sewage, including volatile fatty acids such as acetate.

Table 2.1: Performance of biological phosphorus removal plants.

Type	Flow (m^3 d^{-1})	Sludge age (days)	Influent		Removals		Effluent P ($mg\ L^{-1}$)
			BOD ($mg\ L^{-1}$)	P ($mg\ L^{-1}$)	BOD (%)	P (%)	
Mod AS	4,800	8-69	780	10.5	-	>60	-
Bardenpho	23,000	22-25	225	7	98	94	0.43
Bardenpho	-	-	394	9.6	83	95	0.5
A/O	53,000	-	125	3.5	92	82	0.63
SBR	770	-	170	8.5	95	86	1.2
A/O	12,100	-	145	8.9	94	79	1.8
Bardenpho	5,300	-	164	8.2	98	65	2.9
Mod AS	215,000	<2	220	10.1	-	49	5.2
Bardenpho	150,000	-	570	9.4	90	19	7.1
Mod AS	22,400	3	177	35	87	77	8
Rotanox	35,000	12-18	150	14	95	41	8.3

Source: Bowker & Stensel (1990).

An organic substrate is vital in order to create a biological demand for phosphorus, and many biological treatment works rely on an industrial source of carbon (Table 2.2) (also see Chapter 3). This is perhaps the biggest problem with using biological treatment to reach the possible new consent limit of 0.1 mg L^{-1} phosphorus in the final effluent - securing an economically and operationally sound source of external carbon to enhance the process sufficiently enough. Additionally, because of the combined rainwater / wastewater sewer system in the UK, in periods of high rainfall, microorganisms can be starved as the nutrients they need are diluted.

Table 2.2: Performance of biological phosphorus removal works with varying organic substrates.

Carbon source	**Phosphorus removal (%)**	**Reference**
Septic sludge	97	Morling (2001)
Glucose and acetate (50/50)	90	Kargi & Uygar (2003)
Fermented swine wastes	89	Lee *et al.,* (1997)
Acetic acid	84	Tam *et al.,* (1992)
Fermented organic fraction of municipal solid waste	84	Pavan *et al.,* (1998)
Methanol	80	Nyberg *et al.,* (1996)
Ethanol	80	Nyberg *et al.,* (1996)
Nightsoil	79	Choi *et al.,* (1996)
Fermented food waste	73	Lim *et al.,* (2000)
Anaerobically fermented leachate of food waste	68	Lee *et al.,* (1997)
Glucose	40	Tam *et al.,* (1992)
Wine distillery effluent	40	Bernet *et al.,* (1996)

2.2.1 Understanding how to optimise enhanced biological phosphorus removal

The history of using bacteria to treat wastewater is characterised by empirical development alone. The engineering requirements of an enhanced biological phosphorus removal (EBPR) process are known, but a full understanding of how the biochemical mechanism works is not. The difficulties of isolating pure cultures that demonstrate the complete characteristics of PAOs are well documented (Mino *et al.,* 1998), but some studies are beginning to identify the bacterial species responsible for EBPR (Table 2.3). Until the functions of the microbial species present in the ecosystem of an EBPR plant are understood, the frequent unreliability of the process cannot be addressed (Seviour *et al.*, 2003). There are many factors thought to be responsible for performance deteriorations, including: ready supply of Mg^{2+}, over-aeration, incorrect anaerobic contact and solids retention times, and influent substrate composition, i.e. external carbon.

2.2.2 The role of magnesium

Schonborn *et al.* (2001) artificially enhanced the influent magnesium concentration in a bench scale plant from 15 to 24 mg L^{-1} and 31 mg L^{-1}. This resulted in an increase of phosphorus removal efficiency from 85 to 97 %. The EBPR operation was stable over a long experimental period and the study was able to exclude the effect of the chemical precipitation of magnesium ammonium phosphate. This suggests that magnesium is a key element for EBPR efficiency. The study also investigated the possible role of calcium but found it to be of a much lower significance than magnesium, indeed when magnesium was dosed the ratio of Mg : Ca in the biomass was twice as high. The authors recommend that if an EBPR process is underperforming, the Mg content of the influent should be taken into account.

2.2.3 Over-aeration

It has been found that phosphorus uptake stops due to a gradual depletion of poly-hydroxybutyrate in an over aerated process (from 312 mg L^{-1} to 36 mg L^{-1} in a

Table 2.3: Bacterial species thought to be involved in enhanced biological phosphorus removal (From de Bashan & Bashan and references therein).

Genera or species	Evidence for role in EBPR	Evidence against role in EBPR	Reference
Acinetobacter sp.	Cultures show prevalence in systems exhibiting EBPR Accumulation of polyphosphate and polyhydroxyalkanoate under aerobic conditions	Bias in detection method used. Only present as 10 % of EBPR sludge Acetate uptake mechanism that characterises EBPR is not exhibited by *acinetobacter* spp.	Mino *et al.,* (1998), Christensson *et al.,* (1998),
Microlunatus phosphovorus	Accumulation of polyphosphate under aerobic conditions, and glucose uptake in anaerobic conditions	No acetate uptake or accumulation of PHA under anaerobic conditions	Eschenhagen *et al.,* (2003)
Lampropedia sp.	Accumulate polyphosphate and poly β hydroxybutyrate. Bacteria take up acetate, store it as PHA with polyphosphate degradation and release of orthophosphate	Colonies have a sheet-like organisation which is uncommon in EBPR processes	Stante *et al.,* (1997)
Rodocyclus sp.	Possess key metabolism of PAO, and these groups make up > 81 % of the population of bacteria present in EBPR processes	None	Lee *et al.,* (2003)
Tetrasphaera sp.	Phosphate accumulating coci.	Similar to glycogen accumulating bacteria from activated sludge	Eschenhagen *et al.,* (2003)
Paracoccus denitrificans	Polyphosphate - accumulating bacterium	Does not need an alternating anaerobic / aerobic cycle for phosphate accumulation	Maszenan *et al.,* (1999)
Burkholderia cepacia	Contains intracellular polyphosphate granules	None	Mullan *et al.,* (2002)
Agrobacterium sp., *Aquaspirillum* sp., *Micrococcus* sp., *Staphylococcus* sp., *Acidovorax* sp., *Microsphaera multipartite, Dechlorimonas* sp., yeasts and Cytophaga-Flavobacteria group	Found in large and dominant numbers in EBPR processes	None	Merzouki *et al.,* (1999), Ahn *et al.,* (2002), Melasniemi *et al.,* (1998), Van Ommen Kloeke & Geesey (1999)

study by Brdjanovic *et al.*, (1997)). This occurs because higher dissolved oxygen levels increase protein production and growth, and decrease the need for microbes to produce polyhydroxybutyrate (Chen & Page, 1997).

2.2.4 *Anaerobic contact and solids retention time*

An anaerobic contact time longer than three hours can cause a phosphorus release which is not associated with acetate uptake. When this happens, it shows that the bacteria have not accumulated polyhydroxybutyrate for subsequent oxidation in the aerobic zone (Metcalf & Eddy, 2003), and causes a depletion in cellular energy (Wang & Park, 2001). PAOs with lower cellular energy are likely to be out competed by nonPAOs in EBPR systems (Wang & Park, 2001).

2.2.5 *Influent substrate composition - external carbon*

If the carbon available in the influent to a treatment works is not enough to achieve satisfactory nutrient removal, an additional source must be supplied (Puig *et al.*, 2008). The volatile fatty acid (VFA) acetate ($C_2H_3O_2$) has been successfully tested to improve biological phosphorus removal performance in recent years (Isaacs & Henze, 1995). Other VFAs, such as propionate, butyrate, valerate, isovalerate, and lactate have been used for EBPR purposes (Oehmen *et al.*, 2004; Pijuan *et al.*, 2004), and ratios of the COD these represent to phosphorus removal are variable (Table 2.4). Whilst acetic and isovaleric acids offer the most efficient ratio of dosing to phosphorus removal, there are also economic and broader operational considerations which will determine which VFA to choose.

Table 2.4: Ratios of fatty acids utilised per mg phosphorus removed.

Volatile fatty acid	**mg COD utilised : mg P removed**
Acetic acid	19
Isovaleric acid	24
Propionic acid	32
Isobutyric acid	36
Butyric acid	39
Valeric acid	94

Source: Abu-Ghararah & Randall, 1991.

Isaacs & Henze's (1995) study investigated the effects of both acetate and hydrolysate on the rate of denitrification in an alternating activated sludge process that included biological phosphorus removal. Adding these carbon sources to the anoxic zone caused an instantaneous increase in the denitrification rate. Importantly, the results were reasonably reproducible which means these sources could be used as a control variable to increase the performance of the process. What is slightly unclear is the direct effect of their addition on phosphorus removal (a question still remained about anoxic phosphate release). However, the improvement of denitrification means that the anoxic mixed liquor recycle to the aerobic zone improves conditions for PAOs.

Acetic and propionic acids are the two most common volatile fatty acids present in domestic wastewaters (Chen *et al.*, 2004). Also in 2004, Oehmen *et al.* further developed the idea that propionate is a better substrate than acetate. The authors used propionate as the sole carbon source and found that in comparison to acetate, the organisms produce less CO_2, and hydrolyse less glycogen per mole of VFA uptake. As well as PAOs, glycogen-accumulating organisms (GAOs) take up VFAs via the hydrolysis of glycogen (Puig *et al.*, 2008). As explored above, GAOs do not contribute to phosphorus removal and are considered competitors of PAOs (Mino *et al.*, 1998). Consequently, a lower level of hydrolysed glycogen suggests that conditions were not so favourable for GAOs, which meant less competition for PAOs, which resulted in higher phosphorus removal efficiency. Pijuan *et al.*'s (2004) study also found that propionate use is favourable to acetate, as it resulted in less anaerobic phosphorus release.

Puig *et al.*'s (2008) study attempted to quantify the effects of adding alcohols (ethanol and methanol), or short-chain volatile fatty acids (VFAs) (i.e. acetate and propionate) as the external carbon sources for enhanced biological phosphorus removal (EBPR). The addition of alcohol does work, but an acclimatisation period is required. VFAs result in more dependable phosphorus removal and elicit a much faster response from the microbial community (Puig *et al.*, 2008).

As a result of the high COD : P ratios required for biological systems to meet low effluent consents, biological phosphorus removal plants are usually limited to situations where industrial inputs provide the necessary carbon. In practice, carbon is not added to biological processes to improve phosphorus removal. If plants are underperforming, chemical coagulants are usually added to meet phosphorus consents (See section 2.4).

2.2.6 Phosphorus recovery from the EBPR process

Applying sludge directly to agricultural land as a fertiliser is an attractive prospect for the water industry. Biological sludge, in addition to comparatively high levels of phosphorus, also contains the other nutrients needed to sustain crops. However, direct land application of sludge is not permitted because of concerns about pathogens, odour, and contaminants such as heavy metals (DEFRA, 2009), and industrial waste products. Sludge destined for agricultural land in the UK must undergo further treatment to satisfy the requirements of the Safe Sludge Matrix (ADAS, 2001), which details the levels of further treatment required and the harvest frequencies of crops that have been fertilised with sludge. Additional treatment usually takes the form of anaerobic digestion, chemical treatment or heat treatment. Even after additional sludge treatment, problems remain with predicting and measuring the levels of nutrients present in each load applied to the soil, as nutrient runoff and excessive enrichment must be avoided (DEFRA, 2009).

Whilst some plans are in place to help with applying sludge directly to land (DEFRA, 2009), the most appealing product to the agricultural industry and food consumers alike would be one that is removed from the biomass. In treatment works, a mineral known as struvite (magnesium ammonium phosphate) precipitates out of solution spontaneously and causes a troublesome build up in pipes. However, it can be used as a slow release fertiliser, and the formation of a struvite product from mixed liquors has been detailed in the literature (Forrest *et al.*, 2008), and results in a pure product for which a market is rapidly growing. A recent study of a commercial struvite manufacturing operation at a wastewater treatment plant generated 272,200 kg of struvite, representing 34,500 kg of phosphorus (Britton & Baur, 2010).

There are many problems with relying on EBPR to meet the new consent limits for phosphorus discharge (Table 2.5). Even if the process becomes better understood in the near future to enable greater optimisation, and a single step solution for making the sludge into a safe, marketable product is developed, the extra infrastructure would require heavy investment.

Table 2.5: Advantages and disadvantages of enhanced biological phosphorus removal.

Advantages	Disadvantages
Sludge volumes are similar to those produced by conventional biological treatment processes.	Phosphorus removal is limited by the biochemical oxygen demand (BOD) : phosphorus ratio of the influent stream, specifically low molecular weight substrates.
Installation at existing activated sludge plants requires relatively little new equipment, providing sufficient capacity already exists.	Secondary clarifier performance must be efficient to achieve effluent concentrations of 1 mg phosphorus L^{-1}.
Existing sludge handling methods can be used provided the risks of phosphorus resolubilisation are controlled.	Cannot be used to retrofit fixed film processes.
No chemical additive costs.	Standby chemical treatment is often required in case of low performance or failure of the biological system (due to high rainfall, shock loads of pollutants etc).
Improved process control reduces numbers of filamentous organisms.	Sludge can have poor settling characteristics.
Resulting sludges are enriched in phosphorus and are potentially more useful for agricultural application.	Increased retention time required in activated sludge plants.

Source: EU (2002).

2.3 Chemical phosphorus removal

Chemical removal plants are comparatively easy to incorporate into existing works, and are not limited by the COD : P ratio. Additionally, in comparison to biological systems, they are less susceptible to shock loads, temperature changes, and alterations in feed concentrations. There is no lag time in bringing a chemical plant online, unlike a biological treatment plant where performance slowly improves as the microbial ecosystem becomes established. Consequently, the majority of UK treatment works utilise a chemical precipitation method to both remove suspended particles and reduce phosphorus concentrations, at a variety of treatment stages (at the influent, in the aeration basin of an activated sludge plant, and before or after secondary settlement) (Carliell-Marquet, 2010). Since phosphorus in wastewater occurs mainly as dissolved phosphate species (see Chapter 3), removal by chemical dosing is through a precipitation reaction pathway which forms precipitates of sparingly soluble phosphorus (Metcalf & Eddy, 2003), according to the following reaction:

$$\mathrm{Fe}^{3+} + \mathrm{H}_n\mathrm{PO}_4^{3-n} \Leftrightarrow \mathrm{FePO}_4 + n\mathrm{H}^+$$

In spite of the simplicity of the above equation, there are many competing reactions and the effects of alkalinity, pH, trace elements, and ligands all have a bearing on the dose of chemical needed to remove a given concentration of phosphorus (Metcalf & Eddy, 2003).

The typical molar ratio needed to reach current consent limits is around 2.7 iron to 1 phosphorus by mass, but can vary depending on the chemical used (Table 2.6).

Table 2.6: Chemical : phosphorus ratios required for varying degrees of removal.

Phosphorus removal (%)	**Iron (III) chloride requirement, molar ratio (Fe:P)**	**Iron (III) hydroxide requirement, molar ratio (Fe:P)**	**Iron (III) chloride and hydroxide requirement, molar ratio (Fe:P)**
50	0.57	2.85	0.83
70	1.08	3.86	1.42
80	1.48	>4.80	1.86

Source: (Thistleton et al., 2002).

In order to reach the much lower consent limits expected under the WFD, a dose of 8 Fe to 1 phosphorus is required (see Chapter 8). This would have a severe economical impact on the industry, as well as increasing the production of sludge and its associated problems. The Water Framework Directive may also result in stricter limits being placed on other chemicals, such as those that make coagulants, being released into freshwater systems, perhaps necessitating further treatment downstream of the coagulation stage. It would therefore be beneficial to identify any techniques that might result in an improvement to phosphorus removal rates using chemical methods.

Chemical coagulation is often used upstream of an activated sludge process. This can improve overall phosphorus removal by upwards of 60 % when compared to an activated sludge process alone (Lees *et al.*, 2001). The amount of chemicals needed can also be reduced to metal : phosphorus ratios as low as 0.5 : 1 (Lees *et al.*, 2001).

However, it is likely that for much of the time, a residual amount of coagulant is carried over into the downstream biological treatment process. This is problematic as it can lead to the accumulation of heavy metals in the sludge, a decrease in biological and chemical oxygen demand, suspended solids removal efficiencies, an inhibition of nitrification, a change in the biological ecosystem, and poor biomass flocculation (Lees *et al.*, 2001, and references therein). It has been shown that microbial respiration rates are reduced when the metal based coagulants come into contact with them (Lees *et al.*, 2001 (b); Dorea & Clarke, 2008).

Another way to improve the efficiency of the process is with the addition of coagulant aids. Organic polymers, such as tannic acid have been shown to increase phosphorus removal by 1 - 5 %, (Zhou *et al.*, 2008), and the polyelectrolyte AN913, when added to aluminium chloride increased removal by 30 % (Ozacar, 2003). Effectiveness can also be improved with the use of pre-polymerised inorganic coagulants. The first to be developed were polyaluminium chloride (PAC), described by Dempsey *et al.*, (1984), and polyferric chloride (PFC), described by Leprince *et al.*, (1984). Studies of the coagulation chemistry have shown that it is a range of hydrolysed aluminium or iron species that are responsible for the removal of suspended particles and colloidal impurities (Jiang & Graham, 1998). As a consequence, a range of competing reactions occur that necessitate a higher initial dose (Jiang & Graham, 1998). This means that removal efficiencies are liable to fluctuate depending on the influent water characteristics at any time. To overcome this problem, the water industry usually "overdoses" coagulant to ensure compliance with their consent limits (Jiang & Graham, 1998). Pre-polymerisation offers control over the hydrolysis species that form and can therefore improve performance, and reduce the amount of chemicals required (Table 2.7).

Table 2.7: Removal performance using anionic polymer (Magnafloc 1011) with ferric chloride.

Coagulant used	Phosphorus removal efficiency (%)
Control	26
$FeCl_3$ 30 ppm	54
$FeCl_3$ 30 ppm + polymer 0.25 ppm	60
Polymer 0.5 ppm	19

Source: Poon & Chu, 1999.

An increase in the amount of chemical sludge is inevitable if the water industry is to comply with the much tighter consent limits outlined above. Even if pre-polymerisation is used, or coagulant aids and filters, sludge volumes will be greater than they are presently. Sludge from chemical treatment works shares the same problems as biological sludge when attempting to apply it to land, with the additional complicating factor that the majority of the phosphorus is bound in Fe(III)-hydroxy-phosphate, which is not biologically available (Carliell-Marquet *et al.,* 2010). There are two possible solutions to this problem: recover the phosphorus from the sludge, or recover the coagulant. If it is possible to recover the phosphorus, then a pure product could be formed that would be more palatable to the agricultural industry. If the coagulant could be recovered, then chemical costs could be reduced and so too could the amount of sludge sent for disposal (Parsons & Daniels, 1999). Acid extraction can be applied to remove metals from sludge, which can then be neutralised and blended with fresh coagulants to be reused in treatment (Parsons & Daniels, 1999). The study found that commercial coagulants performed better than those recovered from sludge, but from a sustainability and economic perspective, this process may yet become viable. (Coagulant costs have risen sharply over recent years.)

Overall, especially in the United Kingdom, chemical precipitation is the preferred means by which phosphorus discharge consents are met, because of its advantages over biological methods (Table 2.8).

Table 2.8: Advantages and disadvantages of chemical phosphorus removal.

Advantages	Disadvantages
Chemical precipitation is a reliable, well documented technique.	Operating costs are higher than for biological systems.
The process is easy to control by simply adjusting the dosing rate.	Greater sludge volumes are produced than biological systems, which have poorer dewatering qualities.
Installation at trickling filter or activated sludge plants is relatively straightforward.	Tertiary filtration is required to remove phosphorus in effluent suspended solids.
The sludge can be processed in the same manner as in non phosphorus removal systems.	Effluent may become coloured if iron salts are used.
Coagulant added to the primary clarifier can reduce organic load to the secondary unit by 25 - 35 % by related removal of suspended solids and BOD.	Potentially toxic to downstream biological processes if incorrect dosing is used.
	Metal loads in sludges are problematic for agricultural application.

Source: EU (2002).

However, neither chemical nor biological techniques can be upgraded to reliably result in effluent levels of < 0.1 mg phosphorus L^{-1} without considerable investment. Additionally, they do not provide a cost effective route for the recovery of the phosphorus removed from wastewater streams.

2.4 Adsorbents and ion exchangers

Phosphorus removal via adsorption is considered to be more useful and efficient than chemical precipitation and biological methods (Ugurlu & Salman, 1998), in terms of capacity and the reversibility of the process. Most of the phosphorus in wastewater, especially in final effluents, occurs as phosphate species (Zeng *et al.,* 2004). Phosphate species have high valency and weight in comparison to the other ions present in wastewater, which suggests that materials exhibiting ion exchange properties could be effective at removing them. The ion exchange process can also be reversed and the phosphate recovered.

2.4.1 Natural materials and constructed wetlands

Natural materials represent a group of contact media that are often quoted as being desirable for use in constructed wetlands to enable phosphorus removal simultaneously with the other functions of the process (Johansson Westholm, 2006). A wide range of materials have been trialled, including clays, sands, and calcium rich minerals (Table 2.9), although differences in media size, the scale of the experiments, and water characteristics being treated limit the usefulness of detailed comparison. As such, comparisons have been limited to the material's capacity for phosphorus removal and the design of each trial.

The use of natural materials is desirable because they are usually cheap, readily available, easy to dispose of and environmentally sound. Some disadvantages to using natural materials however, are that their characteristics can vary significantly, with differing compositions leading to altered values of surface area, particle size (for example from 3.5 nm for nanoclays to 12.6 mm for bauxite), hydraulic conductivity, and porosity. In addition, the chemical composition of natural materials can inhibit their

Table 2.9 Natural materials used for phosphorus removal.

Material	Average particle diameter	Feed solution	Type of study	Contact time	Capacity/removal efficiency	Key findings	Challenges	Reference
Allophane nanoclay	3.5 - 5 nm	Model solutions, 2 - 700 mg phosphorus L^{-1}	Batch	40 days	5.62 mg phosphorus g^{-1} from the Freundlich isotherm	Reduction from 1 mg phosphorus L^{-1} to 0.55 mg phosphorus L^{-1}	Source was New Zealand, no commercial availability	Yuan & Wu, 2006
Apatite	0.9 mm	Model, at pH 7, 20 mg phosphorus L^{-1}	Column	Hydraulic loading rate of 1.35 L d^{-1}	13.9 mg g^{-1}, < 2 mg phosphorus in the outlet	Removal mechanism is via surface precipitation	Single use only, biofilm formation adversely affects removal performance	Molle *et al*., 2005
Bauxite	6.8 - 12.6 mm	2.5 - 40 mg phosphorus L^{-1}, pH 5.9	Batch and Column	24 hr batch study, column hydraulic loading rate of 3 L d^{-1}	Batch: 0.355 mg phosphorus g^{-1} Column: 0.16 mg phosphorus g^{-1}	Much higher phosphorus bonding capacity than limestone, zeolite or fly ash	Single use only, consistency in structure and performance	Drizo *et al*., 1999
Calcite	0.075 mm	Artificial phosphate solutions.	Batch	> 1 hour	70 - 80 % removal at pH 7.5 - 8	Complete removal possible (with high initial concentration and pH). Spent adsorbent can be applied directly to acid soils as a fertilizer.	Not likely to remove the levels needed without adjusting pH. Need to trial with real wastewater	Karageorgiou *et al*., 2007
Opoka	0.9 mm	Model, 5- 25 mg phosphorus L^{-1}, at pH 8.3	Batch	20 hours	< 20 % sorption, 0-0.1 mg phosphorus g^{-1}	The presence of the less reactive $CaCO_3$ in Opoka inhibits phosphorus removal when compared to minerals containing CaO	Long term laboratory and field tests required	Johansson (1999)

Material	**Average particle diameter**	**Feed solution**	**Type of study**	**Contact time**	**Capacity/removal efficiency**	**Key findings**	**Challenges**	**Reference**
Sand	Not reported	105 mg phosphorus m^{-2} d^{-1}	Columns	Hydraulic loading rate of 60-120 L m^{-2} d^{-1}	0.417 mg phosphorus g^{-1}	Sand is sensitive to phosphorus loading	Increases in phosphorus sorption capacities of such media are not directly related to lower effluent phosphorus concentrations	Pant *et al.*¸ 2001
Sands	0 - 4 mm	Used model solutions 10 mg phosphorus L^{-1}	Batch and column	12 - 14 hour column retention	0.02 - 0.13 mg phosphorus g^{-1} estimated from Langmuir isotherm	Performance is correlated with Ca content	Variation in sand compositions and time for system to stabilise will prohibit any repeat of this study's trial	Arias *et al.*, 2000
Wollastonite	Mix of pure wollastonite powder and tailings	Secondary wastewater, average 3.4 mg phosphorus L^{-1}	Columns	Hydraulic retention time from 15 to 180 hours	> 80 % removal, rising to 96 % with longer contact (> 40 hours)	Long contact times required and agitation for maximum performance, but effluent phosphorus concentrations of 0.14 to 0.5 mg l^{-1} are possible (average 0.28 mg l^{-1}.)	No regeneration, UK availability	Brooks *et al.*, 2000
Zeolite	Not reported	Model - 500-10000 mg phosphorus L^{-1}	Batch	48 hours	2.15 mg phosphorus g^{-1}	Regeneration is possible	Optimising synthesis	Sakadevan & Bavor (1998)

adsorptive performance (Arias *et al.,* 2000; Johansson Westholm, 2006). These variables make it very difficult to design an operating process that will return consistent levels of phosphorus removal. Many studies of natural materials are carried out in small scale laboratory experiments where critical parameters can be micro managed, such as temperature and hydraulic loading. They also use model water solutions with phosphorus concentrations much higher than in real wastewater effluents (for e.g. the allophane nanoclay, sand, and zeolite studies), and do not attempt to quantify competition from other anions found in real wastewaters. Generally, natural materials, whether applied alone to wastewaters or as a component of a constructed wetland, are slow to take up phosphorus (taking anywhere between 1 hour and 40 days to reach equilibrium in batch experiments), work best when the initial concentration of phosphorus is very high, but cannot provide an effluent containing < 0.1 mg phosphorus L^{-1}, and cannot be regenerated to recover the adsorbed phosphorus and enable repeated use.

2.4.2 Activated natural materials

Natural materials can be altered to enhance their adsorption capabilities. Expanded clay aggregates (Johansson, 1997), and materials doped with rare earth elements, such as clays (Douglas *et al.,* 2004), carbonates (Karageorgiou *et al.,* 2006), and SiO_2 materials (Ou *et al.,* 2007), all exhibit levels of adsorption much greater than in their unaltered state. However, regeneration is rarely considered, or is impossible, adsorption rates are slow, and trials have primarily been carried out in laboratories and not in operational settings.

2.4.3 Industrial by-products

Much work has been done on creating activated carbon adsorbents from industrial by-products (Pollard *et al.,* 1992) to successfully treat wastewaters. Recently, by-products from the metal refining (slags, ochre, red muds, tailings), and energy (fly ash, shale) industries consisting of iron, aluminium, and calcium oxides have been shown to be effective phosphorus adsorbents (Table 2.10). The use of these materials is appealing because of their cost and ready availability. Additionally, their physical properties are

Table 2.10: Industrial by-products used for phosphorus removal.

Material	Average particle diameter	Feed solution	Type of study	Contact time	Capacity/removal efficiency	Key findings	Challenges	Reference
Alumized red mud	Fine powder	Model solution, 10 mg phosphorus L^{-1}	Batch	1 hour	4 mg phosphorus g^{-1}	Maximum performance at pH 4.5	Non specific phosphate binding impacts capacity in presence of competing species	Mohanty *et al.*, 2004
Blast furnace slag	< 3 mm	Raw wastewater, pH 7.7	Batch	Hydraulic loading rate 100 mm d^{-1} onto 8g media	9.15 mg phosphorus g^{-1}	Very wide range of capacity. Effluent levels of 0.26 mg phosphorus L^{-1} achieved	Wide variety of properties depending on specific industrial source	Korkusuz *et al.*, 2007
Electric arc furnace slag	2.5 - 10 mm	Model, no organics, 20 mg phosphorus L^{-1}	Column	Hydraulic loading rate 3 - 4 L d^{-1}	2.2 mg phosphorus g^{-1}, nearly 100 % efficient	Final effluent < 0.1 mg phosphorus L^{-1} for first 116 pore volumes	Maximum capacity is yet to be determined	Drizo *et al.*, 2006
Fe oxide tailings (30 % iron oxide)	0.069 mm	Model, 10 mg phosphorus L^{-1} pH 3.5	Batch	24 hours	8.6 mg phosphorus g^{-1}	Final effluent < 1 mg phosphorus L^{-1}	Capacity is halved at wastewater pH	Zeng *et al.*, 2004
Fly ash	0.125 - 0.063 mm	Stock solutions of 20/50/100 mg phosphorus L^{-1}	Column	1 hour retention time	99 % removal (at 40ºC, and pH > 11)	0.02 mg phosphorus L^{-1} equilibrium concentration	pH and temperature demands	Ugurlu & Salman, 1998

Material	**Average particle diameter**	**Feed solution**	**Type of study**	**Contact time**	**Capacity/removal efficiency**	**Key findings**	**Challenges**	**Reference**
Fly ash (red mud)	< 0.15 mm	155 mg L^{-1} KH_2PO_4, pH 10.1-11.9	Batch	10 hours for equilibrium	113.9 - 345.5 mg phosphorus g^{-1}	High capacity but final effluents were > 1 mg phosphorus L^{-1}	Can it meet a discharge of 0.1 mg phosphorus L^{-1}?	Li *et al.*, 2006
Ochre	0.6 - 2 mm	Model, 1500 - 3000 mg phosphorus L^{-1}, pH 7.2	Batch	48 hours	0.026 mg phosphorus g^{-1} 90 % removal	Final effluent levels < 1 mg phosphorus L^{-1}	Possible market as fertiliser product once saturated with P, but heavy metals may be problematic	Heal *et al.*, 2003, 2005
Ochre (FeO-(OH)	10 mm	Real wastewater, 4 - 7 mg phosphorus L^{-1}	Column	6 hours	4.1	Final effluent 1.8 mg phosphorus L^{-1}	Optimising regeneration and reuse	Frazer-Williams, 2008
Red mud	< 0.002 - 0.2 mm	Secondary effluent from an urban sewage treatment plant 5.2 mg phosphorus L^{-1}	Column	3 hour retention time	100 % removal	Combines phosphorus and heavy metal removal	No regeneration, disposal problematic because of metal content after use	Lopez *et al.*, 1997
Shale	~ 12 mm	2.4 - 40 mg phosphorus L^{-1}, pH 8.2	Batch, column	24 hours	0.65 - 0.73 mg phosphorus g^{-1}	With low loading rates, in a constructed wetland, projected lifespan is 20 years	Can it meet a discharge of 0.1 mg phosphorus L^{-1}?	Drizo *et al.*, 1999
Steel slag Al FeO_3, $CaFeO_3$, $FeCO_3$	10 mm	Real wastewater, 4 - 7 mg phosphorus L^{-1}	Column	25 hours	1.5 mg phosphorus g^{-1}	Final effluent 1.5 mg phosphorus L^{-1}	Optimising regeneration and reuse	Frazer-Williams, 2008

helpful for adsorption because of their small particle size or high porosity. Capacities for phosphorus adsorption vary between 0.026 mg phosphorus g_{media}^{-1} for ochre, to 345.5 mg phosphorus g_{media}^{-1} for the fly ash (red mud), although the latter was observed using model solutions in the laboratory, and was not correlated to low effluent phosphorus concentrations. None of the studies detailed in Table 2.10 used real wastewaters to produce an effluent containing < 0.1 mg phosphorus L^{-1}. Regeneration and recycling are problematic, and with many by-products (for example slags, fly ash and iron and aluminium oxides), the pH of the wastewater needs to be adjusted to increase adsorptive efficiency. Some by-products do not work well at the temperatures of wastewater treatment works (for example fly ash only achieves maximum removal capacity at 40 ° C). Some pre-treatment of the by-products can also be necessary, for example bauxite residue needs to be neutralised with seawater before being used.

2.4.4 Synthetic adsorbent / ion exchange materials

Manufactured materials such as hybrid anion/adsorbent exchangers and polymeric ligand exchangers have the greatest potential for removing phosphorus and for recyclability (Table 2.11). Unlike natural or industrial by-product media, the specific properties needed to optimise removal can be adjusted and a pure product can be synthesised with reliable and consistent adsorptive capacity. Materials can also be designed to have the physical characteristics needed to withstand the mechanical pressures in an operational setting, and can therefore be robust enough to last many cycles of adsorption / regeneration. Selectivity can be a problem for anion exchangers as competing ions in wastewater, such as sulphate, chloride, and bicarbonate, are usually taken up in favour of phosphate because of their greater concentrations, and enhanced electrostatic interaction (Blaney *et al.,* 2007). Other disadvantages of choosing these materials are the price, and the commercial availability. A large proportion of the studied materials have been synthesised by the authors of the studies, such as the polymeric hydrogel (Kofinas & Kioussis 2003). Although some are now being commercially produced, for example the hybrid anion exchanger in Blaney *et al.'s* 2007 study, it is still difficult to replicate the majority of the studies. Again, most of these materials have been studied against phosphate rich model solutions which give inflated capacity numbers in comparison to real wastewaters, either due to differences in

Table 2.11: synthetic materials used for phosphorus removal.

Material	Average particle diameter	Feed solution	Type of study	Contact time	Capacity/removal efficiency	Key findings	Challenges	Reference
Filtralite Fe_2O_4	10 mm	Real wastewater, 4 - 7 mg phosphorus L^{-1}	Column	1 hour	1.2 mg phosphorus g^{-1}	Final effluent 1 mg phosphorus L^{-1}	Optimising regeneration and reuse	Frazer-Williams, 2008
Hybrid anion exchanger - ion exchange beads with a dispersion of ferric oxide nanoparticles	0.69 mm	Model 0.26 mg phosphorus L^{-1}	Column	2 minutes contact time	2.3 mg phosphorus g^{-1}	Effluent of < 0.1 mg phosphorus L^{-1} for 15000 bed volumes. Selective removal of phosphate, small competitive effect from sulphate. Easy to regenerate and recover phosphorus	Optimising process for differing wastewater streams and regenerant regimes	Blaney *et al.*, 2007
Novel inorganic ion exchangers based on individual and mixed hydrous oxides	Not reported	Model solutions, varying phosphorus concentrations	Batch	48 hours	8.23 mg phosphorus g^{-1} at pH 9 for FeAl	Faster kinetics at higher pH, better capacity at lower pH	pH control necessary to optimise process	Chubar *et al.*, 2005
Polymeric hydrogels	Powdered	Aquaculture wastewater 5.22 mg phosphorus L^{-1}	Batch	3 hours	15.3 mg phosphorus g^{-1}	Phosphate selective, binds more than 98% of the phosphate initially present	Expensive, no commercial availability, no details of regeneration procedure	Kofinas & Kioussis, 2003, Kioussis & Kofinas 2005

Material	Average particle diameter	Feed solution	Type of study	Contact time	Capacity/removal efficiency	Key findings	Challenges	Reference
Polymeric ligand exchanger - ion exchange beads loaded with copper	0.3 - 0.8 mm	Secondary wastewater, 2.2 mg phosphorus L^{-1}	Column	8.8 minutes contact time	99 % removal	Effluent < 0.1 mg phosphorus L^{-1} for first 500 bed volumes. Selective phosphate removal and easy regeneration and recovery possible	Commercial availability, optimising process for differing streams and regeneration regimes	Zhao & Sengupta, 1998
Polymeric ligand exchanger - Lanthanum bound to a chelex resin	0.152 - 0.297 mm	Seawater dosed with phosphorus 7.8 mg phosphorus L^{-1}	Column	0.66 minutes contact time	Effluent of < 0.1 mg phosphorus L^{-1} attained	Removal very good, not influenced by chloride and sulphate, and regenerated for reuse by removing the sorbed phosphate by eluting with 6 M HCl	Only 16% of the potential La(III) sites are available for binding phosphate. Regeneration results in some loss of La(III) over time	Wu *et al.*, 2007
Synthetic hydrotalcite	0.5 - 1.7 mm	Model, 200 mg phosphorus L^{-1}	Batch	24 hours	47.3 mg phosphorus g^{-1}	Desorption by NACl solution and regeneration by $MgCl_2$ solution	Competing anions in an operational setting. Expense?	Kuzawa *et al.*, 2006
Ziconium dioxide	Powder	Model, 30 mg phosphorus L^{-1}	Batch	24 hours	29.71 mg phosphorus g^{-1}	Adsorption increased with a decrease of pH – optimum at pH 3. phosphorus adsorption is not completely reversible	Manufactured ZrO_2 has much higher adsorption potential than the commercial product. No regeneration possible, would have to synthesise ZrO_2, not use the commercial product	Liu *et al.*, 2008

phosphorus concentrations in the feed solutions, or the lack of competition from other anions. Additionally, regeneration of the media has not always been considered, a key concept for the commercial success of such materials, and neither has the recovery of phosphorus been fully explored in the majority of the studies.

Despite the drawbacks of some of the studies, the hybrid anion exchanger and the lanthanum and copper polymeric ligand exchangers are the only materials presently investigated that are able to achieve a final effluent concentration of < 0.1 mg phosphorus L^{-1} when contacted with real wastewaters. These media benefit from requiring short contact times of 2 - 8 minutes in column contactors, exhibit selective phosphorus removal, and can all be regenerated.

The capacity of an adsorbent media to remove phosphorus from wastewater determines the quantity of water it can treat before requiring regeneration or replacement. The capacity is not necessarily linked with final effluent concentrations of phosphorus, but for any given media, conditions that result in greater capacities should be encouraged to improve performance.

The pH of wastewater is typically around neutral, but this is not the optimum condition for all of the adsorbents capable of removing phosphorus from wastewater (Figure 2.3). Despite high capacity, some slags need a pH of around 10, and zirconium sulphate requires acidic pHs of around 4. The ideal adsorbent material would require no pH adjustment and return high capacities. In this respect, the polymeric hydrogels, synthetic allophane and iron and aluminium oxides can all operate at their maximum capacities in neutral pH.

The contact time required to reach maximum capacity and low discharge rates is also a critical operational parameter. The range of contact times needed for the media to reach equilibrium with the phosphorus concentration in solution varies widely from 0.66 minutes in a column configuration to 48 hours in batch mode. Shorter contact times are operationally favourable because they reduce both the footprint of the process and the costs for plant and media significantly (see Chapter 8).

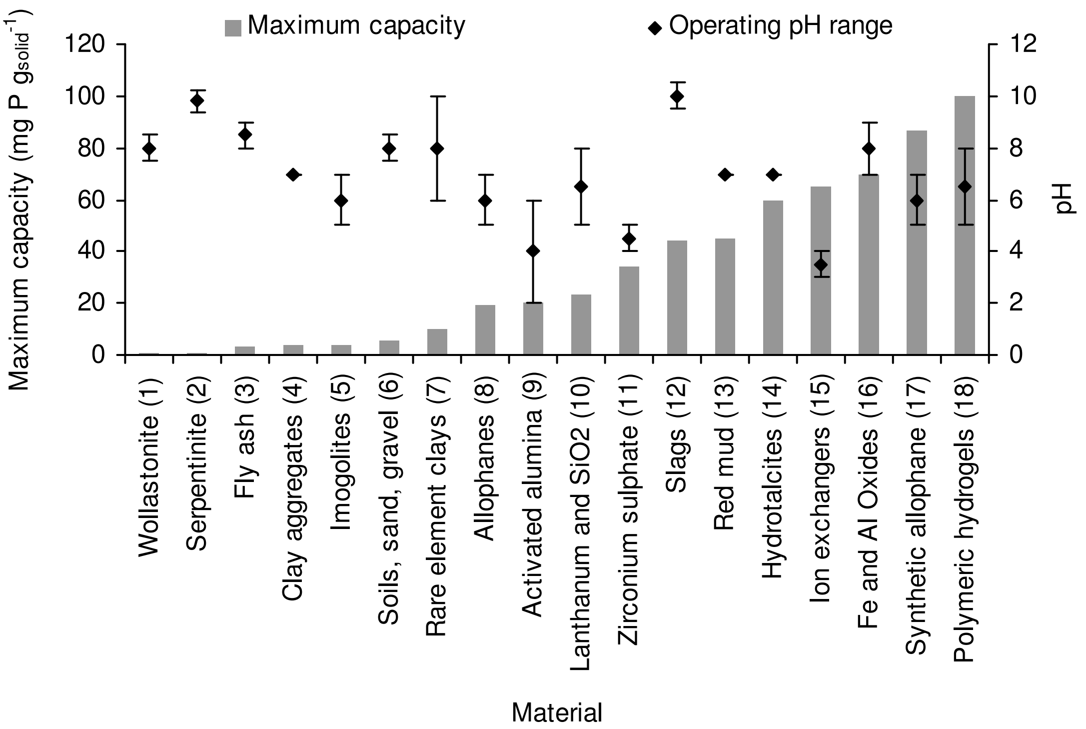

Figure 2.3: Maximum removal capacity and operating pH of a range of phosphorus adsorbers (sources: Hedstrom, (2006), Fukui et al., (2007) (1), Drizo, (2006) (2), Douglas et al., (2004) (3 - 9, 12 - 14, 16, 17), Ou et al., (2007) (10), Lee et al., (2007) (11), Fortin and Karam (2001) (13), Chubar et al., (2007) (15), Kofinas and Kioussis (2003) (18).

Regeneration of the media determines how long it can stay in service for, and therefore has a direct economic influence. Whilst regeneration is not possible or economic with natural or industrial by-product media, the majority of the synthetic media can be reused for many cycles. Typical polymeric ion exchange materials have an operational life of seven years. The regeneration of such media after saturation with phosphorus enables recovery of the phosphorus removed from solution during a service run. Depending on the mechanism of removal, this can be achieved via pH adjustment of the media bed to desorb phosphorus, or by passing a strongly ionic solution through it to reverse the ion exchange (see Chapters 4 - 7). The used regenerant solution can then be passed to a fertiliser manufacturer to process into a marketable product.

The key property that determines the success of any of the adsorbent media is the ability to selectively remove phosphorus from solution. In neutral pH, phosphorus exists as either monodentate or bidentate phosphate species, which are both fairly strong ligands (see Chapter 4). Whilst phosphate can be outcompeted by other ions in wastewater such as sulphate during ion exchange, phosphate is the strongest common ligand in wastewater, and forms inner sphere complexes with transition metals such as iron in the majority of the industrial by-products and in the hybrid anion exchanger, or with copper and lanthanum in the polymeric ligand exchangers.

2.5 Conclusions

Whilst both chemical and biological techniques can be enhanced to improve their phosphorus removal efficiencies, it is unlikely that they will be used in isolation when the Water Framework Directive comes into force. EBPR requires a sustainable source of carbon, ideally from an internal source (i.e. sludge), but this has proven difficult to secure. Biological removal is difficult to manage in the UK under current regulations, and will become even more challenging with tighter consent limits. Shock loads of pollutants can have an instant and debilitating effect on biological plants, and the subsequent time needed for the microbial communities to recover can mean that plants fail to comply with their discharge limits for an extended period after an incident. Chemical treatment can be simply optimised by increasing the dose, or using pre-polymerised coagulants, but both options come at a high price. Additionally, the water industry is working toward chemical free treatment, so increasing the usage of coagulants is not desirable. Overall, enhancing either bacterial or chemical techniques will result in increased sludge volumes, which would require considerable effort to recover the phosphorus from.

New techniques that are not based on conventional means, such as adsorption, are therefore required if the water industry is to comply with the demands of the Water Framework Directive, the reduction of chemical use, and the sustainable use of phosphorus resources. From the literature reviewed in the current study, the key properties of each technique and the main challenges involved in using them to reach a final effluent concentration of 0.1 mg phosphorus L^{-1} shows that both chemical and biological methods are prohibitive, but adsorption only requires optimisation (Table 2.12).

Table 2.12: Key properties required for the investigated methods to reach 0.1 mg phosphorus L^{-1}.

Method	Key property required	Challenge if discharge consent is lowered to 0.1 mg L^{-1}
Biological	COD : P	External carbon source required, increased sludge volumes
Chemical	Fe : P	Excessive expenditure, increased sludge volumes
Adsorption	Transition metal content	Optimising service cycle efficiency and regeneration for phosphorus recovery

The literature investigation clearly points towards adsorbent systems having the greatest potential to meet the new demands of increased removal, and recyclability. Specific polymeric hydrogels for the application of phosphorus removal are not commercially available at present. In the past, the use of manufactured materials such as ion exchangers has not been economically viable for wastewater treatment. Water companies were able to remove phosphorus using cheaper alternatives and still meet their consent limits. Manufactured materials and specifically, hybrid anion exchangers / adsorbent materials appear to now be the best choice for phosphorus removal. These materials can be re-used, and the phosphorus they remove can be recovered, which makes them operationally and economically efficient.

2.6 References

Abu-Ghararah, Z.H., Randall, C.W., (1991). The effect of organic compounds on biological phosphorus removal. *Water Science and Technology* **23** (4-6), pp. 585-594.

ADAS, (2001). *The Safe Sludge Matrix: Guidelines for the Application of Sewage Sludge to Agricultural Land.* Available online at: http://www.adas.co.uk/LinkClick.aspx?fileticket=f_CX7x_v4nY%3d&tabid=211&mid=664 . (Accessed March 2011.)

Ahn, J., Daidou, T., Tsuneda, S., Hirata, A., (2002). Characterization of denitrifying phosphate-accumulating organisms cultured under different electron acceptor conditions using polymerase chain reaction-denaturing gradient gel electrophoresis assay. *Water Research* **36**, pp. 403-412.

Arden, E., Lockett, W.T., (1914). Experiments on the oxidation of sewage without the aid of filters. *The Journal of the Society of Chemical Industry*. **33**, pp. 523-539.

Arias, C.A., Del Bubba, M.D., Brix, H., (2000). Phosphorus removal by sands for use as media in subsurface flow constructed reed beds. *Water Research* **35**, pp. 1159-1168.

Bernet, N., Habouzit, F., Moletta, R., (1996). Use of an industrial effluent as carbon source for denitrification of a high-strength wastewater. *Applied Microbiology and Biotechnology* **32** (9-10), pp. 293-302.

Blaney, L.M., Cinar, S., SenGupta, A.K., (2007). Hybrid anion exchanger for trace phosphate removal from water and wastewater. *Water Research* **41**, pp. 1603-1613.

Bowker, R.P.G., Stensel, H.D., (1990). *Phosphorus removal from wastewater.* Noyes Data Coporation. Park Ridge, New Jersey, USA.

Brdjanovic, D., Slamet, A., van Loosdrecht, M.C.M., Hooijmans, C.M., Alaerts, G.J. and Heijnen, J.J., (1997). Impact of excessive aeration on biological phosphorus removal from wastewater. *Water Research* **32**, pp. 200-208.

Brett, S., Guy, J., Morse, G.K., Lester, J.N., (1997). *Phosphorus Removal and Recovery Technologies* Selper Publications, London, United Kingdom.

Britton, A., Baur, R.O.B., (2010). Phosphorus: A resource in decline. *Journal of the American Water Works Association* **102** (9), pp. 117-118.

Brooks, A.S., Rozenwald, M.N., Geohring, L.D., Lion, L.W., Steenhuis, T.S., (2000). Phosphorus removal by wollastonite: A constructed wetland substrate. *Ecological Engineering* **15**, pp. 121-132.

Carliell-Marquet, C., Smith, J., Oikonomidis, I., Wheatley, A., (2010). Inorganic profiles of chemical phosphorus removal sludge. *Proceedings of the Institution of Civil Engineers Water Management* **163** (WM2), pp. 65-77.

Chen, G., Page, W., (1997). Production of poly-B-hydroxybutyrate by Axotobacter vinelandii in a two-stage fermentation process. *Biotechnology Techniques* **11** (5), pp. 347-350.

Chen, Y., Randall, A.A., McCue, T., (2004). The efficiency of enhanced biological phosphorus removal from real wastewater affected by different ratios of acetic to propionic acid. *Water Research* **38**, pp. 27-36.

Choi, E., Lee, H.S., Lee, J.W., Oa, S.W., (1996). Another carbon source for BNR system. *Water Science and Technology* **34** (1-2), pp. 363-369.

Christensson, M., Blackall, L.L., Welander, T., (1998). Metabolic transformations and characterization of the sludge community in an enhanced biological phosphorus removal system. *Applied Microbiology and Biotechnology* **49**, pp. 226-234.

Chubar, N.I., Kanibolotskyy, V.A., Strelko, V.V., Gallios, G.G., Samanidou, V.F., Shaposhnikova, T.O., Milgrandt, V.G., Zhuravlev, I.Z., (2005). Adsorption of phosphate ions on novel inorganic ion exchangers. *Colloids and Surfaces A: Physicochemical Engineering Aspects* **255**, pp. 55-63.

Cordell, D., Drangert, J., White, S., (2009). The story of phosphorus: Global food security and food for thought. *Global Environmental Change* **19** (2), pp. 292-305.

de-Bashan, L.E., Bashan, Y., (2004). Recent advances in removing phosphorus from wastewater and its future use as fertilizer (1997 - 2003). *Water Research* **38**, pp. 4222-4246.

DEFRA, (2009). *Review of the feasibility of recycling phosphates at sewage treatment plants in the UK.* http://www.defra.gov.uk/environment/quality/chemicals/achs/documents/phosphates-review.pdf (Accessed November 2009).

Dempsey, B.A., Ganho, R.M., and O'Melia, C.R., (1984). The coagulation of humic substances by means of aluminium salts. *Journal of the American Water Works Association* **76**, pp.141-149.

Dorea, C.C., Clarke, B.A., (2008). Effect of aluminium on microbial respiration. *Water, Air, and Soil Pollution* **189** (1-4), pp. 353-358.

Douglas, G.B., Robb, M.S., Coad, D.N., Ford, P.W., (2004). A review of solid phase adsorbents for the removal of phosphorus from natural and waste waters. In: *Phosphorus in Environmental Technologies* (ed. Valsami-Jones, E.), IWA Publishing, London, pp. 20-50.

Drizo, A., Forget, C., Chapuis, R.P., Comeau, Y., (2006). Phosphorus removal by electric arc furnace steel slag and serpentinite. *Water Research* **40**, pp. 1547-1554.

Drizo, A., Frost, C.A., Grace, J., Smith, K.A., (1999). Physico-chemical screening of phosphate-removing substrates for use in constructed wetland systems. *Water Research* **33** (17), pp. 3595-3602.

EA, (2000). EA, *Aquatic eutrophication of England and Wales: a management strategy*, Environment Agency, Bristol (2000) 32 pp.

EA, (2011). *River Basin Management Plans.*
http://www.environment-agency.gov.uk/research/planning/33106.aspx
(Accessed March 2011).

EC, (1991). Council Directive 91/271/EEC of 21 May 1991 concerning urban waste-water treatment.
http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=CELEX:31991L0271:EN:NOT
(Accessed October 2009).

EC, (1998). Commission Directive 98/15/EC.
http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=CELEX:31998L0015:EN:NOT
(Accessed January 2010).

EC, (2000). EC. Directive 2000/60/EC of the European Parliament and of the Council establishing a framework for the Community action in the field of water policy. Official Journal L 327, P. 0001-0073 (22/12/2000); 2000.
http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=CELEX:32000L0060:EN:NOT
(Accessed October 2009).

Eschenhagen, M., Schuppler, M., Roske, I., (2003). The competition between PAOs (phosphorus accumulating organisms) and GAOs (glycogen accumulating organisms) in EBPR (enhanced biological phosphorus removal) systems at different termperatures and the effects on system performance. *Water Science and Technology* **47**, pp. 1-8.

EU Environment Directorate, (2002). *Phosphates and alternative detergent builders - final report.*
http://ec.europa.eu/environment/water/pollution/phosphates/pdf/phosphates.pdf
(Accessed November 2010).

Forrest, A.L., Fattah, K.P., Mavinic, D.S., Koch, F.A., (2008). Optimizing Struvite Production for Phosphate Recovery in WWTP. *Journal of Environmental Engineering* **134** (5), pp. 395-402.

Fortin, J., Karam, A., (2001). Phosphorus sorption by red mud residue as affected by concentration and reaction time. *Agrochimica* **45** 1-2, pp. 55-66.

Frazer-Williams, R.A.D., (2007). Constructed wetlands for advance treatment and reuse. PhD Thesis, Cranfield University, United Kingdom.

Fukui, R., Kurahashi, T., Shiomi, H., Kitaguti, S., Shirakawa, M., (2007). Effect of addition to the gypsum on phosphorous removal properties of wollastonite-type adsorbent. *Zairyo/Journal of the Society of Materials Science, Japan*. **56**, (6), pp. 516-520.

Gilbert, N., (2009). News Feature: The Disappearing Nutrient, *Nature* **461**.

Heal, K.V., Dobbie, K.E., Bozika, E., McHaffie, H., Simpson, A.E., Smith, K.A., (2005). Enhancing phosphorus removal in constructed wetlands with ochre from mine drainage treatment. *Water Science and Technology* **51**, pp. 275-282.

Heal, K.V., Younger, P.L., Smith, K.A., Glendinning, S., Quinn, P., Dobbie, K.E., (2003). Novel use of ochre from mine water treatment plants to reduce point and diffuse phosphorus pollution. *Land Contamination and Reclamation* **11**, pp. 145-152.

Hedstrom, A., (2006). Wollastonite as reactive filter medium for sorption of wastewater ammonium and phosphorus. *Environmental Technology*, **27** (7), pp. 801-809.

Herath, G., (1997). Freshwater Algal Blooms and Their Control: Comparison of the European and Australian Experience. *Journal of Environmental Management* **51**, pp. 217-227.

International Centre for Soil Fertility and Agricultural Development (IFDC), Focus on Fertilizers and Food Security Issue 7 (IFDC, 2008).

Isaacs, S.H., Henze, M., (1995). Controlled carbon source addition to an alternating nitrification-denitrification wastewater treatment process including biological phosphorus removal. *Water Research* **29** (1), pp. 77-89.

Jarvie., H.P., Neal, C., Withers, P.J.A., (2006). Sewage-effluent phosphorus: A greater risk to river eutrophication than agricultural phosphorus? *Science of the Total Environment* **360**, 1-3, pp. 246-253.

Jiang, J-Q., Graham, N.J.D., (1998). Pre-polymerised inorganic coagulants and phosphorus removal by coagulation - A review. *Water SA* **24** (3), pp. 237-244.

Johansson, L., (1999). Industrial by-products and natural substrata as phosphorus sorbents. *Environmental Technology* **20**, pp. 309-316.

Johansson Westholm, L., (2006). Substrates for phosphorus removal – potential benefits for on-site wastewater treatment? *Water Research* **40**, pp. 23-36.

Karageorgiou, K., Paschalis, M., Anastassakis, G.N., (2007). Removal of phosphate species from solution by adsorption onto calcite used as a natural adsorbent. *Journal of Hazardous Materials A* **139**, pp. 447-452.

Kargi, F., Uygar, A., (2003). Effect of carbon source on biological nutrient removal in a sequencing batch reactor. *Bioresource Technology* **89**, pp. 89-93.

Kioussis, D.R., Kofinas, P., (2005). Characterization of anion diffusion in polymer hydrogels used for wastewater remediation. *Polymer* **46**, pp. 9342-9347.

Kofinas, P., Kioussis, D.R., (2003). Reactive phosphorus removal from aquaculture and poultry productions systems using polymeric hydrogels. *Environmental Science and Technology* **37**, pp. 423-427.

Korkusuz, E.A., Beklioglu, M., Demirer, G.N., (2007). Use of blast furnace granulated slag as a substrate in vertical flow reed beds: field application. *Bioresource Technology* **98**, pp. 2089-2101.

Kotabe, H., (1987). Present situation and future of phosphate resources. *Gypsum Lime* **210**, pp. 307-316.

Kuzawa, K., Jung, Y.J., Kiso, Y., Yamada, T., Nagai, M., Lee, T.G., (2006). Phosphate removal and recovery with a synthetic hydrotalcite as an adsorbent. *Chemosphere* **62**, pp. 45-52.

Lee, N., Nielsen, P.H., Aspergen, H., Henze, M., Schleifer, K.H., Jansen, J.L., (2003). Long-term population dynamics and in situ physiology in activated sludge systems with enhanced biological phosphorus removal operated with and without nitrogen removal. *Systematic and Applied Microbiology* **26**, pp. 211-227.

Lee, S.H., Lee, B.C., Lee, K.W., Lee, S.H., Choi, Y.S., Park, K.Y., Iwamoto, M., (2007). Phosphorus recovery by mesoporous structure material from wastewater. *Water Science and Technology*, **55** (1-2), pp. 169-176.

Lee, S.I., Park, J.-O., Ko, K.-B., Koopman, B., (1997). Effect of fermented swine wastes on biological nutrient removal in sequencing batch reactors. *Water Research* **31** (7), pp. 1807-1812.

Lees, E.J., Noble, B., Hewitt, R., Parsons, S.A., (2001) (a). The impact of residual coagulant on downstream treatment processes. *Environmental Technology* **22**, pp. 113-122.

Lees, E.J., Noble, B., Hewitt, R., Parsons, S.A., (2001) (b). The impact of residual coagulant on the respiration rate and sludge characteristics of an activated microbial biomass. *Process Safety and Environmental Protection* **79** (5), pp. 283-290.

Leprince, A., Fiessinger, F., Bottero, J.Y., (1984). Polymerized iron chloride: An improved inorganic coagulant. *Journal of the American Water Works Association* **76**, pp. 93-97.

Li, Y., Liu, C., Luan, A., Peng, X., Zhu, C., Chen, A., Zhang, A., Fan, J., Jia, Z., (2006). Phosphate removal from aqueous solutions using raw and activated red mud and fly ash. *Journal of Hazardous Materials B* **137**, pp 374-383.

Lim, S.-J., Choi, D.W., Lee, W.G., Kwon, S., Chang, H.N., (2000). Volatile fatty acids production from food wastes and its application to biological nutrient removal. *Bioprocess Engineering* **22**, pp. 543-545.

Liu, H., Sun, X., Yin, C., Hu, C., (2008). Removal of phosphate by mesoporous ZrO2. *Journal of Hazardous Materials* **151**, pp. 616-622.

Lopez, E., Soto, B., Arias, M., Nunez., A., Rubinos, D., Barral, M.T., (1997). Adsorbent properties of red mud and its use for wastewater treatment. *Water Research* **32**, pp. 1314-1322.

Maszenan, A.M., Seviour, R.J., Patel, B.K.C., Schumann, P., Rees, G.N., (1999). *Tessaracoccus bendigoensis* gen. nov., sp. nov., a Gram-positive coccus occurring in regular packages or tetrads, isolated from activated sludge biomass. *International Journal of Systematic Bacteriology* **49**, pp. 459-468.

Melasniemi, H., Hernesmaa, A., Pauli, A.S.-L., Rantenen, P., Salkinoja-Salonen, M., (1998). Comparative analysis of biological phosphate removal (BPR) and non-BPR activated sludge bacterial communities with particular reference to *Acinetobacter. Journal of Industrial Microbiology and Biotechnology* **21**, pp. 300-306.

Merzouki, M., Delgenes, J.-P., Bernet, N., Moletta, R., Benlemlih, M., (1999). Polyphosphate-accumulating and denitrifying bacteria isolated from anaerobic-anoxic and anaerobic-aerobic sequencing batch reactors. *Current Microbiology* **38**, pp. 9-17.

Metcalf & Eddy, (2003). *Wastewater Engineering. Treatment and Reuse*. McGraw-Hill, New York.

Mino, T., van Loosdrecht, M.C.M., Heijnen, J.J., (1998). Microbiology and biochemistry of the enhanced biological phosphate removal process. *Water Research* **32** (11), pp. 3193-3207.

Mohanty, S., Pradham, J., Das, S.N., Thakur, R.S., (2004). Removal of phosphorus from aqueous solution using aluminized red mud. *International Journal of Environmental Studies* **61** (6), pp. 687-697.

Molle, P. Lienard, A., Grasmick, A., Iwema, A., Kabbabi, A., (2005). Apatite as an interesting seed to remove phosphorus from wastewater in constructed wetlands. *Water Science and Technology* **51** (9), pp. 193-203.

Morling, S., (2001). Performance of an SBR-plant for advanced nutrient removal, using septic sludge as a carbon source. *Water Science and Technology* **43** (3), pp. 131-138.

Mullan, A., Quinn, J.P., McGrath, J.W., (2002). Enhanced phosphate uptake and polyphosphate accumulation in *Burkholderia cepacia* grown under low-pH conditions. *Microbial Ecology* **44**, pp. 69-77.

Muscutt, A.D., Withers, P.J.A., (1996). The phosphorus content of rivers in England and Wales. *Water Research* **30**, pp. 1258–1268.

Nyberg, U., Andersson, B., Aspergren, H., (1996). Long-term experiences with external carbon sources for nitrogen removal. *Water Science and Technology* **33** (12), pp. 109-116.

Oehmen, A., Zeng, R., Yuan, Z., Keller, J., (2004). Anaerobic metabolism of propionate by polyphosphate-accumulating organisms in enhanced biological phosphorus removal systems. *Water Science and Technology* **50** (10), pp. 139–144.

Ou, A., Zhou, J., Mao, S., Wang, J., Xia, F., Min, L., (2007). Highly efficient removal of phosphate by lanthanum-doped mesoporous SiO2. *Colloids and Surfaces A: Physiochemical Engineering Aspects* **308,** pp. 47-53.

Ozacar, M., Sengil, I.A., (2003). Enhancing phosphate removal from wastewater by using polyelectrolytes and clay injection. *Journal of Hazardous Materials B* **100**, pp. 131-146.

Pant, H.K., Reddy, K.R., Lemon, E., (2001). Phosphorus retention capacity of root bed media of subsurface flow constructed wetlands. *Ecological Engineering* **17**, pp. 345-355.

Parsons, S.A., Daniels, S.J., (1999). The use of recovered coagulants in wastewater treatment. *Environmental Technology* **20**, pp. 979-985.

Pavan, P., Battistoni, P., Traverso, P., Musacco, A., Cecchi, F., (1998). Effect of addition of Anaerobic fermented OFMW (organic fraction of municipal solid waste) on biological nutrient removal (BNR) process: preliminary results. *Water Science and Technology* **40** (2), pp. 159-165.

Pijuan, M., Saunders, A.M., Guisasola, A., Baeza, J.A., Casas, C.,Blackall, L.L., (2004). Enhanced biological phosphorus removal in a sequencing batch reactor using propionate as the sole carbon source. *Biotechnology and Bioengineering* **85** (1), pp. 56–67.

Pollard, S.J.T., Fowler, G.D., Sollars, C.J., Perry, R., (1992). Low-cost adsorbents for waste and wastewater treatment: a review. *The Science of the Total Environment* **116**, pp. 31-52.

Poon, C.S., Chu, C.W., (1999). The use of ferric chloride and anionic polymer in the chemically assisted primary sedimentation process. *Chemosphere* **39** (10), pp. 1573-1582.

Puig, S., Coma, M., Monclus, H., van Loosdrecht, M.C.M., Colprim, J., Balaguer, M.D., (2008). Selection between alcohols and volatile fatty acids as external carbon sources for EBPR. *Water Research* **42** (3), pp. 557-566.

Redfield, A.C., (1958). The biological control of chemical factors in the environment. *American Scientist* **46**, pp. 205-221.

Redfield, A.C., Ketchum, B.H. and Richards, F.A., (1963). The influence of organisms on the composition of sea water. In: *The Sea, II (ed. Hill, M.N.)*, Wiley Interscience, New York, pp. 26-77.

Sakadevan, K., Bavor, H.J., (1998). Phosphate adsorption characteristics of soils, slags, and zeolite to be used as substrates in constructed wetland systems. *Water Research* **32**, pp. 393-399.

Schonborn, C, Bauer, H.D., Roske, I., (2001). Stability of enhanced biological phosphorus removal and composition of polyphosphate granules. *Water Research* **35**, pp. 3190-3196.

Seviour, R.J., Mino, T., Onuki, M., (2003). The microbiology of biological phosphorus removal in activated sludge systems. *FEMS Microbiology Reviews* **27**, pp. 99-127.

Stante, L., Callamare, C., Malaspina, F., Bortone, G., Tilche, A., (1997). Biological phosphorus removal by pure culture of *Lampropedia* spp. *Water Research* **35**, pp. 4191-4199.

Steen, I., (1998). Phosphorus availability in the 21st Century: management of a non-renewable resource. *Phosphorus and Potassium* **217**, pp. 25-31.

Tam, N.F.Y., Wong, Y.S., Leung, G., (1992). Significance of external carbon sources on simultaneous removal of nutrients from wastewater. *Water Science and Technology* **26** (5-6), pp. 1047-1055.

Thistleton, J., Berry, T.-A., Pearce, P., Parsons, S.A., (2002). Mechanisms of chemical phosphorus removal II Iron (III) salts. *Process Safety and Environmental Protection: Transactions of the Institution of Chemical Engineers, Part B* **80** (5), pp. 265-269.

Ugurlu, A., Salman, B., (1998). Phosphorus removal by fly ash. *Environment International* **24**, pp. 911-918.

Valsami-Jones, E., (2004). The Geochemistry and mineralogy of phosphorus. In: *Phosphorus in Environmental Technologies (ed. Valsami-Jones, E.),* IWA Publishing, London, pp. 20-50.

Van Ommen Kloeke, F., Geesey, G.G., (1999). Localization and identification of populations of phosphatase-active bacterial cells associated with activated sludge flocs. *Microbial Ecology* **38**¸ pp. 201-214.

Wang, J.C., Park, J.K., (2001). Effect of anaerobic:aerobic contact time on the change of internal storage energy in two different phosphorus-accumulating organisms. *Water Environment Research* **73**, pp. 436-443.

Weismann, U., Choi, I.S, Dombrowski, E., (2007). *Fundamentals of Biological Wastewater Treatment.* Wiley-VCH Verlag GmbH & CO. KGaA, Weinheim.

Wu, R.S.S., Lam, K.H., Lee, J.M.N., Lau, T.C., (2007). Removal of phosphate from water by a highly selective LA(III)- chelex resin. *Chemosphere* **69**, pp. 289-294.

Yuan, G., Wu, L., (2006). Allophane nanoclay for the removal of phosphorus in water and wastewater. *Science and Technology of Advanced Materials* **8**, pp. 60-62.

Zeng, L., Xiaomei, L., Liu, J., (2004). Adsorptive removal of phosphate from aqueous solutions using iron oxide tailings. *Water Research* **38**, pp. 1318-1326.

Zhao, D., Sengupta, A.K., (1998). Ultimate removal of phosphate from wastewater using a new class of polymeric ion exchangers. *Water Research* **32**, pp. 1613-1625.

Zhou, Y., Xing, X-H., Liu, Z., Cui, L., Yu, A., Feng, Q., Yang, H., (2008). Enhanced coagulation of ferric chloride aided by tannic acid for phosphorus removal from wastewater. *Chemosphere* **72**, pp. 290-298.

3. Molecular weight distribution of phosphorus across sewage treatment works

B.D. Martin, V. Laragione, S.A. Parsons, B. Jefferson

3.1 Introduction

The Water Framework Directive (European Union, 2008) is likely to lower consent limits for phosphorus discharge from municipal wastewater treatment works in the near future. It is thought that the new limits are not able to be practicably achieved using current treatment options (Blaney *et al.*, 2007; Martin *et al.*, 2009), and consequently a need to find enhanced techniques for phosphorus removal exists. New removal options for phosphorus can only be fully exploited if the speciation and particle size distribution of phosphorus through treatment works is understood. These parameters help to determine how mobile the phosphorus is, and can therefore dictate the treatment methods required (Gonzalez Medeiros *et al.*, 2005). The present study seeks to quantify the molecular weight distribution of phosphorus species in a selection of UK wastewater works. For the sake of operational convenience, phosphorus is usually defined as being dissolved if present in a < 0.45 μm filtrate (Hens & Merckx, 2002). However, this is possibly an oversimplification, since the size range defined as colloidal (1 - 1000 nm) straddles this distinction (Hiemenz & Rajagopalan, 1997), and the solute size range is much smaller, at < 1 nm. The present study seeks to compartmentalise wastewater phosphorus into more discrete and useful distinctions, by using multiple membranes in series. These membranes have pore sizes defined by Daltons (Da), a non SI measurement that refers to the atomic mass unit (Figure 3.1).

Solid particles are comparatively easy to remove from wastewater streams by simple depth filtration or sedimentation. The behaviour of colloids however, is harder to predict, and differences in diffusion and agglomeration rates means that they can migrate over long distances, be adsorbed onto solid phases, or settle out by forming large aggregates (Buffle & Leppard, 1995). In addition, the smaller the molecular weight, the more mobile and bio-available the phosphorus, and hence the more profound its ecological impact (Bostrom *et al.,* 1988; Waldeback *et al.*, 1998; Jarvie *et al.,* 2008).

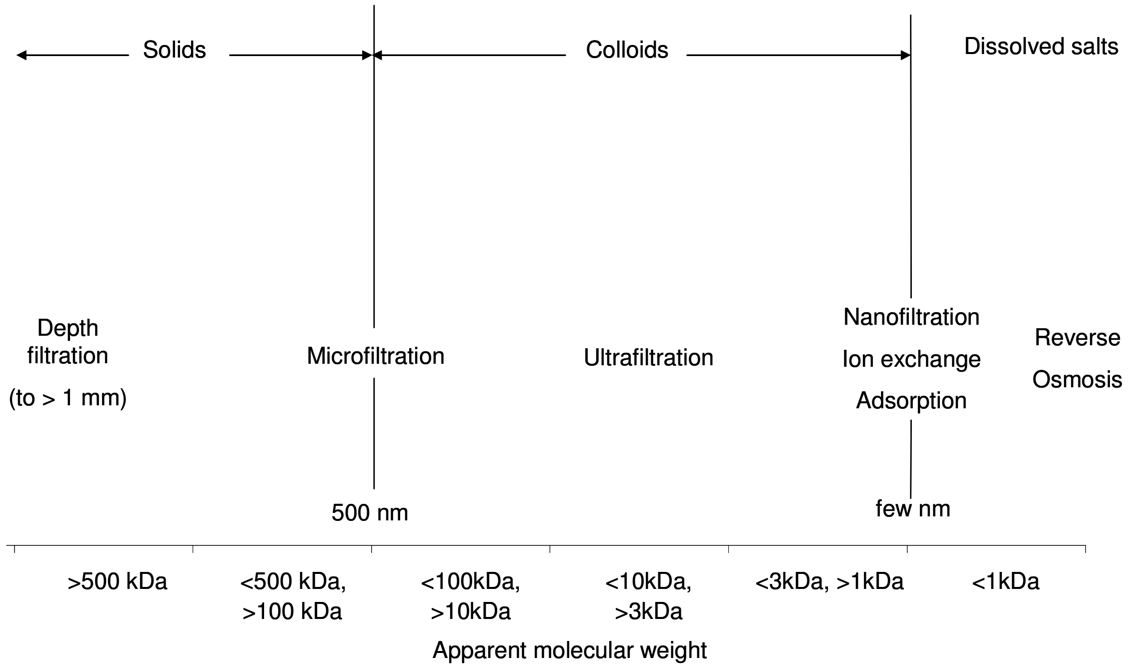

Figure 3.1: Solid, colloidal and dissolved classifications in relation to the Dalton scale and the method of removal required (Adapted from Judd & Jefferson, 2003).

Aims and Scope

Current knowledge of the character of phosphorus species in wastewater assumes the majority are "dissolved," but this distinction fails to differentiate between the colloidal and solute classes. Since potential removal methods differ depending on the distribution between colloids and solutes, it is important to identify where the majority of phosphorus resides in wastewater streams so that new treatments can be designed effectively. This chapter seeks to further the understanding of the molecular weight distribution of phosphorus entering and leaving typical treatment works to this end.

3.2 Materials and methods

3.2.1 Site descriptions

Site 1, a small trickling filter (small TF) is a rural sewage works designed to treat a population equivalence of < 10,000. The site consists of screening, primary sedimentation, biological treatment trickling filters with a humus tank for final settlement before discharge (Figure 3.2). The works is designed to meet a compliance standard of 16 / 30 based on biochemical oxygen demand (BOD) and suspended solids (SS).

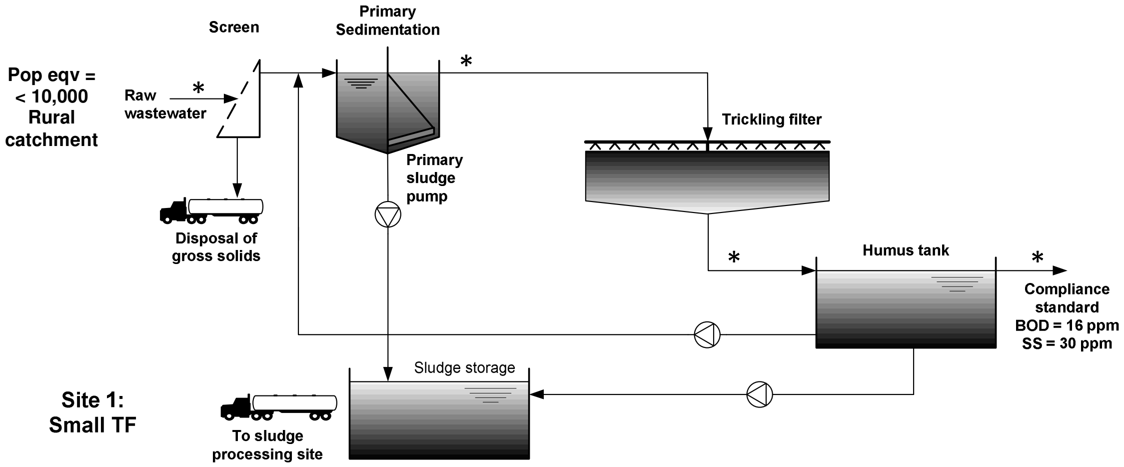

*Figure 3.2: Process flow diagram for site 1 - small trickling filter works. *Sampling points.*

Site 2, a large trickling filter works with chemical addition (large TF) treats the sewage from a town sized to a population equivalence of 12,000. The works is similar to site 1, with the addition of coagulant dosing with ferrous chloride into the flow before and after the primary sedimentation tanks (Figure 3.3). The works is designed to meet a 30 / 16 / 5 / 2 as SS / BOD / ammonia / phosphorus effluent quality.

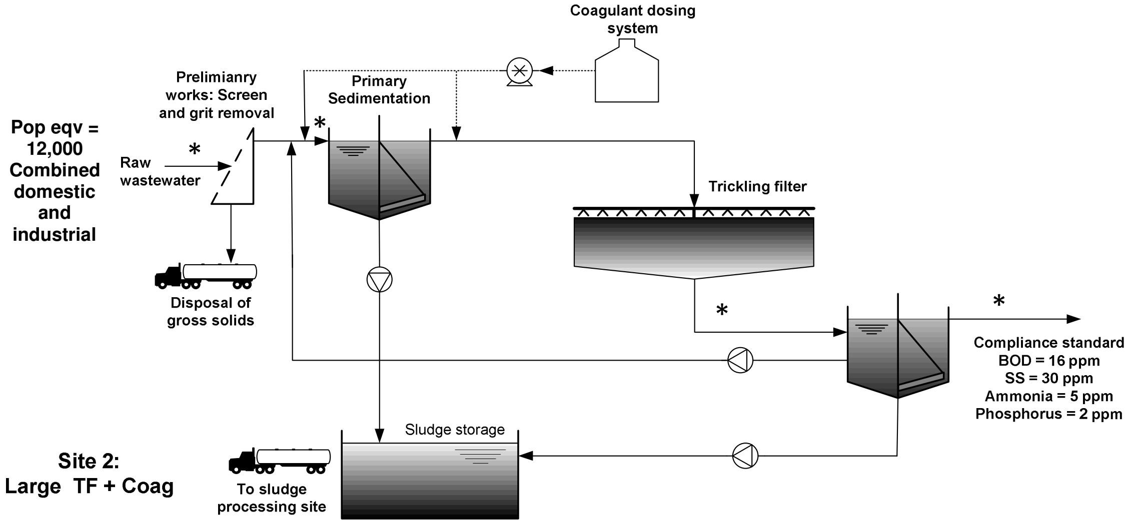

*Figure 3.3: Process flow diagram for site 2 - large trickling filter works. * Sampling points.*

Site 3 is a small activated sludge works (small AS) which undergoes screening and primary sedimentation prior to biological treatment and final sedimentation. The works is sized at a population equivalence of < 10,000 and is designed to meet a 30 / 15 / 5 SS / BOD / ammonia effluent quality (Figure 3.4).

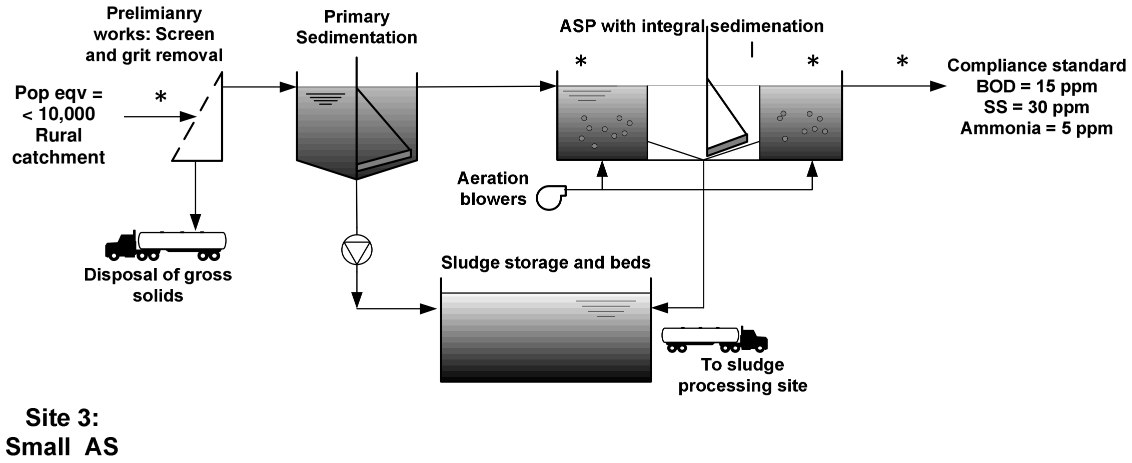

*Figure 3.4: Process flow diagram for site 3 - small activated sludge plant. * Sampling points.*

Sites 1-3 all collect sludge on site for tankering to the local sludge processing site. Site 4 is a large activated sludge plant with chemical addition (large AS), based on a tapered aeration activated sludge works with on site sludge processing through anaerobic digestion and dewatering (Figure 3.5). The site treats both domestic and industrial wastewater and receives sludge imports from the surrounding smaller sewage works. The works doses ferrous chloride for phosphorus removal with coagulant dosed pre and post primary sedimentation. The site treats a population equivalence of 200,000 and meets compliance standards of 30 / 12 / 5 / 1 based on SS / BOD / ammonia / phosphorus.

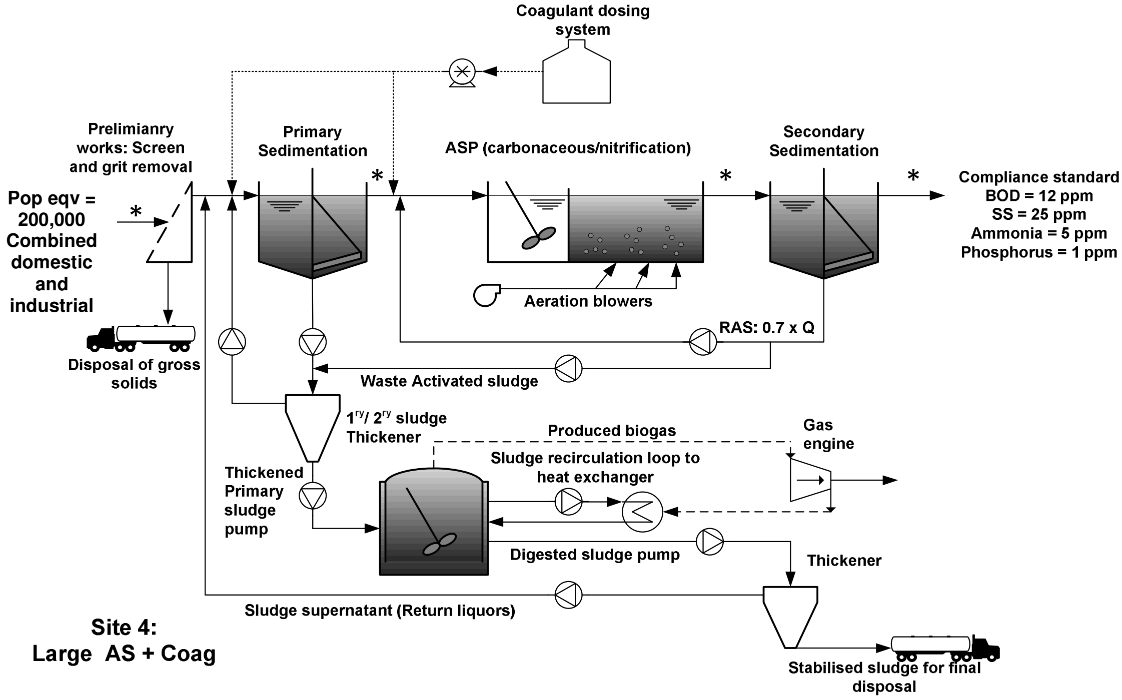

*Figure 3.5: Process flow diagram for site 4 - large activated sludge plant. * Sampling points.*

Site 5 is designed to treat a population equivalence of 236,000 and is based around an activated sludge process (Bio P) configured for biological phosphorus removal and meets a compliance standard of 30 / 20 / 3 / 1 for SS / BOD / ammonia / phosphorus (Figure 3.6). The site contains additional coagulant dosing and includes tertiary sand filters which incorporate a deep bed coarse media configuration.

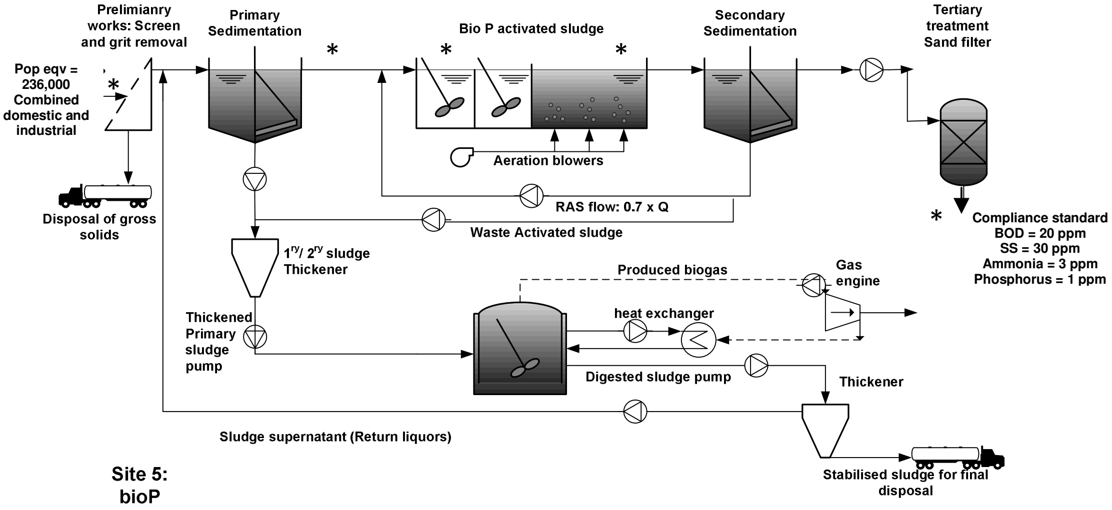

***Figure 3.6**: Process flow diagram for site 5 - enhanced biological phosphorus removal plant.*
** Sampling points.*

Specific geographical details are omitted for company confidentiality concerns but all pertinent date required to meet the aims of the present chapter are included. Data used to generate the resilience curves were obtained from the works manager at each site and include all measurements recorded between September 2008 and September 2010.

3.2.2 Resilience curves

Effluent data from each site was assessed in terms of resilience by plotting percentile values (i.e. the value of a measured parameter under which a certain percent of all the data fall) of the measurements taken over the 2 year period. For example, if a site has a phosphorus discharge limit of 1 mg L^{-1}, and has a 99th percentile value of 1 mg P L^{-1}, this means that for 99 % of the time, it produced an effluent below 1 mg P L^{-1}, and the inference is that it failed this consent 1 % of the time. The key points on the presented resilience curves are found at the percentile value where effluent limits are breached. Additionally, data sets that trend towards the vertical on the presented curves indicate resilience because they show lower variance between the percentile values than a data set trending towards the horizontal. In the present study, a vertical trend would indicate that the site in question consistently achieved its effluent target over the measuring period.

3.2.3 Fractionation process

One litre grab samples were collected from each treatment stage of the five works in October and November 2009. Preliminary work with samples from sites 1 and 4 found that the phosphorus in solid fractions only make up ≤ 10 % of the total phosphorus in raw wastewater streams, dropping to < 3 % in final effluents. These findings are consistent with Sallanko *et al.,* (2006) who found that around 15 % of the phosphorus in a raw wastewater stream was > 0.1 μm. In natural systems, Hens & Merckx (2002) reported that high molecular mass phosphorus compounds were of minor importance, comprising < 8 % of the total phosphorus load in forest soils. Consequently, the present study centrifuged all the samples at 10,000 rpm for ten minutes to separate out any gross solids, and does not include analysis of phosphorus extracted from the resulting sediments.

The membranes used to fractionate the samples were made from a low protein binding modified polyethersulfone (Omega^{TM}, PALL life sciences, supplied by VWR International UK Ltd.). Before use the membranes were prepared by washing with sequences of ultrapure water (0.05 µS conductivity level), 0.1 M NaOH and 0.1 M HCl (supplied by Fisher Scientific UK Ltd.). The alkaline/acid cleaning sequence was repeated after each use and the membranes stored in a 10 % ethanol solution which was frequently replaced. Five separate membrane pore sizes were used: 300, 100, 10, 3 and 1 kDa. The fractionations were conducted in an Amicon 8400 stirred pressure cell (Supplied by Millipore UK Ltd.) driven by nitrogen gas at a pressure of 0.7 atm for the > 100 kDa membranes and 3.7 atm for the others. In all cases the sample was progressively filtered through the series of membranes ensuring a minimum of 60 % retention. The membrane cell was kept in a bath of 2 % nitric acid (reagent grade, supplied by Fisher Scientific UK Ltd) between uses and all glassware and plasticware were washed with alkaline and acid before being stored in 2 % nitric acid between uses.

3.2.4 Analytical technique

Determination of total P, orthophosphate, and indirectly, additional P (assumed to be organic), was made by Spectroquant cell test kits. The method is analogous to EPA 365.2+3, US Standard Methods 4500-P E, and ISO 6878. The method has a standard deviation of ± 0.026 mg P L^{-1}, with a coefficient of variation of ± 1.1 % and a confidence interval of ± 0.05 mg phosphorus L^{-1}. Replicate sample measurements exhibited variances of less than 0.05 mg phosphorus L^{-1}.

3.3 Results

3.3.1 General resilience of the flowsheets

The resilience curves revealed similar BOD profiles for the small TF, small AS and large AS sites with the effluent BODs varying between 0.7 - 5.1 mg L^{-1} up to the 95th percentile. Effluent data from the large TF site was slightly higher with a median BOD of 4.4 mg L^{-1}, and a 95th percentile value of 9.9 mg L^{-1} (Figure 3.7 A). The Bio P plant exhibited a more resilient BOD profile than the other works with a near vertical line between the 25th and 80th percentiles. This reflects the greater need to operate Bio P plants effectively if the process is going to perform. Similar observations were observed in relation to suspended solids, (Figure 3.7 B), reflecting the close connection typically observed between the two measures. In terms of ammonia (Figure 3.7 C), all works operated with similar resilience profiles up to the 80th percentile, as observed by the similarity in the gradients of the curve between the 20th and 50th percentiles. At the sites with compliance standards set for phosphorus discharge (the large TF, large AS, and Bio P plants), the Bio P plant is the most resilient, achieving a 0.43 mg phosphorus L^{-1} discharge up to the 95th percentile (Figure 3.7 D). The large TF achieved a discharge of 1.82 mg phosphorus L^{-1} up to the 95th percentile. The large AS plant was not so resilient, only able to attain a discharge of 0.96 mg phosphorus L^{-1} up to the 60th percentile.

All sites complied with their BOD and SS targets over the 2 year period, and the gradients of the data sets suggest that all except the large TF + coag plant showed good resilience. Ammonia consents were met by all the works apart from the large TF + coag plant, which failed by 1 ppm < 10 % of the time. Where phosphorus consents are in place, each plant failed their target on occasion, with a pronounced difference in resilience between the Bio P plant and the large AS + coag and large TF + coag plants. Consequently, the large AS + coag and large TF + coag plants would generally be characterised as less robust than the others whilst the Bio P plant represents the most robust site. The similarity in the comparison between the small AS and small TF plants indicates the ongoing importance of trickling filter technology, especially at small works.

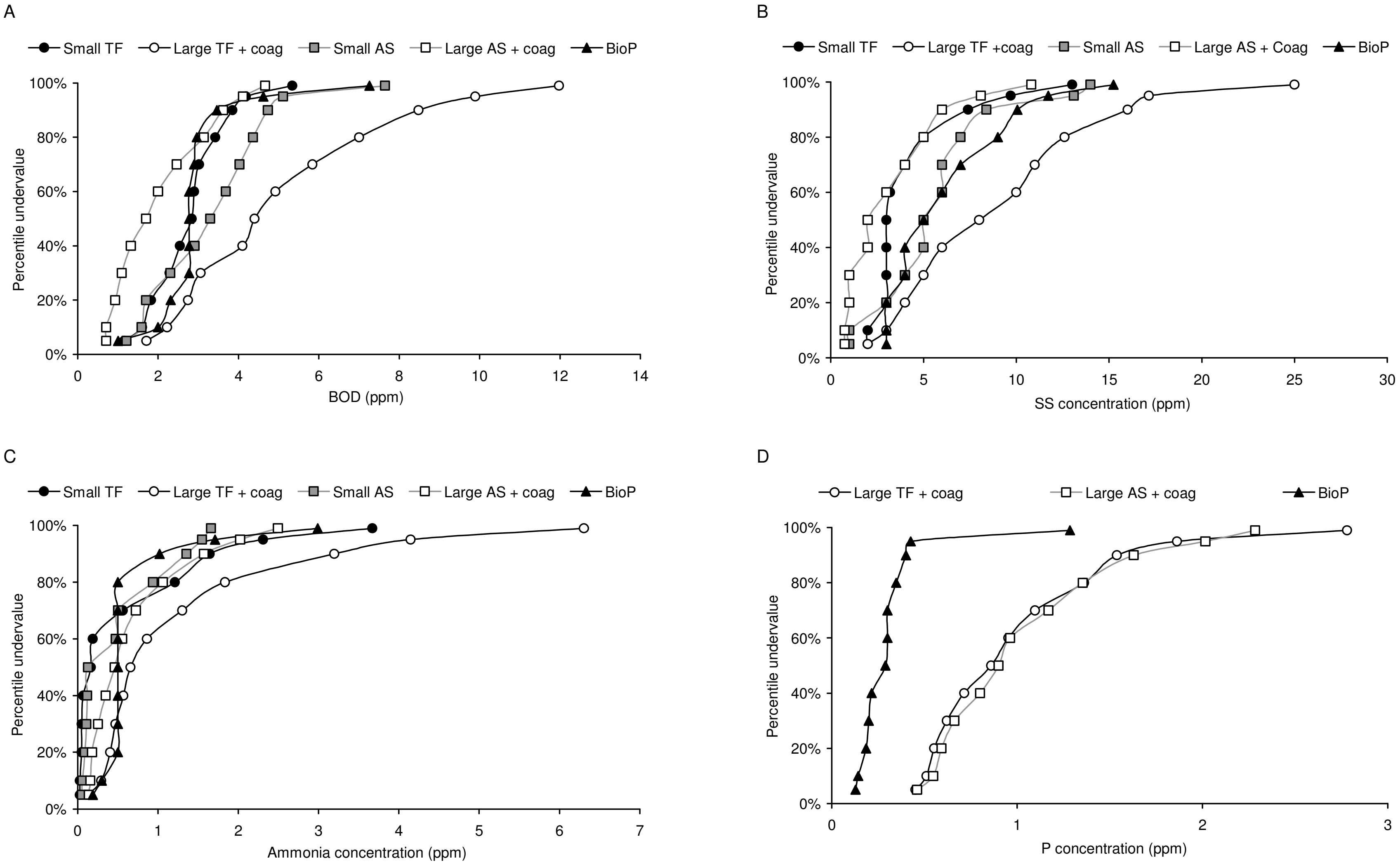

Figure 3.7: Resilience curves for biochemical oxygen demand (A), suspended solids (B), ammonia (C) and phosphorus (D) for the sites under investigation.

3.3.2 Influent phosphorus characteristics

Total phosphorus in the centrifuged supernatant influent samples of the small TF, large TF, small AS, large AS and the Bio P plants respectively had 6.3, 3.8, 10.1, 4.9 and 15.9 % (± 1.1) of their load in molecular weights greater than 300 kDa (Figure 3.8). Similar levels were observed in all size bands apart from the 3 and 1 kDa bands which contained proportionally more phosphorus. To illustrate, across the five works, 74 to 87 % (± 1.1) of the total phosphorus was found in these smallest size bands (Figure 3.8). Further, the dissolved fraction (1 kDa) represented 65, 49, 82, 58 and 59 % (± 1.1) of the total phosphorus for the small TF, large TF, small AS, large AS and Bio P plants respectively.

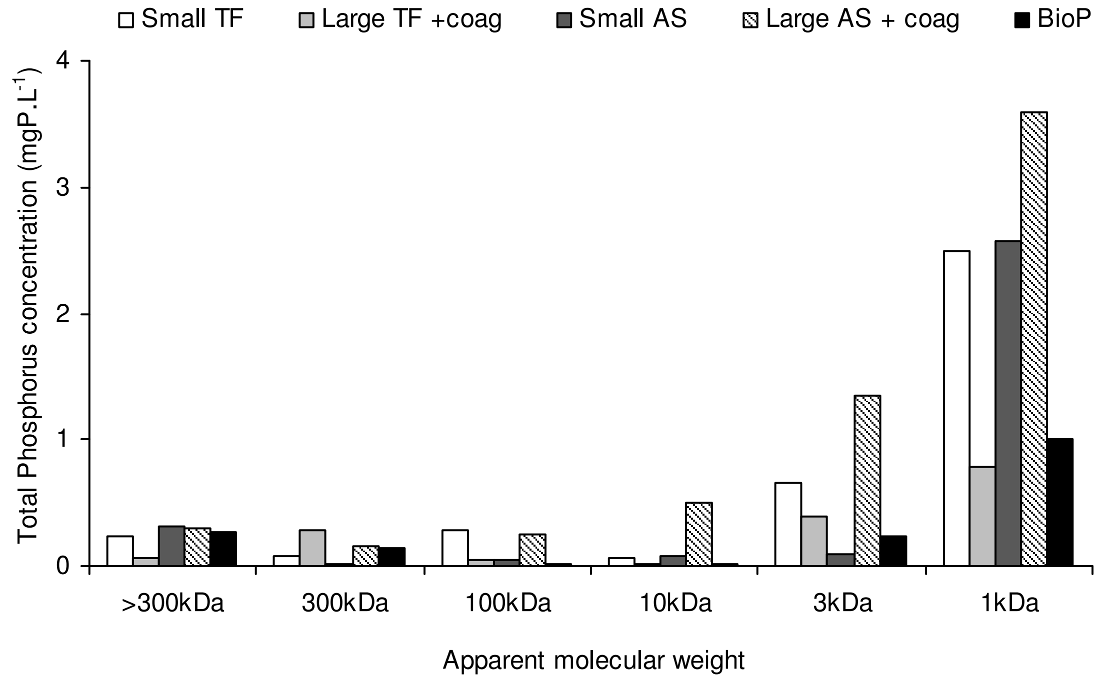

Figure 3.8: Total phosphorus by molecular weight in the influent of the sampled sites.

Total phosphorus in the supernatant of the centrifuged influent samples was 3.8, 1.6, 3.1, 6.1 and 1.7 mg L^{-1} (± 0.05) for the small TF, large TF, small AS, large AS and Bio P plants respectively. The phosphorus was distributed such that between 91 and 100 % (± 1.1) of the measured phosphorus was as phosphate (Figure 3.9) with the exception of the Bio P plant where only 68 % (± 1.1) of the incoming phosphorus was as phosphate. The remaining phosphorus was organically bound with relatively higher concentrations present in the influent to the rural works (small AS, small TF) than the other sites. To illustrate, total organic phosphorus entering the two small sites was between 1.3 - 2 mg L^{-1} (± 0.05) which compared to a range of 0.35 - 1.1 mg L^{-1} (± 0.05) for the other sites.

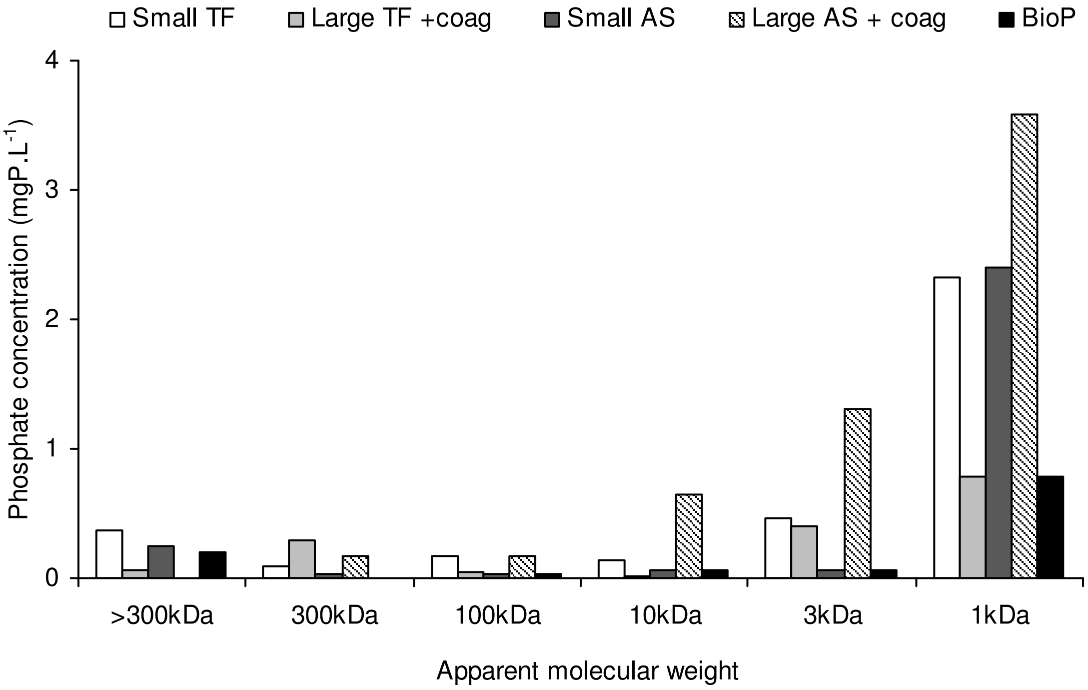

Figure 3.9: Phosphorus as phosphate by molecular weight in the influent of the sampled sites.

Primary sedimentation resulted in net dissolved total phosphorus increases compared to the influent of 0.57, 0.40 and 0.14 mg L^{-1} (± 0.05) in the small TF, large AS and Bio P plants respectively (Figure 3.10) (access was not possible at the large TF and small AS plants).

Comparison between the sedimentation and biological processes in the small TF, and large AS showed that dissolved phosphorus increased by 0.07 and 0.61 mg phosphorus L^{-1} (± 0.05) respectively (Figure 3.11), consistent with earlier work that reported removal or conversion of large inorganic fractions to smaller fractions during contact with biofilm (Sophonsiri & Morgenroth, 2003). In contrast, the Bio P plant reduced the level of dissolved phosphorus by 1 mg L^{-1} (± 0.05), revealing the effectiveness of the enhanced process at reducing this fraction over the standard suspended growth or fixed film methods employed in the other treatment works.

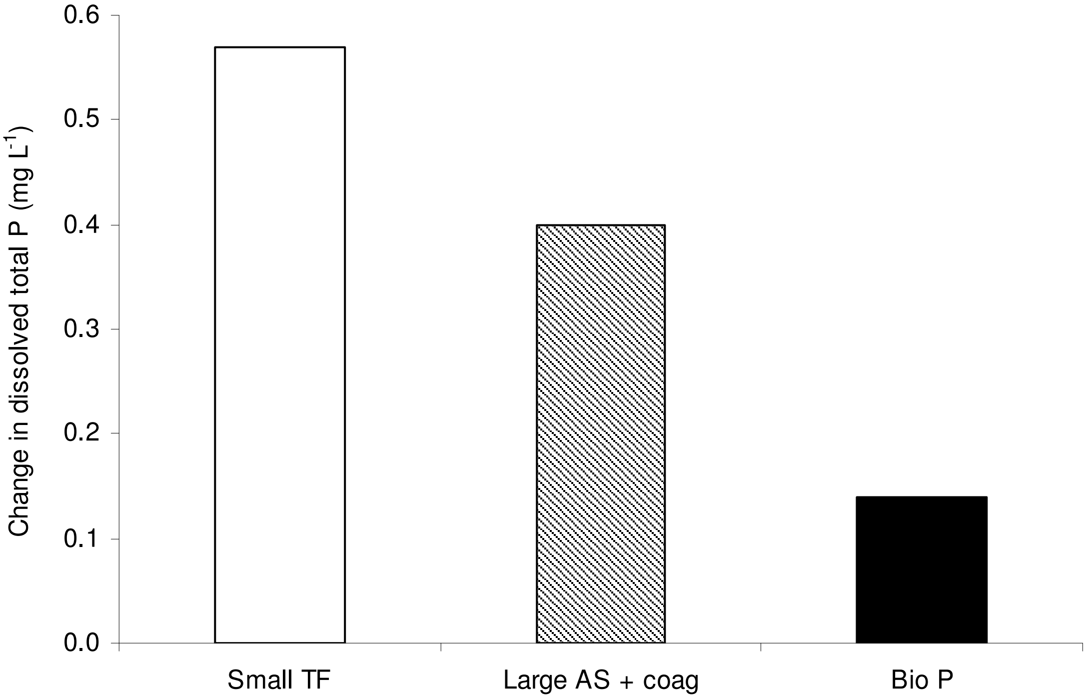

Figure 3.10: Change in total phosphorus in the dissolved (1 kDa) fraction before/after primary sedimentation in each plant.

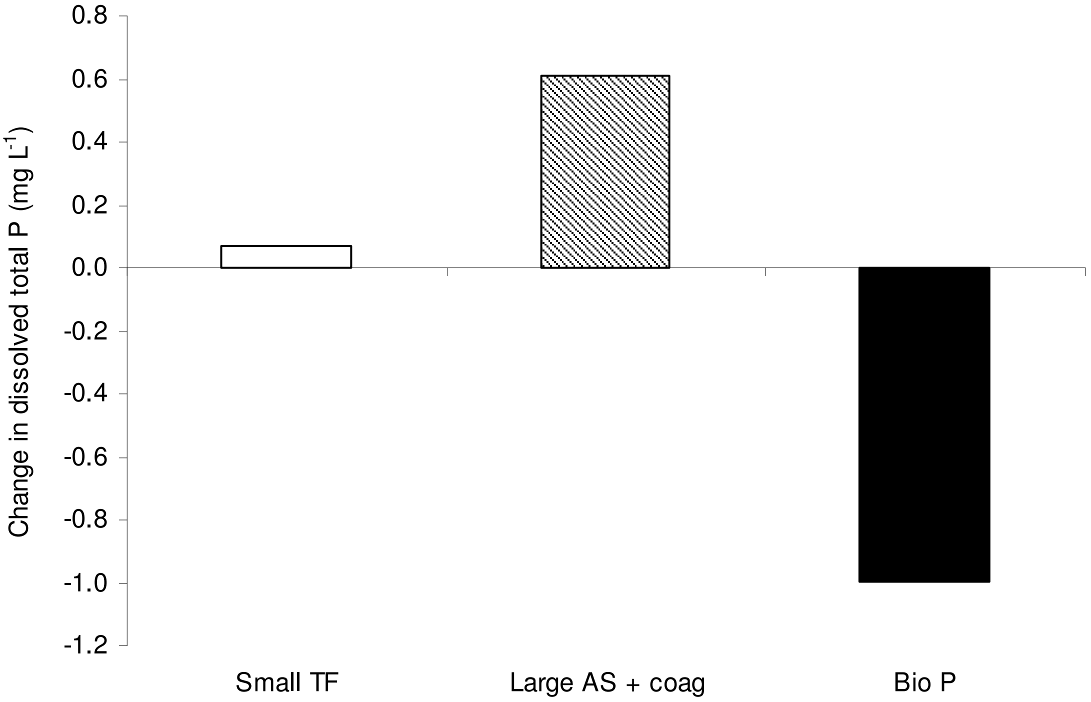

Figure 3.11: Change in total phosphorus in the dissolved (1 kDa) fraction before/after the biological process in each plant.

3.3.3 Effluent phosphorus characteristics

Total phosphorus levels in the final effluent were 4.79 and 3.42 mg L^{-1} (± 0.05) for the small TF and small AS works respectively, and 0.67, 0.83, and 0.18 mg L^{-1} (± 0.05) for the large TF, large AS and Bio P plants respectively, all three within their compliance limits. Of this phosphorus, the larger molecular weights are removed during treatment, and levels occurring at weights > 3 kDa make up less than 30 % (± 1.1) across all the sampled sites (Figure 3.12). Levels of total phosphorus in molecular weights below 1 kDa were 93.0, 70.1, 84.5, 81.9 and 77.8 % (± 1.1) for the small TF, Large TF, small AS, large AS and Bio P plants respectively.

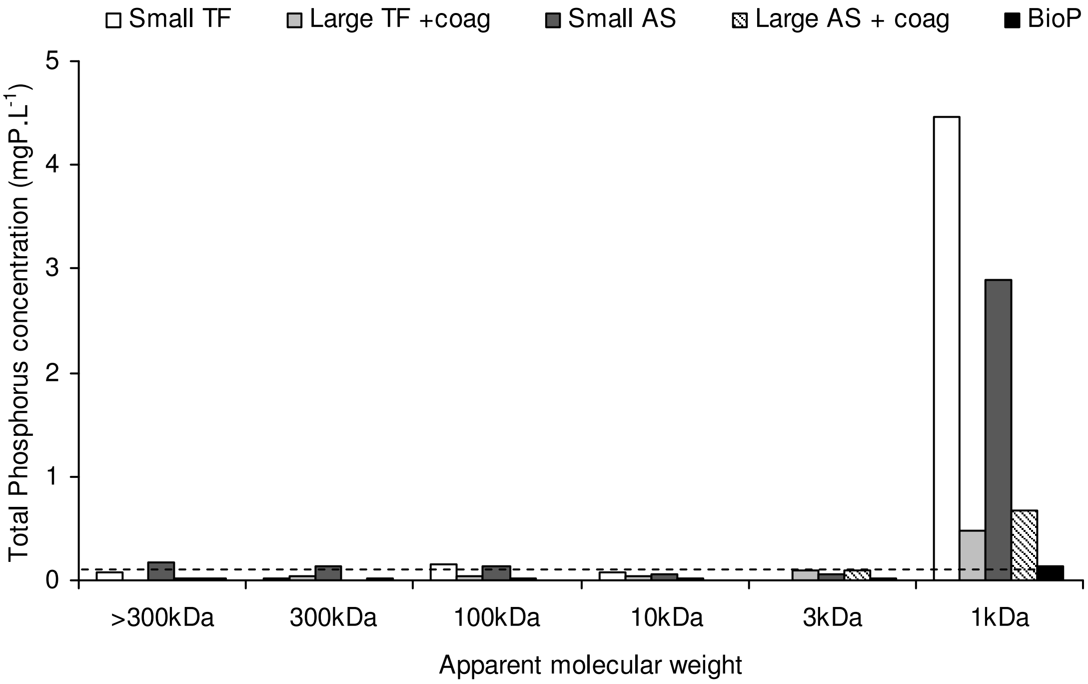

Figure 3.12: Total phosphorus by molecular weight in the final effluent of the sampled sites.

Levels of organically bound phosphorus in the final effluents of all the works were negligible, and are therefore not shown here for brevity. Consequently, the levels of phosphorus as phosphate proceed similarly to the total phosphorus molecular weight distribution, with less than 30 % (± 1.1) on average occurring across all the works at levels greater than 3 kDa (Figures 3.13 and 3.14). Phosphate below 1 kDa in weight made up 89.7, 70.0, 89.6, 50.0, and 100 % (± 1.1) of the final effluents of the small TF, large TF, small AS, large AS and Bio P plants respectively.

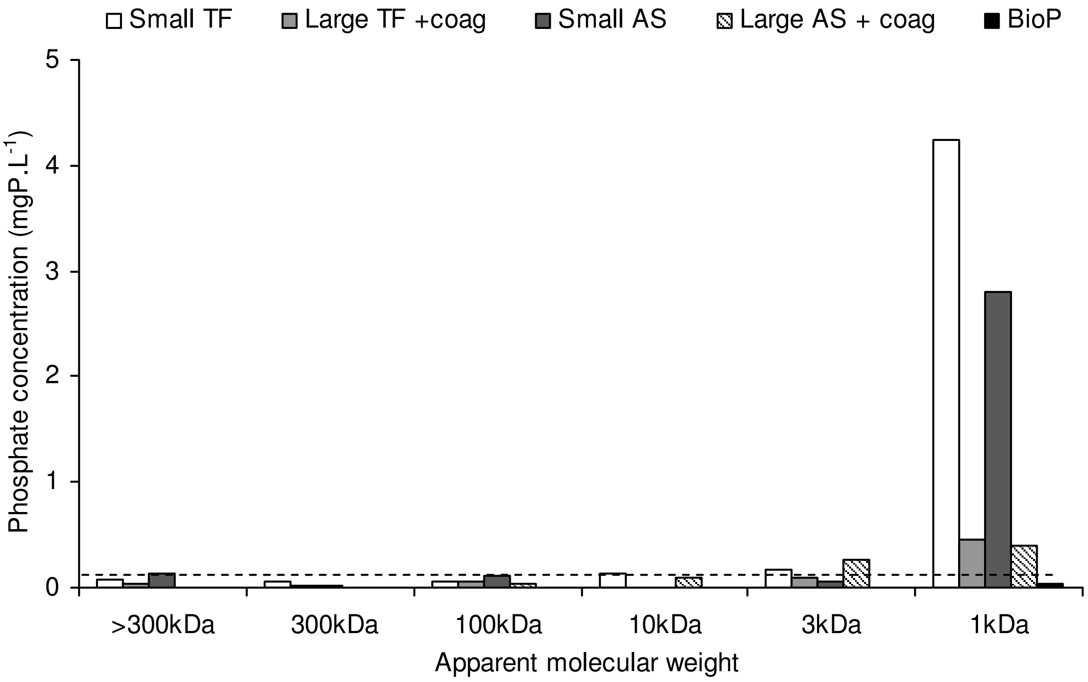

Figure 3.13: Phosphorus as phosphate by molecular weight in the final effluent of the sampled sites.

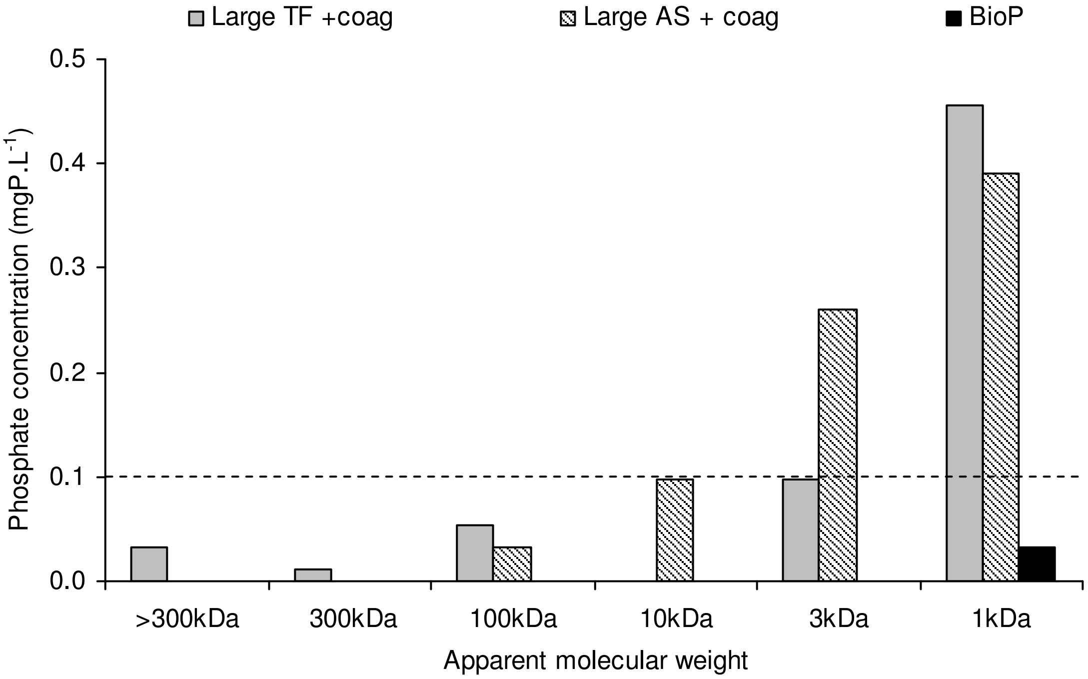

Figure 3.14: Phosphorus as phosphate by molecular weight in the final effluent of the sites with discharge consents.

3.4 Discussion

3.4.1 Implications for future phosphorus removal regimes

Although variations between the works exist in terms of the initial concentrations of phosphorus species entering, and the overall removal performance, the resilience of the sampled works (i.e. achieving phosphorus consents up to the 90th percentile, and overall compliance with the other effluent parameters) allow common traits to be considered. 95 % of the phosphorus in each stage of treatment occurs as phosphate species. At around neutral pH, these are likely to be a 50 / 50 mix of HPO_4^{2-} and $H_2PO_4^-$. The remaining portion is present in organic species. In general, these organic phosphorus species are rapidly taken up by the microbial population in each treatment works, and by the final effluent stage, hardly any is present, and none less than 1 kDa in weight. The majority of the phosphorus resides in inorganic colloidal molecular weight fractions below 10 kDa, and mostly in a dissolved state below 1 kDa.

Previous work (Sallanko *et al.*, 2006) has shown that the amount of phosphorus does not significantly change when membranes as tight as 0.1 μm are used. Attempts have been made to remove phosphorus using filtration techniques, and Nir *et al.,* (2009) used coagulation upstream of an ultrafiltration membrane with a 20 kDa molecular weight cut-off, but this was only able to attain a phosphorus removal of 54 % by weight from an influent of 10 mg L^{-1}. The present study supports this and further quantifies that the majority of phosphorus in wastewater is truly dissolved, not colloidal in nature. Sophonsiri & Morgenroth (2003) found that the size of phosphorus fractions reduced during treatment, either by release of soluble phosphate during biological hydrolysis or oxidation of organic particles, whilst Sallanko *et al.,* (2006) investigated the tendency for phosphorus to dissolve when in storage or in pipes on the way to treatment works. Removing phosphorus from wastewater would be easily achieved if more of it occurred in the particulate range, but since the mechanisms that cause it to dissolve are difficult to remediate, future techniques must be able to improve the removal of phosphorus occurring below 1 kDa. The new consent limit introduced by the Water Framework Directive may be as low as 0.1 mg L^{-1}. If this is implemented, every style of treatment works will need to be upgraded with techniques that enable removal of phosphorus in size fractions below 1 kDa.

In a separate study, final effluent from the large AS works was contacted with a hybrid ion exchange / ferric nanoparticle adsorbent media which removed 87, 91 and 89 % (± 1.1) of the phosphorus at molecular weights of 10, 3 and 1 kDa respectively (Figure 3.15). Materials such as this adsorbent offer a solution to the problem of attaining low phosphorus discharge limits by efficiently removing the dissolved fraction from wastewaters. In addition, they require low chemical inputs (for regeneration of the media only), are insensitive to shock loads and temperature changes, produce no sludge, and offer sustainability advantages over chemical or biological techniques via the recovery of phosphorus in the regeneration step.

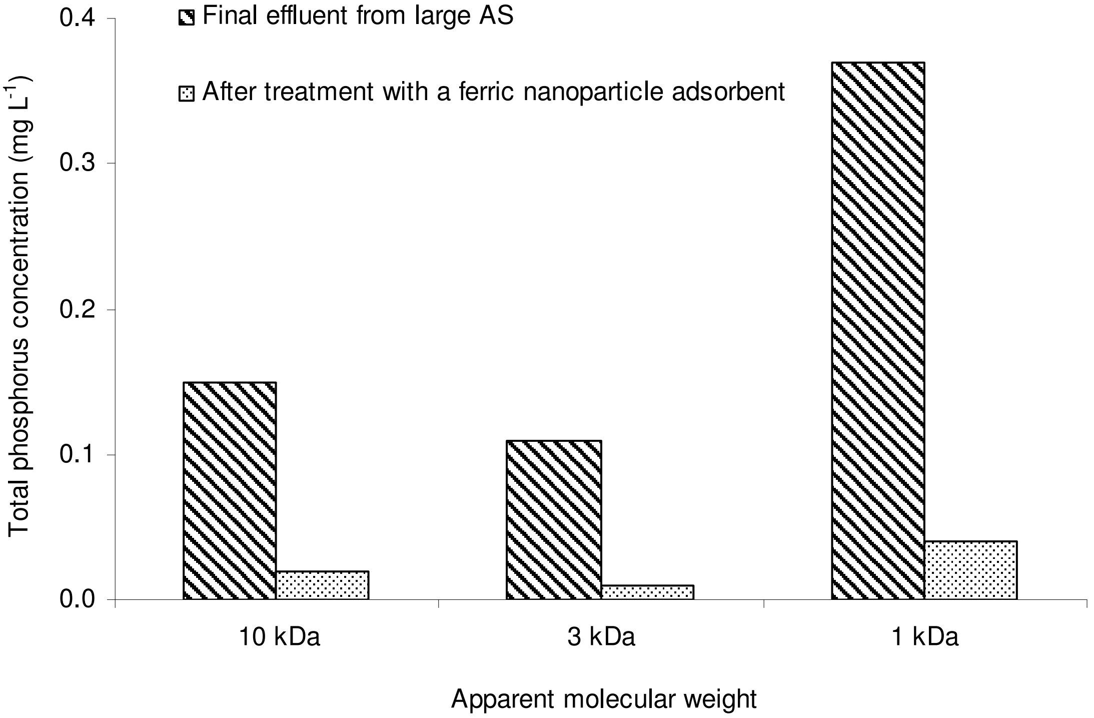

Figure 3.15: Removal of low molecular weight phosphorus using a novel adsorbent.

3.5 Conclusions

The majority of phosphorus in municipal wastewaters is present as inorganic phosphate species, and is mostly distributed in the dissolved fraction, either in the raw influent to the works, or after treatment (Table 3.1).

Table 3.1: Average distribution of total phosphorus in dissolved, colloidal and particulate fractions across all the sampled treatment works

Fraction	Average distribution in influent (%)	Standard deviation (%)	Average distribution in effluent (%)	Standard deviation (%)
Dissolved (< 1 kDa)	**62.9**	**12.5**	**81.5**	**8.4**
Colloidal (3 – 100 kDa)	**22.5**	**14.1**	**11.7**	**9.7**
Particulate (> 300 kDa)	**14.6**	**12.1**	**6.9**	**7.3**

Influent organic species are well distributed across the various weight classes but are reduced to negligible levels during treatment as they are taken up by the biota present in each works. A modest reduction in the comparative amount of large molecular weight phosphorus occurs during treatment in every class of works sampled (Table 3.1). Most of the phosphorus in final effluents is therefore present in molecular weights below 10 kDa, of a colloidal to dissolved nature. Additionally, the distribution of phosphorus in this size fraction is skewed towards the 1 kDa molecular weight band, and is therefore truly dissolved, not colloidal in nature. This means that in order for new phosphorus removal techniques to be successful, they must have the ability to remove a greater amount of phosphorus in the dissolved fraction.

3.6 Acknowledgements

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3.7 References

Blaney, L.M., Cinar, S., SenGupta, A.K., (2007). Hybrid anion exchanger for trace phosphate removal from water and wastewater. *Water Research* **41**, pp. 1603-1613.

Bostrom, B., Persson, G., Broberg, B., (1988). Bioavailability of different phosphorus forms in freshwater systems. *Hydrobiologia* **170** (1), pp. 133-155.

Buffle, J., Leppard, G.G., (1995). Characterization of Aquatic Colloids and Macromolecules. 1. Structure and Behavior of Colloidal Material. *Environmental Science and Technology* **29** (9), pp. 2169-2175.

European Union, (2008). The EU Water Framework Directive - integrated river basin management for Europe. http://ec.europa.eu/environment/water/water-framework/index_en.html. Accessed July 2010.

Gonzalez Medeiros, J.J., Perez Cid, B., Fernandez Gomez, E., (2005). Analytical phosphorus fractionation in sewage sludge and sediment samples. *Analytical and Bioanalytical Chemistry* **381** (4), pp. 873-878.

Hens, M., Merckx, R., (2002). The role of colloidal particles in the speciation and analysis of “dissolved” phosphorus *Water Research* **36,** 6, pp.1483-1492.

Hiemenz, P.C., Rajagopalan, R. (eds), (1997). Colloid and Surface Chemistry: Scope and Variables. In *Principles of Colloid and Surface Chemistry,* Marcel Dekker, New York, pp. 1-56.

Jarvie, H.P., Mortimer, R.J.B., Palmer-Felgate, E.J., Quinton, K. St., Harman, S.A., Carbo, P., (2008). Measurement of soluble reactive phosphorus concentration profiles and fluxes in river-bed sediments using DET gel probes. *Journal of Hydrology* **350** (3-4), pp. 261-273.

Judd, S., Jefferson, B. (2003). *Membranes for Industrial Wastewater Recovery and Re-use.* Elsevier, Oxford, UK.

Martin, B.D., Parsons, S.A., Jefferson, B., (2009). Removal and recovery of phosphate from municipal wastewaters using a polymeric anion exchanger bound with hydrated ferric oxide nanoparticles. Water Science and Technology **60** (10), pp. 2637-2645.

Nir, T., Arkhangelsky, E., Levitsky, I, Gitis, V., (2009). Removal of phosphorus from secondary effluents by coagulation and ultrafiltration. *Desalination and Water Treatment* **8** (1-3), pp. 24-30.

Sallanko, J., Hinkkanen, M., Okkonen, J., (2006). Fractionation of fresh wastewater and solubility of phosphorus in short-term storage. *Journal of Environmental Science and Health Part A* **41**, pp. 1183-1188.

Sophonsiri, C., Morgenroth, E., (2003). Chemical composition associated with different particle size fractions in municipal, industrial, and agricultural wastewaters. *Chemosphere* **55**, pp. 691-703.

Waldeback, M., Rydin, E., Markides, K., (1998). Use of accelerated solvent extraction for determination of ecological important phosphorus in lake sediments. *International Journal of Environmental Analytical Chemistry* **72** (4), pp. 257-266.

4. Removal and recovery of phosphate from municipal wastewaters using a polymeric anion exchanger bound with hydrated ferric oxide nanoparticles

B.D. Martin, S.A. Parsons, B. Jefferson

4.1 Introduction

Phosphorus enters municipal wastewater treatment works from both domestic and industrial sources, with typical concentrations between 4 and 12 mg L^{-1} (Metcalf & Eddy, 2003). Under the Urban Wastewater Treatment Directive (EC, 1991), the levels of phosphorus in municipal wastewater streams must be reduced before discharge to the environment. If natural waters are enriched with phosphorus they are at risk of becoming eutrophic, which has adverse effects on the ecology of freshwater systems and the uses to which the water may be put. Values for phosphorus concentrations that might tip the balance of a natural system towards eutrophication are not well defined, as the characteristics of each water body will influence the response to an enrichment event. What is known is that phosphorus pollution significantly increases the risk of eutrophication, and that point (sewage effluent) rather than diffuse (agricultural) sources of phosphorus pose the most significant risk for river eutrophication (Jarvie *et al.,* 2006). The Urban Wastewater Treatment directive is due to be updated with The Water Framework Directive (EC, 2000), which seeks to further improve surface waters to "good" ecological quality. Phosphorus is of particular concern in this context because of its role in eutrophication. Although there is no widely accepted standard for the background concentration of phosphorus in river waters, a mean of 0.1 mg P L^{-1} has been proposed (EA, 2000). This level refers to the concentration of soluble reactive phosphorus (the portion that is most available to biota). In a survey of 98 UK rivers, 80% failed this target (Muscutt & Withers, 1996). Currently, typical limits for discharge from sewage treatment works are 2 mg L^{-1} P for a 10,000 – 100,000 population equivalent, and 1 mg L^{-1} P for treatment works with a > 100,000 population equivalent (EC, 1991). The Water Framework Directive is expected to impose a reduction in these consent limits to bring the phosphorus concentration in line with the 0.1 mg P L^{-1} found in natural waters. Traditional biological nutrient removal is incapable of achieving an effluent stream of 0.1 mg of P L^{-1} (Blaney *et al.,* 2007). However, it is possible to increase chemical dose to attain this concentration, but the additional cost, sludge production, and the water industry's desire to move towards chemical free treatment makes it an undesirable option. An investigation into new techniques is therefore required, to enable the water industry to comply with the tighter consent limits and so protect the ecology of surface waters. Additionally, estimates of phosphate resources predict that they may be exhausted in as little as several decades (Kotabe, 1987). The dramatic rise in the price of P based fertiliser in 2008, which saw diammonium phosphate prices almost double during the first quarter to $1000/material ton (Coons, 2008), means that sustainable use of this valuable and finite resource is becoming increasingly important. An ideal solution would therefore be a technique that can both remove phosphorus from wastewater streams and recover it as a useful product, such as a fertiliser. This would enable compliance with the new legislation in a sustainable manner, in terms of both resource management and economics.

4.1.1 Ion exchange

Since phosphorus occurs in final effluent wastewater streams predominantly as phosphate anions (Snoeyink & Jenkins, 1980), using an ion exchange process could achieve the twin aims of removal and recovery. Ion exchange is defined as the reversible interchange of ions between a solid phase (the ion exchanger) and a solution phase (Harland, 1994). The affinity of an exchange material for a particular ion is proportional to the valence and weight of the ion. Even though phosphate species have relatively high valency and weight, the phosphate concentration in wastewaters is low in comparison to other anions. This means that in a conventional ion exchange process, removal of phosphate is not very efficient as the exchanger reaches capacity very quickly because all the exchange sites are occupied with the competing anions. Numerous fixed bed sorption/ion exchange trials for the removal of phosphate have been attempted (Eliassen & Tchobanoglous, 1968; Nesbitt, 1969), without great success. The lack of phosphate selectivity and the high operating cost due to the frequent application of regeneration chemicals were sited as major shortcomings affecting the overall viability of the fixed bed process (Zhao & Sengupta, 1998). In all the foregoing studies, phosphate breakthrough from the fixed-bed column always occurred in less than two hundred bed volumes. For ion exchange to work well, an adaption to the standard process or materials is needed.

4.1.2 Effect of hydrated ferric oxide nanoparticles

Based on work by Morel & Hering, (1993), and Zhao & Sengupta, (1998), immobilising particles of a transition metal cation onto a polymer base will enable it to act as an anion exchanger with a high affinity towards anions with strong ligand characteristics such as phosphate. The hybrid anion exchanger (HAIX) used in this study was made using such a process. The parent material is a standard polymeric strong base anion exchanger, into which hydrated ferric oxide (HFO) nanoparticles have been dispersed (Figure 4.1).

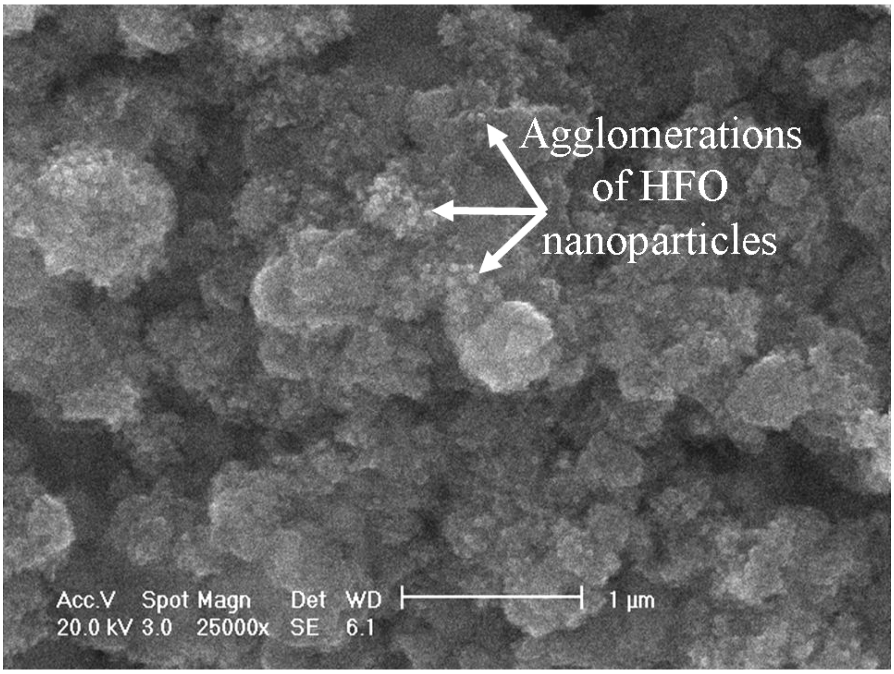

Figure 4.1: SEM image of the surface of an unused HAIX bead.

At above neutral pH the phosphate in wastewater streams exists primarily as the divalent anion HPO_4^{2-} (Zhao & Sengupta, 1998), and its intermediate, the monovalent $H_2PO_4^-$ (Blaney *et al.*, 2007). HPO_4^{2-} is a fairly strong bidentate ligand containing two oxygen donor atoms. Likewise, $H_2PO_4^-$ is a fairly strong monodentate ligand with one oxygen donor atom. The ligand strength of both forms (i.e. their ability to form inner sphere complexes with transition metals - for e.g. ferric iron) is much greater than the other inorganic anions commonly present in wastewater (Zhao & Sengupta, 1998). This enables HAIX to act as a phosphate selective ion exchanger, and because it can be regenerated in the same manner as a conventional exchange resin, the phosphate can be desorbed and recovered.

Similar to the parent resin of HAIX, Amberlite IRA-410 is a strongly basic anion exchange resin in the chlorine form (Figure 4.2). It consists of a styrene-divnylbenzene gel matrix and has an ammonium functional group. Comparing the SEM images, it is apparent that the Amberlite has a much smoother surface due to the lack of nanoparticle agglomerations.

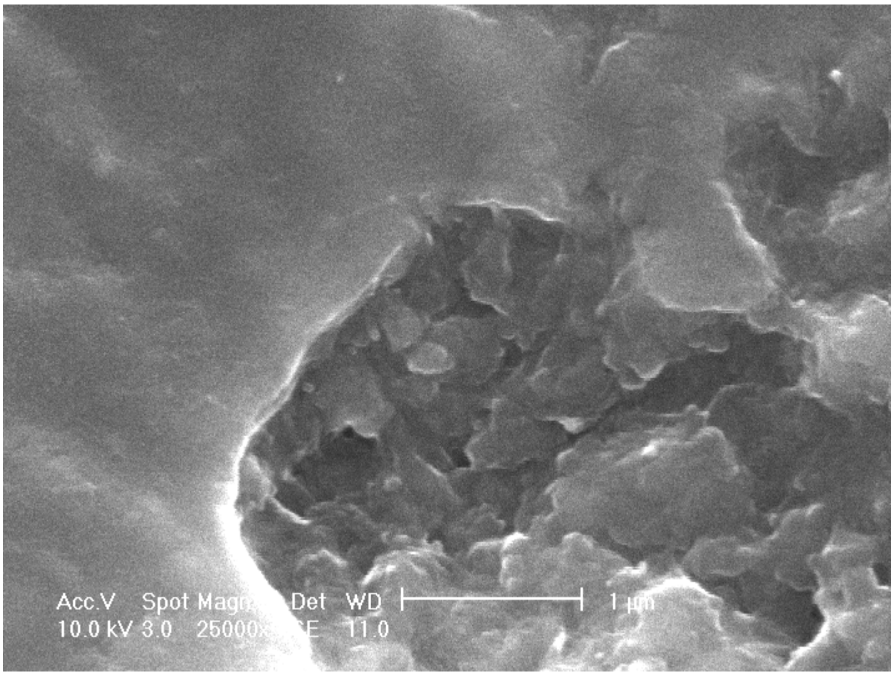

Figure 4.2: SEM image of the surface of an unused Amberlite IRA-410 bead.

Comparing the performance of the Amberlite with the HAIX resin will quantify the effect of adding HFO nanoparticles, and demonstrate the efficiency (or lack thereof) of a standard exchange resin in removing phosphate from wastewater. The aim of this chapter is to provide an initial analysis of the performance of the HAIX material: in terms of differing feed solutions; in comparison with Amberlite; for regeneration and P recovery, and to economically assess its potential for use by the water industry.

4.2 Methods

The hybrid anion exchange resin (trademark: PhosX^{np}) was provided by SolmeteX Co., Massachusetts. Final effluent samples were collected from operating sewage treatment works based on chemical precipitation with ferrous chloride into an activated sludge process (population equivalent > 250,000), and a trickling filter site with no specific phosphorus removal process (population equivalent < 10,000). The sample waters were pumped through a column of 15 mm diameter and 210 mm length containing 10 mL of media, with an empty bed contact time (EBCT) of 2 minutes to compare performance between effluents. The water from the trickling filter works was not pre-filtered, but the sample from the chemical precipitation works was passed through a 1.2 μm filter to minimise fouling risk over the extended run period. The comparison between HAIX and Amberlite IRA-410 (Rohm and Haas, (UK) Ltd, Coventry) was carried out using the same sample water from the trickling filter works, and an identical equipment set up. 10 mL of HAIX and 10 mL of Amberlite were trialled side by side, with an EBCT of 4 minutes. The regenerative tests used the same column and resin bed volume, but extended the EBCT to 4 minutes. The water used was a solution of ammonium phosphate with a PO_4^{3-} concentration of 500 mg L^{-1}. 100 bed volumes of this solution was passed through the column then the media was regenerated with a single bed volume (10 mL) of 4 % NaOH, 2 % NaCl solution, backwashed with deionised water and then put back into service. All experiments were carried out at room temperature (18 - 20 ºC). Determination of total P and phosphate was by Spectroquant cell tests, in triplicate. The method is analogous to EPA 365.2+3, US Standard Methods 4500-P E (Standard Methods, 1995), and ISO 6878.

4.3 Results and discussion

4.3.1 Characterisation of the wastewaters used in the study

The chemical precipitation works uses ferrous chloride and ferric sulphate to remove phosphate, resulting in elevated levels of chloride and sulphate ions in the final effluent when compared to that from the trickling filter works (Table 4.1). The trickling filter performance in terms of P and N removal is poor in comparison to the chemical plant. In both final effluents, the concentration of phosphate anions is much lower than the concentrations of the other anions.

Table 4.1: Characterisation of the final effluents tested with HAIX.

Parameter	Trickling filter works	Chemical precipitation works
pH	6.85 ± 0.20	7.14 ± 0.20
Temp. of sample whilst testing (ºC)	18.00 ± 0.75	18.00 ± 0.75
Phosphate (mg L^{-1})	14.55 ± 1.84	1.89 ± 0.20
Chloride (mg L^{-1})	60.89 ± 6.54	129.82 ± 1.38
Nitrate (mg L^{-1})	156.82 ± 3.70	44.91 ± 0.88
Sulphate (mg L^{-1})	55.93 ± 0.22	169.73 ± 1.96

4.3.2 Comparison with Amberlite IRA-410

The HAIX resin was able to remove a significant proportion of the phosphate and eventually reached capacity after treating 1000 bed volumes (Figure 4.3).

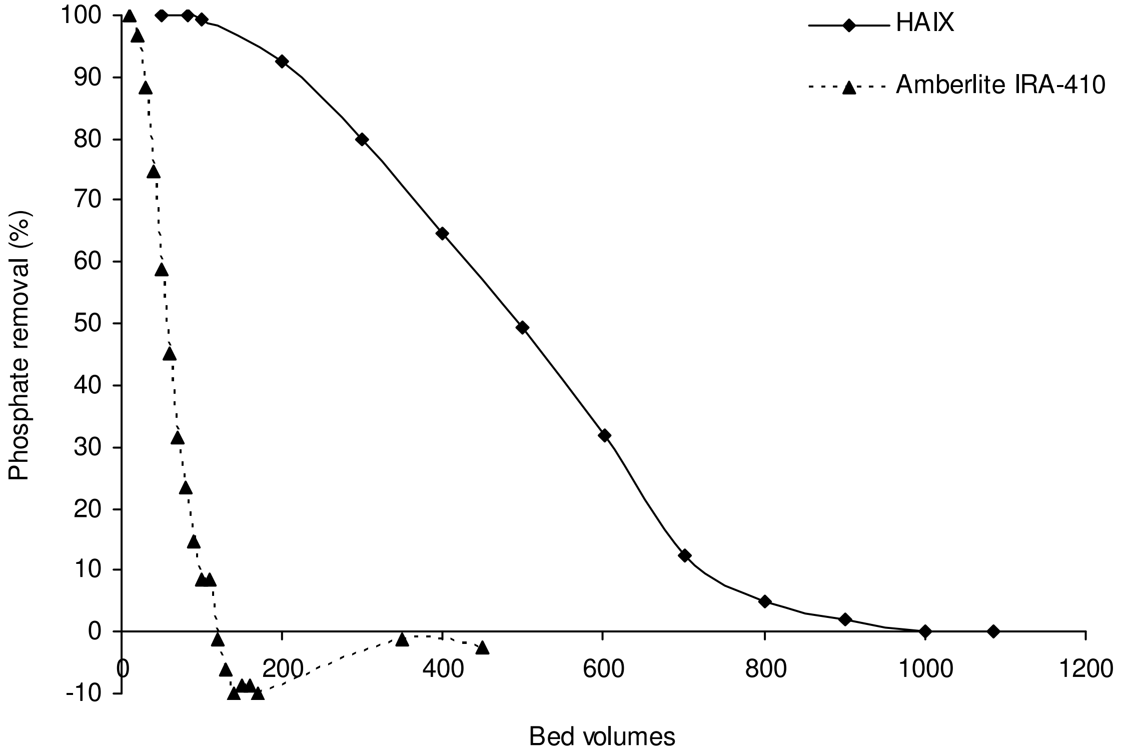

Figure 4.3: Performance comparison of Amberlite IRA-410 and HAIX.

The curve shows a gradual decline in removal rates as the adsorption sites on the resin become associated with phosphate. During the run, the HAIX removed 11.34 mg PO_4^{3-}

g^{-1} resin from the solution, from a starting concentration of 15.2 mg L^{-1}. In contrast, the Amberlite's performance rapidly tailed off and after reaching capacity at around 170 bed volumes, started to elute the phosphate. This is due to the resin's preference for sulphate which results in early breakthrough and chromatographic elution of phosphate (Zhao & Sengupta, 1998). Sulphate concentration in the trickling filter works sample was 60 mg L^{-1}. The Amberlite removed only 0.99 mg PO_4^{3-} g^{-1} resin during its run, from an initial concentration of 16.2 mg L^{-1}. The performance of Amberlite in this trial closely resembles findings in Zhao & Sengupta (1998), and Blaney *et al.,* (2007), where performance was characterised by rapid breakthrough followed by phosphate elution, and a complete lack of removal thereafter. The former study used a total P concentration of 4 mg L^{-1} (approximately 12 mg L^{-1} as phosphate), with sulphate at 100 mg L^{-1}. Breakthrough occurred at around 400 bed volumes, with a dramatic elution spike. The latter investigation used phosphate and sulphate concentrations of 0.26 mg L^{-1} and 120 mg L^{-1} respectively, and phosphate breakthrough occurred at 200 bed volumes, and again, phosphate was eluted. Amberlite is therefore not considered to be an efficient choice for phosphate removal, as its selectivity is poor due to the competition from much higher concentrations of sulphate found in wastewater. Additionally, the elution of phosphate from a column containing Amberlite is clearly an undesirable trait. The HAIX resin has a much higher capacity for phosphate in comparison, and there is no evidence to suggest that it exchanges other ions in preference to phosphate, since none was eluted during any of the trials detailed here, or in previous studies.

4.3.3 HAIX performance with real effluents

Previous work using HAIX (Blaney *et al.*, 2007) demonstrated its effectiveness in removing trace phosphate levels from wastewater (0.26 mg P L^{-1}), even with high concentrations of competing anions. Based on the shape of the curve for the trickling filter works, favourable equilibrium was attained, with a sharp exchange front suggesting good mass transfer characteristics (Figure 4.4).

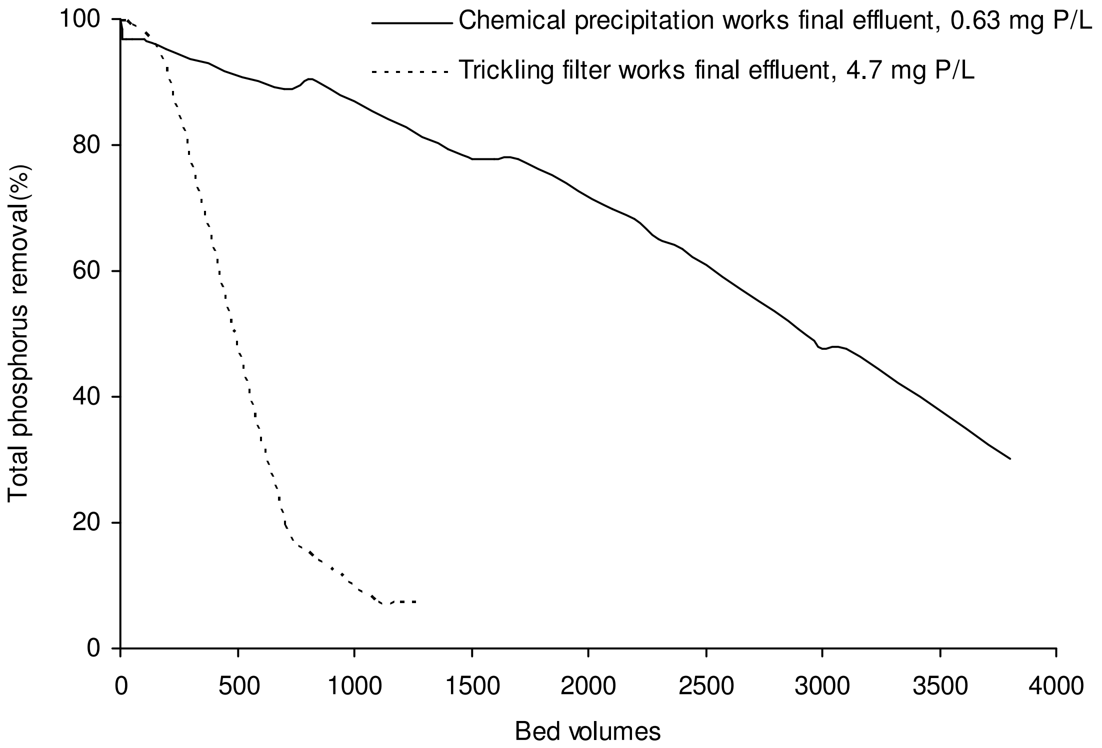

Figure 4.4: Media performance when contacted with low and medium strength phosphate effluents.

Saturation occurred at around 1300 bed volumes. The lower capacity (7.94 mg PO_4^{3-} g^{-1} in comparison to 11.34 mg PO_4^{3-} g^{-1}) returned from the chemically treated wastewater is consistent with the lower starting concentration of phosphate. In addition, the curve for the chemical precipitation works effluent is not so well defined. The exchange front is not sharp, probably as a result of too short a contact time - the exchange rate of the resin was not fast enough to attain equilibrium (Harland, 1994). The results complement those detailed in Blaney *et al.,* (2007), where phosphate breakthrough did not occur until around 15000 bed volumes. The phosphate concentration in the water used in the study was lower than both of the effluents used in the present case, and hence a greater number of bed volumes are expected to be treated. The performance of HAIX in the present study is proportional to Blaney *et al.,* (2007), as it follows the expected curves given the greater starting phosphate concentrations. The difference in capacities and in the shape of the breakthrough curves is more likely to be a result of the different concentration gradients as oppose to the sulphate : phosphate ratio (3.8 : 1 in the trickling filter effluent, and 89.8 : 1 in the chemical precipitation works effluent), which does not significantly affect the kinetics of the adsorption process (see Chapter 6).

4.3.4 Regeneration and phosphorus recovery

80 % of the phosphorus was eluted in the first bed volume, generating a stream with a P concentration of 1250 mg L^{-1} (Figure 4.5). If most of the phosphorus removed from the wastewater stream can be recovered by using just one bed volume of regenerant, then the recovery operation can be run at a very high efficiency. A small volume, highly concentrated phosphorus stream is easier to process into a useful product than a dilute solution. The subsequent regenerant/recovery trial is based on the idea that complete removal of a target ion from an ion exchange resin is not necessary for cyclic column operation (Jelinek & Sorg, 1988).

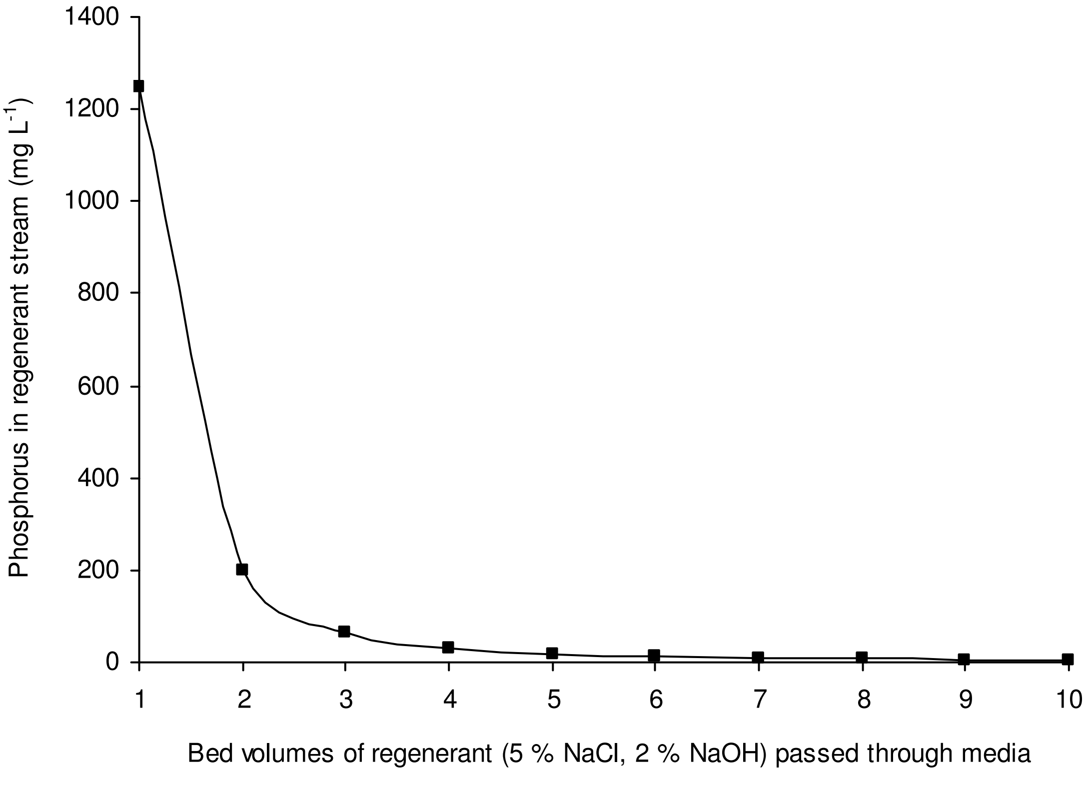

Figure 4.5: Phosphorus elution profile.

Figure 4.5 shows that 20 % of the phosphorus removed during service remains on the resin after the first bed volume of regenerant has passed. It would therefore follow that putting the resin back into service at this point will result in a lower capacity being attainable, given the number of exchange sites already occupied by phosphate. The degree to which capacity is affected, balanced by the efficiency of the recovery operation will determine if this is a realistic way to run a HAIX operation. In this trial, the performance of the resin did not deteriorate after 10 partial regenerations (Figure 4.6). The exchange fronts of all the curves resemble the favourable equilibriums shown in Figures 4.3 and 4.4. The range of phosphate removed by each run was 35 - 50 mg g^{-1} HAIX, with the starting concentration of 500 mg L^{-1} phosphate. Performance was consistently better than with the virgin HAIX. Brand new HAIX beads have iron fines on them from manufacture which need to be washed off before use - in this trial some may have still been present in the first run, inhibiting phosphate removal. Consequently, bead preparation is an important consideration for full scale trials.

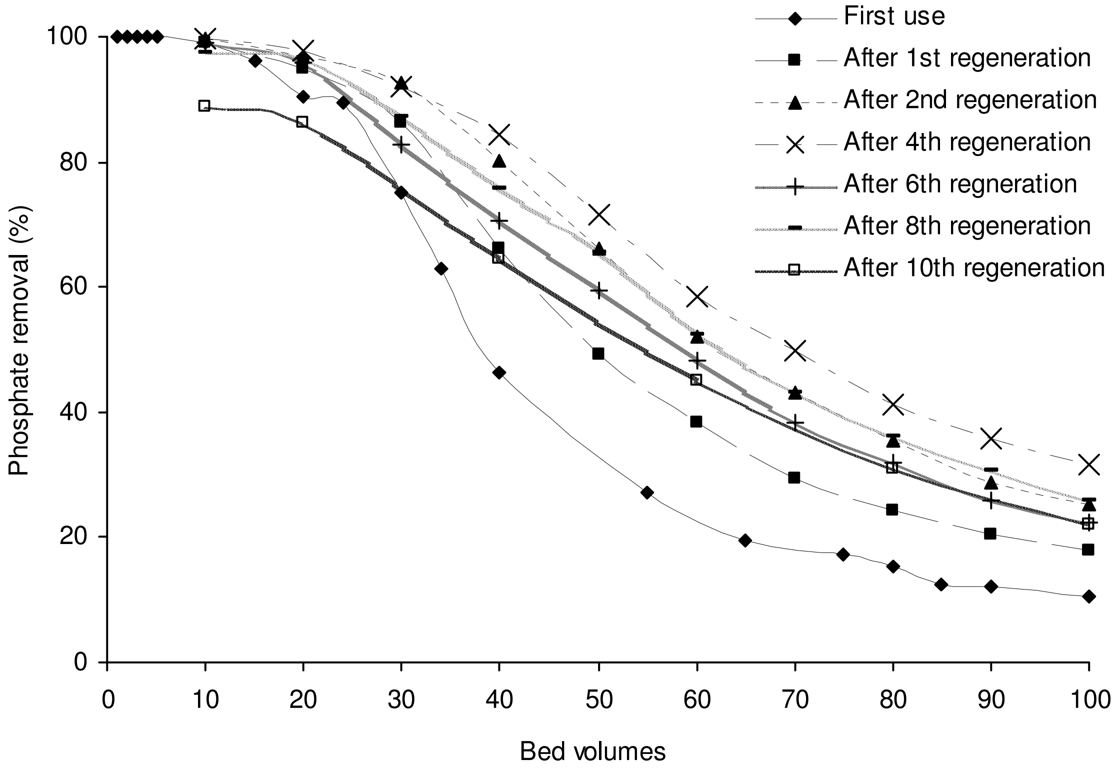

Figure 4.6: HAIX performance after multiple partial regenerations.

The results suggest that optimal elution of phosphate through partial regeneration is possible without adversely affecting subsequent performance. In an operational setting, this means that phosphate recovery can be highly efficient, the service time for regeneration is minimal, and the overall footprint is low.

4.3.5 *Economic assessment*

Over the life cycle of an ion exchange operation, it is the cost of chemicals used to regenerate the resin that is the main limiting factor in its economical success (Wachinski & Etzel, 1997). For the regenerant solution required for the HAIX media, this cost is approximately \$18.2 per cubic metre (based on \$0.35 kg^{-1} for NaOH at 4 %, and \$0.21 kg^{-1} for NaCl at 2 % (Jacob, 2007)). This cost could be offset if the phosphate recovered from a process using HAIX was sold on. In 2008, the cost of phosphate based fertilisers rose dramatically due to a combination of political reasons, increased demand as a result of population growth, and the rising wealth of developing countries (Coons, 2008). Prices have reduced subsequently, but are still much higher than in 2007, and demand for phosphate commodities is expected to outstrip supply in 2011/2012, with Western Europe being a deficit area. As of March 2009, the price of phosphate rock is \$500 per tonne (USGS, 2009). Based on these values, and the performance of the lab scale HAIX operation detailed in this chapter, an initial economic assessment has been carried out (Tables 4.2 and 4.3). Resin cost (\$11.50 L^{-1}) per day has been estimated based on the findings of Blaney *et al.*, 2007, where the same resin was used for over two years with no degradation.

Table 4.2: Economics of HAIX use - Chemical precipitation works.

Flow: 3.56×10^7 L day^{-1}, concentration of P in feed to HAIX: 0.63 mg L^{-1}			
Target effluent concentration (mg L^{-1})	0.1	0.25	0.5
Bed volumes treatable by HAIX	1000	2500	5000
Volume of resin needed per day (litres)	35625	14250	7125
Price of HAIX per day, based on a 2 year life (\$)	561	224	112
Volume of regenerant needed per day (litres)	35625	14250	7125
Price of regenerant used per day (\$)	648	259	130
P recovery per day, based on 80% efficiency (kg)	15	11	4
Value of recovered P per day (\$)	7.55	5.42	1.85
Profit per day (\$)	-1202	-478	-240

With the current price of phosphate commodities, making the process cost neutral does not look achievable, even given the crude analysis detailed here, which does not consider plant costs, energy, processing the regenerant stream into a marketable product, and transport. However, when considered in terms of process selection, the recovery of phosphorus makes using the HAIX a potentially favourable economic option compared to alternative treatments. For instance, the Fe:P coagulant dose required to achieve the current consent of 1 mg P L^{-1} is 2.7:1. To achieve an effluent quality of 0.1 mg P L^{-1}, an Fe:P ratio of 8:1 is required, which would effectively triple the cost of P removal.

Table 4.3: Economics of HAIX use - Trickling filter works.

Flow: 6.75×10^5 L day^{-1}, concentration of P in feed to HAIX: 4.7 mg L^{-1}

Target effluent concentration (mg L^{-1})	0.1	0.25	0.5
Bed volumes treatable by HAIX	10	100	150
Volume of resin needed per day (litres)	67500	6750	4500
Price of HAIX per day, based on a 2 year life ($)	1063	106	71
Volume of regenerant needed per day (litres)	67500	6750	4500
Price of regenerant used per day ($)	1229	123	82
P recovery per day, based on 80% efficiency (kg)	2.5	2.4	2.3
Value of recovered P per day ($)	1.24	1.2	1.13
Profit per day ($)	-2290	-228	-152

4.3.6 Limiting factors and other considerations

The HFO nanoparticles are expected to remain fixed within the exchanger for many operation cycles (Blaney *et al.*, 2007). However, some early work has shown a small decrease of iron from the surface of the resin beads during service by comparing new, used and regenerated beads using X-ray spectroscopy (Figure 4.7).

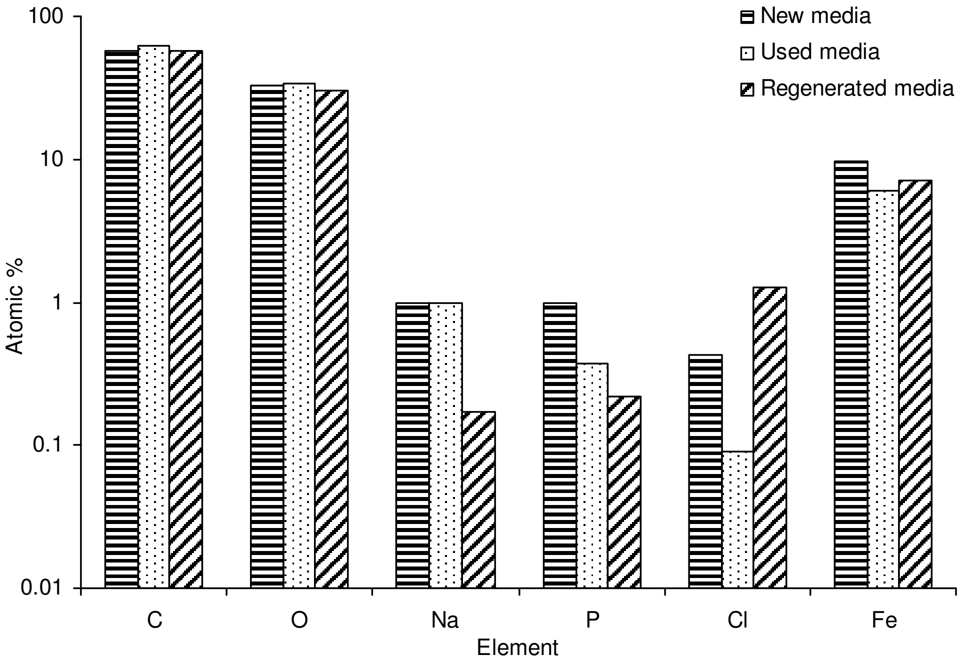

Figure 4.7: X-Ray spectroscopy of new, used and regenerated HAIX media beads.

The values of other elements present on the surface of the beads during the different usage cycles are in line with expectations given the organic nature of the parent bead, the organics present in wastewater, and the composition of the regenerant solutions. Visually, the beads do appear smoother after use, hinting that nanoparticles on the surface are being lost (Figure 4.8), which is confirmed by the X-ray spectroscopy results.

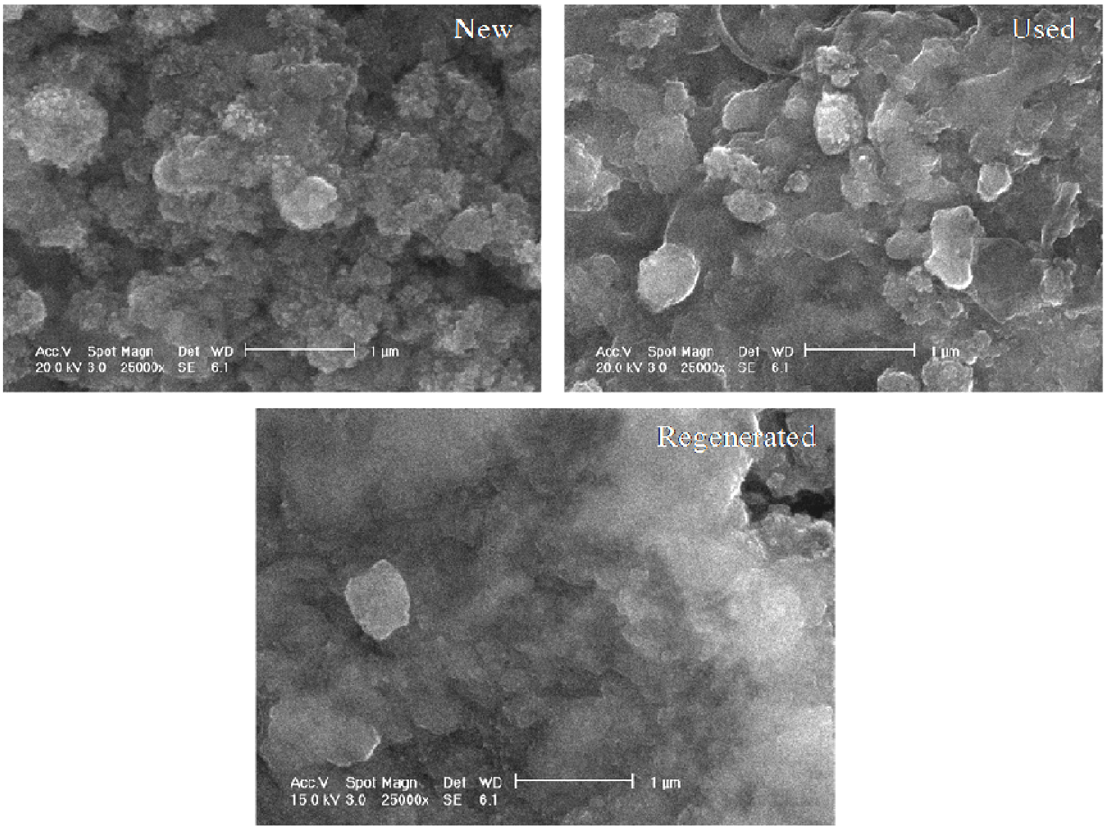

Figure 4.8: SEM images of new, used, and regenerated HAIX beads.

However, spectroscopy only analyses the surface of the material, and since the beads have a microporous structure, further investigation is needed of the inner pore surfaces. Despite the early results suggesting iron loss, no decrease of performance was observed in the present study's trials, which used the same beads multiple times. Any loss of HFO should have a dramatic effect on the selectivity of the HAIX for phosphate.

4.4 Conclusions

- The hybrid anion exchanger shows a much higher capacity (11.34 mg PO_4^{3-} g^{-1}) than a comparable strong base anion exchanger (0.99 mg PO_4^{3-} g^{-1}) when trialled using a real effluent stream containing 14.55 mg PO_4^{3-} L^{-1}.
- The capacity is 7.94 mg PO_4^{3-} g^{-1} with a real effluent containing 1.89 mg PO_4^{3-} L^{-1}, but a contact time longer than 2 minutes is recommended.
- 80 % of the phosphorus removed during a service run can be recovered using a single bed volume of regenerant solution, yielding a solution containing 1250 mg P L^{-1}.
- Partial regeneration of the HAIX had no discernable disadvantage in subsequent service runs.

4.5 Acknowledgements

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4.6 References

Blaney, L.M., Cinar, S., SenGupta, A.K., (2007). Hybrid anion exchanger for trace phosphate removal from water and wastewater. *Water Research* **41**, pp. 1603-1613.

Coons, R., (2008). Prices soar in the first quarter on tight agricultural markets. *Chemical Week* **170** (13).

EA, (2000). EA, Aquatic eutrophication of England and Wales: a management strategy, Environment Agency, Bristol (2000) 32 pp.

EC, (1991). Urban Wastewater Treatment Directive: http://eur-lex.europa.eu/smartapi/cgi/sga_doc?smartapi!celexapi!prod!CELEXnumdoc&lg=en&numdoc=31991L0271&model=guichett (Accessed March 2009).

EC, (2000) EC. Directive 2000/60/EC of the European Parliament and of the Council establishing a framework for the Community action in the field of water policy. Official Journal L 327, P. 0001-0073 (22/12/2000); 2000. www.defra.gov.uk/environment/water/wfd/index.htm, http://europa.eu.int/comm/environment/water/water-framework/index_en.html. (Accessed March 2009).

Eliassen, R., Tchobanoglous, G., (1968). Chemical processing of wastewater for nutrient removal. *Journal of the Water Pollution Control Federation* **40** (5), pp. 171-180.

Harland, C.E., (1994). Ion Exchange: Theory and Practice 2nd Edition. *Royal Society of Chemistry,* Letchworth, UK.

Jacob, C., (2007). Seawater desalination: Boron removal by ion exchange technology. *Desalination* **205**, pp. 47-52.

Jarvie., H.P., Neal, C., Withers, P.J.A., (2006). Sewage-effluent phosphorus: A greater risk to river eutrophication than agricultural phosphorus? *Science of the Total Environment* **360** (1-3), pp. 246-253.

Jelinek, R.T., and Sorg, T.J., (1988). Operating a small full-scale ion exchange system for uranium removal. *Journal / American Water Works Association,* **80** (7), pp. 79-83.

Kotabe, H., (1987). Present situation and future of phosphate resources. *Gypsum Lime* **210**, pp. 307-316.

Metcalf & Eddy, (2003). *Wastewater Engineering. Treatment and Reuse*. McGraw-Hill, New York.

Morel, F.M.M., Hering, J.G., (1993). *Principles and Applications of Aquatic Chemistry.* John Wiley and Sons, Inc., New York, NY.

Muscutt, A.D., Withers, P.J.A., (1996). The phosphorus content of rivers in England and Wales, *Water Res* **30**, pp. 1258–1268.

Nesbitt, J.B., (1969). Phosphorus removal - The state of the art. *Journal of the Water Pollution Control Federation* **41** (5), pp. 701-713.

Snoeyink, V.L., Jenkins, D., (1980). *Water Chemistry.* John Wiley and Sons, New York, NY.

Standard Methods for the Examination of Water and Wastewater, (1995). 19th edn, American Public Health Association/American Water Works Association/Water Environment Federation, Washington DC, USA.

US Geological Survey, (2009). Mineral Commodity Summaries: Phosphate Rock. http://minerals.usgs.gov/minerals/pubs/commodity/phosphate_rock/mcs-2009-phosp.pdf. Accessed March 2009.

Wachinski, A.M., Etzel, J.E., (1997). *Environmental ion exchange: principles and design*. CRC Press LLC, Florida.

Zhao, D., Sengupta, A.K., (1998). Ultimate removal of phosphate from wastewater using a new class of polymeric ion exchangers. *Water Research,* **32** (5), pp. 1613-1625.

5. Phosphorus removal with an iron based nanoparticle adsorbent

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5.1 Introduction

Current discharge consents for phosphorus from sewage treatment vary between no standard for small works, to 1 - 2 mg P L^{-1} depending on the size of the plant and/or the ecological sensitivity of the discharge catchment. Adoption of either chemical precipitation (Yang *et al.,* 2010) and/or enhanced biological reactions (Morse *et al.,* 1998) enables resilient compliance to such standards. However, it is expected that future discharge consents will be based upon the background level of phosphorus in rivers, reported to be around 0.1 mg P L^{-1} (EA, 2000) and in sensitive catchments as low as 0.01 mg P L^{-1} (Hansen, 2006). Processes based on biological P removal are not capable of achieving such tight discharge consents (Kuba *et al.,* 1993) and whilst possible with chemical precipitation, the dose requirements become unsustainable. Whichever treatment route is utilised, phosphorus is removed by converting the dissolved ion into a solid fraction as either inorganic precipitate (coagulation), microbial biomass (biological processes) or plant biomass (extensive systems). Consequently, current approaches do not aid direct recovery, although sludge fertilisation or struvite production from sludge liquors (Saidou *et al.,* 2009) enables phosphorus reuse to a degree. Consequently, the need to achieve such low residual phosphorus concentrations necessitates the consideration of alternative approaches such as contact sorption processes, as they offer greater resilience in meeting very tight discharge concentrations. In addition, some sorption materials offer the added benefit of direct recovery of phosphate as a by-product of the regeneration process. This potentially improves the sustainability of meeting tight consents as well as providing a revenue stream via recovery and reuse of phosphorus which can offset, in part, the additional investment in assets (Martin *et al.,* 2009). Whilst phosphorus recovery from wastewater is not currently practiced, the potential is relatively large with some reports suggesting that a substantial proportion of future phosphorus fertiliser demand could be met through recovery from wastewater.

The application of contact media processes for removal of phosphorus has been previously studied, and has included iron rich industrial by-products such as red mud (Li *et al.,* 2006), hydrated shale oil ash (Kaarsik *et al.,* 2008), ochre from acid mine drainage (Heal *et al.,* 2005), and natural iron oxide containing minerals such as bauxite (Altundogan & Tumen, 2003), laterite (Wood & McAtamney, 1996), and wollastonite (Brooks *et al.,* 2000), with various comparative success as reviewed in Vohla *et al.'s* 2011 study. Reported capacity to retain P varies considerably due to media size, with most media operating at less than 5 mg P g_{media}^{-1} although some report levels as high as 400 mg P g_{media}^{-1} (Vohla *et al.,* 2011). Comparative assessment has resulted in an understanding that media containing polyvalent metals exhibit highly selective removal of phosphorus from wastewater through a ligand exchange reaction where monodentate and binuclear complexes are formed (Parfitt *et al.*, 1975). Whilst the reported capacities suggest suitability for application to full scale use, challenges related to media management and regeneration limit implementation. The main issues relate to the small media sizes often trialled which then require retention by filtration and/or subsequent reduced sorption capacity post regeneration (Zhao *et al.,* 2010). In addition, many of the materials suffer bed compaction and/or fines generation during both operation and regeneration because they are not mechanically strong enough, or do not have sufficient resistance to attrition limiting use to single cycle operation (Genz *et al.,* 2004). Ion exchange resins address such concerns but suffer from a limited capacity, especially where competing ions are present such as sulphate and carbonate (Liberti *et al.,* 1976).

Recently, nanoparticle based adsorbent materials that use ion exchange beads as a scaffold have been developed which provide the combination of required mechanical properties and selectivity towards phosphorus removal (Zhao and Sengupta, 1998, Blaney *et al.,* 2007, Pan *et al.,* 2009). Additionally, the materials can be reused for many service cycles by alkaline regeneration, which deprotonates the hydrated ferric oxide particles, causing an electrostatic repulsion of phosphate back into solution (Pan *et al.,* 2009). The application of such systems is documented for arsenic removal in drinking water (Zhang *et al.,* 2008) and trace phosphorus removal (Blaney *et al.,* 2007). Consequently, looking towards predicted tighter phosphorus consents, nanoparticle based contact resins represent a potential new technology for resiliently and sustainably achieving low target phosphorus consents.

Aim and scope

This chapter builds on recent studies which have proven the effectiveness of iron nanoparticle based contact media in removing phosphorus in a variety of lab based (Zhao & Sengupta, 1998, Blaney *et al.,* 2007, Pan *et al.,* 2009) and small pilot trials (Midorikawa *et al.*, 2008). Overall, the majority of the studies have focussed on media comparison (Pan *et al.,* 2009) and the impact of wastewater characteristics (Midorikawa *et al.,* 2008) with relatively little attention directed towards design issues such as the impact of loading rate and regeneration optimisation. The current study addresses this gap in knowledge and focuses on treatment of the entire phosphorus load (i.e., no other form of P removal involved) from a real sewage works and hence looks at reducing a feed strength of 4.8 mg P L^{-1} down to 0.1 mg P L^{-1} (98% removal). This differentiates from, and compliments, previous studies which have considered removal of trace concentrations at 0.26 mg P L^{-1} (Blaney *et al.,* 2007), synthetic or industrial wastewaters of 2 mg P L^{-1} and 3.8 mg P L^{-1} (Pan *et al.*, 2009) and real wastewaters at 2.2 mg P L^{-1}, with a copper nanoparticle embedded resin (Zhao and Sengupta, 1998).

5.2 Materials and methods

5.2.1 Ferric nanoparticle adsorbent

The adsorbent media, Layne^{RT} (SolmeteX Co., Massachusetts), is a commercially available media, principally used for arsenic removal. The media comprises a strong base gel-type anion exchange resin with a quaternary ammonium functional group. Approximately 26 % of the external and internal surfaces of the material are covered with iron in hydrated ferric oxide form. The base resin has a capacity of 1 meq mL^{-1} (chloride form). The media was initially prepared by fluidisation in deionised water for 30 minutes to remove any remaining fines from the manufacturing process.

5.2.2 *Characterisation of media properties*

Two key media properties were measured during the trials. Initially the media was size graded by dry sieving through a series of 10 inch stainless steel sieves with mesh sizes ranging between 0.18 and 1.18 mm. In addition, the distribution of iron within the beads was measured using an FEI XL30 environmental scanning electron microscope (FEI UK Ltd, Cambridge, United Kingdom) in low-vac mode, and then subjected to elemental spectroscopic analysis using an Oxford Instruments EDX with INCA software (Oxford Instruments, Abingdon, Oxfordshire, United Kingdom). Prior to analysis, the beads were frozen in liquid nitrogen rather than dewatered with heat or solvent to protect their structure. Once frozen, the beads were cut into cross sections to enable imaging of the internal surfaces. Target points for spectroscopy were measured firstly at an area 15 μm from the outer surface of the beads, and then across the diameter of each bead at intervals of 50 μm.

5.2.3 *Equilibrium studies and isotherm modelling*

Batch kinetic and equilibrium studies used 250 mL Erlenmeyer flasks into which 0.4 g of media was placed, with 100 mL of sewage effluent collected from a small trickling filter works containing 4.8 mg P L^{-1}, and 205 mg SO_4^{2-} L^{-1}. A synthetic solution containing 5 mg P L^{-1} and 100 mg SO_4^{2-} L^{-1} was also trialled in the same manner. At the pH range of the experiments, 7.1 - 7.2, the available phosphorus was speciated roughly equally between $H_2PO_4^-$ and HPO_4^{2-} such that each mg of P equates to 0.048 meq. Reporting of phosphorus concentration in this chapter is kept in mass units to provide more direct comparison to other adsorption trials and reflects that the media is considered an adsorption rather than an ion exchange material. Each flask was stirred in an orbital shaker at 200 rpm and 18 ºC for one hour to obtain equilibrium. Kinetic data were obtained by taking sub samples every 10 minutes during a separate test. In all cases after sampling the media was separated from the solution immediately via vacuum filtration. Determination of phosphorus and sulphate concentrations were conducted by Spectroquant cell tests (Supplied by VWR International). The methods are analogous to EPA 365.2+3, and EPA 375.4 respectively. The equilibrium adsorption data was fitted to a number of adsorption models which are commonly used to describe phosphate adsorption:

Freundlich equation: $$q = K_F C_e^{1/n} \tag{5.1}$$

Langmuir equation: $$q = \frac{bK_L C_e}{1 + bC_e} \tag{5.2}$$

Temkin equation: $$q = A + B \ln C_e \tag{5.3}$$

All three are two parameter equations where q is the amount of phosphorus adsorbed per unit weight of media (mg P g_{media}^{-1}), and Ce is the concentration of phosphorus remaining in solution at equilibrium (mg P L^{-1}). All the other terms are constants in the various models. Analysis of kinetic adsorption data was undertaken to compare fits to both intraparticle diffusion and film diffusion limited rate models (Khriasheh *et al.,* 2003; Boyd *et al.,* 1949):

Intra-particle $$q_t = k_{IP} t^{0.5} \tag{5.4}$$

Film diffusion $$Ln(1 - F) = -k_{FD} t \tag{5.5}$$

Where q_t (mg P g_{media}^{-1}) is the solid phase concentration at time t, F is the fractional attainment of equilibrium and k is the rate constant defined in terms of a diffusion model (k_{FD}) (min^{-1}) or an intraparticle model (k_{IP}) (mg $g^{-1}min^{-0.5}$). Both models are plotted in linear form with the appropriateness of the respective models assessed through analysis of the linear regression constant (Choy *et al.*, 2004).

Further analysis was conducted with respect to mass transfer where both the film diffusion coefficient, k_f (cm s^{-1}), and the intraparticle diffusion coefficient, D (cm^2 s^{-1}), were calculated according to the following expressions (Khraisheh *et al.,* 2002; Urano and Tachikawa, 1991):

Intra-particle $$-\left[\log\left(1 - \left\{\frac{Q_t}{Q_e}\right\}^2\right)\right] = \frac{4\pi^2 Dt}{2.3d^2} \tag{5.6}$$

Film diffusion $$\ln\left(\frac{C_t}{C_0}\right) = -k_f \frac{A}{V} t \qquad (5.7)$$

Where *Qt* and *Qe* are the adsorbed amounts at time *t* and at equilibrium (mg P g_{media}^{-1}), *d* is the media diameter (cm), C_t is the concentration at time *t*, C_0 is the initial concentration, *A* is the area (cm^2) and *V* is the solution volume (L). Combining the two coefficients enables calculation of the dimensionless Biot number (*Bi*) which indicates the ratio of the mass transfer resistance in the solid to the mass transfer resistance in the liquid:

Biot Number $$Bi = \frac{k_f d}{D} \qquad (5.8)$$

5.2.4 Column trials

Fixed bed trials using 15 mm diameter, 200 mm long columns fed with final effluent from a small scale trickling filter works were used to generate saturation curves. Equal volumes of the adsorbent media (10 mL) were used in each case, with adjustments to empty bed contact time (of 1, 4, 10, and 20 minutes) controlled with peristaltic pumps. Trials were run until 1000 bed volumes had passed through each column.

5.2.5 Regeneration

Regeneration was undertaken with 40 mL of media that had previously been saturated with phosphorus. Solutions containing 2 % NaOH or 5 % NaCl were passed through the columns using peristaltic pumps at an empty bed contact time of 4 minutes. Each bed volume of regenerant leaving the columns was analysed for phosphate, nitrate and sulphate concentration according to standard methods.

5.3 Results and discussion

5.3.1 Media properties

The size of the carrier bead varied between 0.18 and 1.0 mm with a median size of 0.69 mm and uniformity coefficient of 1.37. The inclusion of the iron nanoparticles increased the specific gravity of the bead to 1.6 which compares to typical levels for ion exchange media of 1.05 - 1.15. Nanoparticle inclusion was found to be evenly spread throughout the beads with analysis of the distribution of iron as a percentage of the total surface area indicating that the distribution of iron ranged from 24 % at the bead edge to 28 % at 220 μm from the edge, the approximate centre of the bead (Figure 5.1). This compliments previous analysis which has indicated that inclusion of nanoparticles within the ion exchange resins restricts the apparent pore diameter by 30 % whilst increasing contact area by 7 % (Pan *et al.,* 2009).

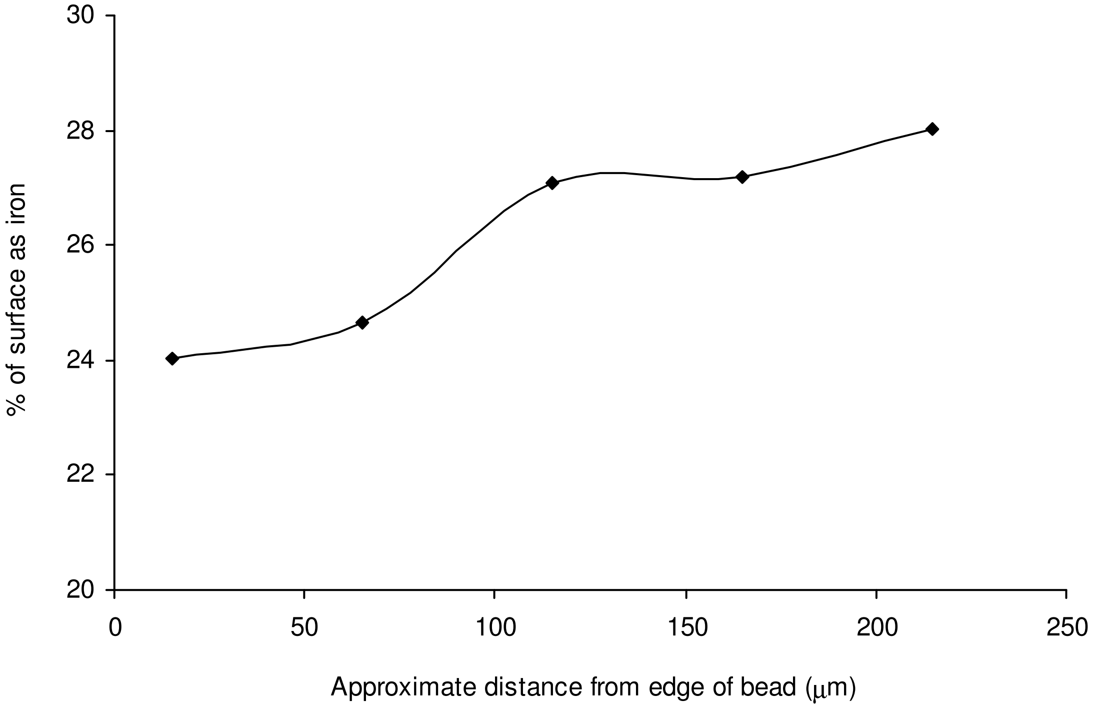

Figure 5.1: Distribution of iron through the depth of a bead.

5.3.2 Equilibrium isotherms

Batch equilibrium trials revealed the equilibrium capacity of the resin to decrease from 2.4 to 1.25 mg P g_{media}^{-1} as the liquid phase equilibrium concentration decreased from 5.2 mg P L^{-1} to 1.2 mg P L^{-1} (Figure 5.2A). Additional trials with a different source of sewage effluent down to lower final phosphorus levels, revealed the capacity at 0.1 mg P L^{-1} to be around 0.1 mg P g_{media}^{-1} (Figure 5.2B) indicating the significance of the target concentration when comparing different media. Comparison of the new media against a standard ion exchange resin akin to the parent resin revealed that around 10 % of the capacity is due to the ion exchange resin alone (Martin *et al.*, 2009). Previous trials with a nanosized hydrated ferric oxide particle embedded into a polystryrene-divinylbenzene resin (Pan *et al.,* 2009) reported capacities ranging between 23.5 mg P g_{media}^{-1} - 27 mg P g_{media}^{-1} at liquid phase concentrations of 5 mg P L^{-1} up to around 47 mg P g_{media}^{-1} for pure solutions with no competing ions. In a solution also containing 100 mg sulphate L^{-1}, the capacity at 5 mg P L^{-1} decreased to around 5.4 mg P g_{media}^{-1}, still over twice that reported in the current case. Explanation for the difference is attributed to iron coverage, which for the reported resin was around 10.2 %. The higher level found in the resin used in the current study, 24 - 28 %, is suggested to cause self agglomeration during the embedding process and thus reduces the available contact area (Pan *et al.,* 2009). Additionally, the parent resin in Pan *et al.*'s (2009) study is also seen to have a higher inherent capacity for phosphorus, at around 60 % of the embedded system, which will account for at least part of the difference.

Analysis of the equilibrium data revealed that all three adsorption models provide an appropriate fit to the observed data for the higher strength trials but only the Langmuir model fit at low concentrations (Figure 5.2B). This is in contrast to work by Zeng *et al.* (2004), who found that the relative appropriateness of the different adsorption models followed the sequence: Temkin ≡ Freundlich > Langmuir with phosphate adsorption onto iron oxide tailings using synthetic solutions. The difference can be explained in relation to competitive adsorption and available adsorption sites. In the case of the current resin, uptake can take place onto both the resin directly and the ferric nanoparticles. The real wastewaters used in the current study contain sulphate, which

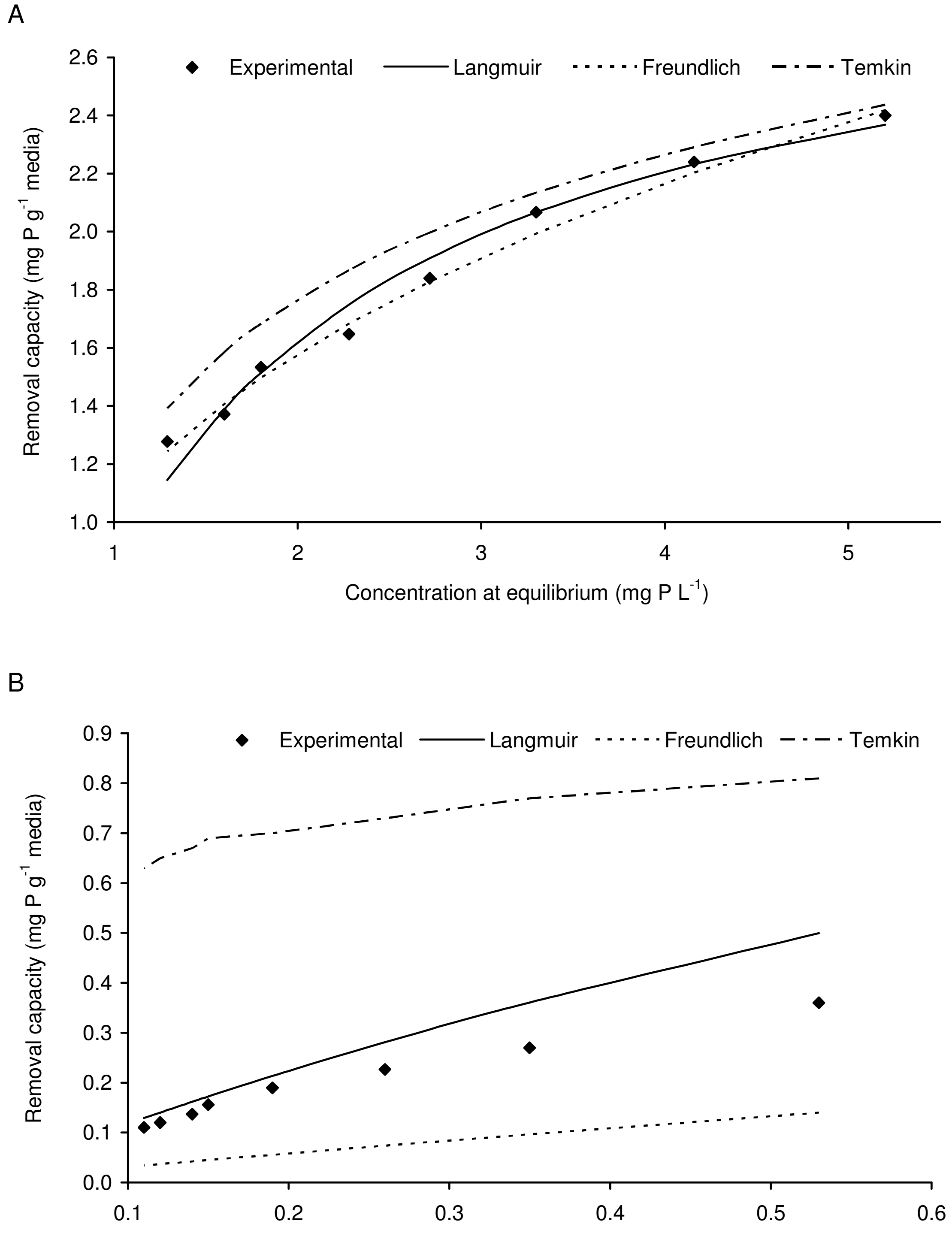

Figure 5.2: Three commonly used adsorption isotherm models fitted to equilibrium data from trials of the ferric nanoparticle adsorbent in wastewaters containing ~ 5 mg phosphorus L^{-1} (A) and ~ 0.5 mg phosphorus L^{-1} (B).

outcompetes phosphate for the ion exchange sites (Blaney *et al.,* 2007), such that phosphate mainly adsorbs onto the ferric nanoparticles. The consequence of which is to generate a pseudo homogeneous system in relation to phosphate uptake, which is better modelled through the Langmuir isotherm. Whereas with other media, the system remains heterogeneous which is then more effectively modelled through either Temkin or Freundlich isotherms.

Comparison of the Langmuir capacity constant, K_L, for a range of materials trialled for phosphorus uptake indicates that the embedded resin has a greater total capacity per mass of media than most of the alternatives, with K_L values ranging from 0.63 in low strength wastewaters (Figure 5.2B) to 0.77 in medium strength wastewaters (Figure 5.2A). To illustrate, example values reported for K_L include 0.612 mg P g_{media}^{-1} for Bauxite (Drizo *et al.,* 1999) and 0.026 mg P g_{media}^{-1} for Ochre (Heal *et al.,* 2003).

5.3.3 Adsorption kinetics

Kinetic experiments with real wastewater (4.8 mg P L^{-1}, 204 mg SO_4^{2-} L^{-1}) and a synthetic solution (5 mg P L^{-1}, 100 mg SO_4^{2-} L^{-1}) revealed that the adsorption of phosphorus was very rapid such that 54 % of the total capacity was utilised within the first 15 minutes and 95 % within the first 60 minutes (Figure 5.3A). No significant difference was observed in P removal between real and synthetic solutions, indicating that other competing ions or solid components in wastewater do not influence overall uptake rate. In comparison, Zeng *et al.,* (2004) reported that 67 % of the capacity was reached within the first 10 minutes using iron oxide tailings, slightly faster than in the current case. Analysis of the kinetic data, in both studies, fit to a three stage model whereby mass transfer initially occurs across the boundary layer surrounding the bead, followed by surface adsorption and then diffusion into the internal structure of the bead (Cheung *et al.,* 2007). Further analysis with respect to rate controlling mechanisms suggests that intraparticle diffusion controls marginally over film diffusion as the rate limiting step (Equations 5.4 and 5.5), with R^2 fit values of 0.98 and 0.84 respectively. This contrasts with commonly used adsorbents such as activated carbon where intraparticle diffusion is reported to dominate as the rate controlling mechanism (Cooney, 1998).

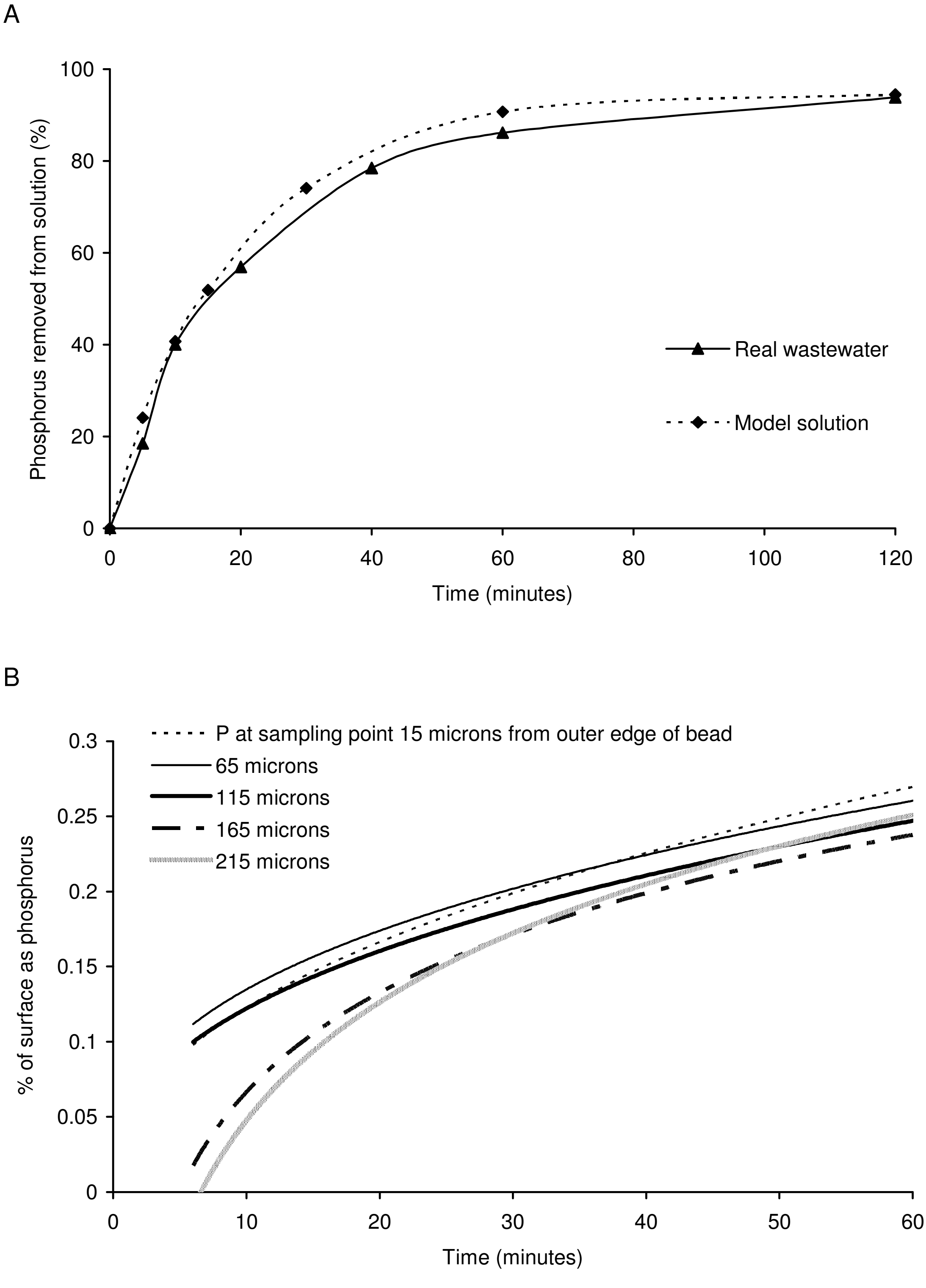

Figure 5.3: Kinetic curve (A) and change in phosphorus coverage within a bead as a function of contact time (B).

Kinetic analysis at different positions within the bead demonstrates the importance of intraparticle diffusion on the overall rate in relation to penetration. Critically, phosphorus coverage within the inner sections of the bead was observed to lag behind those at the surface indicating the switch over of mechanism (Figure 5.3B). To illustrate, phosphorus coverage increased from 0.14 % after 10 minutes to 0.26 % after 60 minutes in a layer extending from the surface to 115 μm into the bead. In contrast, at 165 μm and 215 μm from the bead edge, phosphorus coverage was only 0.07 % and 0.05 % at 10 minutes respectively, only reaching levels consistent with positions closer to the surface after 48 minutes. At this point, 90 % of the total adsorption had been completed. Fitting the data to intraparticle and film diffusion models confirms these observations, based on the criteria of linearity and the need for the line to pass through the origin. A distinct switch in appropriateness of fit was observed such that the outer two layers fit the film diffusion model best and the inner two layers fit the intraparticle diffusion model better (Equations 5.4 and 5.5). The 115 μm layer was intermediate between the two and indicates the zone at which intraparticle diffusion starts to become the dominant mechanism.

Further analysis with respect to mass transfer revealed the intraparticle diffusion coefficient (Equation 5.6) to decrease from 2.6×10^{-6} cm^2 s^{-1} to 1.4×10^{-6} cm^2 s^{-1} as the phosphorus concentration decreased from 105 mg L^{-1} to 5 mg L^{-1} (Figure 5.4). The influence of concentration on D reflects the impact of surface diffusion due to the heterogeneity of the media surface (Cooney, 1998). The corresponding film diffusion coefficient, k_f, was calculated as 2.8×10^{-3} cm s^{-1} (Equation 5.7), which indicates the media operates with a Biot number of 175 (Equation 5.8). The mechanistic implication of which is that the media operates in the intermediate zone where both film and intraparticle diffusion are important but with an emphasis on the latter (Sonetaka *et al.,* 2009). Similarity is found with respect to arsenate and phosphate adsorption onto granular ferric hydroxide with Biot numbers of 182 and 102 respectively (Sperlich *et al.,* 2008). However, comparison with activated carbon reveals smaller Biot numbers (indicating that film diffusion is more important) for metals (Quek & Al Duri, 2007) and pesticides (Baup *et al.,* 2000) and much larger Biot numbers (indicating that intraparticle diffusion is more important) for reactive dye uptake (Khraisheh *et al.,* 2002). The differences are partially related to molecular weight as both k_f and D decrease as molecular weight increases (Walker & Weatherley, 1998). However, comparison across the studies shows the major difference is in terms of *D* with reported values of 0.13-0.61 × 10^{-10} cm^2 s^{-1} for dye adsorption onto activated carbon (Choy *et al.,* 2004), 0.6 × 10^{-10} cm^2 s^{-1} - 4 × 10^{-10} cm^2 s^{-1} for pesticide adsorption on activated carbon (Baup *et al.,* 2000), and 1.2 × 10^{-6} cm^2 s^{-1} for phosphate uptake onto alumina (Urano and Tachikawa, 1991), indicating the relative ease of P uptake into the internal structure of the present media compared to other systems.

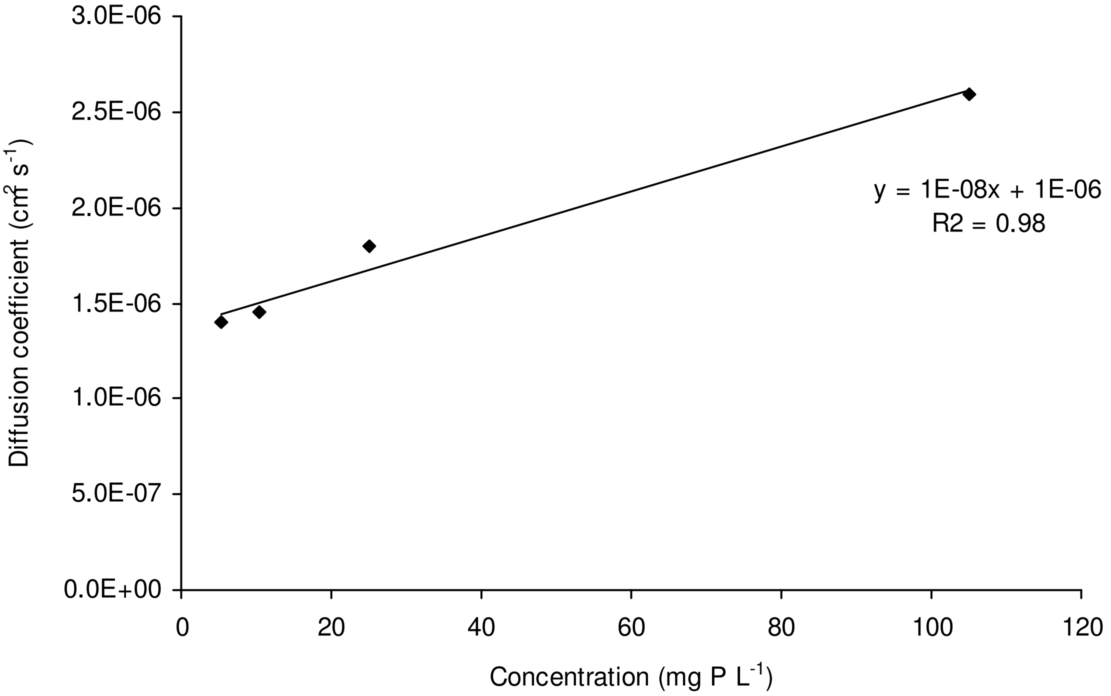

Figure 5.4: The relationship between concentration and the diffusion rate of phosphorus within the bead structure.

5.3.4 Column experiments

Using real wastewater, alteration of the empty bed contact time (EBCT) between 1 and 20 minutes caused a significant change in the shape of the breakthrough curve with the mass transfer zone being more sharply defined as the EBCT increased (Figure 5.5). To illustrate, at an EBCT of 1 minute, immediate leakage of phosphorus is observed with 0.1 mg P L^{-1} exceeded within the first 10 bed volumes. Overall, at an EBCT of 1 minute, the effluent phosphorus increased approximately linearly from 0.39 mg L^{-1} at 100 bed volumes to 4.17 mg P L^{-1} at 900 bed volumes. In contrast, at an EBCT of 20 minutes, no breakthrough was observed for the first 280 bed volumes, with the total capacity reached after 600 bed volumes.

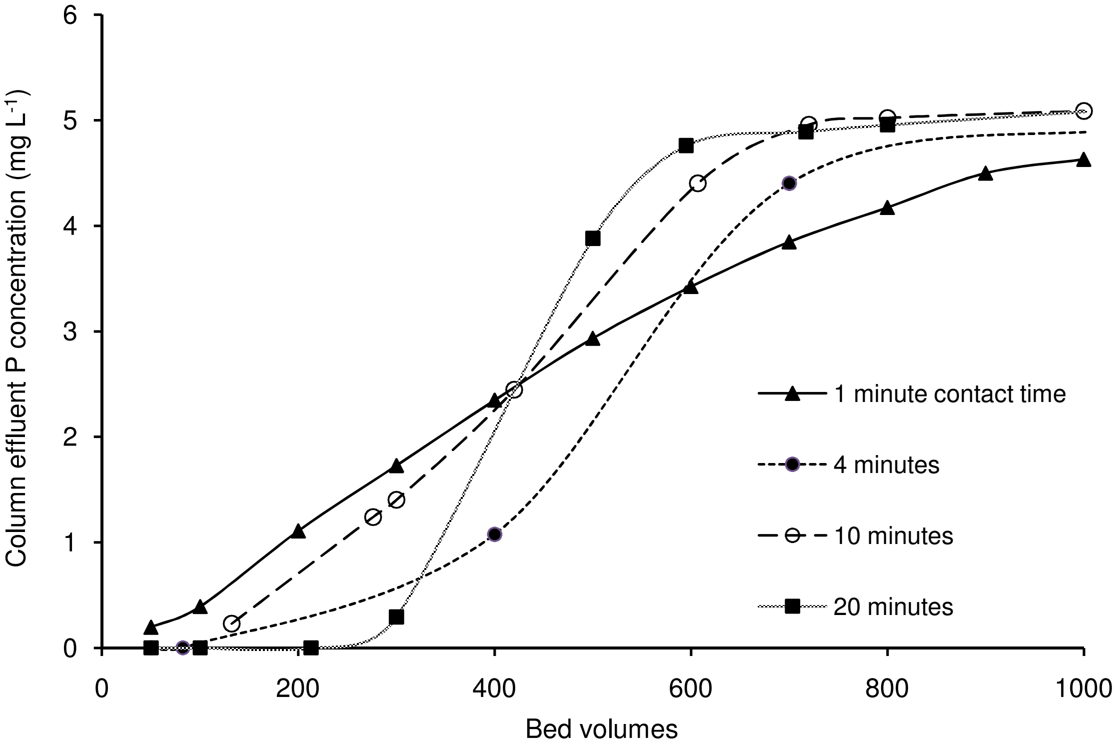

Figure 5.5: Saturation curves for varying empty bed contact times.

Using the same data from the trial described above and in Figure 5.5, but considered in terms of the treatable volume before breakthrough for different final consents and EBCT, the greatest variation was observed at either low or high effluent breakthrough limits (Figure 5.6). For instance, to achieve an effluent concentration of 0.1 mg P L^{-1}, an EBCT of 20 minutes can treat 275 bed volumes, whilst an EBCT of one minute treats less than 10 bed volumes. The difference in treatable volumes between contact times of 1 minute and 20 minutes reduced from 160 bed volumes at 1 mg P L^{-1}, to 50 bed volumes at 2 mg P L^{-1}, suggesting that operational hydraulic rate can be optimised for different final effluent levels. Converted to capacity, the performance ranged between 0.29 mg P g_{media}^{-1} and 0.51 mg P g_{media}^{-1} to meet a 0.1 mg P L^{-1} standard as the EBCT increased from 1 to 20 minutes. Assessment of the operational suitability of these runtimes can be considered with reference to other contact processes typically encountered in water and wastewater treatment such as ion exchange and activated carbon. In the case of the former, typical operating cycles of several hundred bed volumes are common as the media is regenerated on site (McAdam *et al.*, 2010), whereas adsorption processes typically run for thousands of bed volumes between regeneration cycles. However, this reflects the fact that media regeneration has to be completed off site and that dilute components are being adsorbed. Previous trials with the ferric nanoparticle resin treating feed solutions of 0.63 mg P L^{-1} (Martin *et al.,* 2009) and 0.26 mg P L^{-1} (Blaney *et al.,* 2007) reported exhaustive bed lifes of 4000 and 16000 bed volumes respectively. Consequently, the operating cycle of the ferric nanoparticle adsorbent reflects the load being treated but in all cases is similar to existing systems, which should enhance the ease of implementation. The operational capacity is also a function of the permitted effluent phosphorus concentration with compliance to 0.1 mg P L^{-1} reducing the operating capacity to 0.29 - 0.51 mg P g_{media}^{-1} which is only 8 - 13% of the exhaustive capacity.

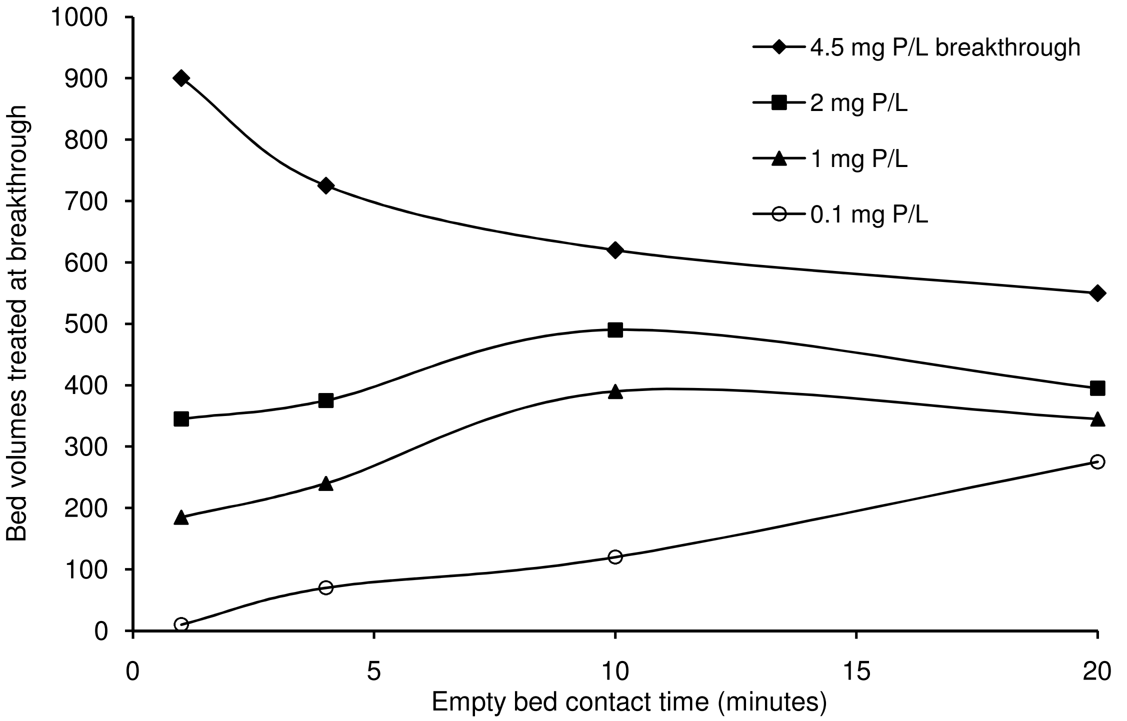

Figure 5.6: Comparison of breakthrough performance with varying contact times.

5.3.5 Regeneration

Regeneration of hybrid adsorbent/ion exchange media typically involves combinations of NaCl and NaOH at concentrations between 2 - 5 % run through a fixed bed of the media for 10 bed volumes (Blaney *et al.,* 2007). Comparison of the efficacy of each component revealed that the majority of desorption occurs within the initial bed volumes such that 65 % and 88 % of the total P desorbed by each solution was eluted by the end of the first bed volume for the 5 % NaCl and 2 % NaOH solutions respectively (Figure 5.7).

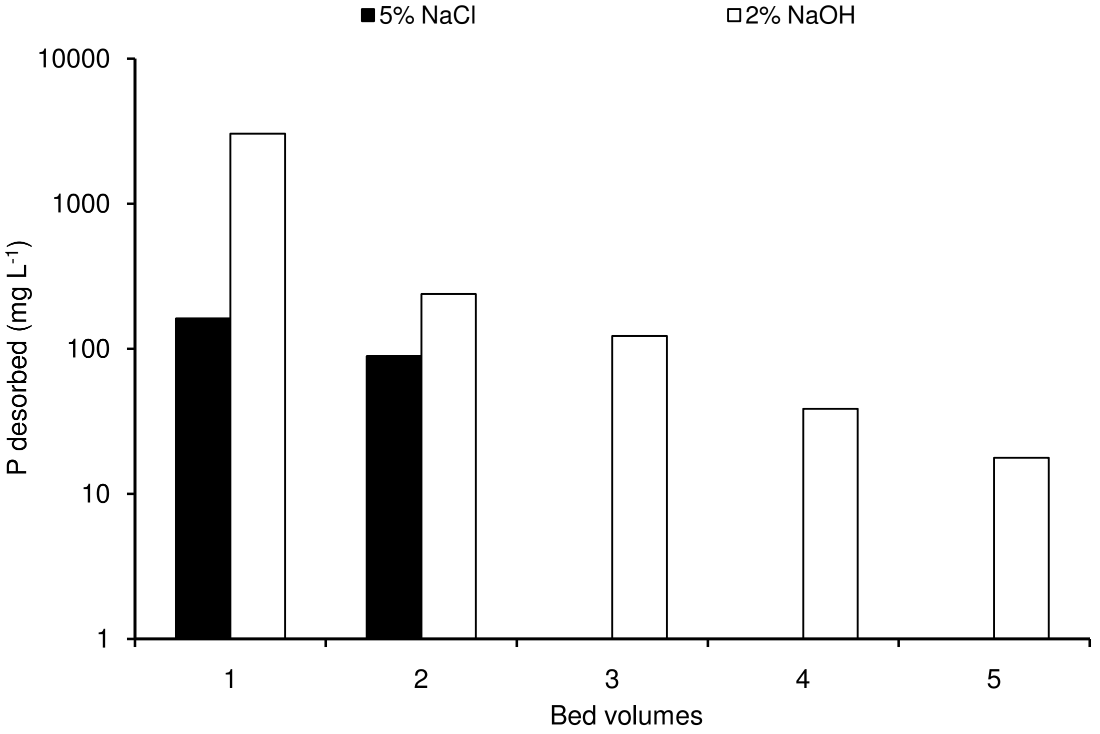

Figure 5.7: P desorption profiles when regenerating the media with different solutions.

Further, desorption ceased within 2 bed volumes with the NaCl solution but continued with the NaOH solution such that no further elution was recorded after 5 bed volumes. The major difference between the effectiveness of the solutions was in terms of the total amount of phosphorus desorbed, which was 3457 mg P L^{-1} using NaOH, and 251 mg P L^{-1} using NaCl. The level associated with the NaCl regeneration is consistent with the level of adsorption ascribed to uptake by the parent resin, of around 10 % (Martin *et al.*, 2009). The NaCl acts mainly on the ion exchange resin, disrupting the electrostatic interaction holding the phosphate ion as an outer sphere complex (Pan *et al.,* 2009). In contrast, the phosphate bound to the ferric nanoparticles is held in an inner sphere complex, the reversal of which requires the ferric to be deprotonated, generating a negatively charged surface that repels the bound phosphate. As a consequence, regeneration with NaOH only acts on the nanoparticles, leaving the ionic material bound to the resin in place. Whilst this reduces capacity by around 10 % in subsequent service runs, it does have the advantage of generating a purer phosphate regenerant stream for downstream recovery. To illustrate, during desorption with the NaOH solution, the average concentration of eluted material over 5 bed volumes was 691 mg P L^{-1}, 39 mg NO_3^- L^{-1} and 55 mg SO_4^{2-} L^{-1}. In contrast, over the same 5 bed volumes, desorption with NaCl produced a solution containing 50 mg P L^{-1}, 1008 mg NO_3^- L^{-1} and 721 mg SO_4^{2-} L^{-1}. A similar contamination issue has been reported elsewhere during the regeneration of activated alumina where the recovered solution contained 2200 mg P L^{-1}, 400 mg SO_4^{2-} L^{-1}, and 1600 mg Al L^{-1} (Urano & Tachikawa, 1991).

5.4 Conclusions

The overall conclusion from the presented work is that the iron nanoparticle embedded resin provides an appropriate means of phosphorus removal down to 0.1 mg P L^{-1}. The implementation of the technology is flexible enough to reflect the complexity of the challenges associated with phosphorus removal such that it can be used to treat the full phosphorus load exerted by wastewater or used to polish a treated stream. The principal impact is on operating cycle time which could vary between 200 and upwards of 1000 bed volumes between regeneration cycles. Previous economic assessments indicate that it is currently more expensive than traditional approaches when treating the full load, as expected (Martin *et al.,* 2009). As such, likely application in the near future will be as a polishing process post chemical and/or biological P removal where extended bed life and reduced regeneration cost can be expected. The present study has shown that there is a limiting EBCT below which mass transfer is negatively impacted through limitations associated with intraparticle diffusion. As such a recommended EBCT of 10 - 20 minutes is suggested which represents mid to high range for traditional adsorption processes. In addition, the economics of the process are heavily tied to the regeneration process (Martin *et al.,* 2009) and the current work indicates that significant savings are possible such that with further optimisation, regeneration based on a maximum of 4 bed volumes or less of NaOH only solutions are likely to greatly reduce chemical costs.

5.5 Acknowledgements

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5.6 References

Altundoğan, H.S., Tümen, F. (2002). Removal of phosphorus from aqueous solutions by using bauxite. 1. Effect of pH on the adsorption of various phosphates, *Journal of Chemical Technology and Biotechnology,* **77,** 77–85.

Baup, S., Jaffre, C., Wolbert, D., Laplanche, A. (2000). Adsorption of pesticides onto granular activated carbon: Determination of surface diffusivities using simple batch experiments. *Adsorption*, **6**, 219-228.

Blaney, L.M., Cinar, S., SenGupta, A.K. (2007). Hybrid anion exchanger for trace phosphate removal from water and wastewater. *Water Research*, **41**, 1603-1613.

Boyd, G.E., Adamson, A.M., Myers, L.S. (1949). The exchange adsorption of ions from aqueous solutions by organic zeolites. II. Kinetics, *Journal of the American Chemical Society*, **69**, 2836-2842.

Brooks, A.S., Rozenwald, M.N., Geohring, L.D., Lion, L.W., Steenhuis, T.S. (2000). Phosphorus removal by wollastonite: a constructed wetland substrate. *Ecological Engineering,* **15,** 121–132.

Cheung, W.H., Szeto, Y.S., McKay, G. (2007). Intraparticle diffusion processes during acid dye adsorption onto chitosan. *Bioresource Technology*, **98**, 2899-2904.

Choy, K.K.H., Porter, J.F., McKay, G. (2004). Intraparticle diffusion in single and multicomponent acid dye adsorption from wastewater onto carbon. *Chemical Engineering Journal*, **103**, 133-145.

Cooney, D.O. (1998). *Adsoprtion design for wastewater treatment*. CRC Press, Florida.

Drizo, A., Frost, C. A., Grace, J., Smith, K. A. (1999). Physico-chemical screening of phosphate-removing substrates for use in constructed wetland systems. *Water Research*, **33**, 3595-3602.

EA, 2000 EA, Aquatic eutrophication of England and Wales: a management strategy, Environment Agency, Bristol.

Genz, A., Kommuller, A., Jekel, M. (2004). Advanced phosphorus removal from membrane filtrates by adsorption on activated aluminium oxide and granulated ferric hydroxide. *Water Research*, **38**, 3523-3530.

Hansen, B. (2006). Engineering news: Environmental engineering: Long-term plan seeks to reduce phosphorus in Spokane River. *Civil Engineering*, **76**, 24-25.

Heal, K., Younger, P.L., Smith, K., Glendinning, S., Quinn, P., Dobbie, K. (2003). Novel use of ochre from mine water treatment plants to reduce point and diffuse phosphorus pollution. *Land Contamination and Reclamation*, **11**, 145-152.

Kaasik, A., Vohla, C., Mõtlep, R., Mander, U., Kirsimäe, K. (2008). Hydrated calcareous oil-shale ash as potential filter media for phosphorus removal in constructed wetlands. *Water Research* **42,** 1315–1323

Khraisheh, M.A.M., Al-Degs, Y.S., Allen, S.J., Ahmad, M.N. (2002) Elucidation of controlling steps of reactive dye adsorption on activated carbon. *Industrial Engineering Chemical Research*, **41**, 1651-1657.

Kuba, T., Smolders, G.J.F., van Loosdrecht, M.C.M., Heijnen, J.J., (1993). Biological phosphorus removal from wastewater by anaerobic-anoxic sequencing batch reactor. *Water Science and Technology,* **27** (5–6), 241–2

Li Y., Liu C., Luan, Z., Peng, X., Zhu, C., Chen, Z., Zhang, Z., Fan, J., and Jia, Z., (2006). Phosphate removal from aqueous solutions using raw and activated red mud and fly ash, *Journal of Hazardous Materials,* **B137**, 374–383.

Liberti, L., Boari, G., Passino, R. (1976). Selective renovation of eutrophic wastes - phosphate removal. *Water Research*, **10**. 421-428

Martin, B.D., Parsons, S.A., Jefferson, B. (2009) Removal and recovery of phosphate from municipal wastewaters using a polymeric anion exchanger bound with hydrated ferric oxide nanoparticles. *Water Science and Technology*, **60**, 2637-2645.

McAdam, E.J., Pawlett, M., Judd, S.J. (2010). Fate and impact of organics in an immersed membrane bioreactor applied to brine denitrification and ion exchange regeneration. *Water Research*, **44**, 69-76.

Midorikawa, I., Aoki, H., Omori, A., Shimizu, T., Kawaguchi, Y., Kassai, K., Murakami, T. (2008). Recovery of high purity phosphorus from municipal wastewater secondary effluent by a high-speed adsorbent. *Water Science and Technology*, **58**, 1601-1607.

Morse, G.K., Brett, S.W., Guy, J.A., Lester, J.N. (1998). Review: Phosphorus removal and recovery technologies. *The Science of the Total Environment* **212**, 69-81.

Pan, B., Wu, J., Pan, B., Lv, L., Zhang, W., Xiao, L., Wang, X., Tao, X., Zheng, S. (2009). Development of polymer-based nanosized hydrated ferric oxides (HFOs) for enhanced phosphate removal from waste effluents. *Water Research*, **43**, 4421-4429.

Parfitt, L., Atkinson, J., Smart, R St.C. (1975). The mechanism of phosphate fixation by iron oxides. *Soil Science Society of America,* **39**, 837-841.

Quek, S. Y., Al-Duri, B. (2007). Application of film-pore diffusion model for the adsorption of metal ions on coir in a fixed-bed column. *Chemical Engineering and Processing: Process Intensification*, **46**, 477-485.

Saidou, H., Ben Moussa, S., Ben Amor, M. (2009). Influence of airflow rate and substrate nature on heterogeneous struvite precipitation. *Environmental Technology*, 30, 75-83

Sonetaka, N., Fan, H., Kobayashi, S., Chang, H., Furuya, E. (2009). Simultaneous determination of intraparticle diffusivity and liquid film mass transfer coefficient from a single-component adsorption uptake curve. *Journal of Hazardous Materials*, **164**, 1447-1451.

Sperlich, A., Werner, A., Genz, A., Amy, G., Worch, E., Jekel, M. (2005). Breakthrough behavior of granular ferric hydroxide (GFH) fixed-bed adsorption filters: Modeling and experimental approaches. *Water Research*, **39**, 1190-1198.

Urano, K., Tachikawa, H. (1991). Process development for removal and recovery of phosphorus from wastewater by a new adsorbent. 2. Adsorption rates and breakthrough curves. *Industrial and Engineering Chemistry Research,* **30,** 1897-1899.

Vohla, C., Koiv, M., Bavor, H.J., Chazarenc, F., Mander, U. (2011) Filter materials for phosphorus removal from wastewater in treatment wetlands – a Review. *Ecological Engineering*, **37** (1), 70-89.

Walker, G.M., Weatherley, L.R. (1998). Fixed bed adsorption of acid dyes onto activated carbon. *Environmental Pollution*, **99**, 133-136.

Wood, R.B., McAtamney, C.F. (1996). Constructed wetlands for waste water treatment: the use of laterite in the bed medium in phosphorus and heavy metal removal. *Hydrobiologia* **340,** 323–331.

Yang, K., Li, Z., Zhang, H., Qian, J., Chen, G. (2010). Municipal wastewater phosphorus removal by coagulation. *Environmental Technology*, **31**, 601-609.

Zeng, L., Li, X., Liu, J. (2004). Adsorptive removal of phosphate from aqueous solutions using iron oxide tailings. *Water Research*, **38**, 1318-1326.

Zhao, D., SenGupta, A.K. (1998). Ultimate removal of phosphate using a new class of anion exchanger. *Water Research*, **32**, 1613-1625.

Zhao, Y., Yue, Q., Li, Q., Gao, B., Han, S., Yu, H. (2010). The regeneration characteristics of various red mud granular adsorbents (RMGA) for phosphate removal using different desorption reagents. *Journal of Hazardous Materials*, **182**, 309-316.

Zhang, Q., Pan, B., Zhang, W., Pan, B., Zhang, Q., Ren, H. (2008) Arsenate removal from aqueous media by nanosized Hydrated Ferric Oxide (HFO)-loaded polymeric sorbents: Effect of HFO loadings. *Industrial and Engineering Chemistry Research*, **47**, 3957-3962.

6. The impact of competing ions and metals on the removal and recovery of phosphate from municipal wastewater by hybrid ion exchange/adsorbent

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6.1 Introduction

Phosphorus has been removed from wastewater streams since the middle of the last century, with the aim of preventing eutrophication and contamination of natural systems. Removal takes the form of either an adapted version of the activated sludge process, where luxury uptake of phosphorus in the biota is encouraged (Comeau *et al.,* 1986), or chemical precipitation, which binds the phosphorus into insoluble metal salts (Morse *et al.,* 1998). These techniques are successful at reducing phosphorus concentrations to the commonly implemented compliance standards of 2 mg L^{-1} or 1 mg L^{-1}, which depend primarily on the size of the population served by the treatment works, and/or the ecological sensitivity of the receiving catchment. However, these compliance standards are expected to be tightened under the Water Framework Directive (EC, 2000), which seeks to elevate all natural water systems to "good" ecological quality. The background concentration of phosphorus in natural systems is reported to be around 0.1 mg L^{-1}, (EA, 2000), and this is expected be the future compliance standard. Biological phosphorus removal processes are not thought to be able to achieve such a low discharge (Blaney *et al.,* 2007), and the additional chemical dosing required (a 155 % excess of ferric chloride) to reach such removal levels is unsustainable (Fytianos *et al.,* 1998). Consequently, new techniques are being evaluated which can sustainably achieve a phosphorus discharge of less than 0.1 mg L^{-1}. One of the most promising is a ferric nanoparticle adsorbent media where the nanoparticles are embedded into an ion exchange resin to provide mechanical support and processing simplicity. The anionic exchange resin used takes advantage of the Donnan membrane effect (Cumbal & Sengupta, 2005; Zhang *et al.*, 2008; Sarkar *et al.*, 2010), whereby the positively charged quaternary ammonium groups that are fixed in the resin structure are effectively behind a semi permeable membrane - they cannot be removed from the solid phase but anions from the solution may pass deep into the bead structure, drawn in by electrostatic attraction from the ammonium groups. This allows phosphate to come into contact with the ferric nanoparticles dispersed within the pore structure, form inner sphere complexes and thus be removed from solution.

As wastewater contains a variety of ionic species, a key consideration is the competitive impact that these may have on the capacity of the media to remove and recover phosphorus. The main inorganic, anionic species present in wastewater that are expected to impact the removal of phosphorus via ion exchange are sulphate and bicarbonate, because of their relatively high atomic weights (96 for sulphate and 61 for bicarbonate) and valencies (divalent for sulphate, monovalent for bicarbonate), in comparison to phosphate (with a mass of 96 for the divalent form and 97 for the monovalent). Relative concentration is also an important factor when implementing the media to remove the total incoming phosphorus load at a treatment works, or as a polishing step installed downstream of biological or chemical phosphorus removal stages. Consequently, expected phosphate concentrations that would contact the media vary from incoming levels around 15 mg phosphate L^{-1}, down to around 3 mg phosphate L^{-1} downstream of chemical or biological stages. In contrast, typical concentrations of sulphate and bicarbonate can be > 200 mg L^{-1} in both raw and treated wastewaters. A larger concentration of an ion can overcome the usual order of uptake onto an ion exchange material - indeed; the regeneration of ion exchangers relies on this phenomenon, and is commonly achieved by employing high strength NaCl solutions (2 - 5 %) to displace much heavier and more highly charged ions on the material with chloride.

Whilst the other ions present in wastewater are not expected to compete for the ferric adsorbent sites, metal species might. Adsorbent materials containing ferric oxides have been used to remove metals from solution (Lopez *et al.*, 1998; Nowack & Stone, 1999; Han *et al.,* 2002). Their influence on the phosphate capacity of hybrid anion exchange/ferric adsorbent materials has yet to be investigated.

Aim and scope

Previous work with similar hybrid anion exchange/adsorbent materials have investigated the impact of sulphate in model solutions (Blaney *et al.*, 2007) and blends of sulphate, sodium chloride and bicarbonate in model solutions (Pan *et al.,* 2009). The present study isolates the impact of separate competing ions on the material's phosphate removal capacity during the loading cycle using model solutions. In addition, the material is contacted with real wastewaters containing varying ratios of phosphate : competing ions to investigate the impact of wastewater character on phosphate adsorption. The removal of metals from a real wastewater is also quantified. Finally, the presence of competing ions in the regeneration step is investigated to assess the purity of the recovered phosphate stream. Studying these parameters will help further understanding of the factors likely to influence the performance of such a hybrid ion exchange/adsorbent material when applied to the removal and recovery of phosphorus at full scale wastewater treatment works.

6.2 Materials and methods

6.2.1 Hybrid ion exchanger/adsorbent

The adsorbent media (trade name Layne^{RT}) was supplied by SolmeteX Co., Massachusetts, USA. The gel-type ion exchange component consists of quartenary amine functional groups in a styrene divnylbenzene copolymer matrix. Approximately 26 % of the external and internal surfaces of the material are covered with iron in hydrated ferric oxide form (Chapter 5). Before first use, the media was placed into a column and run in an upflow configuration with deionised water at a rate high enough to fluidise the bed for 30 minutes. This removed any unbound iron fines left on the media by the manufacturing process.

6.2.2 Kinetic and equilibrium trials for competing ions and limiting mechanism

Batch kinetic and equilibrium studies were conducted using 250 mL Erlenmeyer flasks in an orbital shaker at 200 rpm at 18 ° C. Doses of resin were varied between 0 and 10 g L^{-1}. Model inorganic solutions were made using NH_4HCO_3, $(NH_4)_2SO_4$, and $NH_4H_2PO_4$, (supplied by Fisher Scientific UK Ltd.).

6.2.3 Treatment works sampled

Five wastewater treatment works were chosen to represent the main categories of treatment and scale typically found in the UK (Table 6.1, and see Chapter 3 for detailed descriptions). Small spot samples (1 - 2 L) of final effluent were collected from each works on two consecutive days in June 2010, at around mid-morning. Batch tests were carried out to contact the media with these effluents using doses between 0 and 4 g L^{-1} and an equilibrium time of one hour using the same equipment as described above in section *6.2.2.*

Table 6.1: Class of treatment works sampled.

Treatment method	**Population equivalent**	**Final effluent SO_4^{2-} (mg L^{-1})**	**Final effluent P (mg L^{-1})**	**Current P consent (mg L^{-1})**	**Ratio of SO_4^{2-} meq : PO_4^{3-} meq**
Small trickling filter	< 10,000	130	5.9	No consent	4.7
Large scale trickling filter with Fe dosing	> 10,000, < 100,000	230	0.53	< 2	93.9
Small activated sludge plant with ammonia removal, no Fe dosing	< 10,000	135	4.7	No consent	6.2
Large activated sludge plant with Fe dosing	> 250,000	180	0.83	< 1	30.5
Enhanced biological P removal	> 200,000	270	0.31	< 1	170.3

6.2.4 Isotherm modelling

The equilibrium adsorption data from both the model solutions and real wastewater trials were fitted to adsorption models commonly used to describe phosphate adsorption:

Freundlich equation: $$q = K_F C_e^{1/n} \tag{6.1}$$

Langmuir equation: $$q = \frac{bK_L C_e}{1 + bC_e} \tag{6.2}$$

Temkin equation: $$q = A + B \ln C_e \tag{6.3}$$

All three are two parameter equations where q is the amount of phosphorus adsorbed per unit weight of media (mg g^{-1}), and Ce is the concentration of phosphorus remaining in solution at equilibrium (mg L^{-1}). All the other terms are constants in the various models.

6.2.5 Small scale fixed bed column runs

Fixed bed trials using 15 mm diameter, 20 cm long columns were used to load and regenerate the media, with bed volumes of 10 mL used in each trial. Model solutions (containing 30 mg L^{-1} phosphate, 100 mg L^{-1} of sulphate and nitrate, and 150 mg L^{-1} chloride), in addition to a real wastewater sample from a small trickling filter works to investigate metal uptake (Table 6.2), were passed through at an empty bed contact time of 4 minutes until phosphate saturation occurred. Regenerant solutions of 5 % sodium chloride and 2 % sodium hydroxide were then passed through the saturated media in parallel trials at a rate of 2 bed volumes hr^{-1}.

Table 6.2: Characteristics of the wastewater used in the column tests for metal adsorption.

Parameter	**Value**
pH	7.10 ± 0.20
Temp. of sample whilst testing (ºC)	18.00 ± 0.75
Phosphate (mg L^{-1})	15.41 ± 1.12
Sulphate (mg L^{-1})	58.28 ± 0.31
Bicarbonate (mg L^{-1})	85.31 ± 2.55

6.2.6 Analytical techniques

Determination of total phosphorus, phosphate, and sulphate was by Spectroquant cell tests (supplied by VWR International). The phosphorus method is analogous to EPA 365.2+3, and the sulphate method is analogous to EPA 375.4.

A Perkin Elmer ELAN 9000 ICP Mass Spectrometer was used for the determination of nickel, copper, zinc, cadmium, and lead concentrations. Interference problems exist with the measurement of mercury in the ICP Mass Spectrometer, so a Perkin Elmer AAnalyst 800 Atomic Absorption Spectrometer was used instead. Samples were prepared to match the matrices of the standard solutions by acidification in line with British Standard BS EN ISO 17294-2:2004. Internal and external standards were used in both instruments and measured before each sample run to calibrate the machines, then at halfway through, and at the end of each run to quantify any drift (< 0.1 ppb variance), which has been corrected for in the results presented in the study. Detection limits were 10 - 100 ppt for nickel, copper, zinc, mercury and cadmium, with lead at 1 - 10 ppt.

6.3 Results

6.3.1 Competition from sulphate and bicarbonate - equilibrium

The pH of this trial, and all subsequent tests, rose from an initial value of around 7.1 to a maximum of 8.2. The speciation of phosphate, sulphate and bicarbonate ions were unaltered by the increase of pH. At a media dose of 2 g L^{-1}, the removal of 5 mg L^{-1} phosphorus (0.159 meq) was 99 % (Figure 6.1). The introduction of 100 mg L^{-1} bicarbonate (10.5 meq bicarbonate : 1 meq phosphate) only reduced the phosphorus removal to 97.2 %, but 100 mg L^{-1} sulphate (13 meq sulphate : 1 meq phosphate) reduced it to 80.4 %.

An initial capacity of 8.76 mg phosphorus g_{media}^{-1} for the single phosphorus solution decreased to 7.52 mg phosphorus g_{media}^{-1} with the addition of bicarbonate, and 2.54 mg phosphorus g_{media}^{-1} in the presence of sulphate. These findings are consistent with, if slightly lower than those reported by Pan *et al.,* (2009) who used similar hybrid media but found capacities ranged between 12.2 and 17.8 mg g_{media}^{-1} for a single solution of 10 mg L^{-1} phosphorus, and with a solution containing 10 mg L^{-1} phosphorus and 100 mg L^{-1} sulphate, these capacities dropped to between 5.73 and 5.8 mg g_{media}^{-1}. Zhao & Sengupta (1998), and Blaney *et al.,* (2007) also showed that doubling the sulphate concentration from 120 mg L^{-1} to 240 mg L^{-1} had little impact on the phosphate adsorption capacity of a similar media.

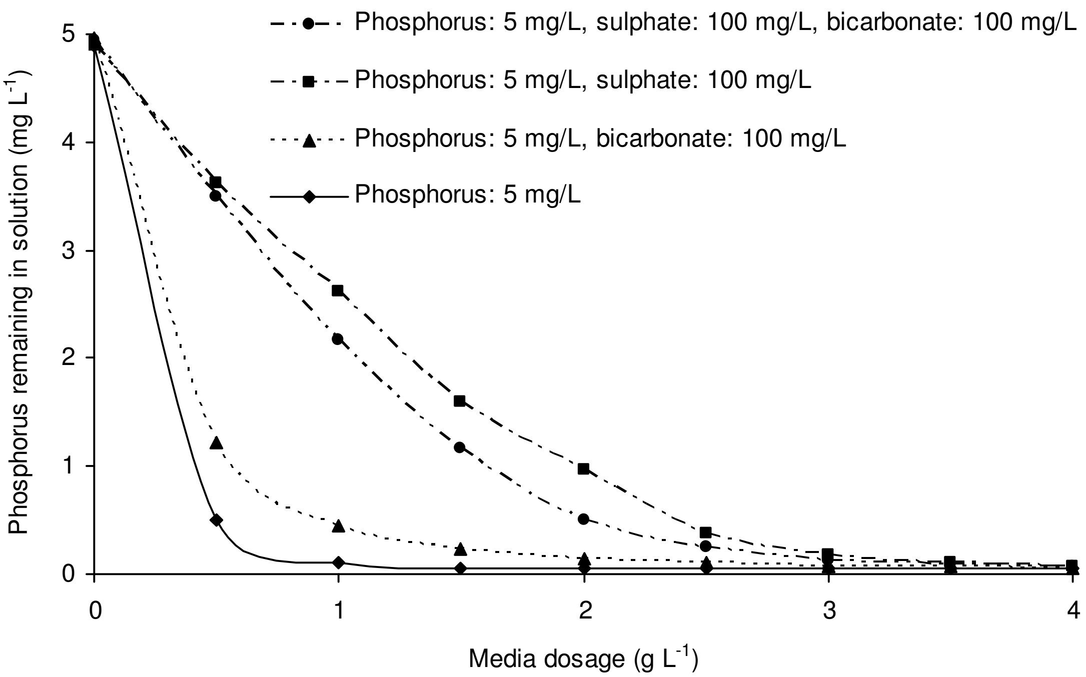


Figure 6.1: Competition effects on phosphorus uptake by the hybrid media in equilibrium studies.

Since neither sulphate nor bicarbonate are strong ligands, the observed decrease in phosphorus removal is a result of them being taken up on the ion exchange sites, and not by adsorption onto the ferric nanoparticles. Sulphate is only able to form outer sphere complexes with ferric oxide at typical wastewater pH (Wijnia & Schulthess, 2000; Lefevre, 2004) and consequently, increases in sulphate concentration do not impact on the adsorptive capability of the media for phosphate (Pan *et al.,* 2009).

The impact of the competing ions decreased in magnitude with increasing media dosages, until at 4 g media L^{-1}, phosphorus removal from all the solutions averaged 98.7

%, with a standard deviation of 0.19. At these high media doses, all the phosphate from the solution is thought to be adsorbed to the ferric nanoparticles, and none competes with the other anions for the ion exchange sites. In these conditions, when the media has not reached full phosphate capacity, the Lewis acid-base adsorption mechanism plays a more significant role than Coulombic ion exchange interaction (Blaney *et al.*, 2007). In practice, this would mean that if large enough media doses were used, the impact of the competing ions on phosphorus removal could be completely eliminated.

6.3.2 Competition from sulphate and bicarbonate - kinetics

The initial rate constant for the single solution of phosphorus is 0.07 mg minute^{-1} (Figure 6.2). The addition of sulphate or bicarbonate, either individually or combined, only reduces the rate constant to 0.06 mg minute^{-1}. Whilst it is clear that the other ions, especially sulphate, exert a detrimental impact on capacity, they have only a negligible effect on the rate at which the media removes phosphorus from solution.

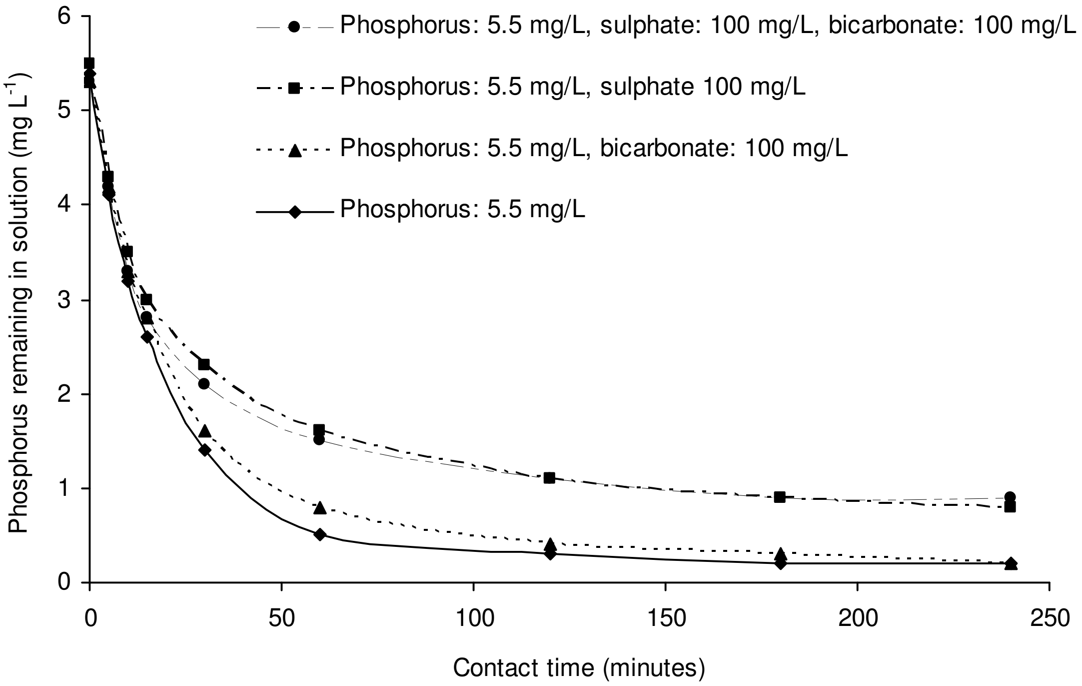


Figure 6.2: Competition effects on phosphorus uptake by the hybrid media in kinetic studies.

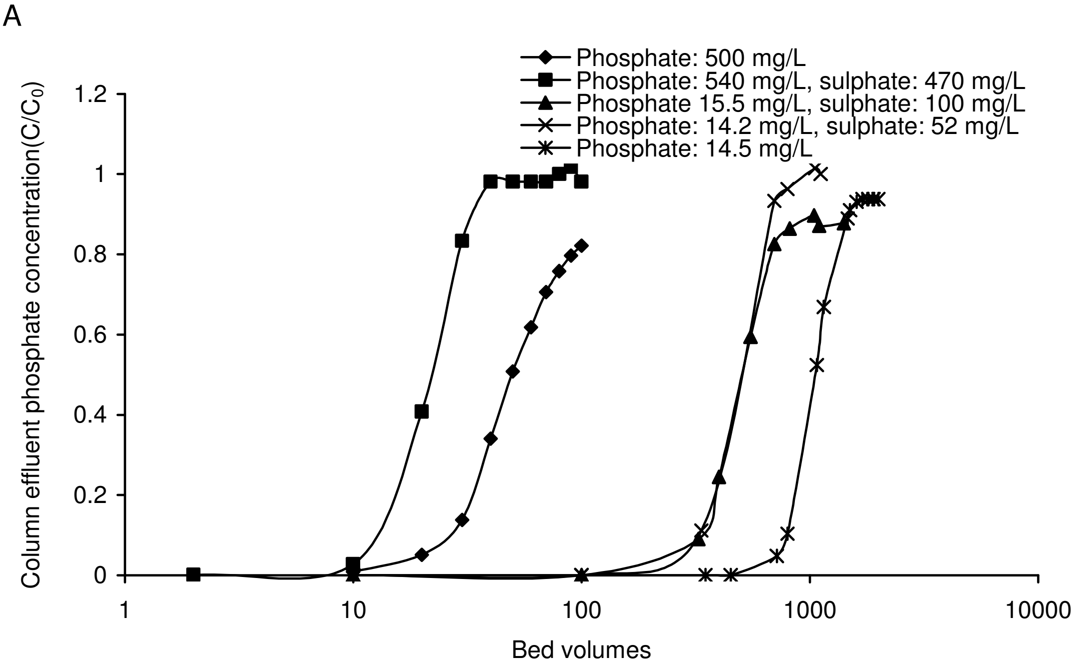
6.3.3 Competition from sulphate - column studies

From a solution containing only phosphate at 14.5 mg L^{-1}, the media was able to treat 590 bed volumes before a breakthrough of 0.1 mg phosphorus L^{-1} occurred. With the addition of sulphate at 52 mg L^{-1}, this was reduced to 181 bed volumes. In line with the equilibrium studies and literature, the doubling of sulphate concentration did not significantly alter this reduction, and at 100 mg L^{-1}, breakthrough occurred at 170 bed volumes. The shape of the phosphate breakthrough curves remains stable across all the tested concentrations (Figure 6.3) indicating that the presence of sulphate does not impact the mass transfer characteristics of the media. However, the backward migration of the curves with increasing sulphate concentrations reveals the impact on the volume of solution treatable.

In relation to overall capacity, in a strong phosphate solution of 500 mg L^{-1}, the media's capacity was 36 mg phosphate g_{media}^{-1} (10.2 meq), which represents the amount removed from solution via both the ion exchange sites on the media and the nanoparticle adsorbent sites dispersed within it. In contrast, a mono-ionic solution of sulphate, at an identical concentration, is removed at a much lower rate, with a capacity of only 17 mg sulphate g_{media}^{-1} (3.3 meq). The phosphate/sulphate separation factor at these identical concentrations can be expressed as (Zhao & Sengupta, 1998):

$$\alpha_{p/s} = \frac{q_P}{C_P} * \frac{C_S}{q_S} \tag{6.4}$$

Where q and C represent the concentrations in the solid phase and aqueous phase respectively, and the $_P$ and $_S$ subscripts represent phosphate and sulphate respectively. The separation factor at equal concentrations of phosphate and sulphate is 2.08, lower than previously reported with a copper based hybrid ion exchanger (Zhao *et al.,* 1998), which reported figures between 10 and 12, but higher than standard commercially available strong base anion exchange media such as IRA-958, reported at between 0.1 and 0.25 (Zhao *et al.,* 1998). This confirms that it is only the ion exchange sites on the media that can remove sulphate from solution. In a strong solution of phosphate (540 mg L^{-1}) and sulphate (470 mg L^{-1}), the media's capacity for phosphate removal is compromised by 50 %, reducing to 18 mg phosphorus g_{media}^{-1} (5 meq) whilst the capacity for sulphate is reduced by 34 %, down to 11 mg sulphate g_{media}^{-1} (2.2 meq).



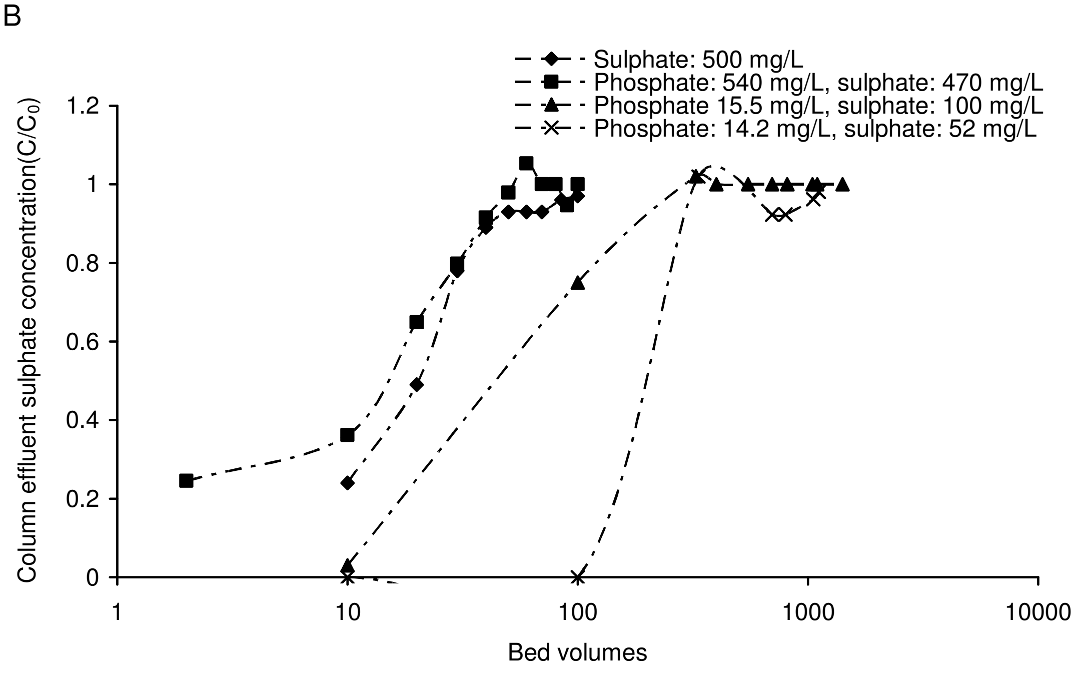


Figure 6.3: Phosphate (A) and sulphate (B) breakthrough curves at varying concentrations.

The reduction in sulphate capacity reflects a repulsive influence of the phosphate adsorbed onto the ferric nanoparticles via Donnan co-ion exclusion (Cumbal *et al.*, 2005). When more environmentally relevant concentrations of sulphate (52 mg L^{-1}) and phosphate (14.2 mg L^{-1}) were passed through the columns, the hybrid media's capacity for phosphate was again compromised by about 50 %, down from 23 mg phosphate g_{media}^{-1} (6.6 meq) from a solution containing only phosphate at 14.5 mg L^{-1}, to 11 mg phosphate g_{media}^{-1} (3.2 meq). The sulphate only competes with the phosphate for the ion exchange sites on the media, and it is the ferric nanoparticles that are responsible for phosphate removal from wastewater feeds in the main. A saturation capacity of 11.19 mg phosphate g_{media}^{-1} (3.2 meq) is achieved from environmentally relevant concentrations of phosphate and sulphate, and it is evident that the presence of sulphate is the largest contributor to the capacity differences between a pure solution (23.04 mg phosphate g_{media}^{-1}) and a real wastewater (9.5 mg phosphate g_{media}^{-1}, reported in Martin *et al.'s* (2009) study).

6.3.4 Isotherm modelling with real wastewaters

Batch equilibrium trials with real wastewaters (and a model solution containing 0.5 mg phosphorus L^{-1} as the only anion) allow an assessment of the media's performance when contacted with varying phosphate concentrations and ratios of sulphate: phosphate that are characteristic of final effluents. The phosphorus concentrations in the effluents from the small scale trickling filter and activated sludge plant works were 5.9 and 4.7 respectively. The other plants all had much lower concentrations (< 1.2 mg phosphorus L^{-1}). Phosphorus removal capacities in the study ranged from a maximum of 2.4 mg phosphorus g_{media}^{-1} from the small trickling filter works effluent, to a minimum of 0.17 mg phosphorus g_{media}^{-1} from the enhanced nutrient removal plant effluent (with a feed strength of 0.31 mg phosphorus L^{-1}) (Figure 6.4).

All three adsorption models fit the observed data for the higher strength trials but only the Langmuir model at low concentrations. This is in contrast to work with phosphate adsorption onto iron oxide tailings from synthetic solutions (Zeng *et al.,* 2004), where Temkin ≡ Freundlich > Langmuir. However, work with media similar to the hybrid

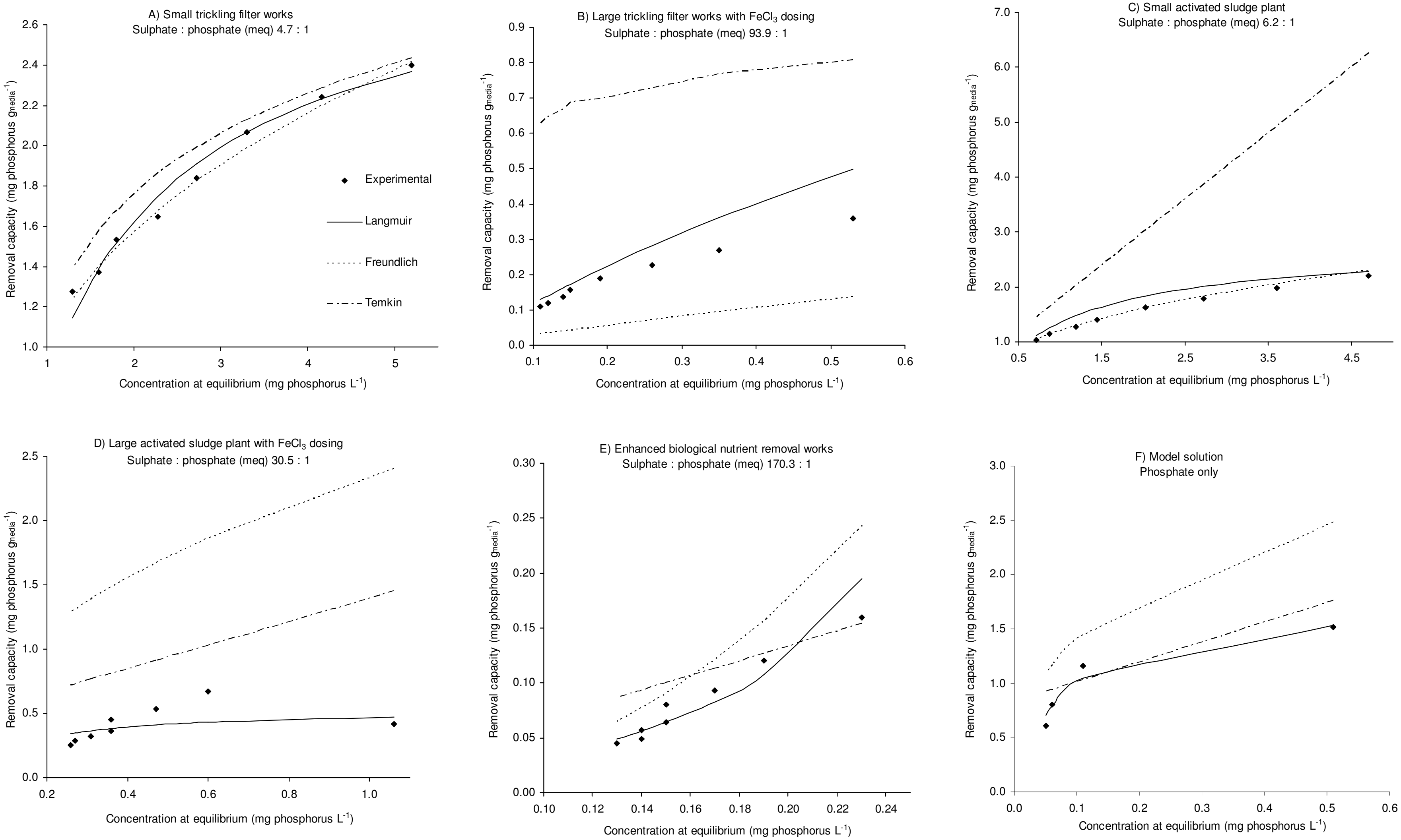


Figure 6.4: Adsorption isotherms for the removal of phosphate from final effluents using the ferric nanoparticle media.

anion exchanger in the present study confirms that the Langmuir model is a better fit (Chubar *et al.*, 2005). In non-hybrid adsorbents such as iron oxide tailings or activated carbons, the frequently amorphous structure of the material gives rise to variations in binding energy, the possibility of more than one monomolecular covering, and non selective adsorption, which are heterogeneous characteristics best modelled by the Freundlich and Temkin isotherms (Johnson & Arnold, 1995). In contrast, when sulphate outcompetes phosphate for the ion exchange sites in the hybrid media, phosphate is removed by selective, homogeneous adsorption onto the ferric nanoparticles. As a result, the good fit of the Langmuir isotherm model also suggests that each site binds only one phosphate molecule with the same adsorption energy throughout the structure, and there are no forces of interaction between adjacently adsorbed phosphate molecules (Cooney, 1998). The sulphate: phosphate ratios at the treatment works are consistent with this, and are 7 : 1 and 9 : 1 by mass and 5 : 1 and 6 : 1 by milliequivalents at the small trickling and small activated sludge plants respectively, conditions which allow some of the phosphate to be removed from solution via ion exchange. The large trickling filter, large activated sludge and enhanced biological phosphorus removal works have much higher sulphate: phosphate ratios of 144 : 1 by mass (94 : 1 meq), 142 : 1 by mass (31 : 1 meq), and 284 : 1 by mass (170 : 1 meq) respectively. At these higher ratios, the experimental data fits most closely with the Langmuir isotherm, consistent with previous studies of hybrid media (Chubar *et al.,* 2005), suggesting the removal mechanism for low strength solutions is homogeneous in nature. This means that in low strength phosphate / high strength sulphate wastewaters, sulphate almost entirely out-competes phosphate for the ion exchange sites.

6.3.5 Removal of metals

Copper, zinc, and lead concentrations were reduced by 44 %, 46 % and 41 % respectively (Figure 6.5). Nickel appears to be eluted during the phosphate loading cycle. Cadmium and mercury concentrations were mostly below the detection limits and are excluded from the Figure.

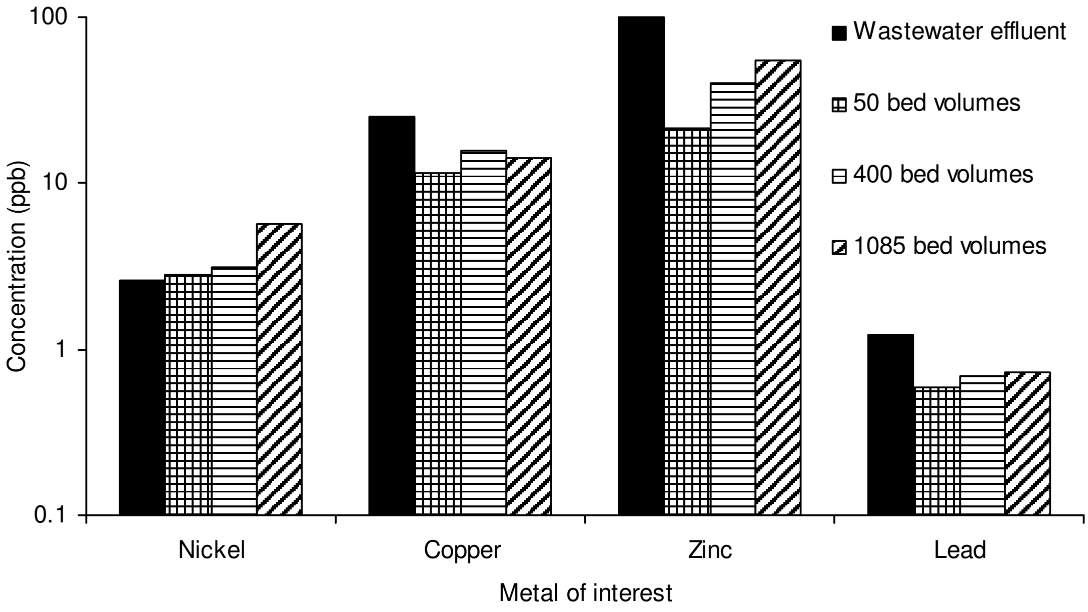


Figure 6.5: Removal of metals from wastewater using the hybrid media.

Comparison to previous trials shows alternative iron based media such as red mud can uptake greater amounts of metal. To illustrate, removals of 100 % (nickel), 68 % (copper), 56 % (zinc) and 89 % (lead) have been reported in column trials with synthetic and real wastewaters (Lopez *et al.,* 1998; Gupta *et al.,* 2001). The relatively low uptake of the metals in the present study is a consequence of the anionic exchange resin used as the base for the hybrid material. If a cationic resin is used with embedded hydrated ferric oxide nanoparticles, metals can be very efficiently adsorbed (Pan *et al.,* 2010). The Donnan membrane effect means that in the present case, the metal cations are unable to access the majority of the adsorption sites in the inner pore spaces of the media because they are repelled by the positively charged quaternary ammonium groups fixed in the resin structure (Sarkar *et al.*, 2010). The metals that are removed by the hybrid media in the present study can therefore only be associated with the ferric nanoparticles dispersed on the outer surface of the resin beads. Phosphate remains the only common ligand in wastewater that has access to the bulk of the adsorbent sites dispersed within the microporous internal surfaces of the resin beads.

6.3.6 Competing ions in the regenerant cycle

Regeneration of the media has been previously undertaken with a mixture of 5 % sodium chloride and 2 % sodium hydroxide (Blaney *et al.,* 2007). Previous analysis of this has revealed that the sodium chloride operates on the ion exchange resin and sodium hydroxide on the ferric nanoparticles, enabling controlled regeneration (see Chapter 7). Extending that to current concerns about competing ions confirms such findings. For instance, regeneration with a 5 % sodium chloride solution resulted in eluted phosphate concentrations of 162 and 89 mg phosphate L^{-1} in the first and second bed volumes respectively (Figure 6.6), representing 6.6 % of the phosphate removed from the feed solution, consistent with the amount ascribed to the ion exchange component of the parent resin. Sulphate does not appear until the third bed volume, but is present at 597 mg L^{-1}. In comparison, regeneration with a 2 % sodium hydroxide solution resulted in an elution profile where 88 % of the total phosphate desorbed during regeneration was present in the first bed volume passed through the bed, with 7 %, 4 %, and < 1 % for the following bed volumes. Over five bed volumes, regeneration with sodium hydroxide removed 91 % of the loaded phosphate from the media, the remaining 9 % spread between the ion exchange sites and the ferric nanoparticles not reached by the solution. The delay in sulphate elution means that optimal phosphate purity and concentration in the regenerant solution is returned in the initial bed volumes, enhancing the opportunities for phosphorus recovery.

The pH of the solution leaving the column decreased from 13.7 to 13.4, suggesting that some of the OH^- ions are being exchanged with the sulphate removed via ion exchange during the loading cycle, allowing it to be eluted from the bed. However, levels of sulphate are very low in comparison to the phosphate concentration, and reach a maximum of 137 mg L^{-1} in the third bed volume, in comparison to the peak phosphate concentration in the first bed volume of 3039 mg L^{-1}. No metals were found in the regenerant stream, which is expected because of the high pH used (Pan *et al.,* 2010).

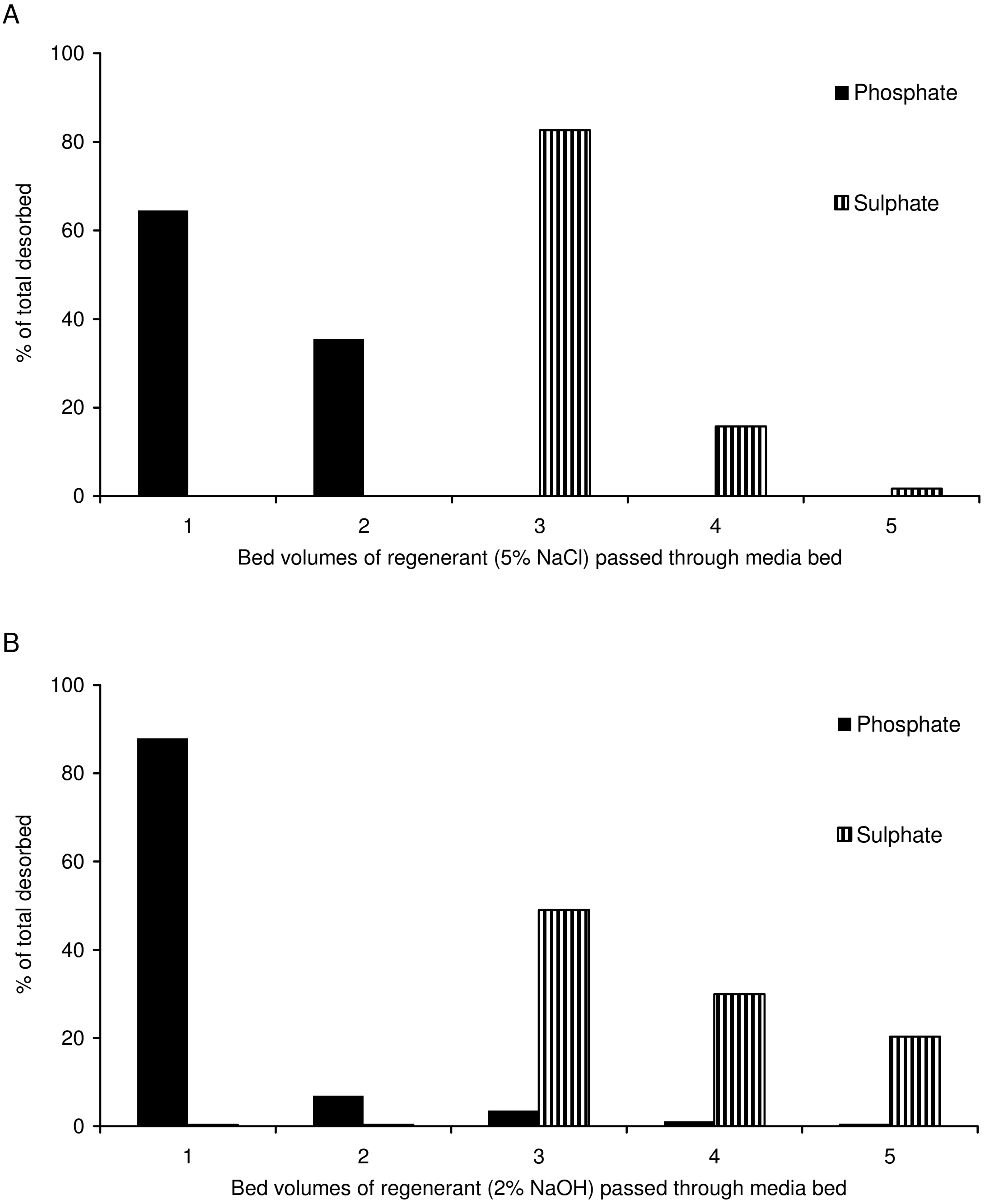


Figure 6.6: Competing ions in regenerant streams using 5 % NaCl (A), and 2 % NaOH (B).

Using sodium hydroxide instead of sodium chloride elutes nearly 19 times more phosphate in the first bed volume. A regime of regeneration in which one or two bed volumes of sodium hydroxide is passed through the bed results in the most efficient phosphate recovery rates. This does not completely regenerate the media, although this is reported to not be essential to the efficiency of such a process (Jelinek & Sorg, 1988). In terms of phosphate recovery, the manufacture of a struvite fertiliser product offers the most marketable option (Forrest *et al.,* 2008). Struvite has a crystalline structure comprised of phosphate, ammonia and magnesium in a 1:1:1 stoichiometric ratio. Currently, the formation of struvite utilises the relatively high phosphorus and ammonia loads in sludge liquors, with typical concentrations of 60 - 100 mg phosphorus L^{-1} and 300 - 700 mg ammonia L^{-1} (Battistoni *et al.,* 2000). Whilst magnesium is present in wastewaters, it is usually dosed into the struvite crystallactor as magnesium chloride. The pH of the process is also controlled by dosing sodium hydroxide (Forrest *et al.,* 2008). Ammonia is therefore present in excess, and it is magnesium and phosphate that limit the process. Adding the phosphate rich regenerant solution from a contact process using the hybrid media could match the concentration of ammonia entering the struvite crystallactor, in addition to easing the sodium hydroxide dosing. This would significantly improve the efficiency of the struvite manufacturing process.

6.4 Conclusion

The work presented in this chapter indicates that the influence of competing ions is observed in relation to overall capacity whilst not influencing phosphorus uptake kinetics. The difference reflects a switch based around the sulphate : phosphate ratio. The operational significance of this concerns whether the process is used to polish a site which already has phosphorus removal or to treat the full phosphorus load.

In the case of polishing sites, the sulphate : phosphate ratio is high, such that phosphorus uptake only occurs on the ferric nanoparticle adsorbent sites, reducing overall capacity. In such cases, regeneration can be undertaken with an alkaline soak, producing a relatively pure phosphorus eluted stream. Whereas when the media is used to treat the full phosphorus load, the sulphate : phosphate ratio is reduced and uptake occurs onto both the parent resin and the ferric nanoparticle adsorbent sites, increasing capacity over that expected just by increasing phosphorus concentrations. Future work is needed to precisely identify the sulphate : phosphate ratio at which heterogeneous adsorption switches with homogeneous adsorption, to build a more complete understanding of the mechanistics of sulphate competition.

Full recovery of the capacity will require a combined sodium chloride / sodium hydroxide soak, although if managed properly this should not lead to contamination as the phosphorus is eluted first in both cases. Based on running the media to full saturation, either removing the full load or as a polish, and using one bed volume of regenerant solution, the concentration of eluted phosphorus remains around 1 g phosphorus L^{-1} (Table 6.3). Removal capacity is comparatively lower when used as a polish using the batch results of the current study, but higher capacities are expected in column runs (Cussler, 1997, and see Chapter 7).

Table 6.3: Implementing full phosphorus load removal or as a polish impacts capacity and recovery.

Implementation	Feed strength (mg P L^{-1})	Removal mechanism	Capacity (mg P_{media} L^{-1})	Regenerant strength (mg P L^{-1})
Full load	5	Ion exchange + adsorption	2.40	1013
Polish	1	Adsorption	0.42	1009

Overall, the ferric nanoparticle media appears suitable for both full load phosphorus removal and polishing applications, enabling compliance to a 0.1 mg phosphorus L^{-1} standard irrespective of feed water chemistry. In addition, the limited metal removal and sequenced release of adsorbed materials means that the relative suitability of the media across all sites is related to the economics of regeneration and recovery. In turn this is directly related to the feed phosphorus concentration. As incoming phosphorus levels increase, capacity will increase slightly but the operating cycle time will decrease. To illustrate, projected bed life to a breakthrough of 0.1 mg phosphorus L^{-1} is 400 bed volumes to remove the entire phosphorus load from the small trickling filter works influent, or 1120 bed volumes for polishing at the enhanced biological nutrient removal works. The economic balance will then depend on the cost of sodium hydroxide and the number of cycles that each batch can be used for before replacement. A potential solution to manage such economics is to precipitate out the phosphate and then reuse the liquid stream again (see Chapters 7 and 8).

6.5 Acknowledgements

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Water, Severn Trent Water, Wessex Water, and Yorkshire Water, and Dr Paul Sylvester, of SolmeteX Co., for supply of the hybrid media sample.

6.6 References

Battistoni, P., Pavan, P., Prisciandaro, M., Cecchi, F., (2000). Struvite crystallisation: a feasible and reliable way to fix phosphorus in anaerobic supernatants. *Water Research* **34** (11), pp. 3033-3041.

Blaney, L.M., Cinar, S., SenGupta, A.K., (2007). Hybrid anion exchanger for trace phosphate removal from water and wastewater. *Water Research* **41**, pp. 1603-1613.

Chubar, N.I., Kanilbolotskyy, V.A., Strelko, V.V., Gallios, G.G., Samanidou, V.F., Shaposhnikova, T.O., Milgrandt, V.G., Zhuravlev, I.Z., (2005). Adsorption of phosphate ions on novel inorganic ion exchangers. *Colloids and Surfaces A: Physicochemical Engineering Aspects* **255**, pp. 55-63.

Comeau, Y., Hall, K.J., Hancock, R.E.W., Oldham, W.K., (1986). Biochemical model for enhanced biological phosphorus removal. *Water Research* **20** (12), pp. 1511-1521.

Cooney, D.O., (1998). *Adsorption design for wastewater treatment.* CRC Press, Inc. Florida, USA.

Cumbal, L., Sengupta, A.K., (2005). Arsenic Removal Using Polymer-Supported Hydrated Iron (III) Oxide Nanoparticles: Role of Donnan Membrane Effect. *Environmental Science and Technology* **39**, pp. 6508-6515

Cussler, E.L., (1997). *Diffusion. Mass transfer in fluid systems. Second Edition.* Cambridge University Press, Cambridge, UK.

EA, (2000). EA, Aquatic eutrophication of England and Wales: a management strategy, Environment Agency, Bristol (2000) 32 pp.

EC, (2000). EC. Directive 2000/60/EC of the European Parliament and of the Council establishing a framework for the Community action in the field of water policy. Official Journal L 327, P. 0001-0073 (22/12/2000); 2000. http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=CELEX:32000L0060:en:HTML. (Accessed November 2010).

Forrest, A.L., Fattah, K.P., Mavinic, D.S., Koch, F.A., (2008). Optimizing struvite production for phosphate recovery in WWTP. *Journal of Environmental Engineering* **134** (5), pp. 395-402.

Frazer-Williams, R.A.D., (2007). *Constructed wetlands for advance treatment and reuse*. PhD Thesis, Cranfield University, United Kingdom.

Fytianos, K., Voudrias, E., Raikos, N., (1998). Modelling of phosphorus removal from aqueous and wastewater samples using ferric iron. *Environmental Pollution* **101** (1) pp. 123-130.

Gupta, V.K., Gupta, M., Sharma, S., (2001). Process development for the removal of lead and chromium from aqueous solutions using red mud - an aluminium industry waste. *Water Research* **35** (5), pp. 1125-1134

Han, S.W., Kim, D.K., Hwang, I.G., Bae, J.H., (2002). Development of pellet-type adsorbents for removal of heavy metal ions from aqueous solutions using red mud. *Journal of Industrial and Engineering Chemistry* **8** (2), pp. 120-125.

Jelinek, R.T., and Sorg, T.J., (1988). Operating a small full-scale ion exchange system for uranium removal. *Journal of the American Water Works Association* **80** (7), pp. 79-83.

Johnson, R.D., Arnold, F.H., (1995). The Temkin isotherm describes heterogenous protein adsorption. *Biochimica et Biophysica Acta - Protein Structure and Molecular Enzymology* **1247** (2), pp. 293-297.

Lefevre, G., (2004). In situ fourier-transform infrared spectroscopy studies of inorganic ions adsorption on metal oxides and hydroxides. *Advances in Colloid and Interface Science* **107**, pp. 109-123.

Lopez, E., Soto, B., Arias, A., Nunez, A., Rubinos, D., Barral, M.T., (1998). Adsorbent properties of red mud and its use for wastewater treatment. *Water Research* **32** (4), pp. 1314-1323.

Martin, B.D., Parsons, S.A., Jefferson, B., (2009). Removal and recovery of phosphate from municipal wastewaters using a polymeric anion exchanger bound with hydrated ferric oxide nanoparticles. *Water Science and Technology* **60** (10), pp. 2637-2645.

Nowack, B., Stone, A.T., (1999). The influence of metal ions on the adsorption of phosphonates onto goethite. *Environmental Science and Technology* **33** (20), pp. 3627-3633.

Pan, B., Qiu, H., Pan, B., Nie, G., Xiao, L., Lv, L., Zhang, W., Zhang, Q., Zheng, S., (2010). Highly efficient removal of heavy metals by polymer-supported nanosized hydrated Fe(III) oxides: Behavior and XPS study. *Water Research* **44** (3), pp. 815-824.

Pan, B., Wu, J., Pan, B., Lv, L., Zhang, W., Xiao, L., Wang, X., Zheng, S., (2009). Development of polymer-based nanosized hydrated ferric oxides (HFOs) for enhanced phosphate removal from waste effluents. *Water Research*, **43** (17), pp. 4421-4429.

Sarkar, S., Sengupta, A.K., Prakash, P., (2010). The Donnan Membrane Principle: Opportunities for Sustainable Engineered Processes and Materials. *Environmental Science and Technology* **44**, pp. 1161-1166.

Wankat, P.C., (1986). *Large-scale adsorption and chromatography*. CRC Press, Inc. Florida, USA.

Wijnia, H., Schulthess, C.P., (2000). Vibrational spectroscopy study of selenate and sulphate adsorption mechanisms on Fe and Al (hydr)oxide surfaces. *Journal of Colloid and Interface Science* **229**, pp. 286-297.

Zhang, Q.J., Pan, B.C., Chen, X.Q., Zhang, W.M., Pan, B.J., Zhang, Q.X., Lv, L., Zhao, X.S., (2008). Preparation of polymer-supported hydrated ferric oxide based on Donnan membrane effect and its application for arsenic removal. *Science in China Series B: Chemistry* **51** (4), pp. 379-385.

Zhao D., Sengupta, K., (1998). Ultimate removal of phosphate from wastewater using a new class of polymeric ion exchangers. *Water Research* **32** (5), pp. 1613-1625.

7. The impact of contactor scale on a ferric nanoparticle adsorbent process for the removal and recovery of phosphorus from municipal wastewater

B. D. Martin, L. De Kock, S. A. Parsons, B. Jefferson

7.1 Introduction

In the present study, an adsorbent that utilises the high ligand strength with which phosphate binds with ferric oxide has been trialled. The adsorbent media consists of "parent" polymeric anionic exchange resin beads that contain a dispersion of ferric oxide nanoparticles. The efficiency of such media in removing phosphorus via ion exchange and adsorption mechanisms from aqueous solutions, and in achieving an effluent concentration of less than 0.1 mg phosphorus L^{-1} has been shown previously at laboratory scale (Blaney *et al.*, 2007; Martin *et al.*, 2009; Pan *et al.,* 2009). After a loading cycle, the adsorption can be reversed and the media regenerated for reuse by contacting it with a sodium hydroxide solution. The high pH deprotonates the ferric oxide, causing the adsorbed phosphate to be repelled back into solution, from which it can be recovered.

A key concern when conducting small scale experiments on adsorption is whether the obtained data can be utilised at full scale. The critical concern relates to spreading of the breakthrough curves through a combination of changes to the internal diffusional resistance, external mass transfer resistance and axial dispersion in the fluid (Cooney, 1998). Commonly, internal diffusion is the most important (see Chapter 5), such that the dimensionless group D_st / R^2, (where D_st is the intraparticle coefficient over time, and R is the external radius of the adsorbent particle) should remain constant during scale up or scale down. Given that D_s and R are likely to remain fixed this means that the fluid residence time (or empty bed contact time, EBCT) should also be fixed between comparisons of scale. In addition, a number of other practical concerns are often reported relating the relative size of media, diameter of column and length of media bed. Schwartz & Smith (1953) presented data that revealed high porosity zones next to the wall of contact vessels, extending inwards by two or three particle diameters. The smaller the column, the larger this effect will be on the overall velocity variation through the bed, resulting in faster contact times for a relatively larger proportion of the media, which causes loss of capacity and early breakthrough. It is generally suggested that this wall effect plays no role when the ratio of the column diameter to particle diameter is greater than 20 (Tobis & Vortmeyer, 1988; Jadhav & Pangarkar, 1990). Column length to particle diameter is only relevant for very shallow beds, of about a dozen layers (Gunn & Malik, 1966; Guedes de Carvalho & Delgado, 2003), which are also exceeded in all the columns in the present study. Irregularities in flow caused by packing are more significant in smaller beds (Van Deemter & Zuiderweg, 1956), and the flow through the bed is likely to be more uniform on average in larger vessels, leading to more clearly defined mass transfer zones and less leakage. Turbulent flow will also cause irregularities in the velocity profile, when Reynolds numbers are greater than 10 (Rhodes, 2008) for a fixed bed. These latter features reflect changes in dispersion profiles typically referred to as Taylor dispersion, where the traditional dispersion front is distorted as diffusion occurs outward in faster flowing sections and inward in slower moving portions. The net result is axial dispersion that blurs the mass transfer front (Cussler, 1997).

A consequence of all the issues stated is that column lengths need to be sufficiently long to enable constant pattern profiles to develop, leading to long experiments. This is avoided in activated carbon by crushing the media for use in rapid small scale column tests (RSSCT), (Crittenden *et al.,* 2005). Such approaches are not appropriate in the current case as the hybrid structure of the media must be maintained to keep the influence of the Donnan membrane effect constant during trials at different scales (Sarkar *et al.,* 2010).

Recent studies with iron nanoparticle adsorbents for the removal of phosphorus have been at laboratory scale (Zhao & Sengupta, 1998; Blaney *et al.,* 2007; Pan *et al.,* 2009), and typical column sizes reported for phosphorus adsorbents with diameters < 1 mm are in the order of 10 mm to 150 mm in diameter (Table 7.1).

Table 7.1: Column sizes reported in literature studies of phosphorus adsorbent/ion exchangers.

Material	**Bed depth (mm)**	**Column ∅ (mm)**	**Ratio of column ∅ : particle ∅**	**Solution**	**Reference**
La (III) Chelex resin	-	10	-	Seawater with 7.8 and 155 mg P L^{-1}	Wu *et al.*, 2007
Hybrid anion exchanger/adsorbent	-	11	15	Synthetic, 0.26 mg P L^{-1}	Blaney *et al.*, 2007
Polymeric ligand exchangers	155	11	22	Real wastewater, 2.2 mg P L^{-1}	Zhao & Sengupta, 1998
Two hybrid anion exchanger/adsorbent	-	12	12 - 20	Real wastewater, 3.8 mg P L^{-1}	Pan *et al.,* 2009
Red mud	47	15	30 - 50	Real wastewater, 5.2 mg P L^{-1}	Lopez *et al.,* 1997
Fly ash	-	50	793 - 2000	Synthetic, 20 - 100 mg P L^{-1}	Ugurlu & Salman, 1998
Apatite	100	85	94	Synthetic, 20 mg P L^{-1}	Molle *et al.*, 2005
Wollastonite powder and tailings	1200	150	-	Real wastewater, 3.4 mg P L^{-1}	Brooks *et al.*, 2000

The expected performance increases in terms of mass transfer and overall removal capacity of the media at larger scales has so far not been quantified. The current study addresses this gap in knowledge by using fixed beds of an iron nanoparticle adsorbent media in columns of 15 mm, 25 mm, 100 mm, 250 mm and 500 mm diameters. Within each contactor, the ratio of bed depth: diameter remained identical, at 2:1. The empty bed contact time also remained identical across the different scales, at 4 minutes. Contact time is more critical than superficial velocity, and is recommended to be kept constant between lab and pilot scale operations (Inglezakis & Poulopoulos, 2006). As a consequence, the Reynolds number (i.e. the degree to which the flow is laminar or turbulent,) increased with column size. Any variations in performance can then be attributed to differences in either scale (lessened wall effect, improvements in packing regularity and therefore contact), or flow characteristics (Reynolds) within the bed.

Aim and scope

The present study seeks to build on the current knowledge of the application of hybrid ion exchange/nanoparticle adsorbents for phosphorus treatment by quantifying changes to removal performance when the media is placed in much larger contact vessels than previous work. The main objectives are to investigate the separate roles of scale and flow regime that have not been addressed by studies such as Zhao & Sengupta, (1998), Blaney *et al.,* (2007) and Pan *et al.,* (2009). These issues are critical in assessing the viability of implementing the hybrid process at full operational scales.

7.2 Materials and Methods

7.2.1 The ferric nanoparticle media

The adsorbent media, Layne^{RT} (SolmeteX Co., Massachusetts) is a commercial product, primarily applied in the removal of arsenic from domestic groundwater supplies. It is known as a hybrid anion exchanger since it comprises a strong base anion exchange resin (gel-type, with a quarternary ammonium functional group), which acts as a scaffold to support a dispersion of ferric oxide nanoparticles (Cumbal *et al.*, 2003). The average particle diameter is 0.69 mm, and coverage of the internal surfaces with iron is approximately 26 % (see Chapter 5). Before use, the media was prepared by fluidisation in de-ionised water for 30 minutes to remove iron fines remaining from the manufacturing process.

7.2.2 Impact of Reynolds number

To assess the possible impact of Reynolds number, a series of trials using laboratory scale columns of 15 mm internal diameter were used at varying contact times. Model solutions containing 4 mg phosphorus L^{-1} were passed through a 10 ml fixed bed of the ferric nanoparticle media at varying speeds (taking between 1 and 4 minutes to move through the bed), using Watson Marlow SciQ 400 and SciQ 323 peristaltic pumps. The Reynolds (Re) number for the column configurations, which relates to the characteristic of the flow through the media bed, is defined as:

$$\mathrm{Re} = \frac{\rho V D}{\mu(1-\varepsilon)} \tag{7.1}$$

Where ρ is the density of the water, V is the superficial velocity of the feed solution through the bed, D is the average diameter of the media particles (0.69 mm), ε is the void fraction (0.3, typical of gel-type ion exchange media (Ping & Sengupta, 2000) and μ is the dynamic viscosity of the water (0.001 Pa.s).

7.2.3 Impact of contactor size

Columns with internal diameters of 15 mm, 25 mm, 100 mm, 250 mm, and 500 mm were used to evaluate the effects of scale on removal efficiency. The trials were normalised to a fixed empty bed contact time of 4 minutes and a fixed aspect ratio of 2:1 (bed height: column diameter). These fixed beds were fed with groundwater (Table 7.2) pumped into an 11 m^3 underfloor reservoir. Phosphorus was dosed into the reservoir to increase its concentration to 4 mg L^{-1} by addition of $NH_4H_2PO_4$, (supplied by Fisher Scientific UK Ltd). Distribution of this water to the columns was achieved using peristaltic and submersible pumps. One column (100 mm) diameter was fed with real wastewater (containing 5 mg phosphorus L^{-1}) at a small trickling filter works to identify any difference in the performance of the media when using the groundwater.

Table 7.2: Ionic characteristics of the groundwater used for the scaling experiments (before P dosing).

Ion	**Average (mg L^{-1})**	**Maximum (mg L^{-1})**	**Minimum (mg L^{-1})**
Chloride ion - as Cl	28	34	19
Nitrate - as N	0.3	0.9	0.2
Nitrite - as N	0.02	0.1	0.00
Orthophosphate - as P	0.29	1.73	0.02
Sulphate - as SO_4	204	304	123
Sulphide - as S	0.02	0.02	0.02

The ratio of column diameter to bed depth as well as the contact time (4 minutes), were kept the same across all the columns, but variations in flow rate, and consequently velocity were necessary to achieve this (Table 7.3).

Table 7.3: Specification of experimental configuration.

Bed depth (cm)	**Column Diameter (cm)**	**Ratio of column ∅ : particle ∅**	**Volume of resin (mL)**	**Surface area (cm^2)**	**Flow rate (mL min^{-1})**	**Liquid velocity (m s^{-1})**	**Reynolds number**
3	1.5	22	5.3	1.8	1.3	1.25E-04	0.09
5	2.5	36	24.5	4.9	6.1	2.08E-04	0.14
20	10.0	145	1570.8	78.5	392.7	8.33E-04	0.58
50	25.0	362	24543.7	490.9	6135.9	2.08E-03	1.44
100	50.0	725	196349.5	1963.5	49087.4	4.17E-03	2.88

7.2.4 Regeneration

Regeneration was undertaken with 40 mL of media that had previously been saturated with phosphorus via contact with final effluent from a small trickling filter works. The media was packed into columns of 25 mm diameter, 200 mm length. Solutions containing varying strengths of sodium hydroxide (0.1, 0.2, 0.5, and 1 M), were passed through the columns using peristaltic pumps, at empty bed contact times of 15 and 60 minutes. Each bed volume of regenerant leaving the columns was analysed for phosphorus concentration.

7.2.5 Analytical techniques

Samples were collected at regular intervals and measured for phosphorus concentration using Spectroquant cell tests. The method is analogous to EPA 365.2+3, US Standard Methods 4500-P E, and ISO 6878.

7.3 Results

7.3.1 Validating the model feed solution

The suitability of the supplemented groundwater as a surrogate feed during the column experiments was confirmed through a comparison of column experiments on both surrogate and real wastewaters. Comparison of the breakthrough curves fed with a real and synthetic solution revealed a statistically similar profile based on an ANOVA F-test, $p < 0.05$ (0.04), indicating that the supplemented groundwater was a suitable surrogate (Figure 7.1).

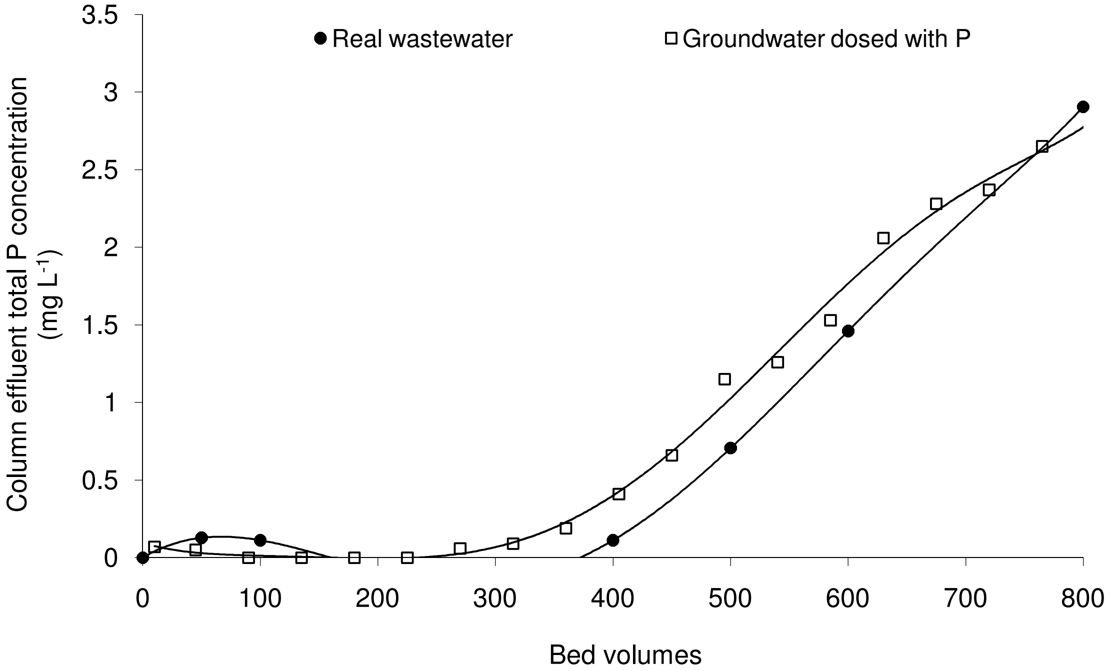

Figure 7.1: No significant difference in media performance between real wastewater and groundwater dosed with phosphorus over a loading cycle (trend lines are polynomial interpolations).

Breakthrough for 0.1, 0.5 and 1 mg phosphorus L^{-1} occurred for the real wastewater at 300, 470, and 540 bed volumes respectively, and for the model solution at 350, 420, and 480 bed volumes respectively.

In wastewater treatment, sulphate is the main competing species with phosphate in ion exchange processes (see Chapter 6, and Blaney *et al.,* 2007). Sulphate levels in the final effluent of five UK wastewater works were measured and were found to be in the range of 130 - 270 mg L^{-1}, with an average of 189 mg L^{-1} (see Chapter 6). Levels in the groundwater used in the present study were consistent with this (Table 2). Chloride and nitrate are typically present at concentrations between 50 mg L^{-1} and 150 mg L^{-1} in final effluents, much higher than those found in the groundwater. However, dosing of these ions into the groundwater was not thought to be necessary because of their negligible competition with phosphate during ion exchange (see Chapter 6).

7.3.2 Saturation curves

Based on a target of 0.1 mg phosphorus L^{-1}, breakthrough occurred in the 250 and 500 mm columns at 650 and 675 bed volumes respectively (Figure 7.2). Media in the largest column produced no detectable levels of phosphorus in its effluent for a full 630 bed volumes. At that point, the levels of phosphorus in the 500, 250, 100, 25, and 15 mm columns were 0.06, 0.11, 1.26, 0.70, and 1.5 mg phosphorus L^{-1} respectively. Further, only the larger columns exhibited consistently favourable mass transfer, with a long flat area at the beginning of the saturation curve, followed by a sharp increase in phosphorus concentrations leaving the column as the media approached its capacity for phosphorus adsorption.

Further evidence of a vessel diameter based impact on the nature of mass transfer is seen by analysing the shape of the mass transfer zone developed in each column (Figure 7.2).

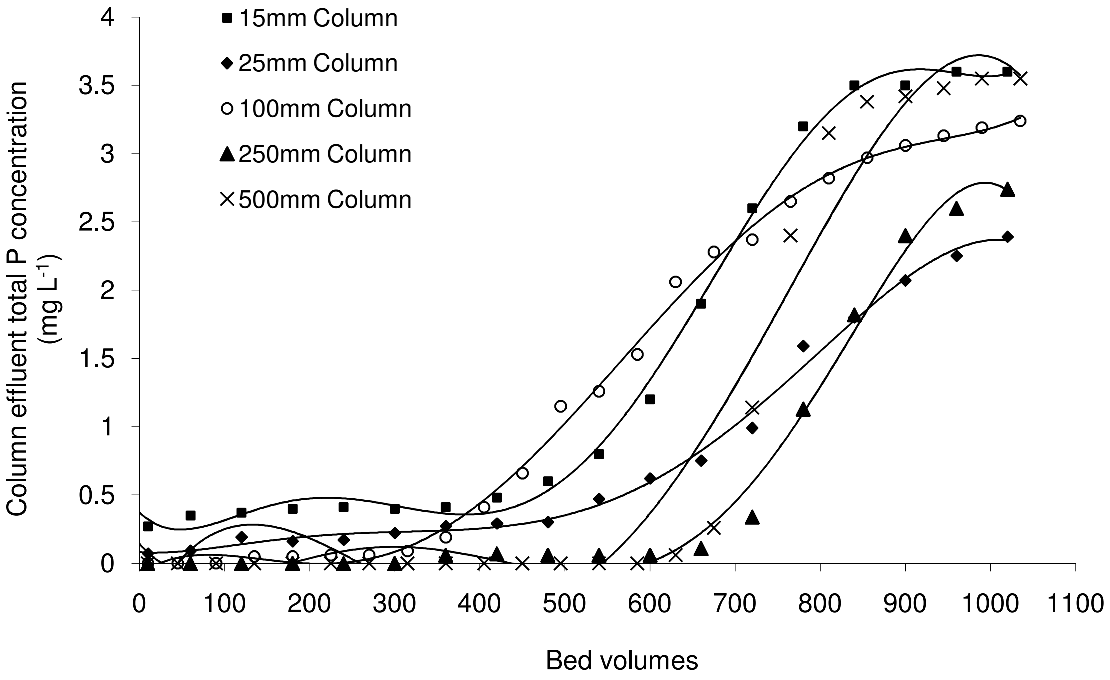

Figure 7.2: Breakthrough curves for different diameter columns (trend lines are polynomial interpolations).

The gradient of the curves increased with column diameter such that gradients of 0.005, 0.006, 0.010 and 0.022 were observed for diameters of 25, 100, 250 and 500 mm respectively. These concentration profiles can be described more conventionally as the fraction of the bed loaded (θ) (Cussler, 1997):

$$\theta = 1 - \frac{(t_E - t_B)}{2t_B} \tag{7.2}$$

Where t_E is the time at equilibrium, and t_B is the time at breakthrough. Additionally, the fraction of the bed that is loaded, θ, can be used to define the length of unused bed l' as (Cussler, 1997):

$$l' = l(1 - \theta) \tag{7.3}$$

Where l is the length of the bed. The loaded fraction of the beds for a given breakthrough concentration becomes greater as column size increases. To illustrate, the fraction of loaded bed increased from 50 % in the 15 mm column up to 84 % in the 500 mm column for a 0.1 mg phosphorus L^{-1} target level. Corresponding levels for a 1 mg phosphorus L^{-1} target were 84 and 86 % respectively, indicating the significant impact of target effluent concentration in relation to the impact of column size. The corresponding length of unused bed for a 0.1 mg phosphorus L^{-1} target outlet was 15 mm and 160 mm for the small and large column respectively.

Leakage rates have a pronounced effect on the effluent quality leaving the smaller columns. For 0.1 mg phosphorus L^{-1} the 15, 25, and 100 mm column effluents broke through at 0, 60, and 320 bed volumes (Figure 7.3). Fluctuations in the shape of the curves for these columns indicate a non ideal flow pattern within the bed, where varying velocities near the wall or by channelling between the media beads play a more significant role than in the larger columns.

Leakage rates also impact the bed life of each column in relation to the volume of feed solution treatable before breakthrough thresholds are met (Figure 7.4), especially for low effluent phosphorus targets. This is observed in relation to the vertical spread of the data points at any given column diameter, with greater variation indicating reduced resilience. To illustrate, for the 15 mm column, there is a gap of 500 bed volumes between breakthrough of 0.1 mg phosphorus L^{-1} and 1 mg phosphorus L^{-1}, whereas in the 500 mm column, for the same breakthrough points, the gap is 50 bed volumes.

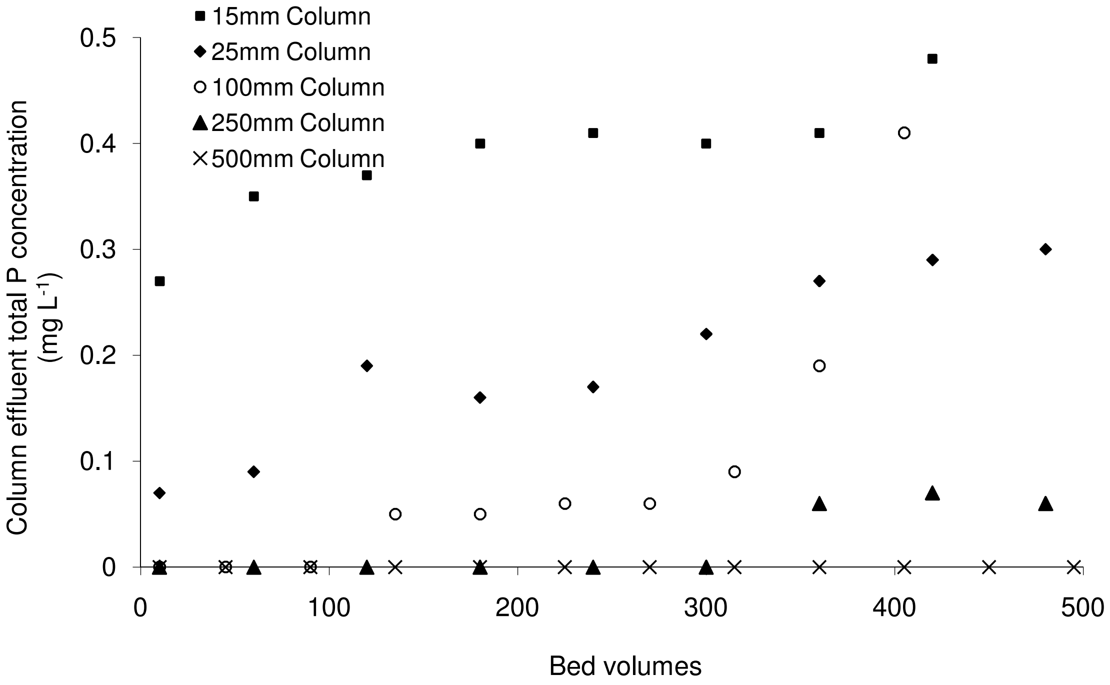

Figure 7.3: Phosphorus leakage at the start of the loading cycle.

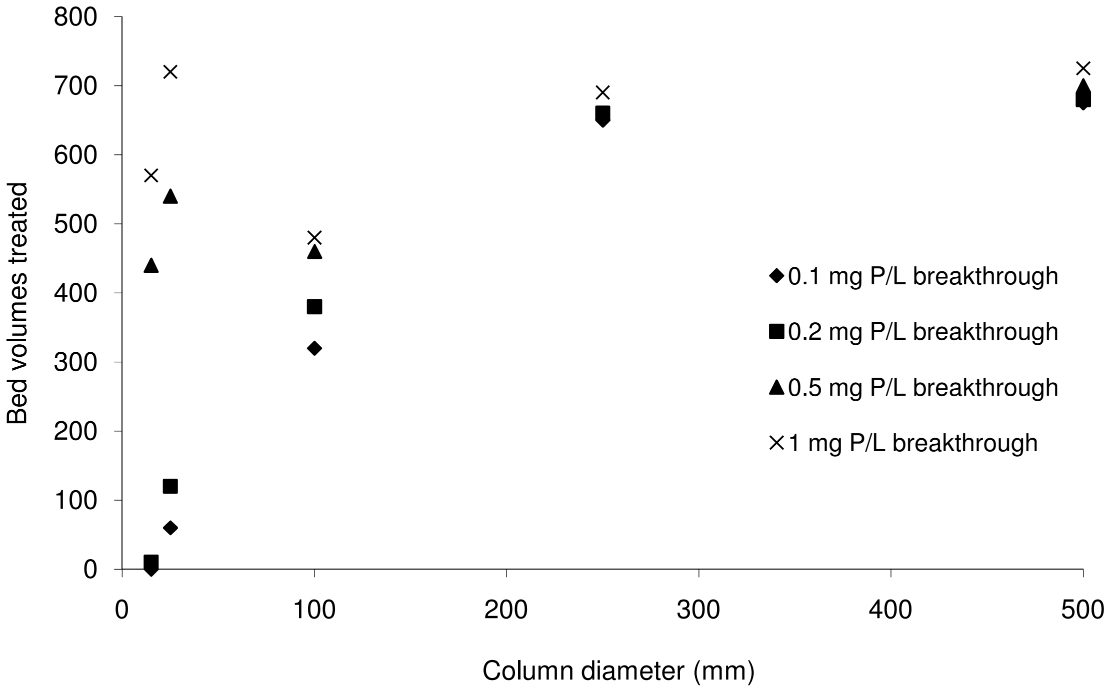

Figure 7.4: Bed life for various phosphorus breakthrough concentrations vs scale.

7.3.3 The effect of scale on removal capacity

The most important impact of column diameter is seen in regard to change in capacity which increased from from 3.37 mg phosphorus g_{media}^{-1} in the 15 mm column, to 6.27 mg phosphorus g_{media}^{-1} in the 500 mm column based on exhaustive capacity (Figure 7.5).

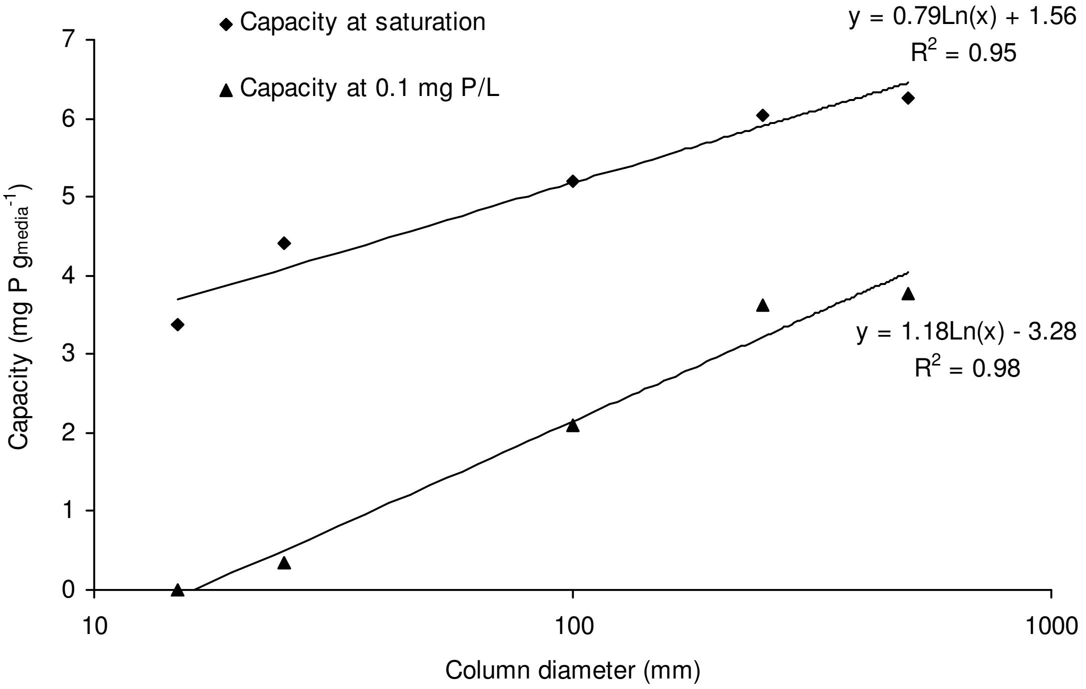

Figure 7.5: The relationship between scale and capacity at a breakthrough of 0.1 mg P L^{-1}, and at saturation (with logarithmic trend lines).

Overall, the data fit to a power law expression with scale exponents of 1.18 and 0.79 for capacity at 0.1 mg phosphorus L^{-1} breakthrough and exhaustion respectively. Capacities at a breakthrough of 0.1 mg phosphorus L^{-1} proceeded similarly, and whilst the 15 mm column has no capacity for the removal of phosphorus to such a low level because of the leakage described above, the 500 mm column exhibited a capacity of 3.76 mg phosphorus g_{media}^{-1}.

7.3.4 Impact of Reynolds number

The basis of the current experiments was to fix the operational parameters of bed length to column diameter and contact time such that both column diameter and superficial velocity change in each trial. Elucidation of the significance of the change in velocity was further considered by analysing a separate trial where different empty bed contact times were operated at a fixed column diameter (15 mm). At Reynolds numbers of 0.16, 0.33, and 0.65 for this column diameter, saturation capacity was 3.1, 2.8 and 2.3 mg phosphorus g_{media}^{-1} respectively (Figure 7.6).

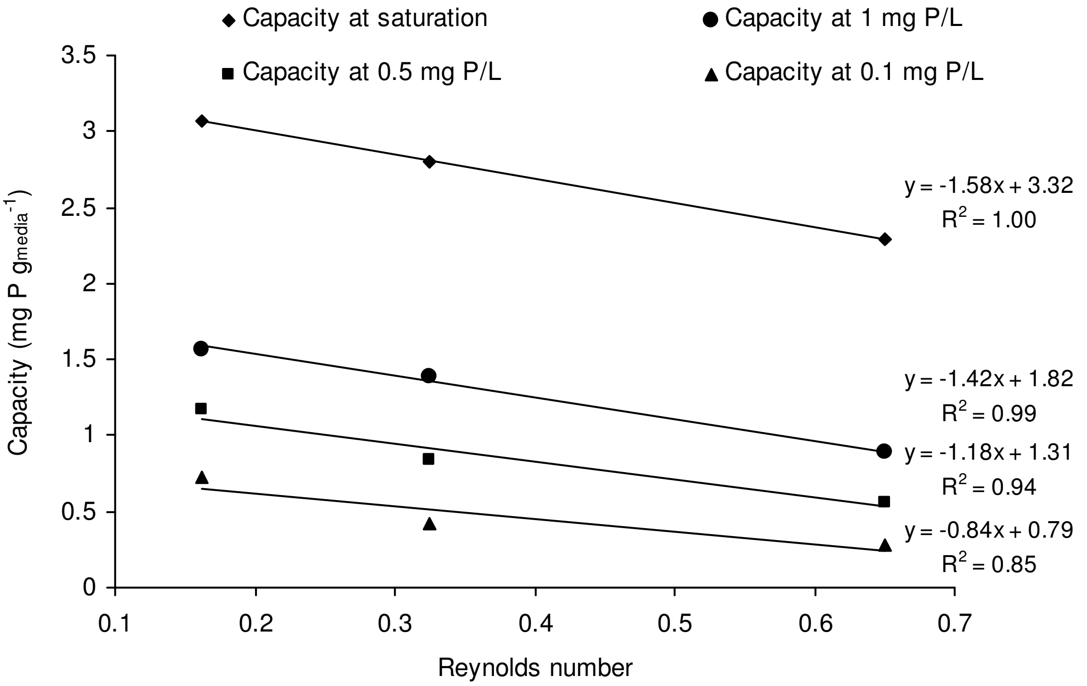

Figure 7.6: The relationship between Reynolds number and capacity at different breakthrough concentrations for a single 15 mm diameter column (with linear trend lines).

The percentage decreases between Reynolds numbers of 0.16 and 0.65 for breakthroughs of 1, 0.5 and 0.1 mg phosphorus L^{-1} are 44, 52 and 62 % respectively. In these trials, a linear decrease in adsorptive capacity is observed as Reynolds numbers rise, and contact time is considered to be the critical controlling factor on uptake in this case.

Consequently, the observed increase in capacity with changing vessel diameters occurs despite the increase in Reynolds number. However, the impact of the Reynolds number is expected to be greatest in smaller diameter columns due to the larger relative impact of Taylor dispersion on the overall flow pattern (Cussler, 1997).

7.3.5 Regeneration

The optimisation of the regeneration process was investigated in terms of the required strength of the sodium hydroxide solution, which was shown to influence both the rate of desorption and the final percentage of phosphorus desorbed (Figure 7.7).

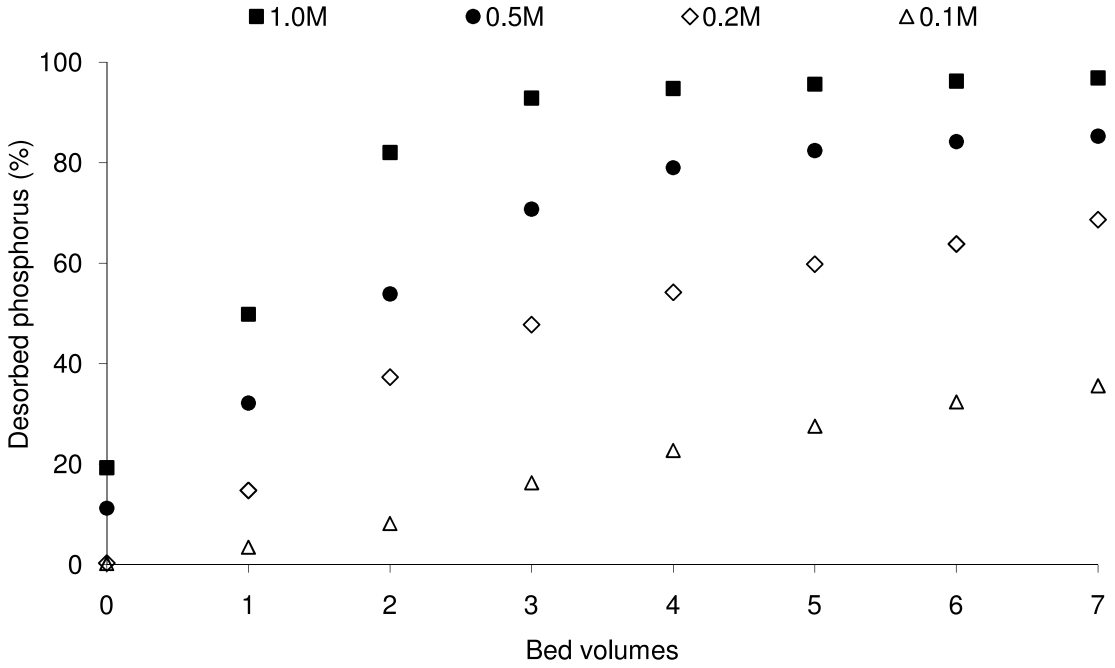

Figure 7.7: Effect of sodium hydroxide strength on phosphorus desorption.

For example, final percentage phosphorus recovery after 7 bed volumes was 35, 68, 85 and 97 % for a 0.1, 0.2, 0.5 and 1.0 M sodium hydroxide solution respectively. Further, the majority of the desorption was seen to occur within the first 3 and 4 bed volumes for the 1.0 M and 0.5 M solutions, which accounted for around 95 % of the total desorption. In contrast, desorption was seen to be more consistent with the weaker strength solutions such that phosphorus desorption followed an approximately linear trend after the second bed volume (Figure 7.7).

The pH of the regeneration solution and hence the media bed was between 13.1 and 13.5 after 4 bed volumes irrespective of the strength of the regenerant solution. The main difference was observed in the initial bed volumes where the regeneration with 0.5 and 1.0 M sodium hydroxide raised the pH to its final value within the first bed volume. In contrast, the weaker strength solutions raised the pH from the initial level of 8 to the final values over the course of the first 4 bed volumes (Figure 7.8).

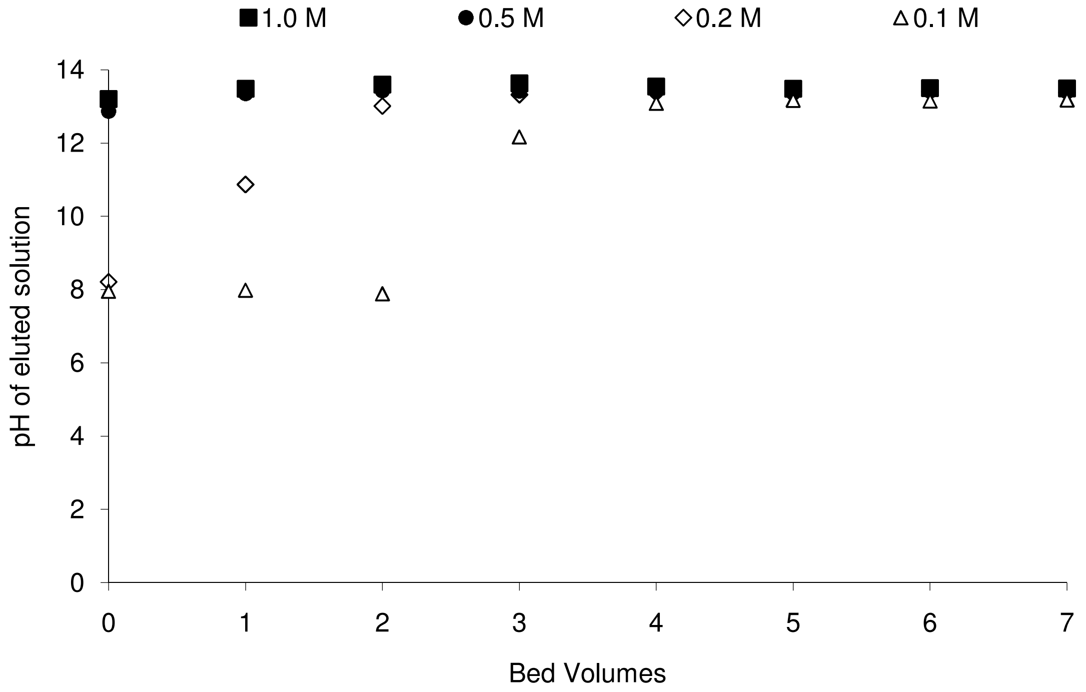

Figure 7.8: Effect of sodium hydroxide strength on effluent pH during a regeneration cycle.

In terms of the desorbed phosphorus, peak eluted concentrations of 999, 675, and 699 mg phosphorus L^{-1} for the 1.0, 0.5 and 0.2 M respectively resulted in net phosphorus concentrations in the regenerant solution of 589, 491, 337 and 138 mg L^{-1} after 4 bed volumes for the 1.0, 0.5, 0.2 and 0.1 M solutions respectively. Previously reported regeneration using such a combined solution revealed a different profile to the current case with a peak in eluted phosphorus of around 500 mg L^{-1} after 4 bed volumes, leading to a recovery of > 95 % of the capacity after 12 bed volumes (Blaney *et al.*, 2007). Similarly, Pan *et al.,* (2009) reported a peak elution at 2 bed volumes at a concentration of 1200 mg L^{-1} with 98 % regeneration after 10 BV based on a 5 % sodium hydroxide, 5 % sodium chloride solution. In part this reflects both the higher overall capacity seen for the latter resin and the greater contribution the parent resin exerts. Overall, regeneration appears to be currently non-optimised, with the potential for further reductions in regenerant use, increase in eluted phosphorus concentration and decrease in contaminants possible. All three have been shown to be critical in relation to the overall economics due to direct cost of the chemical used (Martin *et al.*, 2009) and improvements in the cost of struvite production which improve as a function of the feed P concentration (Vale, 2010).

7.3.6 Implications for implementing the ferric nanoparticle adsorbent for removing the full load of phosphorus in a wastewater stream

At the larger scales reported in the present study, phosphorus concentrations in the effluent leaving a column of 500 mm diameter can be maintained at below 0.1 mg L^{-1} for 675 bed volumes, from an initial phosphorus concentration of 4 mg L^{-1}. The bed life at a breakthrough of 0.1 mg phosphorus L^{-1} in the 500 mm column represents approximately 68 % of the total bed volumes treatable before saturation. Based on the findings of the present study, these conditions appear to be the optimum for mass transfer and overall removal capacity, and a column with a diameter of 3 m, with a bed depth of 6 m (volume of ferric nanoparticle media: 42,412 L, weight: 29,646 kg) would be expected to return a saturation capacity of 7.89 mg phosphorus g_{media}^{-1}, and a 0.1 mg phosphorus L^{-1} breakthrough capacity of 5.37 mg phosphorus g_{media}^{-1}. To illustrate the potential of the process, if a plant were installed to treat a flow of 1 ML day^{-1}, it could remove the entire phosphorus load entering the works down to a level < 0.1 mg phosphorus L^{-1} for 6 days before regeneration was required. The contact time in such a large column would need to be extended beyond the four minutes used in the present study to maintain a Reynolds number below 10. For a bed with a volume of 42,412 L, a depth of 6 m and a flow of 1 ML day^{-1}, the empty bed contact time would be 61.07 minutes, resulting in a Reynolds number of 1.13. Many options are available to optimise the contact method, and since it can be operated in the same way as ion exchange, which the water industry is experienced with through drinking water treatment (Kapoor & Viraraghavan, 1997), the process could be easily implemented. The potential phosphorus available for recovery from a 3 m diameter column would be around 234 kg at the end of each service cycle. However, it is unlikely that complete recovery of the phosphorus would be economically viable. Removing the majority of the adsorbed phosphorus, but not all of it, has been shown to have minimal impact on the subsequent loading capacity of the media (Martin *et al.,* 2009). The easiest route to processing the recovered phosphorus into a marketable product is to add it to a struvite manufacturing process. Struvite (magnesium ammonium phosphate) is an excellent fertiliser since it dissolves very slowly, is very bio-available, and contains phosphate and nitrogen in the optimum ratios needed to support vegetative growth. The formation of struvite from wastewater resources has been detailed in the literature (Forrest *et al.*, 2008), and generates a pure crystalline product for which a market is rapidly growing.

Optimising the chemical use in the regeneration step is critical to the economics of recovery. The market value for a struvite fertiliser product made of 5 to 10 mm diameter pellets is £0.10 kg^{-1} (Vale, 2010). A struvite pellet contains about 12 % phosphorus (Forrest *et al.,* 2008), and so the value of the recovered phosphorus can be estimated at £0.83 kg^{-1} (1 kg struvite / 0.12 kg P in struvite × £0.10 value of struvite kg^{-1}). The bulk value of sodium hydroxide is approximately £0.47 kg^{-1}. (ICIS Chemical Business, 2010). Based on a bed life to saturation of 1000 bed volumes (where 1 m^3 of the media would treat 1 ML of wastewater), with an influent phosphorus concentration of 5 mg L^{-1}, and the % recovery of phosphorus exhibited by the varying NaOH strengths, a 1 M solution appears to be the most efficient choice (Table 7.4).

Table 7.4: Simple economics of phosphorus recovery - based on single use of regenerant.

P recovery target (%)	**Value of P (£ m^3 media^{-1} or £ ML^{-1} wastewater)**	**Cost of recovery by NaOH strength (£ m^3 media^{-1} or £ ML^{-1} wastewater)**			
		0.1 M	**0.2 M**	**0.5 M**	**1 M**
20	0.92	6.58	4.51	1.88	N.A.
40	1.83		8.27	12.22	13.16
60	2.75		18.80	21.62	24.44
80	3.67			39.48	35.72

Re-using the regenerant solution by recirculating it through the exhausted bed would improve the efficiency of the operation, and by re-using it for ten cycles, the value of the recovered phosphate (£36.70) would offset the cost of the 1 M NaOH solution (£35.72) (Figure 7.9).

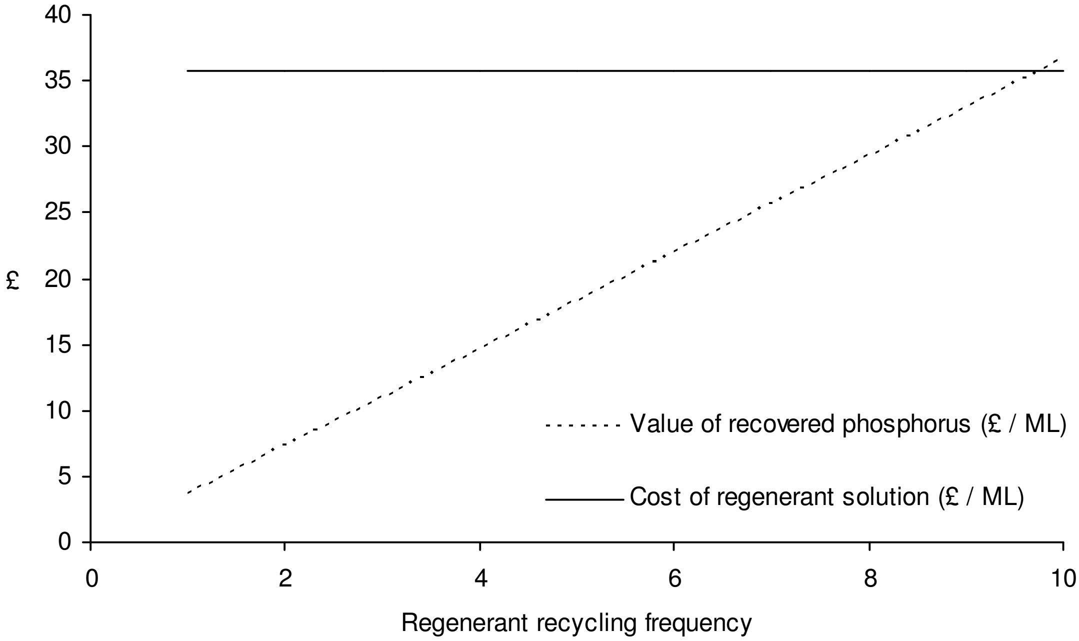

Figure 7.9: Re-using the regenerant solution enables profitability after 10 cycles (data from predictions made in Table 7.4).

Given the solubility of sodium phosphate (15 g L^{-1} at 0 ° C, and 88 g L^{-1} at 25 ° C), and the concentration of phosphorus yielded from the exhausted resin using 1 M NaOH (999 mg L^{-1}), recirculation frequencies greater than ten would be possible before risking supersaturation. The consumption of OH^- ions during the process, and the subsequent lowering of pH might be the limiting factor, and further work is required to identify if this is the case.

A struvite manufacturing process requires pH control, usually by employing NaOH (Forrest *et al.*, 2008). As such, some of its value might be maintained during the process, thus improving the economic value of the regenerant stream. All of this is in contrast to the conventional use of chemicals in wastewater treatment, where the dosing of ferrous chloride costs around £6.30 ML^{-1} (not including associated sludge handling costs and transport) (Wakerley, 2009) to reach a consent limit of 2 mg phosphorus L^{-1}, and there are no economically sound recovery methods for the phosphorus or chemical.

The simple exercise described here shows that although further work is needed to optimise the regeneration step, the flexibility of the nanoparticle adsorbent process allows many options to be considered. Implementing such a process at full scale has the potential to attain a discharge consent of 0.1 mg phosphorus L^{-1}, and provides a method for the sustainable and economically viable recovery of phosphorus, a valuable and finite resource.

7.4 Conclusions

The ferric nanoparticle adsorbent is capable of removing phosphorus from a solution containing 4 mg phosphorus L^{-1} down to levels < 0.1 mg phosphorus L^{-1}, and is a viable process for achieving the new discharge compliances expected under the Water Framework Directive. Increases in contactor size result in logarithmic increases in the phosphorus removal capacity of the ferric nanoparticle adsorbent. In addition, bed life is significantly extended in larger columns. Up-scaling the process increases the efficiency of mass transfer and capacity, and decreases the influence of leakage rates and the wall effect exhibited by columns < 250 mm in diameter.

Regeneration of the media and phosphorus recovery can be achieved using sodium hydroxide, the strength of which can be varied to match the requirements of processing the phosphorus into a marketable product.

Further work at pilot scale with real wastewater is required to fully assess the robustness of the system in terms of varying feed water characteristics. Regeneration at full scale and the conversion of recovered phosphorus into a revenue stream are also yet to be optimised.

7.5 Acknowledgements

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7.6 References

Blaney, L.M., Cinar, S., SenGupta, A.K., (2007). Hybrid anion exchanger for trace phosphate removal from water and wastewater. *Water Research* **41**, pp. 1603-1613.

Brooks, A.S., Rozenwald, M.N., Geohring, L.D., Lion, L.W., Steenhuis, T.S., (2000). Phosphorus removal by wollastonite: A constructed wetland substrate. *Ecological Engineering* **15**, pp. 121-132

Cooney, D.O., (1998). *Adsoprtion design for wastewater treatment.* CRC Press, Florida.

Crittenden, J.C., Rhodes Trussell, R., Hand, D.W., Howe, K.J., Tchobanoglous, G., (2005). *Water Treatment: Principles and Design, second edition.* John Wiley and Sons, Hoboken, New Jersey, USA.

Cumbal, L., Greenleaf, J.E., Leun, D., SenGupta, A.K., (2003). Polymer supported inorganic nanoparticles: characterization and environmental applications. *Reactive and Functional Polymers* **54** (1-3), pp. 167-180.

Cussler, E.L., (1997). *Diffusion. Mass transfer in fluid systems. Second Edition.* Cambridge University Press, Cambridge, UK.

Forrest, A.L., Fattah, K.P., Mavinic, D.S., Koch, F.A., (2008). Optimizing Struvite Production for Phosphate Recovery in WWTP *Journal of Environmental Engineering* **134** (5), pp. 395-402.

Guedes de Carvalho, J.R.F., Delgado, J.M.P.Q., (2003). The effect of fluid properties on dispersion in flow through packed beds. *American Institute of Chemical Engineers Journal* **49**, pp. 1980-1985.

Gunn, D.J., Malik, A.A., (1966). Flow through expanded beds of solids. *Transactions of the Institute of Chemical Engineering* **44**, pp. 371-379.

ICIS, (2010). Chemical Business: http://www.icis.com/StaticPages/p-s.htm#P, accessed 14th September 2010.

Inglezakis, V.J., Poulopoulos, S.G., (2006). *Adsorption, Ion Exchange and Catalysis: Design of Operations and Environmental Applications.* Elsevier, Amsterdam, The Netherlands.

Jadhav, S.V., Pangarkar, V.G., (1990). Particle-liquid mass transfer in three-phase sparged reactors: scale-up effects. *Chemical Engineering Science* **46** (4), pp. 919-927.

Kapoor, A., Viraraghavan, T., (1997), Nitrate removal from drinking water - Review. *Journal of Environmental Engineering* **123** (4), pp. 371-380.

Lopez, E., Soto, B., Arias, M., Nunez., A., Rubinos, D., Barral, M.T., (1997). Adsorbent properties of red mud and its use for wastewater treatment. *Water Research* **32**, pp. 1314-1322.

Martin, B.D., Parsons, S.A., Jefferson, B., (2009). Removal and recovery of phosphate from municipal wastewaters using a polymeric anion exchanger bound with hydrated ferric oxide nanoparticles. *Water Science and Technology* **60** (10), pp. 2637-2645.

Molle, P. Lienard, A., Grasmick, A., Iwema, A., Kabbabi, A., (2005). Apatite as an interesting seed to remove phosphorus from wastewater in constructed wetlands. *Water Science and Technology* **51** (9), pp. 193-203**.**

Pan, B., Wu, J., Pan, B., Lv, L., Zhang, W., Xiao, L., Wang, X., Tao, X., Zheng, S., (2009). Development of polymer-based nanosized hydrated ferric oxides (HFOs) for enhanced phosphate removal from waste effluents. *Water Research* **43**, pp. 4421-4429.

Ping, L., Sengupta, A.K., (2000). Intraparticle diffusion during selective sorption of trace contaminants: the effect of gel versus macroporous morphology. *Environmental Science and Technology* **34**, pp 5193-5200.

Rhodes, M., (2008). *Introduction to particle technology, second edition* pp. 153-155. John Wiley & Sons, Hoboken, USA.

Sarkar, S., Sengupta, A.K., Prakash, P., (2010). The Donnan Membrane Principle: Opportunities for Sustainable Engineered Processes and Materials. *Environmental Science and Technology* **44**, pp. 1161-1166.

Schwartz, C.E., Smith, J.M., (1953). Flow distribution in packed beds. *Industrial Engineering Chemistry.* **45**, pp. 1209-1218.

Tobis, J., Vortmeyer, D., (1988). The near-wall chanelling effect on isothermal constant-pattern adsorption. *Chemical Engineering Science* **43** (6), pp. 1363-1369.

Ugurlu, A., Salman, B., (1998). Phosphorus removal by fly ash. *Environment International* **24**, pp. 911-918.

Vale, P., (2010). *Personal communication,* Severn Trent Water Ltd, Birmingham, UK.

Van Deemter, J.J., Zuiderweg, F.J., (1956). Longitudinal diffusion and resistance to mass transfer as causes of nonideality in chromatography. *Chemical Engineering Science* **5,** pp. 271-289.

Wakerley, T., (2009). *Personal communication,* Cranfield University, Cranfield, UK.

Wu. R.S.S., Lam, K.H., Lee, J.M.N., Lau, T.C., (2007). Removal of phosphate from water by a highly selective La (III)-chelex resin. *Chemosphere* **69**, pp. 289-294.

Zhao, D., SenGupta, A.K., (1998). Ultimate removal of phosphate using a new class of anion exchanger. *Water Research* **32** (5), pp. 1613-1625.

8. Overall implications for phosphorus removal - economics and implementation strategies

8.1 Support of the original hypothesis

The work presented in the previous chapters supports the original hypothesis (*if adsorption can be phosphorus selective and reversible, then greater removal and efficient recovery will be achievable in wastewater treatment*) by showing that a ferric nanoparticle adsorbent media can selectively remove phosphorus from wastewater, and provide a sustainable and economically viable route for its recovery.

8.2 Key findings of the work

The key observations within this thesis with respect to the challenge of achieving a final municipal wastewater effluent concentration of 0.1 mg phosphorus L^{-1} are:

1. Existing chemical and biological techniques cannot be employed to meet this target, either because of prohibitive cost in the case of chemical treatment, or a lack of efficiency and reliability in biological processes.
2. It is the inorganic, dissolved fraction of phosphate that must be targeted for removal in order to achieve lower final effluent concentrations.
3. The dispersion of ferric nanoparticles through an anionic exchanger media removes phosphate from solution, with the rate of removal controlled by a combination of intraparticle and film diffusion mechanisms.
4. Competing ions such as sulphate impact only on the ion exchange component of the parent bead, and not the ferric adsorption sites.
5. Recovery of the adsorbed phosphorus is achieved using a single solution of 1 M sodium hydroxide, producing a highly concentrated stream ideal for further processing into a fertiliser product.

8.3 Operational configuration

As discussed in Chapter 6, the most likely application for the process would be as a final polisher to ensure the dissolved (Chapter 3) phosphorus that remains untreated through either chemical or biological treatment, is reduced to levels in line with the new consent limits expected under the Water Framework Directive, i.e. 0.1 mg phosphorus L^{-1}. Based on column experiments with varying wastewaters, the number of bed volumes treatable by the ferric nanoparticle adsorbent before a breakthrough of 0.1 mg phosphorus L^{-1} is 400, 550, 823, and 1120 from wastewaters containing 5, 2, 1, and 0.5 mg phosphorus L^{-1} respectively, with corresponding values for breakthroughs of 0.2, 0.5, 1, and 2 mg phosphorus L^{-1} where applicable (Figure 8.1).

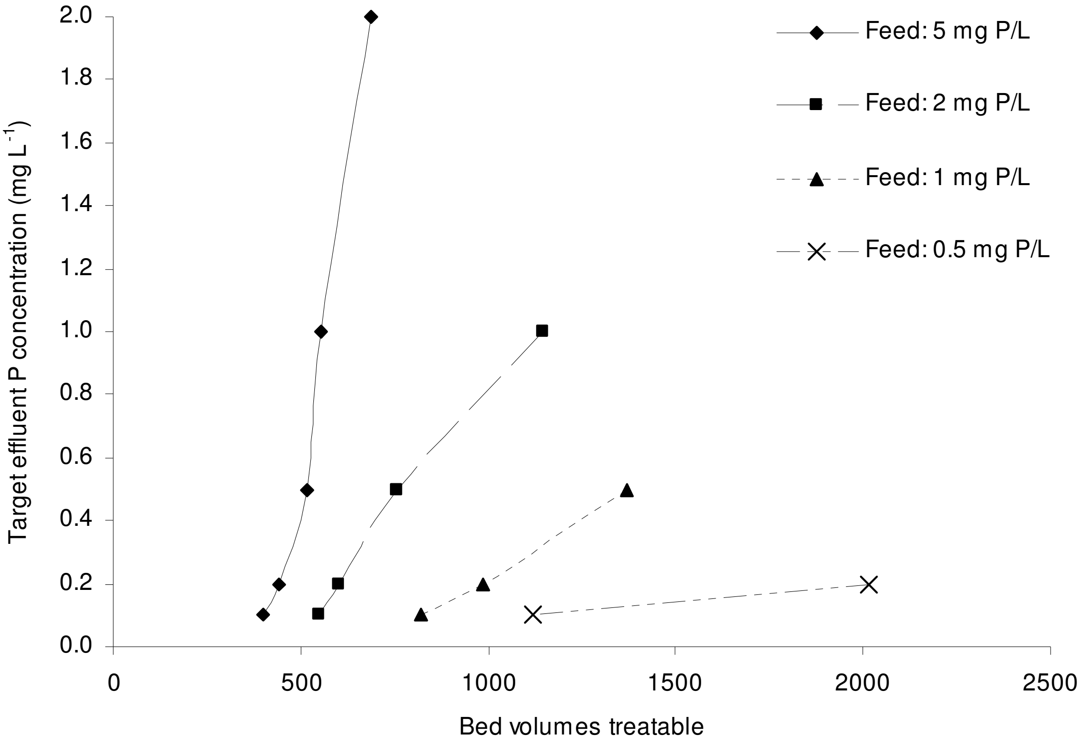

Figure 8.1: Bed volumes treatable by the ferric nanoparticle adsorbent when fed with wastewaters of differing phosphorus concentrations.

The operational benefits of placing the process as a final polishing stage are that greater bed volumes are treatable, and less frequent regenerations are required. However, placing the ferric nanoparticle process downstream of chemical or biological treatments could result in a decrease in the chemical or acetate doses required and consequently, sludge volumes and handling costs. Since the investigation of changes to the upstream parameters that could be made possible by installing the ferric nanoparticle process is beyond the scope of the present project, for the following discussion it will be assumed that they will remain unaltered. The focus will be on the potential for installing the process as a final treatment stage of the entire flow, whether downstream of chemical or biological treatments at large scale wastewater works, or as the sole phosphorus removal technique in the case of a small rural works that currently achieves no phosphorus removal.

8.4 Economic analysis of removal and recovery

The flow and phosphorus load in the final effluent of four typical UK wastewater treatment works (Table 8.1), were used to estimate the amount of ferric nanoparticle media required from the data reported in Figure 8.1.

Table 8.1: Typical UK treatment works used for economic analysis.

Class of treatment works	**Current final effluent concentration (mg P L^{-1})**	**Flow (ML day^{-1})**
Small trickling filter	5	0.18
Large trickling filter with chemical dosing	2	2.16
Activated sludge plant with chemical dosing	1	36
Enhanced biological plant	1	43

Plant costs were based on an ion exchange style contactor consisting of a raw water tank, raw water pumps, ion exchange contact vessels, caustic measure tank, bulk caustic tank, effluent tank, effluent transfer pump and a control panel. Equipment prices based on the required media volumes were given as £500,000, £650,000 and £3,500,000 for 8 m^3, 40 m^3 and 400 m^3 of media respectively (Peckham, 2010). The cost of the ferric nanoparticle media is estimated at a maximum of £7.40 L^{-1} (Sylvester, 2010).

20 year lifecycle costings were based on the plant and media costs outlined above, with a media life of 7 years (typical of ion exchange beads), and an annual interest rate of 8 %. The regeneration regime is critical to the economics of the process, and as outlined in Chapter 7, it is possible to recycle it through an exhausted bed multiple times to allow

its cost to break even with the value of the phosphorus recovered, and for the purposes of the following economic analysis, it is assumed that the regenerant will be recycled ten times. Empirical data concerning the economics of a struvite manufacturing process utilising the regenerant solution from the ferric nanoparticle media are unavailable at this time, but using previous work and industrial experience, the market value for the phosphorus component of a struvite fertiliser product is valued at £0.83 kg^{-1} (Vale, 2010), and the bulk value of sodium hydroxide is approximately £0.47 kg^{-1}. Since sodium hydroxide is required to adjust the pH of a struvite manufacturing process, some its value should be maintained, estimated here at 50 %.

For a small trickling filter works, the plant cost is estimated to be £401,734 with media costing £10,431 every seven years (Figure 8.2).

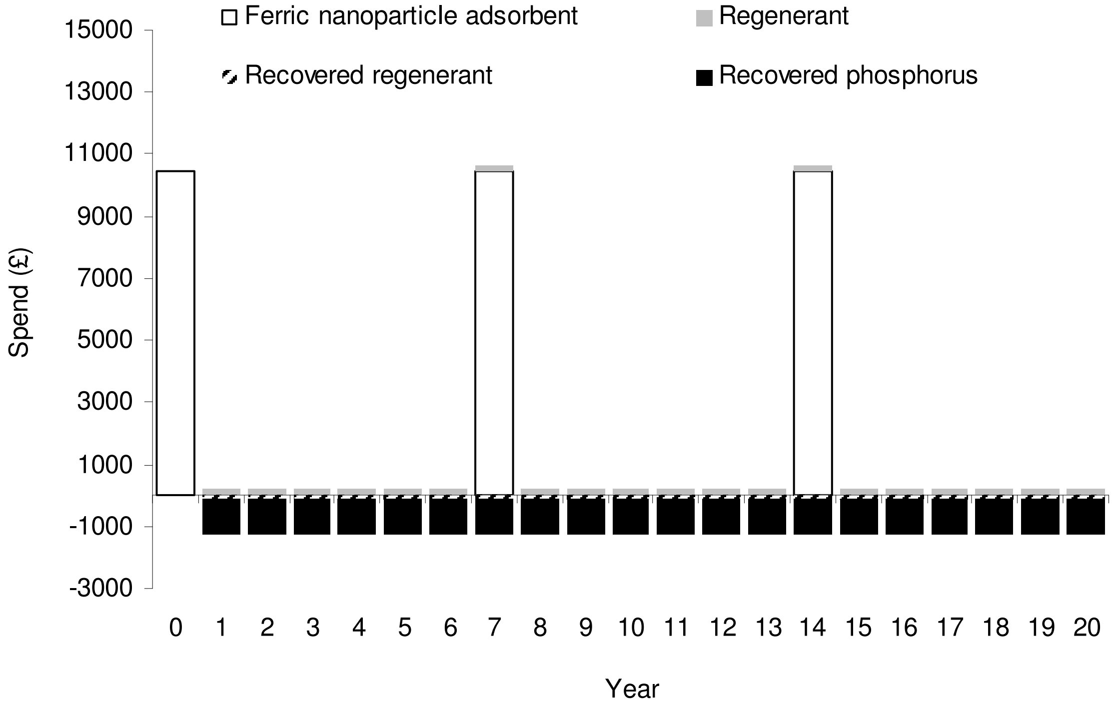

Figure 8.2: Operational spend over 20 year lifecycle for the ferric nanoparticle adsorbent at a small trickling filter plant to reach 0.1 mg P L^{-1} from a feed solution containing 5 mg P L^{-1}.

The regenerant spend (based on 50 % return of its value via struvite manufacture) is £107 each year with a phosphorus yield worth £1153 per year. The cost of the plant to accommodate the ferric nanoparticle process is likely to be prohibitive in this case, despite the regenerant being cost neutral.

In contrast, at the large trickling filter, which currently has a final effluent concentration of 2 mg phosphorus L^{-1}, the plant cost would be £522,102 with a media cost of £125,176 every seven years. The regenerant spend would be £1,859 per year, with a phosphorus value of £10,063 per year (Figure 8.3).

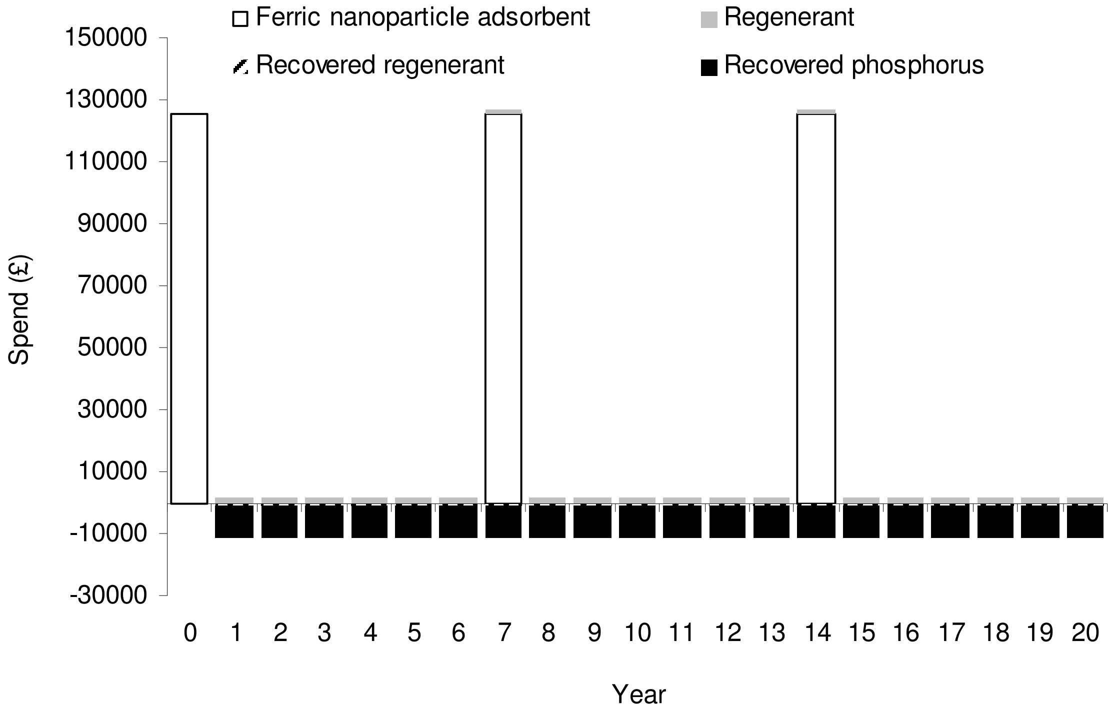

Figure 8.3: Operational spend over 20 year lifecycle for the ferric nanoparticle adsorbent at a large trickling filter (with $FeCl_3$ dosing) to reach 0.1 mg P L^{-1} from a feed solution containing 2 mg P L^{-1}.

In this case the cost of the plant is more favourable in comparison to the value represented by the recovered phosphorus.

The plant cost at a large activated sludge works to achieve a final effluent concentration of 0.1 mg phosphorus L^{-1} is estimated at £2,579,284, with a media cost of £2,086,265 every seven years (Figure 8.4).

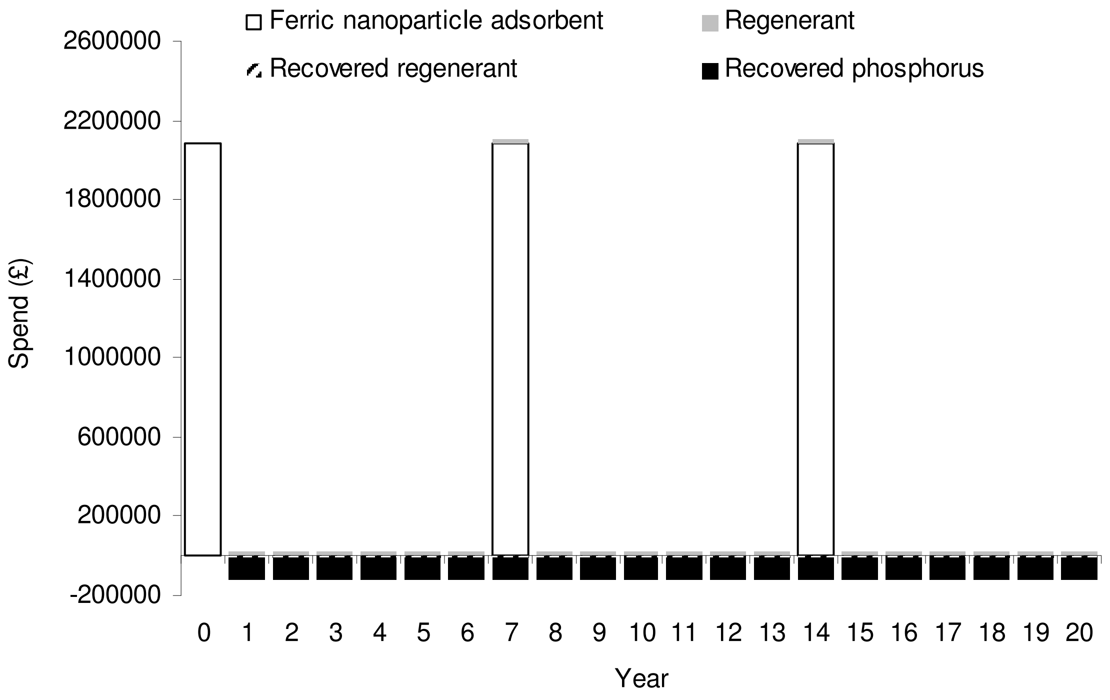

Figure 8.4: Operational spend over 20 year lifecycle for ferric nanoparticle adsorbent at an $FeCl_3$ dosing large activated sludge plant to reach 0.1 mg P L^{-1} from a feed solution containing 1 mg P L^{-1}.

The regenerant cost is £10,353 every year, and the recovery of phosphorus yields a value of £112,081 per year. Economies of scale clearly help in this case, with lower initial capital expenditure required to set up the plant, and a higher relative rate of return from the recovered phosphorus.

For the enhanced biological phosphorus removal works, the plant cost is estimated to be £3,004,824, with a media cost of £2,491,928 every seven years (Figure 8.5). The total regenerant spend would be £12,366 per year and the value of recovered phosphorus from such a site is estimated at £133,875 per year. Similar to the large activated sludge plant, this works would benefit from its large scale in both initial outlay and the value of recovered phosphorus.

Whilst it is possible to increase chemical dosing to achieve tighter discharge consents, the additional spend represents a significant diminishing return (Figure 8.6).

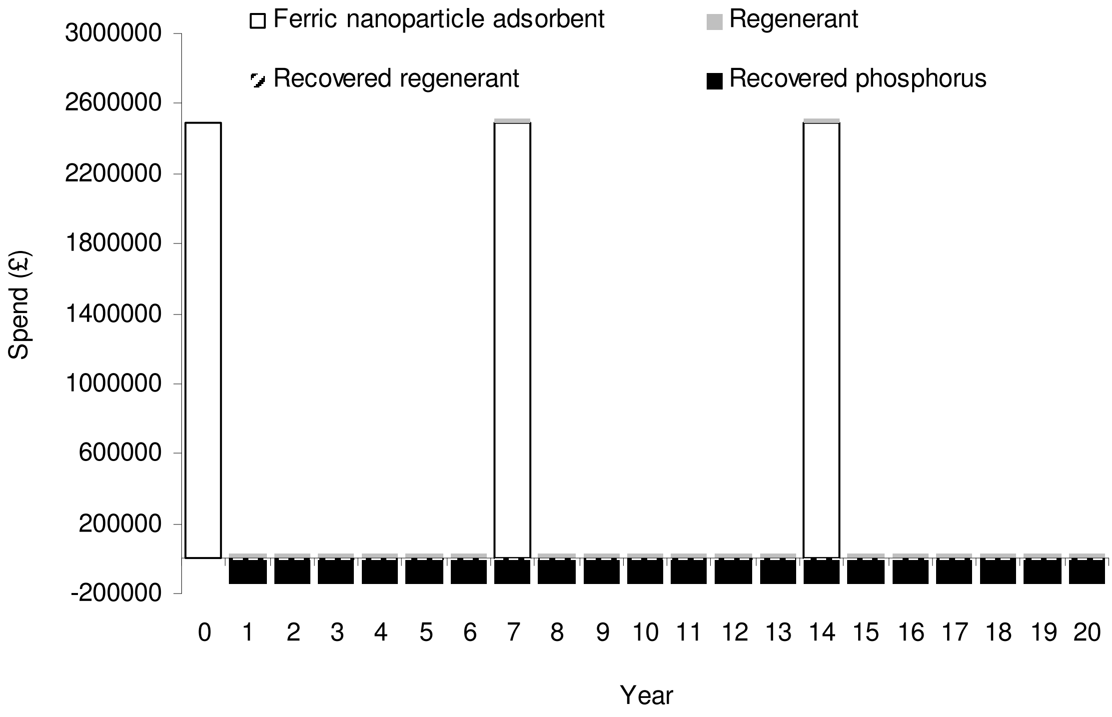

Figure 8.5: Operational spend over 20 year lifecycle for the ferric nanoparticle adsorbent at an enhanced biological plant to reach 0.1 mg P L^{-1} from a feed solution containing 1 mg P L^{-1}.

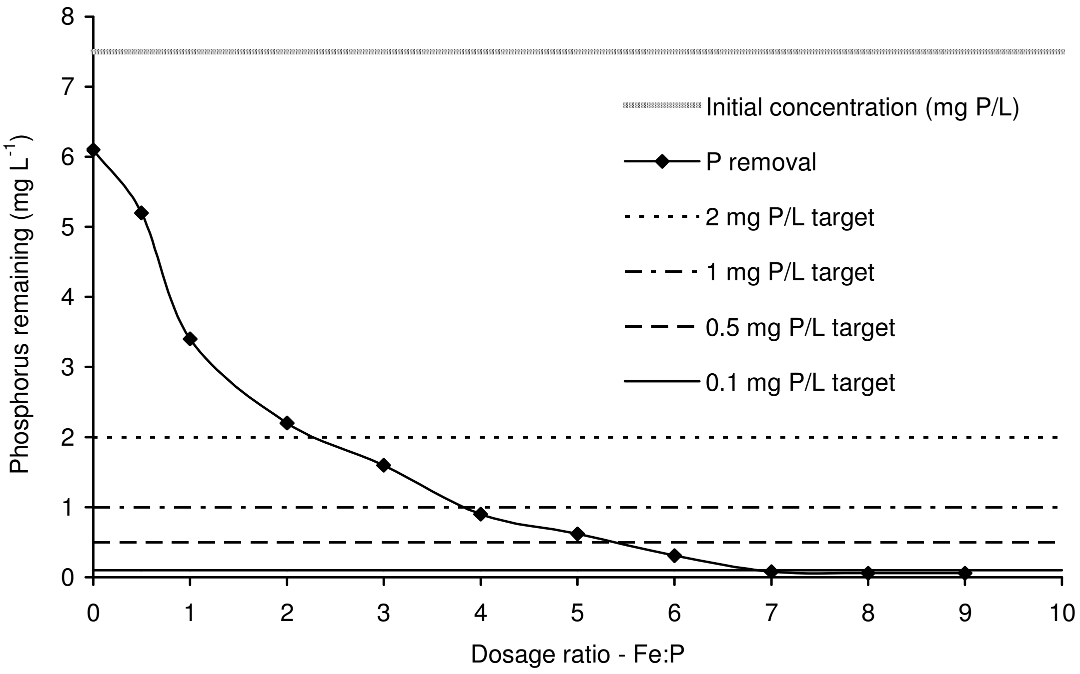

Figure 8.6: Dosage ratios of ferric chloride required to meet discharge targets.

Comparing the operating costs of the ferric nanoparticle process at the discussed works with the necessary increases in chemical use to meet targets of 1, 0.5 and 0.1 mg phosphorus L^{-1}, significant savings may be made at all the treatment works of between 29 and 68 % (Table 8.2). The greatest savings are made when the effluent target is at 0.1 mg phosphorus L^{-1}. Time for payback of the various scenarios (as a fraction of the 20 year period over which the estimates were made), when dividing the adsorbent plant cost with the differences between the operation costs of chemical dosing and the adsorbent process yields 16.34 (326.8 years) for the smallest works, and 0.53 (10.6 years) for the large enhanced biological nutrient removal plant. When the time for payback fraction is < 1, the process can be considered economically viable. At the prices used in the current analysis, using the ferric nanoparticle adsorbent to achieve a final discharge consent of 0.5 mg phosphorus L^{-1} would be economically viable at the large trickling filter, large activated sludge plant and enhanced biological nutrient removal works. Using the media to achieve a consent of 0.1 mg phosphorus L^{-1} becomes viable in the largest works: the activated sludge plant and enhanced biological nutrient removal plant.

The value of phosphorus in struvite is likely to be linked to both standard commercially available fertiliser products such as diammonium phosphate, and the commodity price of phosphate rock. These values have been subject to significant fluctuations over recent years (see Chapter 1), and the sensitivity of the ferric nanoparticle process in relation to this is equally significant. For the small trickling filter works and enhanced biological nutrient removal works, a 100 % increase in struvite value reduces the time to payback by 48 and 32 % respectively (Table 8.3). Whilst other changes to the costs of the various parameters and the operational life of the media can reduce the time to payback across both scenarios by between 9 and 68 %, the entire operation is most sensitive to changes to the cost of the regenerant sodium hydroxide. An increase to this of 50 % results in a lengthening of the time for payback of 64 and 33 % for the small trickling filter and enhanced biological nutrient removal plant scenarios respectively. Whilst the scale of the latter plant is robust enough to accommodate an increase in regenerant cost of 100 %, with a time for payback of < 1, at 0.94 (18.8 years), the small trickling filter works becomes very uneconomic in this situation.

Table 8.2: Net present value (NPV) of the ferric nanoparticle process compared to chemical dosing.

Class of works	Influent feed to ferric nanoparticle process (mg P L^{-1})	Effluent target (mg P L^{-1})	Operating NPV of adsorbent process (£)	Operating NPV of chemical coagulant (£)	Δ NPV (chemical OPEX minus adsorbent OPEX) (£)	Adsorbent plant cost (£)	NPV of adsorbent process including plant (£)	Time for payback (plant cost /Δ NPV) (fraction of 20 year period)
Small Trickling	5	0.1	-57,109	-81,697	24,588	401,734	-458,843	16.34
		0.5	-20,403	-64,336	43,933	394,673	-415,077	8.98
		1	-16,958	-51,060	34,102	394,013	-410,970	11.55
Large Trickling	2	0.1	-691,324	-980,360	289,036	522,102	-1,213,425	1.81
		0.5	-246,759	-772,034	525,275	437,368	-684,126	0.83
		1	-205,933	-612,725	406,792	429,440	-635,373	1.06
Large activated sludge	1	0.1	-11,610,786	-16,339,336	4,728,550	2,579,284	-14,190,070	0.55
		0.5	-4,143,696	-12,867,227	8,723,531	1,167,052	-5,310,748	0.13
Enhanced biological plant	1	0.1	-13,868,435	-19,516,430	5,647,995	3,004,824	-16,873,259	0.53
		0.5	-4,949,415	-15,369,188	10,419,773	1,317,991	-6,267,406	0.13

Table 8.3: Alterations to payback when operating and capital costs are changed.

Parameter	Change	Time for payback at small trickling works, 0.1 mg P L^{-1} target (fraction of 20 year period)	Time for payback at small trickling works, 0.1 mg P L^{-1} target (years)	Time for payback at enhanced biological plant, 0.1 mg P L^{-1} target (fraction of 20 year period)	Time for payback at enhanced biological plant, 0.1 mg P L^{-1} target (years)
Base case	-	16.34	326.8	0.53	10.6
Struvite value	50 % increase	9.66	193.2	0.39	7.8
	100 % increase	8.51	170.2	0.36	7.2
Media life	increase to 10 years	8.53	170.6	0.25	5.0
	increase to 20 years	5.50	110.0	0.17	3.4
Media cost	10 % decrease	13.18	263.6	0.43	8.6
	50 % decrease	7.43	148.6	0.24	4.8
Contactor cost	10 % decrease	14.70	294.0	0.48	9.6
	50 % decrease	8.17	163.4	0.27	5.4
Regenerant (NaOH) cost	50 % increase	45.67	913.4	0.79	15.8
	100 % increase	113.71	2274.2	0.94	18.8

The flexibility of the ferric nanoparticle media provides opportunities for diverse contact methods that could lead to a decrease in the economic sensitivity of the process to the cost of the regenerant. In addition to manipulating the process design of an ion exchange system by varying the scale and consequently, the volumes of media and regeneration solutions required, it could be contacted as an adsorbent system, much like granular activated carbon is employed in drinking water treatment. Even more passive techniques could be investigated, such as using the media as a slow sand filter. Whichever contact method is chosen, it is clear that the ferric nanoparticle adsorbent provides very high phosphorus adsorbing selectivity, capable of treating large wastewater volumes to an effluent strength of 0.1 mg phosphorus L^{-1}, making it ideal as a final stage at an existing works, reducing the need for high coagulant chemical doses, or enhanced biological techniques. The adsorbent also provides an easy method of regeneration and recovery, at levels such that the recovery of phosphorus in the form of struvite becomes economic and provides a route for the cost neutral removal of phosphorus at sewage works.

8.5 References

Forrest, A.L., Fattah, K.P., Mavinic, D.S., Koch, F.A., (2008). Optimizing struvite production for phosphate recovery in WWTP. *Journal of Environmental Engineering* **134** (5), pp. 395-402.

Gerrard, A.M., (2000). Guide to capital cost estimating. Fourth Edition. *Institute of Chemical Engineers,* Rugby, UK.

ICIS Chemical Business, (2010). *Sample reports* http://www.icis.com/StaticPages/p-s.htm#P, accessed 14th September 2010.

Peckham, C., (2010). *Personal communication,* AWE Ltd., (Anderson Water Equipment) Cardiff, UK.

Sylvester, P., (2010). *Personal communication,* SolmeteX Co., Massachusetts, USA.

Vale, P., (2010). *Personal communication,* Severn Trent Water Ltd, Birmingham, UK.

9. Conclusions and recommendations for future work

9.1 Conclusions

The major conclusion is that an adsorption process can be made to selectively remove phosphorus from wastewater, by exploiting the greater ligand strength that phosphate species have over competing anions such as sulphate. The reversible nature of the adsorption onto the ferric nanoparticles in the present case also provides an economically sound route for the recovery and processing of phosphorus into a marketable fertiliser commodity.

Specific conclusions are as follows:

1. Chemical and biological methods of phosphorus treatment are not able to practicably reduce levels to a final effluent target of 0.1 mg phosphorus L^{-1}, expected under the Water Framework Directive.

2. The character of the phosphorus remaining in wastewaters downstream of chemical and biological processes is inorganic, and truly dissolved. The hybrid anion exchanger / ferric nanoparticle adsorbent media was shown to significantly reduce this fraction.

3. The phosphorus removal capacity of the ferric nanoparticle adsorbent is an order of magnitude greater than that exhibited by a standard ion exchange media, and is comparable to other iron oxide rich adsorbent materials such as red mud.

4. The ferric nanoparticle media provides an appropriate means of phosphorus removal down to 0.1 mg phosphorus L^{-1}, either to treat the full phosphorus load in a wastewater stream or as a polishing step post chemical or biological treatment.

5. The removal behaviour closely fits adsorption models such as Langmuir, Freundlich, and Temkin, confirming that the main mechanism of phosphorus removal using the hybrid media is via adsorption.

6. The limiting mechanism on phosphorus uptake is a mix of film diffusion and intraparticle diffusion, with the latter playing a more significant role, indicating the relative ease of phosphorus uptake into the internal structure of the media compared to other adsorbent materials such as activated carbon or activated alumina.

7. Competing ions such as sulphate impact only the ion exchange component of the hybrid material, and phosphorus remains the only common ligand in wastewater removed by the media.

8. The media can be regenerated and re-used for many cycles, with an estimated operational life of seven years based on the properties of the parent ion exchange material.

9. A phosphate rich stream can be produced from the regeneration process with 1 M sodium hydroxide. Partial regeneration has no discernable disadvantage in subsequent service runs, and maximises the concentration of the recovered phosphorus whilst minimising chemical use. Levels of competing ions in this solution are negligible. The regenerant stream can then be added to a struvite manufacturing process, matching ammonia concentrations and assisting with pH adjustment to increase the efficiency and economic viability of recovering the phosphorus into a marketable fertiliser product.

10. Increases in contactor size result in logarithmic increases in the phosphorus removal capacity of the ferric nanoparticle adsorbent. In addition, bed life is significantly extended in larger columns. Up-scaling the process increases the efficiency of mass transfer and capacity, and improvements to both of these performance parameters are expected when the media is installed at a treatment works.

9.2 Future work

A number of areas have been identified during the course of the work that would contribute further knowledge to the field, as follows:

1. Further work at pilot scale, with real wastewater is required to fully assess the robustness and longevity of the system in terms of varying feed water characteristics.

2. A full economic analysis is required to comprehensively assess the impact the ferric nanoparticle process could have on chemical dosing or other parameters upstream (for example reducing chemical use and therefore sludge handling costs).

3. Optimising regeneration by linking it to a struvite manufacturing process, by tailoring the concentration and pH of the phosphorus stream to match the requirements of the crystallactor.

4. Linking the adsorptive removal and recovery of phosphorus with the possibility of ammonia removal and recovery via ion exchange, enabling a struvite manufacturing plant with a much smaller operational and energetic footprint by using highly concentrated nutrient streams.

5. The manufacture and use of other nanoparticle based adsorbents using different transition metals such as titanium and zirconium, and / or the use of different parent ion exchange resins to assess the possibilities of improving on the performance of the ferric based adsorbent reported in this thesis.