

Aerated Blast Furnace Slag Filters for Enhanced Nitrogen and Phosphorus Removal from Small Wastewater Treatment Plants

by

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Abstract

Rock filters (RF) are a promising alternative technology for natural wastewater treatment for upgrading WSP effluent. However, the application of RF in the removal of eutrophic nutrients, nitrogen and phosphorus, is very limited. Accordingly, the overall objective of this study was to develop a low-cost RF system for the purpose of enhanced nutrient removal from WSP effluents, which would be able to produce effluents which comply with the requirements of the EU Urban Waste Water Treatment Directive (UWWTD) (91/271/EEC) and suitable for small communities. Therefore, a combination system comprising a primary facultative pond and an aerated rock filter (ARF) system—either vertically or horizontally loaded—was investigated at the University of Leeds' experimental station at Esholt Wastewater Treatment Works, Bradford, UK.

Blast furnace slag (BFS) and limestone were selected for use in the ARF system owing to their high potential for P removal and their low cost. This study involved three major experiments: (1) a comparison of aerated vertical-flow and horizontal-flow limestone filters for nitrogen removal; (2) a comparison of aerated limestone + blast furnace slag (BFS) filter and aerated BFS filters for nitrogen and phosphorus removal; and (3) a comparison of vertical-flow and horizontal-flow BFS filters for nitrogen and phosphorus removal.

The vertical upward-flow ARF system was found to be superior to the horizontal-flow ARF system in terms of nitrogen removal, mostly through bacterial nitrification processes in both the aerated limestone and BFS filter studies. The BFS filter medium (which is low-cost) showed a much higher potential in removing phosphorus from pond effluent than the limestone medium. As a result, the combination of a vertical upward-flow ARF system and an economical and effective P-removal filter medium, such as BFS, was found to be an ideal option for the total nutrient removal of both nitrogen and phosphorus from wastewater.

In parallel with these experiments, studies on the aerated BFS filter effective life and major in-filter phosphorus removal pathways were carried out. From the standard batch experiments of P_{\max} adsorption capacity of BFS, as well as six-month data collection of daily average P-removal, it was found that the effective life of the aerated BFS filter was 6.5 years. Scanning electron microscopy and X-ray diffraction spectrometric analyses on the surface of BFS, particulates and sediment samples revealed that the apparent mechanisms of P-removal in the filter are adsorption on the amorphous oxide phase of the BFS surface and precipitation within the filter.

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List of Nomenclature and Abbreviations

Symbol	Description	Unit
A	Area	m ²
Alk	Total alkalinity	mg/L as CaCO ₃
AN	Ammoniacal-nitrogen	mg NH ₄ -N/L
BOD ₅	5-day Biochemical Oxygen Demand	mg/L
Chl-a	Chlorophyll-a	µg/L
COD	Chemical Oxygen Demand	mg/L
DO	Dissolved Oxygen	mg/L
NO ₃ -N	Nitrate Nitrogen	mg NO ₃ -N/L
NO ₂ -N	Nitrite Nitrogen	mg NO ₂ -N/L
N _{Tot}	Total Nitrogen	mg N/L
Temp.	Temperature	°C
TKN	Total Kjeldhal Nitrogen	mg NH ₄ -N/L
TP	Total Phosphorus	mg P/L
TRP	Total Reactive Phosphorus	mg P/L
TSS	Total Suspended Solids	mg/L

Abbreviations

ARF	Aerated Rock Filter/s
BFS	Blast Furnace Slag
BNR	Biological nutrient removal
CW	Constructed Wetland Systems
EDX	Energy Dispersive Using X-ray Spectroscopy
HFARF	Horizontal Flow Aerated Rock Filter
HFuaRF	Horizontal Flow Unaerated Rock Filter

N	Nitrogen
P	Phosphorus
p.e.	Population Equivalent
PFP	Primary Facultative Pond
OTE	Oxygen transfer efficiency
r	Removal
RBC	Reed Bed Channel
RF	Rock Filters
SEM	Scanning Electron Microscope
SSF	Subsurface-flow
SSHf-CWs	Subsurface horizontal-flow constructed wetlands
UWWTD	Urban Waste Water Treatment Directive
VFARF	Vertical Flow Aerated Rock Filter
VFUaRF	Vertical Flow Unaerated rock Filter
WSP	Waste Stabilization Pond
WWTP	Wastewater Treatment Plant
XRD	X-ray Diffraction

Chapter 1:

INTRODUCTION

1.1 Background of the study

Nitrogen and phosphorus are recognized as the major nutrients contributing to the increased eutrophication of lakes and other natural waters. Even an increase in phosphorus as low as 0.1 mg P/l could cause eutrophication in which excessive growth of organisms such as algae will decrease the soluble oxygen concentration in waters, causing detrimental effects on the aquatic life as indicated in Henry and Heinke (1989) and Foy and Withers (1998) cited in Alamdari and Rohani (2007). Eutrophication, caused by excessive nitrogen and phosphorus is a common and growing problem in lakes, rivers, estuaries, and coastal oceans (Smith 1998 in Carpenter *et al.*, 1998). Other problems associated with eutrophication include increased purification costs, interference with the recreational and conservation value of water impoundments, loss of livestock and possible sub-lethal effects of algal toxins on humans if eutrophic water were consumed for drinking.

Wastewater generally contains significant quantities of nitrogen and phosphorus, whose removal has become an important facet of wastewater treatment in the past three decades. At such works, phosphorus may be removed by both biological and physicochemical means. As land becomes scarce and more expensive, natural processes for nutrients removal have proved more popular and economical. Rock filter (RF), is an alternative natural treatment method that could be used for upgrading wastewater lagoon or waste stabilisation pond (WSP) effluents. In the last three decades, the use of RF for polishing lagoon and oxidation pond effluents has been studied extensively in the USA.

Initial research on the RF system was primarily focused on the removal of algal suspended solids and organic matter (BOD). As the system rapidly becomes anoxic, removal of ammonia nitrogen becomes negligible.

Middlebrooks (1995) reported that high concentrations of ammonia nitrogen in the RF effluents could limit the application of the process. To remove ammonia nitrogen, the RF must be aerated and past works (Johnson and Mara, 2005) has shown that it is better to treat facultative pond effluents (rather than maturation pond effluents) in aerated rock filter (ARF) so as to reduce the need for maturation ponds and thus save land. An added advantage is the important role of the aeration in its capacity for improving the BOD and TSS removals (Johnson 2005; Mara and Johnson, 2006; Mara 2010). In their works, Johnson and Mara (2007b) showed that an aerated RF could even outperform an un-aerated subsurface horizontal-flow constructed wetland (SSHf-CW). As a matter of fact, aeration has been suggested as a most important operating condition for the operation of the SSHf-CWs, according to Davies and Hart, 1990; Cottingham *et al.*, 1999; Maltais-Landry *et al.*, 2007; Ouellet-Plamondon *et al.*, 2007.

As the new stricter effluent requirements for nutrient removal in urban wastewaters are now applicable under the EU Directive 91/271/EEC, which came into enforcement in 1991, the discharge of nitrogen and phosphorus from small WWTPs (<10,000 p.e.) is limited to 15 mg N/L and ≤ 2 mg P/L, respectively. It is expected that these permissible effluent concentrations would be lowered further in the near future. It is on this basis that the present study, conducted at our experimental station Yorkshire Water's Wastewater Treatment Works at Esholt, Bradford, is focussed on nitrogen and phosphorus removal from a municipal wastewater. Recent works towards this compliance has involved the use of horizontal-flow aerated rock filters (HFARF) for enhanced removal of ammonia and faecal coliforms. These filters have proved effective in removing ammonia (<2 mg N/L) and faecal coliforms (100 per 100 ml) (Johnson and Mara, 2005). However, there is still need to further remove phosphorus from the RF effluent in order to meet the discharge consent limits.

In the present study, the focus however is on the enhancement of simultaneous removal of nitrogen and phosphorus in an aerated rock filter (ARF) that treats a primary facultative pond (PFP) effluent. Mara (2006) showed that a combined system, consisting of a PFP followed by an ARF,

could produce a better quality effluent, require less land, and was even cheaper to operate compared to other systems such as septic tanks or subsurface horizontal-flow constructed wetlands (SSHF-CWs).

To study the performance of the ARF in removing phosphorus, limestone and blast furnace slag (BFS) have been selected as the filter adsorbents due to their high potential and capability in adsorbing phosphorus, as well as their ready availability in the UK. Furthermore, in the final stage of experiments only BFS have been used in both ARF due to its high potential in adsorbing phosphorus from wastewater.

Prior to the nitrogen and phosphorus removal enhancement study; experimental works have been carried out to optimise the nitrogen removal using ARFs in two different flow systems; vertical upward-flow and horizontal-flow. It is noted that in the US (US EPA 2002), the vertical-flow type of aerated rock filters (VFARF) has generally proved to provide the higher level of performance. Although the previous experience at Esholt using the horizontal-flow type of aerated rock filter (HFARF) has proved satisfactory in removing nitrogen and faecal coliforms, the present study, using HFARF and VFARF, is still required in order to confirm the previous findings, although we are yet to prove whether the vertical upward-flow type is superior to the horizontal-flow type.

1.2 Problem Statement

In the UK, the water industry is a major consumer of electrical energy. The energy consumption throughout the UK for sewage treatment works per mega litre (Ml) is reported to have increased from 437 kWh in 1999/98 to 645 kWh in 2003/04 to 663 kWh in 2004/05, and to 756 kWh in 2006/07, with a high of 814 kWh in 2002/03 (Water UK, 2008a; 2008b). The increase has been predominantly a result of the increasingly stringent discharge consents limit, particularly for nutrients (nitrogen and phosphorus), set by the Environment Agency, which stipulates through the EU Urban Waste Water Treatment Directive (91/271/EEC) and the Water Framework Directive (2000/60/EC) that all large wastewater treatment works must remove 75–80% of phosphorus from incoming municipal wastewaters prior to

discharge into 'Sensitive Areas'¹ which are already eutrophic, or which in the near future may become eutrophic if no adequate protective action is taken.

Stricter effluent standards for nutrients may require more advanced wastewater treatment processes. This will be of particular concern for small domestic wastewater treatment plants (WWTPs) operators who will be expected to comply with this regulation in the near future. Larger treatment plants may employ established methods such as modified activated sludge processes for nitrogen and phosphorus removal (generally termed as biological nutrient removal (BNR)). BNR is not only expensive in terms of energy consumption but requires skilled operators due to the complexity of the process. However, the cost of nutrient removal, particularly phosphorus, is significantly higher for the smaller wastewater treatment plants. According to the UK water industry 2005, the cost could increase in the range of £6-60 / kg P to £35 -146 / kg P for small sewage works with PE less than 2,000 (OFWAT, 2007). Thus, the need arises for the development of a simple, low-cost P-removal system in small treatment works (Keplinger *et al.*, 2004) as an alternative technology for improving the effluent quality prior to discharge to the aquatic environment.

1.3 Aim and Objectives of the study

The overall aim of this study is mainly to develop a low-cost RF for enhanced nitrogen and phosphorus removal from WSP effluent to produce effluents that comply with the requirements of the EU Urban Waste Water Treatment Directive (UWWTD) (91/271/EEC). To achieve the aim of the study, the following are the objectives of the experimental works:

- a) To optimize nitrogen removal from municipal wastewaters in the UK environment using aerated limestone filter systems,

¹ The Urban Water and Wastewater Treatment Directive (UWWTD) defined sensitive areas designated under the Directive according to three criteria: (a) waters that are, or have the potential to become, eutrophic if no protective action is taken. (b) drinking water sources that contain or could contain more than 50mg/l of nitrate if no protective action is taken. (c) waters in need of protective action to meet the requirements of other Directives. Waste water discharges over 10,000 PE that pollute Sensitive Areas need treatment that relates to the designation criterion or criteria.

- b) To develop economical ARF for phosphorus removals using the best phosphorus adsorbing filter media (e.g., blast furnace slag).
- c) To investigate the effective life of the pilot-scale subsurface horizontal-flow blast furnace slag filter as well as the mechanism of phosphorus removal in the filter system.

1.4 Scopes of the study

The scope of study, summarised in research framework in Figure 1.1, covers the following aspects:

- (i) To construct a VFARF at the site
- (ii) To collect samples at the respective locations of the VFARF and HFARF
- (iii) To conduct laboratory analyses of the samples for various parameters (BOD, COD, TSS, TKN, ammonium-nitrogen, nitrate-nitrogen, nitrite-nitrogen, chlorophyll-a, alkalinity, pH, DO, and temperature)
- (iv) To compare the performance of the HFARF and VFARF with respect to nitrogen removal based on the performance criteria outlined in (iii) above.
- (v) To study and compare the performance of the HFARF and VFARF systems for simultaneous nitrogen and phosphorus removal, using different filter media:
 - VFARF (limestone + BFS) versus HFARF (BFS)
 - VFARF (BFS) versus HFARF (BFS)
- (vi) To conduct laboratory analyses of the samples for various parameters (BOD, COD, TSS, Total Phosphorus, Total Ortho-phosphorus, ammonium-nitrogen, nitrate-nitrogen, nitrite-nitrogen, chlorophyll-a, alkalinity pH, DO, and temperature)
- (vii) To study the pilot-scale subsurface horizontal-flow BFS effective life in terms of phosphorus removal by performing batch experiments of maximum phosphorus adsorptive

capacity as well as data collection of phosphorus removal at our experimental station.

- (vii) To perform semiquantitative analysis by subjecting the BFS samples to SEM/EDX and XRD; particulates and sediments samples to XRD to investigate the key removal mechanisms in the BFS filter for phosphorus removal or any compounds or precipitates formed on the filter media.

1.5 Chapter Organization

The thesis comprises of 10 chapters, including this introductory section and is organized as follows:

Chapter 2 – Literature Review is focused on the previous research on rock filter system over the globe, possible removal mechanisms of nitrogen and phosphorus from wastewater in a rock filter system, followed by the discussion of the investigated filter media including blast furnace slag (BFS) and limestone as the phosphorus adsorbents in wastewater treatment.

Chapter 3 – Materials and Methods outlines the field works which were carried out at the University of Leeds Experimental Station located at the Esholt Wastewater Treatment Works, Bradford. The chapter presented the details of how each experiment was set up and carried out and the analytical method by which each parameter was performed and analysed to achieve the objectives and scopes of the study.

Chapter 4 – the results from the comparison study of the aerated vertical and horizontal flow system limestone filter for further nitrogen removal from pond effluent will be reported, analysed and discussed. The chapter provide the vertical and horizontal-flow aerated limestone filter system performance data during the monitoring period.

Chapter 5 – reported the results and discussion from the comparison study of two types of adsorbents for phosphorus removal; BFS and limestone in the ARF system. The promising adsorbent which poses the highest potential

of adsorbing phosphorus from wastewater will be selected for further investigation in the ARF system.

Chapter 6 - provided and reported the performance of the aerated vertical and horizontal-flow filter using BFS particularly for simultaneous nitrogen and phosphorus removal.

Chapter 7 – presented the degradation of pollutants in both ARF during two sets of experiments which have been mentioned in chapter 5 and 6.

Chapter 8 – reported the results of the subsurface horizontal-flow BFS filter effective life estimation study as well as the mechanisms of phosphorus removal within the filter.

Chapter 9 – general discussion: this chapter highlights summarises of the outstanding low-cost technology for total nutrient removal as well as its overall removal mechanisms involved from the present scope of study and limitation.

Chapter 10 – overall conclusions and recommendation chapter presents the concluding remarks for the achievements of the study and recommend future work in this area to improve the present study.

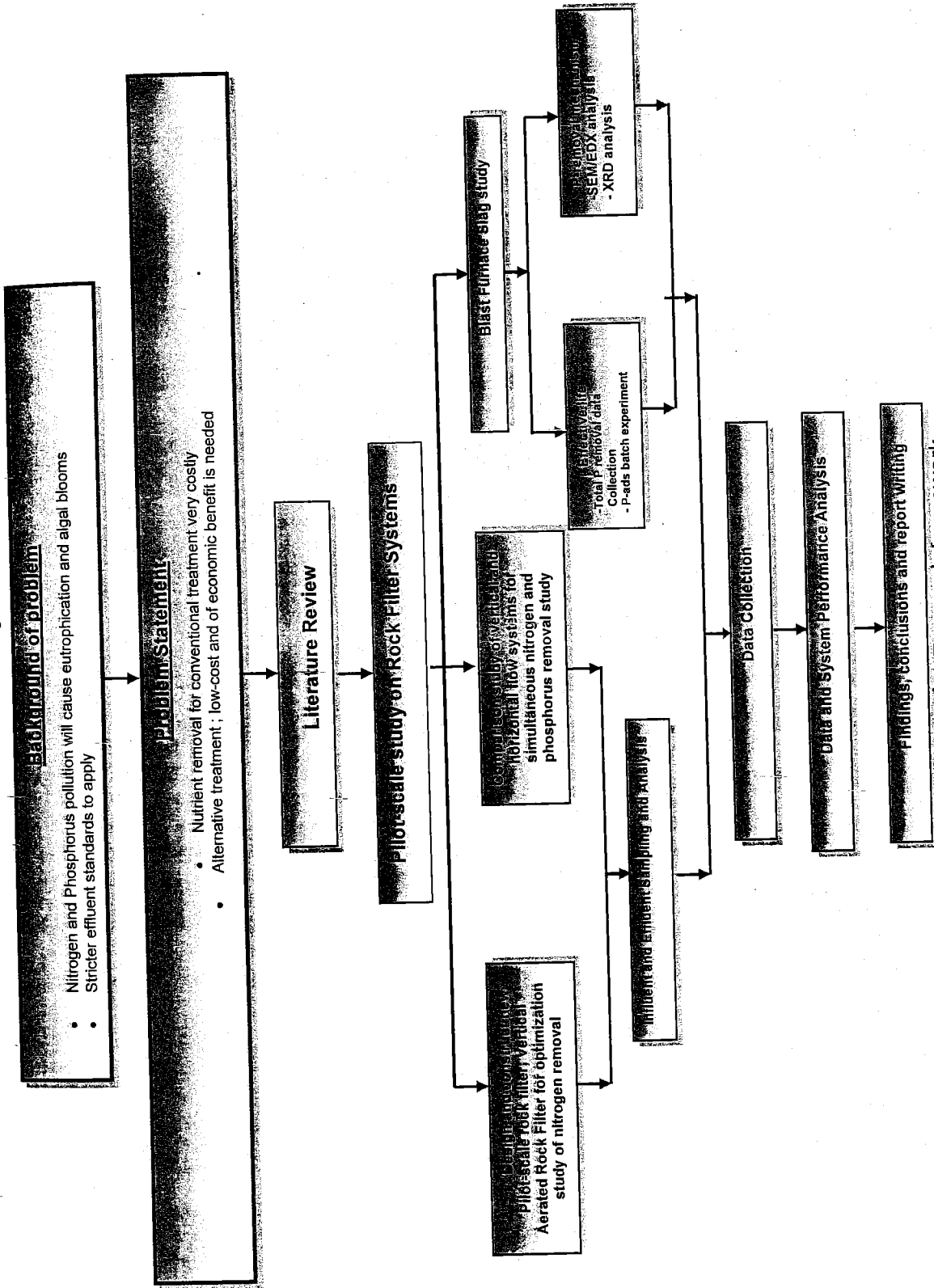


Figure 1.1 Research framework

Chapter 2:

LITERATURE REVIEW

2.1 Introduction

Untreated wastewater causes adverse impacts on the environment and human health due to its hazardous contents. Wastewater must, therefore, receive proper treatment to reduce the harmful pollutants to a harmless or near-harmless level prior to finally discharging it into receiving waters such as streams, rivers or oceans. The wastewater treatment systems include conventional, mechanical, and natural treatment system or a combination of treatment systems. To remove nutrients such as nitrogen and phosphorus from wastewater requires advanced wastewater treatment. Conventional wastewater treatment typically requires large capital investments and consumes large amounts of energy. It is also generally suited to bigger populations. To adopt advanced wastewater treatment technologies in small communities, with lower tax bases and limited resources, the purifying techniques must be low cost, require minimal maintenance, and be easily applicable. This has stimulated the development of alternative wastewater treatment systems which will be more efficient and less expensive than the conventional treatment systems. Natural wastewater treatment system is one of the attractive low-cost technologies for treating small communities' wastewater and one of these systems is the combination of waste stabilization ponds (WSP) and aerated rock filters (ARF).

Waste stabilization ponds have been widely used in all parts of the world for wastewater treatment in small communities. In France and Germany, there are over 2500-3000 and over 3000 WSP systems, respectively, for populations less than 1000 (Racault and Boutin, 2005; Johnson *et al.*, 2007), whilst in the USA more than 7000 WSP systems are serving populations of less than 5000 (Mara, 2004). The popularity of WSP is due to their relatively low initial costs, low operational and maintenance costs and high standards

of reliability in stabilizing the biodegradable organics in raw wastewaters. However, in the UK, WSP's are not popular probably because this treatment method consumes a large area of land and gives a fluctuating effluent quality particularly in terms of suspended solids (SS) and biochemical oxygen demand (BOD) (Johnson *et al.*, 2007).

Nevertheless, with increasing emphasis on higher quality effluents, WSP may need some modification if it is to meet these new stricter effluent requirements. WSP are primarily designed for BOD and SS removal as well as *E coli* and nutrient removals. However, the nutrient removal in a series of WSP often does not comply with the discharge consent. Therefore the effluent from WSP requires further treatment specifically for nitrogen and phosphorus removal. Thus the objective of this study was to carry out further treatment of WSP effluent to remove nitrogen and phosphorus using ARF systems. Two types of ARF systems were designed to study the effectiveness of nutrients removal: a vertical upward-flow ARF and a horizontal-flow ARF.

The overall aim of this study was mainly to develop a low-cost ARF for enhanced nitrogen and phosphorus removal from WSP effluent which is able to produce effluents that comply with the requirements of the EU Urban Waste Water Treatment Directive (UWWTD) (91/271/EEC). The UWWTD makes secondary treatment mandatory for sewerage domestic wastewater as well as all biodegradable industrial wastewater. Requirements to reduce nutrients from wastewater are directly addressed by the Directive as shown in Table 2.1 for those receiving waters that are considered to be at risk from eutrophication.

2.2 Nitrogen, phosphorus and the ecosystem

Nutrient is the term for all chemical substances that an organism requires to survive. Every living organism needs nutrients to grow and carry out crucial life functions. Nutrients are passed between organisms and the environment through the biogeochemical nitrogen and phosphorus cycles which both play prominent roles in the biosphere. Both nitrogen and phosphorus are key elements and are essential for plant and animal cell growth and nourishment.

Nitrogen is used in protein synthesis (e.g., new cell growth) and phosphorus is used for cell energy storage (Scholz, 2006; Conley, *et al.*, 2009).

Table 2.1 The Urban Wastewater Treatment Directive (91/271/EEC) discharge limits for wastewater treatment plants and sensitive water*

Parameter	Population equivalent (p.e)	Maximum concentration	Minimum reduction (%) ¹
BOD ₅ ^{20°C} (without nitrification) ²	-	25 mg O ₂ l ⁻¹	70-90
COD	-	125 mg O ₂ l ⁻¹	75
Total suspended solid	>10,000	35 mg l ⁻¹	90
	2000-10,000	60 mg l ⁻¹	70
Total phosphorus	10,000-100,000	2 mg P l ⁻¹	80
	>100,000	1 mg P l ⁻¹	80
Total nitrogen ³	10,000-100,000	15 mg N l ⁻¹	70-80
	>100,000	10 mg N l ⁻¹	70-80

*Source: Council of the European Communities, 1991

Notes:

- 1 Reduction in relation to the influent load.
- 2 The parameter can be replaced: TOC or TOD if a relationship can be established between BOD₅ and the substitute parameter.
- 3 Total organic means: the sum of Total Kjeldhal Nitrogen, aka TKN, which is the sum of organic N, ammonia (NH₃), nitrate (NO₃) and nitrite (NO₂).

The nitrogen cycle in the environment is given in Figure 2.1 as discussed in Stanley (2001). Nitrogen occurs predominantly in all the spheres as the most abundant gas. The atmosphere is made up of approximately 78% of nitrogen gas (N₂). N₂ is very stable, so breaking it down into atoms that can be incorporated with inorganic and organic chemical forms of nitrogen is the limiting step in the nitrogen cycle. This can be done by exposing it to highly energetic lightning discharges that produce nitrogen oxide. N₂ is also incorporated into chemically bound forms, or fixed by biochemical processes mediated by microorganisms. The biological nitrogen is mineralized to the inorganic form during the biomass decay. The production of gaseous N₂ and

N_2O by microorganisms and the evolution of these gases to the atmosphere complete the nitrogen cycle through the denitrification processes (Stanley, 2001). There are also five possible nitrogen-cycling reactions in the environment: fixation, nitrification, denitrification, assimilation, and ammonification. Reactive nitrogen (biologically active forms such as nitrate, ammonia or organic nitrogen compounds, in contrast to N_2 gas, which not used by organisms except a few nitrogen-fixing species) is supplied by natural resources, as well as industrial N_2 fixation, combustion, and planting of soya beans and other N_2 -fixing crops (Carpenter, 2008). Excess reactive nitrogen then enters groundwater, surface water or the atmosphere.

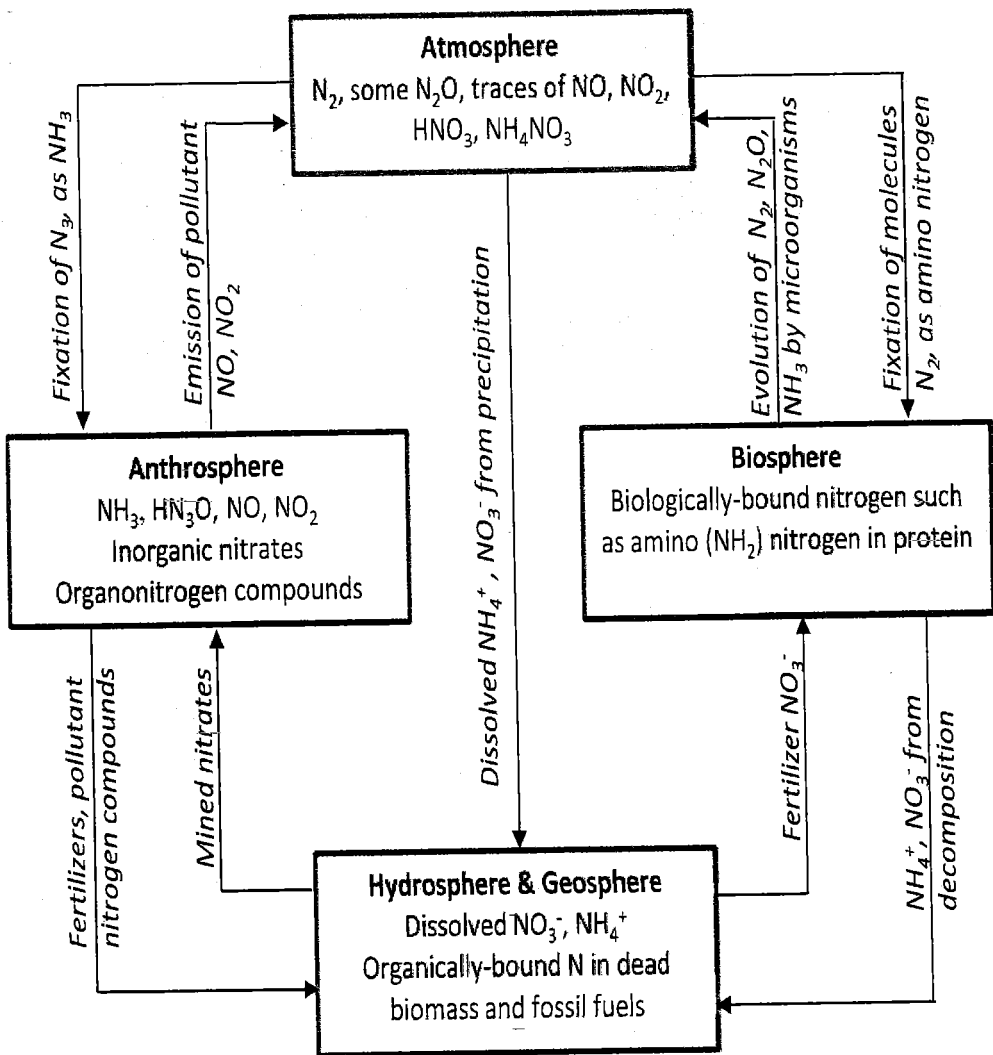


Figure 2.1 Nitrogen Cycle

(Source: Stanley, 2001)

The diagram in Figure 2.2 represents the phosphorus cycle in the environment. Stanley (2001) indicated that the phosphorus cycle was endogenic as there were no common stable gaseous forms of phosphorus in the ecosystem. In the geosphere, phosphorus mainly exists in poorly soluble minerals, such as hydroxyapatite, a calcium salt, deposits of which constitute the major reservoir of environmental phosphates. Moreover, the soluble forms of phosphorus originate from phosphate minerals and other sources such as fertilizers taken up by plants and incorporated into nucleic acids to make up the genetic material of organisms. Mineralization of biomass by microbial decay returns phosphorus to the salt solution from which it may precipitate as mineral matter.

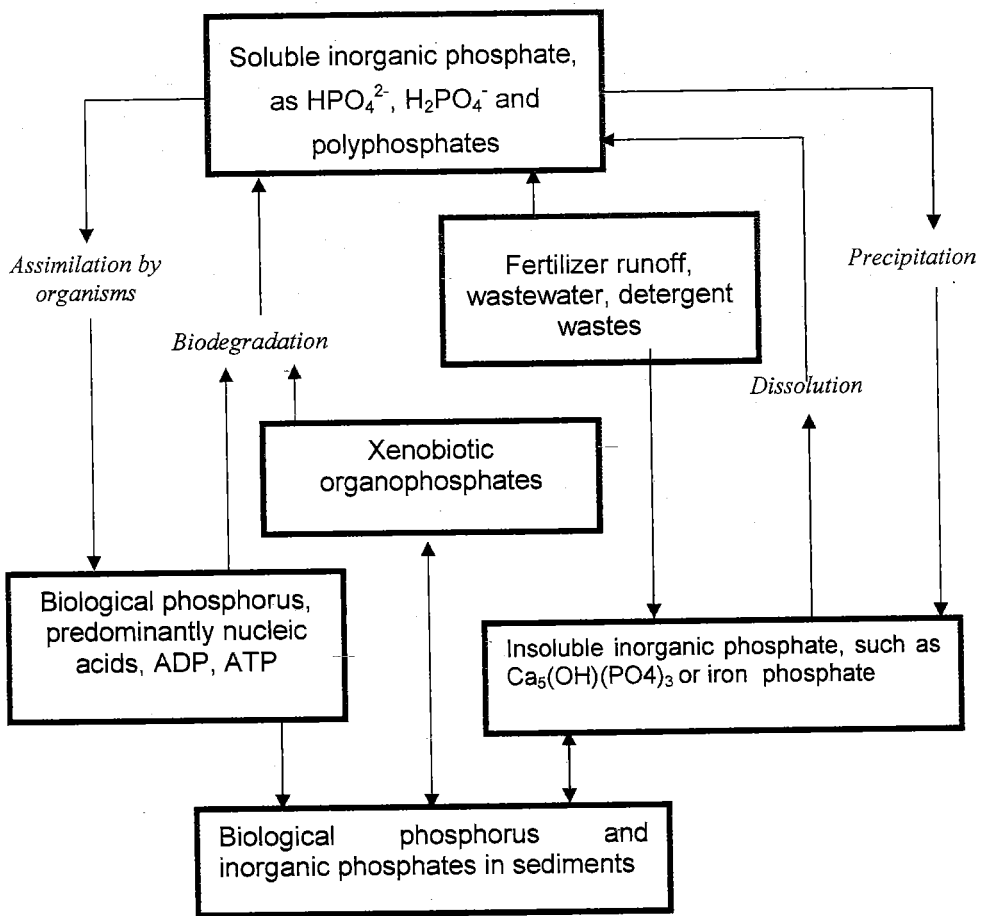
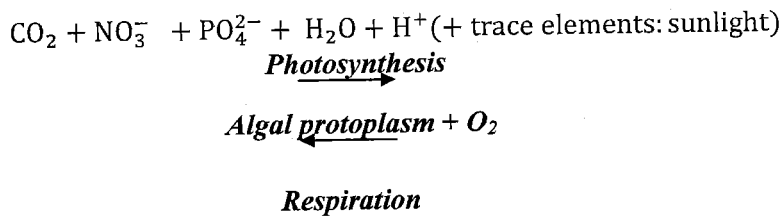


Figure 2.2 Phosphorus cycle

(Source: Stanley, 2001)

Nitrogen and phosphorus are the key elements controlling the growth of algae and aquatic plants in rivers, lakes and shallow areas of the marine environment. For this reason, they are termed life-giving elements. Nitrogen is often the nutrient determining lake productivity, whereas phosphorus is the nutrient limiting growth. The concept of limiting nutrients in water bodies, as described in Burt, *et al.* (1993), relies on the fact that both absolute and relative quantities of essential nutrients regulate primary productivity (mainly algal biomass) in the water bodies. Therefore it is assumed that the ratio at which nutrients are taken up and used by algae reflects the relative composition of these nutrients in their cellular material. On this basis, the ratio 106C:16N:1P has become widely cited as the reference value for assessing the limiting nutrient in water bodies. Carbon is rarely limiting in freshwaters. The assumption is that control of the nitrogen and phosphorus loads entering the water body from its catchment, or manipulation of the ratio of N: P within the water body should control algal growth. The limiting nutrient concept is based on the photosynthesis reaction. Conceptually, the reaction can be expressed as follows (Burt, *et al.* 1993):



This equation suggest that several variables are involved in this reaction. Theoretically, control of any one variable may offer control of eutrophication in water bodies. Most attention has been focused on control of the external nutrient supply, partly because some macro-nutrients, particularly phosphorus, offer a relatively simple means of limiting nutrient control. There is no sharp boundary between phosphorus and nitrogen limitation. However, low N:P ratios favour nitrogen-fixing blue-green algae which are undesirable from a water quality perspective. The biologically available fraction of nitrogen and phosphorus are critical in funding algal blooms. The ratio of nitrogen to phosphorus in the waterbody and comparison with the algae uptake of 16N:1P is an indication of the potential growth-limiting nutrient in the waterbody. If biologically available N and P are measured in

concentration units of mg/L the 16N:1P atomic reference value then corresponds to a mass ratio of 7.2N:1P. Therefore, if the N:P ratio is less than 7N:1P, nitrogen is potentially limiting because the more rapid removal of nitrogen would limit biotic growth; if the ratio is greater than 7N:1P, phosphorus then is limiting. Finally, different uptake and assimilation rates for different primary producers will affect the the response of the waterbody to nutrient limitation. Algal populations will compete for the available nutrient resources. Low N:P ratios encourage dominants by blue-green algae as they usually absent above a total N to total P ratio greater than 29N:1P. Some species of blue-green algae are capable of 'luxury' uptake of limiting nutrients, which are stored for later use. Diatoms, for example, are superior competitors for phosphorus, but inferior competitors for nitrogen. A further complication is that N₂-fixing blue-green algae can be phosphorus limited, while non N₂-fixing algae can be nitrogen-limited.

Therefore, overabundances of nitrogen and phosphorus in the aquatic environment pose a great threat to the biodiversity of surface water ecosystems (rivers, lakes, ocean etc) and also could cause serious environmental and ecological problems, as well as adverse health effects. Human activities have profoundly impacted upon the global biogeochemical cycles of these nutrients as their activities have greatly increased the inputs of reactive nitrogen and phosphorus to the biosphere (Carpenter, 2008). Of these, agriculture and urban activities are major non-point sources of nitrogen and phosphorus which are washed into aquatic ecosystems (Carpenter *et al.*, 1998; Bennet, *et al.*, 2001). Human activities and rapid developments without a strategic plan will eventually give disastrous effects and adverse impacts on the environment. Cultural or anthropogenic "eutrophication" is one of the major global environmental problems. Natural eutrophication is the process by which lakes gradually age and become more productive. It is usually a fairly slow and gradual process, occurring over a period of many centuries.

However, humans, through their various activities and developments, have greatly accelerated this degradation process in thousands of lakes, rivers and estuaries around the globe. This cultural eutrophication is caused by the

inflow of nutrient rich materials, particularly nitrates and phosphates. Nitrates are nitrogen compounds which are mostly produced by bacteria and phosphates are phosphorus compounds. Some nitrate is washed from agricultural land when nitrate is applied as fertilizer, but a lot of nitrate is produced by bacterial oxidation of other forms of nitrogen, including excreted ammonia compounds and proteins in human waste. Phosphates are oxides of phosphorus and are present in many detergents and similar products, so are included in used washing water from domestic and many industrial sources. Both nitrates and phosphates are easily absorbed by plants and needed for growth. However, the use of detergents and chemical fertilizers in daily human activities has greatly increased the amount of nitrates and phosphates that are washed into lakes and water bodies.

Excessive amounts of these nutrients in the water system act as fertilizer for plants and algae which will speed up their growth. Hence, the plants may begin to grow explosively and algal "blooms" or greatly increased density of microscopic plants takes place. As has been discussed by Griffith *et al.*, (1973), the phenomenon occurs due to certain cyanobacterial (blue green algal) species – for example, *Anabena*, *Gleotrichia*, *Aphanizomenon*, and *Nostoc* – which are capable of reproducing rapidly even in the absence of a fixed form of nitrogen through their ability to fix nitrogen from the gaseous atmospheric nitrogen dissolved in the water. Blooms of nitrogen-fixing algae utilize aqueous inorganic phosphorus and immobilize it for the moment.

In the process, the plants and algae consume greater amounts of dissolved oxygen in the water, robbing fish and other species of necessary oxygen. When the huge volumes of algae dies, the bacteria or decomposers require more dissolved oxygen to break down the dead algae. The bacteria then release more phosphate back into the water, which feed more algae. As oxygen levels deplete in the body of water, species such as fish and molluscs literally suffocate to death. Eventually, the lake or pond begins to fill in and becomes choked with plant growth. As the plants die and lakes being filled in with sediment produced from algal biomass, the lake bottom starts to rise. The waters grow shallower and finally the body of water is filled completely and disappears. Figure 2.3 illustrates how excess phosphorus

increases the nitrogen budget of natural waters and hastens the eutrophication process.

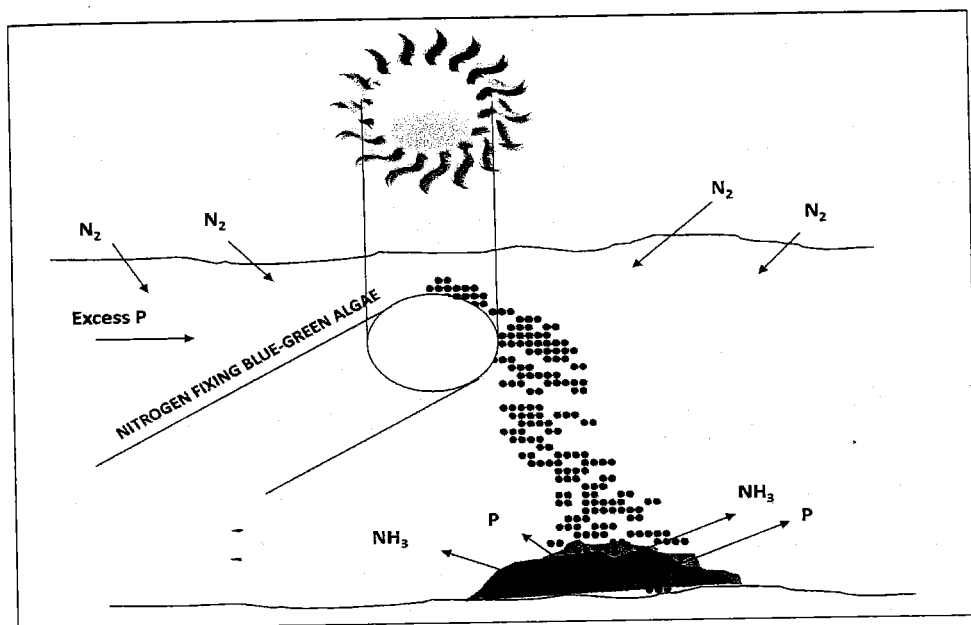


Figure 2.3 Nitrogen, phosphorus and eutrophication

(Adopted from Griffith *et al.* 1973)

2.2.1 Nitrogen and phosphorus in wastewater

Humans and their activities contribute excessive amounts of plant nutrients, primarily phosphorus, nitrogen and carbon, to water bodies in various ways. Untreated, or partially-treated, domestic sewage is another major source of these nutrients in aquatic ecosystems as domestic wastewater is typically rich in nitrogen and phosphorus compounds. From a number of different pieces of research conducted by the UK Environment Agency which provides estimation on the percentage contribution of phosphates from non-agricultural sources to surface water bodies, most indicate that outputs from households (i.e. via sewage treatment works) are much more significant than previously thought. The UK Environment Agency also reported that point sources, predominantly sewage treatment works, comprise about 70% of the phosphorus entering rivers in England and Wales (DEFRA, 2007).

In fresh wastewater, nitrogen is primarily present as proteinaceous matter and urea. This organic nitrogen is rapidly decomposed by bacterial action in the case of proteins or by hydrolysis in the case of urea to ammonia, the

concentration of which in wastewater is indicative to some extent of its age (Gray, 2004).

Nitrogen is present in a variety of forms because of the various oxidation states it can represent. Nitrogen can readily change from one state to another depending on the physical and biochemical reactions present. The total nitrogen in typical municipal wastewaters ranges from about 15 to over 50 mg/L, of which approximately 60% is in the ammonia form, the remainder being in the organic form. Ammonia can be present as molecular ammonia (NH_3) or as ammonium ions (NH_4^+). The equilibrium between these two forms in water is strongly dependent on pH and temperature. At pH 7 essentially only ammonium ions are present and at pH 12 only dissolved ammonia gas (Crites *et al.*, 2006). Organic nitrogen is normally measured separately from ammonia, although occasionally they are expressed together as the total Kjeldhal nitrogen (TKN). The normal concentration range of nitrogen in settled wastewater in the UK is 41–53 mg N/L as ammonia, 16–23 mg N/L as organic nitrogen and 57–76 mg N/L as TKN. The oxidised forms of nitrogen, nitrite and nitrate, are normally absent from fresh wastewater, being products of the biological oxidation processes within the treatment plant. Therefore, as total nitrogen includes all chemical forms of nitrogen, TKN can be assumed to be equivalent to the total nitrogen in raw and settled wastewater (Gray, 2004).

Even though phosphorus has no known health-related significance, it is the wastewater constituent that is most associated with eutrophication of surface waters such as lakes and rivers. Phosphorus is often present in wastewaters almost solely in the form of orthophosphate (PO_4^{3-} , HPO_4^{2-} , H_2PO_4^- and H_3PO_4), polyphosphate and organic phosphates (Reed, *et al.*, 1988; Gray, 2004). Horan (2003) for instance reported that phosphorus concentration in wastewater was approximately 10–30 mg/L; however it varies from one wastewater treatment works to another. Organic phosphate is a minor constituent of wastewater and like the polyphosphates requires further breakdown to the assimilable orthophosphate form, which is normally fairly slow. About 25% of the total phosphorus in settled wastewater is present as orthophosphates, such as PO_4^{3-} , HPO_4^{2-} , H_2PO_4^- , H_3PO_4 , which are available

for immediate biological metabolism. Therefore the inorganic phosphate concentration is important rather than the total phosphorus concentration in terms of utilisation, both in the treatment plant and subsequently in receiving waters. After secondary treatment, approximately 80% of the total phosphorus in a final effluent is in the orthophosphate forms. Typical phosphorus concentrations in wastewater range from 5–20 mg P/L as total phosphorus, of which 1–5 mg/L is the organic fraction and the rest is inorganic (Gray, 2004).

Figure 2.4 shows a typical distribution of phosphorus compounds in municipal wastewater before and after a biological treatment. Polyphosphates are hydrolysed to orthophosphates and the major parts of dissolved organic phosphates also degraded to orthophosphates by the biological degradation of organic matter. Suspended phosphates are normally considered to be organic phosphates, but they may also include chemically precipitated orthophosphates and biologically bound polyphosphates (Arvin and Henze, 1997). Polyphosphates and organic phosphorus are converted to orthophosphate during aeration in an aerated system (IWEM, 1994; Hammer and Hammer Jr., 2005; Scholz, 2006).

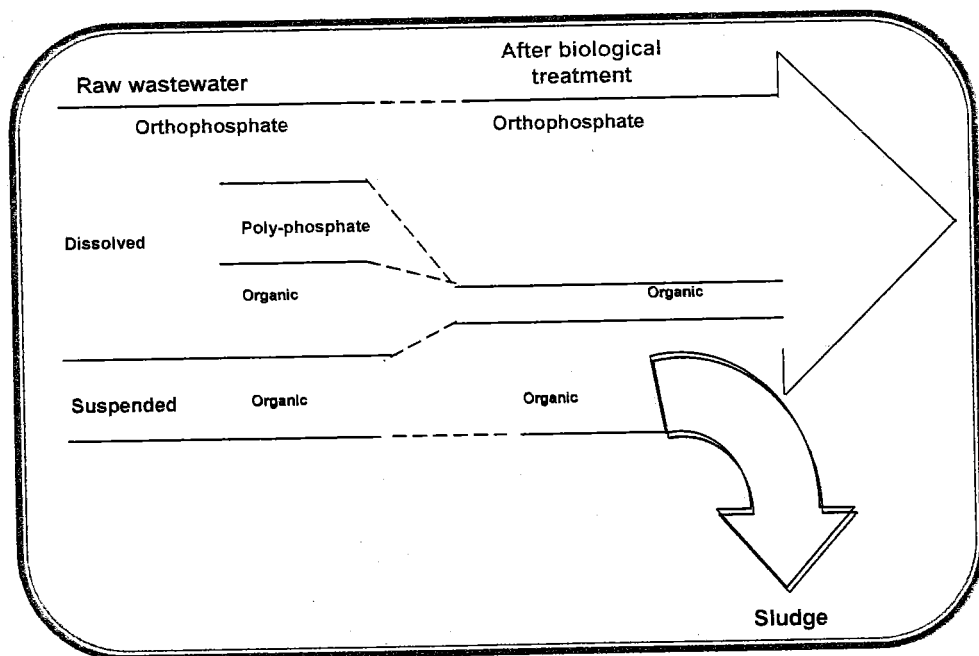


Figure 2.4 Phosphorus fractions in wastewater

(Source: Arvin and Henze, 1997)

2.2.2 Phosphorus removal technologies for wastewater

There are a number of technologies, both established and under development, which can be used to remove phosphorus from wastewater and can potentially be used within a sustainable strategy in response to the issue of eutrophication and the need to reduce the levels of phosphorus entering surface water. Due to global environmental problems stricter nutrients effluent consent limits are now applicable in almost all countries over the world. The effluent limits of nutrients in several countries as shown in Table 2.2.

Table 2.2 Regulation on Nutrient Removal *

Country	Upperlimits		
	Threshold	Nitrogen	Phosphorus
USA	No national regulation	-	1 mg/l P _{total} ¹
Canada	No national regulation	-	1 mg/l P _{total} ¹
Europe	>10, 000 PE in sensitive areas	15 mg/l N _{total} ³	1 mg/l P _{total} ²
Germany	> 10, 000 PE	18 mg/l N _{anorg} ⁴	1 mg/l P _{total} ³
	> 100, 000 PE	18 mg/l N _{anorg} ⁴	1 mg/l P _{total} ³

¹ largest municipal discharge in the Great Lake area ² daily average ³ 2h average sample

*(Adopted from Rolf *et al.*, 1998)

Amongst the developed phosphorus removal technologies, chemical precipitation and biological phosphorus (nitrogen) removal are commonly known processes and widely used despite their relatively high costs. Both methods involve turning the phosphate into particulate form, hence a suspended solid (SS) which can then be removed usually as sludge. Phosphorus removal from sewage works effluent can be achieved by one of the above mentioned methods or a combination of both. A comprehensive review of technologies that remove and recover phosphorus from wastewater and an evaluation of their applicability to phosphorus sustainability has been carried out by Morse *et al.* (1998). They signified that those two previous mentioned treatment methods were amongst the firmly established methods for phosphorus removal in many countries around the world which have been

used since 1950's. The general development and status of all technologies identified is summarised in Table 2.3.

Table 2.3 Phosphorus Removal Technologies

Phosphorus removal/ recovery technology	Development status	Development timescale	Originators/ reference	Country of origin
Chemical precipitation	Commercial	~ 1950 to date	Many	Global
Biological P (and N) removal	Commercial	~ 1960 to date	Many	Global
Phostrip	Commercial	~ 1965	Levin and Shapiro, 1965	USA
Modified Bardenpho	Commercial	~ 1974 to date	Barnard, 1990	South Africa
Phoredux	Commercial	~ 1976 to date	Barnard, 1990	South Africa
A/O	Commercial	~ 1980 to date	Randall et al., 1990	USA
University of Cape Town (UCT)	Commercial	~ 1983 to date	Siebritz et al., 1983	South Africa
Modified UCT	Commercial	~ 1990	Farnell et al., 1990	South Africa
Rotanox	Commercial	~ 1982	Rachwell et al., 1984	UK
Biodenipho	Commercial	~ 1980	Bundgaard and Pedersen, 1991	USA
Crystallisation				
DIIV Crystalactor*	Full-scale	~ 1979 to date	DIIV Consulting Engineers, 1991	Netherlands
CSIR	Laboratory	~ 1992 to date	Momberg and Oellermann, 1992	South Africa
Kurita	Laboratory	~ 1984 to date	Joko, 1984	Japan
Phosnix	Laboratory	~ 1994 to date	Unitika Ltd., 1994	Japan
Sydney Water Board	Laboratory	~ 1993 to date	Angel et al., 1989	Australia
OFMSW	Laboratory	~ 1994 to date	Cecchi et al., 1994	Italy, Spain
Novel nutrient removal				
HYPRO concept	Full-scale	~ 1991 to date	Henze and Harremoës, 1992	Scandinavia
AFBP	Pilot	~ 1994 to date	Shimizu et al., 1994	Japan
Maezawa FBPS	Pilot	~ 1993 to date	Suzuki et al., 1993	Japan
Other wastewater				
RIM-NUT (ion exchange)	Demonstration	~ 1986 to date	Liberti et al., 1986	Italy
Smit-Nymegen (magnetic)	Pilot/FS	~ 1991 to date	Van Velsen et al., 1991	Netherlands
Sirofloc (magnetic)	Demonstration	~ 1979 to date	Dixon, 1991	Australia
Phosphorus adsorbents	Laboratory	~ 1970 to date	Many	Global
Tertiary filtration	Commercial	~ 1900 to date	Many	Global
Slow sand filters	Commercial			
Shallow bed filters	Commercial			
Rapid gravity filters	Commercial			
Rapid deep-bed filters	Commercial			
Moving bed filters	Commercial			
Pressure filters	Commercial			

(Modified from Morse *et al.*, 1998)

2.2.3 Chemical and biological phosphorus removal

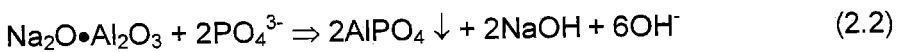
Chemical wastewater treatment for phosphorus removal usually involves changes in the physical properties and chemical structures of the wastewater content due to reactions between the wastewater and the chemical added. Typically in a wastewater treatment system this process involves the addition of a metal salt to enhance the adsorption of the soluble species onto colloids or adsorbent surfaces which consequently precipitate as sediment after chemical reactions occur between the chemical added and the phosphorus

from the wastewater (relying on the low solubility of the metal phosphates). Thus, the phosphate impurity is removed from the wastewater by a settlement or filtration step.

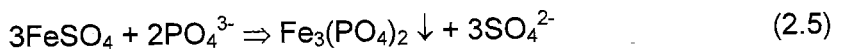
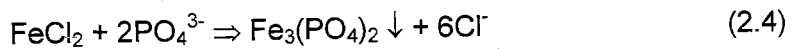
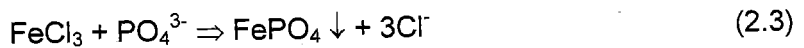
The commonly used chemicals or coagulants to remove phosphorus from wastewater are Al^{3+} , ferric (Fe(III)) or ferrous (Fe(II)) iron, and calcium (Ca(II)) as has been widely discussed in the literature (Bowker and Stensel, 1990; Arvin and Henze, 1997; Scholz, 2006). Lime ($\text{Ca}(\text{OH})_2$) is used as a source of calcium ions; alum ($\text{Al}_2(\text{SO}_4)_3$) and sodium aluminate (NaAlO_2) are sources of aluminium ions; ferric chloride (FeCl_3), ferric sulfate ($\text{Fe}_2(\text{SO}_4)_3$) and ferrous sulphate (FeSO_4) are sources of iron ions. Consequently, different insoluble phosphates will precipitate according to the chemical added. The reaction of alum (hydrated aluminium sulphate) with phosphate can be described by the following equations (Bowker and Stensel, 1990):



Sodium aluminate is sometimes used for phosphorus removal and the reaction of phosphate precipitate can be expressed as (Bowker and Stensel, 1990):



The reactions between ferric chloride, ferrous chloride or ferrous sulphate, and phosphate can be expressed as the following stoichiometry (equations 2.3, 2.4 and 2.5) respectively (Bowker and Stensel, 1990):



A polymer may be used in conjunction with a coagulant (e.g., alum or ferric iron). They are added simultaneously with or subsequent to the coagulant. The function of polymer coagulant aids is to allow small suspended particles, which may not settle, or may block a filter, to come together and combine into large ones, overcoming charges that prevent them from doing so. They cost quite a lot, and require care and expertise choosing the right polymer and getting the dose just right. The benefits may include reduction of dosage of primary coagulant or reduction in the rate of head-loss increase in filtration, and reduction in the rate of sludge production. At the same time, the use of polymer may cause a higher of head-loss increase, i.e., the filter runs are shorter, and there is potential for mud ball formation, particularly if used in excess (Hendricks, 2006).

Biological phosphorus removal relies on designing suspended growth activated sludge systems to remove soluble phosphorus from wastewater. The typical process configurations for biological phosphorus removal include the anoxic-oxic (A-O) process, the Phostrip[®] process, and the modified Bardenpho[®] process (Phredox).

According to Bowker and Stensel (1990), the generally accepted theory for biological phosphorus removal is that anaerobic-aerobic contacting results in competitive substrate utilization, and selection of phosphorus-storing microorganisms. They stated that in the anaerobic zone acetate and other fermentation products are produced from fermentation reactions by facultative bacteria using soluble portion from influent BOD. The fermentation products are preferred and readily assimilated and stored by the microorganisms capable of excessive biological phosphorus removal. During the anaerobic period the assimilation and storage is aided by the energy made from the hydrolysis process of the stored polyphosphates. Later the stored polyphosphate provides energy for active transport of substrate as well as formation of acetoacetate, which is converted to polyhydroxybutyrate (PHB). Furthermore, the stored substrate products are depleted, and soluble phosphorus is taken up in excessive amounts and stored as polyphosphates during aerobic phase. Figure 2.5 shows the proposed biological phosphorus removal mechanisms in a wastewater treatment system.

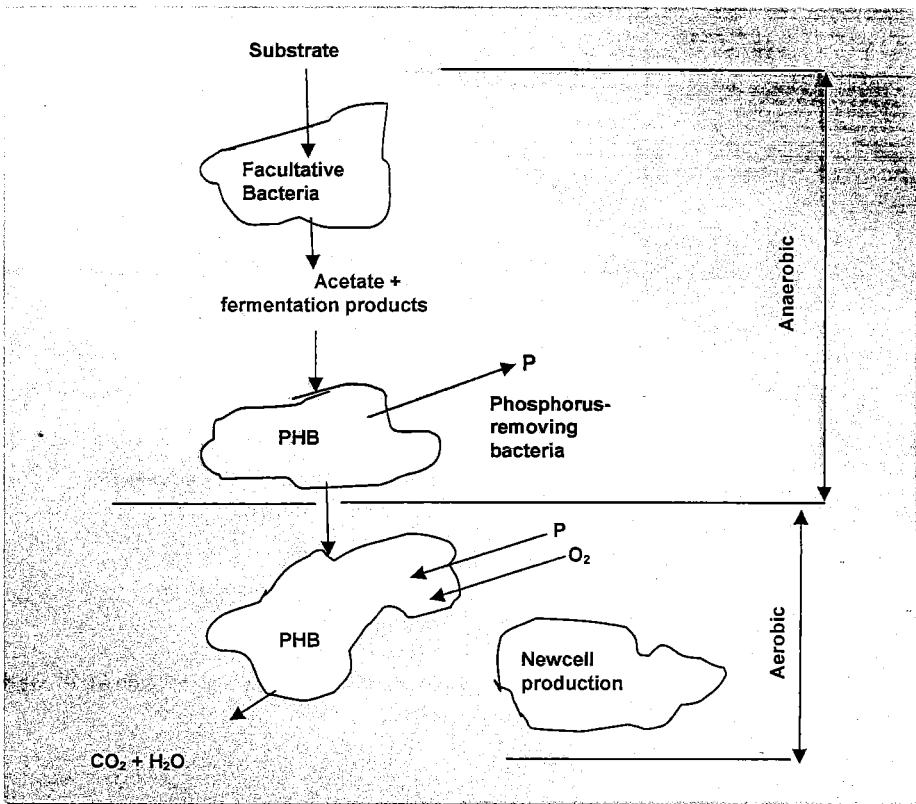


Figure 2.5 Schematic of biological phosphorus removal mechanism

(Source: Bowker and Stensel, 1990)

The A-O process is the main biological phosphorus removal system. Bacteria use phosphate as an energy source. Some bacteria are able to store excess phosphate; they do so only in aerobic conditions. Under anaerobic conditions, these bacteria use their stored phosphate as an energy source to fuel the uptake of carbon substrates. When the activated sludge added into an anaerobic tank after settling, where anaerobic fermentation makes some simple carbon substrate, and as a result the bacteria release all their phosphate into solution. Then, when they are moved into the aerobic zone/tank of the plant, they are short of phosphate, and take up a lot of it very fast. Then, when they have had time to take up lots of excess phosphorus, some of them as surplus activated sludge will be removed, which is how the phosphorus is taken out of the wastewater. Biological phosphate removal is largely independent over the range of 5–20°C. The system depends on a BOD:P ratio >20 in order to achieved a final effluent concentration less than 1 mg P/L, and if the ratio falls below this critical limit

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