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Phosphorus recovery through adsorption using iron modified cellulose

Walquiria Silva Simplicio

Supervisor: Prof. Xinmin Zhan

Co-Supervisor: Dr. Eoghan Clifford

A thesis submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the College of Engineering and Informatics

Submission date: Apr 2020
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Declarations

This thesis or any part thereof, has not been, or is not currently being submitted for any degree at any other university.

___________________
Walquiria Silva Simplicio

The work reported herein is as a result of my own investigations, except where acknowledged and referenced.

___________________
Walquiria Silva Simplicio
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Abstract

Phosphorus is an important non-renewable resource, widely used as fertiliser to maintain high crop yields. As the global phosphate reserves will be exhausted in 40–150 years, there is a need to explore alternatives to phosphate ores. When phosphorus reaches the waterbodies it can result in eutrophication, causing loss of water quality and biodiversity. This study investigated the feasibility of recovering phosphorus from agriculture runoff by adsorption with an adsorbent developed from agricultural by-products.

Adsorbents were prepared from cellulose extracted from grass silage and its adsorption capacity was significantly improved using the metal loading method. The resultant adsorbent was characterised systematically and cellulose was shown to be the backbone of the adsorbent. Brunauer – Emmet – Teller analysis showed an increase in the surface area between grass and iron modified cellulose from 18.3 to 41.8 m²/g, which is favourable to the adsorption process.

Adsorption capacity of iron modified cellulose was further tested in batch and column experiments. The results indicated that iron-modified cellulose presented a maximum adsorption capacity of up to 20.1 mg P/g adsorbent. The isotherm data were best fitted by the Langmuir model, while kinetic data were satisfactorily described by the pseudo-first-order model. Thermodynamic results revealed that the adsorption was feasible, spontaneous, and endothermic. The solution pH did not affect PO₄³⁻ uptake in a wide pH the range of 3 – 10. Iron-modified cellulose demonstrated a high affinity for phosphate, which could be observed by a minor decrease in PO₄³⁻ adsorption when Cl⁻, NO₃⁻, CO₃²⁻ and SO₄²⁻ were tested as competitors for adsorption sites. About 50% desorption efficiency was achieved with a 2.0 M NaOH solution. The column results showed that the highest dynamic adsorption capacity of iron-modified cellulose was 14.6 mg P/g adsorbent. Yoon-Nelson and bed depth service time (BDST) models were most suitable for the description of the column adsorption behaviours.
Cost related investigations revealed that iron modified cellulose was produced cheaper than other lab-scale adsorbents made from agricultural waste by-products. However, it is still more expensive than commercially available adsorbents. The iron modified adsorbent can achieve the additional environmental benefits of the use of renewable materials and waste valorisation. Tests of the bioavailability of phosphorus in iron modified cellulose showed that up to 46.7% of adsorbed phosphorus would be bioavailable to crops. The environmental impacts of iron modified cellulose production were assessed with a life cycle assessment perspective. Electricity input was found to be the largest input to the environmental impacts, and among the chemicals used, ferric chloride and sodium chlorite were found to be the most harmful to the environment.

Iron-modified cellulose could be used in the land as a barrier to prevent phosphorus from reaching adjacent water bodies, and after could be applied to land, as a slow-release fertiliser. This multipurpose characteristic of the adsorbent is believed to be a major contribution of this research to the field of phosphorus recovery.

**Keywords:** Adsorption kinetics; Agricultural waste by-products; Grass silage; Iron modified cellulose; Metal loading; Phosphorus recovery.
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List of Nomenclature

A: Bed cross-sectional area, cm\(^2\)

C\(_0\): Initial concentration of phosphorus, mg/L

C\(_{ad}\): Difference between the initial phosphorus concentration and the effluent phosphorus concentration, mg/L

C\(_b\): Phosphorus concentration at breakthrough time, mg/L

C\(_e\): Equilibrium concentration of phosphorus, mg/L

C\(_t\): Phosphorus concentration at a given time t\(_i\), mg/L

C\(_t\): Concentration of phosphorus at time t, mg/L

EBCT: Empty bed contact time, min

F: Linear velocity, cm/min

k\(_1\): Rate constant of pseudo-first-order adsorption, 1/min

k\(_2\): Rate constant of pseudo-second-order adsorption, g/mg.min

K: Permeability coefficient, m/day

k\(_{AB}\): Adams-Bohart kinetic constant, L/mg.min

K\(_b\): BDST rate constant, L/mg.h

K\(_F\): Freundlich constant, (L/g)

K\(_L\): Langmuir constant related to the energy of adsorption, L/mg

k\(_{TH}\): Thomas rate constant, mL/min.mg

k\(_YN\): Yoon-Nelson rate velocity constant, l/min

MTZ: Length of the mass transfer zone, cm

M: Mass of adsorbent packed in the column, g

m: Mass of dry adsorbent, g
\( m_r \): Mass of empty flask, g

\( m_{f+w} \): Mass of filled volumetric flask + water, g

\( m_{s+f} \): Mass of iron modified cellulose + volumetric flask, g

\( m_{s+f+w} \): Mass of iron modified cellulose + volumetric flask + water, g

\( N_0 \): Sorption capacity of the adsorbent per unit volume of the bed, mg/L

\( Q \): Volumetric flow rate, mL/min

\( q_e \): Equilibrium adsorption capacity of the adsorbent, mg/g

\( Q_{\text{max}} \): Maximum theoretical adsorption capacity, mg/g

\( q_t \): Sorption capacity at time \( t \), mg/g

\( q_{\text{total}} \): Total amount of phosphorus adsorbed onto the column, mg

\( t_b \): Breakthrough time, min

\( t_s \): Exhaustion time, min

\( t_{\text{total}} \): Total time for the column to reach saturation, min

\( V \): Volume of solution, mL

\( V_b \): Volume treated at the breakthrough time, mL

\( v_f \): Flask volume, \( \text{cm}^3 \)

\( V_s \): Volume treated at the exhaustion time, mL

\( W \): Weight of wet adsorbent, g

\( Z_0 \): Critical bed depth, cm

\( Z \): Bed height, cm
**Greek Symbols**

ΔG: Change in Gibbs free energy, kJ/mol

ΔH: Change in enthalpy, kJ/mol

ΔS: Change in entropy, J/mol.K

ΔH: Pressure head change, m

η: Porosity, %

ρₘ: Bulk density, g/cm³

ρₚ: Particle density, g/cm³

ρₗ: Water density, g/cm³

τ: Time required for 50% breakthrough, min
List of Abbreviations

AC: Activated carbon
ATP: Adenosine triphosphate
AWBs: Agriculture waste by-products
AA: Aquatic acidification
AE: Aquatic ecotoxicity
AEut: Aquatic eutrophication
BDST: Bed depth service time
BET: Brunauer, Emmett, and Teller
CMC: Carboxymethyl cellulose
DNA: Deoxyribonucleic acid
DAFM: Department of Agriculture, Food and the Marine
EPC: Effluent phosphorus concentration
EBCT: Empty bed contact time
EPA: Environmental protection agency
EQS: Environmental quality standards
FTIR: Fourier transform infrared spectroscopy
GW: Global warming
GS: Grass silage
HAP: Hydroxyapatite
IV: Intravenous
LCA: Life cycle assessment
MAP: Magnesium ammonium phosphate
MTZ: Mass transfer zone
NAP: National action programme
NFS: National farm survey
NOM: Natural organic matter
NE: Non-renewable energy
OL: Ozone layer depletion potential
PRS: Phosphorus ranking scheme
PHB: Polyhydroxy butyrate
PAOs: Polyphosphate accumulating organisms
RE: Removal efficiency
RI: Respiratory organics
RO: Reverse osmosis
RNA: Ribonucleic acid
SEM – EDX: Scanning Electron Microscopy with X-ray Energy Dispersive Spectrometer
TAN/N: Terrestrial acidification/nutrification
TE: Terrestrial ecotoxicity
TEM: Transmission electron microscope
USEPA United States environmental protection agency
WWTP Wastewater treatment plant
WFD: Water Framework Directive
XRD: Powder X-ray diffraction
Chapter 1 Introduction
1.1 Background

Phosphorus (P) is one of the sixteen elements that are essential for plant growth (Nguyen et al., 2012). It is also a key component of deoxyribonucleic acid (DNA), ribonucleic acid (RNA), adenosine triphosphate (ATP), phospholipids, teeth and bones in animal bodies (Schaum, 2018). Additionally, P is a major material for many important industries, such as fertilisers, detergents, paints, corrosion inhibitors, beverages, and pharmaceuticals (Nguyen et al., 2014b). Though P plays an important role in daily life, it is a non-renewable resource and cannot be artificially synthesised (Karabegovic et al., 2013). Due to the overexploitation for different purposes, the global P reserve is at the risk of being exhausted in 40 – 150 years (Ngatia et al., 2019; de Boer et al., 2019; Ohtake and Tsuneda, 2019). Thus, the search for alternative sources of P has become a matter of urgency (Malila et al., 2019; Schaum, 2018; Hanief and Laursen, 2019).

In another perspective, P level above 0.035 mg/L is likely to lead to eutrophication in Irish rivers, as established by the Water Framework Directive (WFD). Due to the extensive consumption of oxygen for the dead algae decay, the aquatic medium may become deficient of dissolved oxygen, thus threatening the life of aquatic creatures (Jyothi et al., 2012). As a result, loss of water quality, biodiversity, and economic and recreational value may occur (Okochi and McMartin, 2012). To protect the surface water from eutrophication, average concentrations of less than 0.025 mg/l P and less than 0.035 mg/l P have been established in Ireland as legally binding environmental quality standards (EQS) to support the achievement of high and functional ecological status as required by the WFD, respectively. Therefore, appropriate treatment technologies are required to meet stringent regulations (Kalmykova and Fedje, 2013).

Various techniques are available to remove and to recover P from wastewater such as chemical, biological and physical treatment methods. Among the various techniques, adsorption presents significant advantages for being highly effective for the treatment of diluted wastewater, and being easy to operate, and for its performance in the presence of foreign anions and in a wide pH range (Cui et al., 2016; Wang et al., 2016).
Agriculture waste by-products (AWBs) have characteristics that make them attractive to be used to manufacture phosphate adsorbents, such as abundance, low price and non-toxicity. The AWBs’ chemical composition, comprising mainly cellulose and hemicellulose, is appropriate for manufacturing phosphate adsorbents, due to the hydroxyl groups in their structures (Nguyen et al., 2014b, Xu et al., 2010). Another advantage in using AWBs is the reduction in costs related to P recovery, the main challenge in finding competitive techniques to extract phosphorus from phosphate rocks nowadays (Cornel and Schaum, 2009; Lanning, 2008, Tyagi and Lo, 2013).

Although AWBs present as an environmentally friendly option for P recovery, suitable modifications are needed to improve their adsorption capacities. The lack of efficiency in phosphate removal by AWBs is due to a large amount of negatively charged functional groups in its structure (-OH, -COOH), as well as the absence of positively charged ones in its structure (Nguyen et al., 2014b). According to Anirudhan and Senan (2011), modification of AWBs can strengthen lignocellulosic materials, and mitigate the release of organic matter into aqueous solutions.

Metal loading has been used to modify different adsorbents to improve their surface area and adsorption efficiency. In metal loading, AWBs are saturated with metal salts, so the cations in the salts are attained to the AWB surface. It is recommended that the salts used have highly positive charges, so as to effectively sequester phosphate anions during adsorption (Cheng et al., 2013; Liu et al., 2013; Nguyen et al., 2014b).

**1.2 Research Objectives**

The overall aim of this study was to develop a viable process for removing P from wastewater through adsorption onto iron modified cellulose. The specific objectives of this study are:

- Develop P adsorbents from cellulose extracted from grass silage by the metal loading method;
- Investigate the P removal using the selected adsorbent (iron modified cellulose) in batch and column experiments;
• Assess the viability of using the adsorbed material as a fertiliser;
• Conduct an economic and a life cycle assessment of iron modified cellulose development.

1.3 Contribution to knowledge

The usage of cellulose, an adsorbent developed from grass silage, as a P adsorbent will result in double environmental benefits. It does not only give a chance to develop new ways for using grass silage in a greenway but also provide an efficient, beneficial and sustainable technology for P removal. One of the main challenges related to finding a solution for P recovery is cost competitiveness. By the usage of cheap and widely available materials for the adsorbent development, as well as the adoption of simple processes in the modification of adsorbents, this research will make a significant contribution to the process of finding a cost-competitive solution for P recovery from wastewater and for management of agricultural wastes.

1.4 Procedure

The research road map illustrated in Figure 1.1 consists of laboratory experiments and desktop studies. The procedures are summarised here but will be detailed in individual chapters.
### 1.4.1 Synthesis of iron modified cellulose

Cellulose was extracted from grass silage, following a procedure adapted from Morán et al. (2008) and Johar et al. (2012). The grass silage was collected from a farm located in Avoca (County Wicklow, Ireland). Grass silage in different stages of cellulose extraction, and iron modified cellulose before and after adsorption were analysed using a number of techniques: the Fourier Transform Infrared spectra (FTIR), field emission Scan Electron Microscopy (SEM), and Energy dispersive X-ray spectrometer (EDX).

![Figure 1.1 Road map of this study](image-url)
1.4.2 Batch adsorption tests

The P removal ability of iron modified cellulose was evaluated in batch tests. For investigation of the impacts of pH, adsorbent dose, and interference of foreign anions tests, 1 g of iron modified cellulose was added to a 50 ml plastic tube filled with 20 ml of a 10 mg P/L KH$_2$PO$_4$ synthetic solution. For the reaction kinetics test, 250 ml glass flasks filled with 200 ml of the 10mg P/L KH$_2$PO$_4$ solution were used. Samples were taken at intervals for the measurement of P concentrations.

1.4.3 Column adsorption tests

The column adsorption tests were performed in plastic columns with a dimension of 55 cm height and 0.80 cm inner diameter. The column was packed with different amounts of iron modified cellulose to achieve the desired bed height, and a 10 mg P/L KH$_2$PO$_4$ synthetic solution was input continuously. Effluent samples were taken regularly for P measurement.

1.4.4 Bioavailability tests

The bioavailability tests were assessed through the water extraction (Luscombe et al., 1979), iron-oxide impregnated paper (Menon et al., 1989), and Olsen P (Olsen and Watanabe, 1957) tests, respectively.

1.4.5 Economic evaluation and life cycle analysis

For the economic evaluation and life cycle analysis, the costs related to the adsorbent development, as well as all the materials and energy inputs in its synthesis, were assembled. The environmental impacts associated with each step of adsorbent development were evaluated using the software Simapro 7.3 based on the Ecoinvent database to obtain the background data. The software Excel 2013 was used to organise the data and to compare to others available in the literature.
1.5 Structure of dissertation

This thesis consists of seven Chapters. The main contents of each chapter are presented below.

Chapter 1 introduces the context of this study and defines the research questions. The research objectives, main tasks and scope, and significance are highlighted.

Chapter 2 provides a detailed research background for this study. A majority part of this chapter is devoted to evaluating the current technologies for P removal and recovery. The applicability of AWBs based adsorbents for P removal and recovery is discussed. The effects of process parameters are investigated in conjunction with mechanisms and applications. Chapter 2 concludes with key findings from the literature review and determines the proper research direction.

Chapter 3 focuses on the development of the P adsorbents from cellulose extracted from grass silage and characterisation of the adsorbents.

Chapter 4 refers to the performance of iron modified cellulose in adsorption and desorption with batch experiments. The adsorption factors, the maximum adsorption capacity of iron modified cellulose for phosphate, the adsorption isotherm, kinetic models, and the thermodynamic study were carried out.

Chapter 5 investigates the performance of iron modified cellulose with column experiments, and modelling of the column study. Considerations about the phosphorus bioavailability and the economic evaluation of iron modified cellulose were carried out.

Chapter 6 presents the life cycle assessment of iron modified cellulose production in comparison with chemical fertiliser and with other P adsorbents.

Chapter 7 summarises the major findings of this research work. Additionally, the unique contributions of this study to the field of phosphorus removal are highlighted. Chapter 7 ends with recommendations for future research.
Chapter 2 Literature Review
2.1 Overview

This chapter begins with an investigation into the nature of agriculture runoff and phosphorus-related legislation. It reviews the merits and demerits of a wide variety of technologies currently available for P removal and highlights the advantages of adsorption over other methods.

It also discusses the P recovery concerning drivers, technologies and barriers. As the central part of this literature review, it evaluates the potential of using agricultural by-products based adsorbents for P removal and recovery. This section provides deep insights into modification methods, influential factors, mechanisms and applications.

Additionally, this chapter also justifies the selection of the cellulose for the development of P adsorbents in this study.

2.2 Introduction

Phosphorus is an essential element for all forms of life. It is a part of many organic compounds, such as the universal energy currency ATP, the DNA, cell membranes, and bones (Schaum, 2018). Phosphorus deficiency can cause blue-green colouration of leaves, stunting and root weakness in flora, and brittle bones and reduced growth rates of fauna (Bowler et al., 2010). In pristine environments, P enters freshwater systems through the natural weathering and erosion of bedrock and catchment soils, and as inputs of organic matter, such as leaf litter and animal faeces, from the terrestrial environment.

The agriculture sector is nowadays heavily dependent on the supply of reactive P to maintain high crop yields and to promote plant growth. However, while human intervention has increased the availability of P for general societal well-being, this increased availability has provoked several cascading and unintended adverse consequences for a wide range of ecosystem services valued by society (Withers et al., 2014; Rowe et al., 2016).
The primary adverse effect happens when the excess P, as well as other main plant nutrients, reaches surface waters, leading to the extensive growth of phytoplankton, macroalgae and higher plants. In some cases, along with other factors such as reduced flow rates resulting from dams or weirs and changes in the balance of food webs, this can adversely affect invertebrate and fish populations, and even result in the production of toxic substances from algal blooms (Schaum, 2018).

The overall goal of this chapter is to review the main methods used for P removal and recovery from liquid media, in particular, agricultural runoff.

2.3 Agricultural runoff characteristics and phosphorus relevant regulations

Understanding agricultural runoff characteristics is essential for designing and operating the treatment facilities. In order to avoid eutrophication in water bodies, many countries have specific regulations that define the P concentration in effluents, according to the classes of the receiving waterbodies.

2.3.1 Agricultural runoff characteristics

According to the Irish Environmental Protection Agency (EPA), the land area of Ireland is 6.9 million hectares and approximately 4.4 million hectares (67.35%) of the national land cover is agricultural, making it the largest user of land in Ireland (EPA, 2017). The soils of Ireland vary in their physical, chemical and biological characteristics not only at national and regional scales but also within farms and fields. While soils can be managed there are limits to what can be achieved and controlled by management practices alone (EPA, 2016).

A survey was applied by the Teagasc on Irish farms (National Farm Survey – NFS) from 2005 to 2015 about the quantities of macro-nutrients, nitrogen (N), P and potassium (K) and lime applied both on grassland and arable land. Results show that for all three nutrients the application rates on total grassland area decreased gradually between 2005 and 2015. However, the application rates increased in the final years.
For P, for example, the application rate was 9 kg/ha at the beginning of the period, before declining to between 4 - 6 kg/ha from 2008 to 2012. By 2015 the application rate was increased to 8 kg/ha, 11% lower than in 2005. The years of the lowest grassland fertiliser use coincided with the period of the highest fertiliser prices, while higher than average period application rates in 2013 – 2014 were associated with the aftermath of a national fodder shortage (Teagasc, 2018).

In natural water bodies, P may exist in different forms. However, only orthophosphate can accelerate the growth of algae, inducing eutrophication (Bezbaruah et al., 2016). Depending on pH values of aquatic medium, orthophosphate may exist in various species. In strongly alkaline conditions, PO$_4^{3-}$ is the dominant form, while in weakly alkaline conditions, HPO$_4^{2-}$ is dominant. In weakly acidic conditions, H$_2$PO$_4^-$ prevails, whereas H$_3$PO$_4$ is most common in strongly acidic conditions (Figure 2.1) (Pokhrel et al., 2019).

![Figure 2.1 Distribution of phosphate species with pH (Kim et al., 2007)](image)

Phosphorus losses from agricultural systems occur in response to either P accumulation in soils or freshly added applications of inorganic fertiliser or organic P, such as animal manure (Hart et al., 2004). Thus, the presence of P in an agricultural system is the obvious prerequisite for the occurrence of P loss. However, the nature and rate of P transfer and the subsequent concentrations of P in runoff are governed by
chemical (release of P ions into solution), biological (bioaccumulation of P), physical (detachment and entrainment of particles containing P) and hydrological (surface and interflow runoff of P in solution) factors (Dougherty et al., 2004).

Lemunyon and Gilbert (1993) have developed an Index system to identify agricultural sites that are at a high risk of causing P inducing eutrophication of nearby surface waters. Three factors are considered to interfere on P transportation to the edge of a site, being soil erosion, irrigation erosion and runoff class; five factors are used to assess the source availability of P on-site, being soil test P, P fertiliser application rate and method, and organic P application rate and method. To each factor, a weight, assigned using professional judgement, is given, resulting in a final score (Magette et al., 2007). Using this Index system as a guide, Carton and Magette (1999) developed a P ranking scheme (PRS) specifically for Irish grassland systems. The PRS was designed to classify areas within a catchment based on their relative propensity for contributing to P runoff to surface waters. The factors considered for PRS are given in Table 2.1.

Table 2.1 Phosphorus ranking scheme (PRS) for Ireland\(^1\) (Carton and Magette, 1999)

<table>
<thead>
<tr>
<th>Catchment or Field Factor</th>
<th>Weighting Factor</th>
<th>Phosphorus Loss and/or Transport Risk (Value)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Low (1)</td>
</tr>
<tr>
<td>P usage in catchment</td>
<td>0.5</td>
<td>0 - 5 kg/ha</td>
</tr>
<tr>
<td>Condition of receiving waters</td>
<td>0.5</td>
<td>Saline waters, non-impounded waters, free flowing rivers and streams without nutrient problems</td>
</tr>
<tr>
<td>Ratio of land to waters</td>
<td>0.75</td>
<td>Ratio &lt; 36:1</td>
</tr>
<tr>
<td>Farmyard conditions</td>
<td>0.8 (0 if no animals)</td>
<td>Supplement information in Table 2.2</td>
</tr>
<tr>
<td>P usage rate on site</td>
<td>1.0</td>
<td>0-5 kgP/ha</td>
</tr>
<tr>
<td>P application time</td>
<td>0.9</td>
<td>Spring or just prior to crop needs</td>
</tr>
<tr>
<td>Soil test P (based on Morgan’s test)</td>
<td>0.8</td>
<td>0-6 mgP/L</td>
</tr>
</tbody>
</table>
For farmyards, supplemental information has been developed (Table 2.2) evaluating farmyards based on good agricultural practice advice being given at the time (e.g., slurry storage capacity, silage effluent storage capacity, etc.).

**Table 2.2 Supplemental scoring system for farmyards**<sup>1</sup> (Carton and Magette, 1999)

<table>
<thead>
<tr>
<th>Factor</th>
<th>Excellent (3 points each)</th>
<th>Good (2 points each)</th>
<th>Poor (1 point each)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Manure/slurry storage&lt;sup&gt;2&lt;/sup&gt;</td>
<td>&gt; 24 weeks</td>
<td>20 - 24 weeks</td>
<td>&lt; 20 weeks</td>
</tr>
<tr>
<td>Dirty water storage</td>
<td>≥ 12 weeks</td>
<td>12 weeks &gt; x &gt; 2 weeks</td>
<td>&lt; 2 weeks</td>
</tr>
<tr>
<td>Silage effluent storage</td>
<td>Greater than 3 days</td>
<td>3 days</td>
<td>&lt; 3 days</td>
</tr>
<tr>
<td>Dirty areas&lt;sup&gt;3&lt;/sup&gt;</td>
<td>100% covered</td>
<td>50% covered</td>
<td>&lt; 50% covered</td>
</tr>
<tr>
<td>Managerial level&lt;sup&gt;4&lt;/sup&gt;</td>
<td>Top 5% of producers</td>
<td>5% &lt; x &lt; 50%</td>
<td>&lt; 50%</td>
</tr>
<tr>
<td>Fatal flaw&lt;sup&gt;5&lt;/sup&gt;</td>
<td>No</td>
<td>Yes</td>
<td></td>
</tr>
</tbody>
</table>

<sup>1</sup>Scoring - Add points. 13 or more = low risk; 8-12 = medium risk; less than 8 = high risk

<sup>2</sup>Applicable to operations with animals only; allocate 3 points if no animals present; storage periods may require regional adjustment to take account of the shorter winter in southern compared to northern areas.

<sup>3</sup>Implies that roofed areas are fitted with gutters that divert all clean water

<sup>4</sup>Characteristics of exceptional managers should be considered in detail in terms of environmental as well as production issues, e.g., active use of nutrient management planning, well-maintained equipment and facilities (e.g., non-leaking waterers), etc.

<sup>5</sup>A “fatal flaw” is a situation that poses an imminent pollution threat (such as a cracked slurry store, a stream running through a farmyard, or a ‘clean’ water drain very near a pollutant source) and is caused to assign the farmyard an overall high pollution potential, regardless of other factors.

Hubbard et al. (2001) were the first to test the PRS system on two sub-catchments (Omard and Ballina), both in the northeastern portion of the River Shannon catchment using data from the Lough Derg and Lough Ree Catchment Monitoring and Management System (Morton and Engineers, 2001). Subsequently, other researchers
evaluated this tool with data available in different fields and catchments throughout the country (Hughes et al., 2005; Doody et al., 2012; Daly, 2006). All of them reported good accuracy in using the PRS to predict the rank order of P export to water bodies. However, they indicated that applying the method would not be straightforward, once the necessary data used in the scheme would not be widely available.

An assessment on water quality of Irish rivers was done by the Irish Environmental Protection Agency (EPA, 2018), categorising three-year average phosphate concentrations from 1874 individual river sites in 702 rivers into six quality classes for the period 2015 – 2017. Average phosphate concentrations of less than 0.025 mg/l P and less than 0.035 mg/l P have been established in Ireland as legally binding EQS to support the achievement of high and functional ecological status as required by the WFD, respectively. Concentrations of phosphate greater than 0.035 mg/l P are likely to lead to eutrophication. The results of the analysis show that 62.8% of the monitored river sites are classified as either high or good quality based on the phosphate environmental quality standard. The remaining 37.2% of sites are classified as being of moderate or poor quality (Table 2.3).

Table 2.3 Percentage and number of rivers and river sites in each phosphate concentration category for 2015 – 2017 (EPA)

<table>
<thead>
<tr>
<th>mg/l P</th>
<th>Categories of phosphorus concentrations in rivers</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>&lt; 0.025</td>
</tr>
<tr>
<td>no. of sites</td>
<td>905</td>
</tr>
<tr>
<td>% of sites</td>
<td>48.3</td>
</tr>
<tr>
<td>no. of rivers</td>
<td>355</td>
</tr>
<tr>
<td>% of rivers</td>
<td>50.6</td>
</tr>
</tbody>
</table>

Figure 2.2 shows a map of the Republic of Ireland, with the yellow, brown, purple and red dots all indicating levels greater than those likely to lead to nutrient pollution. As can be seen, the north-east, south-east and south of the country have particularly high levels of P (greater than 0.035 mg/l P).
The maximum amount of P allowed to be discharged to water bodies varies in each country. In this way, it is essential to evaluate the legislation in place to verify the most suitable way to remove P from aqueous systems.

### 2.3.2 Phosphorus relevant regulations

According to Awual and Jyo (2011), a maximum permissible level of P lower than 0.01 mg/L is required to protect surface waters from eutrophication. For the same
purpose, the United States EPA has recommended that the total P level in streams that enter lakes and in the flowing streams should not exceed 0.05 mg/L and 0.1 mg/L, respectively (Benyoucef and Amrani, 2011).

To control the P pollution at sources, effluent discharge standards have been developed and applied in several countries. In Europe, most of the legislation regarding P discharges is related to the implementation of the Nitrates Directive (91/676/EEC), in terms of National Action Plans, the Water Framework Directive (2000/60/IEC) in terms of River Basin Management Plans, and the Industrial Emissions Directive (2010/75/EU) (DHPLG, 2018).

Ireland’s first Nitrates Action Programme under the Nitrates Directive came into operation in 2006. Regulations were introduced to put this Action Programme into law. A second Action Programme was finalised in 2010, a third Action Programme was finalised in 2014, and the fourth Action Programme has been agreed and given legal effect by Good Agricultural Practice for Protection of Waters Regulations 2017 and Good Agricultural Practice for Protection of Waters Amendment Regulations 2018.

The main elements of the Nitrates Directive regarding P management in farms are related to time and frequency of manure/fertilisers spreading in the land. The limits established in the Directives follow the rule that the amount of N and P applied to land, being in the form of manure/slurry or fertilisers, should not exceed the crop’s need. For instance, the maximum permissible amount of livestock manure and slurry to be spread per hectare in a year is equivalent to 170 kg of N. Farmers can apply for a nitrates derogation where the 170 kg N/ha limit will be exceeded up to a maximum of 250 kg N/ha. There are times of the year when any manure and fertilisers should not be spread at all on the land. These are called the prohibited spreading periods, and they vary in the country according to the location. Ireland is divided into three zones with different prohibited application periods (Figure 2.3). Research has shown that
prohibited periods are necessary to prevent nutrient loss to water during the most environmentally risky time of the year.

Figure 2.3 Prohibited application periods for fertilisers in Ireland (DAFM, 2018)

A fertilisation plan must be prepared and kept for each grassland farm, describing the crop rotation of the farmland and the planned application of manure and other fertilisers. The fertilisation plan shall comprise at least the following items (Department of Agriculture, Food and the Marine (DAFM), 2018):

- The crop rotation plan, which must specify the acreage of parcels with grass and parcels with other crops, including a sketch map indicating the location of individual parcels;
- The number of livestock on the grassland farm, a description of the housing and storage system, including the volume of manure storage available;
- A calculation of manure N and P produced on the grassland farm;
- The amount, type and characteristics of manure delivered outside the grassland farm or to the grassland farm;
- The foreseeable N and P crop requirements for each parcel;
- Results of soil analysis related to N and P soil status if available;
• The nature of the fertiliser to be used;
• A calculation of N and P application from manure, chemical and other fertilisers for each parcel.

This fertilisation plan should be revised within seven days after any change in agricultural practices at the grassland farm. Periodic N and P analysis in soil should be done for each grassland farm. Sampling and analysis of N and P in soils should be carried out at least once every four years for each homogeneous area of the grassland farm, about crop rotation and soil characteristics.

The Irish National Action Programme (NAP) is recognised across the EU as being comprehensive and robust. Although initial improvements were observed in water quality in response to the NAP since its commencement in 2006, further improvements are still necessary. Conclusions from the EPA’s national assessment covering the years between 2010 and 2015 include:

• The quality of surface and groundwater remained relatively stable;
• The initial target of 13% improvement in water status over the 6 years was not accomplished;
• While a great pollution reduction in the most polluted sites was observed, there was a decline in high-quality water sites;
• 43% of the monitored river waterbodies had a less than good ecological status (DAFM, 2018).

In this way, Ireland’s fourth NAP (contained in the Good Agricultural Practice for Protection of Waters Regulations 2017), effective for 2018 – 2021, takes account of the agricultural pressures on water quality. It provides new measures focusing on intercepting and breaking the pathways that transport N, P and sediment from farmland to waters. It addresses soil fertility problems to improve nutrient use efficiency and productivity for the achievement of sustainable intensification objectives under Food Wise 2025. This comprehends a series of strategies developed by the Department of Agriculture, Food and the Marine that intends to develop the Irish agri-food sector for
the period up to 2025. The strategies aim at employment creation and economic growth in an environmentally sustainable matter among others.

Furthermore, under the fourth NAP, there is a simplification of the regulations for improved understanding and implementation. Taking account of the water quality improvement objectives in Ireland’s River Basin Management Plan, it is crucial that implementation at the farm level of the fourth NAP will take place over 2018 – 2021.

2.4 Phosphorus removal technologies

Removal of P from water streams can be achieved with various technologies, such as membrane filtration, reverse osmosis (Luo et al., 2016), precipitation, coagulation, crystallisation (Ackerman, 2011; Jia, 2014), adsorption (Wang et al., 2016; Xue et al., 2018), ion exchange (Awual and Jyo, 2011; Nur et al., 2014; das Gupta, 2011), magnetic separation (Yan et al., 2015; Tu et al., 2015), biological treatment (Yi et al., 2017; Zou and Wang, 2016), and constructed wetland (Lan et al., 2018). Though chemical precipitation and biological treatment are most common, each method represents its own merits and demerits. In this study, P removal technologies have been grouped into conventional and non-conventional technologies as follows.

2.4.1 Conventional technologies

2.4.1.1 Membrane related processes

Membrane related processes include microfiltration, reverse osmosis, and electrodialysis. These are membrane-related processes. Microfiltration involves a size-exclusion mechanism. Therefore, its removal efficiency does not rely on process parameters, such as influent concentration and pressure (Nguyen et al., 2014b).

In contrast, in reverse osmosis the elimination efficiency is controlled by the influent concentration, pressure, and water flux rate. In the electrodialysis method, the movement of ions is supported by an electric field applied across a semi-permeable membrane. Ions migrate through the membrane and become more concentrated in one
compartment, while decontaminated water remains in the other. While microfiltration suffers from low separation efficiency (≤ 10%), reverse osmosis and electrodialysis are often prone to extremely high costs (Nguyen et al., 2019).

2.4.1.2 Chemical precipitation

Chemical precipitation was first applied in the 1950s, in response to increasing concerns over eutrophication. Chemical methods remove P by addition of salts of multi-valence metal ions to form precipitates of insoluble metal phosphates, which are subsequently separated by sedimentation (Bashar et al., 2018; Biswas et al., 2008; Gibbons, 2009). The most common chemicals employed for this purpose are iron and aluminium chloride or sulphate, or calcium hydroxide. These chemicals combine with phosphate, as shown by the following reactions (Nieminen, 2010).

\[
Al^{3+} + PO_4^{3-} \rightarrow AlPO_4 \downarrow \quad (2.1)
\]

\[
Fe^{3+} + PO_4^{3-} \rightarrow FePO_4 \downarrow \quad (2.2)
\]

\[
5 Ca^{2+} + 3 PO_4^{3-} + OH^- \rightarrow Ca_5(PO_4)_3(OH) \downarrow \quad (2.3)
\]

Chemical removal has the advantage of being simple, efficient and flexible (Biswas et al., 2008). It is reported that up to 90% of the total P can be removed by this method. Though chemical addition can be done at different stages in the wastewater treatment process, the secondary treatment is usually the stage recommended (Nieminen, 2010). Nevertheless, chemical removal method is still subjected to several drawbacks, such as sludge formation, high chemical expense, effluent neutralisation requirement, and inadequate efficiency for P dilute solution (Biswas et al., 2008; Kumar and Pal, 2015; Mallampati and Valiyaveettil, 2013). The sludge handling will increase the treatment cost and require much space (Lanning, 2008; Sengupta and Pandit, 2011). In addition, the sludge formed by chemical methods is non-reusable, due to high impurities and low bioavailability (Biswas et al., 2008; das Gupta, 2011; Kalmykova and Fedje, 2013; Nieminen, 2010). Besides, the identification of optimal dosing conditions is hard to be achieved (Biswas et al., 2008).
2.4.1.3 Biological methods

Biological P removal was developed in the late 1950s, and it has become a firmly established technology (Biswas et al., 2008). Biological methods to remove P from aqueous solutions are characterised by the storage of P in the cells of polyphosphate accumulating organisms (PAOs), followed by the separation of accumulated P in the form of biomass. In anaerobic conditions, PAOs use their intracellular polyphosphate as an energy source to assimilate fermentation products, for example, acetate, to form polyhydroxy butyrates (PHB) and release orthophosphate. When exposed to aerobic conditions, PAOs use PHB as an energy source for oxidising organic matter to provide carbon for new cell growth and synthesising polyphosphate from previously released orthophosphate to store in their cells. The principle of the cell operation for the biological removal method is illustrated in Figure 2.4, while concentrations of participating substances in the process are depicted in Figure 2.5.

![Figure 2.4 Principle of biological P removal process (Nguyen et al., 2014b)]
Biological methods hold several benefits over their chemical counterparts, such as the formation of biological sludge with better value when used in agriculture and P recovery and the absence of chemical usage (Biswas et al., 2008). Nevertheless, biological methods have various shortcomings, namely low removal efficiency (≤ 30%) (Nguyen, 2015), complex configuration and operating regimes (Biswas et al., 2008), high energy consumption and high footprint (das Gupta, 2011; Karachalios, 2012; Peleka and Deliyanni, 2009). Especially, biological removal methods require the addition of readily biodegradable organic carbon, which makes these processes costly (das Gupta, 2011; Nieminen, 2010). The functional micro-organisms (PAOs) are sensitive to the variation of temperature and feed concentrations (Li et al., 2016; Onyango et al., 2007). Furthermore, these processes cannot remove trace levels of P (Sengupta and Pandit, 2011). Hence, chemical methods always stand by the biological methods if stringent P discharge standards are required.

Figure 2.5 Concentrations of involving substances in the biological P removal process (Nguyen et al., 2014b)
2.4.2 Non-conventional technologies

2.4.2.1 Magnetic separation

Magnetic separation was initially investigated in the 1970s. It is considered as an attractive method because this can produce an effluent with the P level of 0.1 - 0.5 mg/L at the same costs as other methods. Magnetic separation can be used as a reliable add-on technology for chemical removal. Lime is employed to precipitate calcium phosphate, which is attached to the magnet. In the next step, calcium phosphate is separated from the magnet in a separator unit using shear forces and a drum operator Figure 2.6. The significant advantages of this process are high elimination efficacy, short process, and low energy consumption (Biswas et al., 2008).

![Figure 2.6 Schematic diagram of magnetic phosphate](image)

2.4.2.2 Crystallisation

The crystallisation technology has been developed since the 1970s, as a result of more stringent regulations and a desire to yield a more marketable end-product (Biswas et al., 2008). This method is based on crystal nucleation and growth chemistry. It includes MAP (magnesium ammonium phosphate) and HAP (hydroxyapatite) processes. However, the high cost makes crystallisation an unattractive option for P pollution treatment. Even so, there are some full-scale wastewater treatment plants (WWTPs)
applying MAP crystallisation technology in Canada, United States, Germany, Japan and Australia (Nieminen, 2010).

### 2.4.2.3 Ion exchange

Ion exchange is defined as the reversible interchange of ions between a solid phase (the ion exchange resin) and a liquid phase (Martin et al., 2009). Ion exchange materials are insoluble and contain loosely held ions in the form of insoluble salts. It allows ion exchange materials to exchange either positively charged ions (cation exchangers) or negatively charged ions (anion exchangers) (Karachalios, 2012). The natural ion exchange materials include proteins, cellulose, living cells, while the most common synthetic resins are those consisting of polystyrene with sulfonate groups (cation exchangers) or amine groups (anion exchangers). Ion exchange method is advantageous because of its simple operation, adaptability to changes in feed flow rates, temperatures and compositions (Awual and Jyo, 2011; Li et al., 2016). However, low selectivity with the presence of co-ions and high operation cost caused by frequent use of generation chemicals are significant hindrances for its widespread application (Biswas et al., 2008; das Gupta, 2011; Karachalios, 2012).

### 2.4.2.4 Adsorption

Adsorption method removes P from water by attracting phosphate ions in a liquid to the surface of a solid adsorbent and holding them by intermolecular forces (Biswas et al., 2008). This method offers various advantages, such as low cost, high efficiency, simple operation, no sludge formation, no influence on wastewater pH (das Gupta, 2011; Zhang et al., 2011; Zach-Maor et al., 2011). Also, adsorption can pre-concentrate P in the solution to a high level, therefore enabling P recovery (Li et al., 2016; Ohura et al., 2011). Besides, it is well-documented that adsorption is efficient in removing P from a dilute solution (Krishnan and Haridas, 2008; Zhang et al., 2014).

Consequently, it is believed that adsorption can promote P recovery from wastewaters characterised by low levels of P, such as municipal wastewater (Ebie et al., 2008; Tan
and Lagerkvist, 2011). Nevertheless, the bottleneck for the use of adsorption in water treatment is the development of low-cost and efficient adsorbent (Li et al., 2016). It is supported by Biswas et al. (2008), who stated that the feasibility of the P adsorption process mostly depends on the preparation of adsorbents.

In the past, activated carbon was used for P removal. However, the problems related to the high cost, no renewability and disposal after use hinder its wide application in developing countries (Karthikeyan et al., 2004). Hence, there is a new trend in using low-cost and abundantly biomaterials, such as agricultural by-products, for this purpose (Biswas et al., 2008). It is desirable to develop adsorbents that have low-cost, abundant availability, high efficiency, high selectivity, potential renewability, and high adaptability to various operating conditions (Ping et al., 2008).

The main advantages and disadvantages of the various P removal technologies are summarised in Table 2.4.

Table 2.4 Summary of advantages and disadvantages of various P removal technologies*

<table>
<thead>
<tr>
<th>Method</th>
<th>Treatment result (mg P/L)</th>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>Membrane Technology</td>
<td>EPC 0.04</td>
<td>Small physical footprint;</td>
<td>High costs in case of RO and electrodialysis;</td>
</tr>
<tr>
<td></td>
<td>(MBR), 0.008</td>
<td>High P removal</td>
<td>Low removal efficiency (&lt; 10%) in case of microfiltration;</td>
</tr>
<tr>
<td></td>
<td>(RO), &lt; 0.005</td>
<td></td>
<td>Fouling</td>
</tr>
<tr>
<td></td>
<td>(electro dialysis)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Magnetic separation</td>
<td>EPC 0.1 - 0.5</td>
<td>High P removal;</td>
<td>Chemicals required;</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Compact process;</td>
<td>Technology is complex</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Low energy consumption</td>
<td></td>
</tr>
<tr>
<td>Chemical precipitation</td>
<td>EPC 0.005 - 0.04</td>
<td>Flexible;</td>
<td>High chemical demand;</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Easy to install;</td>
<td>Chemical sludge generation;</td>
</tr>
<tr>
<td></td>
<td></td>
<td>High P removal;</td>
<td>Effluent neutralisation requirement;</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Less space requirement</td>
<td>Difficult to identify optimal dosing conditions;</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Low bioavailability of end-products;</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Do not promote P recovery;</td>
</tr>
</tbody>
</table>

47
<table>
<thead>
<tr>
<th>Process</th>
<th>EPC</th>
<th>Characteristics</th>
<th>Drawbacks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crystallisation</td>
<td>EPC 0.3 - 1.0</td>
<td>Recycle end-products; Demonstrated technology; MAP produced can be used in agriculture</td>
<td>High cost; Chemicals and operation skills required; Complex process; Unsuitable for wastewater with low P levels</td>
</tr>
<tr>
<td>Ion exchange</td>
<td></td>
<td>Simple operation; High P removal; Adaptability to various solution compositions and flow rates; Can operate in a wide range of temperature</td>
<td>High operation cost; Low selectivity; Materials originated from non-renewable resources</td>
</tr>
<tr>
<td>Adsorption</td>
<td>EPC 0.005 - 0.01 RE &gt; 80</td>
<td>Simple operation; Cost-effectiveness; Few chemicals involved; No sludge formation; No influence on wastewater pH; Suitable for poor P wastewater; Can pre-concentrate P to high levels; Enable P recovery; Multiple regeneration of adsorbents</td>
<td>High cost; Disposal problems after use; The feasibility of P adsorption process relies on the development of adsorbent</td>
</tr>
<tr>
<td>Biological P removal</td>
<td>EPC 0.1 - 0.3 RE ≤ 30</td>
<td>Avoid chemical use; Avoid chemical sludge formation; Produce biological sludge with better value when used in agriculture; Potential P recovery; Established technology</td>
<td>Low removal efficiency; Inability to remove trace P concentration; Can hardly meet discharge standards; Biological sludge handling; Sensitive to changes in P load and temperature</td>
</tr>
</tbody>
</table>

Notation: EPC - Effluent P concentration (mg P/L); RE - Removal efficiency (%).

* Adapted from Biswas et al. (2008); Karachalios (2012); Lanning (2008); Li et al. (2009); Loganathan et al. (2014); Nieminen (2010); Ohura et al. (2011); Strom (2006).
2.5 Phosphorus recovery

2.5.1 Drivers for phosphorus recovery

Phosphorus recovery is a process that can (i) convert P into either plant-available form for reuse as fertiliser or raw material for the P industry, and (ii) separate valuable P from harmful substances (Cornel and Schaum, 2018; Petzet et al., 2012). According to Green et al. (2004), P recovery is defined as a process that allows P to precipitate or crystallise from wastewater, sewage sludge, and ash into a pure product for recycling purposes. Unfortunately, some authors misused ‘P recovery’ for P desorption in the literature, for example, Bottini and Rizzo (2012), Ohura et al. (2011), Das Gupta (2011). In this study, the term ‘P recovery’ is used according to the above definitions.

Recovery of P has become a matter of interest in recent years for many different reasons. Firstly, it is predicted that rock phosphate reserves cannot last for more than 150 years (Figure 2.7) (Kohn et al., 2018; Jia, 2014; Loganathan et al., 2014; Tyagi and Lo, 2013). The increasing scarcity of high-quality P ores leads to the rise in the cost of fertiliser production, and this negatively affects the global economy (Nieminen, 2010). Figure 2.8 shows the evolution of the phosphate rock prices from 2014 to 2019, and the projection prices up to 2030.
Therefore, there is a need to search for alternative P sources. Another reason is that the direct use of sludge/manure in agricultural soils is increasingly restricted. It has contributed to the desire to develop a proper technology for recovering P from
alternative sources (Nieminen, 2010). Thus, the development of appropriate technology for P recovery is necessary.

2.5.2 Routes for P recovery

The most important entry point for P recovery from wastewater – in terms of the amount of P to be recovered – is the sewage collection and treatment system. In urbanised settings, sewage is centrally collected and treated in a WWTP. Sewage treatment includes the removal of P when discharge limits for P are set. The stricter the discharge limits are, the more effective the P removal has to be. In WWTPs, the recovery of P can be performed at several locations (Figure 2.9). Different products of WWTPs may be used as feed materials for P recovery, including (1) direct sludge application in agriculture, (2) P recovery from aqueous sludge phase (a) prior or (b) after dewatering, and (3) incinerated sludge ash.

![Figure 2.9 Hotspots for P recovery from the wastewater stream (Schaum, 2018)](image)

Depending on various products of WWTP utilised for P recovery, the technologies can be classified as precipitation/crystallisation, wet-chemical extraction, and thermal treatment (Sartorius et al., 2012). The crystallisation and precipitation transfer P from liquor into the solid phase using pH adjustment and chemical dosage (Figure 2.10).
The precipitation differs from crystallisation in the reaction speed. Precipitation takes less time than crystallisation. Precipitation results in the amorphous product while crystallisation yields the crystalloid product. The P levels in liquors need to be ≥ 50 mg/L to ensure economically viable P recovery. The pH value can be adjusted with NaOH or CO₂ stripping (Nieminen, 2010). The wet chemical method recovers P bound in sludge and ash by chemical leaching combined with precipitation (Figure 2.11). As P in sludge/ash is in the chemically or biologically bound forms, P needs to be extracted by acid or base leaching before separation through precipitation, ion exchange or nanofiltration.
The thermo-chemical method recovers P from ash by addition of chloride chemicals, for example, KCl, MgCl₂ and then thermal treatment (> 1000 °C), enabling the evaporation of heavy metal chlorides (Figure 2.12). Due to the extensive energy consumption required for incineration plants, the thermo-chemical technology is appropriate for countries where sludge is commonly disposed of by incineration.

![Thermo-chemical technology](image)

*Figure 2.12 Thermo-chemical technology (Adam et al., 2009)*

Recovery of P from sludge or ash may result in higher efficiency than from liquors (Cornel and Schaum, 2009). Nevertheless, this process often suffers from higher costs due to chemical and energy consumption for P leaching and thermal treatment. Thus, from an economic point of view, precipitation/crystallisation technology is usually preferred to wet chemical or thermo-chemical technologies (Nieminen, 2010).

So far, the precipitation/crystallisation technology has been successfully applied in full scale in several countries such as Canada, Japan, Germany and the United States. In contrast, the wet chemical method has found only limited applications in industry. The thermo-chemical process has been restricted to pilot-scale applications.

Calcium phosphate and magnesium ammonium phosphate (MAP) are typical products of P recovery. Calcium phosphate can be recycled in the phosphate industries, while MAP can be used as slow-release fertiliser in agriculture (Tyagi and Lo, 2013). MAP seems to be preferred to some calcium phosphate compounds, due to higher solubility and simultaneous holding of both nitrogen (NH₄⁺) and phosphate (PO₄³⁻) (Ackerman, 2011; Muster et al., 2013). It is reported that the formation of MAP requires P:Mg:N
molar ratio of 1:1:1 and alkaline pH medium of 8 – 10 (Cornel and Schaum, 2009). The additional condition is a low concentration of total suspended solids (Jia, 2014).

Manure provides the biggest potential for nutrient recycling. Centralisation and intensification of livestock production pose a big environmental problem with nutrients faced today (Schaum, 2018). Here, better nutrient management forcing better distribution of nutrients of surplus regions towards deficit regions is the challenge to be coped with. This will provide options to synergise technology development and implementation for the several waste streams. The implementation of the European Nitrates Directive needs to be enforced. In terms of P, manure is estimated to contain 1.8 Mt P and 7 – 9 Mt N in EU 27, whereas wastewater adds 0.3 Mt P and 2 – 3 Mt N (Buckwell and Nadeu, 2016; Leip et al., 2014; Sutton et al., 2011).

Currently, sewage sludge is used as organic fertiliser. The merits and dangers of this practice are widely debated (Healy et al., 2016). Concerns about organic contaminants and pathogens entering the environment and food chain lead to an increasing trend away from agricultural use of sewage sludge, especially in Germany, The Netherlands and Switzerland. Figure 2.13 provides an overview of the different sludge valorisation or disposal routes applied in various European countries (Schaum, 2018).

![Figure 2.13 Sewage sludge valorisation or disposal route in European countries (Schaum, 2018)](image-url)
2.5.3 Barriers to P recovery

Until now, P recovery is still an un-established process. The high cost appears to be the main obstacle to expanding this technology (Lanning, 2008). Low market prices of fossil P based raw materials and products challenge the economic viability of many recovery technologies, especially when these technologies do not provide operational benefits and yield recovered material that is not directly marketable. If there is no prospect of profits, investors will spend their money in other sectors and markets. This is especially notable for technologies requiring significant investments. Here, realistic recovery targets implemented by a form of legislation could motivate or even enforce recovery and recycling (Schaum, 2018).

Tyagi and Lo (2013) claimed that the recovered P was 22 times more costly than mined P. Bottini and Rizzo (2012) reported that the expenditures for P recovered from sludge liquor using the ion exchange method coupled with crystallisation and mined P were 8.2 and 0.652 €/kg, respectively. Taking the annual increase in the mined P cost (0.012 € per kg per annum) into consideration, the P recovery from sludge liquor was expected to be beneficial in the next 10 - 15 years. Molinos-Senante et al. (2011) revealed that the cost of P recovered from wastewater varied between 2 and 8 €/kg P while that of rock phosphate ranged from 35 to 50 $/ton. They concluded that unless environmental benefits were taken into account, P recovery would not be economically viable. Sartorius et al. (2012) predicted that P recovery would become an established process in the next 20 years in developed countries.

Another barrier to P recovery is the quality of the final products (Sartorius et al., 2012). High levels of heavy metals in P recovered from municipal solid waste incineration fly ash prevent them from being used directly in arable lands (Kalmykova and Fedje, 2013). In addition, due to the improper public perception that struvite is a waste product, people tend to avoid using it as fertiliser for their crops (Lanning, 2008).
2.6 Use of Agriculture Waste By-products for P adsorption
2.6.1 Justification of using AWBs based adsorbents for P removal

Agricultural waste by-products have several properties that make them attractive as the material for developing P adsorbents. To begin, AWBs are abundant, cheap, and non-toxic. AWBs have an appropriate chemical composition (cellulose and hemicelluloses) with a large number of active hydroxyl groups. Consequently, AWBs can easily be involved in chemical reactions, for example, metal loading, polymerisation, and graft reaction (Xu et al., 2010). It provides a foundation for AWBs to be converted into some functional polymers with functional groups (Benyoucef and Amrani, 2011). Specifically, the OH groups can combine with alkoxyamine ligands, and hence enhancing their anion exchange abilities (Karthikeyan et al., 2004).

The use of AWBs as P adsorbents is drawing increasing attention (Singh et al., 2018). This practice may result in many benefits. Firstly, it can protect surface water from eutrophication. Secondly, there are huge amounts of AWBs produced worldwide annually, posing a challenge to solid waste disposal. Thus, the recycling of locally available AWBs as phosphate adsorbents not only provides a viable solution to reduce waste materials in a cheap and eco-friendly way but also adds value to AWBs (Anirudhan and Senan, 2011; Eljamal et al., 2013; Ismail, 2012; Tshabalala et al., 2004). It also fits well with the principle ‘use of renewable resources’ of Green Chemistry (Srivastava and Goyal, 2010). In addition, the production of anion exchange resins from abundant, cheap and renewable AWBs may help reduce the cost of P treatment (Liu et al., 2013). The use of AWBs based adsorbents for P decontamination may provide a sustainable, efficient and profitable solution for P pollution management.

2.6.1.1 P removal by AWBs in their natural form

Natural AWBs have received far less attention for being used as phosphate adsorbents than their modified counterparts. Up to date, only a few reports exist, for example, Ismail (2012), Jeon and Yeom (2009), Krishnan and Haridas (2008), Riahi et al.
(2009), Yeom and Jung (2009), and Zhang et al. (2014). Table 2.5 reports phosphate adsorption capacities of natural AWBs and commercial adsorbents for comparison purpose. Natural AWBs display the adsorption capacity for phosphate in the range of 1.10 to 26.66 mg/g. These values are substantially lower than those of many common commercial adsorbents (31.74 – 131.77 mg/g). Obviously, with very few exceptions, the P removal by natural AWBs is not efficient enough for practical application. It can be explained by the fact that as lignocellulosic materials, natural AWBs contain a large number of negatively charged functional groups (-OH, -COOH) on their surfaces. Consequently, raw AWBs are supposed to be less effective in decontaminating anionic contaminants than cationic ones (Mallampati and Valiyaveettil, 2013). Because of the lack of efficacy, the use of natural AWBs for decontaminating PO$_4^{3-}$ from wastewater is still limited.

Table 2.5 The maximum phosphate adsorption capacity of natural AWBs and commercial adsorbents

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Adsorption capacity (mg PO$_4^{3-}$/g)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Natural AWBs</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Palm surface fibres</td>
<td>26.05</td>
<td>Ismail, 2012</td>
</tr>
<tr>
<td>Coir pith</td>
<td>4.35</td>
<td>Krishnan and Haridas, 2008</td>
</tr>
<tr>
<td>Date palm fibres</td>
<td>13.33</td>
<td>Riahi et al., 2009</td>
</tr>
<tr>
<td>Sugarcane bagasse</td>
<td>1.10</td>
<td>Zhang et al., 2012</td>
</tr>
<tr>
<td>Giant reed</td>
<td>0.84</td>
<td>Xu et al., 2011</td>
</tr>
<tr>
<td>Peanut shells</td>
<td>3.13</td>
<td>Liu et al., 2016</td>
</tr>
<tr>
<td>Litchi seed waste</td>
<td>7.65</td>
<td>Shrestha et al., 2018</td>
</tr>
<tr>
<td>Cotton stalks</td>
<td>3.56</td>
<td>Liu et al., 2016</td>
</tr>
<tr>
<td><strong>Commercial adsorbents</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Duolite A-7</td>
<td>31.74</td>
<td>Anirudhan et al., 2006</td>
</tr>
<tr>
<td>Dowex</td>
<td>40.23</td>
<td>Anirudhan and Senan, 2011</td>
</tr>
<tr>
<td>Zirconium loaded Muromac</td>
<td>131.77</td>
<td>Biswas, 2008</td>
</tr>
<tr>
<td>Zirconium ferrite</td>
<td>39.84</td>
<td>Biswas, 2008</td>
</tr>
<tr>
<td>Zr-MCM 41</td>
<td>3.36</td>
<td>Jutidamrongphan et al., 2012</td>
</tr>
<tr>
<td>Zirconium ferrite</td>
<td>27.73</td>
<td>Jutidamrongphan et al., 2012</td>
</tr>
<tr>
<td>Amberlite IRA-400</td>
<td>32.24</td>
<td>Marshall and Wartelle, 2004</td>
</tr>
<tr>
<td>Aluminium oxide</td>
<td>34.57</td>
<td>Peleka and Deliyanni, 2009</td>
</tr>
<tr>
<td>Hydrotalcite</td>
<td>60.00</td>
<td>Peleka and Deliyanni, 2009</td>
</tr>
</tbody>
</table>
2.6.2 Modification of AWBs for efficient P removal

There is a growing trend in using AWBs as materials for the development of phosphate adsorbents. Whereas some natural AWBs can hardly remove P from aqueous solutions, others exhibit very low sorption abilities compared to commercial adsorbents. The lack of efficiency in the phosphate removal of original AWBs can be explained by the abundant availability of negatively charged functional groups (for example −OH, −COOH) as well as the absence of positively charged functional groups (for example −NH₂) on the surface of raw AWBs (Mallampati and Valiyaveettil, 2013). For these reasons, AWBs need to be modified to improve its phosphate sorption abilities. According to Biswas et al. (2008), the feasibility of a P adsorption process is controlled by the preparation of adsorbents.

Besides, modification of AWBs can increase the strength of lignocellulosic materials, and hence mitigating the release of organic matter into aqueous solutions (Anirudhan et al., 2006). Methods of modifying AWBs for better phosphate removal can be grouped into (i) cationization (for example metal loading, and grafting with ammonium type chemicals), (ii) anionization (for example surface coating with sulfate), and (iii) activation (for example thermal, chemical and steam activation). This section aims to gain insight into each method of modification, concerning the principle, procedure, influential factors, application, and limitations of each method.

2.6.2.1 Activation

The activation of AWBs is done through the use of high temperature, pressure or chemicals to improve its adsorption performance.

2.6.2.1.1 Thermal activation

Thermal activation is a process of carbonisation or calcinations of organic matters using high temperature. Huang et al. (2016) used high temperatures to activate oyster shells for better phosphate removal. They discovered that thermal activation
substantially improved the adsorption capacity of oyster shells. Natural oyster shell could not remove any P at the P level of 20 mg/L. Activating oyster shells at 500 °C achieved a removal percentage of 100% after 3 – 4 days. The authors explained the inefficient P removal of raw oyster shell by the attachment of the nacreous layer and the organic mucous membrane to the pores, which prevented phosphate from being adsorbed onto the porous structure. Although the thermal activation boosted the P removal of oyster shells, the weight loss of oyster shells was reported as a side effect. The authors ascribed the weight loss of 1.6% at the temperature 700 °C to the volatility of water and combustion of organic matter. However, they suggested that the decomposition of CaCO₃ would be responsible for the weight loss of 42.4% in the temperature range of 700 – 900 °C. This effect is undesirable since a higher amount of raw oyster shells and more energy are required to produce a certain amount of activated oyster shells. The similar decomposition of CaCO₃ into CaO and increasing surface area were noticed, when waste eggshells were calcinated at 800 °C (Köse and Kivanç, 2011).

Another study on thermal activation was conducted by Peng et al. (2012), in which fast pyrolysis was applied to produce biomass char from pine sawdust. It was shown that the pyrolysis temperature and retention time were primary factors, affecting the phosphate adsorption capacity of biomass char. The phosphate adsorption capacity of biomass char (15.1 g/g) was attributed to the high carbon content and porous structure, which resulted from pyrolysis.

### 2.6.2.1.2 Steam activation

Steam activation is a selective oxidation process of carbonaceous compounds with the presence of air at low temperature/steam, and CO₂/blue gas at high temperature. Namasivayam et al. (2005) employed high-pressure steam (234 °C and 3.0 MPa) to activate oyster shells. Even though natural oyster shells did not adsorb phosphate, 24 g of activated oyster shells lowered the phosphate concentration in 1 L of synthetic wastewater from 50 to 7 mg/l in 7.7 days. The authors assumed that phosphate was adsorbed onto activated oyster shells as amorphous calcium phosphate, which later
was converted into thermodynamically more stable hydroxyapatite. Ca$^{2+}$ was detected in the aqueous solutions during the adsorption performance of activated oyster shells.

Similarly, Abdul and Aberuagba (2005) utilised a steam oxidation process (450 °C, 10 bars) to prepare activated charcoals from three kinds of AWBs. The sorption capacities for different pollutants of activated charcoals were attributed to the developed pore structure and large internal surface area. Among various types of charcoals, corncob proved to be the best. It was ascribed to the contribution of other mechanisms in addition to pore diffusion in the phosphate removal of corncob. They concluded that not only a method of activation but also the raw materials could affect the adsorption features of activated AWBs.

### 2.6.2.1.3 Chemical activation

Chemical activation is a process of carbonisation or calcination, in which inorganic chemicals are employed to degrade and dehydrate the organic compounds. According to Abdul and Aberuagba (2005), the overuse of chemicals in chemical activation may cause environmental contamination or equipment erosion, and thus preventing this method from extensive application. Kumar and Pal (2015) used carbon, prepared from coir pith at 600 °C and activated by H$_2$SO$_4$, for phosphate removal from aqueous solutions. It was found that H$_2$SO$_4$ treated – coir pith activated carbon was a cost-effective phosphate adsorbent. The high phosphate adsorption capacity of coir pith activated carbon (7.74 mg/g) was validated by high Brunauer–Emmett–Teller (BET) surface area and pore size, which were reported to be 727.4 m$^2$/g and 18.79 Å, respectively.

### 2.6.2.2 Cationization

The cationization of AWBs is indented to improve their phosphate adsorption capacity via electrostatic interaction. It consists of the impregnation of the AWBs with metal salts in the metal loading method, or ammonium salts in the quaternization method.
2.6.2.2.1 Metal loading method

It was reported that metal oxides, such as oxides of Fe, Al, Mn, contained in some low-cost materials played important roles in their phosphate removal abilities (Liu et al., 2013, Penn et al., 2007). This suggests a way to improve the phosphate uptake of AWBs based adsorbents, by saturating AWBs with metal salts. It is desirable that the metal-treated AWBs with highly positive charged functional groups can effectively sequester phosphate anions (Cheng et al., 2013). Likewise, since Fe$^{3+}$ exhibits an excellent affinity for PO$_4^{3-}$ ions, Fe$^{3+}$ loaded polymers could be a good choice for phosphate decontamination (Carvalho et al., 2011).

The process is implemented by reacting AWBs with metal salts. Due to the abundance of negatively charged functional groups (for example, $-$OH, and $-$COOH) on their surfaces, AWBs can naturally adsorb metals. Nevertheless, to further boost their metal sequestering ability, it is necessary to graft AWBs with carboxyl ($-$COOH) groups or modify AWBs with bases before metal loading (Eberhardt and Min, 2008). The metal loading procedure is proposed as follows.

**Grafting carboxyl groups onto AWBs**

The integration of carboxylic ($-$COOH) groups into AWBs before their reactions with metal salts can significantly increase their metal adsorption capacities. For this reason, the carboxylic ($-$COOH) group is considered the most important functional group for metal sorption by AWBs (Min et al., 2004). Therefore, one of the well-known methods to improve adsorption ability is through the incorporation of carboxylic ($-$COOH) groups into AWBs. Nada and Hassan (2006) introduced three ways to incorporate carboxylic ($-$COOH) groups into sugarcane bagasse to prepare cationic exchange resins. That is etherification using mono chloroacetic acid (Equation 2.4), esterification using succinic anhydride, and oxidation using sodium chlorite. They discovered that carboxymethylated bagasse displayed the highest cationic exchange ability and thermal stability over that of succinylated and oxidised bagasse.

$$\text{Poly–OH} + \text{Cl–CH}_2\text{–COOH} \rightarrow \text{Poly–O–CH}_2\text{–COOH} + \text{HCl} \quad (2.4)$$
Carvalho et al. (2011) confirmed the efficacy of the etherification method by reporting that the maximum Fe$^{2+}$ adsorption capacity of sugarcane bagasse fibres rose from 16.0 to 75.4 mg/g (371.3%) after the reaction with mono chloroacetic acid. As a consequence, the phosphate removal percentage of carboxymethylated sugarcane bagasse fibres rose 3% compared to the raw material. Similarly, Eberhardt and Min (2008) revealed that the pre-treatment with carboxymethyl cellulose (CMC) augmented the phosphate uptake capacity of Fe$^{2+}$ impregnated wood particles from 2.05 to 17.38 mg/g (748%). They attributed the higher phosphate uptake capacity to additional binding sites to complex iron ions, which were formed by chemical reaction of wood particles with an anionic polymer.

**Base treatment (saponification)**

Another method to enhance the metal sorption ability of AWBs is through base treatment. It is to impregnate the fibres of AWB with a base, being NaOH the most commonly used. It is reported that the (-OH) ions present in the base change the AWBs’ structure, increasing adsorption performance. Min et al. (2004) examined the efficacy of base treatment on the Cd$^{2+}$ sorption by juniper fibre. It was found that base treatment enhanced the maximum Cd$^{2+}$ adsorption capacity almost 3.2 times (from 9.18 to 29.54 mg/g). They explained that hydroxyl ions derived from NaOH changed ester in the wood fibre to carboxylate, which played a significant role in binding Cd$^{2+}$ to AWBs.

\[
\text{R–COO–R’} + \text{H}_2\text{O} + \text{OH}^- \rightarrow \text{R–COO}^- + \text{R’–OH} \tag{2.5}
\]

Equally, the base treatment (saponification) was used before metal loading in many studies (Biswas et al., 2008, Han et al., 2005, Mallampati and Valiyaveettil, 2013). Han et al. (2005) claimed that treatment of juniper mats with 0.5 M NaOH improved their cationic exchange capacity, and hence enhanced the binding ability of Fe irons. As a result, the capture of PO$_4^{3-}$ ions onto juniper mats was strengthened. Mallampati and Valiyaveettil (2013) saponified apple peels with NaOH before impregnation with Zr$^{4+}$ salt. They assumed that the base treatment broke up ester bonds and produced more –OH groups, which were responsible for metal binding onto AWBs.
Deposition of metal ions onto AWBs

It is well recognised that metal ions can attach to AWBs via cationic binding sites on the surface of AWBs, for example, hydroxyl (−OH) groups, and carboxylic (−COOH) groups (Han et al., 2005, Min et al., 2004). Shin et al. (2005) claimed that the ion exchange mechanism might be responsible for La\(^{3+}\) attachment to juniper bark fibre. Their assumption was supported by Powder X-ray diffraction (XRD) patterns, indicating that after La\(^{3+}\) treatment, the height of Ca peak in the material declined compared to the reference peak. In contrast, Ca\(^{2+}\) concentration in the solution increased. Based on obtained data, they concluded that La\(^{3+}\) was retained on juniper bark fibre by replacing Ca\(^{2+}\) in the bark.

The efficacy of AWBs metal loading is found to rely on the type and concentration of loading metals, as well as the method of metal loading. Also, the common metal solutions used for cationization of AWBs consist of Zn\(^{2+}\), Fe\(^{2+}\), Fe\(^{3+}\), La\(^{3+}\), and Zr\(^{4+}\). Wang et al. (2016) reported that the maximum phosphate adsorption capacity of activated carbon (AC)/N-Fe(II) (14.12 mg/g) was greater than AC/N-Fe(III) (8.73 mg/g). The authors ascribed this to the higher intraparticle diffusion and binding energy of AC/N-Fe(II) in comparison with AC/N-Fe(III). Shin et al. (2005) found that the increase in La(NO\(_3\))\(_3\).6H\(_2\)O concentration from 0.01 to 0.1 M led to a rise in phosphate capture ability of La\(^{3+}\) loaded juniper bark fibre, from 20.05 to 33.35 mg/g.

While metal loaded AWBs have been demonstrated to be potential phosphate adsorbents, the metal leakage is a major limitation, hindering their actual application. The significant detachment of loaded metals during their performance is undesirable (Shin et al., 2005). The amount of metal retained on AWBs determines the phosphate adsorption capacity of AWBs. Thus, high metal leakage may lead to the loss of phosphate adsorption capacity after several cycles of operation (Eberhardt and Min, 2008). Besides, the quality of aqueous solutions treated with metal loaded adsorbents can deteriorate, owing to excessive levels of metals. Another detrimental effect is an increase in the cost of water treatment. The reason is that the spent adsorbents need to be repeatedly treated with metal salts to ensure stable sorption capacity (Shin et al., 2005).
Shin et al. (2005) reported that 85% loaded La was leaked at pH 2.5 in the case of removing phosphate by La treated juniper bark. To avoid problems associated with La detachment, the authors suggested using the biosorbent at neutral pH. Similarly, Biswas et al. (2008) discovered the La detachment during desorption test with HCl 0.4 M, when La loaded orange waste gel was employed as a phosphate adsorbent. These findings agree well with a previous study implemented with La loaded activated carbon fibre (Zhang et al., 2011). Both Han et al. (2005) and Nguyen et al. (2014b) revealed that Fe$^{3+}$ ions were vigorously detached from acid mine drainage treated juniper bark and iron-loaded okara during their performance. On the contrary, the Zr leakage was found to be minor in the studies conducted by Biswas et al. (2008), Mallampati and Valiyaveettil (2013), Ohura et al. (2011).

High affinity and selectivity for the phosphate, combined with the stable chemical property, make Zr attractive among various loading metals. However, high cost is a major factor limiting the widespread application of Zr for cationization of AWBs. Since each of the existing loading metals has its own merits and demerits, the search for sustainable, cost-effective loading metals is still ongoing.

### 2.6.2.2 Quaternization method

Quaternization of AWBs is intended to produce anion exchange resins for P removal. It can be implemented by treatment of AWBs with various quaternary ammonium compounds, which provide amino groups for grafting into the structure of AWBs (Wang et al., 2010). Various quaternary ammonium compounds can be utilised, such as poly-allylamine hydrochloride (PAA•HCl) (Karthikeyan et al., 2004; Tshabalala et al., 2004), 3 chloro-2-hydroxypropyl trimethyl ammonium chloride (de Lima et al., 2012; Karthikeyan et al., 2002), trimethylammonium chloride (Marshall and Wartelle, 2004; Wartelle and Marshall, 2006), dimethylamine (Anirudhan et al., 2006; Zhang et al., 2012), triethylamine (Xu et al., 2012, Xu and Shen, 2011, Xu et al., 2009), and urea (Benyoucef and Amrani, 2011; Karachalios, 2012).
Due to the poor interactivity between cellulose and quaternary ammonium compounds, cross-linking agents are used to convert cellulose into more active cellulose ether. The epoxy cellulose ether then is grafted with different amines (Karachalios, 2012; Marshall and Wartelle, 2004). This procedure has been employed in a majority of studies on quaternization by Anirudhan et al. (2006), Wang et al. (2010), and Xu et al. (2012, 2010, 2009). In addition, a cross-linking step has been found to prevent the loss of carboxylated components from lignocellulosic materials (Nada and Hassan, 2006). The most commonly used cross-linking reagent is epichlorohydrin. However, in some cases, choline chloride derivative (Karachalios, 2012), N-(3-chloro-2-hydroxypropyl) (Wartelle and Marshall, 2006), and ethylenediamine (Xu et al., 2011) are used alternatively.

Because epichlorohydrin and quaternary ammonium compounds are not soluble to each other, some organic solvents are employed, such as N, N-Dimethylformamide (DMF) (Anirudhan et al., 2006; Xu et al., 2011; Zhang et al., 2012) and methanol (Xu et al., 2010). Occasionally, pyridine (Anirudhan et al., 2006; Xu et al., 2010; Zhang et al., 2012) and imidazole (Karachalios, 2012) are used as catalysts to open the ring of the epoxide group in the base medium (Xu et al., 2010).

Another method to make the reaction between cellulose and quaternary ammonium compounds occur is to synthesise an aminated intermediate first, which can efficiently react with cellulose later. Xu et al. (2010) utilised this two-step process to synthesise quaternized wheat straw. In the first step, epichlorohydrin (EPI) was reacted with triethylamine in methanol to yield the aminated intermediate. In the second step, wheat straw was reacted with the intermediate in the presence of pyridine to produce aminated wheat straw. Equally, in an earlier study, Tshabalala et al. (2004) proposed a reaction pathway for the synthesis of pine bark anion exchanger. This procedure includes two steps:

Initially, poly-allylamine hydrochloride (PAA•HCl) was reacted with epichlorohydrin (EPI) to form epoxy - PAA•HCl as the aminated intermediate. Next, quaternized pine bark was developed by reacting the epoxy - PAA•HCl with bark polyphenol. As a result, a network of fixed cationic sites of quaternary ammonium, with mobile chloride
ions as anion exchangers, was formed on the bark surface. In the same way, the
quaternization of coconut shell fibres was achieved by epoxide formation, followed by
the reaction between the epoxide and lignin-cellulose materials (de Lima et al., 2012).

Karachalios (2012) claimed that the major problem with the quaternization process
was the use of toxic solvents or reagents. For that reason, the author proposed to utilise
a mixture of choline chloride derivative and urea, in the presence of imidazole for
quaternization of wood residues. The advantage of this procedure was the use of non-
hazardous reagents and bi-functional compounds that played the role of both reagent
and solvent.

It can be noted that, among various quaternary ammonium compounds used for
amination reactions, urea appears to be the best. Remarkably high adsorption
capacities were attained with all sorbents modified with urea, for example, sawdust
(116.25 mgP/g) and wood residues (205.63 mgP/g) (Benyoucef and Amrani, 2011;
Karachalios, 2012). When wood residues were used to prepare cationized adsorbents,
urea modified sorbent showed a phosphate adsorption capacity of 205.63 mg/g, far
superior to that of PAA•HCl modified sorbent, 25.65 mg/g (Karachalios, 2012;
Karthikeyan et al., 2004). Apparently, urea is much better than PAA•HCl in promoting
the phosphate removal capacity of quaternized AWBs. Another promising ammonium
quaternary salt is 2-hidroxypropyltrimethyl ammonium chloride, which resulted in
exceptionally high adsorption capacity of coconut shell fibres, up to 200 mg/g (de
Lima et al., 2012). The results verify the potential of quaternization in enhancing the
phosphate sorption capacity of AWBs.

The quaternization of AWBs is influenced by the nature and dosage of raw
biomaterials, as well as the volume of modifying agents. Wartelle and Marshall (2006)
developed an anion exchange resins from 12 types of AWBs. Comparing their
phosphate adsorptive properties, they discovered that the lignin content of AWBs
determined the efficacy of quaternization. Specifically, AWBs with lower lignin:
cellulose ratios could react more efficiently with N-(3-chloro-2-hydroxypropyl)
trimethylammonium chloride (CHMAC) and yield better anion exchange resins. Xu et
al. (2010) found that reaction temperature, reaction time and dosage of epoxy propyl-
triethyl-ammonium-chloride intermediate were influential factors to the quaternization of wheat straw. The results showed that the maximum phosphate removal was achieved at the following conditions: reaction temperature 55 °C; reaction time 3 h; and intermediate dosage 35 ml. Wang et al. (2010) examined the effect of sorbent dosage, temperature and volume of modifying agents on the phosphate removal of modified giant reed. The results of single-factor experiments indicated that the optimum conditions for quaternization of giant reed were giant reed dosage 4 g; epichlorohydrin dosage 10 ml; DMF (N,N-dimethylformamide) dosage 5 ml; EDA (ethylenediamine triethylamine) dosage 2 ml; and at 60 - 70 °C. Based on the results of orthogonal experiments, they concluded that the dosage of EDA was a critical factor, influencing the preparation of quaternized giant reed.

However, the application of quaternized AWBs is still limited. This can be explained due to loss of the adsorption capacity and mass of adsorbents during adsorption and desorption. Anirudhan et al. (2006) conducted a stability analysis of modified banana stem for four cycles. They discovered a capacity loss of around 12%. Karachalios (2012) revealed a decline of 5.92% in the ability of quaternized wood residues, after five consecutive operation cycles. Notably, de Lima et al. (2012) observed a complete loss of adsorption capacity of modified coconut shell fibres when the modified adsorbent was treated with HCl. The authors attributed this to the physical degradation of the adsorbent by HCl. A weight loss of 12 - 18% of the quaternized wheat straw was reported by Xu et al. (2011) after using 1.0 M HCl as an elution solution. They attributed this to the damage of cellulose/hemicellulose structure, which resulted from the corrosion of HCl. Conversely, Anirudhan et al. (2006) and Karachalios (2012) found minor or negligible loss of capacity and mass. It indicates the significance of selecting the appropriate AWBs and elution solutions to enhance the recyclability of quaternized AWBs.

It should be kept in mind that the removal of phosphate using AWBs based adsorbents has the advantage of being environmentally friendly. Therefore, the use of hazardous solvents and quaternizing agents is considered as a major drawback of the process (Abdul and Aberuagba, 2005; Karachalios, 2012). Xu et al. (2010) claimed that the
formation of large amounts of odoriferous wastewater prevented the wide application of pyridine as a catalyst in the synthesis of quaternized AWBs adsorbents.

On the other hand, the utilisation of neutral salts with high concentrations for desorption of P from AWBs may increase the salinity in arable lands, once P desorbed by this method is recovered and applied as fertilisers (Loganathan et al., 2014).

2.6.2.3 Anionization – sulfate surface coating

The third modification method capable of improving phosphate adsorption ability is the anionization, which is the reaction between AWBs and an anion, being sulfate the most commonly used.

Song et al. (2007) investigated the effect of sodium dodecyl sulfate (SDS) modification on a coconut-based activated carbon adsorbent, regarding its adsorption capacity towards several ions. The best results were achieved for the adsorption of cations. The adsorption capacity of Pb^{2+}, for example, was increased from 5.29 mg/g to 54.47 mg/g when SDS at a solid:liquid ratio of 1:10 was used to modify the coconut-based activated carbon adsorbent. On the other hand, the adsorption capacity of PO_{4}^{2-} did not increase considerably with the sulfate surface coating. When the same conditions were applied, the adsorption capacity went from 32.25 mgP/g to 33.31 mgP/g. This can be explained by the higher affinity between the coconut-based activated carbon adsorbent and sulfate, than between this adsorbent and phosphate.

Table 2.6 shows a summary of the main advantages and disadvantages of the various modification methods presented previously.

<table>
<thead>
<tr>
<th>Method</th>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thermal activation</td>
<td>No consumption of chemicals; Ideal for AWBs with porous structure, high content of CaCO_{3}</td>
<td>High energy consumption; Special equipment requirement; Significant weight loss of adsorbents</td>
</tr>
<tr>
<td>Chemical activation</td>
<td>High efficiency;</td>
<td>Large consumption of chemicals; Environmental contamination; Equipment erosion</td>
</tr>
</tbody>
</table>
### Literature Review

<table>
<thead>
<tr>
<th>Method</th>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>Steam activation</td>
<td>Minimisation of chemical use; Ideal for AWBs with porous structure, high content of CaCO₃</td>
<td>Special equipment is needed</td>
</tr>
<tr>
<td>Metal loading</td>
<td>Simple operation; High efficiency; High selectivity toward phosphate anions; Ideal for AWBs with high affinity toward loading metals; Wide application</td>
<td>High cost of loading metal; Limited stability and reusability of biosorbents due to metal detachment during adsorption; Environmental contamination caused by leaked metals; Extra operational cost due to metal reloading requirement</td>
</tr>
<tr>
<td>Quaternization</td>
<td>High efficiency; High regeneration of adsorbents; Ideal for AWBs with low lignin: cellulose ratios; Wide application</td>
<td>Complicated process; Secondary pollution by toxic solvents or quaternizing reagents; Less selectivity toward PO₄³⁻ anions; Weight and capacity loss of adsorbents after several cycles of operation</td>
</tr>
<tr>
<td>Sulfate coating</td>
<td>Efficacy depends on adsorbents; Limited application</td>
<td>Simplicity</td>
</tr>
</tbody>
</table>

In terms of practical application, cost comparisons between adsorbents developed from AWBs and the commercial ones should be conducted. However, this type of information is particularly rare in the literature. Biswas et al. (2007) predicted that the metal loaded orange waste gel would be cheaper than commercial adsorbents provided that the water treatment plant was adjacent to a juicing factory. The lack of information on the cost/benefit analysis of the process can be considered as a significant research gap, which needs to be filled in future research.

### 2.6.3 Adsorption fundamentals and applications

#### 2.6.3.1 Adsorption mechanisms

Understanding the adsorption mechanisms is necessary for optimising the adsorption process. Several information (pH profile, desorption, kinetic, activation energy) and techniques (FTIR, XRD, TEM) are required to clarify the adsorption mechanism, due
to its complex nature. The mechanisms for adsorption of P onto AWBs based adsorbents have been reported to include ion exchange, ligand exchange, surface precipitation and diffusion.

**Ion exchange**

Ion exchange is associated with very fast, weak and reversible adsorption, which occurs through outer-sphere complex. It replaces an ion on the surface of an ion exchanger by a chemically equal number of another ion while preserving the electroneutrality of the ion exchanger (Loganathan et al., 2014). The ion exchange was found to be the dominant adsorption mechanism in many studies on P removal using AWBs, such as banana stem (Anirudhan et al., 2006), wood residue (Karachalios, 2012), and giant reed (Xu et al., 2011). A typical method to predict the type of adsorption is based on the activation energy (E) magnitude. While E value in the range of 8 – 16 kJ/mol represents the chemical adsorption, the E value lower than 8 kJ/mol stands for physical adsorption (Mahmoud, 2015). The E values for the sorption of P onto modified wheat residue, modified sawdust, and calcined waste eggshell were found to be 3.39, 3.08, 8.04 kJ/mol, respectively. It implies that physical adsorption might be the prevailing sorption mechanism in these cases (Benyoucef and Amrani, 2011; Köse and Kivanç, 2011; Xu et al., 2009). Based on the effect of pH, Anirudhan et al. (2006) concluded that the removal of P using quaternized banana stem (BS) could mainly be attributed to ion exchange between Cl \(^{-}\) of quaternary mine group and HPO\(_4\)^{2-} / H\(_2\)PO\(_4\)^{-} in the solution as follows:

\[
2\text{BS-CH}_2\text{-N}^+\text{(CH}_3\text{)}_2\text{Cl}^- + \text{HPO}_4^{2-} \rightarrow \text{[BS-CH}_2\text{-N}^+\text{H(CH}_3\text{)}_2\text{]}_2\text{HPO}_4^{2-} + 2\text{Cl}^- \quad (2.6)
\]

\[
\text{BS-CH}_2\text{-N}^+\text{(CH}_3\text{)}_2\text{Cl}^- + \text{H}_2\text{PO}_4^- \rightarrow \text{BS-CH}_2\text{-N}^+\text{H(CH}_3\text{)}_2\text{H}_2\text{PO}_4^- + \text{Cl}^- \quad (2.7)
\]

Similarly, Xu et al. (2011) proposed that ion exchange could be an important pathway for the remediation of P by modified giant reed. The replacement of chloride ions in the amine groups of quaternized giant reed by phosphate ions in the solution could occur as follows:

\[
\text{R}^-\text{-N}^+\text{(CH}_2\text{CH}_3\text{)}_3\ldots\text{Cl}^- + \text{H}_2\text{PO}_4^- \rightarrow \text{R}^-\text{-N}^+\text{(CH}_2\text{CH}_3\text{)}_3\ldots\text{H}_2\text{PO}_4^- + \text{Cl}^- \quad (2.8)
\]
From FTIR results, de Lima et al. (2012) suggested that the modification of coconut shell fibres with ammonium quaternary salt led to the integration of $\text{−NH}_2$ groups into the material. Thus, the removal of P using quaternized coconut shell fibres occurred mainly via electrostatic interactions between $\text{−NH}_2$ groups and $\text{PO}_4^{3−}$ anions.

Ligand exchange

Ligand exchange is considered as chemical sorption, which is characterised by fast, strong and less reversible adsorption. It may happen through inner-sphere complex when $\text{PO}_4^{3−}$ anions create a covalent chemical bond with a metallic cation on the surface of AWBs. It leads to the liberation of other anions, which are formerly attached to the metallic cation (Loganathan et al., 2014).

This mechanism was reported for the case of decontaminating P using natural and iron impregnated coir pith (Krishnan and Haridas, 2008). The authors suggested that in the pH range of $2.0 − 3.5$, the ligand exchange occurred between $\text{H}_2\text{PO}_4^−$ ions and surface $\text{OH}^−$ groups to form inner-sphere complexation as follows:

$$\text{CP-OH} + \text{H}_2\text{PO}_4^− + \text{H}^+ \rightarrow \text{CP}-(\text{H}_2\text{PO}_4) + \text{H}_2\text{O} \quad (2.9)$$

$$\text{CP-Fe(OH)} + \text{H}_2\text{PO}_4^− + \text{H}^+ \rightarrow \text{CP-Fe(H}_2\text{PO}_4) + \text{H}_2\text{O} \quad (2.10)$$

From the effect of pH, Biswas et al. (2007) concluded that the adsorption of P onto metal loaded orange waste (SOW) gels was possibly due to a ligand exchange mechanism between $\text{PO}_4^{3−}$ ions in the solution and $\text{OH}^−$ ions coordinated with the metal ions on the orange waste gels. The authors suggested that loaded metal ions could be easily converted into hydrated forms, for example $[\text{Ln}$$\text{(H}_2\text{O})_n]^{3+}$, $[\text{Zr}_4(\text{OH})_8(\text{H}_2\text{O})_{16}]^{8+}$ and $[\text{Zr}_8(\text{OH})_{20}(\text{H}_2\text{O})_{24}]^{12+}$ species with the abundant amount of $\text{OH}^−$ ions and $\text{H}_2\text{O}$ molecules. $\text{H}_2\text{O}$ molecules were deprotonated by releasing $\text{H}^+$ ions to form $\text{OH}^−$ ions, which could be replaced by $\text{PO}_4^{3−}$ ions via ligand exchange mechanism.

Surface precipitation

When the concentration of components of the precipitate surpasses the solubility product of the precipitate, the precipitation of P with metallic ions may take place on the surface of AWBs. This mechanism is described as fast and hardly reversible.
adsorption. With the help of XRD and FTIR results, Shin et al. (2005) verified the contribution of surface precipitation to PO$_4^{3-}$ binding onto La$^{3+}$ loaded bark fibre. Based on kinetic studies, Namasivayam et al. (2005) concluded that the removal of P by oyster shell powder was probably due to the precipitation of P as calcium phosphate.

**Intra-particle diffusion**

This process takes place inside pores and cavities of AWBs. It is characterised by irreversible and very slow adsorption, which may last from several days to months (Loganathan et al., 2014). It is well recognised that if intraparticle diffusion mechanism prevails, a plot between PO$_4^{3-}$ adsorption capacity and the square root of the contact time should be a straight line passing through the origin (Nguyen et al., 2014a). However, the relationship attained in a study by Karachalios (2012) was non-linear. That indicated that intraparticle diffusion could not play a significant role in the sorption of PO$_4^{3-}$ onto quaternized wood residues. Based on TEM results, Riahi et al. (2009) suggested that intraparticle diffusion led to the accumulation of PO$_4^{3-}$ into internal cells of date palm fibres.

**Co-existing mechanisms**

It is quite common that the adsorption process occurs via several co-existing mechanisms. Tshabalala et al. (2004) observed a reduction in PO$_4^{3-}$ uptake with increasing ionic strength and the presence of SO$_4^{2-}$, and NO$_3^-$ anions. For that reason, they suggested that ion exchange and Lewis acid-base interactions might be responsible for the retention of PO$_4^{3-}$ ions onto cationized milled wood residues. From P surface loading and spectroscopic analysis results, Shin et al. (2005) claimed that ion exchange and surface precipitation could contribute to the elimination of P by La$^{3+}$ treated juniper bark fibre. Similarly, physical and chemical sorption mechanisms were found to co-exist in the studies conducted by Benyoucef and Amrani (2011), Mezenner and Bensmaili (2009), and Huang et al. (2010). Also, Karachalios (2012) proposed that the adsorption of PO$_4^{3-}$ onto quaternized pine bark residues resulted from both boundary layer and intraparticle diffusion mechanisms.
2.6.3.2 Desorption mechanisms

Desorption determines the reusability of the adsorbent and recovery of P. Distilled water, salts, acids, and bases can act as agents to P desorption. Distilled water is generally used in an attempt to reduce the cost of desorption chemicals and mitigate adverse impacts on the environment. Namasivayam and Sangeetha (2004) investigated the potential of eluting P from ZnCl$_2$ activated coir pith carbon by distilled water. The authors found that desorption was favoured at pH 2 (30%) and pH 11 (50%), while it was suppressed in the pH range of 3 – 11 (< 10%). The high desorption ability at pH values 2 and 11 could be explained by the dissociation constants of phosphate and the dominant phosphate species at different pH values. At pH 2, unionised H$_3$PO$_4$ species are dominant. These phosphate species have a poor affinity for the sorbent, and thus provide favourable conditions for P desorption. At pH 11, more OH$^-\text{ions}$ are available in the solution, leading to stronger competition among HPO$_4^{2-}$ and PO$_4^{3-}$ for binding sites. Consequently, desorption was efficient at pH 11. Nevertheless, the maximum desorption efficiency was relatively low (50%). The author explained that PO$_4^{3-}$ ions were retained via both ion exchange and chemisorptions mechanisms, and only PO$_4^{3-}$ ions captured by the ion exchange mechanism could be desorbed.

On the other hand, Mallampati and Valiyaveettil (2013) observed a relatively high desorption capacity (90%) in a very short time (10 min), when distilled water at pH 12 was employed in the case of desorbing P from Zr$^{4+}$ loaded apple peels. The successful desorption at high pH value was explained by the replacement of PO$_4^{3-}$ on apple peel surface by OH$^-\text{anions}$ in the solution.

Desorption can also be achieved through the use of salts, such as NaCl and KCl. In some studies, the use of these salts at different concentrations resulted in desorption efficiencies as high as 99.8% for 0.2 M NaCl from quaternized wood residues (Karachalios, 2012); 95.4% for 0.1 M NaCl from wheat straw anion exchanger (WS-AE) (Xu et al., 2010), and 100% for 0.1 M NaCl from modified giant reed (Xu et al., 2011). Conversely, inferior desorption capacities could be detected in other studies, for example, 0.7% for 0.5 M NaCl from calcined waste eggshell (Köse and Kivanç, 2011), and 11.2% and 13% for 0.01 M for KCl from granular date stones and palm
surface fibres, respectively (Ismail, 2012). Loganathan et al. (2014) suggested that neutral salts would work well as desorption solutions just in the case of weak and reversible sorption, whereby ion exchange is an important pathway for the P removal (Karachalios, 2012; Xu et al., 2010). In contrast, for strong and less reversible sorption, which is controlled by ligand exchange, surface precipitation or chemisorptions mechanisms, the efficacy of these salts is usually low (Ismail, 2012; Köse and Kivanç, 2011). The higher concentrations of neutral salts seem to improve desorption ability. A rise in the concentration of NaCl from 0.001 to 0.1 M increased the P desorption efficiency of modified giant reed by 48.7% (Xu et al., 2011). However, the use of neutral salts at high concentrations for desorption will increase the salinity of arable lands once the desorbed P is recovered and applied as fertilisers (Loganathan et al., 2014). The advantage of eluting P using neutral salts is the minor loss of the uptake capacity and mass of the adsorbent after several cycles of operation. Karachalios (2012) reported that the adsorption capacity was decreased by only 5.6% after five cycles of adsorption and desorption using 0.2 M NaCl. Likewise, Xu et al. (2010) revealed that using 0.1 M NaCl as a desorption solution led to the reduction of 9.6% in the P uptake capacity of the adsorbent. The slight weight loss (1 – 3%) was reported when 0.1 M NaCl was used for eluting P from modified giant reed (Xu et al., 2011). The stability of the adsorption capacity and mass of the adsorbents enable their reusability.

To further improve the desorption efficiency of P, acids or bases are often used to substitute distilled water and neutral salts. Among various acids and bases used for this purpose, NaOH and HCl are most commonly used. They usually present extremely high desorption efficiencies. Anirudhan et al. (2006) reported a desorption efficiency of 97.1% when 0.1 M NaOH was used as desorption solution and 85% for 0.4 M HCl. Also, 95% efficiency was reported by Biswas (2008) for 0.2 M NaOH, 97.5% for 0.1 M HCl (Xu et al., 2010), 100% for 0.1 M NaOH and HCl (Xu et al., 2011), and 95.6% for 0.05 M NaOH (Zhang et al., 2012). High efficacy of acids or bases could be explained by the low affinity of H$_3$PO$_4$ (in acidic medium), and HPO$_4^{2-}$ and PO$_4^{3-}$ (in alkaline medium) toward binding sites on AWBs surface. Another reason for that is
the stronger competition in the alkaline medium between OH⁻ ions and \( \text{PO}_4^{3-} \) for binding sites on AWBs.

It is worth mentioning studies conducted by Ismail (2012) and Zhang (2012), where the adsorption was controlled by the chemisorptions mechanism. While 0.01 M KCl exhibited inadequate desorption (11.2 – 13%), satisfactory elution was observed for 0.05 M NaOH (95.6%). This provides strong evidence that bases are superior to neutral salts for P desorption in the case of strong sorption. Both Xu et al. (2011) and Zhang et al. (2012) found that a higher concentration of NaOH promoted desorption. This was probably due to stronger competition between OH⁻ ions and \( \text{PO}_4^{3-} \) for binding sites.

Though HCl and NaOH are proven to be effective eluents, their application could result in some side effects. The loss in the adsorption capacity was shown to be 12% for 0.1 M NaOH (Anirudhan et al., 2006) or 10.53% for 0.1 M HCl (Xu et al., 2010). Particularly, the complete loss of the adsorption capacity of modified coconut shell fibres was recorded after the second cycle of reuse. This could be ascribed to the physical degradation of the adsorbent (de Lima et al., 2012). Xu et al. (2011) revealed a weight loss of 12 – 18% as a result of using 1 M HCl as a desorption solution. They attributed this to the corrosion of the cellulose/hemicellulose structure. In addition, Biswas (2008) reported the release of La³⁺ during desorption when 0.4 M HCl was employed as an eluant. Given the practical application, these effects are undesirable as they may reduce the stability and thus restrict the reusability of AWBs based adsorbents.

### 2.6.3.3 Factors affecting P adsorption performance

Understanding the factors that influence the adsorption performance is fundamental to promote process optimisation. The main factors reported to affect P adsorption performance are solution pH, initial P concentration, adsorbent dose, adsorbent particle size, effect of competing anions and organic matter, contact time and temperature.
Solution pH

The solution pH can affect the dissociation of phosphate species (Figure 2.1), the chemical state of binding sites, and the affinity of phosphate species towards binding sites. The pH profile is useful for elucidating sorption mechanisms, optimising the adsorption process, and selecting proper desorption solutions. Hence, a majority of studies on P adsorption using AWBs based adsorbents have been devoted to determining the ideal solution pH values.

AWBs based adsorbents tend to sequester PO$_4^{3-}$ anions effectively in a specific pH range while extremely acidic or alkaline medium is found to suppress the process. Yue et al. (2010) found that the pH range of 4 – 9 favoured the adsorption of PO$_4^{3-}$ onto modified giant reed. However, the pH value below 4 or above 9 was found to hinder the process. The authors explained this by dissociation constants of phosphate, dominant phosphate species in the solution, and the affinity of phosphate ions towards binding sites. The dissociation constants of H$_3$PO$_4$, H$_2$PO$_4^-$ and HPO$_4^{2-}$ are 2.12, 7.21 and 12.67, respectively (Biswas, 2008). Consequently, the presence of phosphate species in the solution might vary, depending on the solution pH. In the pH range of 4 – 9, H$_2$PO$_4^-$ and HPO$_4^{2-}$ species are dominant. Due to their strong affinity toward binding sites, the sorption of phosphate was enhanced. In contrast, at pH below 4, H$_3$PO$_4$ and HPO$_4^{2-}$ species are the most common. Their inferior affinities toward binding sites led to the unsuccessful decontamination of phosphate. In the same way, at pH above 9, HPO$_4^{2-}$ and PO$_4^{3-}$ species are prevalent. The weak affinity of these species for the active adsorption sites combined with strong competition between OH$^-$ ions and PO$_4^{3-}$ ions for adsorption sites hampered the process. Similarly, the effective pH range was found to be 5 – 7 for modified banana stem (Anirudhan et al., 2006); 7 – 10 for metal loaded orange waste gel (Biswas, 2008); 3.5 – 6 for quaternized pine bark residues (Karachalios, 2012); 3 – 10 for ZnCl$_2$ activated coir pith carbon (Namasivayam and Sangeetha, 2004); 3 – 11 for modified sugarcane bagasse (Zhang et al., 2012); and 4 – 9 for modified giant reed (Yue et al., 2010). The optimum pH values were found to be low, for example, 2 or 3 in work performed by Jeon and Yeom (2009); Krishnan and Haridas (2008); Mallampati and Valiyaveettil (2013). On the
other hand, the best pH values were found to be high, for example, 7.5 or 10 in the studies by Benyoucef and Amrani (2011) and Jyothi et al. (2012). The former result was explained by the dominance of H$_2$PO$_4^-$ species and their affinity for binding sites in acidic medium (Mallampati and Valiyaveettil, 2013). In contrast, the latter finding was ascribed to the possible existence of natural compounds and metal ions, such as Ca, Mg, Fe, Al, Cu, Zn inside these AWBs, which had a strong affinity toward HPO$_4^{2-}$ in alkaline medium (Jyothi et al., 2012). In some studies, the pH had a minor effect on the sorption of P in a wide range, for example, 4-10 for crab shells (Jeon and Yeom, 2009), 5.0 – 10.5 for oyster shell powder (Namasivayam et al., 2005), and 2.0 – 7.5 for scallop shells (Yeom and Jung, 2009). Especially, de Lima et al. (2012) claimed that pH could hardly affect the sorption of PO$_4^{3-}$ onto coconut fibre. The results showed that many AWBs based adsorbents are highly effective in a wide pH range. This property represents an appreciable advantage of AWBs derived adsorbents over conventional adsorbents for PO$_4^{3-}$ removal.

**Initial P concentration**

There is a common trend that the P uptake capacity increases, while the P removal efficiency decreases as the initial concentration of P augments. Riahi et al. (2009) reported that the PO$_4^{3-}$ adsorption capacity of date palm fibres increased from 1.45 to 5.85 mg/g as the initial phosphate concentration increased from 10 to 110 mg/L. These results were consistent with those reported by Anirudhan et al. (2006), Kumar and Pal (2015), Mezenner and Bensmaili (2009), Xu et al. (2009), Yue et al. (2010), and Zhang et al. (2012). Kumar and Pal (2015) and Yue et al. (2010) attributed this to the stronger driving force to convey PO$_4^{3-}$ ions from the solution to the adsorbent’s surface at a greater PO$_4^{3-}$ initial concentration. Higher initial P concentration led to higher PO$_4^{3-}$ availability, increasing the interaction between PO$_4^{3-}$ and binding sites, improving the P uptake capacity of the adsorbent (Mezenner and Bensmaili, 2009; Riahi et al., 2009).

Mezenner and Bensmaili (2009) claimed that the P removal of iron hydroxide eggshell waste decreased from 95 to 64% with increasing initial concentration of P from 2.8 to 110 mg/L. A similar trend was reported for sugarcane bagasse by Zhang et al. (2012). The authors explained this by a higher PO$_4^{3-}$ to the active binding sites ratio at the
higher $PO_4^{3-}$ initial concentration. For a given adsorbent dose, the number of binding sites is constant. Thus, an increase in the initial $PO_4^{3-}$ concentration would lead to a reduction in its percentage removal.

**Adsorbent dose**

The general trend is that the phosphate removal efficiency increases with a rise in the adsorbent dosage to a particular level then remains constant or reduces slightly with further increase in the adsorbent dose. The better $PO_4^{3-}$ removal efficiency at higher AWBs dose is explained by more adsorption sites and larger surface area available at a higher dose (Köse and Kivanç, 2011; Xu et al., 2009; Zhang et al., 2012). The reduction in the $PO_4^{3-}$ removal efficiency when further increase at adsorbent dose beyond its optimum level could be attributed to the higher resistance to mass transfer, particle aggregation and repulsive forces between binding sites (Ismail, 2012; Mezenner and Bensmaili, 2009; Riahi et al., 2009). An increase in the dose of AWBs also results in an increase in the $P$ uptake capacity due to an increase in the available adsorption sites. Riahi et al. (2009) found that the $PO_4^{3-}$ uptake increased from 3.75 to 4.69 mg/g as date palm fibre dose increased from 2 to 6 g/L. However, a further increase in adsorbent dose suppressed the sorption process. This can be explained by weak interaction between $PO_4^{3-}$ ions and the adsorbent as a result of the roll-up of fibres at excessive doses.

**Adsorbent particle size**

Chen et al. (2012) found that $PO_4^{3-}$ uptake capacity increased with a decrease in oyster shell diameter from 590 to 180 μm. Similarly, Yeom and Jung (2009) revealed that 100 mg $PO_4^{3-}$/L could be removed entirely by 1 g of scallop shells of 0.045 mm diameter in 3 h, whereas it was scarcely eliminated by that of 3 mm in 80 h. In the same way, Jeon and Yeom (2009) found that crab shells particles $< 1$ mm in diameter showed a removal percentage $> 85\%$, whereas only $50\%$ was attained by the 3.35 mm particles.
These results prove that the smaller particle size of the adsorbents favoured the P adsorption processes. However, to avoid clogging problems in a packed bed reactor, the optimum particle size needs to be identified and applied.

Co-existing ions

Examining the effects of co-existing ions is necessary to enhance the practical application of the adsorbents. Namasivayam and Sangeetha (2004) reported that Cl\(^-\), NO\(_3\)\(^-\), MoO\(_4\)\(^2-\), and VO\(_3\)\(^-\) slightly affected the PO\(_4\)\(^3-\) removal by ZnC\(_2\) activated coir pith carbon. Equally, Biswas et al. (2007) revealed that the addition of Cl\(^-\), CO\(_3\)\(^2-\), and SO\(_4\)\(^2-\) did not affect the adsorption of PO\(_4\)\(^3-\) onto La\(^3+\) loaded orange waste gel significantly. In a later study, Biswas (2008) revealed that Cl\(^-\) (0.56 mM), CO\(_3\)\(^2-\) (0.33 mM), and SO\(_4\)\(^2-\) (0.42 mM) hardly affected the sorption of PO\(_4\)\(^3-\) (0.20 mM). Köse and Kivanç (2011) claimed that the supplementation of SO\(_4\)\(^2-\), NO\(_3\)\(^-\), and NH\(_4\)\(^+\) with the concentrations ranging from 10 to 50 mg/L had minor influences on the retention of PO\(_4\)\(^3-\) onto calcined waste eggshell. Jyothi et al. (2012) discovered that such foreign anions as Cl\(^-\), SO\(_4\)\(^2-\), NO\(_3\)\(^-\), and CO\(_3\)\(^2-\) with the same concentration as that of PO\(_4\)\(^3-\) hardly interfered with the sorption of PO\(_4\)\(^3-\) by thermally modified barks/stems and their ashes of *Ficus religiosa, Cassia auriculata, Punica granatum* and *Calotropis gigantean*. The adsorption of PO\(_4\)\(^3-\) by AWBs was not strongly affected by the presence of co-anions, implying the high applicability of AWBs derived adsorbents in the real wastewater. However, Namasivayam and Sangeetha (2004) found that the presence of ClO\(_4\)\(^-\), SeO\(_3\)\(^2-\) and SO\(_2\)\(^2-\) with the same concentrations as that of PO\(_4\)\(^3-\) hampered the removal of PO\(_4\)\(^3-\) ions.

Karachalios (2012) claimed that SO\(_4\)\(^2-\) was superior to NO\(_3\)\(^-\) in competing with PO\(_4\)\(^3-\) for binding sites. The higher Cl\(^-\) concentrations resulted in the lower PO\(_4\)\(^3-\) uptake. It is interesting to note that the presence of divalent cationic ions in liquid, for example Ca\(^{2+}\), Mg\(^{2+}\), Cu\(^{2+}\), Zn\(^{2+}\), Fe\(^{3+}\) and Ni\(^{2+}\) with the concentration 10 times greater than that of PO\(_4\)\(^3-\) boosted the PO\(_4\)\(^3-\) extraction by thermally activated barks/stems and their ashes of *Ficus religiosa, Cassia auriculata, Punica granatum* and *Calotropis gigantean* (Jyothi et al., 2012). The positive effect of divalent cationic ions on the adsorption
suggests a way to improve the PO₄³⁻ adsorption capacity of these adsorbents, which is metal loading.

**Natural organic matter (NOM)**

Natural organic matter commonly present in wastewater/manure can reduce P adsorption due to competition for adsorption sites. Boyer et al. (2011) found that NOM impeded phosphate removal of engineered and low-cost adsorbents by occupying adsorption sites or complexing metal ions. Also, Afridi et al. (2019) investigated the effect of citric, humic and oxalic acids on the PO₄³⁻ uptake by anodised iron oxide nanoflakes. Results showed a reduction in the adsorption efficiency of 50%, 40% and 32% for the 3 types of organic matter, respectively. The authors suggested that this was given by the fact that most organic acids exist in the form of anions in water and would compete for the active adsorbent sites.

**Contact time**

The contact time is an indicator of the adsorption kinetics. Therefore, it is a key factor in evaluating the efficacy of AWBs based adsorbents (Eljamal et al., 2013). In many cases, the adsorption was found to be rapid, reaching equilibrium in approximately 1 h. The equilibrium time was reported to be 20 min for quaternized wood residues (Karachalios, 2012), 25 min for modified giant reed (Yue et al., 2010), 40 min for modified sawdust (Benyoucef and Amrani, 2011) and 60 min for natural date palm wastes (Ismail, 2012) and sugarcane bagasse (Zhang et al., 2011). In contrast, longer contact time is necessary for the equilibrium to be reached by other AWBs. The short contact time means that AWBs do not have to be kept in reactors for a long time, and thus space can be saved. It can be considered as an advantageous feature of potential AWBs, from a practical application point of view.

However, it was reported to be 15 h for La³⁺, Ce³⁺ and Zr⁴⁺ loaded SOW gels (Biswa, 2008), 12 h for iron impregnated coir pith (Krishnan and Haridas, 2008), and 6 h for Zr⁴⁺ loaded apple peels (Mallampati and Valiyaveettil, 2013).
Temperature

Normally, the adsorptive removal of PO$_4^{3-}$ by AWBs based adsorbents is temperature sensitive. Some adsorption processes are endothermic while others have an exothermic nature. Mezenner and Bensmaili (2009) found that the retention of PO$_4^{3-}$ by iron hydroxide eggshell was enhanced with a rise in the temperature from 20 to 45 °C. From the positive $\Delta H$ (81.84 kJ/mol), they concluded that the adsorption was endothermic. It was assumed that higher temperature was responsible for the better solubility of iron hydroxide eggshell compound, and this produced more iron and calcium hydrolysis complexes. Consequently, the phosphate precipitation was enhanced. A similar observation was noted by Benyoucef and Amrani (2011), Boujelben et al. (2008), Chen et al. (2012), Kumar et al. (2010), Peng et al. (2012), and Yeom and Yung (2009).

On the contrary, Yue et al. (2010) observed that the P uptake by modified giant reed declined from 19.89 to 17.79 mg/g as the temperature increased from 20 to 60 °C, indicating the exothermic nature of the adsorption process. From negative values of $\Delta G$ and $\Delta H$, Karachalios (2012) concluded that the adsorption of PO$_4^{3-}$ by quaternized pine bark residues was exothermic. These results were in harmony with those reported by Köse and Kivanç (2011) and Xu et al. (2009). They explained that the higher temperature resulted in stronger leakage of PO$_4^{3-}$ ions from AWBs surface into the solution (Xu et al., 2009).

2.6.3.4 P removal by modified AWBs based adsorbents

Since natural AWBs typically exhibit very low affinity for P, they need modification to be efficient in eliminating P from wastewaters (Mallampati and Valiyaveettil, 2013). This section will investigate the P adsorption of AWBs based adsorbents, which are developed by different modification methods.

Krishnan and Haridas (2008) found that impregnation of coir pith with Fe$^{3+}$ solution enhanced the phosphate retention ability of coir pith from 5 to 6 times. Supporting the Eberhardt and Min’s (2008) argument that the phosphate adsorption capacity of modified wood particles was governed by the amount of loaded Fe$^{2+}$, Carvalho et al.
Literature Review

(2011) reported that the phosphate adsorption capacity of Fe\(^{2+}\) impregnated sugarcane bagasse increased 2.25 times as compared to the reference.

The maximum P adsorption capacity (Q\(_{\text{max}}\)) of metal loaded AWBs in the literature varies in a wide range (2.05 – 174.68 mg/g). It can be ascribed to the difference in nature, the composition of AWBs, and the concentration of loading metals.

Among the AWBs that are modified following the metal loading method, Fe\(^{2+}\) treated carboxymethylated sugarcane baggage fibre and saponified Zr\(^{4+}\) loaded SOW gel are the ones that present the highest adsorption capacity, being 49.57 mg/g and 172 mg/g, respectively (Biswas, 2008; Carvalho et al., 2011), values higher than several commercial adsorbents found in the market (Table 2.5). This is a piece of sound evidence for the influence of metal loading on improving P adsorption capacity of AWBs.

Regarding the adsorption performance of AWBs modified by the quaternization method, researchers also show an improvement in comparison with their raw counterparts. Zhang et al. (2012) reported that the phosphate uptake capacity of quaternized sugarcane bagasse (MSBG) and raw sugarcane bagasse (SBG) was 21.30 and 1.1 mg/g, respectively. They attributed this to the higher zeta potential of MSBG (32 mV), as compared to that of SBG (-22 mV). Due to electrostatic interactions, the positive zeta potential of MSBG favoured the retention of phosphate while the negative zeta potential of SBG hampered the adsorption process.

Similarly, Xu et al. (2011) claimed that amino grafted giant reed demonstrated an excellent phosphate adsorption capacity (54.67 mg/g), compared with raw giant reed (0.863 mg/g). Quaternized AWBs based adsorbents are compared with commercial adsorbents, in term of phosphate adsorption capacity, to evaluate their applicability. A comparative study between quaternized soybean hulls and a commercial adsorbent (QA52) showed that quaternized soybean hulls (0.64 mmol/g) were better than QA52 (0.46 mmol/g) in P elimination (Marshall and Wartelle, 2004). Since both of these adsorbents are mainly composed of cellulose, the comparison provides a foundation for the replacement of high-cost, commercial, cellulose-based resins by low-cost, natural AWBs based sorbents in the remediation of phosphate pollution. Given the
search for potential AWBs for quaternization, Wartelle and Marshall, (2006) recommended the use of AWBs with low lignin:cellulose ratio, because of their high affinity for quaternizing reagents. These results highlight the potential of improving the phosphate uptake capacity of AWBs by quaternization.

Thermal activation is efficient in boosting the P removal of AWBs. Huang et al. (2016) found that preheating oyster shell in the temperature range of 100 - 400 °C improved its adsorption capacity for PO$_4^{3-}$ ions. While natural oyster shells could hardly remove any PO$_4^{3-}$ from an 80 mL wastewater solution with 20 g/L of PO$_4^{3-}$, the removal efficiency of preheated oyster shells reached up to 100% after 3 or 4 days. This is attributed to the increase in the pore size and surface area. Peng et al. (2012) found that better PO$_4^{3-}$ uptake was achieved for pine sawdust char produced at higher pyrolysis temperature. Table 2.7 shows the maximum adsorption capacity of modified AWBs, as well as their modification methods.

Table 2.7 The maximum phosphate adsorption capacity of modified AWBs

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Modifying agent</th>
<th>Mechanism</th>
<th>Adsorption capacity (mg/g)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coconut shell fibres</td>
<td>Ammonium quaternary salt</td>
<td>Chemisorption</td>
<td>200</td>
<td>de Lima et al., 2012</td>
</tr>
<tr>
<td>Wood agricultural residues</td>
<td>Chlorocholine chloride</td>
<td>Ion exchange</td>
<td>67.1</td>
<td>Karachalios, 2012</td>
</tr>
<tr>
<td>Sugarcane bagasse</td>
<td>DMA, DMF, EPI*, Pyridine</td>
<td>Chemical process</td>
<td>21.3</td>
<td>Zhang et al., 2012</td>
</tr>
<tr>
<td>Okara</td>
<td>NaOH + 0.25 M FeCl$_3$</td>
<td>Chemisorption + ion exchange</td>
<td>14.66</td>
<td>Nguyen et al., 2015</td>
</tr>
<tr>
<td>Apple peels</td>
<td>NaOH + 0.1 M ZrO$_2$Cl.8H$_2$O</td>
<td>Electrostatic interaction</td>
<td>20.35</td>
<td>Mallampati and Valiaveettil, 2013</td>
</tr>
<tr>
<td>Activated alumina</td>
<td>Sulfate coating</td>
<td>Anion exchange</td>
<td>49.67</td>
<td>Choi et al., 2012</td>
</tr>
<tr>
<td>Pine sawdust char</td>
<td>Fast pyrolysis</td>
<td>Pore diffusion</td>
<td>15.11</td>
<td>Peng et al., 2012</td>
</tr>
</tbody>
</table>

*DMA - Dimethylamine; DMF - N,N-dimethylformamide, EPI - Epichlorohydrin
2.7 Justification of iron modified cellulose as adsorbent

Approximately 91% (4 million ha) of the agricultural land in Ireland is grassland while only 9% is arable land (0.4 million ha) (Hamelinck et al., 2004). Grass is an excellent perennial energy crop with low input and high yield (up to more than 15 t DM/ha/a) (Xie, 2012). The total solids content of grass is about 17%, in which are the cell wall (fibre) and the cell contents (sugars, oil, protein, minerals, others) (Figure 2.14).

The fibre in the grass is measured as neutral detergent fibre (HDF), which is the insoluble fraction composed by cellulose, hemicellulose, pectin and lignin, which remains after boiling in a neutral solution (Teagasc, 2016). Cellulose is the main component of plant fibre, giving the plant rigidity. Cellulose is a biopolymer raw material and has served mankind in numerous applications as a construction material, mainly in the form of intact wood and textile fibres such as cotton or flax, or in the form of paper and board. Cellulose is a versatile starting material for chemical conversions aiming at the production of artificial, cellulose-based threads and films, as well as a variety of stable cellulose derivatives used in many areas of industry and domestic life (Klemm et al., 2005).
In one repeating unit of cellulose molecule, there are methylol and hydroxyl functional groups. Due to the absence of sidechains or branching, cellulose chains can exist in an ordered structure. Therefore, cellulose is a semicrystalline polymer, and it contains both crystalline and amorphous phases. Although it is a linear polymer and contains two types of hydroxyl groups, primary hydroxyl in the methylol group (eCH$_2$OH) at C-6 and secondary hydroxyl groups (eOH) at C-3 and C-4, both of which are hydrophilic, it does not dissolve in water and in common solvents due to strong hydrogen bonds between the cellulose chains (Figure 2.15). As a result, the hydrogen bonds between the cellulose chains and van der Waals forces between the glucose units lead to the formation of crystalline regions in cellulose (Gupta et al., 2016).

Cellulose extracted from grass silage was chosen for investigation in this study due to its insolubility in water, non-toxicity, easy acquiring and abundant availability. Moreover, due to the existence of large amounts of hydroxyl and carboxyl groups on its cell walls, cellulose can quickly and efficiently get involved in chemical modification reactions (Benyoucef and Amrani, 2011).

2.8 Summary

Phosphorus is a crucial nutrient for the fertilisers industry, and there are no known substitutes for it. Besides, as the readily available reserves are becoming scarce, it is
fundamental to find alternative sources. On the other hand, when excess P reaches the waterbodies, it causes severe water pollution.

In this way, there are several known methods capable of removing P from water. In order to reduce the cost associated with P recovery, as well as to add value to waste materials, there is a trend of utilising agriculture waste by-products as the base for the development of adsorbents. Thus, cellulose presents itself as a right choice, due to its chemical structure that allows its involvement in modifications, as well as being low cost, abundant and no toxic.

As agriculture waste by-product adsorbents present low adsorption capacity in their natural form, suitable modifications are required. Among the available methods, metal loading presents excellent adsorption performance with cellulosic materials.
Chapter 3 Development of Iron Modified Cellulose as Phosphorus Adsorbent
3.1 Overview

The choice of a proper adsorbent is fundamental for the success of the adsorption process. This chapter introduces the development of iron modified cellulose as a P adsorbent.

3.2 Introduction

A suitable adsorbent must have high adsorption capacity, high affinity towards the adsorbate, wide availability and relatively low cost. AWBs currently are being investigated as adsorbents, mainly due to their wide availability and low cost. However, as discussed in Chapter 2, in its natural form, AWBs have low adsorption capacities, which need to be increased with surface modifications.

This modification could be thermal or chemical activation. The thermal activation is achieved by carbonisation at high temperatures while chemical activation involves their impregnation with a chemical (Yargic and Ozbay, 2019). After the activation, the porous structure of the material is changed and the pore volume is increased. Surface modification can significantly improve the adsorption capacity of an adsorbent by incorporating functional groups on the surface of the material. This can be done via metal loading (Biswas, 2008; Carvalho et al., 2011; Mallampati and Valiyaveettil, 2013) or quaternization (Benyoucef and Amrani, 2011; de Lima et al., 2012; Karachalios, 2012; Zhang et al., 2012). The grafted functional groups act as adsorption sites for sequestering phosphate from the aquatic medium (Krishnan and Haridas, 2008).

Previous studies have shown that the compounds of multivalence metals have a high affinity for anions, including phosphate (Ruixia et al., 2002). In addition, the metal loading method is quite efficient and straightforward. Hence, recently, the development of P adsorbents from agricultural by-products using metal loading method has received considerable attention (Nguyen et al., 2019). The metal loaded P adsorbents include Fe\textsuperscript{3+} loaded sawdust (Unnithan et al., 2002), Fe\textsuperscript{3+} loaded seed waste
Development of Iron Modified Cellulose as Phosphorus Adsorbent

(Shrestha et al., 2018), Zn$^{2+}$ loaded coir pith activated carbon (Namasivayam and Sangeetha, 2004), La$^{3+}$ loaded juniper fibre (Shin et al., 2005), Fe$^{3+}$ loaded coir pith (Krishnan and Haridas, 2008), Zr$^{4+}$, La$^{3+}$, Ce$^{3+}$, and Fe$^{3+}$ loaded orange waste gels (Biswas et al., 2008), Fe$^{3+}$ loaded eggshell (Mezenner and Bensmaili, 2009), Zr$^{4+}$ loaded apple peels (Mallampati and Valiyaveettil, 2013), Fe$^{2+}$ loaded bagasse fibre (Carvalho et al., 2011), and Zr$^{4+}$ loaded okara (Nguyen et al., 2015).

Although several P adsorbents have been developed from AWBs using the metal loading method so far, it is still necessary to keep investigating new adsorbents developed through this technique to develop a competitive local solution.

Therefore, this study aimed to develop innovative, cost-effective and green P adsorbents from cellulose extracted from grass silage using metal loading method. Cellulose was modified with iron metals (Fe$^{2+}$ and Fe$^{3+}$) to form positively charged functional groups. With the presence of these binding groups, metal modified cellulose would be expected to remove phosphate efficiently from water. For the developed adsorbents, adsorption capacity, desorption and regeneration abilities, and metal leaching needed to be studied. The modification method was then further optimised. Finally, the selected adsorbent was characterised using SEM, EDS, FTIR, and other methods.

3.3 Materials and Methods

This section describes the materials, as well as the procedure executed to develop iron modified cellulose as an adsorbent.

3.3.1 Materials

3.3.1.1 Grass silage

The grass silage used in this study was collected from a farm located in Avoca (County Wicklow, Ireland). The grass silage was manually cut to less than 1.0 cm by a pair of scissors. The grass was washed twice with tap water and once with distilled water to
remove any trace of dirt. It was dried in a temperature controlled chamber at 35 °C for 8 hours. The dried grass was stored in a sealed plastic bag, and it was kept at a cold room (6 °C) until further use. The characteristics of the grass silage are given in Table 3.1.

Table 3.1 Characteristics of grass silage

<table>
<thead>
<tr>
<th>Characteristics</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>4.5</td>
</tr>
<tr>
<td>TS (% fresh weight)</td>
<td>21.6</td>
</tr>
<tr>
<td>VS (% fresh weight)</td>
<td>20.3</td>
</tr>
</tbody>
</table>

Generally, grass silage has an acidic pH due to the presence of lactic acid. Under good conditions, lactic acid bacteria (LAB), which are present on the grass, multiply rapidly and convert available sugars to lactic acid, causing a pH drop (Teagasc, 2016).

3.3.1.2 Chemical reagents

The chemicals used in this work were of analytical grade and were supplied by Sigma–Aldrich (Germany). For the cellulose extraction process, three different solutions were prepared. The sodium chlorite solution was made by adding 26 ml of a 25% sodium chlorite (NaClO₂) solution to a 500 ml volumetric flask. The pH adjustment was made with 99% acetic acid. The total volume was completed with distilled water, and the final solution was stored in a closed glass container protected from sunlight.

For the 10% NaOH solution preparation, 50 g of NaOH were weighted and placed in a beaker. A certain amount of distilled water was added, and this was placed on a magnetic stirrer until complete dissolution of NaOH. The solution was transferred to a 500 ml volumetric flask, which was completed with distilled water. For the NaOH/H₂O₂ solution, 10 g of NaOH were placed in a beaker with water, stirred with a magnetic stirrer until complete dissolution of NaOH. NaOH was then transferred to a 500 ml volumetric flask, where 30 ml of 33% H₂O₂ was added, and the volume was completed with distilled water.
For the metal loading process, 1.0 M of FeCl$_2$ - Fe or FeCl$_3$ - Fe were used, and the adsorption capacity tests were made with a 10 mgP/L KH$_2$PO$_4$ solution, prepared from a 10 M KH$_2$PO$_4$ stock solution.

For the metal modification optimisation process, five different concentrations of FeCl$_3$ - Fe solutions were prepared (0.1, 0.2, 0.3, 0.5, 1.0 M, respectively), and the adsorption capacity of the final adsorbent was tested with a 10 mgP/L KH$_2$PO$_4$ solution, made from a 10 M stock solution.

### 3.3.2 Methods

#### 3.3.2.1 Cellulose extraction

The cellulose extraction procedure adopted was adapted from Morán et al. (2008) and Johar et al. (2012), and it consisted of three main steps, prehydrolysis, pulping and bleaching.

The prehydrolysis aimed to remove the outer layer of grass, remove its green colour and expose the fibre (Figure 3.1). For this process, the dried grass was put in a beaker and the fibres were completely covered with sodium chlorite solution. Then, the pH was adjusted to around 4.0 with concentrated acetic acid, and the beaker was placed in a shaking bath whose temperature was set at 80 °C for 2 hours. If evaporation was observed, more sodium chlorite solution was added to ensure all the fibres were completely soaked at all times. The pH was also measured every 30 minutes and re-adjusted with acetic acid, if necessary. After the two hours, the beaker was left in the fume hood to cool down. The fibres were then put in a 425 µm aperture sieve and were washed 3 times with tap water and twice with distilled water.
The pulping step consisted of cooking of the fibres and removal of the hemicellulose (Figure 3.2). The fibres obtained from the previous step were placed in a beaker, and 10% NaOH solution was added until all the fibres were completely covered. The beaker was placed in the water bath at 75 °C for 3 hours. More NaOH solution was added if obvious evaporation was observed. After three hours, the beaker was left in the fume hood to cool down. The fibres were then put in a 425 µm aperture sieve and were washed three times with tap water and twice with distilled water.

Figure 3.1 Grass silage before (a) and after (b) prehydrolysis

Figure 3.2 Grass silage before (a) and after (b) pulping
The last step, bleaching, aimed at removing the colour of cellulose and further oxidising it (Figure 3.3). This was done by adding a certain volume of NaOH/H₂O₂ solution to a beaker containing the washed grass silage fibres from the previous step. The beaker was placed in a Thermo Scientific MAXQ 3000 orbital shaker at 60 rpm for 24 h. Then, the material was poured on the 425 μm sieve and was washed abundantly with distilled water.

![Grass silage before (a) and after (b) bleaching](image)

*Figure 3.3 Grass silage before (a) and after (b) bleaching*

Prehydrolysis, the first step of cellulose extraction, aimed to remove the lignin layer. The second step, pulping, removed the hemicellulose in grass silage. Finally, the bleaching step further oxidised the material, producing cellulose (Morán et al., 2008; Johar et al., 2012). Based on the mass difference before and after prehydrolysis, before and after pulping, and before and after bleaching, in comparison with the initial grass silage mass, the cellulose, hemicellulose, and lignin contents were found to be 34.3%, 29.6% and 8.6%, respectively.

### 3.3.2.2 Cellulose modification

In order to increase the adsorption performance of cellulose, two different metal salts were tested as cationization agents. For this, the cellulose fibres were put in two
beakers and were soaked in 1.0 M FeCl₃ or FeCl₂ solutions. The beakers were placed in the shaker for 24 h at ambient temperature (12 – 18 °C), allowing the modification reaction to occur. Then, the modified fibres were placed in the sieve and washed several times with distilled water until it was observed that the water was exiting completely clear. The modified cellulose fibres were stored wet in a plastic closed container until further use.

In order to verify the adsorption capacity of the two modified cellulose adsorbents, preliminary adsorption tests were conducted. For this, 1 g of each modified adsorbent was placed in a 50 ml plastic tube, which was filled with 20 ml of a KH₂PO₄ solution with P concentrations ranging from 10 to 300 mg/L, at ambient temperature (12 – 18 °C). The tubes were placed in a Stuart SB3 rotator at 20 rpm for 24 hours. Then, the solution was filtered by a 0.45 µm membrane filter and PO₄-P, iron concentrations in the filtrate were determined using a nutrient analyser (Konelab, Thermo Clinical Labsystems, Vantaa, Finland).

The amount of P adsorbed was calculated by Equation 3.1 (Nguyen et al., 2014a):

\[
q_e = \frac{V(C_o - C_e)}{W}
\]  

(3.1)

where \(q_e\) is the adsorption capacity (mg/g), \(C_o\) is the initial concentration of solution (mg/L), \(C_e\) is the concentration after adsorption equilibrium is reached (mL/L), \(W\) is the weight of adsorbent (g) and \(V\) is the volume of solution (L).

The maximum theoretical adsorption capacity was determined through the Langmuir equation (Nguyen et al., 2013):

\[
\frac{C_e}{q_e} = \frac{C_e}{Q_{max}} + \frac{1}{b} \times Q_{max}
\]  

(3.2)

where, \(b\) is a Langmuir constant related to the adsorption energy; \(Q_{max}\) is the theoretical maximum adsorption capacity (mg/g), also known as monolayer coverage of the surface.

Between the two tested adsorbents, the one that presented better adsorption performance, as well as the least metal leakage, was tested to optimise the metal loading phase. To test this, different concentrations of FeCl₃ – Fe solutions were tested as loading solutions (0.1, 0.2, 0.3, 0.4, 0.5, 0.6 and 0.8 M, respectively), in adsorption
tests. First 1 g of cellulose was placed in a 50 ml plastic tube, which was filled with 20 ml of one of the FeCl₃ solution. The tubes were placed in a Stuart SB3 rotator at 20 rpm for 24 hours. After, the iron modified cellulose was washed abundantly with distilled water and used in adsorption tests, as described previously. The testing was done in triplicate.

3.3.2.3 Characterisation of the adsorbent

The samples were characterised using FTIR, SEM, EDX, and BET surface area techniques. The FTIR of dry samples of grass silage, grass after prehydrolysis, cellulose and iron modified cellulose were obtained using an automatic infrared microscope Shimadzu FTIR AIM-8800 in the range of 400-4000 cm⁻¹. Field emission Scan Electron Microscopy (SEM, Hitachi S-4700) was used to examine the surface morphology of the dry solid samples. Before observation, the samples were fixed on aluminium stubs and coated with a thin layer of palladium-gold alloy. Bruker AXS Quantax 4010 Energy dispersive X-ray spectrometer was used for graphing the elemental make up of the dry samples, creating a map of the image highlighting where selected elements appeared. To measure the surface characteristics of iron modified cellulose, a Micromeritics ASAP 2010 BET instrument (Norcoss, GA, USA) was employed. N and helium gases were used as the adsorbate gas and carrier gas, respectively. The BET tube was loaded with 0.65 – 1.0 g of the sample. A filler rod was placed in the tube to increase the precision of the measurement by reducing the free volume in the tube. Each sample was degassed with helium at room temperature overnight and then immersed into a bath of liquid N. The surface characteristics were measured using N adsorption/desorption isotherms at the liquid N temperature and relative N pressures (P/Po) ranging 0.05 – 1.0. Relative N pressure was the ratio of the N pressure (P) to saturated N vapour pressure (Po) at the liquid N temperature. All data were collected and analysed automatically through the BET instrument software.
Physical properties

Physical characteristics of iron modified cellulose, such as density, porosity and permeability, were investigated according to the procedure outlined by Okochi (2013). For the density calculation, a certain quantity of dry iron modified cellulose was weighted and added to a volumetric flask of known mass. A known mass of distilled water was added to the flask, and the system was weighed. Finally, the flask was emptied, cleaned, dried, filled with distilled water and reweighed. The particle density focused on just the particles, and not the total volume that the particles and pore spaces occupied in a given sample, and it was calculated according to the following equation (Okochi, 2013):

$$\rho_p = \frac{\rho_w (m_{s+f} - m_f)}{(m_{s+f} - m_f) - (m_{s+f+w} - m_{f+w})} \quad (3.3)$$

where $\rho_p$ is the particle density (g/cm$^3$), $\rho_w$ is the water density (g/cm$^3$), $m_{s+f}$ is the mass of iron modified cellulose + volumetric flask (g), $m_f$ is the mass of empty flask (g), $m_{s+f+w}$ is the mass of iron modified cellulose + volumetric flask + water (g), and $m_{f+w}$ is the mass of the volumetric flask filled with water (g).

For the bulk density and porosity calculation, Equations 3.4 and 3.5 were adopted, respectively:

$$\rho_b = \frac{m}{v} \quad (3.4)$$

$$\eta = \left(1 - \frac{\rho_b}{\rho_p}\right) \times 100 \quad (3.5)$$

where $\rho_b$ is the bulk density (g/cm$^3$), $m$ is the mass of iron modified cellulose (g), $v$ is the volume of iron modified cellulose (cm$^3$), $\eta$ is the porosity (%), $\rho_p$ is the iron modified cellulose density (g/cm$^3$), and $\rho_b$ is the bulk density (g/cm$^3$).

The permeability coefficient of iron modified cellulose was determined using Darcy’s law (Nguyen et al., 2013):

$$K = \frac{Q \Delta L}{A \Delta H} \quad (3.6)$$
where $K$ is the permeability coefficient (m/day), $Q$ is the porous medium flow rate ($m^3/s$), $\Delta L$ is the length change (m), $A$ is the cross-sectional area ($m^2$), $\Delta H$ is the pressure head change (m). The apparatus used for permeability measurement is shown in Figure 3.4.

![Figure 3.4 Experimental design to determine the permeability coefficient of iron modified cellulose (Adapted from Nguyuen et al., 2015)](image)

The software Microsoft Office Excel Professional Plus 2013 was used to conduct the modelling and the graphs were created with the software OriginPro 2018 (Northampton, Massachusetts, USA).
3.4 Results and Discussion

In this study, two iron salts (FeCl$_2$.4H$_2$O and FeCl$_3$.6H$_2$O) were tested as metal loading agents for cellulose cationization. A better adsorbent was selected based on the criteria of high adsorption capacity and low metal leaching during adsorption.

3.4.1 Phosphate adsorption capacity

The maximum PO$_4^{3-}$-P adsorption capacity ($Q_m$) of ferric and ferrous chloride modified adsorbents was determined from Langmuir equation. It was found that cellulose modified by ferric chloride had the highest $Q_m$ value (19.0 mg/g), while the one modified by ferrous chloride presented a $Q_m$ value of 12.4 mg/g. The adsorption isotherms of both iron modified salts are given at Figure 3.5.

![Figure 3.5 Adsorption isotherms of ferric and ferrous iron modified cellulose (adsorbent dose 50 g/L, contact time 24 h, temperature 15 – 18 °C, initial P concentration range 10 – 300 mg/L)](image_url)
The \( Q_m \) value of the cellulose without metal loading was 1.39 mg/L. The results indicate that the ferrous and ferric modification increased phosphate adsorption capacities of cellulose by 13.67 and 8.94 times, respectively compared to the natural cellulose. Therefore, loading of the natural cellulose fibres with multi valence metals was an effective way to enhance its phosphate adsorption capacity.

### 3.4.2 Metal leaching from metal loaded adsorbents during adsorption

The leaching of metals, which were earlier loaded on the adsorbent, is evidence for the instability of the adsorbent and it is undesired because it would decrease the adsorption performance in the long term. Nguyen et al. (2019) tested the adsorption performance of zirconium loaded okara in five cycles of operation. Their results showed that the adsorption efficiency was reduced to 46.74% after the fifth cycle, and this reduction was attributed to metal leaching. For ferrous and ferric modified cellulose the leaching observed was 0.7 and 0.3%, respectively. This result provides evidence that the bonding between the cellulose and iron was strong.

This result is in agreement with the findings reported by Micháleková-Richveisová et al. (2017) and Cui et al. (2016) in studies of phosphate adsorption through iron impregnated corn cobs, garden wood waste and wood chips biochars, and ferric hydroxide-coated cellulose nanofibre hybrid, respectively. Their results show good iron retention in the surface of the bioadsorbents.

The results of the adsorption capacity of the tested adsorbents, combined with the metal leaching tests, show that ferric chloride would be a better agent for cellulose cationization and thus was chosen in further trials.

### 3.4.3 Effect of metal loading on adsorption

This study examined the effect of \( \text{FeCl}_3 \) solution concentration on \( \text{PO}_4^{3-} \) adsorption capacity of iron modified cellulose. As ferric chloride modified cellulose presented the
Development of Iron Modified Cellulose as Phosphorus Adsorbent

best adsorption performance and the lowest leaching, the effect of metal loading concentration was only tested for FeCl₃.

Seven different concentrations of FeCl₃ – Fe solutions were tested as loading solutions (0.1, 0.2, 0.3, 0.4, 0.5, 0.6, and 0.8 M, respectively), via adsorption tests. Their PO₄³⁻-P sorption capacities were compared and the results are depicted in Figure 3.6.

![Figure 3.6 Phosphorus percentage removal of iron modified cellulose in different iron loading solution concentrations (adsorbent dose 50 g/L, phosphorus concentration 10 mg/L, temperature 12 – 18 °C, contact time 24 h)](image)

As can be seen, using a FeCl₃ loading solution with a concentration equal to or greater than 0.3 M the adsorption performance was comparable. The larger the amount of Fe³⁺ deposited on the surface of iron modified cellulose, the more the positively charged sites were available, thus enabling the retention of more PO₄³⁻ anions.

Thus, cellulose modified with 0.3 M FeCl₃ solution was used in the subsequent tests.
3.4.4 Adsorbent characterisation

The applicability and the adsorption capacity of iron modified cellulose as an adsorbent rely on the physical characteristics of the material.

It was found that iron modified cellulose had a permeability of 0.0061 m/s, a particle density of 1.35 g/cm$^3$, a bulk density of 1.03 g/cm$^3$, and a porosity of 23.7%. According to Okochi (2013), these parameters for the electric arc furnace steel slag, another P adsorbent, were 0.0043 m/s, 3.732 g/cm$^3$, 1.861 g/cm$^3$ and 50.14%, respectively. It is evident that iron modified cellulose possesses a relatively low density and porosity. As a result, its applicability in column mode with a high bed height could be limited. A high bed height, associated with a low porosity adsorbent, could result in water ponding in the adsorption column.

3.4.5 FTIR analysis

The FTIR analysis was conducted with samples of grass silage, grass silage after prehydrolysis, cellulose and iron modified cellulose. The peaks corresponding to grass silage, grass silage after prehydrolysis and cellulose are depicted in Figure 3.7.
It can be observed that the three curves present similar peaks, in different intensities, because cellulose was a major constituent of grass silage. These peaks correspond to those found in typical cellulose (Morán et al., 2008). The broad band in the 3600 – 3100 cm\(^{-1}\) region is characteristic for stretching vibration of O-H and C-H bonds (Poletto et al., 2011; Rosa et al., 2010). This peak also includes inter- and intramolecular hydrogen bond vibrations in cellulose (Hospodarova et al., 2018). The broad band at 3550 – 3200 cm\(^{-1}\) and the weak peak at 3200 cm\(^{-1}\) are attributed to intermolecular stretching vibration of O-H bond (Rosa et al., 2010). The band at 2894 cm\(^{-1}\) is attributed to CH stretching vibration of all hydrocarbon constituent in polysaccharides. The broad band at 2900 – 2800 cm\(^{-1}\) belong to C-H stretching band in alkanes (Hospodarova et al., 2018). The band at 1642 cm\(^{-1}\) is attributed to the water molecules (Poletto et al., 2011; Rosa et al., 2010). Typical bands assigned to cellulose were observed in the region of 1630 - 900 cm\(^{-1}\). The absorption bands at 1428, 1367, 1334, 1027, and 896 cm\(^{-1}\) belong to stretching and bending vibrations of -CH\(_2\) and -
CH, -OH and C-O bonds in cellulose (Hospodarova et al., 2018). The band at around 1420 – 1430 cm⁻¹ is associated with the amount of the crystalline structure of the cellulose (Hospodarova et al., 2018). The bands at 1650 – 1750 cm⁻¹ are attributed to C=O stretching in carboxylic acids (Poletto et al., 2011).

Two new peaks were observed in FTIR spectra of grass after prehydrolysis and the cellulose compared to the grass. These are located at the 1150 and 900 cm⁻¹ regions, corresponding to C-O stretch and C-H bending, respectively (Socrates, 2004).

### 3.4.6 SEM analysis

SEM images (Figure 3.8) show a big change in the structures between grass and cellulose. The grass looked like a hard plaque, while cellulose presented itself as a fibrous structure.

![SEM images of grass (a), cellulose (b) and iron modified cellulose (c)](image)

*Figure 3.8 SEM images of grass (a), cellulose (b) and iron modified cellulose (c)*

This change in structure was favourable to the adsorption process; a fibrous structure would increase the surface area of cellulose. In the image of iron modified cellulose, it is possible to see spikes in the fibre, and EDS test was undertaken to identify the elements. EDS results show the presence of Fe and a small portion of Cl, as shown in Figure 3.9.
A sample of cellulose was also submitted to EDS test. Results showed a C:O ratio of 4:5 (Figure 3.10).

<table>
<thead>
<tr>
<th>Element</th>
<th>Weight%</th>
<th>Atomic%</th>
</tr>
</thead>
<tbody>
<tr>
<td>C K</td>
<td>41.09</td>
<td>49.94</td>
</tr>
<tr>
<td>O K</td>
<td>53.07</td>
<td>48.43</td>
</tr>
<tr>
<td>Cl K</td>
<td>0.69</td>
<td>0.28</td>
</tr>
<tr>
<td>Fe K</td>
<td>5.14</td>
<td>1.34</td>
</tr>
<tr>
<td>Totals</td>
<td>100.00</td>
<td></td>
</tr>
</tbody>
</table>

Figure 3.10 EDS test for cellulose
3.4.7 BET analysis

Fine particle sizes generally exhibit a higher P adsorption capacity than coarse particle sizes due to a greater relative surface area for adsorption (Okochi, 2013). However, a key concern with too fine particle sizes is that they are more prone to clogging in the P adsorption column, given their lower permeability. Thus, an ideal adsorbent should provide good hydraulic conductivity alongside a large surface area. That is why porosity is an important factor in choosing adsorbents. Particles that are porous will have a greater surface area and more exposed sorption sites, meaning that large grain sizes could still possess good sorption capacity and hydraulic conductivity (Sikdar and Anderson, 2007).

Specific surface area is one of the most important quantities used for the characterisation of various adsorbents (Choma and Jaroniec, 2001). It is defined as the total surface area of a solid or powder (which includes both external and internal accessible surfaces) per unit mass of the material, and largely determines many of its physical and chemical properties (Schroeder-Pedersen et al., 1997). To measure the surface characteristics, a Micromeritics ASAP 2010 BET instrument was employed in these experiments. It was found that the surface area of grass silage and iron modified cellulose were 18.3 and 41.8 m²/g, respectively.

This value was lower than surface areas of other adsorbents reported in the literature. Zhu et al. (2016) tested the surface area of bismuth impregnated biochar, a phosphate adsorbent, and found a value of 87.42 m²/g. Du et al. (2017) synthesised a polyvinyl acetate (PVA) adsorbent by co-precipitation of Fe-Mn oxide, that presented a BET specific surface area of 57.64 m²/g.

Yue et al. (2012) investigated the surface area of cotton fibres, composed mainly by cellulose, and found the value of 8.2 m²/g. The authors explained that the total pore volume and pore size distributions were very sensitive to swelling and drying treatments of the cotton fibre. They observed an irreversible reduction in the pore volume when the fibres were dried. This happened due to the removal of the intramolecular water molecules, allowing the cellulose chains to collapse. Thus, the
Development of Iron Modified Cellulose as Phosphorus Adsorbent

internal surface area of the cotton fibres was inaccessible to N₂ molecules, and the value reported by the BET test referred mainly to the adsorption measurement on the external surface.

3.5 Summary

Cellulose was obtained from grass silage following a simple extraction procedure. In order to improve its adsorption capacity, metal loading was applied. Ferric iron proved to be superior to ferrous iron, concerning adsorption capacity and metal leaching. The optimum metal loading condition was 0.3 M FeCl₃. In addition, the physical properties of iron modified cellulose were tested.
Chapter 4 Batch Study Adsorption with Iron Modified Cellulose
4.1 Overview

This chapter presents the feasibility of iron modified cellulose in P removal with batch studies.

4.2 Introduction

Phosphorus is an essential nutrient to the development of plants, animals and the industrial manufacture (Choi et al., 2012; Karachalios, 2012; Mezenner and Bensmaili, 2009). Phosphorus is often applied in excess to the land and excessive P reaches the water bodies, causing the phenomenon known as eutrophication. As a consequence, the water quality is deteriorated, and the life of aquatic creatures is threatened (Ismail, 2012; Jyothi et al., 2012). Therefore, the excessive amounts of P need to be removed from the water to protect water bodies from this undesirable phenomenon, and to pave the way for the P recovery as well.

Adsorption is a good technology for P removal, especially for its high effectiveness at low P concentrations, besides being simple to operate. On the other hand, commercial adsorbents can present high cost, limiting the usage of this technique worldwide. In an attempt to reduce the treatment cost, there is an emerging trend to use AWBs as P adsorbents (Zhang et al., 2014). The recycling of AWBs as P adsorbents helps the environment by reducing waste in a green way (Ismail, 2012). Moreover, it gives a chance to add values to AWBs and to develop an attractive and economical alternative to existing treatment methods (Peng et al., 2012). Nevertheless, AWBs in its natural forms present low adsorption capacity and, therefore, need to be submitted to modifications.

Considering the various methods of modification for the development of P adsorbents, metal loading seems to be favoured due to the simplicity and effectiveness. Among the different loading metals, Fe$^{3+}$ is usually a good choice due to its strong affinity for phosphate, high selectivity, large surface area, and chemical stability (Biswas, 2008). In Chapter 3, the steps to develop iron modified cellulose from grass silage were presented and discussed. This Chapter extensively investigated iron modified cellulose
in P recovery, with respect to influential factors, adsorption isotherms, solution pH, adsorbent dose, foreign anions, initial P concentration, contact time, temperature thermodynamics, and desorption. The maximum phosphate adsorption capacity was determined and the kinetic study was conducted to identify the rate of the adsorption process.

4.3 Materials and Methods
4.3.1 Materials

The synthesis of iron modified cellulose was described in Chapter 3.

Phosphorous adsorption of iron modified cellulose was tested through batch experiments. The batch tests were done using a 10 mgP/L KH₂PO₄ solution, made from a 10 M stock solution. The pH adjustment was made with dilute NaOH or H₂SO₄, when necessary. The pH, adsorbent dose and interference of foreign anions tests were done in 50 ml plastic tubes filled with 20 ml of the 10 mg P/L KH₂PO₄ solution. The tubes were placed in a Stuart SB3 rotator at 20 rpm. For the reaction kinetics test, 250 ml glass flasks filled with 200 ml of 10 mg P/L KH₂PO₄ solution were used. The flasks were put in a Thermo Scientific MAXQ 3000 orbital shaker.

The tests related to the effect of temperature on adsorption were done using 100 ml glass flasks filled with 50 ml of phosphate solution in varying initial concentrations. The flasks were put in a Thermo Scientific MAXQ 3000 orbital shaker placed inside a controlled temperature chamber.

After adsorption samples were taken from the flasks and were filtered with a 0.45 µm membrane filter. PO₄-P concentrations in the filtrate were determined using a nutrient analyser (Konelab, Thermo Clinical Labsystems, Vantaa, Finland).
4.3.2 Batch sorption experiments

The tests were performed in order to verify the adsorbent performance in different pH conditions, adsorbent doses, initial P concentrations, temperatures, as well as the interference of foreign anions and adsorption kinetics. The conditions adopted for each test are summarised in Table 4.1. All the tests were conducted in triplicate.

*Table 4.1 Batch tests of phosphate adsorption*

<table>
<thead>
<tr>
<th>Kinetic analysis</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>initial P concentration</td>
<td>10 mg/L</td>
</tr>
<tr>
<td>adsorbent dose</td>
<td>6 g/L</td>
</tr>
<tr>
<td>pH</td>
<td>5.6</td>
</tr>
<tr>
<td><em>Variable conditions</em></td>
<td></td>
</tr>
<tr>
<td>sample collection time</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.083, 0.017, 0.25, 0.5, 1, 1.5, 2.0, 5.0, 7.0, 15.0, 18.0, 24.0 h</td>
</tr>
</tbody>
</table>

| Effect of solution pH                   |       |
| adsorbent dose                         | 6 g/L |
| initial P concentration                | 10 mg/L|
| contact time                           | 4 h   |
| *Variable conditions*                  |       |
| pH                                     |       |
|                                        | 3, 4, 5, 6, 7, 8, 9, 10 |

| Effect of adsorbent dose                |       |
| contact time                           | 4 h   |
| pH                                     | 5.6   |
| *Variable conditions*                  |       |
| initial P concentration                |       |
|                                        | 5, 10, 15, 25 mg/L |
| adsorbent dose                         |       |
|                                        | 1, 2, 3, 4, 5, 6, 7, 8, 10 g/L |

| Effect of coexisting anions             |       |
| initial P concentration                | 10 mg/L |
| contact time                           | 4 h   |
| adsorbent dose                         | 6 g/L |
| pH                                     | 5.6   |
| *Variable conditions*                  |       |
| PO₄³⁻-P:SO₄²⁻ ratio                   | 1:10  |
| PO₃⁵⁻-P:Cl⁻ ratio                     | 1:10  |
| PO₄³⁻-P:CO₃²⁻ ratio                   | 1:10  |
| PO₃⁵⁻-P:NO₃⁻ ratio                    | 1:10  |
| PO₄³⁻-P:SO₄²⁻:Cl⁻:CO₃²⁻:NO₃⁻ ratio     | 1:10:10:10:10 |

| Effect of temperature and adsorption isotherm |       |
| contact time                                 | 4 h   |
Batch Study of Phosphate Adsorption with Iron Modified Cellulose

| adsorbent dose | 6 g/L |
| pH             | 5.6   |

**Variable conditions**
- initial P concentration: 10, 20, 50, 100, 150, 200, 250, 300 mg/L
- temperature: 25, 35, 45 °C

After adsorption, the adsorbent was separated from the solution by filtration through Whatman™ 1822-047 Grade GF/C filter paper (diameter: 4.7 cm, pore size: 1.2 μm). The P bearing adsorbent was washed lightly with distilled water to eliminate unbound P.

Desorption investigations were performed with desorption solutions, being distilled water, 0.1 M NaCl, 0.1, 0.2, 0.4, 0.5, 0.6, 1.0, 1.5, 2.0, 2.5, and 3.0 M NaOH, and 0.1, 0.2, 0.4, 0.5, 0.6, 1.0, 1.5, and 2.0 M HCl. 1g of the adsorbent was placed in a plastic 50 mL tube with 20 mL of desorption solution. The tubes were placed in Stuart SB3 rotator at 20 rpm for 24 hours; then the solution was filtered by a 0.45 μm membrane filter and PO₄-P concentration was determined using a nutrient analyser (Konelab, Thermo Clinical Labsystems, Vantaa, Finland).

### 4.3.3 Data analysis

The amount of P adsorbed was calculated through Equation 3.1.

To date, numerous mathematical models have been applied in the kinetic study. In this work, the experimental data were fitted to two well-known kinetic models to explore the main adsorption mechanisms, as well as to predict the adsorption rates. The Pseudo-first order and Pseudo-second order models based on equilibrium adsorption capacity (Nguyen et al., 2013) can be expressed by Equations 4.1 and 4.2, respectively.

\[
\ln(q_e - q_t) = \ln q_e - k_1 t \tag{4.1}
\]
\[
t/q_t = 1/k_2 q_e^2 + 1/t/q_e \tag{4.2}
\]

where \( q_t \) (mg/g) is the phosphate sorption capacity at time \( t \), \( k_1 \) (1/min) and \( k_2 \) (g/mg min) are the rate constant of pseudo-first-order adsorption and the equilibrium rate
constant of pseudo-second-order adsorption, respectively, and $q_e$ (mg/g) is the sorption capacity at equilibrium.

Adsorption isotherms and thermodynamics tests were performed at three different temperatures, 298, 308 and 318 K. Initial P concentrations ($C_i$) ranged from 10 to 300 mgP/L and the adsorbent dose used was 70 g/L. After the equilibrium time of mixing was reached, the equilibrium concentrations of phosphate in the supernatant ($C_e$) were determined. The sorption isotherms were described using the Langmuir, Freundlich and Temkin models, following Equations 3.2, 4.3, and 4.4, respectively (Nguyen et al., 2013; Panagiotou et al., 2018).

\[
\ln q_e = \frac{1}{n} \ln C_e + \ln K_F
\]  

(4.3)

\[
q_e = q_m \ln(K_T C_e)
\]  

(4.4)

where, $K_F$ and $n$ are characteristic constants of the system, and $K_T$ is an indicator for adsorption intensity.

The thermodynamic parameters of the adsorption process were determined from the experimental data obtained at 298, 308 and 318 K after 4 h of adsorption (Cui et al., 2016).

\[
\Delta G_0 = -RT \ln K_0
\]  

(4.5)

\[
K_d = q_e / C_e
\]  

(4.6)

\[
\ln K_0 = \frac{\Delta S_0}{R} - \frac{\Delta H_0}{RT}
\]  

(4.7)

where, $\Delta G_0$, $\Delta H_0$, and $\Delta S_0$ are Gibbs free energy change (kJ/mol), enthalpy change (kJ/mol) and entropy change (J/mol K), respectively; $K_d$ (L/mol) is the distribution coefficient for the adsorption, $T$ (K) is the absolute temperature and $R$ (J/mol K) is the universal gas constant (8.314 J/mol K).

The software Microsoft Office Excel Professional Plus 2013 was used to conduct the modelling and the graphs were created with the software OriginPro 2018 (Northampton, Massachusetts, USA).
4.4 Results and Discussion

This section presents the effects of initial P concentration, contact time, solution pH, temperature and coexisting anions in phosphate adsorption of iron modified cellulose.

4.4.1 Adsorption kinetics

The kinetics study provides information about the adsorption rate, fundamental for system design and practical application. The adsorption kinetics of phosphate on iron modified cellulose was investigated as a function of contact time in the range of 0 – 24 h at ambient temperature (12 – 18 °C). Results show that the adsorption reached 91% of the maximum within 2 h and then increased slowly until the adsorption equilibrium was reached (Figure 4.1).

![Figure 4.1 Adsorption kinetics of phosphate on iron modified cellulose (initial phosphorus concentration 10 mg/L, adsorbent dose 6 g/L, pH 5.6)](image)

This indicated that the adsorption process for phosphate on iron modified cellulose would happen in two different steps: an initial rapid adsorption, that can be attributed to driving force given by the concentration gradient of phosphate in aqueous solution
and a large number of active available sites on the external adsorbent surfaces of iron modified cellulose, and a slow process that continued until the equilibrium was achieved via the diffusion of ions into the pores of inner adsorbent spaces (Cui et al., 2016; Zhao et al., 2011; Al-Qunaibit et al., 2005).

To date, a few mathematical models were developed and applied in kinetics studies. The pseudo-first-order and the pseudo-second-order models (Equations 4.2 and 4.3, respectively) are used to investigate the adsorption kinetics and to predict the adsorption rates. Figure 4.2 presents the curves related to the experimental kinetics, as well as the predicted curves according to the pseudo-first-order and pseudo-second-order models. The sorption capacity at equilibrium considered was given by the Langmuir isotherm (Equation 3.2) and the kinetic parameters are shown in Table 4.2.

![Figure 4.2 Comparison among the experimental, pseudo-first-order, and pseudo-second-order adsorption curves (initial phosphorus concentration 10 mg/L, adsorbent dose 6 g/L, pH 5.6)](image)

As the correlation coefficient of the pseudo-first-order kinetic model ($R^2 = 0.983$) was relatively greater than that of the pseudo-second-order kinetic model ($R^2 = 0.891$), it can be assumed that the adsorption obeyed pseudo-first-order kinetics, and the rate of
adsorption was proportional to the number of unoccupied active sites on the adsorbent surface (Krishnan and Haridas, 2008; Cui et al., 2016).

**Table 4.2 Kinetic parameters of phosphate adsorption on iron modified cellulose**

<table>
<thead>
<tr>
<th>Kinetic parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td><em>Pseudo-first-order</em></td>
</tr>
</tbody>
</table>
| K<sub>1</sub>         | 1.04 h<sup>-1</sup>  
| R<sup>2</sup>       | 0.983  
|  
| *Pseudo-second-order* |  
| K<sub>2</sub>         | 1.31 g/mg.min  
| R<sup>2</sup>       | 0.891  

These results agreed well with those reported by Hokkanen et al. (2014) and Ren et al. (2015), in the cases of phosphate removal by nanostructured microfibrillated cellulose modified with carbonated hydroxyapatite and ferric oxides loaded biochar obtained from cotton stalk, respectively.

**4.4.2 Effect of Solution pH**

The solution pH can affect the chemical state of binding sites, the dissociation of phosphate species in aqueous solutions and the affinity of phosphate species towards binding sites (Nguyen et al., 2013). The effect of pH on phosphate adsorption by iron modified cellulose at the initial concentration of 10 mg P/L is shown in Figure 4.3. The adsorbent reached a 98.2% removal efficiency at pH 4 – 10.
In the pH range studied, phosphate exists in the forms of \( \text{H}_2\text{PO}_4^- \) and \( \text{HPO}_4^{2-} \) (Figure 2.1) (Karageorgiou et al., 2007). High removal efficiency shows that these species had high affinity towards the adsorbent. The presence of \( \text{H}_3\text{PO}_4 \) at pH 3 could also be the reason for the reduction in phosphate removal efficiency. These results are in agreement with that reported by Wang et al. (2016), who found that wheat straw-based amphoteric adsorbent showed maximum phosphate adsorption capacity at pH around 5.0. The researchers affirmed that in low pH conditions the dominant phosphate species was \( \text{H}_3\text{PO}_4 \), and presented a weak interaction with their adsorbent. At high pH range, \( \text{OH}^- \) ions may compete with phosphate for active sites, decreasing adsorption capacity (Nguyen et al., 2013; Cui et al., 2016).

The final pH after adsorption ranged from 2.5 to 3.2, at which phosphate predominant form was \( \text{H}_2\text{PO}_4^- \) (Figure 2.1). There was a final pH reduction when the initial pH ranged from 4 to 10. This could be attributed to adsorption of \( \text{OH}^- \) ions present in the solution (Ismail, 2012; Riahi et al., 2009). This is in agreement with the reported by Nguyen (2015), who observed a final pH range reduction from 3 – 11 to 2.2 – 3.7 in
phosphate adsorption by zirconium loaded okara. They also attributed this reduction to competition between $\text{PO}_4^{3-}$ and $\text{OH}^-$ ions.

Overall, the results show that iron modified cellulose is highly efficient in a broad pH range, which is an advantage when used in practice, saving operational costs related to pH adjustment.

### 4.4.3 Effect of adsorbent dose

The effect of adsorbent dose on P sorption by iron modified cellulose is depicted in Figure 4.4. The P removal efficiency increased from 56.6 to 68.6% when the adsorbent dose was increased from 1 to 2 g/L at initial $\text{PO}_4^{3-}$-P of 5 mg/L.

![Figure 4.4 Effect of adsorbent dose on phosphate adsorption under different initial P concentrations (contact time 4 h, pH 5.6, adsorbent dose range 1-10 g/L)](image)

The increase in P removal performance at higher adsorbent doses can be explained by the greater availability of adsorption sites or larger total surface area (Yue et al., 2010; Zhang et al., 2012). Therefore, for different initial P concentrations of 5, 10, 15, 25
mg/L, the optimal iron modified cellulose doses were determined as 4, 6, 8, 12 g/L, respectively, considering 4 h of contact time and pH 5.6.

4.4.4 Effect of coexisting anions

Coexisting anions such as Cl\(^-\), NO\(_3^-\), CO\(_3^{2-}\) and SO\(_4^{2-}\) are generally present in wastewater, which could interfere with the adsorption of phosphate through competitive adsorption. For this reason, the effects of coexisting anions on the phosphate adsorption were investigated. Results show that the anions did not affect adsorption capacity greatly; the phosphate removal was reduced only from 98.3 to 98.1, 98.1, 97.6, 98.2 and 98.2% for sulphate, chloride, carbonate, nitrate and all ions together, respectively (Figure 4.5).

![Figure 4.5 Effect of coexisting anions on P adsorption (contact time 4 h, pH 5.6, P: ion ratio 1:10)](image)

The results show that the ions had minor interference in P removal, showing high affinity of iron modified cellulose towards phosphate ions. This results are in
agreement with the report of Jyothi et al. (2012), which tested the effects of sulphate, fluoride, chloride, nitrate and carbonate in phosphate adsorption of barks or stems and their ashes of different plants, and observed a minor interference of these ions in phosphate adsorption. Qiu et al. (2015) selected sulphate ion as a representative to test its interference in a biomass-based hydrous zirconium oxide nanocomposite for phosphate adsorption and also found no significant adsorption capacity loss.

4.4.5 Adsorption Isotherms

The adsorption isotherms can provide an opportunity to find the maximum theoretical adsorption capacity and help to identify suitable isotherm models that can be applied in the system design. The phosphate adsorption isotherms of iron modified cellulose were tested at pH 5.6. The results are depicted in Figure 4.6. It can be seen that the adsorption capacity of iron modified cellulose for phosphate increased with increasing temperature.

![Figure 4.6 Adsorption Isotherms of phosphate onto iron modified cellulose (adsorbent dose 6 g/L, pH 5.6, contact time 4 h, initial P concentration range 10 – 300 mg/L)](image_url)
Langmuir, Freundlich and Temkin’s models were applied to the adsorption data at different temperatures, and the calculated parameters are summarised in Table 4.3. The R² values indicated that the Langmuir adsorption (R² = 0.994) model fit the data better compared with the Freundlich (R² = 0.955) and the Temkin models (R² = 0.966), indicating that the process happened in a monolayer fashion (Cui et al., 2016; Mallampati and Valiyaveettil, 2013).

Table 4.3 Isotherms parameters for phosphate adsorption onto iron modified cellulose

<table>
<thead>
<tr>
<th></th>
<th>Temperature (°C)</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>25</td>
<td>35</td>
<td>45</td>
</tr>
<tr>
<td><strong>1. Langmuir</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Qₘ (mgP/g)</td>
<td>19.0</td>
<td>19.0</td>
<td>20.1</td>
</tr>
<tr>
<td>Kₐ (L/mg)</td>
<td>128.9</td>
<td>140.8</td>
<td>177.2</td>
</tr>
<tr>
<td>Rₐ (at C₀ 10 – 300 mg/L)</td>
<td>0.00078 – 0.00003</td>
<td>0.00071 – 0.00002</td>
<td>0.00056 – 0.00002</td>
</tr>
<tr>
<td>R²</td>
<td>0.994</td>
<td>0.986</td>
<td>0.964</td>
</tr>
<tr>
<td><strong>2. Freundlich</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Kₚ (L/g)</td>
<td>159.1</td>
<td>196.3</td>
<td>275.5</td>
</tr>
<tr>
<td>n</td>
<td>1.746</td>
<td>1.731</td>
<td>1.624</td>
</tr>
<tr>
<td>R²</td>
<td>0.955</td>
<td>0.957</td>
<td>0.965</td>
</tr>
<tr>
<td><strong>3. Temkin</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>B (J/mol)</td>
<td>22.3</td>
<td>23.6</td>
<td>27.2</td>
</tr>
<tr>
<td>Kₜ</td>
<td>1.08</td>
<td>1.20</td>
<td>1.44</td>
</tr>
<tr>
<td>R²</td>
<td>0.966</td>
<td>0.950</td>
<td>0.890</td>
</tr>
</tbody>
</table>

The parameters Rₐ is the Langmuir separation factor, that indicates the type of isotherm, being = 1, > 1, 0 < Rₐ < 1 or = 0, linear, unfavourable, favourable or irreversible, respectively, and it is given by the Equation 4.8.

\[
R_L = \frac{1}{1 + K_L C_0}
\] (4.8)

Although Rₐ value is between 0 and 1, meaning the reaction is favourable, the value is close to 0, which is an indication of reaction hardly reversible. The Langmuir adsorption capacity (Qₘ) was determined to be 20.1 mgP/g at 45 °C, which was higher than most of the reported values by other researchers, as shown in Table 4.4.
### Table 4.4 Adsorption capacity of agricultural by-products adsorbents

<table>
<thead>
<tr>
<th>Agricultural by-product</th>
<th>Modifying agent</th>
<th>Adsorption capacity (mgP/g)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>palm surface fibers</td>
<td></td>
<td>8.50</td>
<td>Ismail (2012)</td>
</tr>
<tr>
<td>granular date stones</td>
<td></td>
<td>8.69</td>
<td>Ismail (2012)</td>
</tr>
<tr>
<td>coir pith activated carbon</td>
<td>H₂SO₄</td>
<td>2.52</td>
<td>Kumar et al. (2010)</td>
</tr>
<tr>
<td>date palm fibers</td>
<td>carboxymethylation + FeCl₂</td>
<td>5.85</td>
<td>Riahi et al. (2009)</td>
</tr>
<tr>
<td>sugarcane bagasse</td>
<td></td>
<td>49.57</td>
<td>Carvalho et al. (2011)</td>
</tr>
<tr>
<td>grass silage cellulose</td>
<td>FeCl₃·6H₂O</td>
<td>20.10</td>
<td>this study</td>
</tr>
<tr>
<td>coconut shell fibres</td>
<td>ammonium quaternary salt</td>
<td>65.23</td>
<td>De Lima et al. (2012)</td>
</tr>
<tr>
<td>ficus religiosa bark</td>
<td>ash</td>
<td>30.33</td>
<td>Gregory et al. (2013)</td>
</tr>
<tr>
<td>wheat residue</td>
<td>epichlorohydrin + N,N-dimethylformamide + ethylenediamine + triethylenediamine + triethylamine epichlorohydrin-epichlorohydrin-dimethylamine-trimethylamine epichlorohydrin-epichlorohydrin-trimethylamine</td>
<td>21.88</td>
<td>Xu et al. (2009)</td>
</tr>
<tr>
<td>cotton stalk</td>
<td>diethyleneetriamine-tributylamine</td>
<td>16.81</td>
<td>Xu et al. (2011)</td>
</tr>
<tr>
<td>wheat straw</td>
<td>diethyleneetriamine-tributylamine</td>
<td>19.77</td>
<td>Xu et al. (2011)</td>
</tr>
<tr>
<td>giant reed</td>
<td>dimethylformamide + ethylenediamine + triethylamine</td>
<td>6.49</td>
<td>Yue et al. (2010)</td>
</tr>
<tr>
<td>biochar</td>
<td>magnetite</td>
<td>3.38</td>
<td>Riddle et al. (2018)</td>
</tr>
<tr>
<td>zeolite</td>
<td>Ca(OH)₂</td>
<td>11.11</td>
<td>Markou et al. (2018)</td>
</tr>
<tr>
<td>apple peel</td>
<td>zirconium IV</td>
<td>20.35</td>
<td>Mallampati et al. (2014)</td>
</tr>
<tr>
<td>lignocellulosic butanol residue</td>
<td>ZrO₂</td>
<td>8.75</td>
<td>Zong et al. (2016)</td>
</tr>
</tbody>
</table>

The remarkably high adsorption capacity achieved by Carvalho et al. (2011) and De Lima et al. (2012) was explained by the combined modification method (carboxymethylation and FeCl₂) and by the fibres structure, allied to the modification with ammonium quaternary salt at high temperature, respectively.
4.4.6 Sorption thermodynamics

The thermodynamic parameters ($\Delta G^0$, $\Delta S^0$ and $\Delta H^0$) were calculated using the phosphate equilibrium concentration at different temperatures. Gibbs free energy change ($\Delta G^0$) is used to judge if a reaction is spontaneous, in equilibrium, or impossible, corresponding to $\Delta G^0 < 0$, $\Delta G^0 = 0$ or $\Delta G^0 > 0$, respectively (Stach et al., 2005).

Table 4.5 Thermodynamic parameters for iron modified cellulose phosphate adsorption

<table>
<thead>
<tr>
<th>T (K)</th>
<th>$\Delta G^0$ (kJ/mol)</th>
<th>$\Delta S^0$ (J/molK)</th>
<th>$\Delta H^0$ (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>298</td>
<td>-18.32</td>
<td>142.81</td>
<td>24.43</td>
</tr>
<tr>
<td>308</td>
<td>-19.15</td>
<td></td>
<td></td>
</tr>
<tr>
<td>318</td>
<td>-21.21</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The negative values of $\Delta G^0$ suggest that the adsorption process was spontaneous. The positive values of $\Delta S^0$ and $\Delta H^0$ indicate structural changes in the adsorbent, leading to an increase in the disorder of the solid/liquid system (Fan et al., 2009) and an endothermic process, respectively (Cui et al., 2016; Mezenner and Bensmaili, 2009). A positive value of $\Delta S^0$ reflects the affinity of the adsorbent towards the adsorbate species. The adsorbed solvent molecules, which are displaced by the adsorbate species, gain more translational entropy than is lost by the adsorbate ions, thus allowing for the prevalence of randomness in the system. The magnitude of $\Delta H^0$ may also give an idea about the type of sorption. The heat evolved during physical adsorption is in the range of 2.1 – 20.9 kJ/mol, while the heat of chemisorption generally falls into a range of 80 – 200 kJ/mol (Saha and Chowdhury, 2011). As the magnitude of $\Delta H^0$ fell in between the two ranges, physico-chemical adsorption process is prevalent.

4.4.7 FTIR analysis

The FTIR analysis was conducted with samples of iron modified cellulose after adsorption. The corresponding peaks are depicted in Figure 4.
The curve presents a few peaks characteristic of cellulose (Morán et al., 2008), as it is the base of the analysed material. The broad band observed at 3200 – 3400 cm\(^{-1}\) region is characteristic for stretching vibration of O-H and C-H bonds (Poletto et al., 2011; Rosa et al., 2010). This peak also includes inter- and intra-molecular hydrogen bond vibrations in cellulose (Hospodarova et al., 2018). The peak observed in the 2900 cm\(^{-1}\) band corresponds to the symmetric stretching vibration of CH groups in cellulose (Michell and Higgins, 1999).

The weak band at 2496 cm\(^{-1}\) is characteristic of the NaOH spectra, which could be attached to the cellulose chain after alkali treatment (Fengel and Strobel, 1994). The band located at the 2100 – 2200 cm\(^{-1}\) range was attributed to the CO bond (Mihaylov et al., 2007). The band at 1642 cm\(^{-1}\) corresponded to the presence of water molecules (Poletto et al., 2011; Rosa et al., 2010). Typical cellulose bands were observed in the region of 1630 – 900 cm\(^{-1}\). The absorption bands at 1428, 1367, 1334, 1027 cm\(^{-1}\) and 896 cm\(^{-1}\) belong to stretching and bending vibrations of -CH\(_2\) and -CH, -OH and C-O
bonds in cellulose (Hospodarova et al., 2018). The band at around 1420 – 1430 cm\(^{-1}\) is associated with the amount of the crystalline structure of the cellulose (Hospodarova et al., 2018).

The peaks for 1016 and 1052 cm\(^{-1}\) could be P–OH vibration for P compounds. The peak at 1032 cm\(^{-1}\) could be assigned to the O–C bond vibration of P–OC bond (Gaan and Sun, 2007). The peak observed at the 650 cm\(^{-1}\) band was also attributed to hydrogen bonds (Michell and Higgins, 1999).

### 4.4.8 Desorption Studies

Desorption studies are important to help in the identification of the mechanisms behind the adsorption process and to detect the bond strength between the adsorbate and the adsorbent. This study investigated desorption solutions of NaCl, HCl and NaOH with increasing concentrations, as well as distilled water. Of these, 0.1 M NaCl solution and distilled water showed very poor desorption efficiencies (< 2%). Increasing the concentrations of both HCl and NaOH solutions showed better desorption efficiencies (Figure 4.8).
When increasing the NaOH concentration from 0.1 to 2.0 M, the desorption efficiency increased from 34.5 to 54.6%. The successful desorption can be explained by the replacement of PO$_4^{3-}$ anions adsorbed onto iron modified cellulose by OH$^-$ ions in the desorption solution. The desorption results revealed that ion exchange might be a leading mechanism for the adsorption of PO$_4^{3-}$ by iron modified cellulose. This result was in line with an earlier study conducted by Unnithan et al. (2002), reporting that 98.2% of adsorbed P could be eluted with 0.1 M NaOH.

On the other hand, the desorption efficiency when HCl was used as the desorption agent was constant between 41 and 44% when the solution concentration was increased from 0.1 to 0.6 M. A further increase to 1.0, 1.5 and 2.0 M led to a reduction in the desorption efficiency to 19.9, 5.8 and 1.43%, respectively. This could have happened for cellulose degradation in acidic medium. This was reported by Qiu et al. (2015) in their investigation related to P removal onto a biomass-based hydrous zirconium oxide. They found a 44.3% decrease in phosphate desorption efficiency at pH 2 in comparison with the efficiency at pH 5 and attributed it to degradation of the biomass fibres.
4.5 Summary

This study demonstrated that iron modified cellulose extracted from grass silage had an outstanding ability to remove phosphate from aqueous solutions, with a P removal efficiency of 98%. The adsorbent presented good adsorption capacity in a wide range of pHs and high affinity towards P. The maximum adsorption capacity was found to be 20.1 mg/g, at 45 °C, superior to many other adsorbents developed from AWBs found in the literature. The Langmuir adsorption model fitted the adsorption isotherm and the adsorption system followed pseudo-first-order kinetics. The superior adsorption performance under neutral conditions could represent savings in costs related to pH adjustment. Based on these results, iron modified cellulose can be considered as an efficient and cost-effective approach for environmental remediation.
Chapter 5 Column Study of Phosphate Adsorption by Iron Modified Cellulose
5.1 Overview

This chapter further presents the ability of iron modified cellulose in P removal from aqueous solutions with column studies.

5.2 Introduction

P is an essential macro nutrient for living organisms and a fundamental material of many industries. P is also one of the major environmental concerns (Awual and Jyo, 2011). Recently, there is a growing trend in using low-cost adsorbents for P removal to reduce the cost of water treatment. In this context, several agriculture waste by-products have been tested as P adsorbents, e.g. apple peels, orange waste gel, bagasse, coir pith, and wood particles (Mallampati and Valiyaveettil, 2013; Biswas, 2008; Carvalho et al., 2011; Krishnan and Haridas, 2008; Eberhardt and Min, 2008). However, the biomaterials derived adsorbents often suffer from lack of mechanical strength, inefficiency in column adsorption, and low dynamic adsorption capacity (Awual and Jyo, 2011). To date, a majority of the studies on P adsorption from water and wastewater have been performed in the batch mode experiments (Nur et al., 2014). Though adsorption capacity acquired from batch equilibrium isotherm provides information about the effectiveness of P - adsorbent system, it is impossible to apply the result to continuous flow fixed-bed column, where the contact time is usually shorter than the equilibrium time (Kumar and Bandyopadhyay, 2006). Besides, the column breakthrough curve provides information on the dynamic adsorption capacity (Zach-Maor et al., 2011). Until this present work, little information is available on the sustainable use of agricultural by-products based adsorbents for P removal in the continuous flow fixed-bed column adsorption systems (Bottini and Rizzo, 2012; Li et al., 2013; Paudyal et al., 2013). Therefore, attention should be paid to these aspects to promote the practical application of agricultural by-products derived adsorbents.

In Chapter 4, with the batch mode experiments, iron modified cellulose was proven to be a promising P adsorbent. As the next stage, this Chapter extensively investigated the performance of iron modified cellulose in P removal in the column mode, with respect to different operating variables, such as flow rate, bed depth and initial P concentration. Its dynamic adsorption capacity was also assessed. Mathematical
models were applied in order to predict the breakthrough curve (Adams-Bohart, Thomas, Yoon-Nelson and BDTS). In addition, the adsorbent development cost was estimated from the lab research, and the P bioavailability to plants was also assessed.

5.3 Materials and Methods

5.3.1 Materials

The synthesis of iron modified cellulose was described in Chapter 3.

The column adsorption tests were conducted in plastic columns of 55 cm height and 0.80 cm inner diameter. A 1 cm layer of cotton was placed at the tip of the column to prevent the adsorbent from seeping out with the effluent. The column was packed with different amounts of iron modified cellulose to achieve the desired bed height. At first, iron modified cellulose was stirred thoroughly with distilled water for about 2 minutes to enable swelling and to remove air bubbles. After, the adsorbent was added into the column using the “slurry method” (Zach-Maor et al., 2011), in which the adsorbent was slowly poured into the column with water. A piece of wire was used to gently press the adsorbent from time to time, to ensure the cellulose was evenly distributed along the column. Another layer of cotton was placed on top of the adsorbent, to ensure an even flow of solution. The column filled with iron modified cellulose was left for four hours before the beginning of the adsorption tests, to ensure that the loosely bond water poured with the adsorbent had been drained out.

The column tests were conducted with a known concentration of KH$_2$PO$_4$ solutions, made from a 10 M stock solution. The feed solution containing various initial P concentrations was placed in a 1 L plastic bag, which was positioned on top of the column and was connected to it with an intravenous (IV) line. The device contained a drip chamber and a roller clamp, to adjust the flow rate. In this way, the feed solution was percolated through the column in the downward direction at different flow rates by gravity. Figure 5.1 shows a schematic draw of the column design components.
Effluent samples were collected at defined intervals of time with 2 mL plastic tubes for determination of the P concentration. The solutions collected were filtered by a 0.45 µm membrane filter and PO₄³⁻-P concentration was determined using a nutrient analyser (Konelab, Thermo Clinical Labsystems, Vantaa, Finland).

5.3.2 Column sorption experiments

The column tests were performed in order to verify the performance of iron modified cellulose at different flow rates, bed heights, as well as different initial P concentrations. The conditions adopted for each test are summarised in Table 5.1.
Table 5.1 Column experiment conditions

<table>
<thead>
<tr>
<th>Effect of flow rate</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>adsorbent mass</td>
<td>0.6 g</td>
</tr>
<tr>
<td>bed height</td>
<td>4.0 cm</td>
</tr>
<tr>
<td>initial P concentration</td>
<td>10.0 mg/L</td>
</tr>
<tr>
<td>pH</td>
<td>5.6</td>
</tr>
<tr>
<td>bed volume</td>
<td>2.0 cm³</td>
</tr>
<tr>
<td><strong>Variable conditions</strong></td>
<td></td>
</tr>
<tr>
<td>flow rate</td>
<td>4.1, 5.0, 6.2 mL/min</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Effect of bed height</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>initial P concentration</td>
<td>10.0 mg/L</td>
</tr>
<tr>
<td>flow rate</td>
<td>4.1 mL/min</td>
</tr>
<tr>
<td>pH</td>
<td>5.6</td>
</tr>
<tr>
<td><strong>Variable conditions</strong></td>
<td></td>
</tr>
<tr>
<td>bed height</td>
<td>2.2, 4.0, 6.2 cm</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Effect of initial P concentration</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>flow rate</td>
<td>4.1 mL/min</td>
</tr>
<tr>
<td>bed height</td>
<td>4 cm</td>
</tr>
<tr>
<td>pH</td>
<td>5.6</td>
</tr>
<tr>
<td>bed volume</td>
<td>2.0 cm³</td>
</tr>
<tr>
<td><strong>Variable conditions</strong></td>
<td></td>
</tr>
<tr>
<td>initial P concentration</td>
<td>5.0, 10.0, 15.0 mg/L</td>
</tr>
</tbody>
</table>

5.3.3 Calculation of breakthrough curve parameters

To evaluate the adsorption performance of a column, it is necessary to analyse the breakthrough curve. This can be done by calculating breakthrough curve parameters. The breakthrough time \( t_b \) and treated volume at the breakthrough time \( V_b \) are determined as the time and volume when the outlet P concentration \( C_t \) reached 10% of the inlet P concentration \( C_o \) \( (C_t/C_o = 0.1) \). Similarly, the exhaustion time \( t_s \) and treated volume at the exhaustion time \( V_s \) are defined as the time and volume when the outlet P concentration \( C_t \) reached 90% of the inlet P concentration \( C_o \) \( (C_t/C_o = 0.9) \). The total amount of P adsorbed onto iron modified cellulose column, \( q_{total} \) (mg) and the dynamic adsorption capacity, \( q_e \) (mg/g), are calculated according to the following equations (Paudyal et al., 2013; Sharma and Singh et al., 2013):
\[ q_{\text{total}} = \frac{Q}{1000} \int_{t=0}^{t=\text{total}} C_{\text{ad}} \, dt \approx \frac{Q}{1000} \sum_{i=1}^{n} \frac{1}{2} \left[ (C_i + C_{i+1}) \times (t_{i+1} - t_i) \right] \] (5.1)

\[ q_e = \frac{q_{\text{total}}}{M} \] (5.2)

where \( t_{\text{total}} \), \( Q \), \( M \), and \( C_{\text{ad}} \) are the total time for the column to reach exhaustion (min), volumetric flow rate (mL/min), the amount of adsorbent packed in the column (g), the difference in the initial P concentration and the effluent P concentration at time \( t \) caused by adsorption (mg/L), respectively. \( C_i \) (mg/L) is the effluent P concentration at a given time \( t_i \) (min).

The mass transfer zone (MTZ), which is defined as the length of the adsorption zone in the column, can be obtained from the following equation (Bulgariu and Bulgariu, 2013):

\[ MTZ = Z \left( \frac{t_s - t_b}{t_s} \right) \] (5.3)

where MTZ represents the length of the mass transfer zone (cm); \( Z \) is the bed height (cm); \( t_b \) is the breakthrough time (min); \( t_s \) is the exhaustion time (min). The main parameters of a typical breakthrough curve were shown at Figure 5.2.
The empty bed contact time (EBCT) in the column (min) is a measure of the contact time between the adsorbent and the water that flows through a bed of the particles, and is calculated from the ratio of bed volume (mL) to the flow rate (mL/min) as follows (Ohura et al., 2011):

\[
EBCT = \frac{\text{bed volume}}{\text{flow rate}}
\]  

(5.4)

5.3.4 Breakthrough curve modelling

The prediction of the breakthrough curve is essential for designing a continuous adsorption system. The relation between concentration and time provides insights into the adsorbent affinity, adsorbent surface properties, and adsorption pathways (Foo et
al., 2013). For that reason, several mathematical models have been developed for this purpose. This study investigated the dynamic adsorption behaviour of iron modified cellulose using Adams-Bohart, Thomas, Yoon-Nelson, and BDST models.

5.3.4.1 Adams-Bohart model

Adams-Bohart model assumes that equilibrium is not instant, and the adsorption rate is controlled by external mass transfer (Quintelas et al., 2013). This model is appropriate for analysing the initial part of the breakthrough curve (Ct/C0 = 0 to 0.5) (Long et al., 2014; Sharma and Singh, 2013). The equation of Adams-Bohart model is expressed as follows:

\[
\ln\left(\frac{C_t}{C_0}\right) = K_{AB}C_0t - K_{AB}N_0\frac{Z}{F} \quad (5.5)
\]

where C0 and Ct (mg/L) are the influent and effluent P concentration, K_{AB} (L/mg.min) is the kinetic constant, N_0 (mg/L) is the sorption capacity of the adsorbent per unit volume of the bed, Z (cm) is the bed depth, F (cm/min) is the linear velocity which is calculated by dividing the flow rate (cm^3/min) by the column section area (cm^2). The constants K_{AB} and N_0 of the Adams-Bohart model can be estimated from the linear plot of \ln(C_t/C_0) against t.

5.3.4.2 Thomas model

Thomas model is developed on the assumption that (1) the adsorption is not limited by chemical interactions but by mass transfer at the interface and (2) the experimental data follows Langmuir isotherms and second-order kinetics (Foo et al., 2013). Unlike Adams-Bohart model, Thomas model is appropriate for depicting the whole breakthrough curve (Bulgariu and Bulgariu, 2013). Thomas model can be written in the linear form by the following equation (Paudyal et al., 2013):

\[
\ln\left(\frac{C_0}{C_t} - 1\right) = k_{TH}q_e\frac{M}{Q} - k_{TH}C_0t \quad (5.6)
\]
where \( k_{Th} \) stands for Thomas rate constant (mL/min/mg), \( q_e \) is the adsorption capacity at equilibrium (mg/g), \( M \) is the mass of adsorbent (g), \( Q \) is the feed flow rate (mL/min), and \( t \) is the filtration time (min). The values of \( k_{Th} \) and \( q_e \) were determined from the linear plot of \( \ln(C_t/C_0 - 1) \) against \( t \).

### 5.3.4.3 Yoon-Nelson model

The model developed by Yoon and Nelson is based on the assumption that the rate of decrease in the probability of adsorption for each adsorbate molecule is proportional to the probability of the adsorbate adsorption and the adsorbate breakthrough from the adsorbent (Mthombeni et al., 2018). Similar to Thomas model, Yoon-Nelson model can mitigate limitations of Adams-Bohart model during the later period of the breakthrough curve. The linear expression of Yoon-Nelson model is given by the following equation (Sharma and Singh, 2013):

\[
\ln \left( \frac{C_t}{C_0} - 1 \right) = k_{YN} - \tau k_{YN} \tag{5.7}
\]

where \( k_{YN} \) is the Yoon-Nelson rate constant (min\(^{-1}\)), and \( \tau \) is the time required for 50% P breakthrough (min).

### 5.3.4.4 Bed depth service time (BDST) model

The BDST model proposes a linear relationship between the bed depth and the service time to a given breakthrough concentration. The BDST model does not attempt to predict the full breakthrough curve, but instead predicts the time at which a certain breakthrough concentration will occur for a given bed depth and flow rate. It is reported that BDST model can describe appropriately the initial part (10 to 50%) of the breakthrough curve (Jain et al., 2013). The linear expression of BDST model is given by the following equation (Li et al., 2013; Paudyal et al., 2013):

\[
t = \frac{Z N_0}{C_0 F} - \frac{1}{k_b C_0} \ln \left( \frac{C_0}{C_b} - 1 \right) \tag{5.8}
\]
where \( t \) is the service time of column (h), \( C_b \) is the outlet concentration at breakthrough point (mg/L), \( N_0 \) is the column adsorption capacity (mg/L), and \( K_b \) is the rate constant [L/(mg.h)].

From the plots of time versus bed depth, the BDST parameters, namely \( N_0 \) and \( K_b \), are calculated as follows (Zach-Maor et al., 2011):

\[
\text{slope} = \frac{N_0}{C_0F} \rightarrow N_0 = \text{slope}C_0F \quad (5.9)
\]

\[
\text{intercept} = -\frac{1}{K_bC_0} \ln \left( \frac{C_0}{C_b} - 1 \right) \rightarrow K_b = -\frac{1}{\text{intercept} \times C_0} \ln \left( \frac{C_0}{C_b} - 1 \right) \quad (5.10)
\]

Setting \( t = 0 \) and solving Eq. (5.8) for \( Z \) produces the following equation (Kumar and Bandyopadhyay, 2006):

\[
Z_0 = \frac{F}{K_bN_0} \ln \left( \frac{C_0}{C_b} - 1 \right) \quad (5.11)
\]

where \( Z_0 \) (cm) is called the critical bed depth, which is the minimum bed depth required to yield the desired effluent concentration (\( C_b \)).

The percentage error between the predicted and the observed breakthrough points was determined by the following equation (Miraboutalebi et al., 2017):

\[
\text{Error} = \left| \frac{B_p - B_o}{B_o} \right| \times 100 \quad (5.12)
\]

where \( B_p \) and \( B_o \) are the predicted and observed breakthrough points, respectively.

The software Microsoft Office Excel Professional Plus 2013 was used to conduct the modelling and the graphs were created with the software OriginPro 2018 (Northampton, Massachusetts, USA).

### 5.3.5 Cost of adsorbent development

This study employed analytical grade chemicals for iron modified preparation. Therefore, the cost of developed iron modified cellulose was first estimated based on the prices of analytical grade chemicals and considered: (i) chemicals for cellulose
extraction and modification (NaClO₂, acetic acid, NaOH, H₂O₂ and FeCl₃·6H₂O), and (ii) electricity consumption for drying, heating, and stirring.

The prices of the analytical grade chemicals were supplied by Sigma–Aldrich (Germany), while the prices of industrial grade chemicals were consulted from ChemBell (Orlando, USA). The quantities of chemicals and electricity considered to be inputted in the production of 1 kg of iron modified cellulose were based in the process of adsorbent development, as described in Chapter 3.

5.3.6 Bioavailability tests

The bioavailability tests were carried out with iron modified cellulose after adsorption to evaluate how much of the P attached to the cellulose was readily available for the plants to uptake. Three different tests were conducted – water extraction, iron-oxide impregnated paper and Olsen, respectively.

The method for using distilled water as an extractant to determine P needs of plants was examined in a paper by Luscombe et al. (1979). They found a good correlation between the concentration of water-extractable P and dry matter yields in ryegrass. The method was briefed as follows: 2 g of iron modified cellulose after adsorption was added to 20 mL of distilled water in 50 mL plastic tubes; those tubes were put in a Stuart SB3 rotator at 20 rpm for 1 hour; then the solution was filtered by a 0.45 µm membrane filter and PO₄-P concentration was determined using a nutrient analyser (Konelab, Thermo Clinical Labsystems, Vantaa, Finland).

The use of iron-oxide (FeO) coated paper to test P availability of soil was proposed by Menon et al. (1989), who wanted to develop a soil P test that would estimate plant-available P in tropical soils without mobilising other forms of phosphates. A strip of filter paper impregnated with iron hydroxide functioned as a P sink and adsorbed mobile P from solution, so Menon et al. (1989) called the analysed P, the Pi value (i referring to iron hydroxide). Interest in the method was soon extended to a wider range of soils (Menon et al., 1989). The testing was conducted in three steps:
1. Preparation of FeO paper

Initially, filter papers with 5.5 cm of diameter were put in a 0.65 M FeCl₃ acidified solution and were left overnight. Then, the papers were air dried, put in 2.7 M NH₄OH solution for 30 s and then allowed to drain for 15 s before thoroughly rinsed in distilled water. They were placed in a bucket of clean water for 1 h to permit dissipation of any residual ammonia. After dried, the papers were cut in squares of 4 cm², which were used in the subsequent steps.

2. Phosphorus extraction with FeO paper

In this step, 20 mL 0.01 M CaCl₂ solution was placed in a 50 mL plastic tube with 1 g of iron modified cellulose after adsorption and one strip of FeO paper. The plastic tubes were placed in a Stuart SB3 rotator at 20 rpm for 16 h. Then, the strip was replaced by a new one and the tubes were placed in the rotator for 16 hours. This last step was repeated one more time.

3. Determination of P extracted by FeO paper

In the last step, 40 mL 0.1 M H₂SO₄ solution was added in a 50 mL plastic tube with one paper strip from step 2. This aimed to dissolve FeO with adsorbed P and to make the P soluble. After, the solution was filtered with a 0.45 µm membrane filter and PO₄⁻P concentration was determined using a nutrient analyser (Konelab, Thermo Clinical Labsystems, Vantaa, Finland).

For alkaline and slightly alkaline soils, the Olsen P, or sodium bicarbonate soil test P method is commonly used. It was developed by Sterling R. Olsen and co-workers in 1954 (Olsen et al., 1954) to predict crop response to fertiliser P inputs on calcareous soils. The Olsen P method is best suited for calcareous soils, particularly those with more than 2% calcium carbonate, but has been shown in some research to be reasonably effective for acidic soils too (Sims, 2000). The Olsen P testing procedure was: 20 mL of a 0.5 M NaHCO₃ solution at pH 8.5 was placed in a 50 mL plastic tube with 1 g of iron modified cellulose after adsorption. The tubes were placed in a Stuart SB3 rotator at 20 rpm for 30 minutes. After, the solution was filtered with a 0.45 µm
membrane filter and PO$_4$-P concentration was determined using a nutrient analyser (Konelab, Thermo Clinical Labsystems, Vantaa, Finland).

All the tests were done in triplicate.

5.4 Results and Discussion

This section presents the effects of flow rate, bed height and initial P concentration in the column adsorption test by iron modified cellulose.

5.4.1 Effect of the flow rate

The effect of the flow rate on P adsorption by iron modified cellulose was explored at various flow rates (4.07, 4.93, and 6.22 mL/min) and a constant bed height (4.0 cm), and initial P concentration (10.0 mg/L). The breakthrough curves for the column were determined by plotting $C_t/C_0$ against the number of treated bed volumes. By plotting the breakthrough curves as a function of the treated bed volumes, the effect of the column geometry was eliminated, enabling a better comparison of the different curves. The curves are depicted in Figure 5.3.
As Figure 5.3 shows, a smaller treated bed volumes occurred at a higher flow rate. The treated bed volumes were found to be 604.5, 627.2, and 660.7 at flow rates of 4.07, 4.93, and 6.22 mL/min, respectively. This can be explained by the fact that a larger volume of solution elapsed through the bed at a higher flow rate. As a consequence, more PO$_4^{3-}$ anions got in contact with the binding sites of iron modified cellulose, making them get saturated more quickly. Similarly, a higher adsorption capacity was attained at a lower flow rate. It was probably because lower flow rates resulted in long residence time of P ions in the column. Since phosphate ions had longer contact time with iron modified cellulose, equilibrium can be reached before PO$_4^{3-}$ ions moved out of the column (Jain et al., 2013). According to Damte (2006), the longer contact time led to more efficient diffusion of PO$_4^{3-}$ ions into iron modified cellulose particles, and thus a better adsorption capacity was achieved. These findings agree with the previous studies conducted by Awual and Jyo (2011) and Paudyal et al. (2013).
5.4.2 Effect of initial \( P \) concentration

It is reported that influent \( P \) concentration can also affect the breakthrough curve (Awual and Jyo, 2011). Figure 5.4 illustrates the breakthrough curves at varying feed \( P \) concentrations (5.0, 10.0, and 15.0 mg/L), given a bed height of 4 cm and a flow rate of 4.1 mL/min. The treated bed volumes were 1086.1, 652.7, and 386.3 for influent \( P \) concentration of 5.0, 10.0, and 15.0 mg/L, respectively.

![Breakthrough Curve](image)

Figure 5.4 Effect of influent \( P \) concentration on the breakthrough curve of \( P \) onto iron modified cellulose (bed height 4.0 cm, flow rate 4.1 mL/min, \( pH \) 5.6, bed volume 2.0 cm\(^3\))

Equally, the exhaustion time declined with a rise in the \( P \) initial concentration, from 517.5 min at \( C_0 \) of 5.0 mg/L to 311.0 min at \( C_0 \) of 10.0 mg/L to 184.1 min at \( C_0 \) of 15.0 mg/L. It is evident from Figure 5.4 that the higher the influent \( P \) concentration was, the faster the breakthrough and exhaustion took place. Earlier column saturation
might result from greater concentration gradient and smaller mass transfer resistance at a higher phosphate concentration (Mohammed and Rashid, 2012; Paudyal et al., 2013). A similar trend was reported by Zhang et al. (2014) in case of removing phosphate using activated laterite. The dynamic adsorption capacity of iron modified cellulose for P increased, from 9.7 to 14.6 mg/g with the elevating P inlet concentration from 5.0 to 15.0 mg/L (Table 5.5). These results were in line with those reported by Awual and Jyo (2011) for the removal of P by polymeric anion exchangers.

5.4.3 Effect of bed height

Figure 5.5 described the effect of bed height on the breakthrough curve. As can be seen, at the bed height of 2.2, 4.0, and 6.2 cm, the treated bed volumes increased from 515.5 to 625.0, and 687.8, respectively, which may correspond to a longer contact time. The P uptake capacity of iron modified cellulose was 12.9, 12.6 and 8.4 mg/g for the bed height of 6.2, 4.0 and 2.2 cm, respectively as listed in Table 5.5. The result suggested that reducing the bed height led to a fall in P uptake capacity of iron modified cellulose. Jain et al. (2013) attributed this to the fewer adsorption sites at lower bed height. Conversely, Paudyal et al. (2013) explored that lessening the bed height led to an augmentation of the adsorption capacity of Zr$^{4+}$ loaded dried orange juice residue for fluoride. The authors ascribed this to the greater channelling effect at the higher bed depth and proposed to mitigate this effect by increasing the column diameter.
This study investigates the dynamic adsorption behaviour of iron modified cellulose using Adams-Bohart, Thomas, Yoon-Nelson, and BDST models. Table 5.2 shows the results for Adams-Bohart, Thomas and Yoon-Nelson models.
Table 5.2 Adams-Bohart, Thomas and Yoon-Nelson models parameters for phosphate adsorption in iron modified cellulose column

<table>
<thead>
<tr>
<th>Flow rate (mL/min)</th>
<th>Bed height (cm)</th>
<th>Initial P conc (mg/L)</th>
<th>$k_{AB}$ (L/mg.min)</th>
<th>$N_0$ (mg/L)</th>
<th>$R^2$</th>
<th>$k_{th}$ (mL/min.mg)</th>
<th>$q_0$ (mg/g)</th>
<th>$R^2$</th>
<th>$k_{YN}$ (min$^{-1}$)</th>
<th>$\tau$ (min)</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.07</td>
<td>4.0</td>
<td>10</td>
<td>0.0047</td>
<td>2.95</td>
<td>0.670</td>
<td>3.29</td>
<td>17.33</td>
<td>0.865</td>
<td>38.82</td>
<td>164.90</td>
<td>0.922</td>
</tr>
<tr>
<td>4.93</td>
<td>4.0</td>
<td>10</td>
<td>0.0049</td>
<td>2.64</td>
<td>0.920</td>
<td>2.49</td>
<td>20.94</td>
<td>0.755</td>
<td>35.42</td>
<td>124.38</td>
<td>0.886</td>
</tr>
<tr>
<td>6.22</td>
<td>4.0</td>
<td>10</td>
<td>0.0076</td>
<td>2.00</td>
<td>0.919</td>
<td>1.71</td>
<td>23.71</td>
<td>0.537</td>
<td>29.63</td>
<td>89.26</td>
<td>0.726</td>
</tr>
<tr>
<td>4.07</td>
<td>2.2</td>
<td>10</td>
<td>0.0099</td>
<td>1.69</td>
<td>0.761</td>
<td>2.80</td>
<td>23.92</td>
<td>0.575</td>
<td>44.97</td>
<td>61.51</td>
<td>0.768</td>
</tr>
<tr>
<td>4.07</td>
<td>4.0</td>
<td>10</td>
<td>0.0041</td>
<td>3.24</td>
<td>0.883</td>
<td>3.25</td>
<td>17.40</td>
<td>0.879</td>
<td>38.39</td>
<td>165.13</td>
<td>0.932</td>
</tr>
<tr>
<td>4.07</td>
<td>6.2</td>
<td>10</td>
<td>0.0014</td>
<td>4.61</td>
<td>0.946</td>
<td>1.05</td>
<td>26.64</td>
<td>0.930</td>
<td>14.39</td>
<td>340.04</td>
<td>0.971</td>
</tr>
<tr>
<td>4.22</td>
<td>4.0</td>
<td>5</td>
<td>0.0040</td>
<td>2.50</td>
<td>0.965</td>
<td>1.96</td>
<td>19.83</td>
<td>0.817</td>
<td>13.86</td>
<td>301.33</td>
<td>0.929</td>
</tr>
<tr>
<td>4.22</td>
<td>4.0</td>
<td>10</td>
<td>0.0042</td>
<td>3.34</td>
<td>0.867</td>
<td>3.29</td>
<td>17.99</td>
<td>0.865</td>
<td>38.79</td>
<td>165.01</td>
<td>0.921</td>
</tr>
<tr>
<td>4.22</td>
<td>4.0</td>
<td>15</td>
<td>0.0040</td>
<td>4.09</td>
<td>0.937</td>
<td>3.06</td>
<td>22.44</td>
<td>0.899</td>
<td>56.21</td>
<td>134.33</td>
<td>0.963</td>
</tr>
</tbody>
</table>
Adams-Bohart model assumes that equilibrium is not instant and it is used to analyse the initial part of the breakthrough curve \( (C_t/C_0 = 0 \text{ to } 0.5) \). The kinetic constant \( k_{AB} \) presented no significant change when increasing the initial P concentration, but it decreased from 0.0076 to 0.0047 L/mg.min when decreasing the flow rate from 6.22 to 4.07 mL/min, respectively. Also, an increase in the bed height from 2.2 to 6.2 cm led to decreasing of the kinetic constant from 0.0099 to 0.0014 L/mg.min. The capacity of the adsorbent \( (N_0) \) decreased from 2.95 to 2.0 mg/L with increasing the flow rate from 4.07 to 6.22 mL/min, respectively. An increase in \( N_0 \) values from 1.69 to 4.61 mg/L and from 2.50 to 4.09 mg/L were observed when increasing both the bed height from 2.2 to 6.2 cm and the initial influent P concentration from 5 to 15 mg/L, respectively. These results suggest that better adsorption performance of the column, characterised by higher adsorption capacity \( (N_0) \) and lower kinetic constant \( (k_{AB}) \), can be achieved with higher bed height \( (Z) \), but at a lower feed flow rate \( (Q) \) (Bulgariu and Bulgariu, 2013).

Unlike Adams-Bohart model, Thomas model can be used to analyse the whole breakthrough curve. This model is based on the assumption that adsorption is limited by mass transfer at the interface and that the data follows Langmuir isotherms and second-order kinetics. As the flow rate increased from 4.07 to 6.22 mL/min, the Thomas rate constant decreased from 3.30 to 1.71 mL/min.mg, whereas the dynamic adsorption capacity increased from 17.3 to 23.7 mg/g. An increase in initial P concentration from 5.0 to 15.0 mg/L led to an elevation in both Thomas rate constant from 1.97 to 3.02 mL/min.mg and adsorption capacity from 18.8 to 22.4 mg/g. The increase in the bed depth from 2.2 to 6.2 cm resulted in a decrease in the Thomas rate constant from 2.8 to 1.0 mL/min.mg, but growth in the uptake capacity from 23.9 to 26.6 mg/g. A higher uptake capacity at the higher feed P concentration can be attributed to the larger concentration gradient and higher driving force (Paudyal et al., 2013). A similar trend was reported by Bulgariu and Bulgariu (2013), Long et al. (2014) and Samuel et al. (2013).

Regarding the Yoon-Nelson model, it was found that both \( k_{YN} \) and \( \tau \) decreased from 38.8 to 29.7 min\(^{-1}\) and from 194.9 to 89.3 h, respectively, with an increase in flow rate.
from 4.07 to 6.22 mL/min. When increasing the bed height from 2.2 to 6.2 cm, the $k_{YN}$ values decrease from 45.0 to 145.4 min$^{-1}$, while $\tau$ increased from 89.3 to 165.1 h. A change in the initial P concentration from 5 to 15 mg/L was responsible for an increase in the $k_{YN}$ values from 13.9 to 56.2 min$^{-1}$ and a decrease in $\tau$ from 301.3 to 134.3 h. Sharma and Singh (2013) explained these results by the faster saturation of the column at a higher flow rate and inlet P concentration. Nevertheless, $\tau$ was extended at higher bed depths. Similar trends were reported by Chen et al. (2012) and Long et al. (2014). The $\tau$ values predicted by Yoon-Nelson model were quite similar to those obtained from experiments. Also, the investigation of correlation coefficients showed that Yoon-Nelson model was more satisfactory than Adams-Bohart and Thomas models in describing the phosphate adsorption by iron modified cellulose process.

5.4.4.1 Bed depth service time (BDST) model

The BDST model represents the relationship between bed depth and service time. It is reported that BDST model can describe appropriately initial part (10 to 50%) of the breakthrough curve (Jain et al., 2013). The BDST model for 10, 30, 50, and 90% breakthrough is depicted in Figure 5.6.
Column Study of Phosphate Adsorption by Iron Modified Cellulose

Figure 5.6 BDST model for 10, 30, 50, and 90% breakthrough (inlet P concentration 10 mg/L, flow rate 4.07 mL/min)

Table 5.3 represents BDST model constants (N₀, Kₜ) and corresponding critical bed depth (Z₀) for various breakthrough points (10, 30, and 50%) at a constant initial P concentration (10 mg/L) and flow rate (4.07 mL/min). The high correlation coefficients (R² > 0.995) demonstrated that BDST model could efficiently depict the phosphate – iron modified cellulose dynamic adsorption system.

<table>
<thead>
<tr>
<th>Breakpoint (%)</th>
<th>N₀ (mg/L)</th>
<th>Kₜ (L/mg.h)</th>
<th>Z₀ (cm)</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>61.59</td>
<td>0.154</td>
<td>1.87</td>
<td>0.999</td>
</tr>
<tr>
<td>30</td>
<td>68.34</td>
<td>0.064</td>
<td>1.57</td>
<td>0.995</td>
</tr>
<tr>
<td>50</td>
<td>79.81</td>
<td>0.000</td>
<td>1.39</td>
<td>0.996</td>
</tr>
</tbody>
</table>

The mass transfer zone (MTZ), can be defined as the adsorbent layer through which the effluent concentration changes from 10 to 90% of the influent concentration. MTZ is identified as the horizontal distance between these two lines in the BDST plot.
Equation 5.8 allows predicting the breakthrough time ($t_b$) for a new bed depth ($Z$) without conducting further experiments. The prediction utilises $N_0$, and $K_b$ values determined at the same initial P concentration ($C_0$) and velocity ($F$). Table 5.4 represents the predicted (pred) and observed (obs) breakthrough times for varying bed depths. It was found that the breakthrough times calculated by BDST model were quite similar to those obtained from the experiment. It validates the applicability of BDST model to P – iron modified cellulose dynamic adsorption system.

<table>
<thead>
<tr>
<th>Bed depth (cm)</th>
<th>10% breakthrough</th>
<th>30% breakthrough</th>
<th>50% breakthrough</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pred $t_b$ (h)</td>
<td>Obs $t_b$ (h)</td>
<td>Error (%)</td>
<td>Pred $t_b$ (h)</td>
</tr>
<tr>
<td>2.2</td>
<td>0.25</td>
<td>0.0</td>
<td>0.54</td>
</tr>
<tr>
<td>4</td>
<td>1.62</td>
<td>0.0</td>
<td>2.06</td>
</tr>
<tr>
<td>6.2</td>
<td>3.30</td>
<td>0.3</td>
<td>3.93</td>
</tr>
</tbody>
</table>

5.4.5 Column adsorption capacity of iron modified cellulose

The dynamic adsorption capacity of iron modified cellulose for P at the breakthrough time and exhaustion time was calculated for different operating conditions (Table 5.5). The highest P adsorption capacity of iron modified cellulose at the exhaustion time was 14.59 mg/g, value achieved at a bed height of 4 cm, flow rate of 4.22 mL/min and initial P concentration of 15 mg/L. The influent pH was not adjusted for this tests, and it was measured as 5.6.
Table 5.5 Breakthrough curve parameters for P adsorption onto iron modified cellulose at different operating conditions

<table>
<thead>
<tr>
<th>Flow rate (mL/min)</th>
<th>Bed height (cm)</th>
<th>Initial P conc (mg/L)</th>
<th>t_b (min)</th>
<th>V_b (L)</th>
<th>t_s (min)</th>
<th>V_s (L)</th>
<th>q_e (mg/g)</th>
<th>MTZ (cm)</th>
<th>EBCT (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.07</td>
<td>4</td>
<td>10.0</td>
<td>97.22</td>
<td>0.40</td>
<td>309.85</td>
<td>1261.08</td>
<td>12.65</td>
<td>2.74</td>
<td>0.49</td>
</tr>
<tr>
<td>4.93</td>
<td>4</td>
<td>10.0</td>
<td>52.57</td>
<td>0.26</td>
<td>246.60</td>
<td>1215.73</td>
<td>10.64</td>
<td>3.15</td>
<td>0.41</td>
</tr>
<tr>
<td>6.22</td>
<td>4</td>
<td>10.0</td>
<td>27.29</td>
<td>0.17</td>
<td>215.06</td>
<td>1337.67</td>
<td>9.80</td>
<td>3.49</td>
<td>0.32</td>
</tr>
<tr>
<td>4.07</td>
<td>2.2</td>
<td>10.0</td>
<td>15.12</td>
<td>0.06</td>
<td>140.06</td>
<td>570.06</td>
<td>8.39</td>
<td>1.96</td>
<td>0.27</td>
</tr>
<tr>
<td>4.07</td>
<td>4</td>
<td>10.0</td>
<td>97.18</td>
<td>0.40</td>
<td>308.76</td>
<td>1256.64</td>
<td>12.58</td>
<td>2.74</td>
<td>0.49</td>
</tr>
<tr>
<td>4.07</td>
<td>6.2</td>
<td>10.0</td>
<td>198.32</td>
<td>0.81</td>
<td>526.65</td>
<td>2143.45</td>
<td>12.90</td>
<td>3.87</td>
<td>0.77</td>
</tr>
<tr>
<td>4.22</td>
<td>4</td>
<td>5.0</td>
<td>123.01</td>
<td>0.52</td>
<td>517.47</td>
<td>2183.71</td>
<td>9.66</td>
<td>3.05</td>
<td>0.48</td>
</tr>
<tr>
<td>4.22</td>
<td>4</td>
<td>10.0</td>
<td>80.25</td>
<td>0.34</td>
<td>311.00</td>
<td>1312.42</td>
<td>13.11</td>
<td>2.97</td>
<td>0.48</td>
</tr>
<tr>
<td>4.22</td>
<td>4</td>
<td>15.0</td>
<td>92.32</td>
<td>0.39</td>
<td>184.07</td>
<td>776.77</td>
<td>14.59</td>
<td>1.99</td>
<td>0.48</td>
</tr>
</tbody>
</table>

The MTR is the region where P is most effectively and rapidly adsorbed. This zone moves downward with a constant velocity as the upper regions become saturated. The EBCT is the time the effluent is in touch with the adsorbent, assuming a constant velocity.

Table 5.6 indicates that iron modified cellulose is favourably comparable to most of the reported adsorbents in term of P adsorption capacity.

Table 5.6 Comparison of iron modified cellulose and various adsorbents in term of the P dynamic adsorption capacity

<table>
<thead>
<tr>
<th>Agriculture by-product</th>
<th>Modifying agent</th>
<th>Adsorption capacity (mg/g)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>sugarcane bagasse</td>
<td>carboxymethylation + FeCl_2</td>
<td>12.50</td>
<td>Carvalho et al. (2011)</td>
</tr>
<tr>
<td>grass silage cellulose</td>
<td>FeCl_3.6H_2O</td>
<td>14.59</td>
<td>this study</td>
</tr>
<tr>
<td>orange waste gel</td>
<td>zirconium IV</td>
<td>10.00</td>
<td>Biswas et al. (2008)</td>
</tr>
<tr>
<td>orange waste gel</td>
<td>lanthanium III</td>
<td>13.63</td>
<td>Biswas et al. (2008)</td>
</tr>
<tr>
<td>wood particles</td>
<td>Carboxymethyl cellulose + Ferrous chloride Epichlorohydrin-diethylenetriamine-trimethylamine</td>
<td>2.32</td>
<td>Eberhardt and Min (2008)</td>
</tr>
<tr>
<td>cotton stalk</td>
<td></td>
<td>16.01</td>
<td>Xu et al. (2011)</td>
</tr>
</tbody>
</table>
The result shows that iron modified cellulose can effectively remove P in the continuous adsorption systems. The reasonably high adsorption capacity of this iron modified cellulose column for P can be explained by the fact that Fe$^{3+}$ loading resulted in the development of effective binding sites for phosphate anions on the surface of cellulose.

### 5.4.6 Economic assessment and bioavailability

#### 5.4.6.1 Costs of adsorbent development

This study employed analytical grade chemicals for iron modified cellulose preparation. Therefore, the cost of iron modified cellulose development was first estimated based on the prices of analytical grade chemicals. This included the following items: (i) cellulose extraction and loading chemicals (NaClO$_2$, CH$_3$COOH, NaOH, H$_2$O$_2$ and FeCl$_3$.6H$_2$O) and (ii) electricity input for heating, drying and stirring. The costs are depicted in Table 5.7. The electricity price per kWh was considered to be 0.15 € (SEAI, 2019).

<table>
<thead>
<tr>
<th>Material</th>
<th>Adsorbent Details</th>
<th>Cost (€)</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>wheat straw</td>
<td>Epichlorohydrin-diethylenetriamine-trimethylamine Epichlorohydrin + N,N-dimethylformamide + Ethylenediamine + Triethylamine</td>
<td>13.67</td>
<td>Xu et al. (2011)</td>
</tr>
<tr>
<td>giant reed</td>
<td>Epichlorohydrin + N,N-dimethylformamide + Ethylenediamine + Triethylamine</td>
<td>19.89</td>
<td>Yue et al. (2010)</td>
</tr>
<tr>
<td>okara</td>
<td>FeCl$_3$</td>
<td>16.43</td>
<td>Nguyen et al. (2013)</td>
</tr>
</tbody>
</table>
Table 5.7 Iron modified cellulose development cost

<table>
<thead>
<tr>
<th>Chemicals Used</th>
<th>Usage/kg</th>
<th>Analytical grade price (€)</th>
<th>Cost/kg (€)</th>
<th>Industrial grade price (€)</th>
<th>Cost/kg (€)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaClO₂</td>
<td>171.24 mL</td>
<td>87.84/1000 mL</td>
<td>15.04</td>
<td>881.00/1000 L</td>
<td>0.15</td>
</tr>
<tr>
<td>acetic acid</td>
<td>13.17 mL</td>
<td>79.5/1000 mL</td>
<td>1.05</td>
<td>528.69/1000 L</td>
<td>0.01</td>
</tr>
<tr>
<td>NaOH</td>
<td>329.30 g</td>
<td>38.8/500 g</td>
<td>25.55</td>
<td>264.33/1000 kg</td>
<td>0.09</td>
</tr>
<tr>
<td>H₂O₂</td>
<td>98.80 mL</td>
<td>51.7/1000 mL</td>
<td>5.11</td>
<td>334.82/1000 L</td>
<td>0.03</td>
</tr>
<tr>
<td>FeCl₃·6H₂O</td>
<td>111.27 g</td>
<td>82.9/500 g</td>
<td>18.45</td>
<td>405.28/1000 kg</td>
<td>0.05</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td></td>
<td></td>
<td><strong>65.20</strong></td>
<td></td>
<td><strong>0.32</strong></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Electricity Usage</th>
<th>Electricity consumption (kW)</th>
<th>Usage time/kg (h)</th>
<th>Cost/kg (€)</th>
</tr>
</thead>
<tbody>
<tr>
<td>oven</td>
<td>4.1</td>
<td>26.34</td>
<td>16.20</td>
</tr>
<tr>
<td>shaking bath</td>
<td>1</td>
<td>16.46</td>
<td>2.47</td>
</tr>
<tr>
<td>mechanical shaker</td>
<td>0.115</td>
<td>79.03</td>
<td>1.36</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td></td>
<td></td>
<td><strong>20.03</strong></td>
</tr>
</tbody>
</table>

The cost of iron modified cellulose prepared from analytical grade chemicals was estimated to be 85.23 €/kg. In an attempt to reduce the cost of adsorbent development, the calculation of the cost of iron modified cellulose development was made based on the prices of industrial grade chemicals and, in this case, the cost was reduced to 20.35 €/kg. The results indicated that the use of industrial grade chemicals significantly reduced the cost of the developed adsorbent.

In order to compare the performance of iron modified cellulose in terms of cost with other agriculture waste by-products adsorbents or commercial adsorbents, the adsorption capacity must be considered. Table 5.8 shows the development costs of two adsorbents made from agriculture waste by-products, as well as three commercial ion exchange resins.
### Table 5.8 Cost comparison of adsorbents considering the adsorption capacity

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Price (€/Kg)</th>
<th>Adsorption capacity (mg/g)</th>
<th>Price (€/gP)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zirconium loaded okara</td>
<td>185.03</td>
<td>15.1</td>
<td>12.25</td>
</tr>
<tr>
<td>Quaternized corn stover</td>
<td>27.48</td>
<td>16.81</td>
<td>1.63</td>
</tr>
<tr>
<td><strong>Iron modified cellulose</strong></td>
<td><strong>20.35</strong></td>
<td><strong>20.10</strong></td>
<td><strong>1.01</strong></td>
</tr>
<tr>
<td>DOWEX ion exchange resins</td>
<td>0.88</td>
<td>40.05</td>
<td>0.02</td>
</tr>
<tr>
<td>Hydrotalcite</td>
<td>2.19</td>
<td>60</td>
<td>0.04</td>
</tr>
<tr>
<td>Aluminium oxide</td>
<td>4.24</td>
<td>35</td>
<td>0.12</td>
</tr>
</tbody>
</table>

Considering the adsorption capacity, iron modified cellulose presented the lowest cost among the investigated adsorbents developed from agriculture waste by-products. Commercial adsorbents still presented lower prices and greater adsorption capacities. It is worth pointing out that the use of adsorbents developed from agriculture waste by-products, besides the P removal, also promotes the valorisation of a product that was going to be waste, adding a beneficial value to it.

### 5.4.6.2 Bioavailability of the produced adsorbent

Besides knowing the adsorption capacity of the adsorbent, it is important to evaluate how much of the adsorbed P is bioavailable to plants. The bioavailable P is considered to be the amount of inorganic P, which a P-deficient soil can utilise throughout 24 h or longer (Sonzogni et al., 1982). There are a few methods to assess the P bioavailability in soils, depending on the soil pH and usage. Three different tests were done, considering that iron modified cellulose would be used as fertiliser in acidic, alkaline or slightly acidic to alkaline soils, being water extraction, iron-oxide impregnated paper and Olsen, respectively.

The P portion that can be extracted from iron modified cellulose using water as the extractant was 1.3%.

For acidic and slightly acidic soils, iron-oxide impregnated paper is one of the most applied methods (Menon et al., 1989; Sharpley, 1993). Sharpley (1993) observed that the iron-oxide strip P content of runoff was closely related to the growth of several...
algal species incubated for 29-d with runoff as the sole source of P. As the resin membranes and iron-oxide strips act as a P sink, they simulate P removal from soil or sediment-water samples by plant roots and algae. In this study, the results were 46.7% of bioavailable P in the first strip, 10.4% in the second strip and 3.2% in the third strip.

The Olsen P, or sodium bicarbonate soil test P method is commonly used for alkaline and slightly alkaline soils. The Olsen P method is best suited for calcareous soils, particularly those with > 2% calcium carbonate (Fixen and Grove, 1990). Using this method, the bioavailable P was measured as 35.9%.

The SMART Fertiliser Management Group (2018) stated in their report about P in soil and plants that the acceptable concentration of P in soil can be as low as 30 – 50 ppm, depending on the soil use. Considering iron modified cellulose’s adsorption capacity and bioavailability, its concentration would be 6821 and 8873 ppm, for alkaline and acidic soils, respectively. This means that iron modified cellulose could be applied as land P fertiliser both in alkaline and acidic soils.

5.5 Summary

Chapter 5 investigated P removal by iron modified cellulose packed bed column. The results demonstrated that it was feasible to remove P from aqueous solutions using this adsorbent in a dynamic adsorption system. The effects of column design parameters, such as flow rate, inlet P concentration, and bed depth were examined. The results revealed that a lower flow rate, higher bed depth and intermediate feed P concentration facilitated the adsorption performance of the column, which was evidenced by longer service time and higher treated volume.

The highest dynamic adsorption capacity of iron modified cellulose for P was obtained at the flow rate of 4.22 mL/min, influent P concentration of 15 mg/L and bed depth of 4.0 cm. It was estimated to be 14.59 mg P/g adsorbent.

Thomas model fitted the data relatively well and returned a maximum theoretical adsorption capacity of 26.64 mg/g. Both the BDST and Yoon-Nelson model fitted well
the experimental data. The BDST model predicted accurately the breakthrough time for the change of bed depth.

Investigations regarding the adsorbent development cost revealed that iron modified cellulose is cheaper to be produced than other adsorbents made from agriculture waste by-products. The bioavailability tests show good results with the iron-oxide impregnated paper test, showing 46.7% of bioavailable P in the first strip, 10.4% in the second and 3.2% in the third, for acidic and slightly acidic soils.
Chapter 6 Environmental Life Cycle Analysis of Iron Modified Cellulose
6.1 Overview

This chapter presents the life cycle analysis of iron modified cellulose and compares its usage as a fertiliser, with a chemical fertiliser, and as a phosphate adsorbent, with three adsorbents made from activated carbon.

6.2 Introduction

Iron modified cellulose is a low-cost alternative for P removal from liquid. It can be used as a slow release fertiliser, reducing the application rate of chemical fertilisers on land. However, the production of iron modified cellulose involves the input of chemicals and energy, and produces waste, as described in Chapter 3.

In this way, environmental impacts must be considered when selecting the appropriate method of P removal or the best land fertiliser to avoid creating a worse impact on the environment. Therefore, a complete environmental assessment of any of these solutions must be carried out. Life cycle assessment (LCA) can be used for such assessment. LCA is a tool that aims to assess the environmental aspects of a process and potential environmental impacts during this process (ISO 14040, 2006).

A LCA includes the definition of goal and scope, inventory analysis, impact assessment and interpretation of results, as illustrated in Figure 6.1.
Activated carbon is a widely used adsorbent for pollutants removal from wastewater, due to its high porosity, large surface area, high surface reactivity and ease of compaction into a packed bed (Shen et al., 2019). The environmental impacts associated with a specific activated carbon vary because it can be produced from various carbonaceous materials by physical or chemical activation or by a combination of the two processes (Tan et al., 2017).

In relation to fertilisers, many different physical and chemical forms are available. Among the chemical fertilisers, triple super phosphate (P$_2$O$_5$) is commonly used, for being suitable for all crops and soils (Beecher and Elliott, 2016). Life cycle assessment of fertilisers indicates that despite the technological improvements in its manufacturing and use during the last 100 years, greater production intensity increases emissions of pollutants (N$_2$O, NO$_x$, NH$_3$, PO$_4^{3-}$) contributing to the greenhouse effect, acidification, and eutrophication. Fertilisers containing heavy metals (Cd, Zn, Co, Se, Hg) also have a toxic effect on water, land, and human beings (Skowrońska and Filipek, 2014). The
negative environmental impacts of the production and use of P fertilisers are mainly due to the greenhouse effect (transport of raw materials and products) and eutrophication (dispersion of phosphates during fertiliser production and accumulation of phosphogypsum) (Cordell et al., 2009).

The goal of this study was to quantify the environmental impacts associated with iron modified cellulose production process prepared after cellulose extraction from grass silage. Such information is relevant to identify the environmental weaknesses in the production process.

The environmental performance of iron modified cellulose was compared with three activated carbon adsorbents from different substrates, and with P$_2$O$_5$, a chemical fertiliser.

6.3 Materials and Methods
6.3.1 Data origin

The data used in the Life Cycle Analysis were based on the laboratory production of iron modified cellulose, described in Chapter 3. A major drawback in utilising lab scale data for LCA was the lack of industrial-scale data, which would result in a much higher impact when comparing to materials and energy input in industrial scale. Optimised process and scaling effects of the latter result in advantageous material and energy efficiencies (Piccinno et al., 2015).

The quantities of chemicals used, as well as the electricity consumption in the lab production of iron modified cellulose, is summarised in Table 6.1.
Table 6.1 Inputs of chemicals and electricity considered for the LCA of iron modified cellulose

<table>
<thead>
<tr>
<th>INPUTS</th>
<th>Chemicals</th>
<th>Usage/batch</th>
<th>Usage/kg of cellulose (g/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>NaClO₂ (25 %)</td>
<td>52.0 ml</td>
<td>428.1</td>
</tr>
<tr>
<td></td>
<td>Acetic acid (98 %)</td>
<td>4.0 ml</td>
<td>13.83</td>
</tr>
<tr>
<td></td>
<td>NaOH (99.9 %)</td>
<td>100.0 g</td>
<td>329.3</td>
</tr>
<tr>
<td></td>
<td>H₂O₂ (33 %)</td>
<td>30.0 ml</td>
<td>143.24</td>
</tr>
<tr>
<td></td>
<td>FeCl₃.6H₂O (97 %)</td>
<td>33.75 g</td>
<td>111.3</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Electricity</th>
<th>Electricity consumption/batch (kW)</th>
<th>Usage time/batch (h)</th>
<th>Usage/kg of cellulose (kWh/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>oven</td>
<td>4.1</td>
<td>8</td>
<td>108.0</td>
</tr>
<tr>
<td>shaking bath</td>
<td>1</td>
<td>5</td>
<td>16.5</td>
</tr>
<tr>
<td>mechanical shaker</td>
<td>0.23</td>
<td>48</td>
<td>18.0</td>
</tr>
<tr>
<td>total</td>
<td></td>
<td></td>
<td>142.6</td>
</tr>
</tbody>
</table>

Note: The cellulose mass produced per batch was 303.67 g (wet mass). The numbers between brackets represent the concentration of the chemicals used in the laboratory experiments. The densities of NaClO₂, acetic acid, and H₂O₂ are 2.5, 1.05, 1.45 g/cm³, respectively (PubChem, 2017).

For the assessment of iron modified cellulose as a phosphate adsorbent, the comparison was made with three activated carbon based adsorbents found in the literature, named wood waste (Kim et al., 2018), coconut shells (Kim et al., 2018), and olive waste cake (Hjaila et al., 2013).

The environmental impacts associated with electricity, NaClO₂, acetic acid, NaOH, H₂O₂, FeCl₃.6H₂O, and P₂O₅ fertiliser are sourced from the Ecoinvent database v 2.2 (Swiss Centre for Life Cycle Inventories, SCLCI, 2010).

6.3.2 Application of LCA methodology

In this study, the environmental impacts associated with each step were evaluated using the software Simapro 7.3 based on the Ecoinvent database v 2.2 (Swiss Centre for Life Cycle Inventories, SCLCI, 2010) to obtain the background data. The impact assessment method used was Impact 2002 +. The impact categories considered in this study were (Humbert et al., 2005):
• Ozone layer depletion potential (OL) (kg CFC-11 eq.). It represents the ability of different gases to damage the ozone layer, reducing its ability to prevent ultraviolet (UV) light entering the earth’s atmosphere, increasing the amount of carcinogenic UVB light reaching the earth’s surface;

• Respiratory inorganics (RI) (kg C₂H₄ eq). It refers to respiratory effects which are caused by inorganic particulate matter in the air;

• Aquatic ecotoxicity (AE) (kg triethylene glycol (TEG) water). The characterisation factors of aquatic ecotoxicity are given for emissions into air, water and soil and quantify the ecotoxicity effects on fresh water (referring to streams and lakes);

• Terrestrial ecotoxicity (TE) (kg TEG soil). Terrestrial ecotoxicity characterisation factors are calculated in a similar way as aquatic ecotoxicity for emissions into air, water and soil, but the effects are quantified on the soils;

• Terrestrial acidification/nutrification (TAN/N) (kg SO₂ eq). Acidic gases such as sulphur dioxide (SO₂) react with water in the atmosphere to form “acid rain”, a process known as acid deposition. When this rain falls, often a considerable distance from the original source of the gas, it causes ecosystem impairment of varying degree, depending upon the nature of the landscape ecosystems. Gases that cause acid deposition include ammonia (NH₃), nitrogen oxides (NOₓ) and sulphur oxides (SOₓ);

• Aquatic acidification (AA) (kg SO₂ eq). Freshwater becomes acidic when acid inputs surpass the quantity of bases produced in the reservoir through weathering of rocks, or by the reduction of acid anions, like sulphate and nitrate within the lake. The main causes of aquatic acidification are atmospheric depositions and soil leaching of SOₓ and NOₓ;

• Aquatic eutrophication (AEut) (kg PO₄³⁻ - P eq). Eutrophication is the build-up of a concentration of chemical nutrients in an ecosystem which leads to abnormal productivity. This causes excessive plant growth like algae in rivers which causes severe reductions in water quality and animal populations.
Emissions of ammonia, nitrates, nitrogen oxides and phosphorous to air or water all have an impact on eutrophication;

- Global warming (GW) (kg CO$_2$ eq). Climate change can be defined as the change in global temperature caused by the greenhouse effect due to the release of “greenhouse gases” by human activity creates. Climate change is one of the major environmental effects on economic activity, and is one of the most difficult to handle because of its broad scale;

- Non-renewable energy (NE) (MJ primary). Characterisation factors for non-renewable energy consumption, in terms of the total primary energy extracted, are calculated using upper heating values. Damage characterisation factors are expressed in MJ total primary non-renewable energy.

The concentrations of the chemicals used for iron modified cellulose production described in Chapter 3 are different from the concentrations of the chemicals given by the Ecoinvent database. Therefore, the chemical usage was adapted accordingly, and the adjustment was shown in Table 6.2.

Table 6.2 Chemicals usage adjustment

<table>
<thead>
<tr>
<th>Chemicals</th>
<th>Concentration (%)</th>
<th>Usage</th>
<th>Concentration in database (%)</th>
<th>Adjusted Usage</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaClO$_3$</td>
<td>25.0</td>
<td>52 mL</td>
<td>99</td>
<td>13.1 mL</td>
</tr>
<tr>
<td>acetic acid</td>
<td>98.0</td>
<td>4 mL</td>
<td>98</td>
<td>4.0 mL</td>
</tr>
<tr>
<td>NaOH</td>
<td>99.99</td>
<td>100 g</td>
<td>50</td>
<td>200.0 g</td>
</tr>
<tr>
<td>$\text{H}_2\text{O}_2$</td>
<td>33.0</td>
<td>30 mL</td>
<td>50</td>
<td>19.8 mL</td>
</tr>
<tr>
<td>FeCl$_3$.6H$_2$O</td>
<td>97.0</td>
<td>33.75 g</td>
<td>40</td>
<td>81.8 g</td>
</tr>
</tbody>
</table>

6.3.2.1 Functional unit

The functional unit, as defined by the ISO 14040 (2006), is the unit of the product or service whose environmental impacts will be assessed or compared. In this study, the functional unit was defined as the production of 1 kg of iron modified cellulose.
For the activated carbon based adsorbents, the functional unit adopted was also 1 kg of adsorbent produced. For the P₂O₅ fertiliser, the functional unit given by the database was also 1 kg of fertiliser produced.

### 6.3.2.2 System boundary

The system boundary is a set of criteria specifying which unit processes are part of the product system (ISO 14040, 2006). Figure 6.2 shows the iron modified cellulose production system, which comprises 5 steps, drying, prehydrolysis, pulping, bleaching, and iron modification. For each step, the input flow was identified.

![Mass flow input of iron modified cellulose production](image)

*Figure 6.2 Mass flow input of iron modified cellulose production*

The software Microsoft Office Excel Professional Plus 2013 was used to conduct the modelling and the graphs were created with the software OriginPro 2018 (Northampton, Massachusetts, USA).
6.4 Results and discussion

6.4.1 Environmental assessment results for iron modified cellulose production

In the analysis of iron modified cellulose production, the inputs of chemicals and electricity in every step were considered. The results, depicted in Table 6.3, show that electricity contributes with more than 90% of the total environmental impact in all of the assessed categories.

*Table 6.3 Environmental impacts of iron modified cellulose production process*

<table>
<thead>
<tr>
<th>Impact category</th>
<th>Unit</th>
<th>Electricity (%)</th>
<th>Acetic acid (%)</th>
<th>NaOH (%)</th>
<th>FeCl₃ (%)</th>
<th>H₂O₂ (%)</th>
<th>NaClO₂ (%)</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>OL</td>
<td>kg CFC-11 eq</td>
<td>92.63</td>
<td>0.18</td>
<td>1.74</td>
<td>4.21</td>
<td>0.40</td>
<td>0.83</td>
<td>2.97E-06</td>
</tr>
<tr>
<td>RO</td>
<td>kg C₂H₄ eq</td>
<td>94.93</td>
<td>0.48</td>
<td>0.68</td>
<td>1.28</td>
<td>1.50</td>
<td>1.13</td>
<td>4.30E-03</td>
</tr>
<tr>
<td>AE</td>
<td>kg TEG water</td>
<td>97.58</td>
<td>0.12</td>
<td>0.01</td>
<td>1.01</td>
<td>0.33</td>
<td>0.96</td>
<td>2.58E+03</td>
</tr>
<tr>
<td>TE</td>
<td>kg TEG soil</td>
<td>97.79</td>
<td>0.06</td>
<td>0.05</td>
<td>1.15</td>
<td>0.22</td>
<td>0.72</td>
<td>7.10E+02</td>
</tr>
<tr>
<td>TAN/N</td>
<td>kg SO₂ eq</td>
<td>97.87</td>
<td>0.04</td>
<td>0.46</td>
<td>0.62</td>
<td>0.14</td>
<td>0.86</td>
<td>8.74E-01</td>
</tr>
<tr>
<td>AA</td>
<td>kg SO₂ eq</td>
<td>97.85</td>
<td>0.04</td>
<td>0.60</td>
<td>0.57</td>
<td>0.14</td>
<td>0.81</td>
<td>2.93E-01</td>
</tr>
<tr>
<td>AEut</td>
<td>kg PO₄³⁻P-lim</td>
<td>96.11</td>
<td>0.10</td>
<td>0.05</td>
<td>1.89</td>
<td>0.37</td>
<td>1.49</td>
<td>7.16E-03</td>
</tr>
<tr>
<td>GW</td>
<td>kg CO₂ eq</td>
<td>98.54</td>
<td>0.03</td>
<td>0.31</td>
<td>0.36</td>
<td>0.14</td>
<td>0.62</td>
<td>7.90E+01</td>
</tr>
<tr>
<td>NE</td>
<td>MJ primary</td>
<td>98.47</td>
<td>0.06</td>
<td>0.38</td>
<td>0.33</td>
<td>0.18</td>
<td>0.58</td>
<td>1.16E+03</td>
</tr>
</tbody>
</table>

The electricity that is provided in Ireland is generated using a number of different fuel sources, like coal, gas, peat, and renewables. Ireland also uses oil and non-biodegradable fraction of waste (waste energy i.e. the non-renewable portion of electricity generated from incineration of municipal waste), which are listed in the “other” category. Ireland’s renewable energy is predominantly sourced from wind (CRU, 2018). The contribution from each source is shown in Figure 6.3.
According to Ireland’s Greenhouse Gas Emissions Projections report (EPA, 2019), fossil fuels are key contributors to CO₂ emissions from the power generation sector. However, a significant reduction in emissions over the long term is projected as a result of the expansion of renewables (e.g. wind), assumed to reach 41 – 54% by 2030, with a move away from coal and peat.

It is worth noting that the usage of electric equipment in this study was not optimised. In one batch of cellulose production, about 3 times more of cellulose (about 1 kg) could be produced. This would reduce the impact associated with electricity consumption.

Figure 6.4 shows the relative impact contributions of the chemicals used in the iron modified cellulose production process. As can be observed, FeCl₃·6H₂O and NaClO₂ are the chemicals that present the major contribution in the total environmental impact in the majority of the assessed categories, such as ozone layer depletion, aquatic ecotoxicity, terrestrial ecotoxicity, and aquatic eutrophication; and terrestrial acidification/nutrification, aquatic acidification, global warming potential, and non-renewable energy, respectively.
According to the FeCl₃·6H₂O Safety Data Sheet (2010), this is not considered toxic, but it can exist in effluents at acutely toxic levels when the concentration is above 3000 mg/L because the resulting salinity can exceed the tolerance of the most freshwater organisms. Incidental exposure to inorganic chloride may occur in occupational settings where chemicals management policies are improperly applied. FeCl₃·6H₂O increases the electrical conductivity of water and thus increases its corrosivity. In metal pipes, chloride reacts with metal ions to form soluble salts thus increasing levels of metals in drinking water.

Zhang et al. (2017) studied the effect of iron on freshwater cyanobacteria bloom formation and discovered that cyanobacterial growth in eutrophic lakes can be
suppressed by controlling iron availability. This would explain the major contribution of this chemical in the aquatic eutrophication category. The authors, however, demonstrate the major role of other pollutants in eutrophication, such as P and N.

NaClO₂ is used as an antimicrobial pesticide at numerous use sites. Its antimicrobial registered uses fall into several major categories including use in the treatment of human drinking water systems; in industrial process and water systems; as a materials preservative; and as a general disinfectant in medical, residential, agricultural, commercial and industrial settings (US EPA, 2006).

For terrestrial animals, studies show that toxicity of NaClO₂ to birds range from highly to slightly toxic on an acute oral basis and from slightly toxic to practically non-toxic in a subacute dietary basis. For freshwater aquatic animals, the results of studies examining the toxicity of NaClO₂ to freshwater fish indicate it is from slightly toxic to practically non-toxic on an acute basis (ATSDR, 2004). For aquatic invertebrates, the studies indicate that the toxicity ranges from very highly toxic for technical grade NaClO₂ to practically non-toxic for the formulated product on an acute basis. For estuarine/marine invertebrates, studies indicate that NaClO₂ is slightly toxic on an acute basis. For plants, results of toxicity studies indicate NaClO₂ is moderately toxic to terrestrial and aquatic plants (US EPA, 1991).

All these findings indicate although FeCl₃.6H₂O and NaClO₂ are the chemicals that present the major environmental impact in the iron modified cellulose development process, these are not highly toxic to the environment.

6.4.1.1 Environmental assessment results considering electricity optimisation

Since the electricity usage is the component that presents the major environmental impact during the iron modified cellulose production process, in this section an evaluation of the reduction in environmental impact was assessed, considering an optimisation on the electricity usage and an increase in the renewable share in the Irish fuel mix, as predicted by the Irish Environmental Protection Agency (2019).
Each batch of iron modified cellulose produced about 300 g of adsorbent, when about 1 kg could have been produced. This statement was made based on observations of the lab equipment loading capacities. Also, the share in the Irish fuel mix corresponding to renewables is about 36.2%, and this is expected to reach 41–54% by 2030, with a move away from coal and peat (EPA, 2019). The reduction in the total environmental impact of iron modified cellulose production considering the above described scenarios is shown in Figure 6.5, where $E_0$, $E_1$, $41\% R – E_0$, $54\% R – E_0$, $41\% R – E_1$, $54\% R – E_1$ are the reference electricity input, the optimised input considering 1 kg of iron modified cellulose being produced per batch, the reference electricity input considering 41% of renewables in the fuel mix, the reference electricity input considering 54% of renewables in the fuel mix, the optimised electricity input considering 41% of renewables in the fuel mix, and the optimised electricity input considering 54% of renewables in the fuel mix, respectively.

Figure 6.5 Comparison of total environmental impact of iron modified cellulose production considering alternative electricity scenarios
In this, E0 was considered the reference scenario, with a relative total environmental impact of 100%. The relative total environmental impact of the other scenarios was presented as a percentage of E0. As can be observed, the relative total environmental impacts follow the order: E0 > 41% R – E0 > 54% R – E0 > E1 > 41% R – E1 > 54% R – E1. It was observed a reduction of about 10 and 30% in the total environmental impact in all the assessed categories considering an increase of 41 and 54% in the renewables energy grid share, when compared to the reference, respectively.

A comparison between the reference environmental impact and the impact considering electricity optimisation (E1) showed a reduction of about 65% in the total environmental impact in all the categories. This is a substantial reduction, which can be achieved by loading the equipment to its maximum capability.

6.4.2 Comparison of environmental impacts with alternative adsorbents

The comparison between iron modified cellulose’s environmental performance and other adsorbents is necessary. This study compared the environmental impact categories of ozone layer depletion (OL), respiratory organics (RO), aquatic ecotoxicity (AE), terrestrial ecotoxicity (TE), terrestrial acidification/nutrification (TA/N), aquatic acidification (AA), aquatic eutrophication (AEut), global warming (GW), and non-renewable energy (NE) among iron modified cellulose and activated carbon prepared from, wood waste (Kim et al., 2019), coconut shells (Kim et al., 2019), and olive-waste cake (Hjaila et al., 2013). The results are depicted in Table 6.4.
Table 6.4 Characterised environmental impacts for 1 kg of iron modified cellulose production in comparison with other adsorbents

<table>
<thead>
<tr>
<th>Impact category</th>
<th>Unity</th>
<th>This study</th>
<th>Literature data</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Iron modified cellulose</td>
<td>Olive waste AC</td>
</tr>
<tr>
<td>OL</td>
<td>kg CFC-11 eq</td>
<td>2.97E-06</td>
<td>5.5E-07</td>
</tr>
<tr>
<td>RO</td>
<td>kg C₂H₄ eq</td>
<td>4.30E-03</td>
<td>7.0E-03</td>
</tr>
<tr>
<td>AE</td>
<td>kg TEG water</td>
<td>2.58E+03</td>
<td>4.9E+00</td>
</tr>
<tr>
<td>TE</td>
<td>kg TEG soil</td>
<td>7.10E+02</td>
<td>1.6E-02</td>
</tr>
<tr>
<td>TAN/N</td>
<td>kg SO₂ eq</td>
<td>8.74E-01</td>
<td>5.3E+00</td>
</tr>
<tr>
<td>AA</td>
<td>kg SO₂ eq</td>
<td>2.93E-01</td>
<td>1.1E-01</td>
</tr>
<tr>
<td>AEut</td>
<td>kg PO₄³⁻ P-lim</td>
<td>7.16E-03</td>
<td>3.3E-02</td>
</tr>
<tr>
<td>GW</td>
<td>kg CO₂ eq</td>
<td>7.90E+01</td>
<td>1.1E+01</td>
</tr>
<tr>
<td>NE</td>
<td>MJ primary</td>
<td>1.16E+03</td>
<td>1.7E+02</td>
</tr>
</tbody>
</table>

As can be observed, iron modified cellulose presents a greater environmental impact in all the selected categories, except for terrestrial acidification/nutrification and aquatic eutrophication. For the wood waste and the coconut shells activated carbon, the lower impact can be explained by the larger amount of adsorbent developed (approximately 1 ton of raw material produced 118 and 127 kg of wood waste and coconut shell waste activated carbon, respectively). This large scale of production was responsible for an optimisation of the process, especially with regard to the electricity usage, biggest contributor in the total environment impact in all of the three cases, as demonstrated in section 6.4.1 and by Kim et al. (2019).

In relation to activated carbon produced from olive waste, the main contribution was due to the use of phosphoric acid, especially in the terrestrial acidification/nutrification, and the aquatic acidification categories (Hjaila et al., 2013). Another big contributor to the total environmental impact was identified as the electricity usage, an important component in the activated carbon preparation process. That is one of the reasons why the authors reinforce the importance of the application of an energetic policy of renewable sources (Hjaila et al., 2013). Considering an optimisation in the electricity usage during iron modified cellulose development process, as well as a change in the renewable energy share in the Irish grid, as ascribed in section 6.4.1.1, the impact is comparable with the other 3 adsorbents presented.
Environmental Life Cycle Analysis of Iron Modified Cellulose

(Table 6.5), except for the categories of aquatic acidification and aquatic eutrophication.

**Table 6.5 Characterised environmental impacts for 1 kg of iron modified cellulose production in comparison with other adsorbents considering electricity optimisation**

<table>
<thead>
<tr>
<th>Impact category</th>
<th>Unit</th>
<th>This study</th>
<th>Literature data</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Iron modified</td>
<td>Olive</td>
<td>Wood</td>
</tr>
<tr>
<td></td>
<td></td>
<td>cellulose</td>
<td>waste AC</td>
</tr>
<tr>
<td>OL</td>
<td>kg CFC-11 eq</td>
<td>7.80E-07</td>
<td>5.46E-07</td>
</tr>
<tr>
<td>RO</td>
<td>kg C\textsubscript{2}H\textsubscript{4} eq</td>
<td>1.05E-03</td>
<td>7.00E-03</td>
</tr>
<tr>
<td>AE</td>
<td>kg TEG water</td>
<td>5.76E+02</td>
<td>4.90E+00</td>
</tr>
<tr>
<td>TE</td>
<td>kg TEG soil</td>
<td>1.57E+02</td>
<td>1.60E-02</td>
</tr>
<tr>
<td>TAN/N</td>
<td>kg SO\textsubscript{2} eq</td>
<td>1.93E-01</td>
<td>5.26E+00</td>
</tr>
<tr>
<td>AA</td>
<td>kg SO\textsubscript{2} eq</td>
<td>6.46E-02</td>
<td>1.08E-01</td>
</tr>
<tr>
<td>AEut</td>
<td>kg PO\textsubscript{4}\textsuperscript{3-}P-lim</td>
<td>1.68E-03</td>
<td>3.30E-02</td>
</tr>
<tr>
<td>GW</td>
<td>kg CO\textsubscript{2} eq</td>
<td>1.70E+01</td>
<td>1.11E+01</td>
</tr>
<tr>
<td>NE</td>
<td>MJ primary</td>
<td>2.50E+02</td>
<td>1.68E+02</td>
</tr>
</tbody>
</table>

It is noteworthy that besides the environmental impact caused by the adsorbent development, other factors should be considered when selecting a proper adsorbent, such as adsorption/desorption performance, adsorption capacity, quality of the final product, among others. The analysis made in this section only aimed at environmental impact assessment.

### 6.4.2.1 Comparison of environmental impacts results considering the adsorption capacity

Another factor to be considered when selecting a proper adsorbent is its adsorption capacity (Priyanka and Saravanakumar, 2018). So, a comparison of the environmental impact caused by iron modified cellulose production and activated carbon made from olive waste (Fernando et al., 2009), wood waste (Kilpimaa et al., 2014), and coconut shells waste (Braun et al., 2018) was assessed in terms of adsorbed PO\textsubscript{4}\textsuperscript{3-} - P.

Although the production process of the activated carbons adopted for comparison in section 6.4.1 is different from the ones given in this section, it will be considered that their adsorption capacity is similar. In this way, the adsorption capacity of activated carbon from olive waste, wood waste, and coconut shells is considered to be 2.8, 3.48,
and 2.6 mg/g, respectively. For iron modified cellulose the adsorption capacity was considered as 19.0 mg/g, as demonstrated in Chapter 4. The environmental impacts of iron modified cellulose and activated carbon made from olive, wood, and coconut shells waste per g of PO$_4^{3-}$ - P adsorbed was demonstrated in Table 6.6.

Table 6.6 Characterised environmental impacts for iron modified cellulose production with and without electricity optimisation per g of adsorbed P in comparison with other adsorbents

<table>
<thead>
<tr>
<th>Impact category</th>
<th>Unit</th>
<th>This study</th>
<th>Literature data</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Iron modified cellulose –</td>
<td>Iron modified cellulose –</td>
</tr>
<tr>
<td></td>
<td></td>
<td>E0</td>
<td>54% R – E1</td>
</tr>
<tr>
<td>OL</td>
<td>kg CFC-11 eq/g</td>
<td>1.57E-07</td>
<td>4.11E-08</td>
</tr>
<tr>
<td>RO</td>
<td>kg C$_2$H$_4$ eq/g</td>
<td>2.26E-04</td>
<td>5.52E-05</td>
</tr>
<tr>
<td>AE</td>
<td>kg TEG water/g</td>
<td>1.36E+02</td>
<td>3.03E+01</td>
</tr>
<tr>
<td>TE</td>
<td>kg TEG soil/g</td>
<td>3.74E+01</td>
<td>8.26E+00</td>
</tr>
<tr>
<td>TAN/N</td>
<td>kg SO$_2$ eq/g</td>
<td>4.60E-02</td>
<td>1.01E-02</td>
</tr>
<tr>
<td>AA</td>
<td>kg SO$_2$ eq/g</td>
<td>1.54E-02</td>
<td>3.40E-03</td>
</tr>
<tr>
<td>Aeut</td>
<td>kg PO$_4^{3-}$P-lim/g</td>
<td>3.77E-04</td>
<td>8.85E-05</td>
</tr>
<tr>
<td>GW</td>
<td>kg CO$_2$ eq/g</td>
<td>4.16E+00</td>
<td>8.95E-01</td>
</tr>
<tr>
<td>NE</td>
<td>MJ primary/g</td>
<td>6.10E+01</td>
<td>1.32E+01</td>
</tr>
</tbody>
</table>

Among the investigated adsorbents, wood waste activated carbon presents the lower environmental impact in all the assessed categories, except for non-renewable energy. This happened because, among the 3 activated carbon adsorbents, wood waste activated carbon presented the highest adsorption capacity. This, combined with the electricity optimisation during the adsorbent manufacturing, was responsible for reducing the total environmental impact of wood waste activated carbon in the majority of the assessed categories.

The adsorption capacity of iron modified cellulose is about 6.8, 5.4, and 7.3 times higher than the activated carbon adsorbents made from olive waste, wood waste, and coconut shells, respectively. This was responsible for a great decrease in the environmental impact of iron modified cellulose in face of the others. Considering electricity optimisation, iron modified cellulose presented a lower total environmental impact than olive waste and coconut shells activated carbon in all the evaluated categories, except for aquatic and terrestrial ecotoxicity. This demonstrated the
importance of considering the adsorption capacity when assessing the environmental impact of an adsorbent.

6.4.3 Comparison of environmental impact results with alternative fertilisers

Iron modified cellulose can be used as a slow release fertiliser. Consequently, it is important to compare its environmental performance to chemical fertiliser. For this, the environmental impact categories of ozone layer depletion (OL), respiratory organics (RO), aquatic ecotoxicity (AE), terrestrial ecotoxicity (TE), terrestrial acidification/nutrification (TA/N), aquatic acidification (AA), aquatic eutrophication (AEut), global warming (GW), and non-renewable energy (NE) were assessed and compared between iron modified cellulose with and without electricity optimisation and increase in the Irish grid renewable share, and P₂O₅, as given by the Ecoinvent database. The results are depicted in Table 6.7.

<table>
<thead>
<tr>
<th>Impact category</th>
<th>Unit</th>
<th>This study</th>
<th>Ecoinvent</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Iron modified cellulose – E0</td>
<td>Iron modified cellulose 54% R – E1</td>
</tr>
<tr>
<td>OL</td>
<td>kg CFC-11 eq</td>
<td>2.97E-06</td>
<td>7.80E-07</td>
</tr>
<tr>
<td>RO</td>
<td>kg C₂H₄ eq</td>
<td>4.30E-03</td>
<td>1.05E-03</td>
</tr>
<tr>
<td>AE</td>
<td>kg TEG water</td>
<td>2.58E+03</td>
<td>5.76E+02</td>
</tr>
<tr>
<td>TE</td>
<td>kg TEG soil</td>
<td>7.10E+02</td>
<td>1.57E+02</td>
</tr>
<tr>
<td>TAN/N</td>
<td>kg SO₂ eq</td>
<td>8.74E-01</td>
<td>1.93E-01</td>
</tr>
<tr>
<td>AA</td>
<td>kg SO₂ eq</td>
<td>2.93E-01</td>
<td>6.46E-02</td>
</tr>
<tr>
<td>AEut</td>
<td>kg PO₄³⁻P-lim</td>
<td>7.16E-03</td>
<td>1.68E-03</td>
</tr>
<tr>
<td>GW</td>
<td>kg CO₂ eq</td>
<td>7.90E+01</td>
<td>1.70E+01</td>
</tr>
<tr>
<td>NE</td>
<td>MJ primary</td>
<td>1.16E+03</td>
<td>2.50E+02</td>
</tr>
</tbody>
</table>

As can be observed, the total environmental impact of iron modified cellulose production without electricity optimisation is greater than the P₂O₅ production in all the analysed categories. With electricity optimisation, the total environmental impacts would be less in the global warming category and are similar in all the other analysed categories.
The \( \text{P}_2\text{O}_5 \) production process, as used by the Ecoinvent database, was derived from literature studies and specifications from the manufacturers, relevant for the European production (Moreno Ruiz et al., 2016). There are a few methods of producing \( \text{P}_2\text{O}_5 \) from phosphate rocks; this means the impacts associated with its production may vary. The gypsum disposal represents one of the main concerns in the chemical fertiliser’s production process, once it contains fluorine compounds, which are toxic if disposed in freshwater, and radioactive trace elements. Land application is the main gypsum disposal route, meaning that there is an impact associated with land requirement that was not considered in this study. About 5 tonnes of gypsum are generated per tonne of \( \text{P}_2\text{O}_5 \) produced (EFMA, 2000).

The main emissions from the process are gaseous fluorides. 10 – 15\% of the fluorine contained in the phosphate rock is released during the acidulation and filtration stages and the gaseous emissions must be scrubbed. The final result is an emission containing less than 10 mg.Nm\(^{-3}\) as fluorine. The secondary emission is dust originating from the unloading, handling and grinding of phosphate rock (EFMA, 2000).

In this way, although the total environmental impact of \( \text{P}_2\text{O}_5 \) and iron modified cellulose are similar, the chemical fertiliser production process generates fumes and solid waste that are difficult to be disposed of. Also, it is worth mentioning that iron modified cellulose was produced in lab scale and productions in industrial scale are more optimised and, consequently, less harmful to the environment per kg of material produced. Also, \( \text{P}_2\text{O}_5 \) is produced from phosphate rocks, whose reserves are becoming scarce (EFMA, 2000), while iron modified cellulose’s substrate is grass silage, abundant and renewable resource.

### 6.4.3.1 Comparison of environmental impacts considering the P bioavailability

Only a portion of P present in fertilisers is available to plants. In this way, this section was focused on the assessment of the environmental impact of iron modified cellulose and \( \text{P}_2\text{O}_5 \) chemical fertiliser, considering their P bioavailability.
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The P bioavailability is affected by a number of factors, such as soil pH, balanced crop nutrition, organic matter, soil texture, application timing, and soil temperature, aeration, moisture, and compaction, among others (Wang et al., 2017).

As stated in Chapter 5, the bioavailability of iron modified cellulose varied from 35.9 to 46.7%, following the methods for alkaline and acidic soils, respectively. Also, as demonstrated in Chapter 4, iron modified cellulose’s adsorption capacity is 19 mg/g, which means about 1.9% of iron modified cellulose is composed of P. For the chemical fertiliser, about 45% of it is composed of P, and something between 85 and 90% of this is bioavailable (Conde et al., 2014). In this way, the bioavailable P for iron modified cellulose and P₂O₅ was considered as the average values, 0.78 and 39.38%, respectively. The total environmental impact of iron modified cellulose with and without electricity optimisation, as well as the impact of P₂O₅ production per g of bioavailable P, was depicted in Table 6.8.

Table 6.8 Characterised environmental impacts for iron modified cellulose production with and without electricity optimisation and P₂O₅ per g of bioavailable P

<table>
<thead>
<tr>
<th>Impact category</th>
<th>Unit</th>
<th>This study Iron modified cellulose – E0</th>
<th>Iron modified cellulose 54% R – E1</th>
<th>P₂O₅</th>
</tr>
</thead>
<tbody>
<tr>
<td>OL</td>
<td>kg CFC-11 eq/g</td>
<td>3.79E-07</td>
<td>9.94E-08</td>
<td>4.88E-10</td>
</tr>
<tr>
<td>RO</td>
<td>kg C₂H₄ eq/g</td>
<td>5.47E-04</td>
<td>1.34E-04</td>
<td>1.45E-06</td>
</tr>
<tr>
<td>AE</td>
<td>kg TEG water/g</td>
<td>3.29E+02</td>
<td>7.34E+01</td>
<td>2.12E+00</td>
</tr>
<tr>
<td>TE</td>
<td>kg TEG soil/g</td>
<td>9.04E+01</td>
<td>2.00E+01</td>
<td>3.41E-01</td>
</tr>
<tr>
<td>TAN/N</td>
<td>kg SO₂ eq/g</td>
<td>1.11E-01</td>
<td>2.46E-02</td>
<td>1.74E-04</td>
</tr>
<tr>
<td>AA</td>
<td>kg SO₂ eq/g</td>
<td>3.73E-02</td>
<td>8.23E-03</td>
<td>5.63E-05</td>
</tr>
<tr>
<td>AEut</td>
<td>kg PO₄³⁻P-lim/g</td>
<td>9.13E-04</td>
<td>2.14E-04</td>
<td>1.25E-05</td>
</tr>
<tr>
<td>GW</td>
<td>kg CO₂ eq/g</td>
<td>1.01E+01</td>
<td>2.17E+00</td>
<td>5.25E-03</td>
</tr>
<tr>
<td>NE</td>
<td>MJ primary/g</td>
<td>1.48E+02</td>
<td>3.19E+01</td>
<td>9.02E-02</td>
</tr>
</tbody>
</table>

The P bioavailability of the chemical fertiliser P₂O₅ is 50 times higher than the P bioavailability of iron modified cellulose. In this way, even considering iron modified cellulose manufacturing with electricity optimisation, the total environmental impact of P₂O₅ production is smaller than the total environmental impact of iron modified cellulose production in all the assessed categories.
It is noteworthy that the production of $P_2O_5$ is given in industrial scale, which reduces the total environmental impact per kg of fertiliser produced, and it produces solid and gaseous waste of difficult disposal. Also, the reserves of high quality phosphate rocks, raw material to produce $P_2O_5$, are becoming scarce (Scholtz et al., 2019). This factors should also be considered when selecting the best option of P fertiliser.

6.5 Summary

This study evaluated the environmental impacts of iron modified cellulose. Electricity usage was found to be the main factor affecting its total environmental impacts, being responsible for more than 90% in the majority of the analysed categories. Among the chemicals used, $FeCl_3.6H_2O$ and $NaClO_2$ were found to be the most harmful to the environment, being responsible for over 20% of the total environmental impacts caused by chemical usage in all the selected categories. A comparison between iron modified cellulose’s performance with other activated carbon based adsorbents shows that optimisation in the electricity usage could improve its performance in face of the others. The environmental impact of iron modified cellulose’s production was also compared to the one of chemical fertiliser. Results show that if the fertiliser’s P bioavailability is considered, the environmental impact of iron modified cellulose is greater than of $P_2O_5$. 
Chapter 7 Conclusions and Recommendations
7.1 Overview

The previous chapters provided insights into different aspects of P removal from the liquid media by adsorption onto iron modified cellulose. The overall concluding remarks of this thesis, the unsolved research questions, and the direction for future work were discussed in Chapter 7.

7.2 Main Conclusions

This study demonstrated that grass could be used as a raw material to develop a cheap adsorbent for P. Its adsorption capacity was efficiently activated by the metal loading method. Fe$^{3+}$ cationic ions deposited on iron modified cellulose were responsible for the retention of PO$_4^{3-}$ anionic ions onto the adsorbent.

Batch experiments indicated that iron modified cellulose worked efficiently in a wide pH range (4 – 10) and in the presence of coexisting anions (SO$_4^{2-}$, NO$_3^-$, CO$_3^{2-}$ and Cl$^-$). This can be considered an advantage of iron modified cellulose when used in treating real wastewater. The P adsorption capacity of iron modified cellulose was up to 20.1 mg P/g adsorbent, which is favourable compared to other adsorbents reported in the literature. This was probably owing to the existence of positively charged Fe$^{3+}$ cationic ions on the adsorbent. The kinetic study demonstrated that P removal by iron modified cellulose happened in two different steps: an initial rapid adsorption, which can be attributed to the increase in the driving forces given by the concentration gradient of phosphate in aqueous solution and the large number of available active sites on the external adsorbent surfaces of iron modified cellulose, and a slow process until the adsorption equilibrium was achieved. The pseudo-first-order model most satisfactorily described the kinetic data. The P removal rate achieved was 98% and a desorption efficiency of 54.6% was observed when a 2.0 M NaOH solution was used as desorption agent.

The column experiments showed that it was feasible to remove P from water using an iron modified cellulose packed bed column. The lower flow rate, higher bed depth, and smaller feed P concentration resulted in a higher treated volume and longer service time. The highest dynamic adsorption capacity of iron modified
Conclusions and Recommendations

cellulose obtained was 14.59 mg P/g adsorbent. The Yoon-Nelson and BDST models satisfactorily described the column adsorption behaviour.

An economic assessment showed that iron modified cellulose could be produced at a cost of 20.35 €/kg, considering it was produced with industrial grade chemicals. This can be produced cheaper than other adsorbents developed from agriculture waste by-products reported in the literature, although it is still more expensive than commercial adsorbents. The cost can be greatly reduced by considering large-scale industrial development. Furthermore, additional benefits should also be considered, as the use of renewable materials and waste valorisation. The bioavailability tests showed that 46.7 and 35.9% of P adsorbed were available to acidic and alkaline soils, respectively.

An evaluation related to the environmental impacts associated with iron modified cellulose development showed a big contribution of electricity usage. An optimisation in electricity usage, as well as an increase in the share of renewable sources could significantly reduce the total environmental impacts of iron modified cellulose development. Among the chemicals used, FeCl₃.6H₂O and NaClO₂ were found to be the most harmful to the environment, being responsible for over 40% of the total environmental impact caused by chemicals in all the analysed environmental categories.

7.3 Contributions to the field

The original contributions of this PhD research to the field of P removal and recovery include the use of grass, a renewable and abundant material in Ireland, as the raw material to develop a P adsorbent. The adsorbent development included a simple extraction technique, which is believed to be the first of its kind.

The developed adsorbent could be used as a barrier to prevent P from agriculture runoff from reaching water bodies and, subsequently, could be applied to land, as a slow release fertiliser. The development of an adsorbent with this versatile characteristic is also an original contribution of this study.
Also, the bioavailability tests are normally applied to assess the bioavailable soil P. The application of this type of test to assess the bioavailability of P in adsorbents was not reported before.

7.4 Recommendations for future research

7.4.1 Evaluation of iron modified cellulose safety

This study showed that iron modified cellulose did not suffer from Fe\(^{3+}\) leaching during its performance. However, if the adsorbed material is used directly in the land as a fertiliser, it is necessary to conduct a site study to evaluate if the presence of iron in its structure will pose any harm to the environment.

7.4.2 Agronomic study of the developed adsorbent

The bioavailability tests showed a good theoretical P uptake by plants. However, in reality, the efficacy of the material can vary, depending on the pH, the type of soils on which the adsorbent is applied, and the crop types. Thus, it is suggested that the field tests with the reclaimed iron modified cellulose after adsorption should be conducted to verify its agronomic values in the real conditions.

7.4.3 Alternative sources of chemicals and energy

The adsorbent development requires the input of chemicals for cellulose extraction process, metal loading, and pH alteration, and the input of energy for heating and mixing. To make P recovery through iron modified cellulose process economically viable, the industrial use chemicals should be explored.

Moreover, a study on the use of renewable energy (solar, wind energy) or the incorporation of energy produced in other phases of water treatment is also necessary.
7.4.4 Use of iron modified cellulose for other ions removal

The similarities in chemistry between phosphate (PO$_4^{3-}$) and arsenate (AsO$_4^{3-}$) have been well-documented in the literature. As iron modified cellulose was found to have a strong affinity for PO$_4^{3-}$ anions, it is expected to be effective in eliminating AsO$_4^{3-}$ anions as well. Therefore, it is recommended to use iron modified cellulose for purification of arsenate contaminated underground waters. If it is successful, the practical application of iron modified cellulose will be extended.
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