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Evaluation of the impact of coagulant choice on phosphorus removal
from municipal wastewater

Faculty of Engineering and Applied Sciences
Research Degree

PhD
Academic Year: 2021 - 2025

Supervisor: Dr Marc Pidou
Associate Supervisor: Professor Bruce Jefferson
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This thesis is submitted in partial fulfilment of the requirements for
the degree of PhD

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Academic integrity declaration

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- the thesis submitted has been written by me alone.
- the thesis submitted has not been previously submitted to this university or any other.
- that all content, including primary and/or secondary data, is true to the best of my knowledge.
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Abstract

Phosphorus removal is a critical objective in municipal wastewater treatment due to its role in eutrophication and the tightening of regulatory discharge limits. Chemical coagulation remains the most widely adopted method for phosphorus control; however, its effectiveness is influenced by coagulant type, pH conditions, dosing location, and wastewater matrix composition. This thesis aimed to advance the understanding of how these operational and chemical variables govern the mechanisms of phosphorus removal, with the goal of optimising coagulant selection and application strategies under real-world conditions.

A comprehensive screening of 17 coagulants, including ferric, aluminium, rare earth, zinc, and calcium-based formulations, was conducted under both uncontrolled and pH-adjusted conditions. Ferric sulphate, polyaluminium chloride (PACL), and aluminium sulphate emerged as the most effective agents, achieving residual total phosphorus concentrations as low as 0.35 mg/L, 0.15 mg/L and 0.6 mg/L, respectively, under controlled pH conditions, particularly under neutral pH, where stable hydroxide flocs are favoured. Rare earth coagulants demonstrated high phosphate affinity but formed fragile flocs, limiting their practical application. Floc characterisation revealed that compact, shear-resistant aggregates correlated strongly with higher removal efficiency.

To investigate the role of pH, a detailed comparative analysis of ferric sulphate (FS), aluminium sulphate (ALS), and PACL was performed across a pH range of 4-8. The results confirmed that coagulant solubility, hydrolysis potential, and metal speciation significantly impact phosphorus removal efficiency. FS and ALS were better than PACL under acidic conditions due to more complete hydrolysis and formation of stable flocs. Phosphorus fractionation and turbidity data supported these trends, identifying pH 6-7 as the optimal window for coagulant performance and floc settleability.

The final phase of the study examined how dosing location in the crude influent, after primary settling tanks (PST), and in the final effluent (FE) influences coagulant performance. FS showed enhanced phosphorus removal even in high-

strength crude wastewater, though required careful pH control to avoid over-acidification. ALS and PACL were more effective at PST and FE, where organic loading and particulate interference were lower. A two-point dosing strategy applied to crude wastewater was found to enhance phosphorus removal while reducing total coagulant demand, offering a practical route for chemical cost optimisation.

Collectively, this thesis delivers critical insights into the physicochemical and operational factors driving chemical phosphorus removal. The findings inform coagulant selection and deployment in diverse wastewater environments, support compliance with future phosphorus discharge standards, and contribute to the development of cost-effective and environmentally sustainable treatment strategies.

Keywords: phosphorus; municipal wastewater; coagulation; selection; pH; floc; dosing strategy; ferric sulphate; polyaluminium chloride; environmental compliance.

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List of Abbreviations

2PD	Two-point dosing
AFM	Atomic force microscopy
AHP	Acid-hydrolysable phosphorus
ALC	Aluminium chloride
ALCH	Aluminium chlorohydrate
ALS	Aluminium sulphate
BOD	Biochemical oxygen demand
BPR	Biological phosphorus removal
CC	Cerium chloride
CH	Calcium hydroxide
COD	Chemical oxygen demand
CP	Condensed Phosphorus
CPR	Chemical phosphorus removal
CS	Cerium sulphate
D/I	Dose-to-influent ratio
DOM	Dissolved organic matter
EBPR	Enhanced biological phosphorus removal
EEM	Excitation emission matrix
EU	European Union
FC	Ferric chloride
FD	Fractal dimension

FE	Final effluent
FERC	Ferrous chloride
FERS	Ferrous sulphate
FS	Ferric sulphate
FTIR	Fourier transform infrared spectroscopy
ICP-MS	Inductively coupled plasma-mass spectrometry
LC	Lanthanum chloride
LCA	Cycle assessment
LC-OCD	Liquid chromatography organic carbon detection
LS	Lanthanum sulphate
NMR	Nuclear magnetic resonance
NOM	Natural organic matter
Ortho-P	Orthophosphate
PACL	Polyaluminium chloride
PAFC	Polyaluminium ferric chloride
OH	Hydroxide ions
PFS	Polyferric sulphate
PST	Primary settling tanks
REEs	Rare earth elements
RP	Reactive phosphorus
STW	Sewage treatment works
TEA	Techno-economic analysis

TP	Total phosphorus
TSS	Total suspended solids
UF	Unfiltered fraction
UK	United Kingdom
UP	Unreactive Phosphorus
EUWWTD	European Union's urban wastewater treatment directive
WFD	Water Framework Directive
WWTPs	Wastewater treatment plants
XRD	X-ray diffraction
ZC	Zirconium chloride
ZIC	Zinc chloride
ZIS	Zinc sulphate
ZS	Zirconium sulphate

Chapter 1

1 Introduction

1.1 Background

Phosphorus is a vital nutrient for biological productivity in both natural ecosystems and agricultural systems. However, excessive phosphorus concentrations in aquatic environments have become a leading cause of eutrophication, resulting in harmful algal blooms, hypoxia, loss of biodiversity, and degradation of water quality (Jia-Qian et al., 1998; Morse et al., 1998; Ansari et al., 2010). These environmental consequences seriously threaten public health, drinking water supplies, and ecosystem services.

Municipal wastewater is a significant source of phosphorus, largely derived from human excreta, food residues, and synthetic detergents. The typical concentration of total phosphorus (TP) in municipal wastewater ranges from 6 to 8 mg/L (Parsons and Smith, 2008), with orthophosphates accounting for approximately 50%, condensed phosphates (polyphosphates) for 35%, and organic phosphates for the remaining 15% (Owodunni *et al.*, 2023). Orthophosphates (PO_4^{3-}), the most reactive and bioavailable form, are directly assimilable by microorganisms and plants, making them the primary target in phosphorus removal. Polyphosphates are condensed forms of inorganic phosphorus used in detergents and food additives, which can hydrolyse into orthophosphates under biological and chemical conditions in wastewater treatment processes. Organic phosphates are phosphorus bound within organic molecules, often requiring enzymatic or chemical breakdown to release reactive orthophosphate (Nadeem *et al.*, 2022).

Managing phosphorus levels in municipal wastewater is essential for protecting environmental health and complying with international and regional regulatory frameworks. The European Union's Urban Wastewater Treatment Directive (UWWTD), originally adopted in 1991, mandated reductions in nutrient discharges, including phosphorus, to mitigate eutrophication and protect water bodies (European Commission, 1991). In 2024, the EU adopted a modification of the UWWTD introducing stricter phosphorus discharge limits. Under the revised

directive, all urban wastewater treatment plants serving over 150,000 population equivalents must implement tertiary treatment for nitrogen and phosphorus removal by 2039 (Council of the European Union, 2024). This modification reflects the EU's commitment to enhancing the ecological status of water bodies and aligns with the broader objectives of the European Green Deal.

Complementing the UWWTD, the Water Framework Directive (WFD) (Water Framework Directive, 2000) takes a more integrated approach by establishing a framework for achieving “good ecological and chemical status” in surface and groundwater bodies. Phosphorus control is a central objective of the WFD, given its well-documented role in nutrient enrichment and degradation of water quality. Member states are required to implement measures, including enhanced phosphorus removal from wastewater, to meet water quality objectives across designated river basin catchments.

Although the United Kingdom (UK) is no longer obligated to follow EU legislation following Brexit, the legacy of these frameworks continues to shape UK environmental policy. The UK retains the original provisions of the 1991 UWWTD and incorporates elements of the WFD into its domestic water legislation. However, it is not bound to adopt the stricter phosphorus discharge limits set by the 2024 UWWTD recast, a divergence that could influence future policy decisions. Currently, the Environment Agency in England and Wales sets phosphorus discharge consents based on the sensitivity of receiving water bodies, typically requiring wastewater treatment plants (WWTPs) to achieve final effluent concentrations or limits of 1.0 – 0.5 mg/L for less sensitive areas to as low as 0.1 - 0.3 mg/L for Special Areas of Conservation or Sites of Special Scientific Interest (SSSIs) (DEFRA, 2014; Environment Agency, 2019). It's worth noting that more recent updates, such as the Water Industry National Environment Programme (WINEP) 2021–2027 and the Environment Act 2021, have introduced stricter phosphorus targets, including an 80% reduction in phosphorus loadings from wastewater by 2038 (DEFRA, 2014; Colloide, 2025). Similarly, in Scotland, the Scottish Environment Protection Agency (SEPA) enforces tiered phosphorus limits under the Controlled Activities Regulations

(CAR) to meet River Basin Management Plans, with treated effluent targets as stringent as 0.3 mg/L TP for discharges into eutrophication-sensitive water bodies (SEPA, 2025). In this context, the 0.3 mg/L TP benchmark adopted in this study represents a realistic yet stringent target by the wastewater treatment company in Scotland, actually a strict target that most utilities are facing in the UK, and yet a stringent target that aligns with current UK and EU regulatory requirements for sensitive water bodies. Moreover, the work undertaken could anyway be able to evaluate for even lower levels of phosphorus concentrations. It serves as a practical performance criterion for evaluating the effectiveness of various coagulants and dosing strategies under diverse wastewater treatment conditions.

Against this regulatory backdrop, achieving low residual phosphorus concentrations in treated effluent has become a critical goal for WWTPs. Various treatment methods are available for phosphorus removal, including enhanced biological phosphorus removal (EBPR) and chemical precipitation. EBPR relies on the metabolic activity of specific microorganisms, often struggling to achieve consistently low effluent phosphorus concentrations and requiring a significant amount of energy for aeration, which contributes to 50-67% of wastewater treatment plant energy consumption (Foley et al., 2010; Lozano et al., 2020; Siatou et al., 2020; Chen et al., 2022; Qambar and Al Khalidy, 2022). In contrast, chemical coagulation has emerged as a reliable and controllable method, particularly under varying operational conditions and stricter discharge requirements.

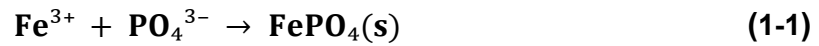
Chemical coagulation involves the addition of metal-based coagulants such as aluminium or iron salts, which react with phosphate ions to form insoluble precipitates that are removed through sedimentation or filtration. This method not only enables effective phosphorus removal to meet stringent standards but also offers operational advantages in terms of process stability, simplicity, and compatibility with existing infrastructure (Kim et al., 2005; Farah Ateeq, 2016b). However, more stringent discharge regulations necessitate a greater amount of coagulant usage, resulting in increased sludge generation and a subsequent rise

in operational costs. Additionally, the chemical supply chain remains a concern, emphasising the need for optimised and sustainable coagulant use.

When metal-based coagulants such as ferric sulphate ($\text{Fe}_2(\text{SO}_4)_3$), aluminium sulphate ($\text{Al}_2(\text{SO}_4)_3$), or polyaluminium chloride (PACL) are introduced into wastewater, they undergo rapid hydrolysis in water, producing hydrolysis species such as Fe^{3+} , $\text{Fe}(\text{OH})^{2+}$, $\text{Fe}(\text{OH})_3$, Al^{3+} , $\text{Al}(\text{OH})^{2+}$, and $\text{Al}(\text{OH})_3$. These species play critical roles in destabilising colloidal particles and removing phosphorus through the following primary mechanisms (Figure 1-1):

Precipitation:

Dissolved phosphate ions (PO_4^{3-}) directly react with metal ions (Fe^{3+} or Al^{3+}) to form insoluble precipitates such as ferric phosphate (FePO_4) or aluminium phosphate (AlPO_4), which are subsequently removed through sedimentation or filtration (Ebeling *et al.*, 2003). These reactions can be expressed as:



Adsorption and Sweep Flocculation:

The hydrolysis of coagulants produces amorphous metal hydroxide flocs such as $\text{Fe}(\text{OH})_3$ and $\text{Al}(\text{OH})_3$. These flocs have large surface areas that adsorb dissolved phosphorus species and entrap particulate phosphorus and other impurities through enmeshment (Jarvis *et al.*, 2005).

Pre-hydrolysed coagulants like PACL introduce preformed Al polymeric species (e.g., $\text{Al}_{13}\text{O}_4(\text{OH})_{24}^{7+}$), which enhance charge neutralisation and adsorption efficiency. However, their performance is strongly influenced by pH and wastewater characteristics.

The effectiveness of these mechanisms depends on several factors, including the type of coagulant, dosage, wastewater pH and alkalinity, and the concentrations of suspended solids, organic matter and mixing conditions. Maintaining near-neutral pH (6-7) is critical for optimising the formation of metal hydroxides and

phosphate precipitates. At lower pH, the excessive solubility of metal-phosphate complexes can lead to re-dissolution, whereas high pH favours the formation of soluble hydroxide species, such as $\text{Al}(\text{OH})_4^-$, which reduces coagulation effectiveness (Wilfert *et al.*, 2015; Zhao *et al.*, 2016).

These mechanisms of precipitation and adsorption underscore the reliability of chemical coagulation in achieving stringent phosphorus discharge limits in municipal wastewater treatment. Understanding these interactions is critical for optimising coagulant use in achieving stringent phosphorus limits.

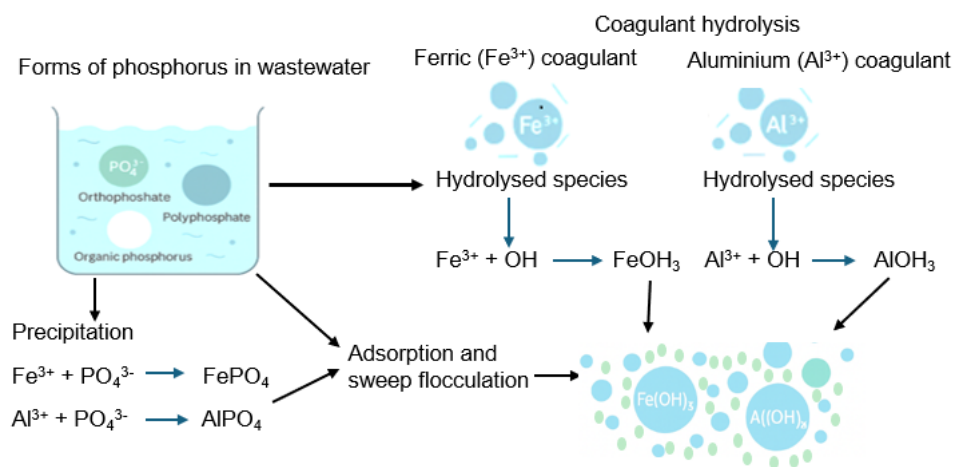


Figure 1-1: Illustration of phosphorus removal mechanisms in municipal wastewater via chemical coagulation. Orthophosphates (PO_4^{3-}) react with ferric (Fe^{3+}) or aluminium (Al^{3+}) coagulants to form insoluble precipitates (FePO_4 , AlPO_4) and are captured within flocs formed by metal hydroxide polymers. Condensed and organic phosphorus are first transformed into reactive forms before being adsorbed or precipitated.

1.2 Justification for Coagulant Selection

The selection of coagulants in this study was guided by their varied chemical properties, operational behaviours, and environmental implications. Iron-based (ferric sulphate, ferrous salts) and aluminium-based (aluminium sulphate, pre-hydrolysed PACL) coagulants are widely used in full-scale wastewater treatment plants due to their proven performance, availability, and cost-effectiveness. Pre-hydrolysed coagulants, such as PACL, offer potential advantages in floc formation and pH stability, but have shown variable performance under different wastewater characteristics.

Rare earth elements (lanthanum and cerium-based coagulants) and zirconium salts are being increasingly investigated for their high phosphate binding affinity and potential to achieve ultra-low residual phosphorus levels. However, their high cost, limited supply, and environmental footprint pose significant scalability challenges. Zinc-based coagulants and calcium hydroxide were also included to explore their dual functionality in phosphorus removal and pH adjustment. In particular, zinc salts are known to facilitate the removal of other pollutants, which may offer additional benefits in the co-removal of phosphorus and other compounds in a single step. This comprehensive selection enables a comparative assessment of conventional and advanced coagulants across diverse operational scenarios, providing valuable insights for sustainable coagulant management strategies.

1.3 Research Gap

Although extensive research has been conducted on chemical phosphorus removal, most studies have focused on individual coagulants or idealised synthetic wastewater matrices. There remains a lack of comparative evaluations of multiple coagulant types under controlled pH and real municipal wastewater conditions. While the influence of pH on coagulation is well established, it is often overlooked in wastewater treatment due to the cost implications. However, as the sector moves toward optimising coagulation efficiency and reducing coagulant consumption, pH adjustment may potentially be a valuable strategy for enhancing phosphorus removal while minimising environmental and economic costs. Furthermore, the influence of coagulant dosing location within a treatment train on phosphorus removal efficiency and floc characteristics has not been systematically investigated. This limits the development of evidence-based dosing strategies that account for site-specific wastewater characteristics, operational constraints, and emerging regulatory requirements.

This thesis addresses these gaps by:

1. Evaluating a broad range of coagulants (including conventional, pre-hydrolysed, and rare earth-based formulations) under both uncontrolled and controlled pH conditions.

2. Investigating the influence of coagulant dosing location (raw wastewater, after primary settling, final effluent) on treatment performance and floc properties.
3. Providing new insights into floc formation dynamics and coagulant efficiency under real wastewater conditions to inform sustainable and adaptive phosphorus removal strategies for wastewater treatment plants.

1.2 Coagulant types and known mechanisms

Phosphorus removal using chemical coagulation is a widely adopted and effective method in municipal wastewater treatment. The effectiveness of coagulants depends on their chemical composition, the physicochemical properties of the wastewater, and the operational parameters.

1.2.1 Inorganic coagulant

Inorganic coagulants, particularly aluminium and iron salts, are widely employed in municipal wastewater treatment due to their availability, low cost, and effective phosphorus removal, and include aluminium sulphate (alum), aluminium chloride, ferric chloride, and ferric sulphate (Peter, 2001; Bolto and Gregory, 2007; Kweinor et al., 2020). These coagulants exhibit well-characterised chemical behaviours, especially in relation to their hydrolysis, floc formation capability, and interactions with phosphorus in solution.

Upon introduction to wastewater, aluminium- and iron-based coagulants dissociate into trivalent metal ions (Al^{3+} or Fe^{3+}) that undergo hydrolysis to form a variety of monomeric and polymeric hydrolysed species such as $\text{Al}(\text{H}_2\text{O})_6^{3+}$, $\text{Al}(\text{OH})^{2+}$, $\text{Fe}(\text{H}_2\text{O})_6^{3+}$, and other polynuclear complexes (Tzoupanos and Zouboulis, 2008; Lee et al., 2014; Yang et al., 2016). These species possess a high cationic charge that destabilises negatively charged colloidal particles through charge neutralisation, leading to their aggregation into flocs (Gupta et al., 2012). At low dosages, this charge neutralisation mechanism predominates, but at higher concentrations, sweep flocculation becomes more prominent (Snodgrass et al., 1984). In sweep flocculation, metal hydroxide precipitates form voluminous networks that enmesh colloidal and suspended particles, facilitating

their removal through sedimentation or filtration (Packham, 1965; Franceschi et al., 2002; Wang et al., 2009; Yang et al., 2016).

In addition to destabilisation, aluminium and iron salts contribute to phosphorus removal through chemical precipitation and surface complexation. Ferric or aluminium-based coagulants react with phosphate ions to form insoluble compounds such as FePO_4 , $\text{Fe}_{2.5}\text{PO}_4(\text{OH})_4$, $\text{Fe}_{1.6}\text{H}_2\text{PO}_4(\text{OH})_{3.8}$, or amorphous $\text{Al}(\text{OH})_3$, which precipitate out of solution (Bai *et al.*, 2010; Liu and Zhou, 2022).

The performance of these coagulants has been reported to be highly dependent on operational conditions such as pH, coagulant dosage, and mixing intensity. Optimal hydrolysis and floc formation typically occur within a pH range of 5.5-7.5 for aluminium coagulants and a broader range from 4.5 for ferric salts (Yang et al., 2010; Bai et al., 2010; Gon Kim et al., 2015). Within these ranges, metal hydroxide species are most stable and reactive, enabling efficient destabilisation of particles and phosphorus removal. The deviations from the optimal pH can significantly impair performance: low pH values can favour soluble metal complexes over precipitates, while high pH may lead to negatively charged hydrolysis species that re-stabilise colloids, undermining coagulation (Trinh and Kang, 2015; Owodunni *et al.*, 2023).

Conversely, overdosing may saturate binding sites, lead to the re-stabilisation of particles, and contribute to elevated residual metal concentrations in the treated effluent, and often produce more sludge, which increases treatment costs and creates further challenges for dewatering and disposal (Ren *et al.*, 2020).

Despite the effectiveness of inorganic coagulants, they are particularly sensitive to variations in pH and temperature, require relatively high doses to achieve stringent phosphorus discharge limits, and tend to generate substantial quantities of sludge (Bolto and Gregory, 2007; Kweinor et al., 2020). Moreover, excessive residual aluminium or iron in the treated water may pose ecological and health concerns, especially if further treatment steps are not implemented to remove these metals (Jia-Qian et al., 1998; Kweinor et al., 2020; Krupińska, 2020; Zheng et al., 2022).

1.2.2 Pre-polymerised

Pre-polymerised coagulants have emerged as advanced alternatives to conventional aluminium and iron coagulants in municipal wastewater treatment, particularly for phosphorus removal. These coagulants, such as polyaluminium chloride (PACL), aluminium chlorohydrate (ALCH), polyaluminium silicate sulphate (PAS), and polyaluminium ferric chloride (PAFC), are composed of inorganic metal oligomers that have undergone partial or complete hydrolysis prior to application (Matilainen et al., 2010; Daud et al., 2015; Mahdavi et al., 2017). This pre-hydrolysed state enhances their structural stability and reactivity, distinguishing them from traditional coagulants like alum and ferric chloride.

A key attribute of pre-polymerised coagulants is their high basicity, defined by the molar ratio of hydroxide ions (OH^-) to metal atoms in their structure (Lei *et al.*, 2009; Mancuso *et al.*, 2021). This characteristic results in highly charged, polymeric species with increased cationic charge density, which enhances their ability to destabilise negatively charged colloidal particles. The increased level of polymerisation contributes to the formation of larger and more compact flocs, promoting efficient solid-liquid separation and improving overall treatment performance (Peter, 2001). Additionally, the structural integrity of these coagulants enables them to perform effectively across a broad pH range from slightly acidic to neutral conditions, making them particularly advantageous in wastewater treatment (Sinha *et al.*, 2004; Lei *et al.*, 2009; Li *et al.*, 2019; Nadeem *et al.*, 2022).

The mechanisms by which pre-polymerised coagulants achieve phosphorus removal include charge neutralisation, sweep flocculation, adsorption, and polymer bridging (Jia-Qian et al., 1998; Devanathan et al., 2024). Their preformed polymeric structure allows for rapid floc formation and improved floc stability, especially during the sedimentation and filtration stages. Unlike conventional coagulants that rely heavily on in-situ hydrolysis, the controlled hydrolytic state of these coagulants allows them to act immediately upon contact with wastewater, accelerating the coagulation-flocculation process and reducing reaction time (Chu *et al.*, 2018). This has been reported to lead to more robust and shear-

resistant flocs that enhance phosphorus capture efficiency and reduce turbidity in the treated effluent (Sinha et al., 2004; Lei et al., 2009; Li et al., 2019; Nadeem et al., 2022).

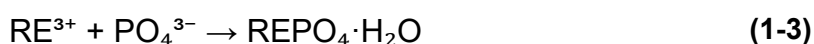
Previous studies have demonstrated the high efficacy of pre-polymerised coagulants, where PACL has achieved phosphorus removal rates exceeding 90% under optimal dosing and operating conditions in municipal wastewater treatment (Kim et al., 2022). ALCH has also shown considerable effectiveness in forming stable, dense flocs, which improve sedimentation rates and overall treatment outcomes. In addition to high removal efficiency, these coagulants contribute to operational benefits such as reduced sludge production and improved sludge dewaterability (Zouboulis and Tzoupanos, 2010; Gan et al., 2021).

Regardless of these advantages, the challenge of pre-polymerised coagulants is their comparatively higher cost relative to traditional coagulants, which may be a barrier to widespread adoption, particularly in resource-limited settings. Additionally, while their performance is generally more stable across varying pH and temperature ranges, their effectiveness can still be compromised under extreme conditions or with inappropriate dosing strategies. Overdosing can lead to increased residual aluminium concentrations or unintended shifts in pH, requiring careful monitoring and optimisation (Matilainen et al., 2010; Daud et al., 2015).

1.2.3 Rare earth elements

Rare earth elements (REEs), particularly salts of lanthanum and cerium such as lanthanum chloride, lanthanum sulphate, cerium chloride, and cerium sulphate, have gained increasing attention as high-performance coagulants for phosphorus removal in municipal wastewater treatment. Their most notable attribute reported is their strong chemical affinity for anions like phosphate (PO_4^{3-}) and carbonate (CO_3^{2-}), which stems from their unique electronic configuration that favours the formation of stable, insoluble complexes, which allows REEs to achieve phosphorus removal efficiency at low dosages (Haneline et al., 2015; Kajjumba and Marti, 2022b).

The dominant mechanism of phosphorus removal by REEs is chemical precipitation. Upon addition to wastewater, REEs dissociate into trivalent cations (La^{3+} , Ce^{3+}), which react directly with phosphate ions to form rare earth phosphate minerals like rhabdophane ($\text{REPO}_4 \cdot \text{H}_2\text{O}$), a stable and naturally occurring compound (Clavier et al., 2018; Pan et al., 2024). This direct precipitation is supplemented by other coagulation mechanisms, including charge neutralisation, adsorption, and sweep flocculation, which contribute to the formation of dense and compact flocs with enhanced settleability and dewatering characteristics (Yuan et al., 2018; Kajjumba et al., 2021). The overall reaction can be represented as:



where RE^{3+} refers to either La^{3+} or Ce^{3+} ions.

The most compelling advantage of REE coagulants is their efficiency at low molar ratios. Studies have demonstrated that phosphorus removal exceeding 90% can be achieved using a near 1:1 molar ratio of REE to phosphate, which reduces overall chemical consumption and associated costs (Haneline et al., 2015). In addition to their effectiveness, REEs are relatively abundant in the Earth's crust and, at environmentally relevant concentrations, are considered to have low toxicity, making them attractive for broader environmental applications (Michael, 2013). Their ability to maintain performance consistency under varying wastewater characteristics makes them particularly suitable for advanced treatment systems targeting low phosphorus discharge levels, such as <0.1 mg/L-P, a requirement already being met by facilities in the United States using REE technology (Haneline et al., 2015).

However, the relatively high market price of REEs compared to aluminium and iron salts may restrict their widespread adoption, particularly in low-budget or developing regions. Additionally, concerns exist around the long-term environmental impact of REE accumulation in sludge and ecosystems, as their behaviour in natural waters and soils is not yet fully understood. While their toxicity is generally low, prolonged or excessive usage may still present

ecological risks that require further investigation (Pan et al., 2024). Moreover, the availability and supply chain of REEs can be influenced by geopolitical and industrial factors, which may affect procurement and pricing stability.

1.2.4 Organic polymers

Organic polymers have emerged as a significant class of coagulants and coagulant aids in municipal wastewater treatment, primarily due to their adaptable properties, high removal efficiency, and reduced environmental impact. Unlike conventional metal-based coagulants, organic polymers produce lower volumes of sludge, exhibit superior biodegradability, and function effectively across a broad range of water chemistries (Vadapalli, 2005; Bolto and Gregory, 2007; Kweinor et al., 2020). These attributes make them especially attractive for sustainable and cost-effective phosphorus removal strategies in both municipal and industrial settings.

These polymers are typically synthesised by combining functional monomers to create macromolecules with tailored charge properties, which are classified into four main types based on ionic character: cationic, anionic, non-ionic, and amphiphilic (Duan and Gregory, 2003; Lee et al., 2014b). The cationic polymers, such as polyamines, carry a strong positive charge that facilitates charge neutralisation of negatively charged colloids. This mechanism promotes rapid destabilisation and aggregation of particles into flocs, particularly under acidic conditions where particle surfaces are more negatively charged. Anionic and non-ionic polymers, by contrast, primarily rely on adsorption and bridging mechanisms. Their long polymer chains can connect multiple particles simultaneously, promoting the formation of large, shear-resistant flocs with improved settling and filtration characteristics (Vadapalli, 2005; Dao et al., 2016; Naceradska et al., 2019; Heiderscheidt et al., 2020; Khairul et al., 2021).

Amphiphilic polymers, which contain both hydrophilic and hydrophobic segments, extend the applicability of organic coagulants to more complex wastewaters. These polymers can interact with a wide variety of contaminants through combined mechanisms such as charge neutralisation, hydrophobic bonding, and

polymer bridging, making them suitable for treating variable industrial effluents and mixed wastewater streams (Dao et al., 2016; Khairul et al., 2021).

Previous studies have substantiated the effectiveness of organic polymers in phosphorus removal, where cationic polyamines have been shown to achieve over 90% phosphorus removal in municipal wastewater treatment, demonstrating performance comparable to or better than some inorganic coagulants (Yue et al., 2008; Kolya and Kang, 2023). Similarly, amphiphilic polymers have exhibited strong flocculation performance in industrial wastewater, where contaminant profiles are more heterogeneous (Das et al., 2021). In addition to high removal efficiency, organic polymers are typically less sensitive to fluctuations in pH and temperature, offering operational stability under changing process conditions (Kweinor et al., 2020).

Consequently, the effectiveness of organic polymers can be highly dependent on precise dosage and the specific wastewater matrix, requiring careful optimisation to avoid overdosing, which may lead to re-stabilisation of particles or increased residual polymer in effluent. Additionally, while generally considered less toxic than metal salts, some synthetic polymers may raise concerns regarding their long-term environmental persistence and potential by-products from degradation (Dao et al., 2016). The cost of high-performance organic polymers may also limit their use in low-resource settings when compared to more affordable inorganic alternatives.

Furthermore, various coagulants have been reported to perform well in phosphorus removal from municipal wastewater, and many studies highlight their strengths, such as high removal efficiency, broad pH tolerance, or low sludge production. However, results often vary depending on wastewater characteristics, operational conditions, and coagulant formulation. In some cases, findings are inconsistent or even contradictory, with no universally accepted consensus on the most effective option. These discrepancies highlight the need for a more systematic and comparative evaluation of coagulant types to better understand their mechanisms, limitations, and practical suitability in different treatment scenarios.

1.3 Treatment performance

The relationship between the dose-to-influent phosphorus ratio (D/I) and the resulting total phosphorus (TP) concentration for a wide range of coagulants reported in the literature is illustrated in Figure 1-2. Despite covering both aluminium- and iron-based coagulants, the data reveal a high degree of scatter with no consistent trend between D/I ratios and TP removal. For similar D/I values, TP concentrations vary significantly, sometimes ranging from near-complete phosphorus removal to concentrations exceeding 10 mg/L. These inconsistencies are observed across conventional coagulants, such as alum and ferric chloride, and advanced formulations like PACL and polyferric sulphate (PFS).

Reported removal efficiencies also vary widely among studies in the literature. For instance, Liu and Zhou, (2022) reported that 0.9 mg/L of PFS achieved 98.7% TP removal, while Letelier-Gordo and Fernandes, (2021) found that ferric chloride dosed at a 10.4:1 molar ratio and aluminium sulphate at over 7.8:1 removed 95% and 92% of phosphorus, respectively. Similarly, a 50 mg/L dose of PACL/PFS achieved a residual TP of 0.18 mg/L (94% removal) (Dai *et al.*, 2021). Other studies with municipal wastewater using aluminium sulphate, aluminium chloride, and PACL at doses of 4, 2, and 1 mg/L reported residual TP values of 0.49, 0.17, and 0.23 mg/L, respectively (Bai *et al.*, 2010; Valerijus *et al.*, 2011; Fundneider *et al.*, 2020). In another study with municipal wastewater, ferric sulphate and ferric chloride at doses of 4 mg/L and 30 mg/L produced the same residual TP of 0.5 mg/L (Georgantas and Grigoropoulou, 2005a; Bai *et al.*, 2010).

These highlight the difficulty in comparing results across the studies in the literature, as similar coagulants can produce vastly different outcomes, and different coagulants can yield indistinguishable results (Table A- 1 in Appendix). The influence of uncontrolled variables such as pH, temperature, wastewater composition, and dosing protocols further complicates interpretation. The lack of standardised conditions and reporting practices across studies limits the comparability and reproducibility of the findings. Together, the scattered data and conflicting reports highlight the necessity for a more systematic, controlled evaluation of coagulants, as pursued in this study.

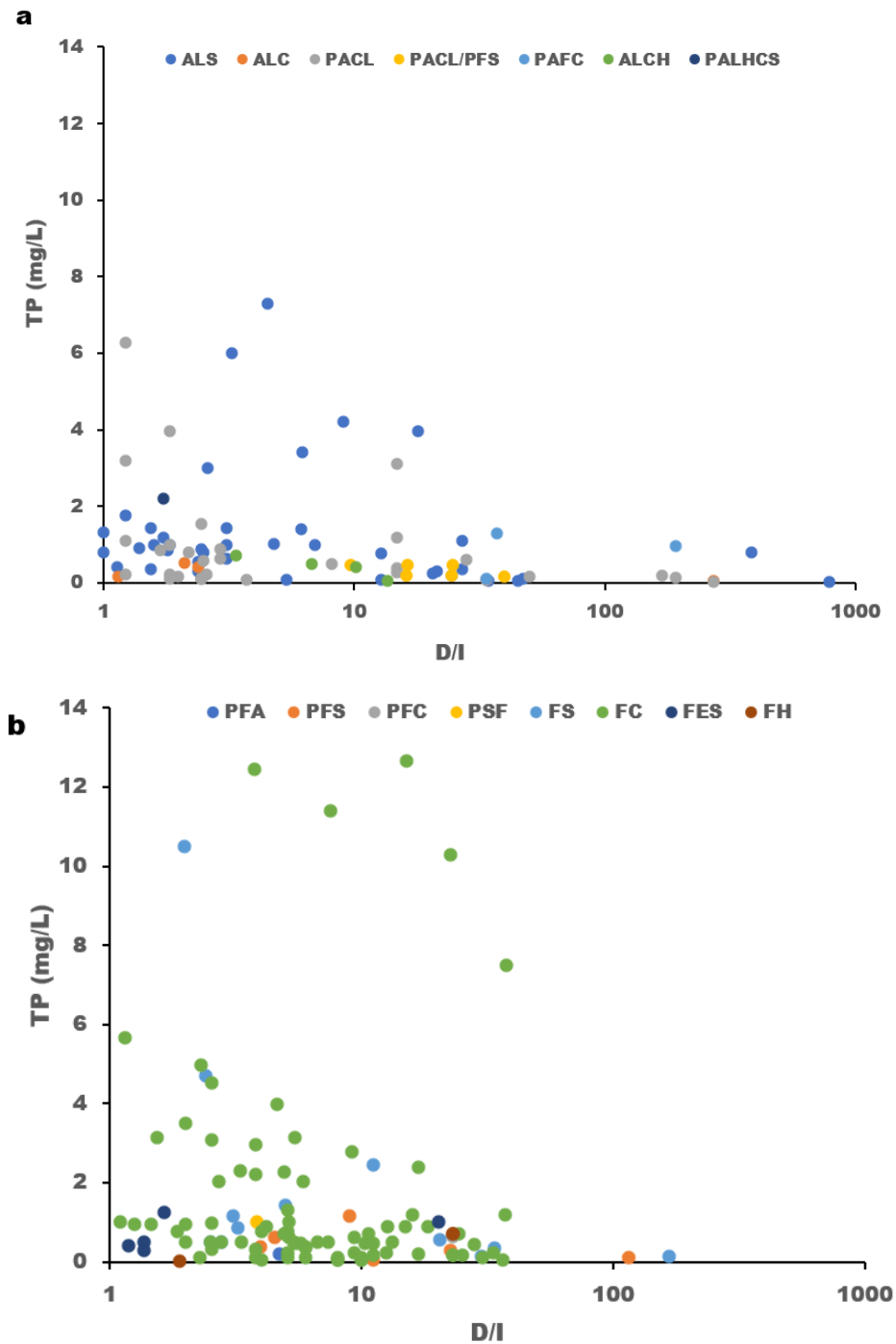


Figure 1-2: Variability in total phosphorus removal efficiency across aluminium-based (a) and Ferric-based (b) coagulants at different dosing ratios, D/I refers to the chemical dose (mg/L) divided by the influent phosphorus concentration (mg/L): Evidence from the literature (Table A- 1 in the Appendix).

1.4 Factors influencing the coagulation process

1.4.1 Operating conditions

A complex interplay of physicochemical parameters and operational conditions governs effective phosphorus removal via coagulation. The following are operating conditions that influence coagulation, and understanding how these factors interact is essential for optimising treatment performance in municipal wastewater systems.

Coagulant dosage plays a central role in determining treatment efficiency. At optimal levels, aluminium and ferric based coagulants promote the formation of larger and denser flocs that effectively settle and remove phosphorus (Langer *et al.*, 2017). However, overdosing can lead to saturation of particle surfaces, resulting in the formation of smaller, more fragile flocs, increased residual metal concentrations, and higher sludge production (Szabó *et al.*, 2008; Farah Ateeq, 2016a; Teh *et al.*, 2016). Coagulant demand is also influenced by the initial phosphorus concentration, requiring precise dosage adjustments based on wastewater characteristics (Lees *et al.*, 2010).

Mixing intensity and time are reported to significantly affect floc formation and structural integrity. Rapid mixing ensures even distribution of coagulants and facilitates initial destabilisation of particles, while slow mixing encourages floc growth through aggregation (Langer *et al.*, 2017). Studies indicate that shorter rapid mixing times produce larger flocs, but extended mixing may enhance compactness and shear resistance (Ayoub *et al.*, 2011; BinAhmed *et al.*, 2014; Teh *et al.*, 2016). However, excessive mixing can cause floc disintegration, reducing settleability and treatment efficacy durations (Bai *et al.*, 2010; Liu *et al.*, 2021a). Optimal mixing speeds generally range from 20 to 200 rpm, depending on coagulant type and treatment objectives (Nadeem *et al.*, 2022).

Settling duration is also critical, enabling solid-liquid separation after flocculation. Longer settling times allow the complete sedimentation of flocs, particularly larger and denser ones formed through sweep flocculation (Dong *et al.*, 2009; Chunjuan and Qingye, 2011). However, excessively long settling times

may lead to the compaction of sludge, which can pose challenges in sludge removal and processing (Zhao et al., 2011).

In principle, longer settling times can improve phosphorus removal, but they may not be feasible for high-throughput treatment facilities with limited space and time. Hence, optimising other parameters, such as coagulant dosage and mixing intensity, becomes crucial to compensate for shorter settling durations (Y. Liu *et al.*, 2021; Zheng *et al.*, 2022).

Additionally, properly optimised settling times, combined with adequate coagulant dosage and mixing intensity, can enhance the formation and stability of flocs, leading to more effective phosphorus removal (Peng *et al.*, 2022). Conversely, inadequate settling times can result in incomplete floc removal, higher turbidity, and elevated phosphorus concentrations in the treated effluent (Droppo et al., 2008).

1.4.2 Floc properties

The **floc size** is a primary determinant of phosphorus removal efficiency. Larger flocs settle more rapidly due to their increased mass and surface area (Ebeling et al., 2003; Gonzalez-Torres et al., 2014). pH influences floc size, with alum showing optimal performance in the narrow range of 6.5–7.5, while ferric chloride performs effectively across a wider pH range (Ebeling et al., 2003; Li et al., 2006).

Floc strength governs the resilience of aggregates under shear, and flocs formed through different coagulation mechanisms exhibit varying strengths. Flocs formed by bridging mechanisms, such as those induced by polymer flocculants, tend to be stronger and more resistant to breakage than those formed by charge neutralisation or sweep flocculation (Yu *et al.*, 2011). The strength hierarchy is typically: bridging > sweep > charge neutralisation (Lee et al., 2014b). Lower pH levels can weaken aluminium-based flocs due to increased solubility, (Tang *et al.*, 2014).

Floc density impacts both sedimentation and effluent clarity. Denser flocs are more likely to settle effectively and resist re-entrainment during clarification (Kim et al., 2001). Ferric hydroxide flocs have been shown to demonstrate relatively

consistent density across a wide pH range, enhancing performance compared to the more pH-sensitive aluminium hydroxide flocs (Ebeling *et al.*, 2003). While density is essential for sedimentation, it plays a less critical role in filtration-based systems, where floc strength and structure are more influential.

The internal structure of flocs, including their porosity and compactness, significantly influences the effectiveness of phosphorus removal. Flocs with a highly porous and loosely connected structure may exhibit lower settling velocities and be more prone to breakage. In contrast, compact and dense flocs are more stable and settle more efficiently. The fractal dimension, a measure of floc compactness, indicates that flocs formed under sweep flocculation are more compact compared to those formed under charge neutralisation (Kajjumba and Marti, 2022). This compactness enhances the physical capture and settling of phosphorus-laden particles. pH determines the structure of the flocs; at lower pH values, the solubility of metal coagulants such as aluminium and ferric salts increases, resulting in a higher concentration of dissolved and hydrolysed metal species (e.g., Al^{3+} , Fe^{3+}) in solution. These soluble species rapidly undergo polymerisation and precipitation as hydroxides (e.g., $\text{Fe}(\text{OH})_3$, $\text{Al}(\text{OH})_3$), facilitating the formation of denser and more cohesive flocs. The abundance of reactive hydrolysed species enhances inter-particle bridging and aggregation, resulting in flocs with reduced porosity and greater mechanical strength. Conversely, as the pH increases, the solubility of coagulants decreases, and fewer reactive hydrolysis products are available in solution. This limits polymeric network formation and leads to the development of more loosely bound and porous floc structures, which negatively affect sedimentation efficiency (Li *et al.*, 2006).

Floc age also been shown to play a role in removal efficiency, and younger flocs are generally more reactive and efficient at trapping and settling phosphorus-rich particles. As flocs age, they undergo compaction and structural changes that can reduce their reactivity and sedimentation potential (Yan *et al.*, 2008; Zhao *et al.*, 2011). Maintaining optimal floc age through controlled mixing and treatment timing is crucial for sustaining phosphorus removal performance.

Floc breakage and re-growth are dynamic processes influenced by shear forces, coagulant chemistry, and mixing conditions. Floc breakage is an inevitable aspect of the coagulation-flocculation process, particularly in systems with high-shear environments. The ability of flocs to resist breakage and maintain their integrity is crucial for effective phosphorus removal. Flocs formed by hydrolysing metal salts, such as alum and ferric chloride, tend to be weaker and more prone to breakage under high shear conditions (Duan and Gregory, 2003). However, polymeric coagulants can enhance the structural integrity of flocs, reducing their susceptibility to breakage (Liang *et al.*, 2009). The pH of the wastewater influences floc breakage. At lower pH values, the increased solubility of coagulants like aluminium sulphate can weaken the flocs, making them more susceptible to breakage. Conversely, ferric coagulants provide more stable flocs over a broader pH range, reducing breakage risks (Zhao *et al.*, 2011). While flocs re-grow, the ability of flocs to reform to a significant extent after breakage ensures continued effective removal of suspended solids and phosphorus. Re-growth potential is also affected by coagulation mechanisms; flocs formed through charge neutralisation exhibit greater re-formability than those formed by sweep flocculation (Yu *et al.*, 2011b; Yang *et al.*, 2016). It is also pH-dependent, with optimal pH conditions enhancing charge neutralisation and reducing solubility, thereby promoting the re-formation of stable flocs (Zhao *et al.*, 2011).

1.4.3 Water characteristics

1.4.3.1 Alkalinity and pH

The pH and alkalinity of municipal wastewater significantly influence the chemical reactions involved in coagulation, the stability and structure of flocs, and the overall effectiveness of phosphorus removal. The efficiency of different coagulants varies across pH ranges due to the solubility and hydrolysis behaviour of their active components.

Aluminium-based coagulants, such as aluminium sulphate and polyaluminium chloride, perform optimally in slightly acidic to neutral pH conditions, typically between pH 6 and 7.5. Within this range, aluminium salts hydrolyse to form aluminium hydroxide precipitates that provide surfaces for phosphate adsorption

and subsequent precipitation (Bai et al., 2010; Gon Kim et al., 2015; Wei et al., 2015; Langer et al., 2017). Deviations from this pH range hinder the formation of $\text{Al}(\text{OH})_3$, thereby reducing floc formation and phosphorus removal efficiency.

In contrast, iron-based coagulants, such as ferric chloride (FeCl_3) and ferrous sulphate (FeSO_4), offer a broader effective pH range, generally between 4 and 8. Ferric ions react with phosphate to form ferric phosphate precipitates, maintaining removal efficiency even under fluctuating pH conditions (Dong *et al.*, 2009). However, extremely low or high pH levels can affect the solubility of ferric phosphate and disrupt coagulation dynamics.

Alkalinity plays a pivotal role in buffering pH changes during the coagulation process. The hydrolysis of aluminium and iron salts releases hydrogen ions, which can acidify the water; hence, adequate alkalinity helps to neutralise these hydrogen ions, thereby maintaining pH within the optimal operational condition (Bai et al., 2010; Zhao et al., 2011; Farah Ateeq, 2016a). In systems with low alkalinity, the addition of acidic coagulants like alum or ferric chloride can lead to sharp pH declines, suppressing the formation of metal hydroxide flocs and decreasing phosphorus removal efficiency (Bai *et al.*, 2010; Zheng *et al.*, 2022).

The interaction between alkalinity and coagulant dosage is also critical. In high-alkalinity wastewaters, the natural buffering capacity can resist pH changes caused by coagulant addition, which may require higher doses of coagulants to lower the pH sufficiently for effective phosphorus removal (Yan *et al.*, 2008). Conversely, in low-alkalinity waters, where there is minimal buffering capacity, careful management of coagulant dosage and pH adjustment is necessary to avoid excessive acidification, which can impair coagulation reactions and compromise floc stability.

Furthermore, the solubility of metal-phosphate complexes and metal hydroxides is strongly pH-dependent. Maintaining pH within the coagulant-specific optimal range ensures that metal ions remain in reactive forms capable of effectively precipitating phosphate (Hafsteinsdóttir *et al.*, 2015). Therefore, the operational control of both pH and alkalinity, through pre-treatment or continuous dosing

strategies, is thus essential for optimising coagulation conditions and achieving high phosphorus removal efficiency.

1.4.3.2 Suspended Solids

The concentration of suspended solids in municipal wastewater can significantly impact phosphorus removal efficiency during coagulation and improve flocculation. It serves as nuclei for floc formation, providing surfaces for coagulants to adhere to and form larger, more settleable flocs. High suspended solids can enhance phosphorus removal by increasing the chances for coagulant-particle interactions (Lv *et al.*, 2019)

However, excessively high concentrations of suspended solids can pose challenges. While they provide more surfaces for flocculation, they also increase the demand for coagulants, as more coagulant is required to effectively bind the larger mass of particles. This increased coagulant demand can raise operational costs and complicate the management of residuals. The optimal coagulant dosage must be carefully managed in wastewater with very high suspended solids to avoid excessive chemical use and ensure effective phosphorus removal (Bilotta and Brazier, 2008).

Moreover, the nature and composition of suspended solids can influence coagulation efficacy. Organic and inorganic suspended solids interact differently with coagulants. Organic suspended solids, which include biological matter and organic particles, can complicate the coagulation process due to their varying surface charges and hydrophobic properties. In contrast, inorganic suspended solids, such as clay and silt, tend to have more predictable interactions with coagulants, often leading to more efficient floc formation (Bilotta and Brazier, 2008).

Sedimentation, filtration, and other pre-treatment methods help manage the load of suspended solids, ensuring that the coagulation process operates within optimal parameters. Pre-treated wastewater with reduced suspended solids concentration requires lower coagulant dosages while achieving high phosphorus removal efficiency (Khan and Farooqi, 2011).

The interaction between suspended solids concentration and coagulant type must be carefully considered. Different coagulants have varying affinities for different types and concentrations of suspended solids. For example, PACL has performed well in wastewater with moderate to high suspended solids concentrations, forming stable flocs that enhance phosphorus removal. Conversely, alum and ferric chloride may require more precise control of suspended solids to achieve similar efficiency (Ebeling et al., 2004; Hamidi et al., 2007; Bai et al., 2010).

1.4.3.3 Ions and Metals

The presence of various ions and metals significantly influenced the effectiveness of phosphorus removal from municipal wastewater by coagulation; they can either enhance or impede the coagulation process, affecting the efficiency of phosphorus removal.

Divalent cations, such as calcium (Ca^{2+}) and magnesium (Mg^{2+}), enhance coagulation by bridging negatively charged particles, aiding the formation of larger and more stable flocs, which improve phosphorus removal by promoting the adsorption of phosphate onto the flocs (Chakraborty *et al.*, 2017). Specifically, calcium can precipitate as calcium phosphate, further reducing the soluble phosphorus concentration in the treated water (Song et al., 2010).

However, competing anions, such as sulphate (SO_4^{2-}) and chloride (Cl^-), can adversely affect the coagulation process; high concentrations of sulphate, for instance, can form insoluble complexes with aluminium or ferric ions, thereby reducing the availability of these coagulants for phosphorus removal. This competition necessitates higher coagulant dosages to achieve the desired phosphorus removal efficiency, leading to increased operational costs and potential residual coagulant issues (Saxena et al., 2018).

Heavy metals, like iron (Fe) and manganese (Mn), play a significant role in the coagulation process because they can form insoluble complexes with phosphate, facilitating its removal from wastewater. Iron, either added as a coagulant or naturally occurring, enhances phosphorus removal by forming ferric phosphate (FePO_4) precipitates and ferric hydroxide [$\text{Fe}(\text{OH})_3$] flocs, which serve as

adsorption sites for precipitates (Tang *et al.*, 2014). However, excessive concentrations of these metals can lead to the overproduction of metal hydroxides, which may aggregate rapidly into dense particles with reduced surface area. This can limit the availability of reactive adsorption sites for phosphate binding, potentially reducing phosphorus removal efficiency (Li *et al.*, 2016; Feng *et al.*, 2022). While the formation of metal hydroxides is essential for effective phosphorus adsorption and removal, their excessive accumulation can compromise the overall coagulation process; hence, direct precipitation of compounds like FePO_4 is generally more effective for achieving low residual phosphorus concentrations.

Organic matter in wastewater can interact with metal ions, affecting their availability for phosphorus removal. High dissolved organic carbon levels can complex with metal ions such as aluminium and iron, reducing their effectiveness as coagulants. This interaction can hinder the coagulation process and decrease phosphorus removal efficiency. Organic matter can significantly alter the dynamics of metal ion availability, necessitating adjustments in coagulant dosage and pH management to maintain effective phosphorus removal (Omoike and vanLoon, 1999; Wilfert *et al.*, 2015). However, despite the extensive research on coagulation-based phosphorus removal, the literature is marked by inconsistencies in reported performance across different coagulants, doses, and operational conditions. These discrepancies are further compounded by the influence of wastewater matrix variability, organic load, pH, and other interacting parameters that are often not standardised across studies. As a result, it remains difficult to draw generalisable conclusions or identify best practices. This highlights the need for a more systematic and comparative evaluation of coagulants under controlled conditions to better understand their performance and establish reliable operational guidelines.

1.5 Aim and objectives

The overall aim of this thesis is to understand the impact of coagulant choice on the mechanisms controlling phosphorus removal from municipal wastewater, in order to establish an evidence-based framework for optimising chemical dosing

strategies across different treatment stages. To achieve this, the primary operational and chemical parameters influencing coagulant performance, such as pH, dosing location, and phosphorus speciation, were identified and systematically evaluated. The influence of selected coagulants on phosphorus removal efficiency, floc formation dynamics, and residual metal concentrations were investigated under both controlled and uncontrolled conditions. Furthermore, the practical implications of coagulant selection were examined through laboratory-scale studies using real wastewater samples, thereby contributing to improved understanding of process optimisation for enhanced phosphorus removal in municipal treatment facilities. To meet the aim stated, the following objectives will be addressed:

Objective 1 (Chapter 2): To determine the effectiveness of a broad range of coagulants in treating real municipal wastewater, focusing on floc formation and phosphorus removal under both uncontrolled and controlled pH conditions. This includes investigating how wastewater characteristics and coagulant selection influence floc properties—such as size, shape, and strength—as well as assessing the overall performance of the coagulation process in removing phosphorus.

Objective 2 (Chapter 3): To establish the behaviour and performance of high-efficiency coagulants in municipal wastewater across varying pH conditions. The assessment will again focus on floc formation and phosphorus removal efficiency.

Objective 3 (Chapter 4): To assess the impact of coagulant dosing location within a sewage treatment plant. The effectiveness of high-performing coagulants will be evaluated at different dosing points—namely, crude influent, primary settling tanks, and final effluent—within a selected case study site.

1.6 Thesis Structure

The thesis is presented as chapters, each formatted as an individual journal paper, in accordance with Cranfield University guidelines. The thesis comprises an overall introduction (Chapter 1) and three technical papers (Chapters 2, 3, and

4). The relationships between the various thesis objectives and chapters are illustrated in Table 1-1.

Ehizuelen Franklin Imafidon was the lead author of all the chapters in this PhD thesis, with editing and revision provided by Dr Marc Pidou and Prof Bruce Jefferson. All experimental works were designed and performed by Ehizuelen Franklin Imafidon, with the support of Nuannat Simmons for ICP-MS analysis. The contribution of each chapter is outlined below.

Chapter 2 tackles objective 1 of the thesis, focusing on the comparative performance of 17 metal-based coagulants (iron, aluminium, rare earth, zinc, and calcium-based) for total phosphorus (TP) removal from municipal wastewater. The chapter investigates the effectiveness of these coagulants under controlled and uncontrolled pH conditions, analysing factors such as charge, solubility, hydrolysis behaviour, metal speciation, and phosphate affinity. Key insights into the role of pH, coagulant dose, and floc characteristics were established, providing a comprehensive evaluation under standardised experimental conditions. This work enhances the understanding of how coagulant chemistry impacts phosphorus removal performance and offers guidance for selecting coagulants in wastewater treatment processes. In preparation for submission to *Environmental Technology*

Chapter 3 focuses on objective 2 of the thesis, which aims to investigate how pH influences the performance of three commonly used coagulants: Ferric sulphate, aluminium sulphate and polyaluminium chloride, in phosphorus removal from municipal wastewater. The chapter builds on the coagulant selection work from Chapter 2 by providing a controlled and systematic comparison of treatment performance, floc formation, and phosphorus fractionation across a range of pH conditions. This study delivers a comprehensive mechanistic understanding of the pH-dependent behaviour of coagulants, highlighting the strengths and limitations of each. It establishes key insights into coagulant selection for low-level phosphorus discharge compliance. Intended for submission to *Water Research*

Chapter 4 addresses objective 3 of the thesis, which aims to determine the optimum location for coagulant dosing in municipal wastewater treatment processes. The chapter evaluates phosphorus removal performance at three key dosing locations: raw wastewater (Crude), post-primary settling (PST), and final effluent (FE) with varying water characteristics using ferric sulphate, aluminium sulphate and polyaluminium chloride. The study examines the impact of wastewater matrix characteristics and pH conditions on coagulant effectiveness, supported by a detailed analysis of phosphorus fractionation, floc formation, turbidity, total suspended solids (TSS), and chemical oxygen demand (COD) removal. A two-point dosing strategy was also tested to enhance coagulant distribution and phosphorus removal efficiency. The findings provide practical insights into coagulant selection and strategic dosing to meet stringent phosphorus discharge limits in municipal sewage treatment works. Manuscript in preparation for submission to the *Journal of Water Process Engineering*

Chapter 5 is an overall discussion of the key implications of this thesis's results for practical application.

Chapter 6 presents opportunities for further research stemming from the findings of the presented thesis.

Chapter 7 summarises the vital conclusions of the findings of the study.

Table 1-1: Thesis contents and the publication proposal progression

Chapter	Paper	Title	Objective linked to	Proposed journal
1		Introduction		
2	1	Impact of coagulant choice on phosphorus removal from wastewater	1	Environmental Technology
3	2	To evaluate the impact of pH on the effectiveness of ferric sulphate, aluminium sulphate and PACL for phosphorus removal	2	Water Research
4	3	To understand the impact of the location on the effectiveness of ferric sulphate, aluminium sulphate and PACL for P removal from sewage	3	Journal of Water Process Engineering
5	-	Implications of the work: Overall discussions	2,3,4	
6	-	Further work	2,3,4	
7		Conclusions	2,3,4	

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Appendix A

Table A- 1: Summary of phosphorus removal efficiency from literature sources across various wastewater types

Type of wastewater	Coagulant	Dosage (mg/L as metal)	Influent TP (mg/L)	Effluent TP (mg/L)	D/I	Reference
Municipal wastewaters	Aluminium sulphate	11.0	4.6	0.5	2.4	(Pratt et al., 2012)
Municipal wastewaters	Aluminium sulphate	8.0	4.6	1.2	1.7	(Pratt et al., 2012)
Real wastewater	Aluminium sulphate	27.0	5.7	1.0	4.8	(Park et al., 2016)
Real wastewater	Aluminium sulphate	13.5	5.7	0.3	2.4	(Park et al., 2016)
Real wastewater	Aluminium sulphate	9.0	5.7	1.0	1.6	(Park et al., 2016)
Municipal wastewater	Aluminium sulphate	10.8	2.0	0.1	5.3	(Kim et al., 2008)
Model wastewater	Aluminium sulphate	50.0	11.1	7.3	4.5	(Song et al., 2008)
Model wastewater	Aluminium sulphate	10.0	11.1	4.2	9.0	(Song et al., 2008)

Type of wastewater	Coagulant	Dosage (mg/L as metal)	Influent TP (mg/L)	Effluent TP (mg/L)	D/I	Reference
Model wastewater	Aluminium sulphate	20.0	11.1	4.0	18.0	(Song et al., 2008)
Model wastewater	Aluminium sulphate	30.0	11.1	1.1	27.0	(Song et al., 2008)
Model wastewater	Aluminium sulphate	50.0	11.1	0.1	45.1	(Song et al., 2008)
Model wastewater	Aluminium sulphate	2.3	1.5	1.4	1.5	(Song et al., 2008)
Model wastewater	Aluminium sulphate	4.5	1.5	1.4	3.1	(Song et al., 2008)
Model wastewater	Aluminium sulphate	9.0	1.5	1.4	6.2	(Song et al., 2008)
Model wastewater	Aluminium sulphate	18.0	1.5	1.5	12.3	(Song et al., 2008)
Model wastewater	Aluminium sulphate	30.0	1.5	0.2	20.6	(Song et al., 2008)
Model wastewater	Aluminium sulphate	50.0	1.5	0.1	34.3	(Song et al., 2008)

Type of wastewater	Coagulant	Dosage (mg/L as metal)	Influent TP (mg/L)	Effluent TP (mg/L)	D/I	Reference
Municipal wastewater	Aluminium sulphate	40.0	3.1	0.8	12.8	(Kwak and lee, 2015)
Domestic wastewater	Aluminium sulphate	1.1	16.3	0.7	0.1	(Dong and Pan, 2011)
Municipal wastewater	Aluminium sulphate	7.2	4.0	0.9	1.8	(Yang et al., 2010)
Domestic wastewater	Aluminium sulphate	62.1	2.9	0.3	21.4	(Banu et al., 2008)
Domestic wastewater	Aluminium sulphate	8.4	7.4	0.4	1.1	(Dong et al., 2009)
Domestic wastewater	Aluminium sulphate	11.4	7.4	0.4	1.5	(Dong et al., 2009)
Municipal wastewater	Aluminium sulphate	27.0	11.0	0.9	2.5	(Diamadopoulos et al., 2007)
Municipal wastewater	Aluminium sulphate	20.2	11.0	1.0	1.8	(Diamadopoulos et al., 2007)
Municipal wastewater	Aluminium sulphate	13.5	11.0	1.8	1.2	(Diamadopoulos et al., 2007)

Type of wastewater	Coagulant	Dosage (mg/L as metal)	Influent TP (mg/L)	Effluent TP (mg/L)	D/I	Reference
Influent water	Aluminium sulphate	40.0	0.1	0.2	78.0	(Wang et al., 2014)
Municipal wastewater	Aluminium sulphate	4.0	1.7	0.5	2.4	(Bai et al., 2010)
Sewage treatment plant	Aluminium sulphate	23.0	4.9	0.1	47.4	(Wang et al., 2005)
Municipal wastewater	Aluminium sulphate	15.0	10.8	0.9	1.4	(Georgantas and Grigoropoulou, 2005)
Wastewater effluent	Aluminium sulphate	1.8	6.5	0.4	26.9	(Al-Rehaili and Misbahuddin, 2001)
Municipal wastewater	Aluminium sulphate	5.0	8.1	6.6	0.6	(Lee et al., 2001)
Municipal wastewater	Aluminium sulphate	25.0	8.1	0.6	3.1	(Lee et al., 2001)
Return activated sludge	Aluminium sulphate	3.5	10.0	1.7	0.4	(Lee et al., 2001)
Return activated sludge	Aluminium sulphate	10	10	1.3	1.0	(Lee et al., 2001)

Type of wastewater	Coagulant	Dosage (mg/L as metal)	Influent TP (mg/L)	Effluent TP (mg/L)	D/I	Reference
Municipal wastewater	Aluminium sulphate	67.5	2.8	0.2	24.4	(Kajjumba et al., 2021)
Municipal wastewater	Aluminium sulphate	27.0	8.7	1.0	3.1	(Sima et al., 2021)
Dairy soiled water	Aluminium sulphate	11.0	43.0	3.0	2.6	(Mohamed et al., 2020)
Primary wastewater	Aluminium sulphate	25.0	10.0	0.8	2.5	(Lee et al., 2001)
Glycine wastewater	Aluminium sulphate	30.0	7.8	0.8	38.0	(Liu and Zhou, 2022)
Municipal wastewater	Aluminium sulphate	40.0	3.1	0.1	12.8	(Kwak and lee, 2015)
Municipal Wastewater	Recovered Aluminium sulphate	54.0	8.7	3.4	6.2	(Chakraborty et al., 2017)
Municipal wastewater	Spent sludge	alum 75.0	10.8	1.0	6.9	(Georgantas and Grigoropoulou, 2005)
Municipal Wastewaters	Aluminium chloride	11.0	4.6	0.4	2.4	(Pratt et al., 2012)

Type of wastewater	Coagulant	Dosage (mg/L as metal)	Influent TP (mg/L)	Effluent TP (mg/L)	D/I	Reference
Conventional WW	Aluminium chloride	2.0	1.8	0.2	1.1	(Fundneider et al., 2020)
Municipal wastewater	Aluminium chloride	3.5	1.7	0.5	2.1	(Bai et al., 2010)
Influent water	Aluminium chloride	50.0	0.2	0.1	27.0	(Wang et al., 2014)
Domestic sewage	Aluminium chloride	1.7	5.0	0.1	33.5	(Cai et al., 2020)
Municipal Sewage Treatment Plant	Polyaluminium chloride	11.0	4.0	0.6	27.9	(Wang et al., 2022)
Glycine wastewater	Polyaluminium chloride	15.0	7.8	0.1	19.0	(Liu and Zhou, 2022)
Municipal wastewater	Polyaluminium chloride	11.0	7.3	0.4	14.8	(Rathnaweera et al., 2019)
Municipal wastewater	Polyaluminium chloride	11.0	7.3	3.1	14.8	(Rathnaweera et al., 2019)
Municipal wastewater	Polyaluminium chloride	11.0	7.3	0.3	14.8	(Rathnaweera et al., 2019)

Type of wastewater	Coagulant	Dosage (mg/L as metal)	Influent TP (mg/L)	Effluent TP (mg/L)	D/I	Reference
Municipal wastewater	Polyaluminium chloride	11.0	7.3	1.2	14.8	(Rathnaweera et al., 2019)
Municipal wastewater	Polyaluminium chloride	1.7	9.3	2.9	0.2	(Väänänen et al., 2016)
Municipal wastewater	Polyaluminium chloride	2.4	8.7	4.1	0.3	(Väänänen et al., 2016)
Municipal wastewater	Polyaluminium chloride	13.0	0.8	0.2	17.0	(Scherrenberg et al., 2012)
Municipal wastewater	Polyaluminium chloride	1.0	0.4	0.2	2.6	(Gasiūnas and Aškinis, 2011)
Municipal wastewater	Polyaluminium chloride	6.8	4.0	0.9	1.7	(Yang et al., 2010)
Influent water	Polyaluminum chloride	50.0	0.2	0.4	27.0	(Wang et al., 2014)
Municipal wastewater	Polyaluminium chloride	16.0	4.3	0.1	3.7	(Kim and Chung, 2014)
Municipal wastewater	Polyaluminium chloride	16.0	7.3	0.8	2.2	(Kim and Chung, 2014)

Type of wastewater	Coagulant	Dosage (mg/L as metal)	Influent TP (mg/L)	Effluent TP (mg/L)	D/I	Reference
Municipal wastewater	Polyaluminium chloride	16.0	6.4	0.6	2.5	(Kim and Chung, 2014)
Municipal wastewater	Polyaluminium chloride	16.0	5.5	0.9	2.9	(Kim and Chung, 2014)
Municipal wastewater	Polyaluminium chloride	16.0	8.1	0.2	2.0	(Kim and Chung, 2014)
Domestic wastewater	Polyaluminium chloride	6.9	16.3	0.4	0.4	(Dong and Pan, 2011)
Municipal wastewater	Polyaluminium chloride	27.0	11.0	1.5	2.5	(Diamadopoulos et al., 2007)
Municipal wastewater	Polyaluminium chloride	20.2	11.0	4.0	1.8	(Diamadopoulos et al., 2007)
Municipal wastewater	Polyaluminium chloride	13.5	11.0	6.3	1.2	(Diamadopoulos et al., 2007)
Municipal wastewater	Polyaluminium chloride	27.0	11.0	0.1	2.5	(Diamadopoulos et al., 2007)
Municipal wastewater	Polyaluminium chloride	20.2	11.0	1.0	1.8	(Diamadopoulos et al., 2007)

Type of wastewater	Coagulant	Dosage (mg/L as metal)	Influent TP (mg/L)	Effluent TP (mg/L)	D/I	Reference
Municipal wastewater	Polyaluminium chloride	13.5	11.0	3.2	1.2	(Diamadopoulos et al., 2007)
Municipal wastewater	Polyaluminium chloride	27.0	11.0	0.1	2.5	(Diamadopoulos et al., 2007)
Municipal wastewater	Polyaluminium chloride	20.2	11.0	0.2	1.8	(Diamadopoulos et al., 2007)
Municipal wastewater	Polyaluminium chloride	13.5	11.0	1.1	1.2	(Diamadopoulos et al., 2007)
Municipal wastewater	Polyaluminium chloride	27.0	11.0	0.1	2.5	(Diamadopoulos et al., 2007)
Municipal wastewater	Polyaluminium chloride	20.2	11	0.1	1.8	(Diamadopoulos et al., 2007)
Municipal wastewater	Polyaluminium chloride	13.5	11.0	0.2	1.2	(Diamadopoulos et al., 2007)
Sewage wastewater	Polyaluminium chloride	24.0	4.9	0.2	50.1	(Wang et al., 2005)
Domestic sewage	Polyaluminium chloride	17.0	5.0	0.1	33.5	(Cai et al., 2020)

Type of wastewater	Coagulant	Dosage (mg/L as metal)	Influent TP (mg/L)	Effluent TP (mg/L)	D/I	Reference
Municipal wastewater	Polyaluminium chloride	19.5	2.4	0.5	8.1	(Guo et al., 2015)
Dairy soiled water	Polyaluminium chloride	13.0	43.0	0.6	2.9	(Mohamed et al., 2020)
Mine production wastewater	PACL/PFS	25.0	1.0	0.5	24.8	(Dai et al., 2021)
Mine production wastewater	PACL/PFS	40.0	1.0	0.2	39.6	(Dai et al., 2021)
Mine production wastewater	PACL/PFS	30.0	1.8	0.5	16.3	(Dai et al., 2021)
Mine production wastewater	PACL/PFS	45.0	1.8	0.2	24.5	(Dai et al., 2021)
Mine production wastewater	PACL/PFS	30.0	3.1	0.5	9.7	(Dai et al., 2021)
Mine production wastewater	PACL/PFS	50.0	3.1	0.2	16.1	(Dai et al., 2021)
Mine production wastewater	PACL/PFS	25.0	1.0	0.5	24.8	(Dai et al., 2021)

Type of wastewater	Coagulant	Dosage (mg/L as metal)	Influent TP (mg/L)	Effluent TP (mg/L)	D/I	Reference
Mine production wastewater	PACL/PFS	40.0	1.0	0.2	39.6	(Dai et al., 2021)
Mine production wastewater	PACL/PFS	30.0	1.8	0.5	16.3	(Dai et al., 2021)
Mine production wastewater	PACL/PFS	45.0	1.8	0.2	24.5	(Dai et al., 2021)
Mine production wastewater	PACL/PFS	30.0	3.1	0.5	9.7	(Dai et al., 2021)
Mine production wastewater	PACL/PFS	50.0	3.1	0.2	16.1	(Dai et al., 2021)
Glycine wastewater	PAFC	15.0	7.8	1.0	19.0	(Liu and Zhou, 2022)
Domestic wastewater	PAFC	13.0	3.5	1.3	37.1	(Liu YinSong et al., 2014)
Domestic sewage	PAFC	17.0	5.0	0.1	33.5	(Cai et al., 2020)
Municipal wastewater	Aluminium chlorohydrate	16.9	5.0	0.7	3.4	(Heronemus et al., 2021)
Municipal wastewater	Aluminium chlorohydrate	33.7	5.0	0.5	6.7	(Heronemus et al., 2021)

Type of wastewater	Coagulant	Dosage (mg/L as metal)	Influent TP (mg/L)	Effluent TP (mg/L)	D/I	Reference
Municipal wastewater	Aluminium chlorohydrate	50.6	5.0	0.4	10.1	(Heronemus et al., 2021)
Municipal wastewater	Aluminium chlorohydrate	67.5	5.0	0.1	13.5	(Heronemus et al., 2021)
Domestic wastewater	Polyauminium hydroxy chloro sulphate	10.0	5.8	2.2	1.7	(Kim et al., 2015)
Phosphate-kaolin synthetic water	Polyferric acetate	24.0	5.1	0.2	4.7	(Wei et al., 2017)
Municipal WWTP	Polyferric sulphate	11.0	10.0	0.1	11.2	(Ping et al., 2023)
Phosphate-kaolin synthetic water	Polyferric sulphate	20.0	5.1	0.4	4.0	(Wei et al., 2017)
Glycine wastewater	Polyferric sulphate	90.0	7.8	0.1	12.0	(Liu and Zhou, 2022)
Synthetic wastewater	Polyferric sulphate	89.9	10.0	1.2	9.0	(Ruihua et al., 2011)
Synthetic wastewater	Polyferric sulphate	89.9	4.0	0.3	22.5	(Ruihua et al., 2011)

Type of wastewater	Coagulant	Dosage (mg/L as metal)	Influent TP (mg/L)	Effluent TP (mg/L)	D/I	Reference
Municipal wastewater	Polyferric sulphate	18.0	4.0	0.6	4.5	(Yang et al., 2010)
Municipal sewage	Polyferric chloride	40.0	1.7	0.7	23.0	(Xie et al., 2020)
Municipal sewage	Polyferric chloride	40.0	1.7	0.7	23.0	(Xie et al., 2020)
Mustard tuber wastewater and municipal wastewater	Polysilicate ferric	33.5	8.7	1.0	3.9	(Sima et al., 2021)
Glycine wastewater	Ferric sulphate	13.0	7.8	0.1	17.0	(Liu and Zhou, 2022)
Municipal wastewater	Ferric sulphate	21.0	4.2	0.7	5.0	(Holba et al., 2012)
Municipal wastewater	Ferric sulphate	21.0	8.7	4.7	2.4	(Holba et al., 2012)
Municipal wastewater	Ferric sulphate	21.0	10.6	10.5	2.0	(Holba et al., 2012)
Synthetic wastewater	Ferric sulphate	12.0	4.0	0.2	30.0	(Ruihua et al., 2011)

Type of wastewater	Coagulant	Dosage (mg/L as metal)	Influent TP (mg/L)	Effluent TP (mg/L)	D/I	Reference
Synthetic wastewater	Ferric sulphate	82.1	4.0	0.6	20.5	(Ruihua et al., 2011)
Municipal wastewater	Ferric sulphate	4.0	1.6	0.5	2.5	(Bai et al., 2010)
Municipal wastewater	Ferric sulphate	11.0	10.0	2.4	11.2	(Ping et al., 2023)
Sewage wastewater	Ferric sulphate	16.0	4.9	0.4	33.8	(Wang et al 2005)
Municipal wastewater	Ferric sulphate	30.0	10.8	0.5	2.8	(Georgantas and Grigoropoulou, 2005)
Municipal wastewater	Ferric sulphate	25.0	8.1	1.2	3.1	(Lees et al., 2001)
Primary wastewater	Ferric sulphate	50.0	10.0	1.4	5.0	(Lees et al., 2001)
Return activated sludge	Ferric sulphate	1.7	10.0	4.5	0.2	(Lees et al., 2001)
Return activated sludge	Ferric sulphate	5.0	10.0	1.7	0.5	(Lees et al., 2001)
Return activated sludge	Ferric sulphate	8.4	10.0	1.5	0.8	(Lees et al., 2001)

Type of wastewater	Coagulant	Dosage (mg/L as metal)	Influent TP (mg/L)	Effluent TP (mg/L)	D/I	Reference
Screened municipal wastewater	Fresh ferric sulphate	20.0	6.2	0.9	3.2	(Keeley et al., 2016)
Synthetic wastewater	Ferric chloride	20.0	10.0	0.5	2.0	(Zhiqiang et al., 2006)
Synthetic wastewater	Ferric chloride	20.0	10.0	3.5	2.0	(Zhiqiang et al., 2006)
Real wastewater	Ferric chloride	5.6	5.7	3.7	1.0	(Park et al., 2016)
Real wastewater	Ferric chloride	27.9	5.7	2.3	4.9	(Park et al., 2016)
Real wastewater	Ferric chloride	18.6	5.7	2.3	3.3	(Park et al., 2016)
Municipal wastewater	Ferric chloride	7.5	6.5	5.7	1.2	(El-Shafai et al., 2023)
Municipal wastewater	Ferric chloride	15.0	6.5	5.0	2.3	(El-Shafai et al., 2023)
Municipal wastewater	Ferric chloride	30.0	6.5	4.0	4.6	(El-Shafai et al., 2023)
Municipal wastewater treatment	Ferric chloride	60.0	6.5	2.8	9.2	(El-Shafai et al., 2023)

Type of wastewater	Coagulant	Dosage (mg/L as metal)	Influent TP (mg/L)	Effluent TP (mg/L)	D/I	Reference
Municipal wastewater	Ferric chloride	12.0	6.5	0.9	18.4	(El-Shafai et al., 2023)
Model wastewater	Ferric chloride	50.0	13.3	12.5	3.8	(Song et al., 2008)
Model wastewater	Ferric chloride	10.0	13.3	11.4	7.6	(Song et al., 2008)
Model wastewater	Ferric chloride	20.0	13.3	12.7	15.1	(Song et al., 2008)
Model wastewater	Ferric chloride	30.0	13.3	10.3	22.6	(Song et al., 2008)
Model wastewater	Ferric chloride	50.0	13.3	7.5	37.7	(Song et al., 2008)
Municipal Sewage	Ferric chloride	11.0	4.0	0.5	27.9	(Wang et al., 2022)
Municipal wastewater	Ferric chloride	12.5	5.0	0.7	24.3	(Heronemus et al., 2021)
Municipal wastewater	Ferric chloride	18.0	5.0	0.1	36.4	(Heronemus et al., 2021)
Municipal sewage	Ferric chloride	40.0	1.7	0.2	23.0	(Xie et al., 2020)
Conventional wastewater	Ferric chloride	4.0	1.8	0.1	2.3	(Fundneider et al., 2020)
Domestic wastewater	Ferric chloride	13.0	3.5	1.2	37.1	(Liu YinSong et al., 2014)

Type of wastewater	Coagulant	Dosage (mg/L as metal)	Influent TP (mg/L)	Effluent TP (mg/L)	D/I	Reference
Municipal wastewater	Ferric chloride	8.0	4.3	0.8	1.9	(Kim and Chung, 2014)
Municipal wastewater	Ferric chloride	8.0	7.3	1.0	1.1	(Kim and Chung, 2014)
Municipal wastewater	Ferric chloride	8.0	6.4	1.0	1.3	(Kim and Chung, 2014)
Municipal wastewater	Ferric chloride	8.0	5.5	0.9	1.5	(Kim and Chung, 2014)
Municipal wastewater	Ferric chloride	8.0	8.1	1.1	1.0	(Kim and Chung, 2014)
Municipal wastewater	Ferric chloride	4.0	1.6	0.5	2.5	(Bai et al., 2010)
Municipal wastewater	Ferric chloride	16.8	4.0	0.9	4.2	(Yang et al., 2010)
Artificial sewage	Ferric chloride	54.0	10.0	0.5	5.4	(Zhou et al., 2008)
Artificial sewage	Ferric chloride	54.0	5.0	0.4	10.8	(Zhou et al., 2008)
	Ferric chloride	54.0	9.2	2.0	5.9	(Zhou et al., 2008)
Effluent wastewater	Ferric chloride	54.0	5.2	0.5	10.3	(Zhou et al., 2008)

Type of wastewater	Coagulant	Dosage (mg/L as metal)	Influent TP (mg/L)	Effluent TP (mg/L)	D/I	Reference
Effluent of the pilot-scale wastewater	Ferric chloride	54.0	4.1	0.5	13.3	(Zhou et al., 2008)
	Ferric chloride	54.0	5.1	0.7	10.7	(Zhou et al., 2008)
	Ferric chloride	54.0	35.0	3.2	1.5	(Zhou et al., 2008)
Sewage from the primary sedimentation tank	Ferric chloride	54.0	5.8	0.6	9.3	(Zhou et al., 2008)
	Ferric chloride	54.0	9.2	2.0	5.9	(Zhou et al., 2008)
Sewage from the secondary sedimentation tank	Ferric chloride	54.0	5.2	0.5	10.3	(Zhou et al., 2008)
Pesticide industrial wastewater	Ferric chloride	54.0	4.1	0.5	13.3	(Zhou et al., 2008)
Effluent of the anaerobic digestion of leachate of a municipal landfill	Ferric chloride	54.0	5.1	0.7	10.7	(Zhou et al., 2008)
Effluent of the bioreactor	Ferric chloride	54.0	35.0	3.2	1.6	(Zhou et al., 2008)

Type of wastewater	Coagulant	Dosage (mg/L as metal)	Influent TP (mg/L)	Effluent TP (mg/L)	D/I	Reference
Effluent of the pilot-scale bioreactor	Ferric chloride	54.0	5.8	0.6	9.3	(Zhou et al., 2008)
Sewage from the primary sedimentation tank	Ferric chloride	60.0	9.0	0.5	6.7	(Marguti et al., 2008)
Sewage from the secondary sedimentation tank	Ferric chloride	80.0	5.0	1.2	16.0	(Marguti et al., 2008)
Pesticide industrial wastewater	Ferric chloride	60.0	4.0	0.9	15.0	(Marguti et al., 2008)
Effluent of the anaerobic digestion of leachate of a municipal landfill	Ferric chloride	11.0	10.0	0.5	11.2	(Ping et al., 2023)
Raw Sewage	Ferric chloride	10.0	4.0	0.2	25.1	(Chen et al., 2024)
Final effluent	Ferric chloride	10.0	6.0	0.2	16.8	(Chen et al., 2024)
Final effluent	Ferric chloride	10.0	8.0	0.2	12.6	(Chen et al., 2024)
Municipal wastewater	Ferric chloride	11.0	10.0	0.2	11.2	(Chen et al., 2024)

Type of wastewater	Coagulant	Dosage (mg/L as metal)	Influent TP (mg/L)	Effluent TP (mg/L)	D/I	Reference
Synthetic wastewater	Ferric chloride	11.0	12.0	0.2	9.3	(Chen et al., 2024)
Synthetic wastewater	Ferric chloride	55.9	11.0	1.3	5.1	(Diamadopoulos et al., 2007)
Synthetic wastewater	Ferric chloride	41.9	11.0	2.2	3.8	(Diamadopoulos et al., 2007)
Synthetic wastewater	Ferric chloride	27.9	11.0	4.5	2.5	(Diamadopoulos et al., 2007)
Synthetic wastewater	Ferric chloride	55.9	11.0	0.8	5.1	(Diamadopoulos et al., 2007)
Municipal wastewater	Ferric chloride	41.9	11.0	3.0	3.8	(Diamadopoulos et al., 2007)
Municipal wastewater	Ferric chloride	27.9	11.0	3.1	2.5	(Diamadopoulos et al., 2007)
Municipal wastewater	Ferric chloride	55.9	11.0	0.11	5.9	(Diamadopoulos et al., 2007)
Municipal wastewater	Ferric chloride	41.9	11.0	0.11	3.8	(Diamadopoulos et al., 2007)

Type of wastewater	Coagulant	Dosage (mg/L as metal)	Influent TP (mg/L)	Effluent TP (mg/L)	D/I	Reference
Municipal wastewater	Ferric chloride	27.9	11.0	0.3	2.5	(Diamadopoulos et al., 2007)
Municipal wastewater	Ferric chloride	55.9	11.0	0.2	5.1	(Diamadopoulos et al., 2007)
Municipal wastewater	Ferric chloride	41.9	11.0	0.3	3.8	(Diamadopoulos et al., 2007)
Municipal wastewater	Ferric chloride	27.9	11.0	1.0	2.5	(Diamadopoulos et al., 2007)
Municipal wastewater	Ferric chloride	20.0	6.0	0.5	3.3	(Zhiqiang et al., 2006)
Municipal wastewater	Ferric chloride	30.0	10.8	0.5	2.8	(Georgantas and Grigoropoulou, 2005)
Municipal wastewater	Ferric chloride	70.0	5.5	0.9	12.7	(Al-Rehaili and Misbahuddin, 2001)
Municipal wastewater	Ferric chloride	15.0	19.3	3.5	0.8	(Realı et al., 2001)
Synthetic wastewater	Ferric chloride	30.0	19.3	0.9	1.6	(Realı et al., 2001)

Type of wastewater	Coagulant	Dosage (mg/L as metal)	Influent TP (mg/L)	Effluent TP (mg/L)	D/I	Reference
Synthetic wastewater	Ferric chloride	17.0	10.0	2.4	16.8	(Zhou et al., 2008)
Synthetic wastewater	Ferric chloride	30.0	5.0	0.4	6.0	(Zhou et al., 2008)
Synthetic wastewater	Ferric chloride	25.0	9.2	2.0	2.7	(Zhou et al., 2008)
Synthetic wastewater	Ferric chloride	30.0	5.2	0.5	5.8	(Zhou et al., 2008)
Artificial sewage	Ferric chloride	30.0	4.1	0.5	7.4	(Zhou et al., 2008)
Artificial sewage	Ferric chloride	25.0	5.1	0.7	5.0	(Zhou et al., 2008)
Effluent of the bioreactor	Ferric chloride	19.0	35.0	3.2	5.4	(Zhou et al., 2008)
Effluent of the pilot-scale bioreactor	Ferric chloride	30.0	5.8	0.6	5.2	(Zhou et al., 2008)
Sewage from the primary sedimentation tank	Ferric chloride	40.0	1.7	0.2	23.0	(Xie et al., 2020)

Type of wastewater	Coagulant	Dosage (mg/L as metal)	Influent TP (mg/L)	Effluent TP (mg/L)	D/I	Reference
Sewage from the secondary sedimentation tank	Ferric chloride	17.0	5.0	0.2	33.5	(Cai et al., 2020)
Pesticide industrial wastewater	Ferric chloride	44.7	8.7	1.0	5.1	(Sima et al., 2021)
Effluent of the anaerobic digestion of leachate of a municipal landfill	Ferric chloride	24.0	43.0	0.5	5.5	(Sima et al., 2020)
Municipal sewage treatment plant	Ferric chloride	6.0	7.0	0.2	0.9	(Philp, 1985)
Domestic sewage	Ferric chloride	83.8	2.8	0.1	30.2	(Kajjumba et al., 2021)
Mustard tuber wastewater and municipal wastewater	Ferric trichloride	3.1	16.3	0.4	0.2	(Dong and Pan, 2011)
Dairy soiled water	Ferrous sulphate	11.1	8.1	0.5	1.4	(Wang et al., 2014)
Raw wastewater	Ferrous sulphate	9.7	8.1	0.4	1.2	(Wang et al., 2014)
Municipal wastewater	Ferrous sulphate	8.2	5.0	1.3	1.6	(Li et al., 2014)

Type of wastewater	Coagulant	Dosage (mg/L as metal)	Influent TP (mg/L)	Effluent TP (mg/L)	D/I	Reference
Domestic wastewater	Ferrous sulphate	11.1	8.1	0.3	1.4	(Wang et al., 2014)
Municipal wastewater	Ferrous sulphate	111.0	5.5	1.0	20.3	(Banu et al., 2008)
Municipal wastewater	Ferric hydroxide	40.0	1.7	0.7	23.0	(Xie et al., 2020)
Domestic wastewater	Ferric hydroxide	40.0	1.7	0.7	23.0	(Xie et al., 2020)
Municipal wastewater	Hydrous ferric oxide	2.9	6.0	0.6	0.5	(Newcombe et al., 2008)
Synthetic domestic wastewater	Hydrous ferric oxide	5.0	6.0	0.1	0.8	(Newcombe et al., 2008)
Municipal sewage	Hydrous ferric oxide	11.3	6.0	0.01	1.9	(Newcombe et al., 2008)
Municipal sewage	Titanium salt	8.0	2.2	0.9	3.7	(Jia et al., 2022)
Municipal wastewater	Titanium salt	20.0	2.2	0.4	9.3	(Jia et al., 2022)
Municipal wastewater	Titanium salt	60.0	2.2	0.3	27.9	(Jia et al., 2022)

Type of wastewater	Coagulant	Dosage (mg/L as metal)	Influent TP (mg/L)	Effluent TP (mg/L)	D/I	Reference
Municipal wastewater	Acid mine drainage	78.7	4.0	0.3	19.7	(Ruihua et al., 2011)
SBRs wastewater	Acid mine drainage	89.9	4.0	0.3	22.5	(Ruihua et al., 2011)
SBRs wastewater	Cerium chloride	17.0	2.8	0.03	60.7	(Kajjumba et al., 2021)
SBRs wastewater	Lanthanum chloride	17.0	2.8	0.05	60.2	(Kajjumba et al., 2021)
Municipal effluent	Zirconium tetrachloride	50.0	15.2	1.0	3.3	(Uysal and Boyacioglu, 2021)
Synthetic wastewater	Sodium aluminate	48.6	2.8	0.3	17.5	(Kajjumba et al., 2021)
Municipal wastewater	Magnesium hydroxide	75.4	1.3	0.2	59.3	(Kajjumba et al., 2021)
Municipal wastewater	Polyethersulfone	2.1	16.3	0.4	0.1	(Dong and Pan, 2011)
Industrial wastewater	Tannic acid	20.0	10.0	0.5	2.0	(Zhou et al., 2008)
Municipal wastewater	Powdered activated carbon	50.0	0.7	0.1	69.4	(Altmann et al., 2015)

Chapter 2

2 Impact of coagulant choice on phosphorus removal from wastewater

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Abstract

The removal of phosphorus is crucial in wastewater treatment as excess phosphorus discharge into water bodies can lead to eutrophication, resulting in harmful algal blooms, oxygen depletion, and biodiversity loss. Coagulants play a vital role in the reduction of phosphorus levels by promoting its precipitation and subsequent removal, making their evaluation essential for optimising treatment processes and meeting increasingly stringent environmental regulations. This study investigated the efficacy of 17 coagulants, including iron-based, aluminium-based, rare-earth metal-based, and zinc-based compounds, in the removal of total phosphorus (TP) from municipal wastewater. Using a series of coagulation-flocculation experiments under uncontrolled and controlled pH conditions (pH 7), the research evaluated the impact of coagulant type, dosage, and pH control on TP removal efficiency. The experimental setup employed jar tests, coupled with a particle size analyser, to monitor floc formation, breakage, and regrowth dynamics in real-time. Coagulant performance was assessed by measuring residual TP, suspended solids, and COD alongside floc strength and fractal dimension to analyse floc characteristics.

The results indicate that ferric sulphate and polyaluminium chloride demonstrated the highest TP removal efficiency, particularly under controlled pH conditions, where flocs were more stable and compact. Rare earth metal coagulants, notably cerium sulphate, also exhibited strong TP removal capabilities, although their high cost may limit their use to specialised applications. Zinc-based coagulants and calcium hydroxide showed moderate TP removal performance, primarily functioning in pH adjustment and supplementary roles. The study confirms that pH control plays an important role in optimising coagulant efficiency and enhancing phosphorus removal and floc stability.

This research contributes to the optimisation of coagulation processes by comprehensively comparing coagulants under varying conditions, providing insights into their specific performance dynamics. Where ferric and aluminium-based coagulants consistently achieve lower residual TP levels due to their stable hydroxide formation, which enhances phosphate adsorption. Rare earth coagulants, despite their strong phosphate-binding affinity, exhibited limitations in floc stability, leading to lower overall efficiency. Thus, this highlights the crucial role of pH in influencing coagulant performance, as significant deviations from the optimal range resulted in reduced phosphorus removal efficiency due to solubility shifts and destabilisation of hydroxide species. These insights provide a framework for selecting coagulants based on wastewater characteristics and operational requirements, ensuring efficient phosphorus removal while minimising chemical usage and sludge production and advancing knowledge in phosphorus removal methodologies.

Keywords: Coagulation; Flocculation; Phosphorus; Floc formation; Optimisation

2.1 Introduction

Phosphorus removal from wastewater is essential to mitigate eutrophication, threatening aquatic ecosystems by reducing oxygen levels, harming biodiversity, and degrading water quality (Dorgham, 2014; Glibert, 2017; Ayele and Atlabachew, 2021). To address these environmental risks, stringent regulations mandate low effluent phosphorus discharge limits for wastewater treatment plants (WWTPs). For instance, the European Union (EU) Directive 91/271/EEC requires total phosphorus concentrations to be under 1.0 mg/L for large treatment facilities, with some cases demanding levels as low as 0.1 mg/L (Tran *et al.*, 2012; Carrillo *et al.*, 2024). Achieving such low concentrations, particularly with diverse wastewater compositions, poses challenges for WWTPs, which have widely adopted coagulation for phosphorus removal due to its effectiveness, ease of application, adaptability, and energy efficiency (Jin *et al.*, 2024; Reza *et al.*, 2024; Xu *et al.*, 2024).

Coagulation involves adding metal salts, commonly iron or aluminium compounds, to react with the phosphorus and also destabilise colloidal particles, enabling aggregation into flocs that can be removed through sedimentation or filtration (Tahraoui *et al.*, 2024; Zaki *et al.*, 2024). The effectiveness of the coagulation process depends not only on the chemical composition of the coagulant but also on the characteristics of the wastewater. Different coagulants exhibit distinct characteristics, such as variations in charge density, solubility, hydrolysis rates, and affinity for phosphate ions, influencing their performance. As shown in Table 1, coagulants reported in the literature for phosphorus removal vary widely in their chemical properties. Iron-based coagulants, such as ferric sulphate (FS) and ferric chloride (FC), rely on extensive hydrolysis and polymerisation to form stable flocs, while aluminium-based coagulants, such as polyaluminium chloride (PACL), are known for their pre-polymerised structure, which allows for rapid floc formation and reduced sludge production (Mohamed *et al.*, 2024). Rare-earth metal-based coagulants, like cerium sulphate (CS) and lanthanum sulphate (LS), demonstrate high phosphate-binding affinities; however, at higher dosages, whereas calcium hydroxide (CH) is primarily used

for pH adjustment to trigger precipitation of calcium phosphate compounds. These differences highlight the need to adapt coagulant selection to the specific wastewater characteristics for optimal phosphorus removal.

Studies have evaluated various, more conventional, coagulants to assess their effectiveness in phosphorus removal. For instance, municipal wastewater treated with aluminium sulphate (ALS), aluminium chloride (ALC), and PACL at dosages of 4, 11, and 16 mg/L achieved total phosphorus (TP) residual levels of 0.49, 0.41, and 0.88 mg/L, respectively, from initial concentrations of 1.67, 4.6 and 5.5 mg/L (Bai *et al.*, 2010; Pratt *et al.*, 2012; Kim and Chung, 2014). Similarly, municipal wastewater with an initial TP concentration of 1.59 mg/L treated with ferric sulphate at a dose of 4 mg/L achieved a TP residual of 0.5 mg/L (Bai *et al.*, 2010). Synthetic wastewater treated with ferric chloride at a dose of 8 mg/L resulted in TP residuals of the initial 4.3 mg/L to 0.77 mg/L (Kim and Chung, 2014).

As an alternative, rare earth metal-based coagulants, such as cerium and lanthanum, have been reported to show a strong affinity for phosphate ions, forming stable complexes that enhance phosphorus removal under varied pH conditions (Lu *et al.*, 2024; Yingqi Li *et al.*, 2024). Zirconium and zinc-based coagulants similarly exhibit strong metal-ligand complexation, with zirconium demonstrated to achieve low TP residuals at lower dosages compared to traditional coagulants (Akram *et al.*, 2020; Wang *et al.*, 2021). Calcium hydroxide (CH), while less effective as a primary coagulant, is widely used for pH adjustment, promoting phosphorus precipitation as calcium phosphate and improving sludge dewatering (Nie *et al.*, 2019; Lv *et al.*, 2022). Previous research has demonstrated the effectiveness of rare earth coagulants, particularly lanthanum and cerium, in phosphate removal within the range pH of 4.0–9.0 of wastewater centrate; LaCl_3 and CeCl_3 achieved phosphorus removal, reducing the initial phosphate concentration of 8.5 mg PO_4^{3-} /L to a residual TP of 4.25 mg/L (>50%) at dosages of 80.78 mg/L for LaCl_3 and 81.18 mg/L for CeCl_3 at pH ≥ 6.0 . Notably, even at lower pH levels (≤ 5.0), their performance remained

unaffected, with residual TP further decreasing to 1.28 mg/L (85%) at the same dosage (Kajjumba *et al.*, 2021).

The hydrolysis of coagulants, particularly those with high-valence cations such as Al^{3+} or Fe^{3+} , is highly pH-sensitive. Under optimal pH conditions, these cations react with phosphate ions (PO_4^{3-}) to form insoluble phosphate precipitates, which can be efficiently removed through solid-liquid separation (Tran *et al.*, 2012). The effectiveness of this process is closely linked to the speciation of the metal coagulants, as shown in Figure 2-1. These speciation diagrams illustrate how different coagulants are influenced by pH, with distinct speciation profiles for iron-based, aluminium-based, and rare-earth metal-based coagulants.

The speciation of ferric ion (Fe^{3+}), in Figure 2-1a, indicates that at low pH (< 2), ferric ion primarily exists as Fe^{3+} , which is soluble and ineffective in phosphorus precipitation. However, as the pH increases to around 4-5, $\text{Fe}(\text{OH})^{2+}$ and $\text{Fe}(\text{OH})_3(\text{am})$ become dominant species. The formation of $\text{Fe}(\text{OH})_3$, a solid precipitate, is most effective in the pH range of 5-8, as corroborated by previous studies that highlight this pH range as optimal for phosphorus removal (Amirtharajah and Mills, 1982; Millero, 2001; Mezenner and Bensmaili, 2009; Lů *et al.*, 2013; Ping *et al.*, 2023). Above pH 8, $\text{Fe}(\text{OH})_4^-$ dominates, indicating a transition to soluble hydroxide complexes, reducing coagulation efficiency.

In contrast, the ferrous ion (Fe^{2+}) is the dominant species across a much broader pH range (up to pH 8-9), with $\text{Fe}(\text{OH})^+$ and $\text{Fe}(\text{OH})_2$ appearing only at higher pH values (> 9) (Figure 2-1b). This behaviour explains why ferrous coagulants are generally less effective in phosphorus removal than ferric coagulants under typical wastewater treatment conditions (pH 6-8) (Jones *et al.*, 2014; Bratby, 2016).

Aluminium (Al^{3+}) displays a similar behaviour as ferric with only Al^{3+} at low pH (< 4). As the pH increases to between 5 and 6, $\text{Al}(\text{OH})_2^+$ and $\text{Al}(\text{OH})_3(\text{am})$ form, with $\text{Al}(\text{OH})_3$ being the primary precipitate responsible for phosphorus removal (Figure 1c). $\text{Al}(\text{OH})_4^-$ becomes dominant at pH values greater than 8. Aluminium ions

were reported to be most effective as coagulants in the pH range of 5-7 (Pa Ho Hsu, 1976; Amirtharajah and Mills, 1982).

The rare earth metals cerium (Ce^{3+}) and lanthanum (La^{3+}) show similar behaviour, with both metals forming hydroxide species around neutral pH values (Figure 2-1d and e). In the cerium diagram, $\text{Ce}(\text{OH})_2^+$ and $\text{Ce}(\text{OH})_3$ dominate at pH values between 7 and 9, while $\text{Ce}(\text{OH})_4^-$ appears at higher pH values (> 10). These hydroxide species facilitate the precipitation of phosphate. Similarly, lanthanum forms $\text{La}(\text{OH})_2^+$ and $\text{La}(\text{OH})_3(\text{amorphous})$ in the pH range of 7-9, which have been reported to be effective in phosphorus capture (Lu *et al.*, 2024). Zirconium (Zr^{4+}) exhibits robust phosphorus removal capacity due to the formation of $\text{Zr}(\text{OH})_2^{2+}$ and $\text{Zr}(\text{OH})_4(\text{am})$ at pH values between 4 and 8 (Figure 2-1f) (Kajjumba and Marti, 2022). However, these observations have primarily been made under controlled laboratory conditions and high doses (Liu, Liang and Wu, 2024; Altaf *et al.*, 2025), and their performance in real wastewater treatment applications remains less extensively validated. This highlights the need for further investigation under uniform experimental conditions, as undertaken in this study, to determine their true efficacy compared to conventional coagulants.

Zinc (Zn^{2+}) shows a different behaviour, with Zn^{2+} being the dominant species across a wide pH range up to 6.5. Zinc hydroxides ($\text{Zn}(\text{OH})_2$) begin to form at pH values greater than 8 (Figure 2-1g).

Ultimately, calcium (Ca^{2+}), represented in the last diagram, shows that Ca^{2+} is dominant up to pH 10, where CaOH^+ begins to form (Figure 2-1h). Calcium is typically used in wastewater treatment for pH adjustment rather than direct phosphorus removal, though it can promote phosphate precipitation as calcium phosphate at higher pH values (Lin *et al.*, 2024).

This highlights the critical role of pH in the determination of the dominant species of coagulants and their subsequent impact on phosphorus removal efficiency (Yitao *et al.*, 2024). Despite technological advancements, consistent phosphorus removal remains challenging under varying operational conditions, as optimal coagulant performance depends on factors like pH control, coagulant dosage,

and flocculation parameters (Hernandez-Ramirez and Thompson, 2024). Consequently, selecting the appropriate coagulant is critical, as the impact on floc stability, phosphorus capture efficiency, and sludge production can vary significantly across coagulants. However, it is important to note that only a limited number of studies have investigated multiple coagulants under the same conditions, making direct comparisons of performance challenging. The wide range of experimental conditions, such as variations in wastewater composition, pH, and coagulant dosages used in different studies, further complicates efforts to evaluate and standardise coagulant efficiency.

Therefore, this research aims to deepen the understanding of how different coagulants perform in phosphorus removal under controlled and uncontrolled pH conditions in real wastewater by testing a wide range of coagulants in the same conditions. Specifically, the study's objectives are to assess the impact of coagulant selection on treatment performance and to evaluate the effects of chemical addition on floc formation and breakage. To explore the dynamics of phosphorus species removal, laboratory-scale coagulation experiments were conducted using real municipal wastewater under varying coagulant concentrations and pH conditions. The findings from this research are expected to contribute to the optimisation of coagulation processes in wastewater treatment plants that support compliance with stringent environmental regulations and protect aquatic ecosystems.

Table 2-1: Properties of the different coagulants tested

Coagulant	Traditional/ Emerging	Availability	Effective pH	Solubility	Hydrophilicity/ Hydrophobicity	Mechanism	Reference
FS	Traditional	Widely available	Effective in a wide pH range	High	Hydrophilic	Adsorption, charge neutralisation, precipitation, sweep flocculation and bridging	(Tang <i>et al.</i> , 2014; Zhang <i>et al.</i> , 2015)
FC	Traditional	Widely available	Effective in a wide pH range	High	Hydrophilic	Adsorption, charge neutralisation, precipitation, sweep flocculation and bridging	(Ebeling <i>et al.</i> , 2003; Ren <i>et al.</i> , 2020)
FERS	Traditional	Readily available	Effective pH 7–8	Moderate	Hydrophilic	Charge neutralisation, oxidation to Fe ³⁺ followed by precipitation, sweep flocculation and bridging	(Zhang <i>et al.</i> , 2013; Bratby, 2016)
FERC	Traditional	Readily available	Effective pH 7–8	Low	Hydrophilic	Charge neutralisation, oxidation to Fe ³⁺ followed by precipitation, sweep flocculation and bridging	(Ebeling <i>et al.</i> , 2003; Zhang <i>et al.</i> , 2013)
ALS	Traditional	Widely available	Most effective between pH of 5.5 and 6.5	High	Hydrophilic	Charge neutralisation, precipitation, sweep flocculation and bridging	(Duan and Gregory, 2003; Ebeling <i>et al.</i> , 2003)
ALC	Traditional	Available	Most effective between pH of 5.5 and 6.5	High	Hydrophilic	Charge neutralisation, precipitation, sweep flocculation and bridging	(Duan and Gregory, 2003; Zheng <i>et al.</i> , 2022)
ALCH	Traditional	Available	Less pH impacted	High	Hydrophilic	Charge neutralisation, adsorption, and bridging	(Duan and Gregory, 2003; Wang <i>et al.</i> , 2009)
PACL	Traditional	Widely available	Less pH impacted	High	Hydrophilic	Charge neutralisation, adsorption, and bridging	(Kim <i>et al.</i> , 2001; Zhao <i>et al.</i> , 2011)
CS	Emerging	Limited	Effective under varying pH conditions	Moderate	Hydrophilic	Precipitation, charge neutralisation, adsorption, and sweep flocculation	(Yan <i>et al.</i> , 2008; Kajjumba and Marti, 2022)
CC	Emerging	Limited	Effective under varying pH conditions	Moderate	Hydrophilic	Precipitation, charge neutralisation, adsorption, and sweep flocculation	(Yan <i>et al.</i> , 2008; Kajjumba and Marti, 2022)
LS	Emerging	Limited	Wide working pH range	Moderate	Hydrophilic	Precipitation, charge neutralisation, adsorption, and sweep flocculation	(Zheng <i>et al.</i> , 2022; Lu <i>et al.</i> , 2024)
LC	Emerging	Limited	Wide working pH range	Moderate	Hydrophilic	Precipitation, charge neutralisation, adsorption, and sweep flocculation	(Zheng <i>et al.</i> , 2022; Lu <i>et al.</i> , 2024)
ZS	Emerging	Limited	Optimal pH values of 6–7	High	Hydrophilic	Precipitation, charge neutralisation, adsorption, and sweep flocculation	(Kajjumba and Marti, 2022; Haoming <i>et al.</i> , 2023)
ZC	Emerging	Limited	Optimal pH values of 6–7	Moderate	Hydrophilic	Precipitation, charge neutralisation, adsorption, and sweep flocculation	(Kajjumba and Marti, 2022; Haoming <i>et al.</i> , 2023)
ZIS	Traditional	Available	Optimal pH 4 - 6	Low	Hydrophilic	Precipitation of zinc phosphate and sweep flocculation	(Ebeling <i>et al.</i> , 2003; Kovo <i>et al.</i> , 2013; Sinha <i>et al.</i> , 2020; Zhao <i>et al.</i> , 2021)
ZIC	Traditional	Available	Optimal pH 4 - 6	Low	Hydrophilic	Precipitation of zinc phosphate and sweep flocculation	(Ebeling <i>et al.</i> , 2003; Kovo <i>et al.</i> , 2013; Zhao <i>et al.</i> , 2021)
CH	Traditional	Widely available	Effective pH 10-12 increases the pH of wastewater	Low	Hydrophilic	Precipitation of calcium phosphate Ca ₃ (PO ₄) ₂	(Bai <i>et al.</i> , 2010; Owodunni and Ismail, 2021; Zheng <i>et al.</i> , 2022)

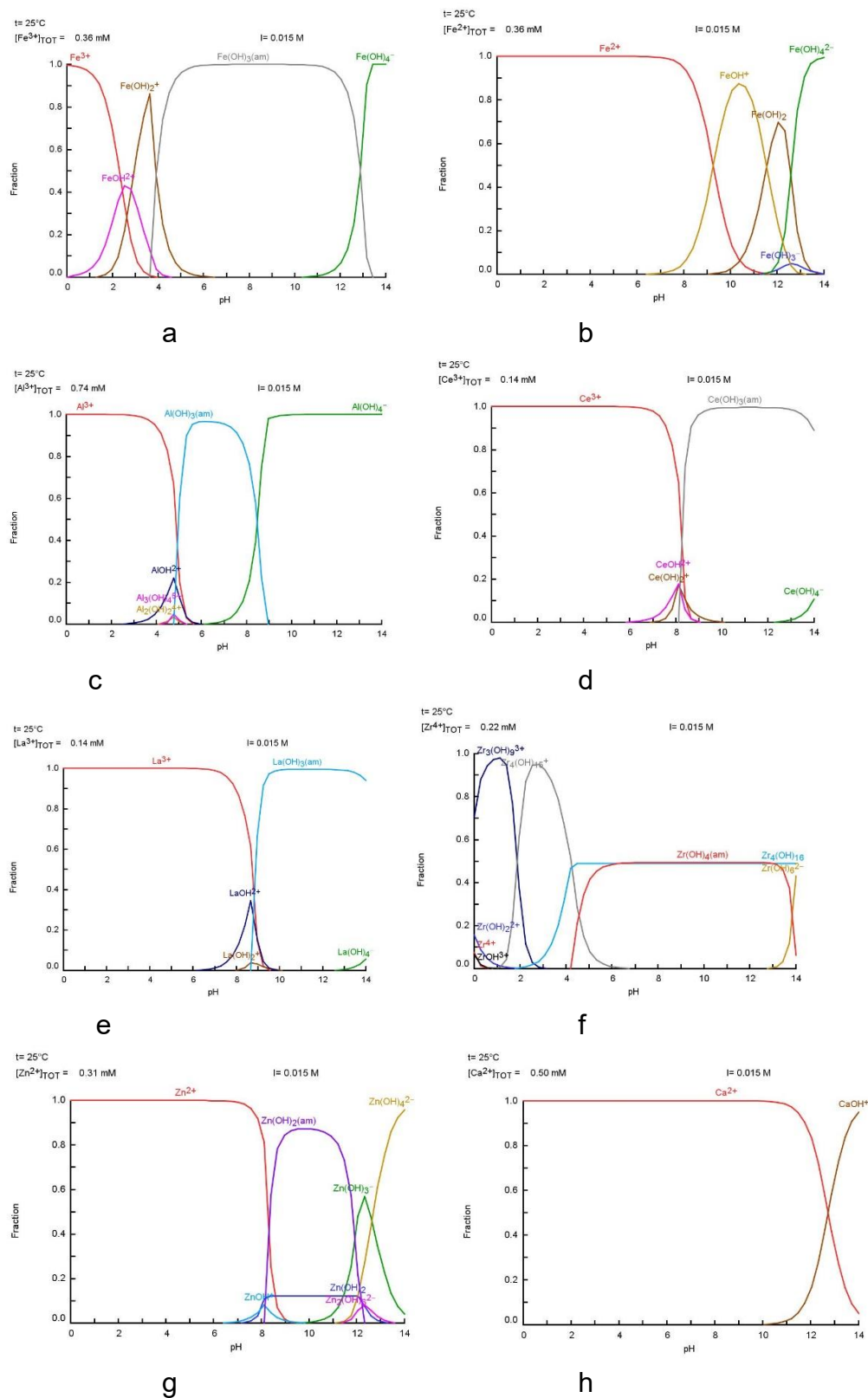


Figure 2-1: Speciation diagram for (a) ferric, (b) ferrous, (c) aluminium, (d) cerium, (e) lanthanum, (f) zirconium, (g) zinc, and (h) calcium

2.2 Materials and Methods

2.2.1 Municipal Wastewater Sample Collection and Characterisation

Municipal wastewater samples were collected from the sewage treatment facility at Cranfield University. The samples were collected from the final effluent tank after treatment through screens, primary sedimentation, a combination of trickling and submerged aerated filters, and final clarification. These samples served as the primary substrate for all experimental procedures and provided a consistent baseline for the evaluation of the performance of various coagulants under controlled-temperature laboratory conditions.

To ensure a comprehensive understanding of the wastewater matrix, the collected samples were characterised for key physico-chemical parameters prior to experimentation (Table 2-2 and

Table 2-3). The parameters characterised included pH, alkalinity, turbidity, total suspended solids (TSS), chemical oxygen demand (COD), total phosphorus (TP), and orthophosphate (Ortho-P) concentrations with the following method:

- pH: Measured using a calibrated multiparameter probe (Jenway 4330 pH meter).
- Alkalinity: Alkalinity measurements were performed using a Hanna Instruments alkalinity checker.
- Turbidity: Determined using a portable turbidity meter (Hach 2100Q), expressed in Nephelometric Turbidity Units (NTU).
- TSS: Quantified gravimetrically by filtering a known volume of wastewater through pre-weighed glass fibre filters and drying at 105°C using a standardised filtration method (Federation and Aph Association, 2005).
- TP, Ortho-P, and COD: concentrations were determined with the use of Merck cell test kits and measured colorimetrically using the ascorbic acid method after persulfate digestion for TP with a spectrophotometer, Merck Spectroquant NOVA 60 system.
- Target metal concentrations were quantified using Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) on a Nexion 350D system.

- Dionex ICS – 1600 and ICS – 900 thermo-scientific Ion chromatography was employed to analyse key anions and cations.

This initial characterisation provided a reliable basis for interpreting coagulation performance, floc formation behaviour, and phosphorus removal efficiency under varying treatment conditions.

2.2.2 Coagulant Selection

Seventeen coagulants were selected for this study to assess their efficacy in phosphorus removal and establish the impact of their properties (Table 2-1 and Figure 2-1). For information, the speciation diagrams reported in Figure 2-1 were obtained using Hydra-Medusa software under thermodynamic equilibrium conditions (Puigdomenech, 2020). The calculations were based on solubility constants and metal-ligand interactions from established databases. The input parameters included a temperature of 25°C, an ionic strength of 0.015 M, and a pH range of 0-14. This pH range was chosen not to represent typical wastewater treatment conditions, which typically range from 6 to 8, but rather to illustrate the full spectrum of potential chemical species that can form under varying pH environments. These diagrams illustrate the dominant metal species at different pH levels, providing insights into their role in phosphorus removal and helping to interpret the observed coagulation performance. The iron-based coagulants included Iron (III) sulphate hydrate (FS, 97%) and Iron (III) chloride (FC, reagent grade, 97%), along with Iron (II) sulphate heptahydrate (FERS, 99.5% for analysis) and Iron (II) chloride tetrahydrate (FERC, 98%), all acquired from Fisher Scientific. For aluminium-based coagulants, Aluminium chloride (ALC, reagent grade, 98%) and Aluminium sulphate octa-decahydrate (ALS, ≥97%) were obtained from Sigma-Aldrich, Polyaluminium chloride (PACL) and Aluminium chlorohydrate (ALCH, also known as Polygold) were sourced from Airedale Chemical Company Limited.

Rare earth metal coagulants included Cerium (III) chloride heptahydrate (CC, 99%), Cerium (IV) sulphate (CS, 99%), Zirconium (IV) sulphate tetrahydrate (ZS, 98+%, metals basis), Zirconium (IV) chloride (ZC, 98%, anhydrous), Lanthanum chloride (LC, hydrated, ACS reagent) and Lanthanum (III) sulphate (LS,

anhydrous, 99.9% REO), all procured from Fisher Scientific. Zinc-based coagulants, including Zinc chloride (ZIC, 98.5%) and Zinc sulphate heptahydrate (ZIS), were sourced from Thermo Scientific Chemicals. Calcium hydroxide (CH, ACS reagent, $\geq 95.0\%$) was obtained from Sigma-Aldrich.

2.2.3 Coagulation–Flocculation Experiment

The coagulation-flocculation experiments were conducted using standard practice testing to evaluate the required chemicals, dosages, and conditions for optimal results. The experiments used a Phipps & Bird Six-Paddle Stirrer. The jar test method commenced with a rapid mixing phase at 200 rpm for 2 minutes to ensure thorough dispersion of the coagulant within the wastewater matrix, both with and without pH adjustment, followed by the addition of the designated coagulant dose (5, 10, 15, 30 and 40 mg/L). This was succeeded by a slow mixing phase at 30 rpm for 15 minutes to promote floc formation, which were then allowed to settle by gravity for 30 minutes. For experiments that require pH control, the pH was adjusted and maintained at 7 from the start of the trial before the addition of the coagulant. After the settling phase, the supernatant from each jar was collected for further analysis. Each test was conducted in triplicate to ensure the reliability and reproducibility of the results.

2.2.4 Floc Formation and Breakage Assessment

To further understand the dynamics of floc formation and stability, specialised coagulation experiments were conducted with selected conditions (Table B-1) using a single paddle stirrer jar tester integrated with a particle size analyser. The experimental setup involved cylindrical 2L jars, each equipped with port holders for inflow and outflow tubing, containing 1L of the final effluent with a strictly controlled pH of 7. A Malvern Mastersizer was employed to continuously monitor and quantify floc size distribution throughout the coagulation and flocculation processes. The setup included two tubes arranged opposite each other at a depth of 2 cm above the paddle. During the experiment, water was continuously drawn through the Mastersizer optical unit and returned to the jar through a peristaltic pump with a 5 mm internal diameter tubing at a flow rate of 1.5 L/hr. Floc size

measurements were recorded every minute and processed via a connected PC to ensure precise data acquisition.

The experimental procedure mirrored the conditions outlined in the initial coagulation tests, with a rapid mixing phase at 200 rpm for 2 minutes, followed by a slow mixing phase at 30 rpm for 15 minutes to promote floc growth. Subsequently, the suspension was subjected to increased shear by raising the mixing speed to 200 rpm for an additional 15 minutes to assess floc breakage and strength. Finally, the mixing speed was reduced back to 30 rpm for 15 minutes to evaluate the potential for floc regrowth. As before, all experiments were conducted in triplicate.

2.2.5 Floc Size and Fractal Dimension

Several key floc properties were calculated from the experimental data with the laser diffraction instrument (Malvern Mastersizer 2000). The floc strength factor (FSF) was determined using the formula:

$$\text{Floc Strength Factor} = \frac{d_2}{d_1} \times 100 \quad (2-1)$$

Where d_1 represents the mean floc size immediately before breakage, and d_2 represents the mean floc size after breakage (Jarvis *et al.*, 2005; Bratby, 2016). Floc size measurements were collected during coagulation tests using the Mastersizer at key time points to capture growth (after slow mixing), breakage (after high shear), and regrowth (after shear reduction). The Mastersizer's software calculated particle volume distributions from intensity data, which were used to establish the mass (M) of flocs. The mass–size relationships were then used to derive Df for each stage.

This methodology provides valuable insights into the structural characteristics of flocs and their resilience to shear forces, contributing to understanding the performance of different coagulants in phosphorus removal.

Floc regrowth factor (FRF) was calculated as follows:

$$\text{Floc Re-growth Factor} = \frac{d_3 - d_2}{d_1 - d_2} \times 100 \quad (2-2)$$

Where d_3 represents the mean floc size after the regrowth phase, d_2 after breakage, and d_1 before breakage. This parameter indicates the ability of flocs to reform after being subjected to shear forces (Jarvis *et al.*, 2005; Bratby, 2016). Floc fractal dimension was determined using the mass length scaling approach based on particle size distribution data obtained from the Malvern Mastersizer. The Mastersizer uses laser diffraction to measure scattered light intensity at multiple angles, generating detailed size distribution profiles for flocs during growth, breakage, and regrowth phases. These data allow the estimation of the floc mass–size relationship expressed as:

$$M \propto L^{D_f} \quad (2-3)$$

where M is the mass of the floc, L is the characteristic length scale (e.g., floc diameter), and D_f is the fractal dimension. Plotting $\log M$ against $\log L$ produces a straight line, where the slope corresponds to D_f (Waite *et al.*, 2001; Wu *et al.*, 2002; Jarvis *et al.*, 2008). Higher D_f values indicate denser and more compact flocs, whereas lower values signify more open and porous structures. This method accounts for the irregular geometry and scaling properties of flocs and is widely applied in coagulation and flocculation studies.

2.2.6 Justification for pH selection and control

The choice to control the pH at 7.0 during specific experiments was deliberate and based on both practical and scientific considerations. pH 7.0 was selected as it represents a neutral condition and is within the typical pH range encountered in municipal wastewater treatment systems (approximately 6.5-7.5). This makes it a realistic and relevant pH for assessing the performance of coagulants under conditions commonly observed in operational wastewater treatment environments. By maintaining a stable pH at 7.0, variability due to pH fluctuations was minimised, allowing for a direct comparison of coagulant performance in removing phosphorus.

It is acknowledged that the solubility and speciation of metal-based coagulants such as ferric sulphate, aluminium sulphate, and polyaluminium chloride are pH-dependent. As shown in Figure 2-1, different hydrolysis species dominate at

different pH values, which directly affects the formation of metal-phosphate precipitates. Therefore, by selecting pH 7.0 as the controlled condition, this study specifically investigated which coagulants achieve effective phosphorus removal at neutral pH, rather than determining the optimal pH for each coagulant. This approach reflects a practical scenario in which operators may not adjust pH extensively, but instead rely on treatment efficiency within existing wastewater pH ranges.

Furthermore, we recognise that fixing the pH at 7.0 may not represent ideal conditions for all coagulants tested, as some may exhibit superior performance at more acidic or alkaline pH levels. However, this constraint was intentional, as it allowed us to evaluate and compare the robustness of each coagulant's phosphorus removal capacity under a standardised and environmentally relevant condition.

We also performed parallel tests under uncontrolled pH conditions. These tests provided insights into how natural pH variations in wastewater influence coagulant performance, allowing for a more comprehensive assessment of their behaviour. Together, these two approaches, controlled pH at 7.0 and uncontrolled pH, offer a balanced evaluation of coagulant efficacy across realistic operational scenarios.

2.2.7 Analytical Techniques

Various analytical techniques were employed to measure the relevant parameters of the treated wastewater samples. The pH levels were measured using a Jenway 4330 pH meter. Target metal concentrations were quantified using Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) on a Nexion 350D system.

Dionex ICS – 1600 and ICS – 900 thermo-scientific Ion chromatography was employed to analyse key anions and cations. Chemical oxygen demand (COD), total phosphorus (TP), and orthophosphate concentrations were determined with the use of Merck cell test kits and measured with a spectrophotometer Merck Spectroquant NOVA 60 system. Alkalinity measurements were performed using

a Hanna Instruments alkalinity checker. Total suspended solids (TSS) were quantified using a standardised filtration method (Federation and Aph Association, 2005), and turbidity was measured with a Hach 2100Q turbidity meter, and to ensure accuracy, each sample was analysed in triplicate.

Table 2-2: Wastewater characterisation for controlled pH 7 without coagulant

	FS		FC		FERS		FERC		ALS		ALC		ALCH		PACL		CS		CC		LS		LC		ZS		ZC		ZIS		ZIC		CH	
Parameter	Mean	Stdev	Mean	Stdev	Mean	Stdev	Mean	Stdev	Mean	Stdev	Mean	Stdev	Mean	Stdev	Mean	Stdev	Mean	Stdev	Mean	Stdev	Mean	Stdev	Mean	Stdev	Mean	Stdev	Mean	Stdev	Mean	Stdev	Mean	Stdev	Mean	Stdev
TP (mg/L)	7.9	0.0	8.8	0.5	6.7	0.3	6.8	0.5	8.2	0.2	4.9	1.1	7.3	0.8	8.1	0.1	7.8	0.2	7.7	0.2	6.1	0.3	7.9	0.3	9.0	0.4	7.9	0.2	6.2	0.4	5.6	0.5	8.1	1.3
Ortho-P (mg/L)	6.9	0.0	7.1	0.1	5.9	0.0	6.4	0.2	6.9	0.1	7.1	0.1	7.2	0.1	7.3	0.1	7.0	0.2	7.1	0.1	5.4	0.1	7.2	0.1	8.0	0.2	7.1	0.2	5.6	0.1	4.8	0.0	7.8	0.1
pH	7.1	0.0	7.3	0.1	6.7	0.0	7.0	0.1	7.1	0.1	7.0	0.0	6.4	0.0	6.5	0.1	6.4	0.0	6.5	0.0	7.1	0.0	6.5	0.0	6.4	0.0	6.5	0.0	7.1	0.0	7.1	0.0	6.5	0.0
Alkalinity (mg/L)	73.3	1.3	69.7	4.5	40.3	4.1	96.0	2.9	49.0	3.7	55.7	6.0	36.0	7.8	32.3	4.5	27.0	5.7	37.7	1.7	75.0	1.4	35.0	3.6	24.3	1.3	31.3	5.3	78.3	5.3	72.0	2.9	25.3	0.9
TSS (mg/L)	63.3	0.0	61.3	0.0	76.7	0.0	50.0	0.0	64.0	0.0	63.3	0.0	72.7	0.0	54.7	0.0	64.7	0.0	57.3	0.0	56.0	0.0	81.3	0.0	73.3	0.0	70.7	0.0	69.3	0.0	66.0	0.0	85.3	0.0
Turbidity (NTU)	24.4	1.4	23.9	0.6	22.2	0.4	23.8	2.5	27.5	0.8	25.2	0.5	34.4	0.7	35.2	1.8	38.8	1.1	28.5	1.7	28.7	1.5	28.4	1.3	41.1	0.4	33.1	1.0	26.5	1.3	23.5	1.6	44.9	2.5
COD (mg/L)	84.3	5.0	81.0	5.4	97.7	5.4	93.3	4.1	86.0	20.6	81.0	11.2	98.3	6.8	99.7	6.9	96.0	7.8	80.0	8.0	77.3	12.3	99.3	11.7	99.7	7.9	97.3	2.5	79.7	9.5	92.7	17.8	98.7	2.5
Chloride (mg/L)	87.3	0.1	78.2	0.2	72.0	0.2	70.3	0.3	75.0	0.1	74.9	0.3	77.4	0.2	79.6	0.5	76.1	0.1	74.7	0.3	97.1	0.3	74.4	0.1	74.7	0.2	75.5	0.2	98.1	0.2	64.1	0.2	74.6	0.1
Sulphate (mg/L)	55.1	0.0	55.7	0.1	49.4	0.2	73.8	0.2	54.9	0.1	54.6	0.3	50.5	0.1	53.6	0.4	50.6	0.1	50.5	0.2	63.2	0.2	50.2	0.2	53.5	0.2	51.0	0.3	63.2	0.2	58.5	0.2	54.0	0.1
Ferric (mg/L)	-0.3	0.3	-0.4	0.2	0.0	1.1	-0.1	0.4	-0.4	0.7	-0.5	0.4	0.6	49.8	-0.4	0.1	-0.1	0.1	-9.9	2.5	0.0	0.2	0.1	9.9	0.0	0.2	0.0	0.2	-1.7	0.2	-0.1	0.4	0.0	0.2
Aluminium (mg/L)	-1.2	0.2	-0.2	0.1	0.0	0.2	0.0	0.0	-0.1	0.2	-0.1	0.1	89.8	81.5	-0.1	0.3	0.0	2.9	-0.2	0.1	0.0	0.1	9.2	510.3	-0.6	0.4	-1.0	0.1	0.0	0.2	0.0	0.1	0.0	0.2
Zinc (mg/L)	0.0	0.3	0.0	0.2	0.1	0.2	0.0	0.3	0.0	0.6	0.0	0.1	0.6	36.8	0.0	0.4	0.1	0.2	0.1	0.2	0.0	0.1	0.1	2.2	0.1	0.3	0.1	0.1	0.1	1.6	0.1	1.5	0.1	0.3
Calcium (mg/L)	40.7	9.4	41.3	89.9	42.7	49.2	72.5	73.6	42.9	49.9	42.9	94.6	47.7	80.1	44.7	59.1	44.8	42.4	40.7	69.4	57.0	28.3	44.5	20.6	46.6	89.8	45.3	87.3	56.7	172.5	55.9	36.8	46.9	89.6

Table 2-3: Wastewater characterisation for uncontrolled pH without coagulant

	FS		FC		FERS		FERC		ALS		ALC		ALCH		PACL		CS		CC		LS		LC		ZS		ZC		ZIS		ZIC		CH	
Parameter	Mean	Stdev	Mean	Stdev	Mean	Stdev	Mean	Stdev	Mean	Stdev	Mean	Stdev	Mean	Stdev	Mean	Stdev	Mean	Stdev	Mean	Stdev	Mean	Stdev	Mean	Stdev	Mean	Stdev	Mean	Stdev	Mean	Stdev	Mean	Stdev	Mean	Stdev
TP (mg/L)	4.1	0.4	3.5	0.1	6.9	0.2	6.9	0.2	4.4	0.2	4.5	0.3	4.0	0.7	4.9	0.1	6.7	0.0	4.6	0.2	4.5	0.4	4.5	0.1	4.7	0.3	4.6	0.2	6.9	0.2	6.9	0.2	4.7	0.2
Ortho-P (mg/L)	4.3	0.0	3.4	0.1	5.9	0.0	5.9	0.0	4.5	0.2	8.2	0.1	4.2	0.0	4.5	0.1	7.4	0.1	4.9	0.0	4.4	0.4	4.7	0.1	4.8	0.1	4.6	0.1	5.9	0.0	5.9	0.0	4.7	0.0
pH	7.2	0.0	7.6	0.0	6.8	0.0	6.8	0.0	7.1	0.1	7.4	0.0	7.1	0.0	6.7	0.0	7.0	0.0	6.8	0.0	6.6	0.0	6.7	0.0	7.7	0.0	7.3	0.1	6.8	0.0	6.8	0.0	7.3	0.0
Alkalinity (mg/L)	160.3	26.6	192.3	0.5	51.0	1.4	51.0	1.4	130.3	9.0	108.5	0.5	107.3	0.5	115.7	0.9	59.0	1.4	53.7	1.3	85.3	2.6	49.0	5.1	94.3	2.1	51.7	3.1	51.0	1.4	51.0	1.4	122.0	28.3
TSS (mg/L)	48.0	0.0	48.0	0.0	45.3	0.0	45.3	0.0	52.0	0.0	58.0	0.0	26.0	0.0	51.5	0.0	31.3	0.0	35.3	0.0	58.7	0.0	58.7	0.0	42.7	0.0	57.3	0.0	45.3	0.0	45.3	0.0	32.0	0.0
Turbidity (NTU)	20.8	0.6	25.1	3.2	14.2	2.4	14.2	2.4	16.5	4.1	25.2	0.8	9.8	0.3	9.7	1.1	21.9	0.4	4.6	0.1	22.7	2.4	51.2	1.8	12.5	0.9	21.8	2.4	14.2	2.4	14.2	2.4	12.0	0.9
COD (mg/L)	43.0	7.8	52.0	5.0	43.3	4.1	43.3	4.1	31.3	5.4	44.5	0.5	15.3	0.5	18.0	1.4	35.0	5.0	11.7	2.1	101.0	29.4	87.7	9.8	39.7	6.9	47.3	6.6	43.3	4.1	43.3	4.1	30.3	5.0
Chloride (mg/L)	59.8	0.1	57.5	0.2	68.7	0.4	68.7	0.4	61.9	0.1	45.8	0.2	na	na	na	na	70.3	0.1	68.8	0.1	21.8	0.0	na	na	59.7	0.2	na	na	68.7	0.4	68.7	0.4	66.1	0.1
Sulphate (mg/L)	61.7	0.0	65.9	0.1	45.8	0.1	45.8	0.1	66.9	0.6	49.3	0.2	na	na	na	na	55.1	0.1	54.1	0.1	17.2	0.0	na	na	60.1	0.1	0.0	0.0	45.8	0.1	45.8	0.1	63.2	0.1
Ferric (mg/L)	-0.1	1.2	0.0	0.4	0.0	0.0	0.0	0.0	0.0	0.6	-0.1	2.4	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	-0.2	2.1	-0.2	2.1	0.0	0.8

Aluminium (mg/L)	0.0	0.6	0.0	0.1	0.0	0.0	0.0	0.0	0.0	0.9	-0.1	6.3	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	94.6	69.3	94.6	69.3	0.0	0.9
Zinc (mg/L)	0.8	0.2	0.0	0.0	3.3	35.6	3.3	35.6	1.0	0.3	0.1	0.1	2.8	2.5	1.9	1.0	2.1	1.3	3.3	35.6	-0.4	0.5	-0.2	0.1	-0.3	0.1	-0.3	0.4	0.0	0.4	0.0	0.4	1.1	2.3
Calcium (mg/L)	65.7	17.0	68.1	54.4	47.3	452.4	47.3	452.4	63.8	82.9	43.9	90.3	63.9	73.2	60.6	16.3	44.9	59.1	47.3	452.4	40.0	29.4	35.9	30.9	33.0	24.5	36.6	66.8	44.7	82.2	44.7	82.2	61.0	51.0

Note: A total of 103 samples were collected from the Cranfield sewage works; a total of 306 samples were analysed for the 17 coagulants, with and without pH control conditions during the laboratory experiment.

2.3 Results

It is essential to note that the starting concentrations of phosphorus, TSS, COD, and other wastewater parameters for each coagulant varied, reflecting natural variations in the collected wastewater samples. While the discussion largely focuses on residual TP concentrations as the target for discharge in the environment, this does not necessarily reflect the total mass of phosphorus removed by each coagulant. For example, a coagulant tested with a higher initial TP concentration may remove a greater absolute mass of phosphorus but still leave a higher residual concentration. Consequently, comparisons based solely on residual TP levels may overlook cases where significant phosphorus removal occurred but did not reach low residual TP levels. Consequently, comparisons based solely on residual TP levels may overlook cases where significant phosphorus removal occurred but did not reach low residual TP levels. For instance, several coagulants demonstrated high removal efficiency when treating influent with elevated phosphorus concentrations, even though the final residual TP exceeded target levels. They may have been potentially capable of achieving the residual TP target if the influent TP concentration were lower.

2.3.1 Total Phosphorus

The overall trends in TP removal for the various coagulants tested show a gradual decrease in residual TP as the dosage increases. However, some of the coagulants, FS, ALS, and PACL, reached low TP levels at low doses and then plateaued with very minimal further change as the doses were further increased. In Figure 2-2 a and b, FS achieved a residual TP from an initial concentration of 4.1 mg/L to 0.12 mg/L at a 30 mgFe/L (0.54 mol/L) dosage under uncontrolled conditions and from 7.9 mg/L to 0.35 mg/L at 40 mgFe/L (0.72 mol/L) under controlled pH conditions. FC showed TP residual from 3.5 to 0.37 mg/L at a 10 mgFe/L (0.18 mol/L) dosage under uncontrolled conditions. However, under controlled pH conditions, a higher dosage of 30 mgFe/L was required to achieve residual TP from 8.8 to 0.83 mg/L.

ALS reduced TP to 0.22 mg/L at 10 mgAl/L (0.37 mol/L) under uncontrolled conditions and further to 0.15 mg/L at 15 mgAl/L (0.56 mol/L), Figure 2-2c and d. With pH control, ALS reduced TP to 0.6 mg/L at a 30 mgAl/L (1.11 mol/L) dosage. Under controlled pH, ALC performed more predictably, achieving a TP residual of 0.26 mg/L at 15 mgAl/L (0.56 mol/L). PACL exhibited similar efficiency, achieving a residual TP of 0.55 mg/L at 10 mgAl/L (0.37 mol/L) under uncontrolled conditions and 0.15 mg/L at 30 mgAl/L (1.11 mol/L) under controlled pH. These results align with previous studies, where ALS and FS at 40 and 30 mg/L doses achieved residual TP levels of 0.78 mg/L and 0.5 mg/L, respectively (Georgantas and Grigoropoulou, 2005; Kwak and Lee, 2015).

In contrast, some coagulants exhibited only a slight decrease in TP, which maintains nearly flat performance curves across the dosage range, particularly under uncontrolled pH conditions. Ferrous-based coagulants require much higher dosages to reduce TP levels but still perform poorly. Residual TP for these coagulants remained above 4 mg/L under uncontrolled conditions and improved only to around 2.4 mg/L with pH control Figure 2-2a and b. In Figure 2-2h, Zinc-based coagulants also exhibited limited performance, with residual TP reductions to 1 and 1.8 mg/L, even at the higher dosages of 40 mg/L.

Some of the rare earth coagulants attained a residual TP of 1 mg/L at higher doses of 30-40 mg/L, particularly CC and LS (Figure 2-2e and f). In contrast, the other coagulants (ZS, ZIS, ZIC and CH) could not reach the residual TP of either 0.3 or 1 mg/L.

The trends observed for ortho-P (Figure B-1) were very similar to those seen for TP across all coagulants and dosage conditions, as ortho-P was the main fraction of TP. However, the Ortho-P:TP ratio remained constant across different doses, suggesting that all phosphorus fractions were removed to the same level at all tested dosages.

Iron- and aluminium-based coagulants effectively reduce TP to low levels, especially under controlled pH conditions. Some rare earth metal-based coagulants, such as CC and LC, also demonstrate adequate TP removal at

higher dosages. However, their performance was generally less consistent than iron and aluminium coagulants.

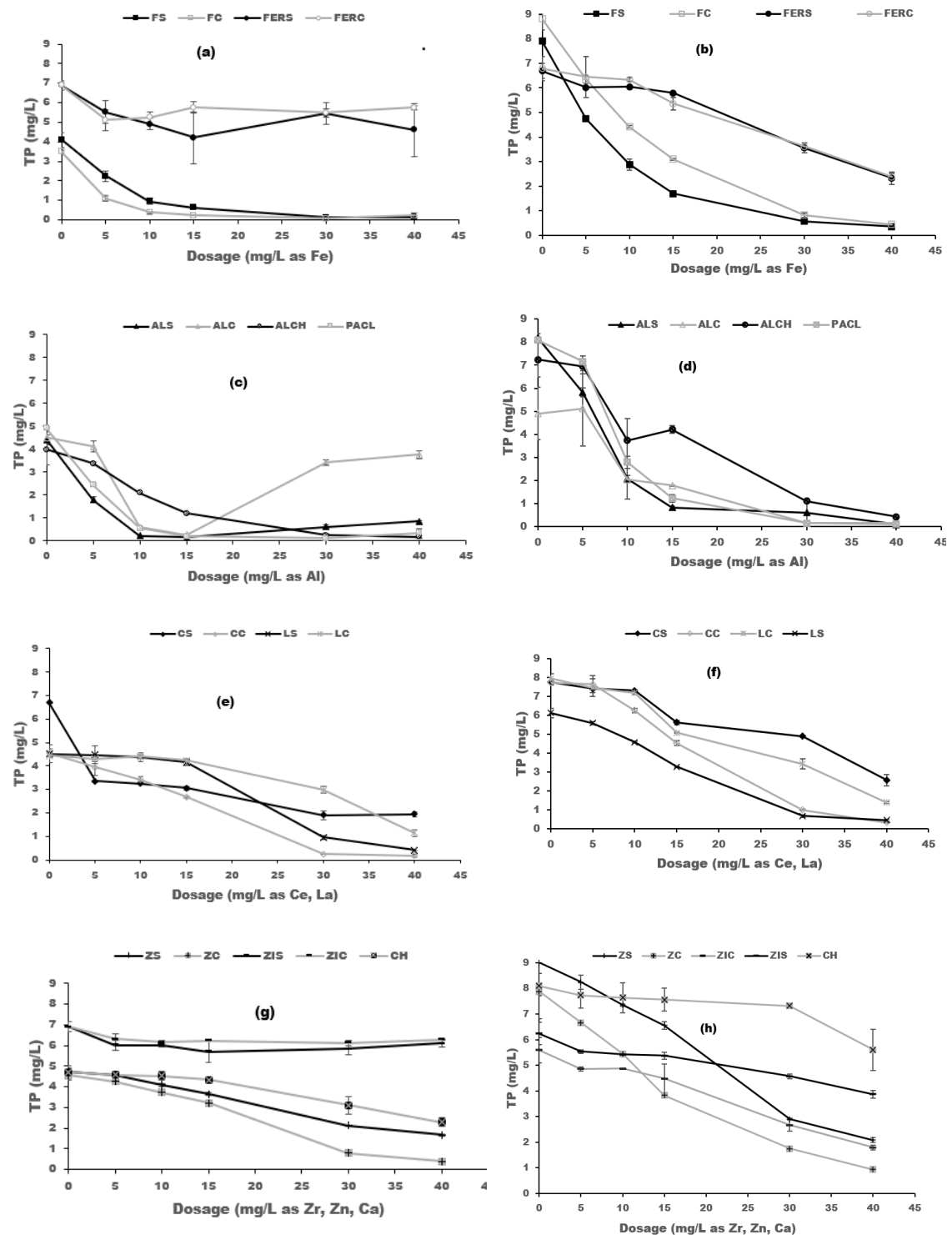


Figure 2-2: Residual total phosphorus without (a, c, e, g) and with (b, d, f, h) pH control.

2.3.2 Influence of pH and Alkalinity

Under uncontrolled pH conditions (Figure 2-3), both iron- and aluminium-based coagulants caused a significant drop in pH, decreasing from an initial range of 6.5-7.5 to around 4.0 at a 40 mg/L dosage. This drop in pH is directly linked to the rapid consumption of the wastewater's alkalinity as a result of the hydrolysis of coagulants, especially in cases where metal salts such as FS and ALS were used. As the alkalinity, initially 130-190 mg/L CaCO_3 (Figure B-2), was depleted to less than 20 mg/L CaCO_3 and even zero for ALS at dosages 40 mg/L, the buffering capacity was depleted, resulting in the sharp pH drop observed.

Coagulants such as PACL and ALCH, which are pre-polymerised, exhibited more stable pH profiles (7.1-5.3) even at higher dosages due to their lower acidification tendencies compared to conventional coagulants (Khairul et al., 2021). Conversely, ferrous-based, zinc-based, and rare earth coagulants (Figure 2-3a, e and g) had negligible impacts on pH, with only a slight decrease observed for CS, LS, ZS, and ZC at higher dosages of 30-40 mg/L. However, calcium hydroxide (CH) significantly increased pH from 7.0 to 10.2 at a 40 mgCa/L dosage due to hydroxide ions (OH^-) released during hydrolysis. Previous studies observed similar pH increases, with calcium hydroxide raising pH from 6.5 to 10 (Marshall et al., 2017).

Under controlled pH conditions (Figure 2-3e, f, g and h), all coagulants maintained near-neutral pH levels with minimal fluctuations. High initial alkalinity helped maintain stability during coagulation and allowed for consistent phosphorus removal, particularly with ferric-based coagulants and ALS.

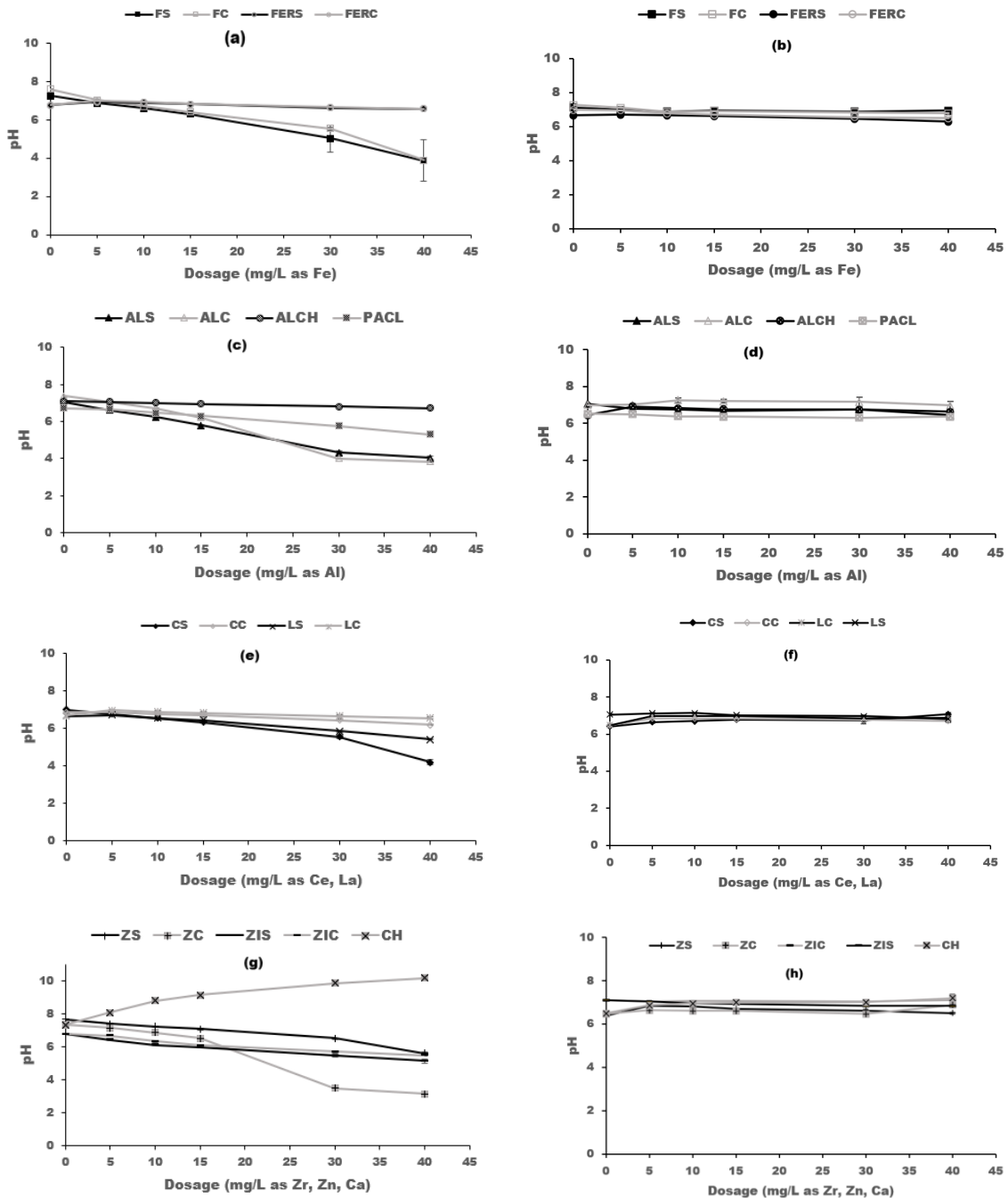


Figure 2-3: Influence of pH without (a, c, e, g) and with (b, d, f, h) pH control.

2.3.3 Total Suspended Solids

The impact of the coagulants on TSS was also evaluated under uncontrolled and controlled pH conditions. Across all coagulants, a significant initial reduction in TSS was observed as the dosage increased, particularly under controlled pH conditions, where TSS levels were generally more stable. There was generally a

gradual decrease in TSS when the dose increased (Figure 2-4), but then there was an increase for the highest dose for several coagulants tested.

Under uncontrolled pH, FS and FC initially showed a steady reduction in TSS from 48.0 mg/L to 2.7 mg/L and 0.7 mg/L at a dosage of 30 mgFe/L, respectively (Figure 2-4a). However, an increase in TSS was observed at higher dosages, with FS reaching 10 mg/L at a dosage of 40 mg/L, while low and stable TSS levels were maintained under pH-controlled conditions. In contrast, ferrous-based coagulants exhibited different behaviours. FERS showed an initial decrease in TSS but experienced a subsequent rise at higher dosages. Again, they performed better under controlled pH.

Significant differences in TSS levels were observed under uncontrolled and controlled pH conditions (Figure 2-4c and d) for aluminium-based coagulants. Under uncontrolled conditions, ALS showed stable TSS levels, reducing from 52 mg/L to 5 mg/L at a 15 mgAl/L dosage, and this performance was sustained across higher dosages. ALC, however, exhibited more variability, with TSS initially dropping at lower dosages but increasing at higher concentrations, particularly at 30 mgAl/L and 40 mgAl/L. Under controlled pH conditions, all aluminium-based coagulants improved performance, as they could reduce TSS more consistently. For instance, ALS and PACL achieved TSS levels below 7 mg/L at a 15 mgAl/L dosage and maintained this across increasing dosages. ALC and ALCH also showed improved TSS removal under controlled pH, though ALC slightly increased at higher dosages. The pre-hydrolysed coagulants, PACL and ALCH, exhibited more stable TSS performance across increasing dosages under uncontrolled and controlled pH conditions.

The rare earth metal-based coagulants demonstrated significant TSS variations under uncontrolled pH, with CS showing the most pronounced fluctuation. However, TSS levels stabilised under controlled pH, with all rare earth coagulants achieving improved floc formation and sedimentation. LS and LC reduced TSS to below 10 mg/L at higher dosages.

Zirconium and zinc-based coagulants exhibited similar trends. Under uncontrolled pH, TSS fluctuated for both ZS and ZC, with ZS peaking at 41 mg/L

before stabilising, and ZC showed more consistent reductions. Under controlled pH, both coagulants achieved more stable TSS profiles, with ZS reduced TSS to 35 mg/L and ZC maintaining 24 mg/L at higher dosages. Zinc-based coagulants showed gradual TSS reductions across increasing dosages under controlled conditions, though they exhibited more significant variability under uncontrolled pH. ZIS decreased TSS to 13 mg/L at 40 mgZn/L under pH control. CH was unique in that it increased the pH significantly, which caused variability in TSS across the dosage range. Under uncontrolled pH, CH fluctuated from 41 mg/L at low dosages to 24 mg/L at 40 mgCa/L. Even under controlled pH, CH exhibited fluctuations. When pH was controlled at 7, the overall TSS performance improved for most coagulants. As shown in the results, FS, FC, and PACL maintained consistently low TSS levels across the dosage range.

Furthermore, the TSS trends show that ferric and aluminium-based coagulants consistently performed better in reducing TSS and maintained low levels across the range of dosages. Under controlled pH conditions, the improvement in TSS for most coagulants indicates more effective floc formation, leading to enhanced sedimentation and, subsequently, better phosphorus and particulate residuals, as further evidenced in turbidity (Figure B-3). Systems with low alkalinity showed rapid pH drops when acidified coagulants were added, which disrupted floc formation and reduced the overall efficiency of phosphorus and TSS removal.

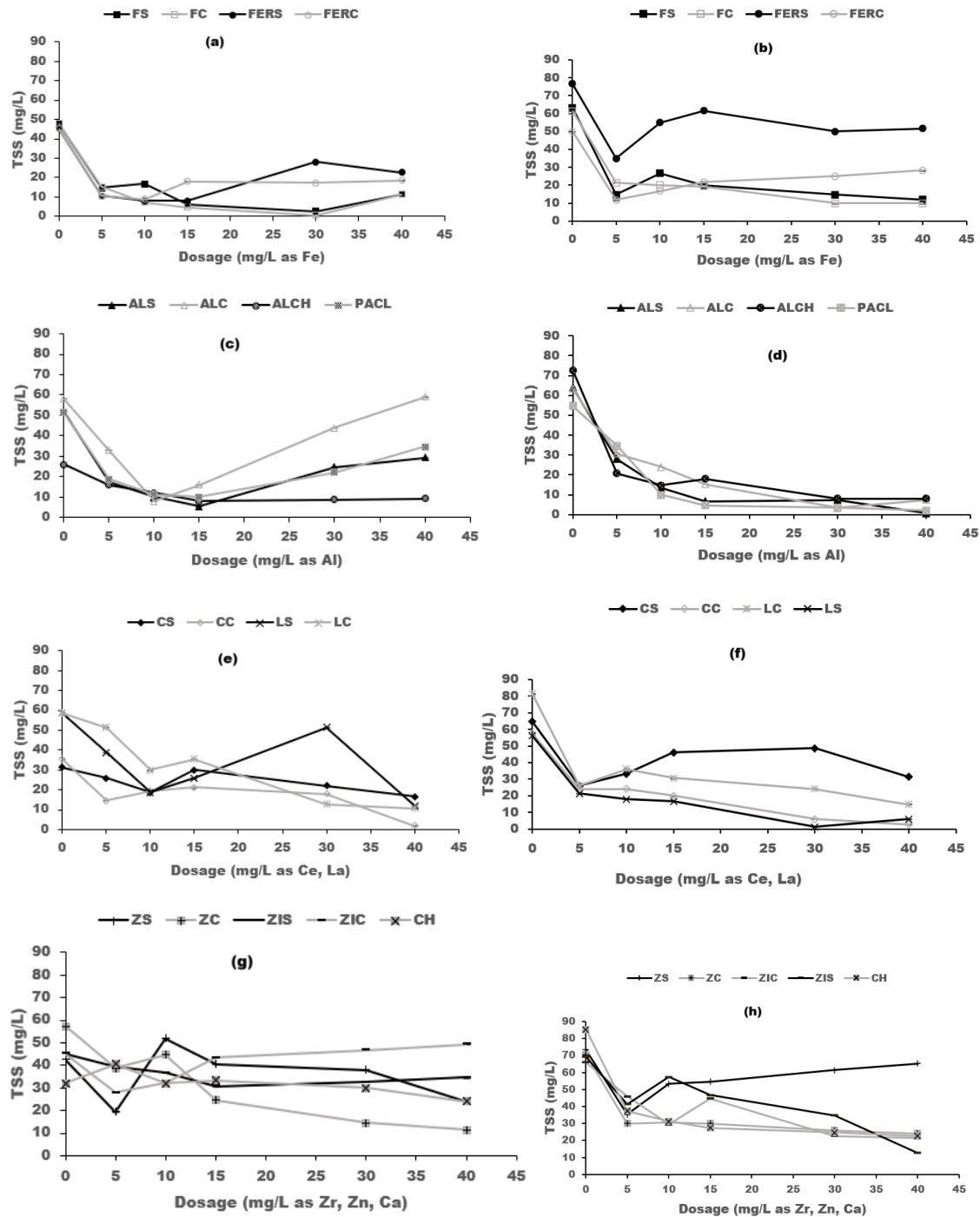


Figure 2-4: Residual TSS without (a, c, e, g) and with (b, d, f, h) pH control

2.3.4 Chemical Oxygen Demand

Under uncontrolled pH conditions, most coagulants demonstrated an initial reduction in COD as the dosage increased, but the extent of improvement varied significantly across coagulant types (Figure 2-5). Ferric-based coagulants were

the most effective, reducing COD from 43 mg/L to 12 mg/L and 20 mg/L, respectively, at a dosage of 30 mgFe/L. Ferrous-based coagulants were less efficient, achieving higher residual COD values of 38 mg/L and 36 mg/L, respectively, even at similar dosages.

Under controlled pH, COD removal improved across all coagulants, with FS and FC showing the most significant reduction, lowered COD from approximately 95 mg/L to 25 mg/L and 23 mg/L at 30 mgFe/L. Ferrous-based coagulants also performed better under pH control and reduced COD to 28 mg/L (FERS) and 21 mg/L (FERC) at the same dosage, though their overall efficiency remained lower than ferric-based coagulants.

Under uncontrolled pH, the residual COD of the wastewater treated with aluminium-based coagulants was initially low and maintained across the dosage range, with ALS and PACL showing the most effectiveness. With controlled pH, all coagulants showed improved efficiency, with ALS and PACL maintaining COD levels below 30 mg/L from an initial COD of about 100 mg/L (Figure 2-5c and d).

Rare earth metal-based coagulants displayed variable COD removal efficiency under uncontrolled pH, with CS and CC reducing COD to 19 mg/L and 9 mg/L, respectively, at a 15 mg/L dosage. LS and LC performed similarly, achieving COD residuals of 24 mg/L and 19 mg/L at 30 mg/L dosages. Controlled pH significantly enhanced their performance, with CS reducing COD to 26 mg/L and CC achieving 9 mg/L at a 40 mg/L dosage (Figure 2-5e and f).

The COD residual efficiencies under uncontrolled pH were relatively stable. COD residuals were maintained, with CH being the least effective, while, under controlled pH, slight improvements were observed Figure 2-5g and h.

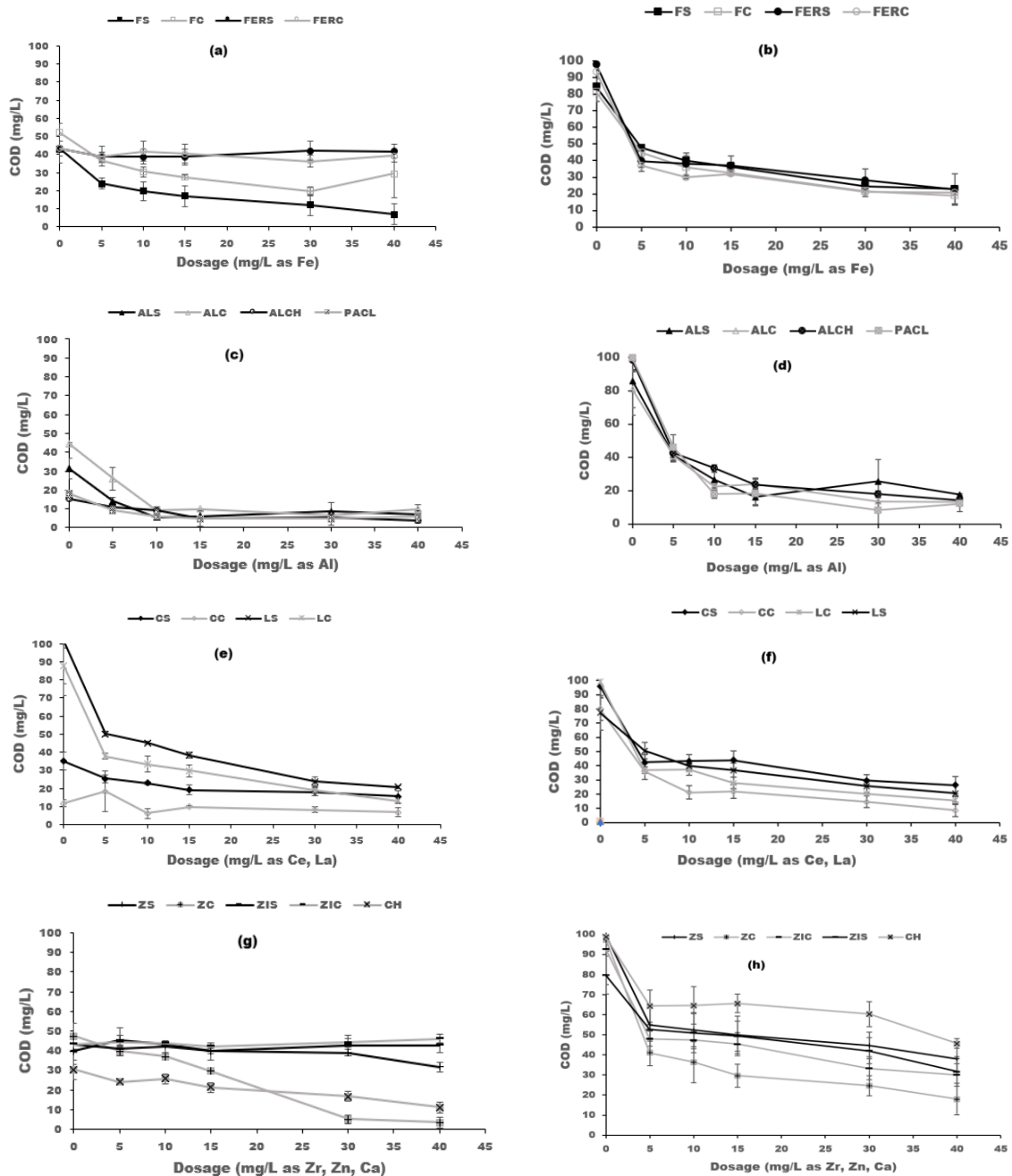


Figure 2-5: Residual COD without (a, c, e, g) and with (b, d, f, h) pH 7 controlled

2.3.5 Floc formation

The properties of flocs under controlled pH 7 conditions show distinct characteristics across the different coagulants in terms of floc size, strength, re-growth potential, and fractal dimension, all of which are factors that influence phosphorus removal efficiency in wastewater treatment (Figure 2-6 and Table 2-4).

Among the iron-based coagulants, FS formed moderately sized, stable flocs (300 μm) with a fractal dimension increasing slightly from 2.38 to 2.45 after breakage and regrowth. FC formed smaller flocs (250 μm) but had the highest re-growth capacity (39.53). Ferrous-based coagulants, FERS and FERC, generated larger flocs with high floc strength (58.5 and 62.3), but their re-growth capacity was significantly lower (14.9), suggesting that while they form strong flocs, they are less resilient after shear.

Aluminium-based coagulants demonstrated more compact and generally smaller flocs compared to iron coagulants. PACL exhibited the highest compactness, with a fractal dimension increasing from 2.44 to 2.6 and strong floc strength (52.2), whereas ALS and ALCH followed similar trends, forming stable but less dense flocs. ALC produced the least compact flocs (FD: 2.27) with the lowest floc strength (44.7), indicating weaker sedimentation potential.

Rare earth metal-based coagulants formed the largest initial flocs but were highly fragile, breaking down easily even without an increase in shear in the first phase of the test. CS and CC had lower fractal dimensions (2.30 and 2.50) and weak floc strength (29.73), while LC displayed higher strength (44.84) but low re-growth capacity (9.97). The rapid formation and subsequent structural breakdown suggest that these coagulants may be less effective in processes requiring sustained floc stability.

Zirconium and zinc-based coagulants generally formed moderately compact flocs, with ZS producing porous flocs (FD: 2.00) and ZIC generating the densest flocs (FD: 2.62). CH displayed the highest floc strength (71.5) but with lower compactness (FD: 2.07), which may impact settling velocity. However, its high re-growth potential (28.60) suggests resilience, which is crucial for maintaining consistent phosphorus removal.

These results collectively emphasise the importance of floc characteristics such as size, strength, and compactness in determining the effectiveness of coagulants in phosphorus residual. The controlled pH 7 environment ensured that the observed flocculation behaviours were primarily due to the intrinsic properties

of the coagulants, without the confounding effects of pH variability, allowing for a clearer comparison of their performance in wastewater treatment.

Table 2-4: Floc properties for controlled pH 7

Coagulant	Fractal Dimension	Floc Strength	Floc Re-growth
FS	2.43	43.3	14.7
FC	2.39	37.4	39.5
FERS	2.59	58.5	14.9
FERC	2.53	62.3	-27.9
ALS	2.38	49.5	5.7
ALC	2.27	44.7	9.4
ALCH	2.49	45.3	36.5
PACL	2.53	52.2	10.4
CS	2.30	29.7	26.7
CC	2.45	43.9	-3.9
LS	2.37	43.6	0.4
LC	2.37	44.8	9.9
ZS	1.99	54.9	37.0
ZC	2.37	46.6	19.9
ZIS	2.58	40.0	22.7
ZIC	2.62	41.9	52.0
CH	2.07	71.5	28.6

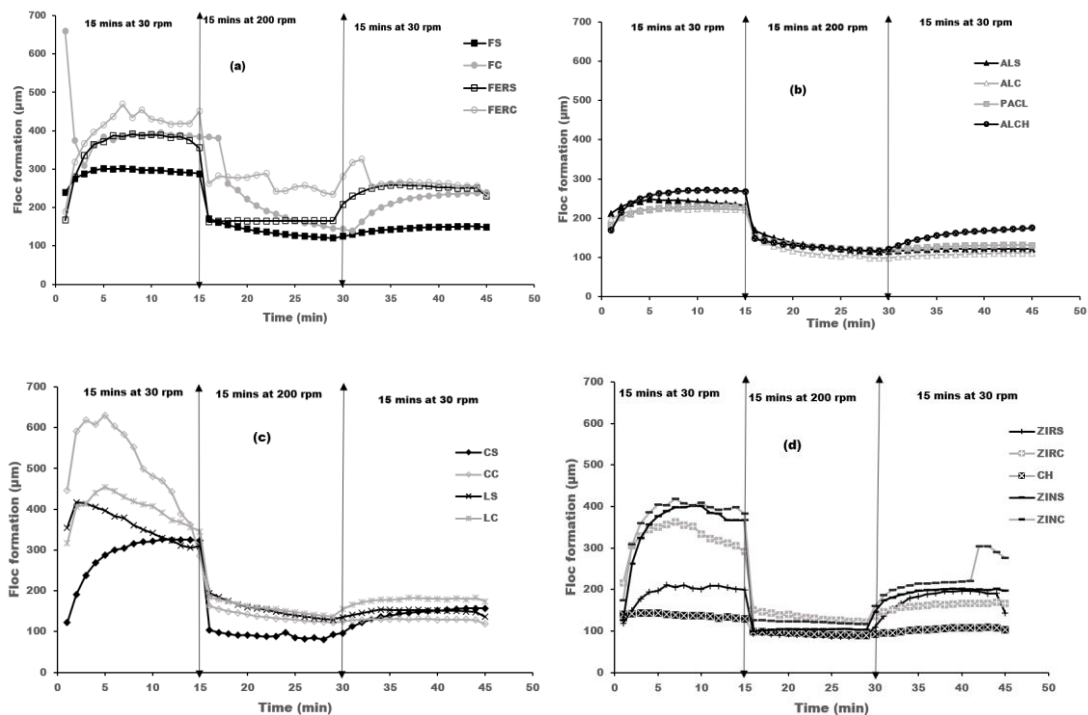


Figure 2-6: Floc formation with (a, b, c, d) pH 7 controlled

2.4 Discussion

While comparisons are primarily based on residual TP levels, it is important to note, as highlighted in the results, that starting phosphorus concentrations varied slightly among coagulants. This means that some coagulants with higher residual TP may still have removed substantial absolute quantities of phosphorus, but not enough to meet the target residual levels. This context should be taken into account when interpreting comparative performance.

2.4.1 Impact of Coagulation on Residual Total Phosphorus

The coagulation experiments conducted in this study evaluated the effectiveness of different metal-based coagulants in removing TP from municipal wastewater. These properties affected interactions between the coagulants and phosphorus, leading to varying TP residual concentrations across different conditions (Table 2-5). Understanding these mechanisms provides insight into the optimal selection of coagulants for wastewater treatment applications.

When comparing coagulants at similar concentrations, ferric and aluminium-based coagulants consistently exhibited better TP removal compared to rare earth and other metal-based coagulants. FS, ALS and PACL achieved residual TP concentrations of 0.35, 0.6 and 0.15 mg/L, respectively, at optimal coagulant dosages, demonstrating the highest efficiency. Their effectiveness can be attributed to their ability to neutralise negatively charged colloidal particles, which agrees with previous research (Zhou et al., 2008; Jin et al., 2021; Mourdikoudis and Dominguez-Benetton, 2025). The formation of $\text{Fe}(\text{OH})_3$ and $\text{Al}(\text{OH})_3$ species around neutral pH 7 enhanced phosphorus removal by providing a surface area for adsorption (Figure 2-1a and c). However, since a significant fraction of phosphorus in wastewater is present in a soluble form, additional mechanisms, such as precipitation and complexation, contribute to the removal efficiency. The literature has reported that metal hydroxide complexes are significant in phosphorus capture through adsorption and precipitation (Bacelo *et al.*, 2020; Zhao *et al.*, 2025).

The solubility is used to evaluate the behaviour of specific compounds formation depending on pH, as illustrated in (Figure B-3) (Levlin and Hultman, 2014), both

FePO_4 and AlPO_4 exhibit distinct pH-dependent solubility trends that significantly influence their ability to form and remain stable during treatment.

The solubility curves demonstrate that FePO_4 is slightly more soluble than AlPO_4 in the pH range of 5.5 to 7.5, indicating a broader window of stability for ferric phosphate precipitates within this near-neutral zone. At lower pH values (below pH 5), the solubility of both compounds increases markedly; however, AlPO_4 becomes substantially more soluble than FePO_4 under these acidic conditions. This behaviour contrasts with their respective hydroxides, where ferric hydroxide generally dissolves more readily than aluminium hydroxide at low pH. In the case of the phosphates, the greater solubility of AlPO_4 promotes enhanced resolubilisation of phosphate into the aqueous phase, as Al^{3+} , Fe^{3+} , and PO_4^{3-} ions are released back into solution (Singer and Liang, 2004).

This reduction in phosphate retention under acidic conditions is further exacerbated by the solubility behaviour of their respective hydroxide forms, aluminium hydroxide ($\text{Al}(\text{OH})_3$) and ferric hydroxide ($\text{Fe}(\text{OH})_3$), which are amphoteric in nature and are more soluble at low pH, thereby decreasing the effectiveness of coagulant performance due to increased solubility of the metal species (Hung *et al.*, 2004). Thus, at low pH, two effects occur: (i) reduced formation of stable metal phosphate precipitates, and (ii) increased solubility of the metal coagulants. These conditions compromise the performance of ferric and aluminium coagulants for phosphorus removal, both in precipitation and in sweep flocculation, which rely on optimal hydroxide formation and enmeshment of colloidal particles. In contrast, within the near-neutral pH range, phosphate solubility decreases, enabling better removal through precipitation and adsorption mechanisms.

The performance of ferrous-based coagulants was notably lower, with FERS achieving a TP residual of 4.2 mg/L, indicating the need for higher dosages to compensate for its less effective charge interaction and achieve comparable TP removal. The lower valency of Fe^{2+} reduces its ability to form stable phosphate complexes, supported by the speciation diagrams in Figure 2-1 and Table 2-5, thereby limiting its efficiency compared to Fe^{3+} (Piasecki *et al.*, 2019; Jianzhi *et*

al., 2021). Similarly, Aluminium-based coagulants exhibited varying effectiveness, with PACL demonstrating the highest efficiency due to its pre-polymerised nature, which enhances charge neutralisation and reduces sludge production (Youssef *et al.*, 2023). In contrast, ALC exhibited less stable phosphorus removal, likely due to its high solubility and the tendency to cause pH reduction under uncontrolled conditions. This corroborates existing research that coagulant solubility influences floc formation and phosphorus adsorption capacity (Lapointe *et al.*, 2023; Liu *et al.*, 2021).

Rare earth metal-based coagulants, such as cerium and lanthanum coagulants, have been reported to have strong phosphate-binding affinity (Bacelo *et al.*, 2020) but did not achieve TP levels as low as iron and aluminium-based coagulants, possibly due to the less stable floc structures they form. The speciation diagrams (Figure 2-1d and e) indicate that $\text{Ce}(\text{OH})_3$ and $\text{La}(\text{OH})_3$ formation is pH-dependent, with optimal performance occurring at pH 6-8. However, their large initial flocs exhibited fragility, leading to structural failure under shear forces, which impacted operational stability. As a result, while rare earth coagulants may be effective in controlled environments and require more settling time, their limited structural stability makes them less ideal for large-scale wastewater treatment applications where hydraulic shear forces are present.

Zirconium and zinc-based coagulants exhibited moderate phosphorus removal efficiency, with ZIC producing the most compact flocs, characterised by a high fractal dimension and enhanced sedimentation properties. However, their efficiency remained lower than Fe- and Al-based coagulants, particularly under uncontrolled pH conditions, where solubility changes influenced their performance. Calcium hydroxide ($\text{Ca}(\text{OH})_2$) primarily functioned as a pH adjuster (Marshall *et al.*, 2017), promoting the precipitation of calcium phosphates, but its effectiveness was decreased in wastewater with low alkalinity (Yuting Li *et al.*, 2024). These findings emphasised the importance of pH buffering in ensuring optimal coagulant performance.

Hydrophilicity and hydrophobicity are significant in determining coagulant performance. Hydrophilic coagulants, such as PACL and FS, readily dissolve in

water before hydrolysing to form insoluble hydroxide flocs that facilitate coagulation through charge neutralisation and adsorption (Duan and Gregory, 2003; Davis and Edwards, 2014; Nan *et al.*, 2016); demonstrated effective phosphorus removal due to their ability to rapidly dissolve and disperse in wastewater, forming hydroxide flocs with a high affinity for phosphate ions. This supports the findings documented in the literature that hydrophilic coagulants enhance floc formation and pollutant adsorption (Tubić *et al.*, 2016; Lapointe *et al.*, 2021). Conversely, coagulants with lesser hydrophilicity characteristics (Zhang *et al.*, 2025), such as CH, demonstrated inadequate phosphorus removal efficiency but required higher dosages to maintain stability in the system due to their limited solubility (Lapointe *et al.*, 2021).

The role of pH in coagulant performance was evident across all chemicals tested. The speciation diagrams in Figure 2-1 illustrate that coagulant effectiveness strongly depends on metal-hydroxide species' stability under different pH conditions. Ferric coagulants predominantly form $\text{Fe}(\text{OH})_3$ at neutral pH, which serves as an efficient adsorbent for phosphate ions due to its large surface area, facilitating strong electrostatic interactions with negatively charged phosphate species (Sun *et al.*, 2019). However, when pH drops below 4 due to insufficient buffering, ferric ions remain in their soluble Fe^{3+} form and do not precipitate into hydroxide flocs, significantly reducing coagulation potential and resulting in a higher residual TP and other parameters, as observed for the solids and organic matter. Aluminium-based coagulants exhibit even greater sensitivity to pH fluctuations, as small changes can shift the equilibrium between soluble and hydroxide forms, influencing phosphorus removal efficiency (Duan and Gregory, 2003; Lin *et al.*, 2009). Similarly, rare earth and zirconium-based coagulants rely on stable pH conditions to maintain hydroxide precipitation, as evidenced by the trends observed in controlled pH experiments.

The trends in TSS and COD removal further highlighted the impact of the coagulant dose on removal. The correlation between TSS and phosphorus removal suggests that higher TSS residual levels generally resulted also in poorer phosphorus residuals due to the resuspension of fine particles that failed to settle efficiently. In some cases, increased dosing led to the formation of smaller

particles that were less efficient at settling, reducing overall phosphorus removal efficiency. This result corroborates previous studies, which show that excessive coagulant dosing can hinder floc sedimentation and reduce treatment performance (Tsai *et al.*, 2022).

While COD and TP removal occur through coagulation and flocculation and highlight a trade-off in coagulant application, they do not always enhance each other. Instead, they may compete for coagulant binding sites, as coagulants simultaneously interact with organic matter and phosphorus compounds; excessive organic matter in wastewater may consume coagulant ions, reducing their availability for phosphate precipitation (El-Shafai *et al.*, 2023). Higher dosages improved COD and TP removal, but dosage optimisation was necessary to ensure sufficient coagulant availability for both processes without excessive chemical addition in wastewater treatment operations.

Largely, pH control emerged as a crucial factor, as fluctuations influenced coagulant speciation and floc stability, ultimately affecting phosphorus removal performance. In practical applications, this suggests that wastewater treatment plants using ferric and aluminium-based coagulants must implement pH buffering strategies to prevent efficiency losses due to speciation shifts. This can be achieved by pre-alkalinisation of influent wastewater to maintain pH stability and maximise coagulant performance, as demonstrated in municipal wastewater treatment processes in this study.

Table 2-5: Summary of the different properties of coagulants tested

Coagulant	Doses in molar conc.(mol/L)					Residual TP in molar conc.(mol/L)					pH	Speciation	Floc Strength	Floc Regrowth	Fractal Dimension	Floc Size
	5	10	15	30	40	5	10	15	30	40						
FS	0.090	0.179	0.269	0.537	0.716	0.153	0.093	0.055	0.018	0.011	6.87	Fe(OH) _{3(am)}	Moderate	Moderate	Dense	Moderate
FC	0.090	0.179	0.269	0.537	0.716	0.205	0.143	0.100	0.027	0.014	6.85	Fe(OH) _{3(am)}	Weak	High	Dense	Moderate
FERS	0.090	0.179	0.269	0.537	0.716	0.194	0.195	0.187	0.115	0.075	6.44	Fe ²⁺	Strong	Moderate	Dense	Moderate
FERC	0.090	0.179	0.269	0.537	0.716	0.208	0.205	0.173	0.117	0.077	6.56	Fe ²⁺	Strong	Low	Dense	Large
ALS	0.190	0.371	0.556	1.112	1.482	0.188	0.067	0.027	0.019	0.003	6.75	Al(OH) _{3(am)}	Moderate	Low	Moderately Dense	Small
ALC	0.190	0.371	0.556	1.112	1.482	0.166	0.066	0.057	0.005	0.005	6.16	Al(OH) _{3(am)}	Moderate	High	Less Dense	Small
ALCH	0.190	0.371	0.556	1.112	1.482	0.224	0.121	0.136	0.036	0.014	6.74	Al(OH) _{3(am)}	Moderate	High	Dense	Moderate
PACL	0.190	0.371	0.556	1.112	1.482	0.231	0.090	0.039	0.005	0.004	6.31	Al(OH) _{3(am)}	Strong	Moderate	Dense	Large
CS	0.036	0.071	0.107	0.214	0.285	0.239	0.236	0.181	0.158	0.083	6.75	Ce ³⁺	Weak	Moderate	Less Dense	Small
CC	0.036	0.071	0.107	0.214	0.285	0.246	0.201	0.146	0.032	0.010	6.77	Ce ³⁺	Moderate	Low	Dense	Large
LS	0.036	0.072	0.108	0.216	0.289	0.180	0.232	0.106	0.022	0.045	6.97	La ³⁺	Moderate	Low	Moderately Dense	Large
LC	0.036	0.072	0.108	0.216	0.288	0.241	0.149	0.164	0.111	0.015	6.86	La ³⁺	Moderate	Moderate	Moderately Dense	Large
ZS	0.055	0.110	0.164	0.329	0.438	0.266	0.237	0.212	0.093	0.067	6.62	Zr(OH) _{4(am)}	Strong	High	Porous	Large
ZC	0.055	0.110	0.164	0.329	0.110	0.215	0.176	0.123	0.057	0.175	6.46	Zr(OH) _{4(am)}	Moderate	Moderate	Moderately Dense	Moderate
ZIS	0.055	0.438	0.164	0.329	0.438	0.179	0.030	0.173	0.148	0.125	6.83	Zn ²⁺	Moderate	Moderate	Dense	Small
ZIC	0.076	0.153	0.229	0.459	0.612	0.157	0.157	0.145	0.086	0.058	7.05	Zn ²⁺	Strong	High	Very Dense	Moderate
CH	0.125	0.250	0.374	0.749	0.998	0.249	0.246	0.244	0.236	0.181	7	Ca ²⁺	Very Strong	Moderate	Porous	Small

2.4.2 The Difference Between Sulphate and Chloride

Sulphate and chloride, the counterions in the coagulants tested here, may also influence their behaviour in coagulation for TP removal from wastewater treatment. Sulphate-based coagulants, such as FS and ALS, formed denser flocs that settle more efficiently (Table 2-5), resulting in lower residual TP levels in treated effluent. The data in Figure 2-2 showed that under pH-controlled conditions, FS reduced TP to 0.35 mg/L at 40 mg/L, and FC achieved a TP residual of 0.83 mg/L at the same dosage. Similarly, ALS reduced TP to 0.15 mg/L at 30 mg/L dosage, while ALC showed a residual TP of 0.26 mg/L at the same dosage. These results are in line with previous studies that observed that sulphate ions contribute to more compact and stable floc formation, which enhances phosphorus precipitation and removal (Bratby, 2016; Liu *et al.*, 2024).

Chloride-based coagulants are soluble and immediately available for phosphate precipitation; the lower floc density may reduce settling efficiency and increase the risk of re-suspension as they form lighter, more fragile flocs, which can be less stable under certain conditions. Previous reports noted that while chloride-based coagulants remain effective, their performance in TP residual is often less consistent than sulphate-based coagulants in situations where floc stability is critical (Liu *et al.*, 2024).

Comparing sulphate and chloride-based coagulants across the different metal coagulants for TP removal, the results indicate that sulphate achieves lower TP levels than chloride under both pH conditions, which highlights the structural benefits that sulphate ions contribute to floc formation (Cao *et al.*, 2011; El-taweel *et al.*, 2023). Sulphate acts as an effective coagulation aid because it can precipitate such colloidal mixed salts by neutralising the excess positive charge but cannot compete with PO_4^{3-} for Fe^{3+} . Fe^{3+} has a stronger affinity for PO_4^{3-} and a stronger hydrolysis power than Al^{3+} (Pa Ho Hsu, 1976). Similar phenomena hold for most of the other coagulants tested (Table 2-5). However, it is essential to mention that while sulphate-based coagulants perform better in phosphorus removal, the difference in effectiveness is only marginal and depends on the specific wastewater characteristics. In high-turbidity waters or where rapid

coagulation is needed, chloride-based coagulants may provide significant advantages due to their high solubility and immediate availability of reactive species (Liu *et al.*, 2024). Additionally, adjustments in coagulant dosage or a combination of sulphate and chloride coagulants could mitigate the differences in performance and maximise the benefits of both counterions.

2.4.3 The Impact of Coagulant Choice

The choice of coagulant has significant implications for phosphorus removal efficiency, operational requirements, and sustainability of wastewater treatment processes. The differences among the coagulants tested were highlighted, each providing unique benefits and limitations impacting phosphorus removal. Ferric-based coagulants, particularly FS, demonstrate high phosphorus removal efficiency across pH conditions, forming dense, stable flocs that efficiently capture and precipitate phosphorus and achieve residuals as low as 0.35 mg/L. Similarly, aluminium-based coagulants, such as PACL, perform well, particularly under controlled pH conditions and achieve low TP levels at minimal dosages due to rapid floc formation and reduced sludge production. While the importance of pH in coagulation is recognised, this study provides empirical evidence that pH control significantly improves the performance of coagulants, particularly iron and aluminium-based like FS and PACL (Yang *et al.*, 2010; Wei *et al.*, 2015; Naceradska *et al.*, 2019). The research also provides new insights into the comparative performance of rare earth metal-based coagulants, demonstrating a high potential for TP residual efficiencies, although more expensive (Kajjumba and Marti, 2022). The findings also offer a slightly different perspective on zinc-based coagulants and CH, emphasising their roles in multifunctional treatment processes, particularly in pH adjustment. This complexity adds to the understanding of coagulant selection and emphasises the need for a tailored approach that considers not only residual efficiency but also specific operational requirements.

2.5 Conclusion

The findings of this research highlight the critical role of coagulant selection in optimising TP removal from wastewater, with a clear emphasis on the importance of pH control and the intrinsic properties of various coagulants (hydrolysis behaviour, phosphate affinity, solubility, and metal speciation). While comparisons focus on residual TP levels, it is worth noting that starting phosphorus concentrations varied among coagulants, which may have influenced their apparent relative performance. The evaluation of a diverse set of coagulants, which includes iron-based, aluminium-based, rare-earth metal-based, zinc-based, and calcium hydroxide compounds, has demonstrated distinct differences in their TP removal efficiencies, floc formation behaviours and operational parameters. Ferric and aluminium based coagulants, particularly FS and ALS, emerged as the most effective in TP removal, supported by their strong charge-neutralisation capabilities and ability to form dense, stable flocs that efficiently precipitate phosphorus even under varying pH conditions. This aligns with previous research and highlights the robustness of ferric and aluminium coagulants, particularly under controlled pH that possibly favour the best out of the Fe and Al coagulants and that other conditions may be needed to improve the performance of the other coagulants, where TP levels were reduced to as low as 0.35 mg/L.

The performance of aluminium-based coagulants, such as PACL, was also highly notable, particularly under controlled pH conditions, where rapid floc formation and lower sludge production made them highly effective in reducing TP to low levels. Rare earth metal-based coagulants like CS and CC demonstrated potential for phosphorus removal, particularly under stringent phosphorus removal scenarios, offering high phosphate-binding affinity and forming stable complexes that may enhance TP residual efficiency. Although more expensive, their potential application is significant in sensitive environments where stringent phosphorus discharge limits are required.

Zinc-based coagulants and CH displayed moderate TP removal efficiency, primarily serving as a pH adjuster rather than a primary coagulant. However, the

role of CH and zinc-based coagulants in multifunctional treatment processes, such as pH adjustment and micronutrient provision, adds a layer of complexity to the coagulant selection process and highlights the need for a tailored approach to coagulant choice, where specific wastewater characteristics, operational objectives, and regulatory requirements must be balanced to achieve optimal phosphorus removal.

A key intellectual contribution of this study is the empirical evidence of the significant impact of pH control on the effectiveness of various coagulants, particularly those based on iron and aluminium. Under controlled pH conditions, Ferric and aluminium coagulants predominantly form hydrolysed species such as $\text{Fe}(\text{OH})_3$ and $\text{Al}(\text{OH})_3$, which are known to facilitate effective charge neutralisation and sweep flocculation. These hydroxide precipitates enhance phosphorus removal by providing a high surface area for adsorption and a strong binding affinity for phosphate ions. The improved performance observed in this study corresponds with the pH ranges (6.5-7.5) that favour the formation of these optimal hydrolysed species (Table 2-5 and Figure 2-1). Additionally, it extends the understanding of the comparative performance of rare earth metal-based coagulants, offering practical insights into their application in wastewater treatment processes. The findings highlight the importance of the chemical composition of coagulants and their operational dynamics of floc formation, stability, and re-growth, providing a comprehensive framework for the improvement of TP removal processes in wastewater treatment plants. This work thus adds valuable knowledge to the field and provides a new perspective on advanced coagulants, offering practical insights into wastewater treatment processes.

However, it is important to note certain constraints of this study. The experiments were conducted under controlled laboratory conditions, allowing precise pH adjustments and stable temperatures that may not fully represent the dynamic and variable environment of full-scale wastewater treatment plants. Such conditions favoured optimal performance of Fe- and Al-based coagulants but may not reflect real-world challenges like fluctuating flow or cost-effective pH control.

Additionally, long-term operational factors such as sludge production, handling, and overall sustainability of the coagulants were not assessed. Speciation diagrams provided mechanistic insights but were based on equilibrium models, which may not capture dynamic reactions occurring in practical systems.

2.6 References

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Appendix B

Table B-1: Selected coagulant dosages applied at controlled pH 7 conditions for floc formation assessment

Coagulant	FS	FC	FERS	FERC	ALS	ALC	ALCH	PACL	CS	CC	LS	LC	ZS	ZC	ZIS	ZIC	CH
Dosage (mg/L)	40	40	40	40	40	30	40	30	40	40	40	40	40	40	40	40	40

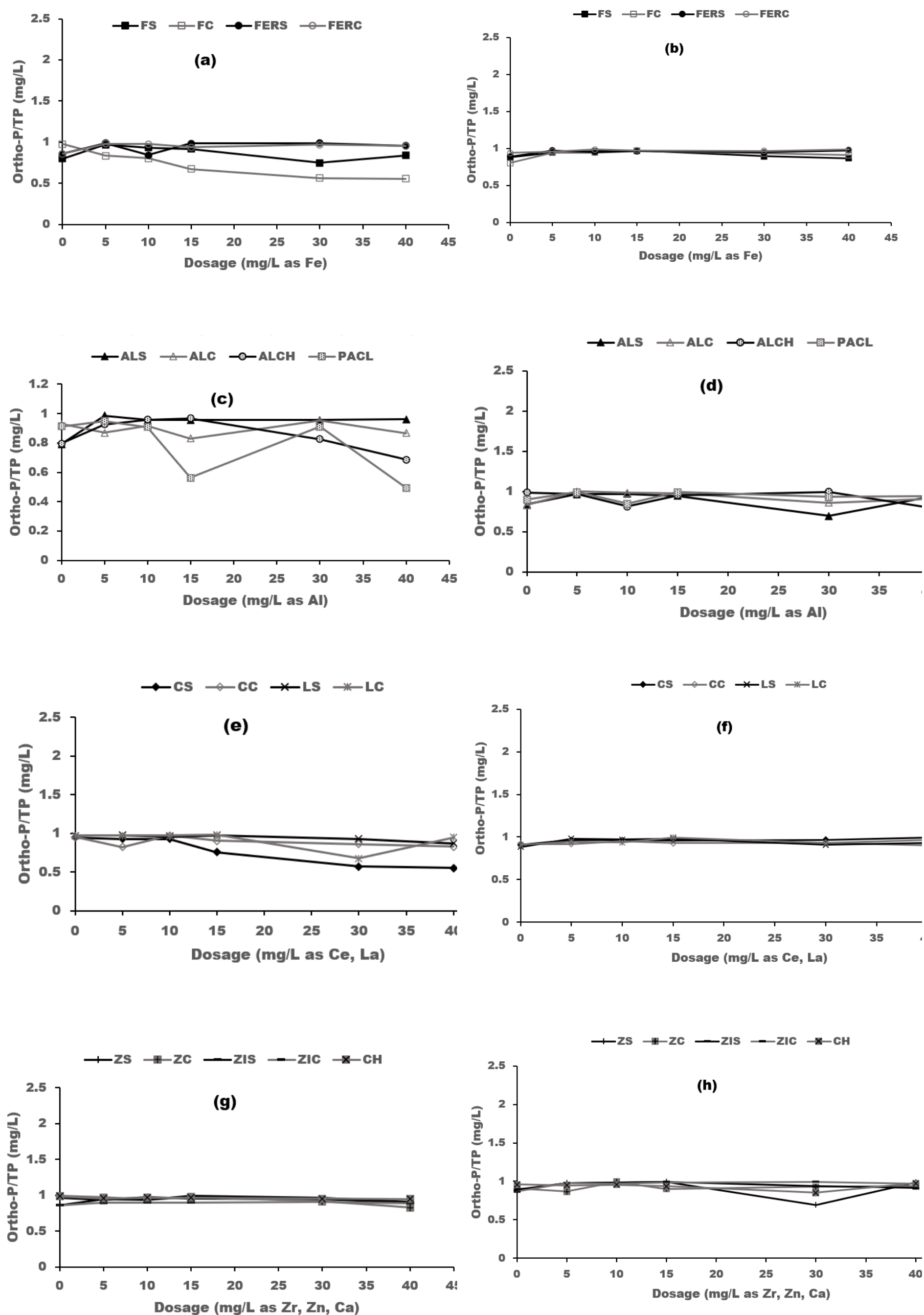


Figure B-1: Residual Ortho-P/TP ratio of treated wastewater without (a, c, e, g) and with (b, d, f, h) pH control

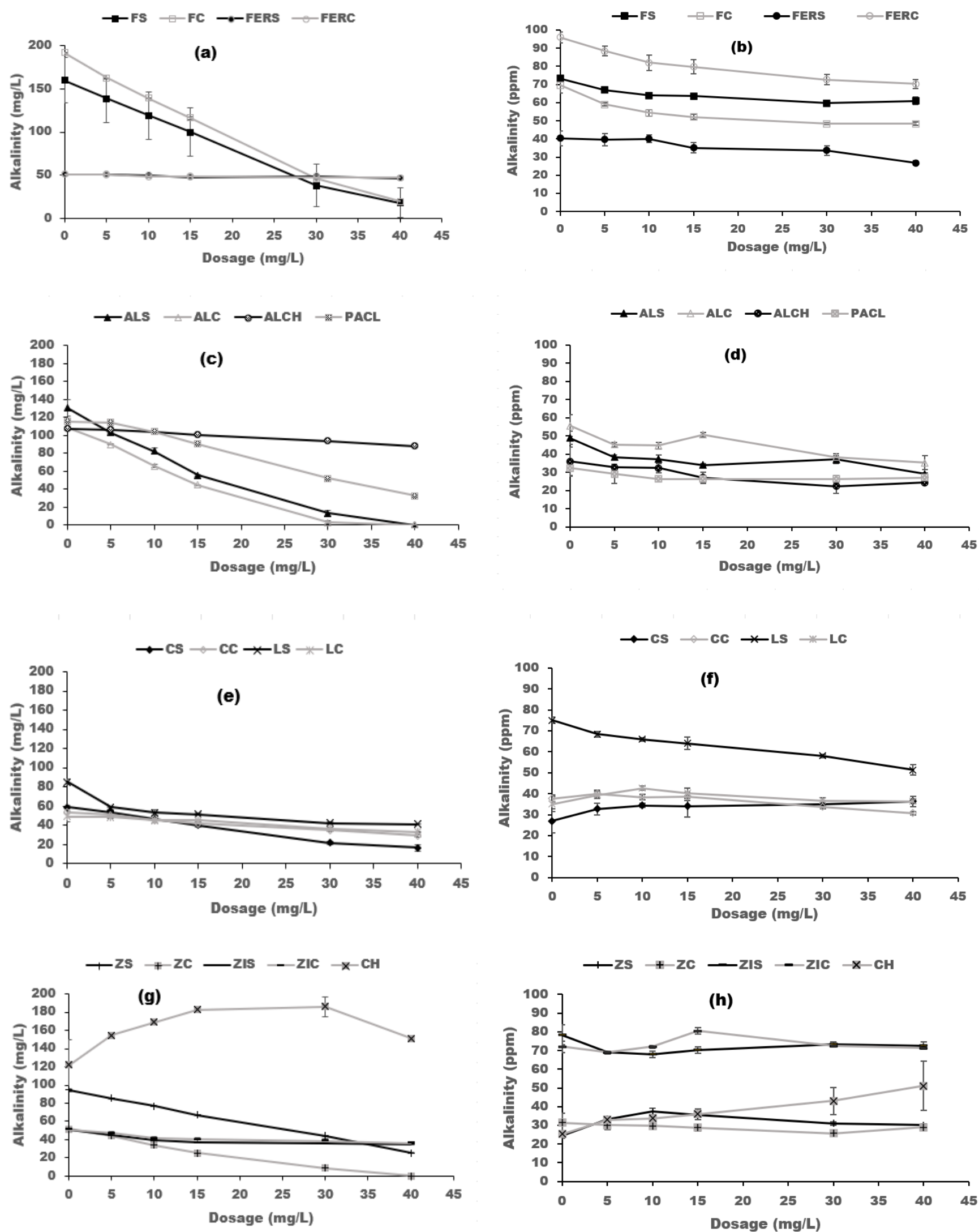


Figure B-2: Influence of alkalinity on treated wastewater without (a, c, e, g) and with (b, d, f, h) pH control

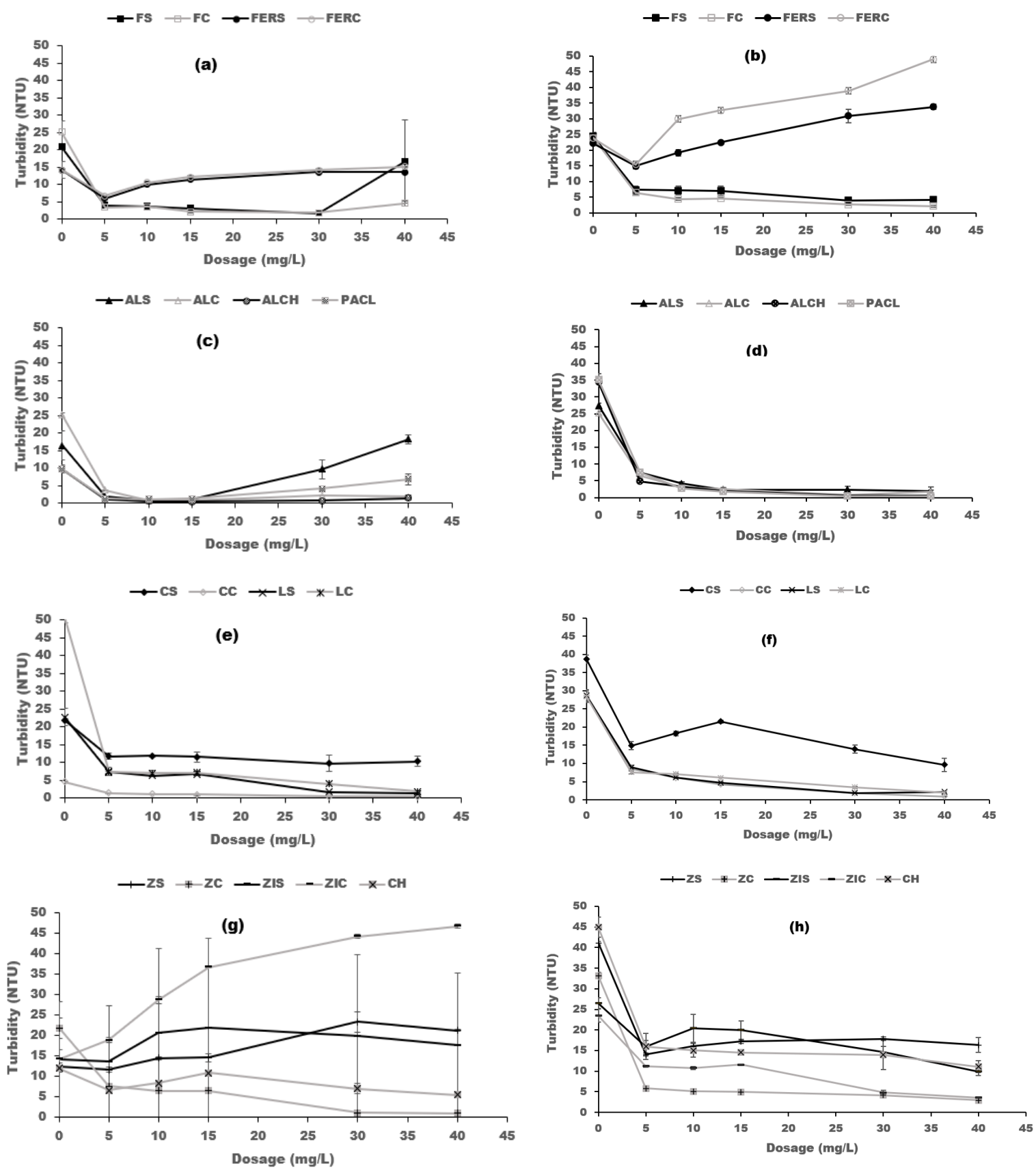


Figure B-3: Impact of Turbidity on treated wastewater without (a, c, e, g) and with (b, d, f, h) pH control

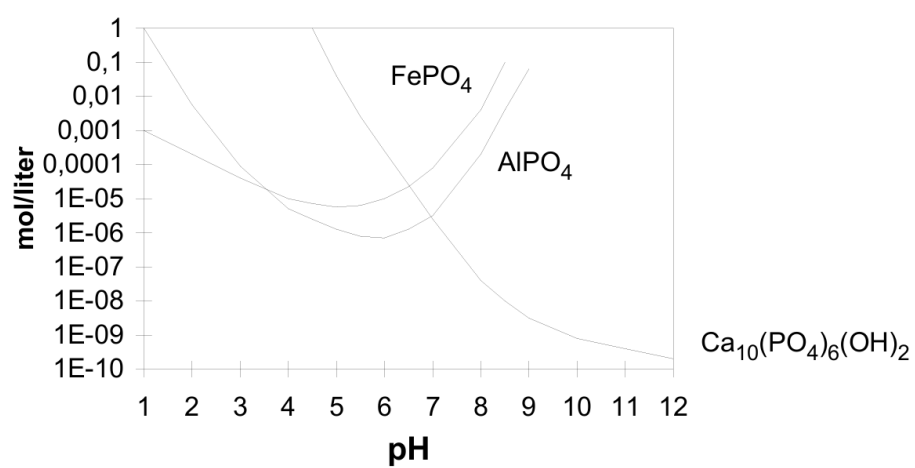


Figure B-4: Solubility for ferric and aluminium phosphate compounds (Levlin and Hultman, 2014).

Table B-2: Chloride and sulphate anion concentrations across coagulant types and dosages (all measured in mg/L) under uncontrolled pH conditions

	Dosage	FS	FC	FERS	FERC	ALS	ALC	PACL	ALCH	CS	CC	LS	LC	ZS	ZC	ZIS	ZIC	CH
Chloride	0	59.8	57.5	68.7	68.7	61.9	45.9	na	na	70.3	68.8	na	na	59.7	na	68.6	68.6	66.1
	5	58.4	74.6	98.2	104.2	61.9	59.5	na	na	70	73.3	na	na	61.2	na	181.3	187.6	66.2
	10	58.4	95.2	98.2	111.2	62.5	73	na	na	70	77.2	na	na	60.7	na	180.6	193.2	66.5
	15	59	114.5	98.9	117.1	62.1	86.7	na	na	70.7	80.1	na	na	61.1	na	180.8	200	66.2
	30	59	174.3	98.4	137.4	63.1	126.8	na	na	70.2	93.6	na	na	61.2	na	180.6	217	65.9
	40	58.6	214.4	98	150.1	62.6	153.5	na	na	70.4	99.7	na	na	61.2	na	182.3	229.7	65.8
Sulphate	0	61.7	65.9	45.8	45.8	66.9	49.3	na	na	55.1	54.1	na	na	60.1	na	45.8	45.8	63.2
	5	82.5	64.1	104.6	94.6	91.5	50.1	na	na	61.6	54.7	na	na	68.6	na	101.1	96.7	63.2
	10	102.9	65	115	97.5	117.2	49.6	na	na	68.2	54.5	na	na	78.4	na	110	97	63.5
	15	126.6	65.3	126	95.8	143.5	49.2	na	na	76.4	53.8	na	na	89.6	na	118.2	95.6	63
	30	186	63.1	158.1	100.3	229.9	60.3	na	na	97	53.8	na	na	126.6	na	139.6	96.8	62.5
	40	235.4	47.4	175.2	102.1	292.2	63.6	na	na	110.3	51.5	na	na	151.1	na	155.6	96.5	62.2

Table B-3: Chloride and sulphate anion concentrations across coagulant types and dosages (all measured in mg/L) under controlled pH conditions

	Dosage	FS	FC	FERS	FERC	ALS	ALC	PACL	ALCH	CS	CC	LS	LC	ZS	ZC	ZIS	ZIC	CH
Chloride	0	87.2	78.2	71.9	70.3	75	74.9	79.6	77.4	76.1	74.7	97.1	74.4	74.7	75.5	98.1	64.1	74.6
	5	88.8	91.5	73	77.9	76.8	99.6	92.8	133.4	118.2	80.9	98.2	79.2	76	85.8	104.6	75.6	80.7
	10	88.8	101.5	71.9	84.6	77.6	120.7	104.1	100.3	118.7	83	97.6	81.5	76.1	93.8	105.3	77.3	83.1
	15	88.2	112.3	48.4	91.1	77.3	142.7	116.3	103	117.4	87.8	97.5	84.6	76.4	99.4	103.2	83.7	90.8
	30	87.7	142.9	72.2	111.4	76.2	221.9	148.7	113	118.6	99.1	97.1	91.9	76.7	127.5	105.2	100.9	110.5
	40	86.2	165.9	71.9	123.3	76.8	234.8	171.5	120	117.7	106.9	97.4	96.6	77.4	142.2	104.8	112.7	121.9
Sulphate	0	55.1	55.7	49.4	73.8	54.9	54.6	53.6	50.5	50.6	50.5	63.2	50.1	53.5	51	63.2	58.5	54

Dosage	FS	FC	FERS	FERC	ALS	ALC	PACL	ALCH	CS	CC	LS	LC	ZS	ZC	ZIS	ZIC	CH
5	78.7	57	59.8	74.5	86.3	55.7	54.4	58.3	77.4	50.6	69.1	79	65	51.5	71.8	195.9	56.6
10	100.8	56.8	66.6	74.4	115.2	55.5	53.8	57	87.6	49.4	73.5	78.4	74.3	51.5	79.5	59.7	54.6
15	122.8	56.8	50.9	74.5	144.4	55.1	53.6	64.7	91.5	50.6	79.9	79.4	84.3	50.4	85.6	60	53.7
30	192.1	56	101.6	73.7	230.5	53.5	49.9	59.3	113.1	49.6	95.1	90.1	117.2	52.1	109.6	59.3	53.3
40	234.7	56.1	118.4	73	283.7	53	48.3	59.4	127.8	51.2	105.9	93.9	139.1	53.6	124.8	58.7	52.8

Table B-4: Residual metal concentrations (Fe, Al, Zn, Ca) (all measured in mg/L) across coagulant types and dosages under uncontrolled pH conditions

Coagulant	Dose (mg/L)	FS	FC	FERS	FERC	ALS	ALC	PACL	ALCH	CS	CC	LS	LC	ZS	ZC	ZIS	ZIC	CH
Fe	0	0	0	0	0	0	-0.1	0	0	0	0	0	0	0	0	-0.2	-0.2	0
	5	0.4	0	1.2	1.7	0	-0.1	0	0	0	0	0	0	0	0	-0.2	0.1	0
	10	1.1	0	2.3	3.9	0	-0.1	0	0	0	0	0	0	0	0	-0.2	-0.1	0
	15	0.9	0	4.2	7	0	-0.1	0	0	0	0	0	0	0	0	-0.2	-0.1	0
	30	0	0	17.2	19.9	0	-0.1	0	0	0	0	0	0	0	0	-0.2	-0.1	0
	40	0.1	0	27.9	29.3	0	0	0	0	0	0	0	0	0	0	-0.2	-0.1	0
Al	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	-0.57	-0.57	0
	5	0	0	0	0	0.5	0.8	0	0	0	0	0	0	0	0	-0.1	-0.2	0
	10	0	0	0	0	0	-0.1	0	0	0	0	0	0	0	0	-0.1	-0.2	0
	15	0	0	0	0	0	7.2	0	0	0	0	0	0	0	0	-0.1	-0.2	0
	30	0	0	0	0	3.6	25	0	0	0	0	0	0	0	0	-0.1	-0.2	0
	40	0	0	0	0	12.1	33.9	0	0	0	0	0	0	0	0	-0.1	-0.2	0
Zn	0	0.8	0	3.3	3.3	1	0	1.8	2.8	2.1	3.3	-0.4	-0.2	-0.3	-0.3	0	0	1.1
	5	0.2	0	0.1	0.1	0.5	0	0.9	0.9	1.8	1.3	-0.5	-0.2	-0.3	-0.3	5.5	6.6	1
	10	0.4	0	0.1	0.1	0.9	0.1	0.9	0.5	1.8	1.2	-0.5	-0.1	-0.3	-0.3	9.5	12	1.2
	15	0.5	0	0.1	0.1	1	0.1	1.2	0.3	1.6	1.1	-0.5	-0.2	-0.2	-0.3	14.8	16.6	1.1
	30	0.9	0	0.3	0.1	1.4	0.1	1.6	0.3	1.7	2	-0.5	-0.2	-0.2	-0.2	27.9	34.4	0.7
	40	0.8	0.1	0.3	0.1	1.4	0.1	1.8	0.3	2.4	2.4	-0.5	-0.2	-0.1	-0.2	37.1	46.5	0.5
Ca	0	65.7	68.1	47.3	47.3	63.8	43.9	60.6	63.9	44.9	47.3	40	35.9	33	36.6	44.7	44.7	61
	5	64.3	65.1	51.8	49.2	64.5	43.1	62.6	62.1	42.7	41.9	39.9	36	31.7	37.9	43.8	51.8	64.9
	10	65.2	66.5	49.5	49.5	65.1	44.7	61.3	61	42.9	40.7	40.1	36.7	30.9	37.3	42.1	52.7	67.5
	15	65.9	65.5	49.9	49.7	66	43.9	62.3	60.3	42.6	40	40.3	36.1	31	37.7	44.1	51.1	71.9
	30	66.5	67.9	50.5	48.4	66.2	44.3	63.8	59.9	42.1	42	39.7	35.2	31.5	37.7	42.1	51.9	67.6
	40	66.7	69.2	50.7	49.2	63.6	47.8	61.4	58.6	42.2	63.1	40	35.1	32.9	38.1	44.6	50.9	63.5

Table B-5: Residual metal concentrations (Fe, Al, Zn, Ca) (all measured in mg/L) across coagulant types and dosages under controlled pH conditions

Coagulant	Dose (mg/L)	FS	FC	FERS	FERC	ALS	ALC	PACL	ALCH	CS	CC	LS	LC	ZS	ZC	ZIS	ZIC	CH
Fe	0	-0.3	-0.4	0	-0.1	-0.4	-0.5	-0.4	0.6	-0.1	-9.9	0	0.1	0	0	-1.7	-0.1	0
	5	1.8	1.3	1.4	1	-0.3	-0.5	-0.4	-0.3	0	-9.2	0	0	0	-0.1	-1.7	-0.1	0.1
	10	2.3	1.5	3.9	2.3	-0.4	-0.5	-0.4	-0.3	0	-9.9	0	-0.1	0	0	-1.7	-0.1	0
	15	2	1.9	6.1	3.4	-0.3	-0.5	-0.4	-0.3	0.1	-10	0	0	0	0	-1.7	-0.1	0.1
	30	1.1	0.8	8.1	1.8	-0.4	-0.5	-0.4	-0.4	-0.1	-10	-0.1	-0.1	0	-0.1	-1.7	-0.1	0.1
	40	0.6	0.3	6.7	1.2	-0.4	-0.5	-0.4	-0.4	-0.1	-10.1	0	0	0	-0.1	-1.7	-0.1	0
Al	0	1.2	-0.2	0	0	-0.1	0	-0.1	89.8	0	-0.1	0	9.2	-0.6	-1	0	0	0
	5	-1.2	-0.2	0	0	1.9	1.9	2.2	1	124.9	-0.1	0	1.4	-0.5	-1	0	0	141.3
	10	-1.2	-0.2	0	0	1.1	1.3	0.9	1.5	124.6	-0.1	0	1.2	-0.5	-1	0	0	71.4
	15	-1.2	-0.2	0	0	0.6	0.7	0.4	89.2	233.4	-0.1	0	1.2	-0.5	-1	0	0	76.7
	30	-1.2	-0.2	0	0	0.2	0.1	21	4.3	57.1	-0.2	0	1.2	-0.5	-1	0	0	79.3
	40	-1.2	-0.2	0	0	0	0.1	94.6	4.2	66.7	-0.2	0	2.4	-0.6	-1	0	0	78
Zn	0	0	0	0.1	0	0	0	0	0.6	0.1	0	0	0.1	0.1	0.1	0.1	0.1	0.1
	5	0	0	0	0	0	0	0	0	0.1	0	0.1	0.1	0.1	0	5.7	10.4	0.1
	10	0	0	0	0	0	0	0	0	0.1	0	0.1	0.1	0.1	0	10.6	20.8	0.1
	15	0	0	0.1	0	0	0	0	0	0.1	0	0.2	0	0.1	0	16.2	12.4	0.1
	30	0	0	0	0	0	0	0	0	0	0	0.1	0	0.1	0	32.1	23.7	0.1
	40	0	0	0	0	0	0	0	0	0	0	0.3	0	0.1	0	43.3	34.2	0.1
Ca	0	40.7	41.3	42.7	72.5	42.9	42.9	44.7	47.7	44.8	40.7	57	44.5	46.6	45.3	56.7	55.9	46.9
	5	39.7	39.4	43.4	79.2	43.3	44.3	45.3	46.5	47	42.2	57.9	44.5	48.8	31	58.3	59.8	53.4
	10	38.7	39.5	43.6	76.1	42.7	43.6	43	45.6	47.1	42.4	56.5	46.6	48.4	45.3	56.4	58.7	55.8
	15	37.3	39	44	77.4	43.2	37.8	43.5	45.5	47.5	41.5	56.4	44.9	48.3	45.2	57.5	58.2	59.9
	30	37.1	38.5	42.1	76.5	42.1	42.5	43.7	44.9	45.4	39.6	57.3	44.1	47.8	45.1	57.4	57.7	71.1
	40	36.8	38	41.9	78.9	42.7	42.3	43.3	45.9	44.8	40.6	58.1	43.6	47.4	43.1	59.6	57.8	77.3

Chapter 3

3 Evaluating the Impact of pH on the Effectiveness of Ferric Sulphate, Aluminium Sulphate and PACL for Phosphorus Removal

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Abstract

Phosphorus removal from municipal wastewater is a critical process in preventing eutrophication and ensuring compliance with increasingly stringent discharge regulations. This study investigates the impact of pH on the effectiveness of ferric sulphate (FS), aluminium sulphate (ALS), and polyaluminium chloride (PACL) in phosphorus removal. Coagulation-flocculation experiments were conducted across a pH range of 4-8, with dosages varying between 5 and 40 mg/L as metal to determine optimal operational conditions for total phosphorus (TP) removal. The results revealed significant differences in the performance of the three coagulants, primarily dictated by their hydrolysis, solubility, and speciation dynamics. FS demonstrated efficient phosphorus removal across all pH levels, achieving residual TP concentrations below 0.3 mg/L at neutral to alkaline conditions (pH 6-8). ALS exhibited comparable performance but required lower dosages at high pH, which aligned with the minimum solubility of $\text{Al}(\text{OH})_3$ in the pH 6.5-7.5 range. PACL displayed inconsistent phosphorus removal trends, particularly at low pH, where hydrolysis limitations and weaker floc formation resulted in higher residual TP levels. Fractionation analysis indicated that FS and ALS effectively converted dissolved phosphorus into particulate solids, enhancing sedimentation, while PACL retained a higher proportion of colloidal phosphorus, particularly at pH 4. The floc formation analysis demonstrated that FS produced larger, more resilient flocs with superior strength and regrowth potential, contributing to its higher phosphorus removal efficiency across all conditions tested. Turbidity and total suspended solids (TSS) trends further reinforced the differences in coagulant performance, with FS achieving the most

stable turbidity reductions, followed by ALS, while PACL exhibited greater variability. The findings highlight the crucial role of pH in optimising coagulant selection and dosing strategies. The study provides new insights into coagulant behaviour, highlighting the importance of solubility and speciation in phosphorus removal efficiency. These results directly allow for wastewater treatment optimisation, particularly in meeting stricter regulatory discharge limits more sustainably.

Keywords: phosphorus removal, wastewater treatment, ferric sulphate, aluminium sulphate, polyaluminium chloride, coagulation, pH effect, floc formation, speciation, solubility

3.1 Introduction

Phosphorus (P) is a key nutrient responsible for the eutrophication of aquatic systems, which has become a global environmental issue, leading to the degradation of water quality and biodiversity loss (Zahed *et al.*, 2022). Excessive phosphorus in water bodies promotes harmful algal blooms, depletes dissolved oxygen, and threatens aquatic life (Xu *et al.*, 2024). Addressing this issue requires stringent control over phosphorus levels in wastewater effluent, particularly as discharge regulations become more rigorous under frameworks such as the European Water Framework Directive (Vale and Fernández, 2021).

Municipal wastewater typically contains phosphorus concentrations ranging from 4 to 12 mg/L, while the effluent limits in some regions now target values as low as 0.1 mg/L to prevent eutrophication (Zhang *et al.*, 2015). Conventional biological phosphorus removal processes, such as Enhanced Biological Phosphorus Removal (EBPR), have been widely implemented in many countries. However, EBPR presents limitations, particularly in cases of diluted wastewater or high nitrate loads in the anaerobic compartment (Xu *et al.*, 2024). These challenges necessitate supplementary chemical treatments to meet stricter discharge limits.

Chemical phosphorus removal (CPR) is often employed alongside biological processes in wastewater treatment to achieve compliance with phosphorus discharge limits. Coagulants such as ferric chloride, aluminium sulphate, and polyaluminium chloride (PACL) are commonly used for phosphorus removal in chemical precipitation processes. In Chapter 2, these coagulants demonstrated excellent performance in phosphorus removal, making them the focus of this study for further evaluation under controlled pH conditions. They promote the formation of flocs, which can be easily separated from wastewater through sedimentation or filtration (Xie *et al.*, 2020). Indeed, the addition of these metal salts to wastewater reacts with phosphorus to form precipitates through the metal-phosphorus complex formation and the hydrolysis of the metal ions in water, leading to the generation of metal hydroxides that further facilitate phosphorus adsorption and removal (Jiang and Graham, 1998). Despite the

effectiveness of chemical phosphorus removal, several operational challenges remain. Excessive use of metal salts can lead to increased sludge production and associated disposal costs (Ojo and Ifelebuegu, 2019). Additionally, the accumulation of metal ions in effluent may pose environmental and public health risks, particularly when alum is used in large quantities (Li *et al.*, 2017). Furthermore, the increasingly stringent discharge consents and the introduction of regulatory limits on sites that previously had none; as a result, higher chemical dosages are required to meet compliance, placing additional pressure on the supply chain for coagulants. Consequently, there is a growing emphasis on optimising coagulant use to enhance phosphorus removal efficiency and minimise chemical consumption and sludge production, thereby ensuring sustainable and cost-effective wastewater treatment operations.

The removal of phosphorus then relies on the optimal dosing of coagulants, pH control, and the formation of stable flocs that can be effectively removed during treatment (Cao *et al.*, 2010). The pH of the system plays a critical role in this process, influencing both the charge of the metal hydroxides and the speciation of phosphorus in the wastewater (Mohammed and Shanshool, 2009). For instance, ferric sulphate and aluminium sulphate have been reported to exhibit optimal phosphorus removal efficiency within a specific pH range, typically 4 to 8. Experimental results from the literature show that final effluent treated with ferric sulphate at a pH of 5 and a dosage of 15 mgFe/L reduced phosphorus concentrations from an initial 3.37 to 0.28 mg/L (Mohammed and Shanshool, 2009). Similarly, aluminium sulphate effectively reduced phosphorus concentrations to 0.26 mg/L at a dosage of 15 mgAl/L. Polymeric coagulants like PACL, a pre-hydrolysed coagulant, have also been reported to improve floc strength and phosphorus removal efficiency due to their ability to neutralise particle surface charges more effectively than traditional coagulants (Zhu *et al.*, 2016).

Floc formation is a crucial aspect of the phosphorus removal process, as the size and strength of flocs directly affect their removal efficiency (Cao *et al.*, 2010). The growth rate and strength of the flocs are influenced by the wastewater's pH and

the type of coagulant used. For instance, ferric-based coagulants have been reported to form stronger flocs at lower pH levels, while PACL has been reported to produce larger, more stable flocs over a wider pH range (Zhu *et al.*, 2016). While the impact of pH on coagulation performance has been widely studied, limited research has systematically evaluated multiple coagulants under identical conditions using the same wastewater source for different pHs.

Although coagulant dosing is widely used in wastewater treatment to achieve P removal, the role of pH in influencing both removal efficiency and the underlying mechanisms, particularly floc formation, remains insufficiently understood. Most existing studies have been conducted under idealised or synthetic conditions, with limited insight into how coagulants behave in real wastewater matrices where variable pH, competing ions, and organic matter may affect performance. Furthermore, comparative data across different coagulant types under controlled pH conditions in real wastewater are scarce, which limits the development of robust, broadly applicable dosing strategies. This chapter aims to evaluate the impact of pH on the effectiveness of ferric sulphate, aluminium sulphate, and PACL in phosphorus removal. Specifically, the study will investigate the influence of pH on both phosphorus removal efficiency and floc formation under controlled pH conditions. By examination of the phosphorus fractions in municipal wastewater and the performance of different coagulants, this research seeks to enhance the understanding of how pH affects the coagulation mechanism for phosphorus removal. The outcomes of this study will provide insights into the optimisation of chemical phosphorus removal processes and contribute to the ongoing efforts to meet stringent phosphorus discharge limits.

3.2 Materials and Methods

3.2.1 Municipal wastewater sample collection and Characterisation

Municipal wastewater samples were obtained after treatment from the final effluent of the sewage treatment facility at Cranfield University. The treatment train includes an inlet screen, balance tank, primary lamella clarifiers, trickling filters and submerged aerated filters, secondary lamella clarifiers, and final clarifier. These samples served as the primary substrate for all experimental

analyses, providing a reliable and consistent matrix to assess the performance of various coagulants under controlled laboratory conditions.

To ensure a robust understanding of the wastewater matrix, all samples were characterised for essential physico-chemical parameters prior to experimental analysis (Table 3-1). The parameters assessed included pH, alkalinity, turbidity, total suspended solids (TSS), chemical oxygen demand (COD), total phosphorus (TP), and orthophosphate (Ortho-P), using the following analytical methods:

pH: Measured using a calibrated multiparameter pH meter (Jenway 4330).

Alkalinity: Determined using a Hanna Instruments alkalinity checker.

Turbidity: Measured in Nephelometric Turbidity Units (NTU) using a Hach 2100Q portable turbidity meter.

Total Suspended Solids: Quantified gravimetrically by filtering known volumes of wastewater through pre-weighed glass fibre filters, followed by drying at 105°C, in accordance with standard methods (Federation and Aph Association, 2005).

Total Phosphorus, Orthophosphate, and COD: Analysed using Merck Spectroquant cell test kits and quantified colorimetrically with the ascorbic acid method. TP analysis was preceded by persulfate digestion. Measurements were carried out on a Merck Spectroquant NOVA 60 spectrophotometer.

Metal concentrations: Key target metals were quantified via Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) using a Nexion 350D instrument.

Ionic species: Major cations and anions were analysed using ion chromatography on Dionex ICS-1600 and ICS-900 thermo scientific systems.

This characterisation established a reliable baseline for evaluating coagulation performance, phosphorus fractionation, and floc behaviour under controlled treatment conditions.

Table 3-1: Wastewater characterisation for uncontrolled pH and without a coagulant

Parameter	Mean	Stdev
TP (mg/L)	3.4	0.0
Ortho-P (mg/L)	3.0	0.0
COD (mg/L)	79.7	7.4
TSS (mg/L)	65.3	0.0
Turbidity (NTU)	31.4	6.1
Alkalinity (mg/L)	111.0	2.2
Chloride (mg/L)	64.5	0.3
Sulphate (mg/L)	52.8	0.3
Ferric (mg/L)	-0.3	0.2
Aluminium (mg/L)	-0.5	0.2
Zinc (mg/L)	-0.1	0.3
Calcium (mg/L)	38.9	38.6

Note: A total of 65 samples were collected from the Cranfield sewage works, while A total of 270 samples were analysed for the 5 pH conditions and three coagulants during the laboratory experiment.

3.2.2 Coagulant selection and preparation

In this study, ferric sulphate (FS), aluminium sulphate (ALS), and polyaluminium chloride (PACL) were selected for further evaluation based on their better performance in phosphorus removal, as identified in the previous chapter. These coagulants were prepared following the manufacturer's specifications to ensure consistent application during the experiments. Ferric sulphate heptahydrate (99.5% for analysis) and aluminium sulphate octadecahydrate ($\geq 97\%$) were sourced from Fisher Scientific and Sigma-Aldrich, while Airedale Chemical Company Limited supplied PACL.

3.2.3 Coagulation–flocculation experiment

Standard coagulation-flocculation jar testing protocols were used to evaluate the optimal conditions and chemical dosages required for effective phosphorus removal. A Phipps & Bird Six-Paddle Stirrer was employed for all jar tests. Each experiment began with a rapid mixing phase at 200 rpm for 2 minutes to ensure the uniform dispersion of the coagulant within the wastewater matrix, followed by

the addition of designated coagulant dosages (5, 10, 15, 30, and 40 mg/L as metal). This was followed by a slow mixing phase at 30 rpm for 15 minutes to promote floc formation. The flocs were then allowed to settle by gravity for 30 minutes.

For experiments that require pH control, the pH of the wastewater was adjusted and maintained at 4, 5, 6, 7 and 8 using hydrochloric acid before the coagulant was added. After the settling phase, the supernatant and settled solids were carefully separated for further analysis. All tests were performed in triplicate to ensure reproducibility and reliability.

3.2.4 Floc formation and breakage assessment at optimised dosage for residual TP

Based on the results from the previous coagulation tests, only a selected set of dosages that achieved the target residual TP, as shown in Table C-1, was evaluated to gain a deeper understanding of the formation, stability, and regrowth potential of flocs, additional experiments were conducted using a jar tester connected to a particle size analyser. These experiments were carried out in cylindrical 2L jars containing 1L of the Cranfield University final effluent with pH strictly controlled at 4, 5, 6, 7 and 8. A Malvern Mastersizer 3000 laser diffraction instrument continuously monitored and analysed floc size distribution throughout the coagulation and flocculation processes.

The experiments followed the same initial procedure as the standard coagulation tests, with rapid mixing at 200 rpm for 2 minutes to disperse the coagulant evenly, followed by slow mixing at 30 rpm for 15 minutes to facilitate floc formation. The formed suspension was then subjected to a high shear phase by increasing the mixing speed to 200 rpm for 15 minutes to evaluate floc strength. Afterwards, the speed was reduced back to 30 rpm for another 15 minutes to observe floc regrowth potential. Floc size measurements were taken every minute, with water drawn through the Mastersizer optical unit at a flow rate of 1.5 L/hr using a peristaltic pump fitted with 5 mm internal diameter tubing. The data collected was processed in real-time on a connected PC.

To ensure the robustness of the results, all experiments were repeated in triplicate, and several floc properties were derived from the recorded data, including the fractal dimension, floc strength factor, floc breakage factor, and floc regrowth factor, calculated as follows:

$$\text{Floc Strength Factor} = \frac{d_2}{d_1} \times 100 \quad (3-1)$$

Where d_1 represents the mean floc size immediately before breakage, and d_2 represents the mean floc size after breakage (Jarvis *et al.*, 2005; Bratby, 2016)..

Floc size measurements were recorded at three critical stages during the coagulation tests: after floc growth (post-slow mixing), after floc breakage (post-high shear), and after regrowth (post-shear reduction). The Mastersizer software computed particle volume distributions from the light scattering intensity data, which were then used to infer the floc mass.

Floc Regrowth Factor (FRF) was determined to assess the flocs' ability to reform after breakage, using the equation:

$$\text{Floc Re-growth Factor} = \frac{d_3 - d_2}{d_1 - d_2} \times 100 \quad (3-2)$$

Where d_1 is the floc size before breakage, d_2 is the floc size after breakage, and d_3 is the floc size after regrowth. This parameter indicates the ability of flocs to reform after being subjected to shear forces (Jarvis *et al.*, 2005; Bratby, 2016).

Fractal Dimension (D_f) was calculated to characterise the structural complexity of flocs. The fractal dimension describes how the floc mass scales with size and provides insight into floc compactness. It was estimated using the mass–length scaling relationship:

$$M \propto L^{D_f} \quad (3-3)$$

where M is the mass of the floc, L is the characteristic length scale (e.g., floc diameter), and D_f is the fractal dimension. Plotting $\log M$ against $\log L$ produces a straight line, where the slope corresponds to D_f (Waite *et al.*, 2001; Wu *et al.*,

2002; Jarvis et al., 2008). Higher D_f values denote denser, more compact flocs, while lower values reflect open and loosely bound structures.

This methodology allows for detailed assessment of floc formation, resilience, and structural integrity across coagulant types and pH conditions, offering valuable mechanistic insights into phosphorus removal performance.

3.2.5 Phosphorus fractionation protocol

The same approach of only a selected set of conditions (Table C-1) from the previous coagulation tests for the phosphorus fractionation experiments were employed to measure different phosphorus species in the wastewater, categorised into reactive, unreactive, and condensed forms. This process involved several stages: filtration, digestion, complexation, measurement, and calculations.

3.2.5.1 Filtration

Wastewater samples were filtered using 0.45 μm and 0.025 μm filter papers to fractionate the samples by size. A Buckner filtration apparatus connected to a vacuum pump was used. Three fractions were then obtained:

Unfiltered fraction (u): No filtration step was required.

0.45 μm filtered fraction f(0.45): Samples were passed through a 0.45 μm filter to remove the particulates.

0.025 μm filtered fraction f(0.025): Samples were then passed through a 0.025 μm filter to remove the colloids.

3.2.5.2 Digestion

The samples were digested to transform some phosphorus species into molybdenum-reactive phosphorus. After filtration, 5.0 ml of the sample was transferred to a glass test tube and digestion agents were added according to the phosphorus fraction:

Molybdenum-Reactive Phosphorus (RP) required no digestion.

Acid-hydrolysable phosphorus (AHP) was treated with 0.2 ml of 5.25 N sulfuric acid, heated at 100°C for 30 minutes, and then neutralised with 0.2 ml of 5.0 N sodium hydroxide.

Total Phosphorus (TP) was digested using persulfate at 120°C for 30 minutes.

3.2.5.3 Complexation and Measurement

Following digestion, molybdate salts were added to the samples to form a blue molybdenum-phosphate complex, with antimony tartrate acting as a catalyst to accelerate the reaction. The solution was thoroughly mixed and allowed to develop for 60-90 minutes to ensure complete colour formation. After the reaction period, the absorbance of the molybdenum-phosphate complex was measured using a spectrophotometer. Appropriate dilutions were performed for samples exceeding the calibrated range, and the measured concentrations were adjusted accordingly to account for the dilution factor.

3.2.5.4 Calculations

The unreactive and condensed phosphorus fractions were calculated by subtracting the measured reactive and hydrolysable phosphorus from the total phosphorus values. For instance:

$$\text{Unreactive Phosphorus (UP)} = \text{TP} - \text{AHP}$$

$$\text{Condensed Phosphorus (CP)} = \text{AHP} - \text{RP}$$

$$>0.45 \text{ micron fraction} = \text{U-fraction} - \text{f}(0.45) \text{ fraction}$$

$$0.45\text{-}0.025 \text{ micron fraction} = \text{f}(0.45) \text{ fraction} - \text{f}(0.025) \text{ fraction}$$

3.2.6 Analytical Techniques

Various analytical techniques were employed to measure the relevant parameters of the treated wastewater samples. The pH levels were measured using a Jenway 4330 pH meter, ensuring precise pH control throughout the experiments with regular calibrations. Target metal concentrations were quantified using Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) on a Nexion 350D system.

Ion chromatography was employed to analyse key anionic (lithium, sodium, ammonium, potassium, magnesium and calcium) and cations (fluoride, chloride, nitrate, phosphate and sulphate). Chemical oxygen demand (COD), total phosphorus (TP), and orthophosphate (Ortho-P) concentrations were determined with the use of Merck cell test kits and measured with a spectrophotometer (Merck Spectroquant NOVA 60). Alkalinity measurements were performed using a Hanna Instruments alkalinity checker. Total suspended solids (TSS) were quantified using a standard filtration method, and turbidity was measured with a turbidity meter (Hach, 2100Q). To ensure accuracy, each sample was analysed in triplicate.

3.3 Results

3.3.1 Total phosphorus

The experimental data revealed the effectiveness of FS, ALS, and PACL in the TP and Ortho-P removal under controlled pH conditions (4, 5, 6, 7, and 8) and varied dosages (5-40 mg/L). Figure 3-1a-c illustrate the trends in TP removal as a function of pH and dosage for FS, ALS, and PACL, respectively. In contrast, Figure 3-1d-f shows the corresponding behaviour for Ortho-P and the Ortho-P/TP ratio, as presented in Figure C-1a-c, which provided further insights into the relative contributions of each phosphorus fraction during coagulation.

Across all the coagulants tested, TP and Ortho-P concentrations generally decline with increasing coagulant dosage, consistent with the expected behaviour of metal-based coagulants in the formation of insoluble precipitates that remove phosphorus from wastewater. The removal efficiencies improved as the pH was increased across the tested coagulants, although significant variability was observed between coagulants in their ability to achieve low residual TP levels. The performance of FS and ALS were particularly notable, as they achieved rapid reductions in TP and Ortho-P across the pH range from the lowest dose tested of 5 mg/L, with then generally smaller further removal for dosages exceeding that value. For FS, this was especially observed at pH 7 and 8, where residual TP concentrations were consistently below the target levels of 0.3 mg/L for doses of 10 mg/L and above (Figure 3-1a, d), while doses of 15 mg/L and above were

needed to achieve this value at the other pHs. Interestingly, ALS displayed better performance across most pHs and achieved the residual TP of 0.3 mg/L at a dose of 5 mg/L at pH 6. However, at acidic pH values, particularly at pH 4, ALS showed poorer phosphorus removal efficiency, with residual TP concentrations remaining above the target residual TP level of 0.3 mg/L even at the higher coagulant dosages (Figure 3-1b, e). To illustrate, at pH 4 and a dosage of 10 mgAl/L, residual TP was at approximately 1.8 mg/L, and even at 40 mgAl/L, the residual TP only reduced to 1.7 mg/L. ALS may not achieve optimal phosphorus precipitation at such low pH. PACL depicted a slower decline in residual TP efficiency with dose, with significant variations across pH levels. Its performance was notably weaker at lower pH values (pH 4-6), as evidenced by higher residual TP levels (Figure 3-1c, f). Increasing the PACL dosage did not result in a proportional decrease in residual TP at these acidic pH levels. For instance, at pH 4, the residual TP was 1.4 mg/L at 15 mg/L dosage and increased to 2.9 mg/L at 40 mg/L dosage, indicating that higher doses led to poorer phosphorus removal efficiency under these conditions. PACL only met the target for doses of 30 and 40 mg/L at pHs of 6 and 7.

Previous studies reported that ferric sulphate, aluminium sulphate and PACL achieved total phosphorus removal efficiency of 87.3%, 95.6% and 93.97% minimum residual phosphorus of 0.35, 0.12 and 0.16 mg/L at pH 7, 6.3, and 5.4 respectively. However, removal efficiency declined at higher pH levels with PACL due to altered polymeric aluminium species, supporting the observed trends in this study (Wang *et al.*, 2005). Another study reported alum coagulation at pH 7 produced effluent with a total residual phosphorus content of 0.3 mg/L (Banu *et al.*, 2008). These findings suggest PACL performance is more sensitive to pH fluctuations than FS and ALS.

The Ortho-P/TP ratio exhibited some variability across different pH and coagulant dose conditions, indicating that the removal rates of phosphorus fractions were not uniform, and in certain conditions, Ortho-P may have been removed more effectively than other phosphorus fractions. Conspicuously, PACL displayed deviations in the Ortho-P/TP ratio at pH 6 and 7, particularly at 15 mg/L dosages,

which align with the PACL lower rate of TP reduction observed in Figure 3-1c and f. This shows differential removal efficiencies between TP fractions and is likely due to limitations in its ability to form stable flocs at lower dosages.

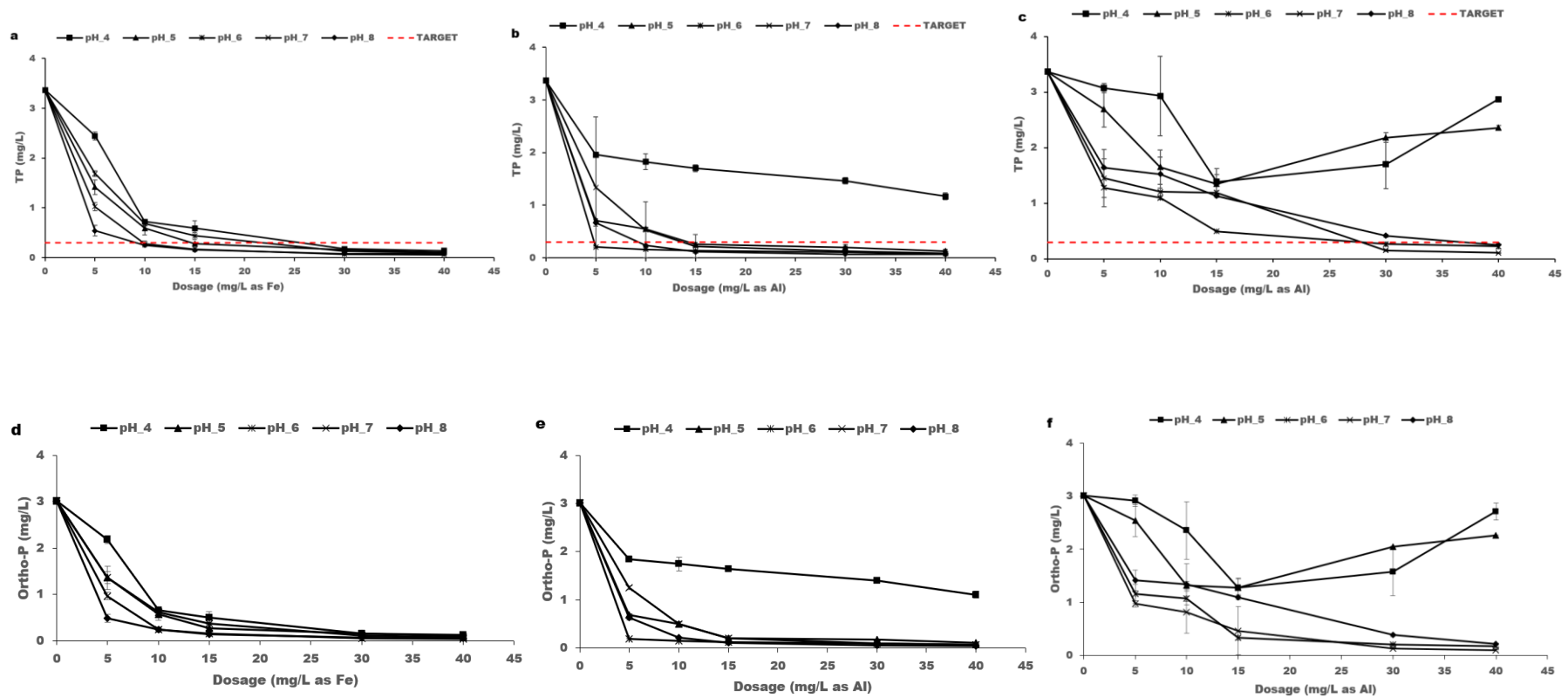


Figure 3-1: Effect of controlled pH conditions on residual TP (a, b, & c) and ortho-P (d, e & f) using FS (a, d), ALS (b, e), and PACL (c, f)

3.3.2 Fractionation

The fractionation results (Figure 3-2a-c) provide insights into the distribution of phosphorus across different fractions: dissolved, colloidal, and particulate - under the controlled pH conditions (4, 5, 6, 7, and 8) for the coagulants FS, ALS, and PACL. The wastewater effluent (WW) predominantly consisted of soluble reactive phosphorus, as evidenced by the dominance of the dissolved fraction ($<0.025\ \mu\text{m}$). With the addition of coagulants, a significant shift was observed in the phosphorus fractions, with, for all conditions tested, the residual TP mostly in particulate form.

FS, which, as shown above, performed well at all pHs, consistently achieved very low levels of all fractions. ALS exhibited a similar trend to FS, but the higher residual observed at pH 4 was essentially converted to particulates. This trend was even more pronounced for PACL at pHs of 4 and 5, as elevated particulate phosphorus levels across were observed, further confirming its weaker performance in phosphorus removal compared to FS and ALS (Figure 3-2a-c) yet, suggesting again that the reaction and floc formation happened, but the particles were not removed by settling.

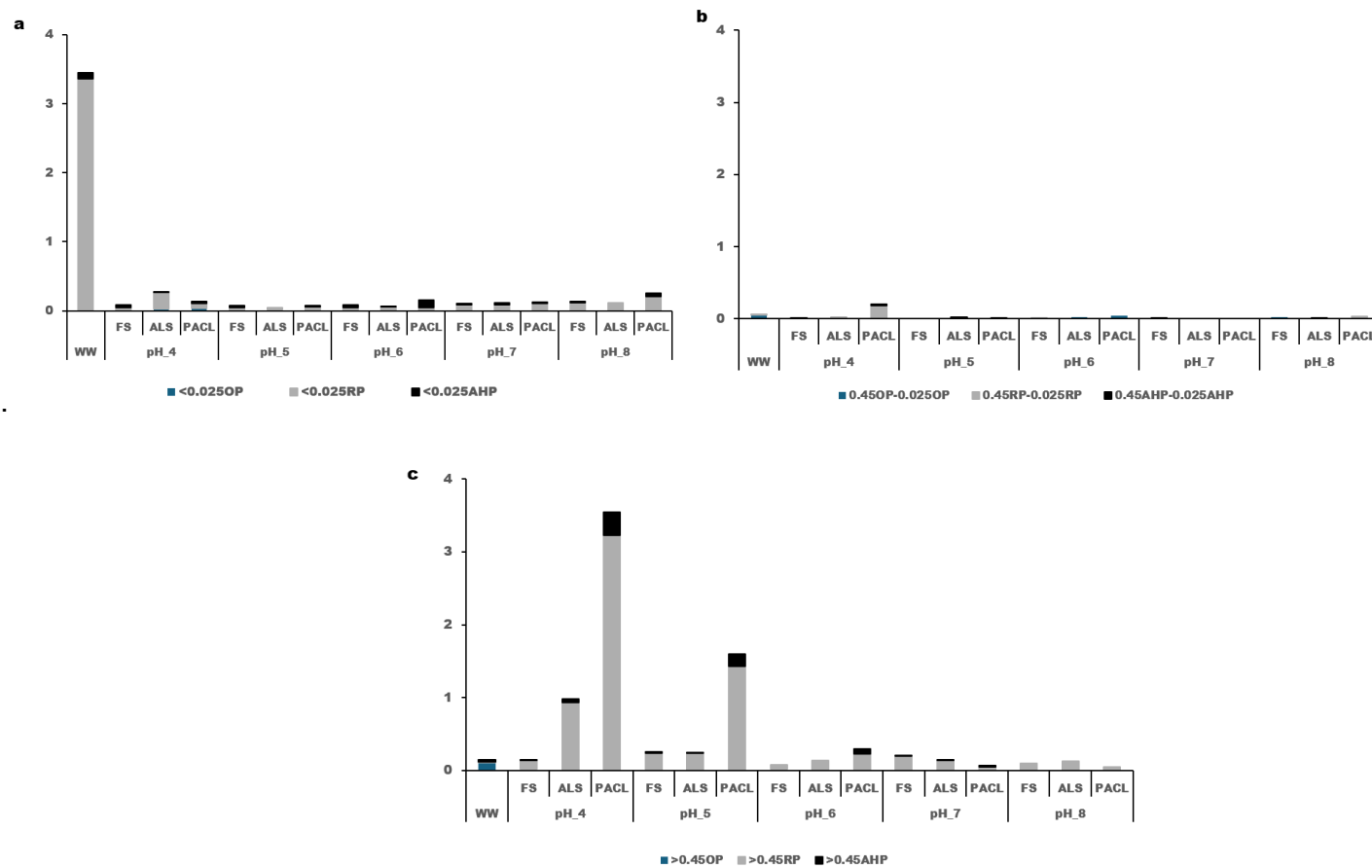


Figure 3-2: Phosphorus fractionation for (a) soluble, (b) colloidal and (c) particulate material under controlled pH conditions

3.3.3 Dose vs pH

The coagulant dosage required to achieve the target TP level of 0.3 mg/L for FS, ALS, and PACL under controlled pH conditions is shown in Figure 3-3. The relationship between dosage and pH exhibited apparent differences among the three coagulants and highlighted their distinct pH-dependent behaviours.

FS demonstrated the lowest dosage requirements at pHs of 7 and 8 with doses of about 10 mgFe/L. Doses of 15 to 25 mgFe/L were then needed to meet the target TP at lower pHs. ALS exhibited a low point with an optimal dosage of only 5 mgAl/L at pH 6. ALS dosage requirement increased for pHs on either side of this value, with a dose of 10-15 mgAl/L needed at pHs 5, 7 and 8. PACL, however, deviated significantly from this pattern, as significantly higher doses were required, between about 27 and 37 mgAl/L, for pHs of 6 to 8.

These highlight that FS and ALS achieved the target TP levels with lower dosages, particularly around neutral pH, while PACL required higher dosages and did not achieve the target phosphorus removal levels at lower pH values.

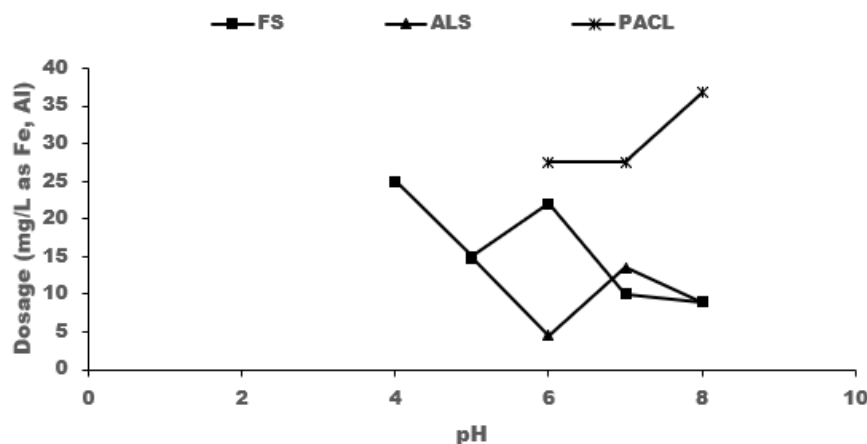


Figure 3-3: Dose of coagulant and pH required to achieve the target TP level of 0.3 mg/L

3.3.4 Turbidity and solids

The turbidity and TSS results (Figure C-2a-f) reported as the turbidity/TSS ratio (Figure 3-4a-c) across the coagulants, show a distinct pattern in dose-response relationships under controlled pH conditions. FS showed a generally low

turbidity/TSS ratio except for pH 4 across all dosages (Figure 3-4a), suggesting a greater presence of smaller and colloid particles. However, the fractionation data showed that there were no colloids. It is important to note that for the test at that pH, the turbidity/TSS ratio was already high in the effluent to be treated, which may have influenced the performance. At pH 5 and above, the ratio remained low, indicating more effective floc formation and separation. ALS also displayed low turbidity/TSS ratios with a stable trend observed beyond 10 mg/L, particularly for neutral to alkaline pH (6-8) (Figure 3-4b). At the lower pHs, with ALS, higher ratios were observed again, indicative of the presence of smaller particles, which corroborate both the poorer performance for TP removal and the fractionation results. More surprisingly, PACL exhibited consistently low turbidity/TSS ratios across all pH levels. However, as shown in the fractionation results, the particulate levels increased, but so did the turbidity, suggesting that PACL at these pH levels formed particles that were not settleable (Figure 3-4c).

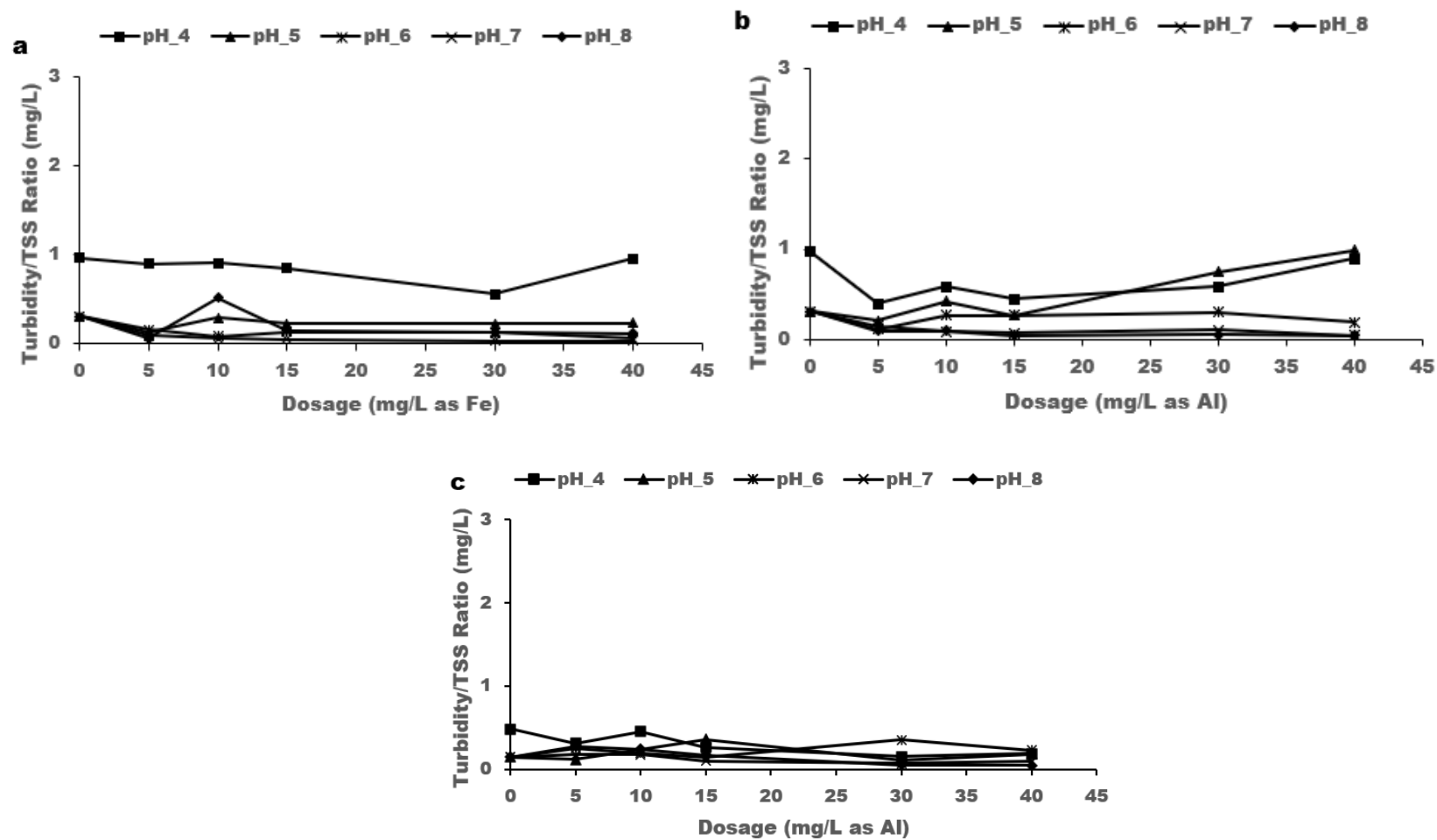


Figure 3-4: Effect of controlled pH conditions on residual turbidity and TSS ratio using FS (a), ALS (b), and PACL (c)

3.3.5 Chemical Oxygen Demand

Across all coagulants, a significant reduction in COD was observed at low dosages (5-10 mg/L), irrespective of pH, reflecting the ability of these coagulants to aggregate and remove organic and colloidal material (Figure 3-5a-c). FS demonstrated consistent performance, achieving stable COD reductions beyond 10 mg/L across all pH levels. ALS displayed greater variability in COD removal efficiency across pH levels. Indeed, higher residual COD levels were observed at low pHs (pH 4 and 5). COD removal stabilised at neutral and alkaline pH levels (pH 6-8) with dosages exceeding 10 mg/L, suggesting improved coagulation and flocculation processes. PACL showed the highest degree of variation among the three coagulants tested, particularly at acidic pH values (pH 4-5), where residual COD levels fluctuated significantly. At higher pH levels, PACL required greater dosages (>15 mg/L) to stabilise COD removal, indicating its weaker performance relative to FS and ALS. This variability highlights differences in floc stability and the ability of PACL to aggregate and remove organic material effectively under these pH conditions.

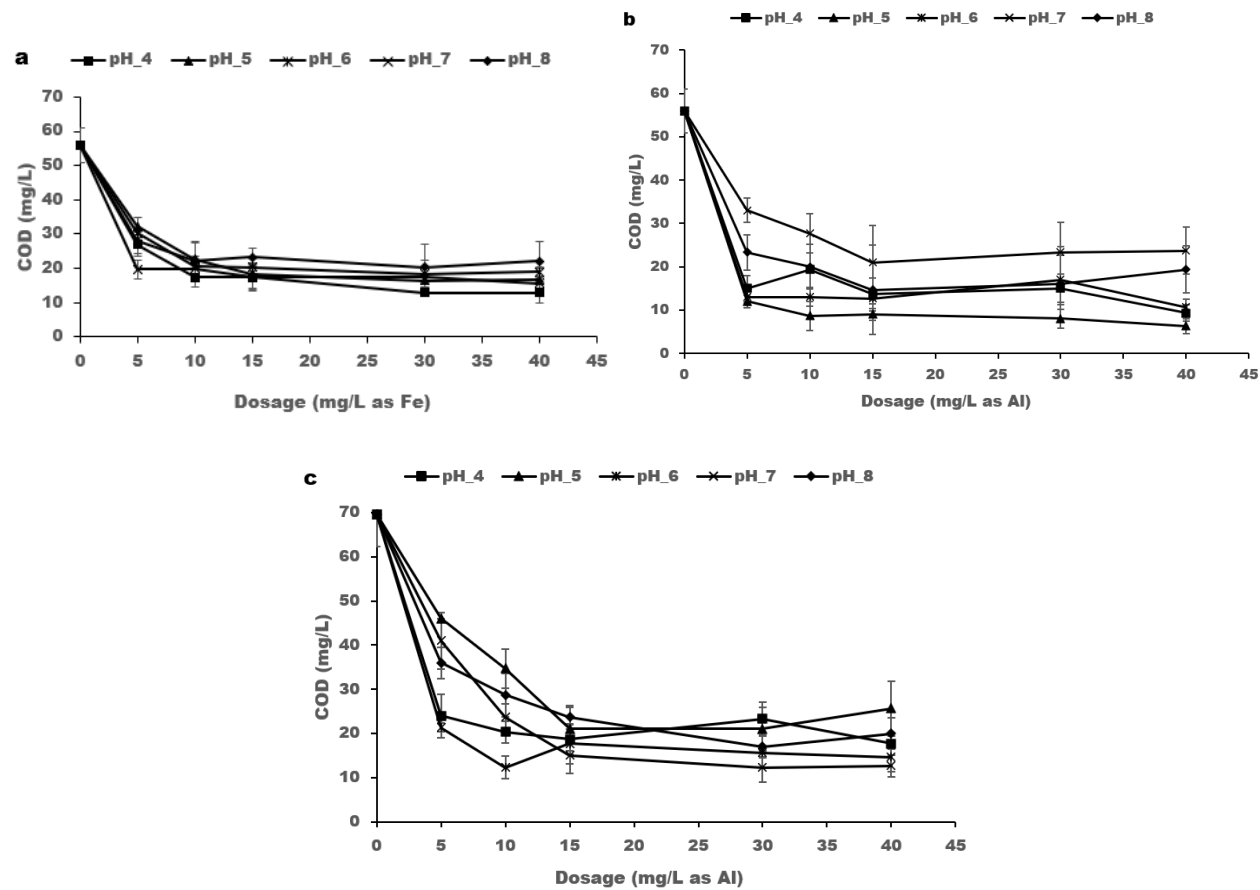


Figure 3-5: Influence of controlled pH on residual COD using FS (a), ALS (b), and PACL (c)

3.3.6 Floc Formation

The floc formation results (Figure 3-6a-c) depict distinct patterns among the three coagulants FS, ALS, and PACL, under controlled pH conditions. The floc size at pH 7 and 8 for FS and ALS reached approximately 150-200 μm during the growth phase, and PACL has a broader range with floc size above 200 μm for some pHs. The break phase at 200 rpm resulted in a significant reduction in floc size for all coagulants and stabilised in a similar range of between 80–150 μm , while PACL exhibited again greater variability.

The floc strength (Table 3-2) displayed a clear dependence on pH and coagulant type. FS and ALS displayed similar behaviours with decreasing floc strength as the pH was increased. Interestingly, for these two chemicals, an inverse trend was also observed for the floc regrowth, as more regrowth was observed at the higher pHs. Overall, the floc strength values were generally greater for ALS than for FS, suggesting stronger flocs for the aluminium-based coagulant. Although no clear pattern could be found for the fractal dimension in relation to the pH. On average, lower fractal values were obtained for ALS than for FS, confirming that more compact flocs were formed for the latter. More variability was observed with PACL, with the highest floc strength observed at pH 7 and the lowest at pH 6 and 8. Similar to ALS, PACL displayed poor to no regrowth potential, with negative values obtained, indicative of continued breakage even when shear was reduced.

The particle size distribution curves from the tests at pH 7 (Figure 3-6d-f) demonstrate the comparable trends observed for FS and ALS with significant breakage and limited regrowth but still greater for FS. The curves are much more compact for PACL, in this case forming smaller flocs that were marginally broken and regrown.

The role of pH in the modulation of coagulant performance is evident, especially for FS and ALS, with floc formation and regrowth profiles showing a distinct trend for each coagulant.

Table 3-2: Effect of controlled pH on floc strength, re-growth, and fractal dimension using ferric sulphate, aluminium sulphate, and polyaluminium chloride coagulants

Coagulant	Tested pH	Floc strength	Floc Re-growth	FD
FS	4	77.9	-3.6	2.67
	5	54.8	2.6	2.71
	6	50.1	10.6	2.71
	7	44.4	12.7	2.74
	8	47.8	15.4	2.76
ALS	4	98.9	-81.8	2.42
	5	64.6	-24.8	2.33
	6	71.8	-13.3	2.31
	7	64.2	-1.3	2.64
	8	55.3	5.5	2.62
PACL	4	65.8	-17.5	2.39
	5	63	-21.9	2.51
	6	50.5	-18.1	2.58
	7	88.2	-17.2	2.71
	8	50.5	7.6	2.93

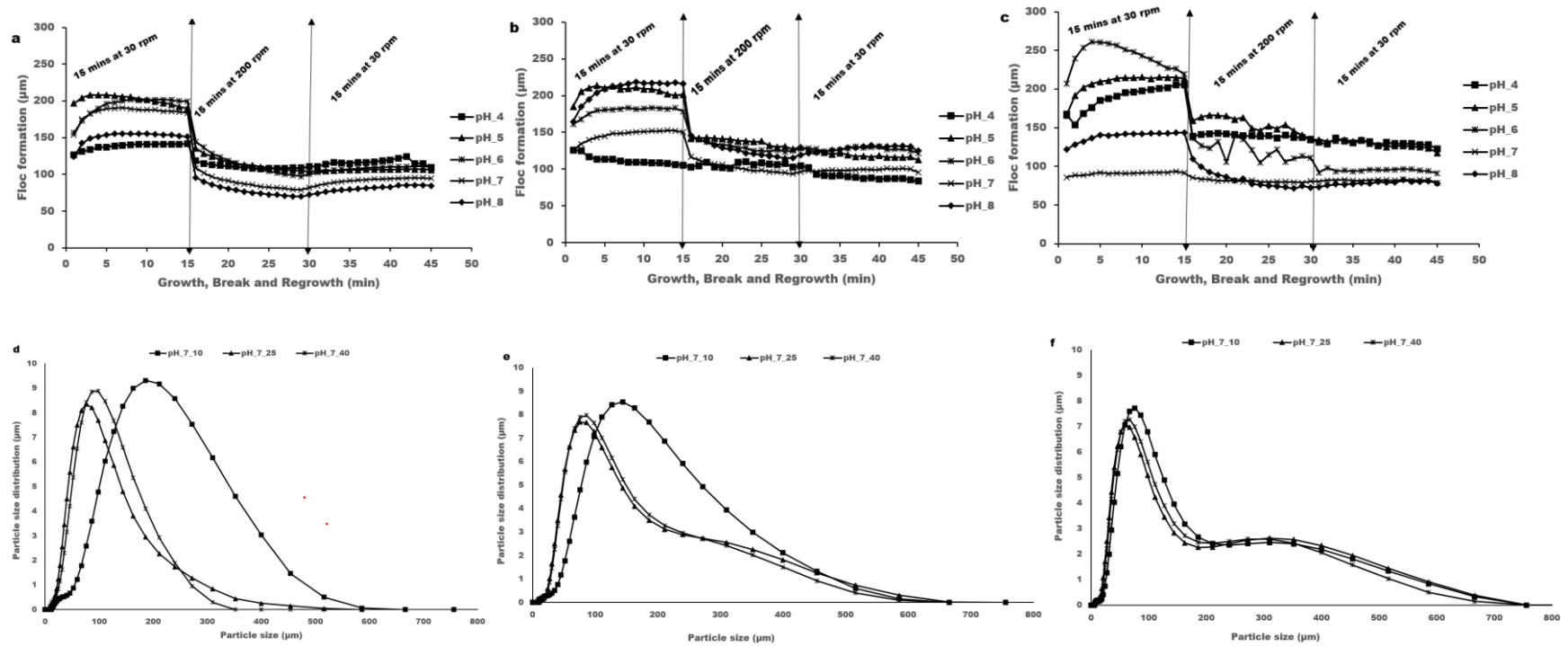


Figure 3-6: Floc formation and particle size distribution at pH and 10, 25 and 40 minutes of the tests for FS (a & d), ALS (b & e) and PACL (c & f) under controlled pH conditions

3.4 Discussion

The experimental results of this research show that ferric sulphate consistently achieved phosphorus removal efficiency across all tested pH levels, with the most significant decrease observed at pH 6-8 (Figure 3-1a). As seen in the Fe(III) speciation diagram (Figure 2-1a), ferric ions readily hydrolyse in this pH range in water to form ferric hydroxide $[\text{Fe}(\text{OH})_3]$, which has a high affinity and acts as an efficient adsorbent for phosphorus binding and removal (Zhang *et al.*, 2020). The Fe(III) species exhibit reduced solubility at pH 7-8, promoting the formation of $\text{Fe}(\text{OH})_3$ precipitates, which enhances phosphorus removal by facilitating the incorporation of phosphate into solid-phase aggregates. The ferric-based coagulants seem most effective at neutral to slightly alkaline pH conditions due to their increased phosphorus adsorption onto ferric hydroxide precipitates, which undergo extensive polymerisation, forming stable precipitates (El Samrani *et al.*, 2004; Yu *et al.*, 2007). At lower pH levels (pH 4-5), ferric ion solubility increases, reducing the precipitation of $\text{Fe}(\text{OH})_3$ and consequently leading to higher residual phosphorus concentrations (Figure 3-1a). However, the rapid formation of strong flocs further supports the high efficiency of FS, as floc size and compactness enhance sedimentation and phosphorus removal.

ALS exhibited a better trend, achieving optimal residual phosphorus at pH 6, where residual TP targets were reached at a low dosage of 5 mgAl/L (Figure 3-1b). The Al(III) speciation diagram (Figure 2-1c) confirms that aluminium ions hydrolyse to form aluminium hydroxide $[\text{Al}(\text{OH})_3]$ in this pH range, which has a high affinity for phosphorus adsorption. The solubility (Table 2-1) indicates that $\text{Al}(\text{OH})_3$ reaches minimum solubility at pH 6.5-7.5. At neutral to alkaline pH, $\text{Al}(\text{OH})_3$ precipitates provide a large surface area for phosphorus adsorption, explaining the observed efficiency of ALS in this pH range. However, at lower pH values (pH 4-5), aluminium remains more soluble as Al^{3+} , leading to weaker phosphorus precipitation and higher residual phosphorus concentrations because low-pH conditions limit aluminium-based coagulants' hydrolysis and coagulation effectiveness. Additionally, at very high pH (>8), aluminium salts form soluble $\text{Al}(\text{OH})_4^-$ (Georgantas and Grigoropoulou, 2007). This phenomenon

explains the slight increase in residual phosphorus concentrations observed in this study at pH 8. The relationship between pH and dosage (Figure 3-3) aligns with the solubility, with ALS requiring its lowest dosages for effective phosphorus removal at pH 6-7. Despite its higher phosphorus residuals at low pH, the fractionation results suggest that ALS primarily converted residual phosphorus into particulate form.

PACL behaviour was distinct from FS and ALS, characterised by inconsistent phosphorus removal, particularly at low pH values (Figure 3-1c). The pre-hydrolysed nature of PACL likely influenced its speciation and adsorption mechanisms (Figure 2-1c), with polymeric forms undergoing further hydrolysis depending on the pH of the wastewater. At lower pH values (4-5), PACL displayed weaker phosphorus removal, suggesting that the pH changes affected the preformed species more, likely due to partial hydrolysis and reduced availability of active polymeric species for phosphate binding (Choi et al., 2013; Wang et al., 2014). The solubility (Table 2-1) indicates that PACL remains soluble across different pH levels, making it less effective in forming phosphorus precipitates under certain conditions due to its pre-hydrolysed aluminium species exhibiting reduced phosphate adsorption efficiency under variable pH conditions due to speciation instability (Choi et al., 2013).

The fractionation results (Figure 3-2) and turbidity and TSS trends (Figure 3-4) provide additional insights into the aggregation efficiency and settleability of the different coagulants. FS, which consistently performed well across all pH conditions, achieved very low residual phosphorus levels across all fractions, indicating effective coagulation and sedimentation. ALS exhibited a similar trend to FS, but at pH 4, the residual phosphorus was primarily transformed into particulate form, suggesting that while coagulation occurred, the resulting flocs may have had weaker settleability. This trend was even more pronounced for PACL at pH 4 and 5, where higher particulate phosphorus levels were observed (Figure 3-2a-c).

The increase in particulate phosphorus without a corresponding decrease in residual phosphorus suggests that while coagulation and floc formation occurred,

the flocs produced were too small or weak to settle effectively. This limitation in settleability is further supported by the turbidity and TSS measurements (Figure 3-4), which highlight differences in aggregation behaviour. FS consistently achieved effective reductions in turbidity and TSS across all pH levels, reflecting its strong ability to aggregate and remove particulate matter. ALS followed a similar trend but required slightly higher dosages to achieve comparable reductions. In contrast, PACL exhibited higher turbidity and TSS values at lower pH (4-5), aligning with the fractionation data, which showed an increase in particulate phosphorus that was not effectively removed. This suggests that PACL at low pH formed particulates that remained in suspension rather than settling out, further confirming its weaker phosphorus removal performance compared to FS and ALS. These findings indicate that PACL's poor performance at low pH was not due to ineffective coagulation but rather the formation of smaller, less compact flocs that were inefficiently removed by sedimentation (Su *et al.*, 2021).

The low turbidity/TSS ratio observed for PACL in (Figure 3-4) at all pH levels, when considered alongside the fractionation results, suggests that phosphorus removal inefficiencies were more likely due to the formation of particulates that were not effectively removed through sedimentation, rather than a limitation in reactive species availability. Additionally, the stable Ortho-P/TP ratio across conditions indicates that all phosphorus fractions were removed at a similar rate, further supporting that the inadequacies observed with PACL were not due to the selective removal of specific phosphorus species but rather the inability of the formed particulates to settle effectively. At higher pH, PACL performed slightly better but still required higher dosages than FS and ALS to achieve comparable phosphorus removal, reaffirming the limitations of its pre-hydrolysed structure in adapting to changing pH conditions.

Floc formation properties further support the observed phosphorus removal trends, as shown in Figure 3-6. ALS produced higher floc strength values, particularly at acidic to alkaline pH. The fractal dimension data (Table 3-2) demonstrate that FS flocs were more compact and resistant to breakage,

enhancing sedimentation and phosphorus removal efficiency. ALS produced higher floc strength values with limited regrowth compared to FS, suggesting a slightly lower resistance to breakage. This may indicate differences in the internal cohesion and compactness of the flocs formed by each coagulant, ultimately influencing their sedimentation and phosphorus removal efficiency. PACL produced the weakest flocs, particularly at low pH (Figure 3-6c), where polymeric aluminium species were less effective in promoting aggregation and likely contributed to its lower phosphorus removal efficiency (Gheraout and Gheraout, 2012; Xiao et al., 2019). The fractal dimension analysis further confirmed that PACL flocs were less compact and more prone to fragmentation, which explains the higher residual phosphorus levels observed under certain pH conditions.

Generally, the distinct removal efficiencies observed for FS, ALS, and PACL are largely dictated by the hydrolysis of the metal ions and the formation of precipitates that facilitate phosphorus adsorption, precipitation and sedimentation. These processes govern the transformation of soluble phosphorus into particulate fractions, which impacts overall treatment performance. The effectiveness of these coagulants is strongly influenced by their solubility, speciation, and hydrolysis dynamics, which are all pH-dependent (Yan et al., 2007; Zhao et al., 2016; Dayarathne et al., 2021; Weiss et al., 2021).

3.5 Conclusion

In the literature, studies evaluating the impact of pH on phosphorus removal using FS, ALS, and PACL have largely focused on individual coagulants or treatment efficiency alone. There is limited reporting on the mechanisms governing phosphorus removal under identical conditions and their implications for floc formation, settleability, and overall coagulation performance. This study integrated and expanded previous research by systematically assessing the impact of the direct link between pH-dependent hydrolysis mechanisms on the coagulation efficiency of these three commonly used coagulants, considering both treatment performance and floc properties. Conducting a side-by-side evaluation under the same wastewater matrix and controlled pH conditions allowed for a direct comparison of their hydrolysis behaviour, phosphorus fractionation, and floc dynamics, providing a comprehensive insight into their operational effectiveness across a wide pH range. Additionally, this study provides new insights into coagulant selection and dosing strategies for achieving low phosphorus discharge limits in wastewater treatment.

The results showed that both FS and ALS were highly effective in achieving low residual phosphorus concentrations (<0.3 mg/L) under optimal pH conditions. ALS demonstrated a dose advantage at pH 5-8, achieving the target TP with 5 mg Al/L, compared to FS at dosages of 10 mg Fe/L and above at pH 4-8. This suggests that ALS is more dose-efficient under certain conditions. The hydrolysis of Al^{3+} into aluminium hydroxide $[\text{Al}(\text{OH})_3]$ provided an effective surface for phosphorus adsorption, but at lower pH levels (4-5), ALS remained more soluble, leading to weaker precipitation. Additionally, at pH levels greater than 8, ALS formed soluble $\text{Al}(\text{OH})_4^-$, further decreasing its phosphorus removal efficiency. However, FS performance was more consistent across a broader pH range (4-8), with robust floc formation and greater resilience to breakage, making it advantageous in wastewater treatment systems with fluctuating pH conditions. The results align with previous studies that highlight the pH-dependent nature of aluminium-based coagulants, with optimal performance within a narrower pH range.

PACL exhibited the most variable performance, with particularly weak phosphorus removal at pH 4-5, likely due to incomplete hydrolysis and reduced availability of active polymeric species for phosphorus binding. Even at neutral and alkaline pH conditions, PACL required higher dosages than FS and ALS to achieve comparable removal efficiencies. The fractionation analysis confirmed that PACL resulted in higher residual particulate phosphorus levels, suggesting that coagulation and floc formation occurred, but the flocs remained too small or weak to settle effectively. These findings indicate that PACL's pre-hydrolysed nature does not provide significant advantages over conventional ferric and aluminium coagulants in phosphorus removal under the tested conditions.

Floc characterisation experiments further supported these observations, highlighting distinct differences in floc strength, regrowth potential, and settleability among the coagulants. FS produced the most stable and resilient flocs, particularly at neutral to alkaline pH. ALS flocs had the highest growth but exhibited lower regrowth potential, while PACL flocs were the weakest, particularly at low pH, where polymeric aluminium species showed reduced aggregation efficiency. Fractal dimension analysis further confirmed that FS flocs were more compact and resistant to breakage, enhancing overall phosphorus removal performance.

The dose and pH analysis reinforced the unique solubility and hydrolysis behaviours of the three coagulants. FS and ALS required lower dosages at their optimal pH ranges, whereas PACL consistently required higher dosages across all conditions. The turbidity and TSS analysis further demonstrated that FS and ALS achieved more effective solid-phase separation, while PACL's performance was hindered by weaker flocculation and sedimentation characteristics.

For practical applications, these findings highlight the importance of tailoring coagulant selection based on wastewater pH and treatment objectives. The inadequacy of PACL at low pH suggests that its use should be carefully considered in environments where acidic conditions prevail.

However, the constraints of this work must be acknowledged. The experiments were conducted at laboratory scale using final effluent samples under controlled

pH conditions. While representative, they do not capture the full operational variability of large-scale systems, such as fluctuating flows, temperatures, and influent compositions. The requirement for acid and base addition (HCl and NaOH) to maintain tight pH control raises questions about scalability, cost-effectiveness, and environmental sustainability, particularly for systems with low buffering capacity. Additionally, only final effluent was assessed; coagulant performance at other treatment stages (e.g., crude wastewater or PST) may yield different insights.

3.6 References

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Appendix C

Table C-1: Selected pH and dosage conditions evaluated for achieving 0.3 mg/L TP Target

Coagulant	pH	Dosage (mg/L)	0.3 mg/L TP target
FS	4	30	Yes
	5	15	Yes
	6	30	Yes
	7	10	Yes
	8	10	Yes
ALS	4	40	No
	5	15	Yes
	6	5	Yes
	7	15	Yes
	8	10	Yes
PACL	4	15	No
	5	15	No
	6	30	Yes
	7	30	Yes
	8	40	Yes

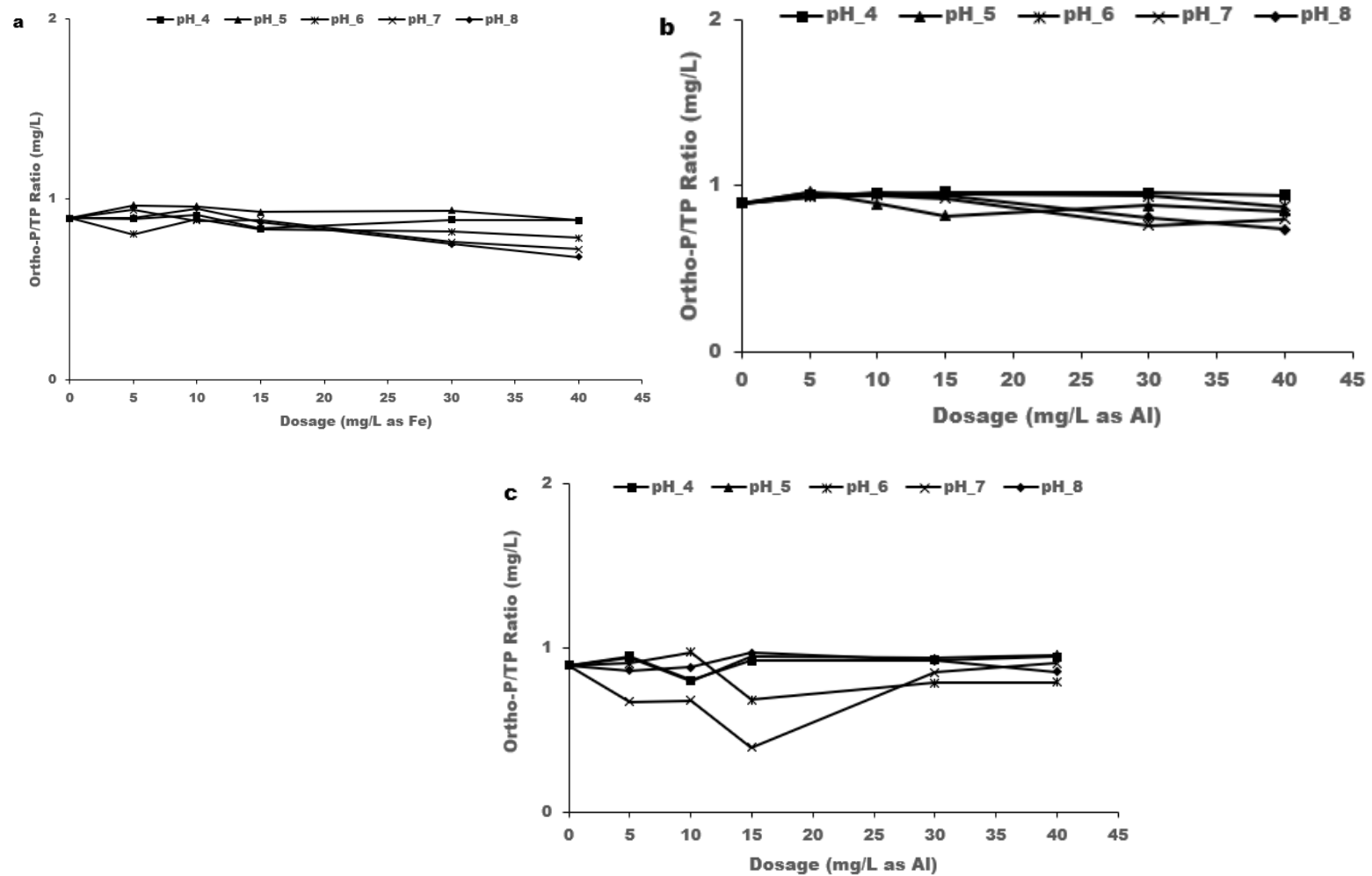


Figure C-1: Effect of pH and coagulant dosage on Ortho-P/TP Ratio for different coagulants

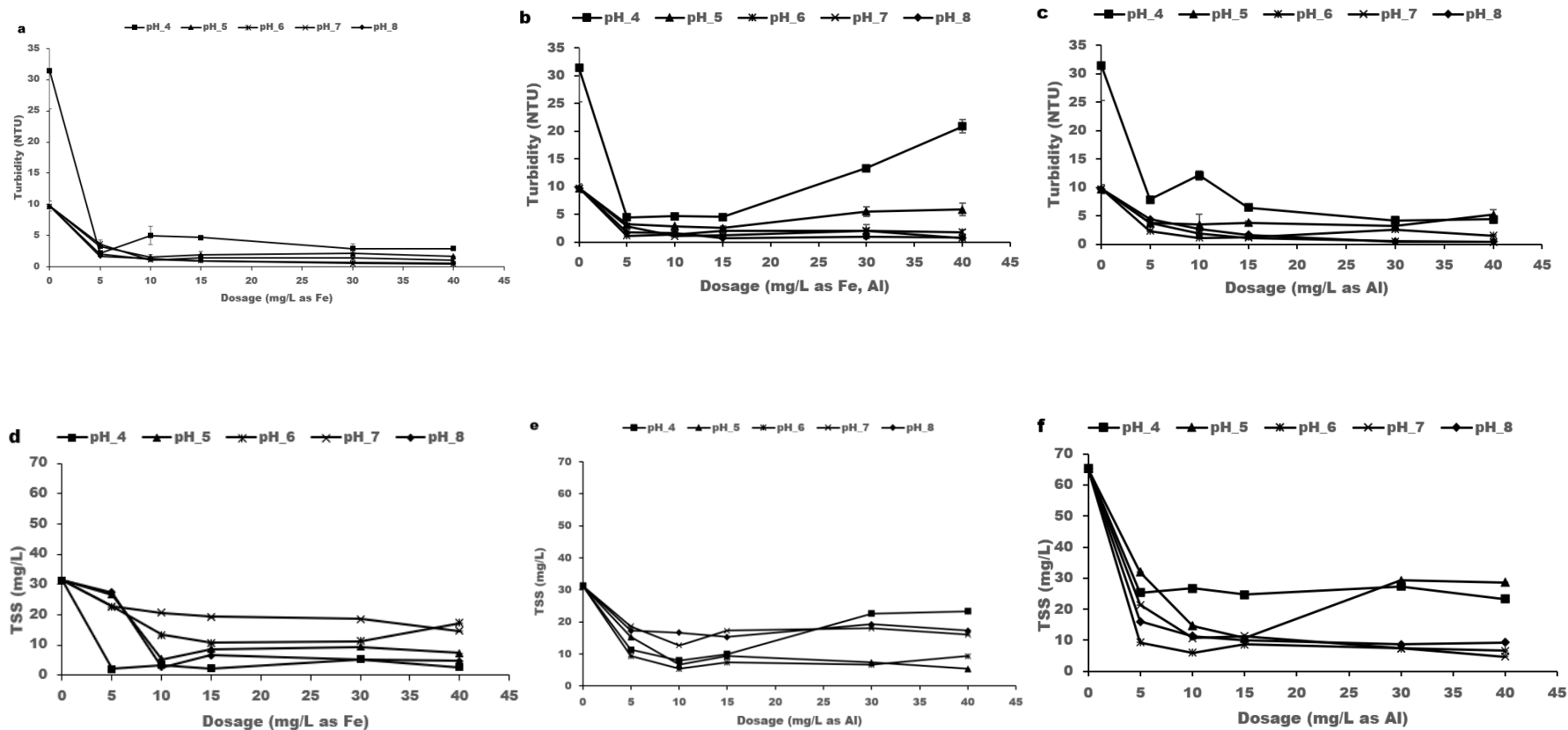


Figure C-2: Effect of controlled pH and coagulant dosage on turbidity (a-c) and TSS (d-f) removal using different coagulants

Table C-2: Influence of pH and coagulant dosage on chloride and sulphate anion concentrations (measured in mg/L) in treated wastewater using ferric sulphate, aluminium sulphate, and polyaluminium chloride

Coagulant	pHs Dosage (mg/L)	4		5		6		7		8	
		Chloride	Sulphate	Chloride	Sulphate	Chloride	Sulphate	Chloride	Sulphate	Chloride	Sulphate
FS	0	64.5	52.7	64.5	52.7	64.5	52.7	64.5	52.7	64.5	52.7
	5	129.6	83.6	115.5	74.6	99.2	77.2	42	81.5	34.2	82.8
	10	113.6	112.5	93.8	97.1	88.8	98.8	41.7	104.8	34	105.5
	15	97.4	134.5	85.5	117.6	62.3	123.1	41.9	127.8	33.9	127.7
	30	61.5	197.1	62.3	184.1	62.1	196.1	41.6	200.4	34	202.7
	40	61.3	242.2	62	224.9	61.2	240.8	41.3	248.7	33.7	250.5
ALS	0	64.5	52.7	64.5	52.7	64.5	52.7	64.5	52.7	64.5	52.7
	5	115.5	115.5	98.2	88.7	72.8	88.8	61.8	80	35.5	90.6
	10	111.4	148.5	78.5	111.1	55.1	117.2	61.6	106.7	35.1	118.8
	15	136.8	36.8	63	135.9	34.3	141.8	61.3	135.5	35.3	149.7
	30	91.2	322.8	33.5	233	33.9	227.5	61.2	223.5	34.5	240.4
	40	76	344.4	33.6	281.3	34.2	281.7	60.8	278.4	34.5	300.8
PACL	0	64.5	52.7	64.5	52.7	64.5	52.7	67	46.6	64.5	52.7
	5	136.2	46.4	143.9	50	123.7	47.3	80.5	47.6	77.8	46.2
	10	140.8	45.8	149.6	53	121.4	46.6	90.5	47.2	87.8	45.6
	15	144.1	46.9	136.9	55.6	125.4	46	102.4	47.5	98.6	45.5
	30	157.5	68.7	177.2	68.8	135.1	41.3	136.7	45.9	134.7	45.7
	40	158.4	69.7	196.3	71.2	157.9	37.9	156.9	44.4	155	45.1

Table C-3: Effect of pH and coagulant dosage on residual metal concentrations (Fe, Al, Zn, Ca measured in mg/L) in treated wastewater using ferric sulphate, aluminium sulphate, and PACL

pH		4				5				6				7				8			
Coagulant	Dosage (mg/L)	Fe	Al	Zn	Ca	Fe	Al	Zn	Ca	Fe	Al	Zn	Ca	Fe	Al	Zn	Ca	Fe	Al	Zn	Ca
FS	0	-0.2	-0.5	-0.1	38.9	-0.2	-0.5	-0.1	38.9	-0.2	-0.5	-0.1	38.9	-0.4	-0.1	0	23.3	-0.2	-0.5	-0.1	38.9
	5	0.2	-0.5	0	38.4	0.8	-0.5	0	39.1	1.4	-0.5	-0.1	40.3	0.3	-0.5	-0.1	44.8	0.2	-0.5	-0.1	50.4
	10	0.2	-0.5	0	37.2	0.3	-0.5	-0.1	37.8	0.3	-0.5	-0.1	40.1	0.1	-0.5	-0.1	48.4	0.1	-0.5	-0.1	50
	15	0.2	-0.5	-0.1	37.8	0.1	-0.5	-0.1	37.2	0.4	-0.5	-0.1	38.7	0.1	-0.5	-0.1	43	0	-0.5	-0.1	46.6
	30	0	-0.5	-0.1	23.3	0	-0.5	-0.1	38.1	0	-0.5	-0.1	41.4	-0.1	-0.5	-0.1	47	-0.1	-0.5	-0.1	49.1
	40	0.1	-0.5	-0.1	37.9	0	-0.5	-0.1	39.1	0	-0.5	-0.1	38.5	-0.2	-0.5	-0.1	46.5	-0.2	-0.5	-0.1	43.8
ALS	0	-0.2	-0.5	-0.1	38.9	-0.2	-0.5	-0.1	38.9	-0.2	-0.5	-0.1	38.9	-0.4	-0.1	0	23.3	-0.2	-0.5	-0.1	38.9
	5	-0.1	9.3	5.92	53.5	-0.4	0.9	0	52.9	-0.4	0.1	0	53.6	-0.2	0.4	-0.1	35.6	-0.3	0.5	0	49.9
	10	-0.1	10.4	0	53.5	-0.4	1.2	0	52.8	-0.4	0.2	0	54.3	-0.2	-0.3	-0.1	39.3	-0.3	0.2	0	51
	15	-0.1	9.1	-0.1	53.5	-0.4	1.1	0	53.2	-0.4	0.2	0	56.6	-0.2	-0.5	-0.1	37.2	-0.3	0.1	0	49.3
	30	-0.2	21.7	-0.1	53.3	-0.4	2	0	51.3	-0.4	0.3	0	55.5	-0.2	-0.5	-0.1	35	-0.4	0.1	0	51.7
	40	-0.2	28.1	-0.1	53.9	-0.4	1.9	0	52.5	-0.4	0.3	0	51.6	-0.2	-0.6	-0.1	34.4	-0.4	0.1	0	52.7
PACL	0	-0.2	-0.5	-0.1	38.9	-0.2	-0.5	-0.1	38.9	-0.2	-0.5	-0.1	38.9	-0.4	-0.1	0	23.3	-0.2	-0.5	-0.1	38.9
	5	-0.3	2.5	0.1	28.8	-0.4	1	0	32.9	0	0.3	0.1	37.1	-0.3	0.8	0	22.7	-0.3	1.5	0	27.4
	10	-0.3	1.6	0.3	30.5	-0.4	0.7	0.1	30.3	0	0.1	0.1	37	-0.4	0.7	0	21.8	-0.4	1.1	0	25.7
	15	-0.3	2.7	0.1	29.1	-0.4	1.4	0	32.2	0	0.1	0.1	38.8	-0.4	0	0	23.7	-0.4	0.7	0	24.7
	30	-0.3	11.2	0	28.5	-0.4	7.2	0	28.1	0	0.1	0.1	37.1	-0.4	-0.1	0	24.2	-0.4	0.1	0	24.5
	40	-0.3	18.5	0.1	28.3	-0.4	12.6	0	29.7	0	0.2	0.1	37.9	-0.4	-0.1	0	23.2	-0.4	0.1	0	24.1

Chapter 4

4 Understand the impact of the dosing location on the effectiveness of ferric and aluminium coagulants for P removal from sewage

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Abstract

Phosphorus pollution from municipal wastewater is a major contributor to eutrophication, prompting stringent regulatory limits on effluent discharge. Chemical coagulation remains a widely employed strategy for phosphorus removal, yet its effectiveness is highly dependent on coagulant type, dosing location, and wastewater characteristics. This study systematically evaluates the performance of ferric sulphate, aluminium sulphate, and polyaluminium chloride across three key dosing locations - crude wastewater, post-primary settling, and final effluent - to determine optimal treatment strategies for enhanced phosphorus removal.

Jar tests and analytical techniques were employed to assess total phosphorus removal, floc formation, particle size distribution, and coagulant interactions with organic matter. FS consistently demonstrated the highest phosphorus residual efficiency, achieving TP concentrations below 0.3 mg/L at PST and FE locations, while ALS and PACL exhibited more variable performance, particularly in high-strength crude wastewater. The study identified two-point dosing as an effective strategy for improving phosphorus removal in raw wastewater, enhancing coagulant distribution, and reducing overall chemical demand.

This research provides practical insights for optimising coagulant selection and dosing location in municipal wastewater treatment plants, ensuring compliance with stringent phosphorus discharge regulations while minimising chemical costs and environmental impact.

Keywords: phosphorus removal, wastewater treatment, chemical coagulation, ferric sulphate, polyaluminium chloride, dosing optimisation, floc formation, and eutrophication prevention.

4.1 Introduction

Phosphorus is a key driver of eutrophication, which leads to excessive algal blooms, oxygen depletion, and the degradation of aquatic ecosystems (Tran *et al.*, 2012). To address these concerns, regulations such as the European Union Water Framework Directive mandate that wastewater treatment plants (WWTPs) reduce phosphorus concentrations in their effluent to as low as 0.1 mg/L in sensitive areas (Langer *et al.*, 2017). This regulatory push has driven WWTPs, to explore more efficient and cost-effective phosphorus removal technologies.

In most WWTPs, phosphorus is removed through either biological phosphorus removal (BPR) or coagulation. While BPR involves microorganisms that uptake phosphorus, it is highly sensitive to operational conditions such as carbon availability and the balance between biochemical oxygen demand (BOD) and phosphorus (Xie *et al.*, 2020). In contrast, coagulation, which involves the addition of coagulants such as ferric or aluminium based salts, is more robust and capable of achieving the very low phosphorus concentrations needed to meet regulatory limits (Xu *et al.*, 2024). Coagulants react with phosphate (PO_4^{3-}) in the wastewater to form insoluble phosphorus compounds that can be removed through sedimentation or filtration (Xu *et al.*, 2024).

The dosing location can greatly influence phosphorus removal effectiveness, as different stages of the treatment process present varying levels of suspended solids, organic matter, and phosphorus speciation. In previous research where 5 mgAl/L of ALS was dosed at different treatment stages of total phosphorus (TP) concentration of 5.60-9.00 mg/L, specifically in raw wastewater, after primary sedimentation, and before the secondary clarifier, phosphorus removal efficiency varied significantly. The most effective removal occurred when ALS was dosed before the secondary clarifier, achieving a TP concentration of 0.3 mg/L (Ge *et al.*, 2018). This highlights the importance of selecting the correct dosing location to maximise coagulant efficiency. Dosing in raw wastewater, which contains high levels of organic matter and particulates, may reduce coagulant performance or lead to excess dosing due to interference with coagulation mechanisms. Dosing after primary settling is often more effective because a significant portion of the suspended solids and organic material has already been removed, allowing the coagulant to interact more efficiently with the

phosphorus (Xie *et al.*, 2020). Additionally, final stage dosing before effluent discharge is sometimes necessary to ensure that the stringent phosphorus limits imposed by environmental regulations are met. However, dosing at the final stage also introduces the potential risk of residual metal discharge, which is itself a regulated concern. If not properly managed, metals such as aluminium and iron can accumulate in the effluent, potentially leading to secondary pollution and non-compliance with discharge regulations (Vale and Fernández, 2021).

Studies have shown that coagulant choice is crucial for optimising phosphorus removal efficiency, hence, comparing FS, ALS, and PACL revealed that FS was more effective for TP removal at specific locations within the treatment train, particularly when dosed after primary settling, with pH of 5.5 to 6.5 range achieves TP removal of 0.33 mg/L at a dosage of 30 mgFe/L (Li *et al.*, 2017). In a similar study, TP concentrations in raw sewage were found to be as high as 9.0 mg/L, but dosing 5 mgAl/L of ALS after the aeration tank reduced soluble phosphorus to 0.13 mg/L (Ge *et al.*, 2018). FC, on the other hand, performs at a pH range of 4.5 to 5.0, achieving up to 90% phosphorus removal at a dosage of 40 mgFe/L (Xie *et al.*, 2020). It was also shown that FC and ALS are highly effective at this point, achieving TP concentrations below 0.17 mg/L with dosages of 40 mgFe/L and 30 mgAl/L, respectively (Li *et al.*, 2017). While existing studies indicate that both the location of coagulant dosing and the type of chemical used significantly influence phosphorus removal performance, there remains no clear accepted recommendation for the optimal combination of these factors. Variability in wastewater characteristics, treatment plant configurations, and regulatory constraints means that trade-offs often exist between dosing efficiency, residual metal discharge, and operational costs. Therefore, it is essential to conduct a systematic evaluation of both dosing location and coagulant selection to identify optimal treatment strategies that maximise phosphorus removal while minimising potential drawbacks.

Furthermore, floc formation, which occurs during the coagulation process, is essential for phosphorus removal. Effective floc formation allows phosphorus to be captured and removed through sedimentation or filtration. Studies compared the performance of different coagulants and found that ALS generally produces more stable flocs than FC, which leads to better phosphorus removal, particularly when dosed after primary settling (Zahed *et al.*, 2022). However, when overdosed, any coagulant can cause floc

destabilisation and reduced phosphorus removal efficiency, as noted in studies on both ALS and FS (Smoczyński *et al.*, 2014). While existing research provides insight into how coagulant type influences floc formation and stability, there is currently no comprehensive study evaluating the combined impact of both coagulant choice and wastewater characteristics at different dosing locations. Given that the effectiveness of coagulation depends not only on the chemical itself but also on the composition of the wastewater at each treatment stage, understanding these interactions on floc formation and stability is critical.

This study then aims to address this knowledge gap by systematically assessing the interplay between coagulant selection, wastewater characteristics, and dosing location, providing insights into how these factors can be optimised in municipal wastewater treatment for phosphorus removal while mitigating risks of floc destabilisation and secondary pollution. Samples were taken from three key points in the treatment process at a full-scale site: raw wastewater, after primary settling, and final effluent.

4.2 Materials and Methods

4.2.1 Municipal Wastewater Sample Collection and Characterisation

Municipal wastewater samples used in this study were sourced from a sewage Treatment Works (STW) located near Glasgow in Scotland, a municipal treatment facility designed to remove organic matter, nutrients, and suspended solids before effluent discharge. The treatment process follows a conventional train, beginning with preliminary screening to remove large debris, followed by primary settling tanks (PST) where a significant portion of suspended solids and organic matter is removed. The wastewater then undergoes biological treatment through an activated sludge process, which further degrades organic contaminants and removes nutrients. The final stage includes secondary clarification, where residual solids are settled before the treated effluent is discharged.

Currently, coagulant dosing at this site is applied at the back end of the biological process, just before the secondary clarifier, to aid phosphorus removal. This means that phosphorus levels in the final effluent samples collected for this study had already undergone some treatment. Therefore, the tests in this study evaluated the potential

for additional phosphorus removal to achieve very low effluent phosphorus concentrations, ensuring compliance with stringent environmental discharge regulations. All samples were handled and stored according to standard protocols to maintain their integrity throughout the experimental period.

Prior to experimental analysis, municipal wastewater samples were comprehensively characterised to understand the baseline physico-chemical properties of the matrix (Table 4-1). This initial assessment was essential for interpreting subsequent coagulation performance, floc formation dynamics, and phosphorus removal efficiency. The following parameters were analysed using standard methods:

- **pH:** Measured with a calibrated multiparameter pH meter (Jenway 4330) to determine the hydrogen ion concentration of the samples.
- **Alkalinity:** Assessed using a Hanna Instruments alkalinity checker to evaluate the buffering capacity of the wastewater.
- **Turbidity:** Determined with a portable turbidity meter (Hach 2100Q), with results expressed in Nephelometric Turbidity Units (NTU), reflecting the clarity of the samples.
- **Total Suspended Solids (TSS):** Quantified gravimetrically by filtering a known volume of wastewater through pre-weighed glass fibre filters, followed by drying at 105°C. This was conducted in accordance with the standardised method outlined by the American Public Health Association (APHA) (Federation and Aph Association, 2005).
- **Total Phosphorus (TP), Orthophosphate (Ortho-P), and Chemical Oxygen Demand (COD):** These were measured using Merck Spectroquant cell test kits. TP was determined following persulfate digestion and analysed colorimetrically using the ascorbic acid method. All measurements were carried out using a Merck Spectroquant NOVA 60 spectrophotometer.
- **Metal Concentrations:** Target metal ions were quantified using Inductively Coupled Plasma Mass Spectrometry (ICP-MS), conducted on a Nexion 350D system to ensure high sensitivity and precision.

- **Anions and Cations:** Key ionic species were analysed using ion chromatography (IC) with Dionex ICS–1600 and ICS–900 (Thermo Scientific), providing detailed profiling of the wastewater's ionic composition.

This baseline characterisation enabled the identification of site-specific conditions that could influence the chemical speciation of phosphorus, coagulant behaviour, and overall treatment efficiency across the different dosing locations.

Table 4-1: Scottish wastewater characterisation without coagulants

Parameter	Crude		PST		FE	
	Mean	Stdev	Mean	Stdev	Mean	Stdev
TP (mg/L)	4.4	0.1	3.4	0.1	0.7	0.1
Ortho-P (mg/L)	3.4	0.1	3.1	0.1	0.7	0.0
pH	6.6	0.0	6.5	0.0	6.6	0.1
Alkalinity (mg/L)	179.0	0.8	203.7	2.1	101.0	2.9
TSS (mg/L)	181.7	0.0	78.7	0.0	28.7	0.0
Turbidity (NTU)	64.9	1.6	51.1	1.6	4.2	0.7
COD (mg/L)	284.0	9.9	203.3	7.7	15.7	2.1
Chloride (mg/L)	175.3	0.3	86.6	0.0	49.2	0.3
Sulphate (mg/L)	82.6	0.1	31.9	0.0	38.0	0.2
Ferric	0.1	1.4	0.3	1.9	-0.3	1.6
Aluminium (mg/L)	0.0	0.2	0.0	0.1	0.0	0.1
Zinc (mg/L)	0.0	0.3	-0.4	12.2	0.0	0.2
Calcium (mg/L)	25.8	49.0	41.5	129.7	38.7	12.5

Note: Bulk one-time samples were collected for each of the locations from Scottish Water in Scotland. A total of 162 samples were analysed for the three locations and coagulants during the laboratory experiment.

4.2.2 Coagulant Selection and Preparation

In this study, ferric sulphate (FS), aluminium sulphate (ALS), and polyaluminium chloride (PACL) were selected for further evaluation due to their demonstrated effectiveness in phosphorus removal, as observed in the preceding chapter. To ensure consistency in application, these coagulants were prepared according to the manufacturer's guidelines. Ferric sulphate heptahydrate (99.5% analytical grade) and aluminium sulphate octadecahydrate ($\geq 97\%$ purity) were obtained from Fisher

Scientific and Sigma-Aldrich, respectively, while PACL was supplied by Airedale Chemical Company Limited.

4.2.3 Coagulation–Flocculation Experiment

A standardised coagulation-flocculation approach was utilised to determine the optimal conditions and dosages for phosphorus removal. Jar tests were performed using a Phipps & Bird Six-Paddle Stirrer to ensure controlled mixing. Each experiment commenced with a rapid mixing stage at 200 rpm for 2 minutes, allowing uniform dispersion of the coagulant within the wastewater matrix. This was immediately followed by adding coagulant at doses of 5, 10, 15, 30, and 40 mg/L, and two-point dosing was carried out with doses 16, 17, 18, 20 and 25 mg/L from the initial 15 mg/L dosage. A slow mixing phase at 30 rpm was maintained for 15 minutes to promote floc formation, after which the flocs were left to settle under gravity for 30 minutes.

4.2.4 Assessment of Floc Formation and Breakage

Floc formation, stability, and regrowth potential were further analysed on selected dosages that achieved the target residual TP using a jar tester equipped with a particle size analyser. These experiments were conducted in cylindrical 2L jars, each containing 1L of crude, PST and final effluent from Philipshill STW. A Malvern Mastersizer laser diffraction instrument was used to continuously monitor and assess floc size distribution throughout the coagulation-flocculation process.

The experimental procedure began with a rapid mixing stage at 200 rpm for 2 minutes to ensure even coagulant dispersion, followed by a slow mixing phase at 30 rpm for 15 minutes to promote floc formation. To evaluate floc strength, the suspension was exposed to high shear stress at 200 rpm for 15 minutes before reducing the speed back to 30 rpm for another 15 minutes to assess floc regrowth potential. Floc size measurements were recorded every minute using a peristaltic pump with a flow rate of 1.5 L/hr and 5 mm internal diameter tubing, with real-time data processing via dedicated software.

Floc Size and Fractal Dimension

Key floc characteristics were assessed during the coagulation–flocculation experiments using a laser diffraction instrument (Malvern Mastersizer 2000). Three main parameters were derived: floc strength factor (FSF), floc regrowth factor (FRF),

and fractal dimension (Df), all of which provide insight into the structural integrity and behaviour of flocs under shear conditions.

Floc Strength Factor (FSF) was calculated to evaluate the resistance of flocs to breakage, using the equation:

$$FSF = \frac{d2}{d1} \times 100 \quad (4-1)$$

where d1 is the average floc size before the application of shear (end of slow mixing), and d2 is the floc size after breakage (following high shear mixing)(Jarvis *et al.*, 2005; Bratby, 2016).

During the tests, particle size measurements were recorded at three key stages: after slow mixing (growth), after high shear mixing (breakage), and after subsequent low shear mixing (regrowth). These measurements were obtained using the Mastersizer, which determines particle volume distributions based on scattered light intensity. From this data, the Floc Regrowth Factor (FRF) was calculated using:

$$FRF = \frac{d3-d2}{d1-d2} \times 100 \quad (4-2)$$

Where d1 is the floc size before breakage, d2 is the floc size after breakage, and d3 is the floc size after regrowth. This parameter quantifies the ability of flocs to recover following shear-induced breakage (Jarvis *et al.*, 2005; Bratby, 2016).

The floc fractal dimension (Df) was used to describe the internal structure and compactness of flocs. It was calculated through the mass length scaling relationship derived from the size distribution data generated by the Mastersizer. The relationship is expressed as:

$$M \propto L^{Df} \quad (4-3)$$

where M represents the mass of the floc, L is the characteristic length scale (e.g., diameter), and Df is the fractal dimension. A log–log plot of floc mass versus floc size yields a slope corresponding to Df. Higher Df values indicate more compact and dense flocs, while lower values represent looser and more porous aggregates (Waite *et al.*, 2001; Wu *et al.*, 2002; Jarvis *et al.*, 2008). By combining FSF, FRF, and Df, the methodology provides a complete assessment of floc formation dynamics and

resilience, enhancing our understanding of how different coagulants influence floc structure and performance during phosphorus removal.

Each experiment was conducted in triplicate to ensure data reliability and reproducibility.

4.2.5 Fractionation of Phosphorus Procedure

Phosphorus in wastewater was classified into reactive, unreactive, and condensed fractions, and its fractionation involved a series of sequential steps, including filtration, digestion, complexation, measurement, and calculation with the selected set of conditions.

For filtration, samples were processed using a vacuum-assisted Buckner filtration system and sequentially passed through 0.45 µm and 0.025 µm filters to separate different phosphorus fractions based on particle size.

Chemical treatments were applied during digestion to convert various phosphorus species into molybdenum-reactive phosphorus for quantification. Molybdenum-reactive phosphorus required no digestion, while acid-hydrolysable phosphorus (AHP) was digested using sulfuric acid, and total phosphorus (TP) was oxidised using persulfate at elevated temperatures.

Following digestion, molybdate salts were introduced into the samples to facilitate complexation, forming a blue molybdenum-phosphate complex. Antimony tartrate was added as a catalyst to accelerate the reaction, and the mixture was left to develop for 60-90 minutes to ensure complete colour formation. Absorbance was measured using a spectrophotometer, with appropriate dilutions performed for samples exceeding the calibrated range. The measured concentrations were subsequently adjusted to account for the dilution factor.

The unreactive and condensed phosphorus fractions were then derived mathematically by subtracting the measured reactive and hydrolysable phosphorus concentrations from the total phosphorus values:

$$\text{Unreactive Phosphorus (UP)} = \text{TP} - \text{AHP}$$

$$\text{Condensed Phosphorus (CP)} = \text{AHP} - \text{RP}$$

$$>0.45 \mu\text{m fraction} = \text{U-fraction} - \text{f}(0.45) \text{ fraction}$$

$0.45\text{--}0.025\ \mu\text{m fraction} = f(0.45)\text{ fraction} - f(0.025)\text{ fraction}.$

4.2.6 Two-Point Dosing Strategy

For the two-point dosing (2PD) experiments, the coagulation–flocculation procedure was modified to divide the total coagulant dose into two sequential applications. Initially, ferric sulphate was dosed at 15 mg Fe/L and mixed rapidly at 200 rpm for 2 minutes, followed by slow mixing at 30 rpm for 15 minutes to facilitate floc formation. The suspension was then allowed to settle under gravity for 30 minutes.

After settling, the supernatant was carefully decanted and subjected to a second coagulation cycle. Additional ferric sulphate was introduced into the supernatant at doses of 1, 2, 3, 5, 10, and 15 mg Fe/L, resulting in total cumulative doses of 16, 17, 18, 20, and 30 mg Fe/L, respectively. This second treatment followed the same coagulation protocol: rapid mixing (200 rpm, 2 minutes), slow mixing (30 rpm, 15 minutes), and settling (30 minutes).

Following the second settling period, the treated supernatant was collected for analysis. All two-point dosing tests were conducted in triplicate to ensure accuracy and reproducibility.

4.2.7 Analytical Methods

A range of analytical techniques was employed to ensure precise measurement of wastewater parameters. pH levels were monitored using a Jenway 4330 pH meter, while metal concentrations were quantified through Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) using a Nexion 350D system, shown in Table D-1.

Chemical oxygen demand (COD), total phosphorus (TP), and orthophosphate concentrations were measured using Merck cell test kits, with spectrophotometric analysis performed using a Merck Spectroquant NOVA 60 system. Alkalinity was assessed with a Hanna Instruments alkalinity checker, and total suspended solids (TSS) and turbidity were determined using standardised filtration techniques and a Hach 2100Q turbidity meter. All analyses were conducted in triplicate to ensure the accuracy and reliability of the results.

4.3 Results

4.3.1 Total Phosphorus

In Figure 4-2(a-c), the general trend shows a reduction in TP concentrations across all coagulant dosages and locations, achieving below the target level of 0.3 mg/L. For the crude location in the wastewater using FS as a coagulant, the target TP removal of 0.3 mg/L was achieved at dosages 30 and 40 mg/L, where the TP values are 0.18 and 0.2 mg/L, respectively. After the PST, the target was also achieved at dosages 30 and 40 mg/L, where the TP value is 0.13 and 0.11 mg/L, respectively. The FE achieved the target level at a low dosage of 5 mg/L and maintained the low residual for higher doses of 10, 15 and 30 mg/L, where the TP values are 0.13, 0.06, 0.06, and 0.15 mg/L, respectively. The improvement in TP value for these dosages is due to the existing backend dosage. However, the 40 mg/L dosages in the FE did not meet the target.

In Figure 4-2b, ALS did not meet the target TP removal in the crude for all dosages tested. The analysis shows using ALS in the PST achieved the TP removal target for all dosages above 5 mg/L. However, in the FE using ALS, the target TP was met at all dosages applied in this study. Similarly, with PACL (Figure 4-2c), it was observed that crude did not achieve the target TP level at all the dosages (5-40 mg/L), while the target TP levels were achieved in the PST location at dosages 10 to 40 mg/L where TP residual was 0.29, 0.26, 0.15 and 0.22 mg/L, respectively. In the FE, the target TP levels were achieved at a dosage of 5 mg/L with a TP residual of 0.13 mg/L, and even lower TP levels of 0.09 and 0.07 mg/L were achieved at dosages of 10 and 15 mg/L, respectively. However, at higher dosages 30 and 40 mg/L, the target TP level was not achieved, where the TP level went back up to 0.51 and 0.56 mg/L, respectively.

There is no significant difference between the analysed results of TP and Ortho-P because Ortho-P forms the vast majority of the TP (Figure 4-2d, e and f). Indeed, the ortho-P/TP ratio (Figure D-1(g, h and i)) remained stable for all doses tested in all locations with FS and ALS. However, more variations were observed with PACL, but with no clear trend.

Two-point dosing (2PD) applied to the crude wastewater achieved residual TP concentrations comparable to those obtained with single-point dosing but with a significantly reduced coagulant dose. Specifically, while a single dosing point required 30 mg/L to meet the target effluent quality, the same residual TP efficiency was achieved with just 16–17 mg/L when the dose was split across two points (Figure 4-1). The additional dosing point likely enhanced FS's distribution and reaction efficiency within the high organic and particulate matrix of crude wastewater, leading to TP levels comparable to those observed at PST and FE in the single dosing point. This suggests that a two-point dosing strategy optimises coagulant utilisation, potentially reducing the overall chemical requirement to achieve the same phosphorus removal efficiency. Therefore, strategically splitting the coagulant addition makes the coagulation process more effective, minimising excess chemical usage while maintaining stringent effluent quality standards.

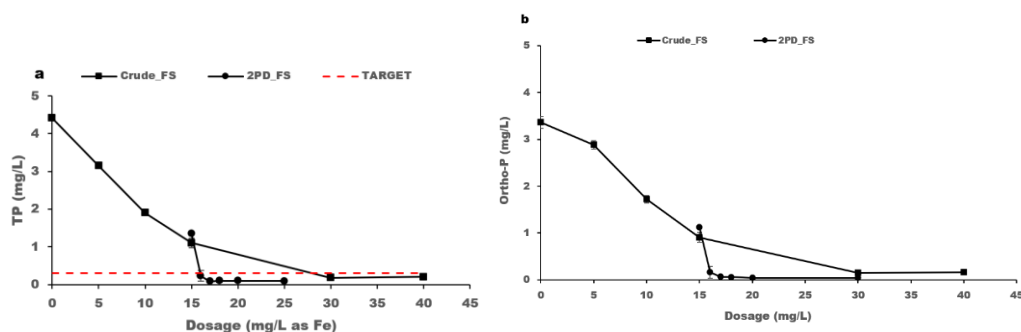


Figure 4-1: TP (a) and Ortho-P (b) removal from crude wastewater samples with 2PD treated with FS, achieved TP target limits at a minimised dosage

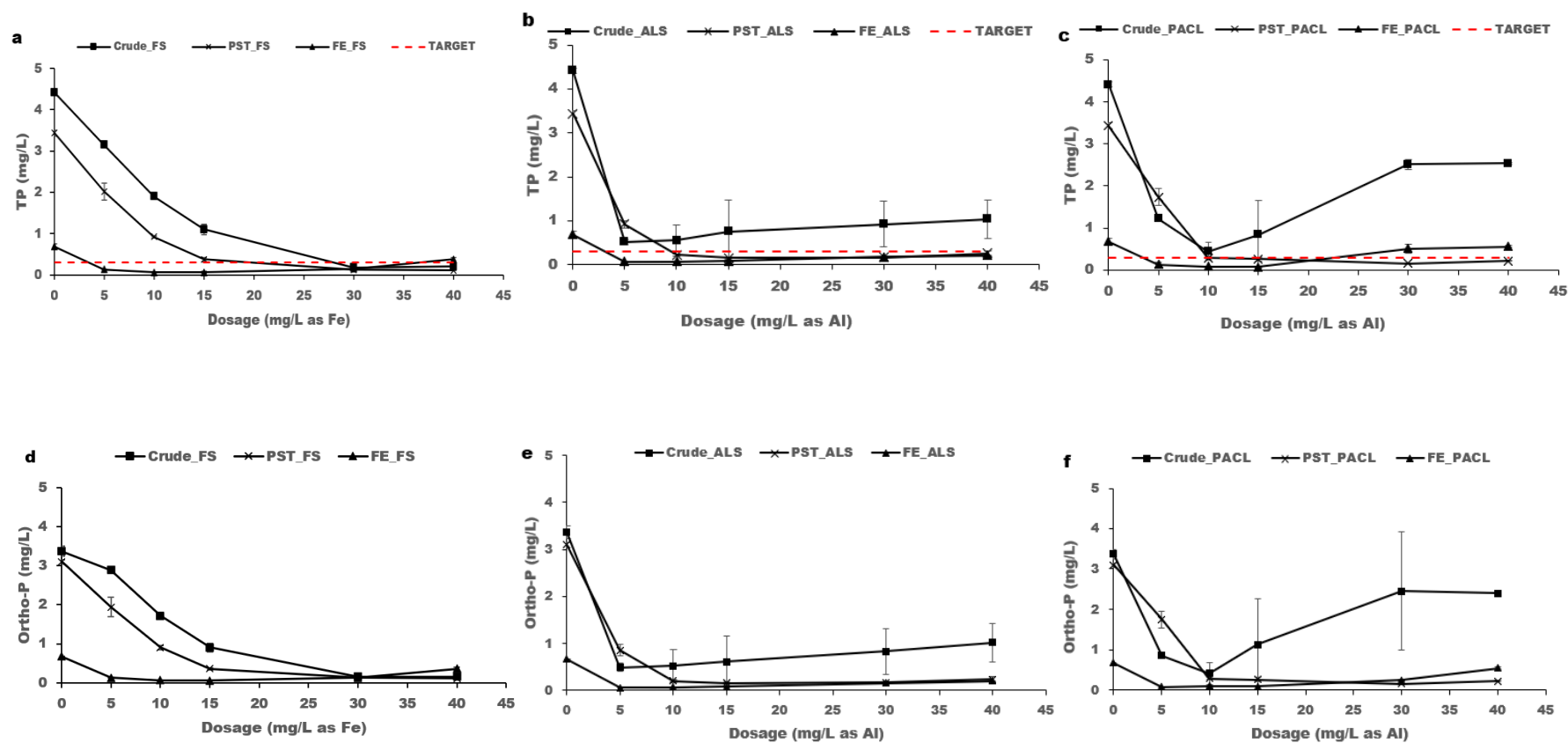


Figure 4-2: Total Phosphorus residuals treated with (a) FS, (b) ALS and (c) PACL and Ortho-P with (d) FS, (e) ALS and (f) PACL in the wastewater samples from the three locations (Crude, PST, and FE)

4.3.2 TP Fractionation

The fractionation shows that all three sources of water contained mainly soluble reactive phosphorus, which was significantly reduced following coagulation by all 3 coagulants (Figure 4-3a). The presence of phosphorus-related colloids (0.45-0.025 μm) was minimal across all locations (Figure 4-3b).

The particulate fraction ($>0.45 \mu\text{m}$) exhibited a distinct distribution across locations (Figure 4-3c). In the crude wastewater and final effluent, the fraction was a mixture of different phosphorus forms, whereas in the PST effluent, only acid-hydrolysable phosphorus (AHP) remained. In all cases, particulates were effectively removed, either through incorporation into the flocs formed during coagulation or by direct settling. Interestingly, with mainly reactive phosphorus remaining.

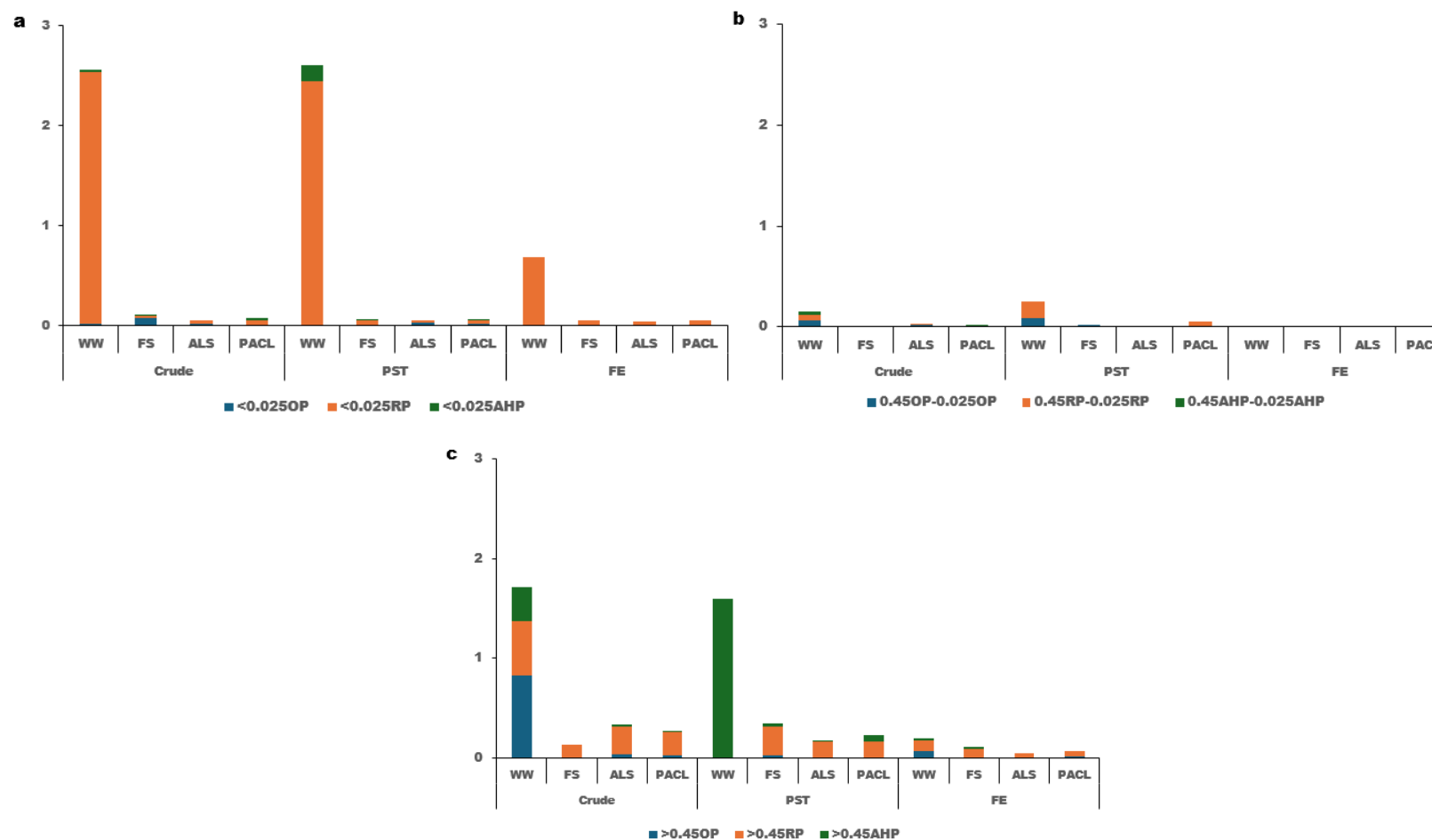


Figure 4-3: Phosphorus fractionation of wastewater samples from three locations (Crude, PST, and FE) treated with FS, ALS, and PACL, categorised by size fractions-(a) <0.025 μ m, (b) 0.45-0.025 μ m, and (c) >0.45 μ m

4.3.3 pH and Alkalinity

The pH for all the coagulants demonstrates a general decline with increased dosage. For FS (Figure 4-4a), the pH reduction was most obvious in the FE, where it dropped from approximately 7.0 to below 4.0 at dosages above 30 mg/L. A similar but less dramatic trend was observed in the PST and Crude, with pH values stabilised around 5.7 at the same dosage. For ALS (Figure 4-4b), the pH decreased steadily across all locations, with the final pH ranging between 4.0 and 5.0 at dosages of 30-40 mg/L. The reduction was less steep than with FS but still sufficient to significantly alter the chemical speciation of metals. As indicated by the speciation diagrams (Figure 2-1), the varying pH levels observed during dosing would have influenced the hydrolysis products of the metal coagulants, potentially shifting from monomeric to polymeric species. These species, such as $\text{Al}(\text{OH})^{2+}$ and $\text{Al}_{13}\text{O}_4(\text{OH})_{24}^{7+}$ in the case of aluminium-based coagulants, have different charge densities and affinities for phosphate binding, which may explain the differences in phosphorus removal efficiency and floc characteristics at different dosing points. PACL (Figure 4-4c) exhibited the most stable pH, consistently above 4.5 to 5.0 across all locations, even at higher dosages.

The initial alkalinity levels varied across the different wastewater locations, with Crude (179 ppm), PST effluent (204 ppm), and FE (101 ppm) exhibiting distinct starting values (Figure 4-4d, e, f). Interestingly, the PST effluent displayed a higher initial alkalinity than the crude wastewater, which is unexpected and may be attributed to site-specific factors or potential variations in influent composition over time.

As coagulant dosage increased, alkalinity consistently decreased across all locations, reflecting the consumption of carbonate and bicarbonate species during coagulant hydrolysis. For FS (Figure 4-4d), alkalinity reductions were most pronounced at the FE stage, where it dropped from an initial value of 101 ppm to zero at dosages of 30 mg/L and above. In contrast, Crude and PST effluents gradually declined, stabilising at approximately 55 ppm at higher dosages.

ALS (Figure 4-4e) followed a similar trend, with alkalinity reductions more gradual than FS but still significant, particularly in the FE. PACL (Figure 4-4f) has the least reduction in alkalinity, with residual values remaining above 50 ppm across all locations and dosages. The higher alkalinity consumption for FS aligns with its stronger acidic nature and higher hydrolysis demand than ALS and PACL.

Notably, the 2PD maintained comparable pH levels in the crude when compared with an equivalent total single-dose application, indicating that the distribution of coagulant across 2PD did not exacerbate acidification.

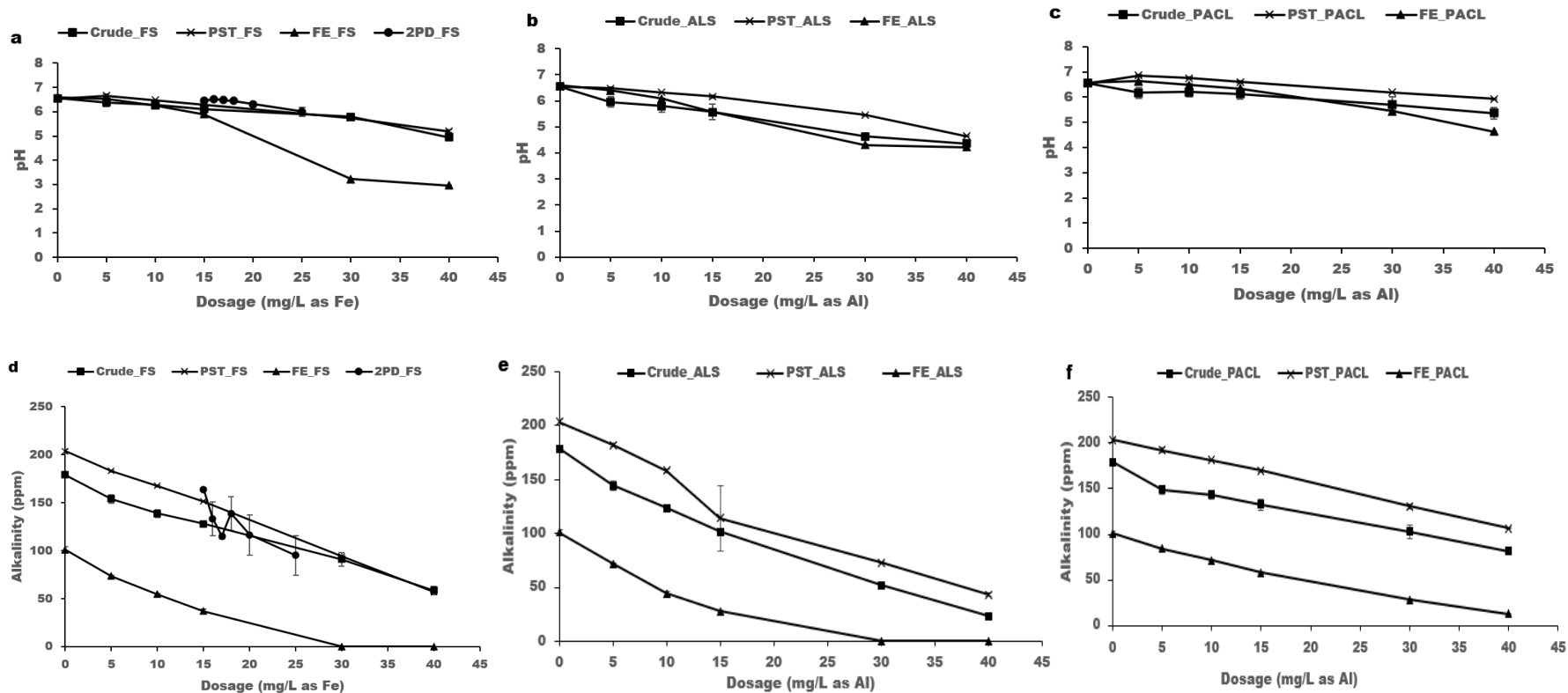


Figure 4-4: Changes in pH (a-c) and alkalinity (d-f) of wastewater samples treated with FS (a, d), ALS (b, e), and PACL (c, f) at varying dosages from three sampling location-crude, PST, and FE

4.3.4 Turbidity and TSS

For the aluminium-based coagulants, turbidity showed a sharp initial decrease at the lowest tested dosage, after which effluent turbidity remained consistently low across all higher dosages (Figure 4-5b and c), in particular in the crude and PST effluent. However, PACL-treated crude wastewater retained higher turbidity levels (~20 NTU) even at elevated dosages, suggesting incomplete particulate removal in this matrix. In contrast, FS showed a more gradual turbidity reduction between 5 and 15 mg Fe/L, after which turbidity levels stabilised at consistently low values (<10 NTU), indicating that effective particle aggregation and removal occurred within this dosage range.

A notable observation across all treatment locations was the increase in turbidity and suspended solids (SS) at the highest coagulant dosages, particularly at 30 mg/L. While higher doses promoted particle formation, these newly formed solids were not always efficiently removed, especially in the FE, likely due to floc instability and impaired settling. This highlights the importance of optimising dosage to prevent unintended increases in effluent turbidity, which could compromise discharge quality. Among the coagulants, FS demonstrated the most consistent turbidity reduction, achieving levels below 7 NTU at dosages above 15 mg/L across all sampling points, particularly in the crude and PST effluents, where initial turbidity was highest. ALS also provided substantial reductions, stabilising around 10 NTU within the 15–30 mg/L range, though it was slightly less effective than FS. PACL performed well at lower dosages (5–15 mg/L), especially in the PST effluent and FE, but showed higher residual turbidity in the crude wastewater relative to FS and ALS. These trends reinforce the need for careful dosage selection to balance floc formation and stability for effective solids removal.

In Figure 4-5d, e, f, TSS removal was observed at coagulant dosages above 10–15 mg/L, particularly with FS, demonstrating the ability to aggregate and settle particulate matter across all sampling locations. Notably, the initial TSS concentrations varied significantly between the locations, approximately 180 mg/L in crude wastewater, 80 mg/L in PST effluent, and 22 mg/L in the FE.

Despite these large differences in initial particulate loads, FS achieved similar low residual TSS concentrations at optimal doses across all locations. This highlights not only FS's robust performance but also the effectiveness of both direct settling and incorporation of solids within flocs, allowing for efficient removal even under high solids load. ALS and PACL showed comparable performance in the PST and FE, achieving residual TSS concentrations of approximately 15-20 mg/L at 10-15mg/L dosages. However, in the crude wastewater, both coagulants were less effective. With ALS, a TSS concentration of around 50 mg/L was recorded at a dose of 30 mg/L, while PACL resulted in a slightly higher residual of 59 mg/L at the same dosage. Notably, PACL performance improved at a 40 mg/L dose, where TSS levels dropped, suggesting enhanced flocculation and settling at higher concentrations. The 2PD strategy further enhanced TSS removal in the crude and highlighted the advantages of targeted dose strategies in high-strength wastewater.

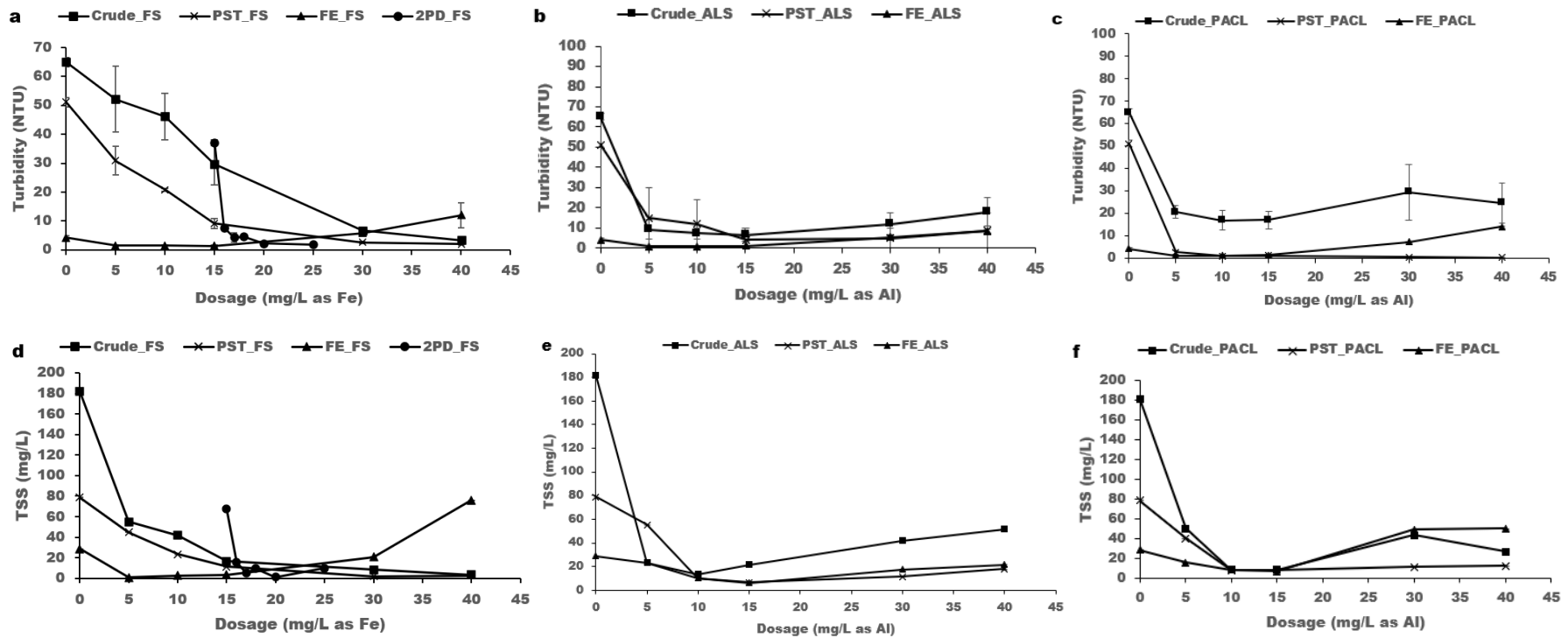


Figure 4-5: Turbidity (a-c) and TSS (d-f) removal from wastewater samples treated with FS (a, d), ALS (b, e), and PACL (c, f) at varying dosages from three sampling locations-crude, PST, and FE

4.3.5 Chemical Oxygen Demand

In the crude samples, a more pronounced COD reduction was observed at lower dosages, with minimal additional improvement at higher doses for all chemicals tested. To illustrate, with FS in the crude wastewater, COD decreased from approximately 284 mg/L to below 150 mg/L at the lowest tested dosage, with additional reductions observed as the dosage increases up to 15 mg/L, with a COD residual achieved of 123 mg/L. Beyond this point, COD levels remain relatively stable. A similar trend is observed for ALS and PACL in Figure 4-6b, c, where the most significant COD reduction occurs at the lowest tested dosage, after which further increases in coagulant dosage do not result in notable additional removal. Ultimately, at higher dosages, COD removal by all three coagulants stabilised within a similar range (100-150 mg/L), indicating that beyond a certain threshold, coagulation contributes minimally to further organic matter removal. The PST samples exhibit relatively minor COD reductions, stabilising at approximately 80-100 mg/L for all coagulants from an initial concentration of about 200 mg/L. The FE samples show limited improvements as their initial COD concentration was already low at about 15 mg/L, and with the residuals generally between 4-10 mg/L for FS and ALS, while PACL demonstrates a slight increase at dosages above 30 mg/L.

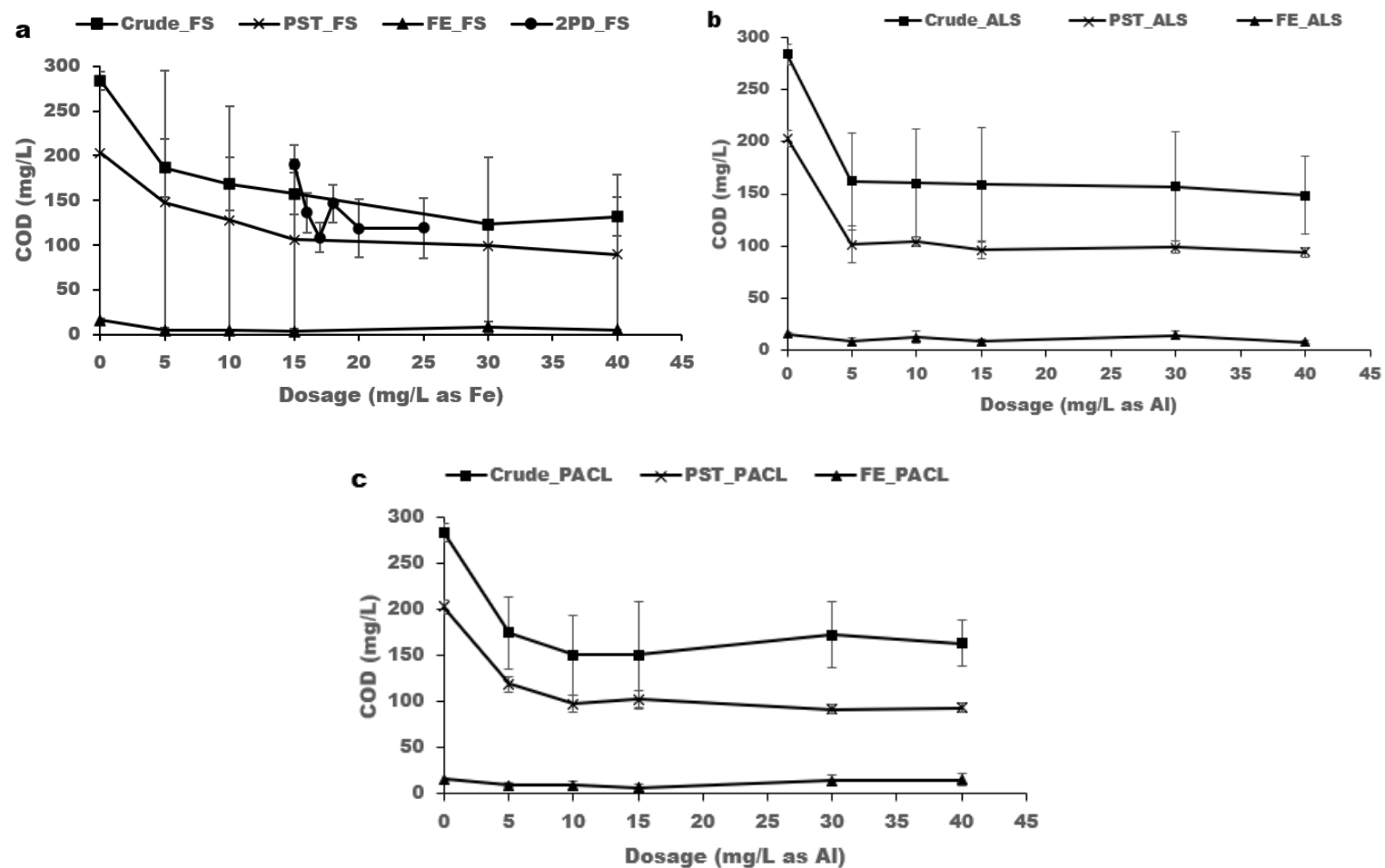


Figure 4-6: COD removal at varying coagulant dosages for wastewater samples treated with FS (a), ALS (b), and PACL (c) from three sampling locations-crude, PST, and FE

4.3.6 Floc formation

The floc formation results in Figure 4-7a-c and Table 4-2 for FS, ALS, and PACL coagulants across crude, PST, and FE samples exhibit distinct trends that indicate varied performance under different wastewater conditions. For FS, the FE sample demonstrated the largest initial floc size, which reached approximately 250 μm during the initial 15-minute growth phase at 30 rpm. This peak was followed by a sharp reduction to around 100 μm during the 15-minute break phase at 200 rpm. Regrowth during the final 15-minute phase at 30 rpm reached a plateau of approximately 120 μm , with a floc regrowth of 15.4 and a floc strength factor of 39.7. Conversely, FS performance in Crude and PST samples showed consistently smaller flocs, with initial sizes peaking at 186 μm and 152 μm , respectively, and regrowth values of 24 for Crude and 10.4 for PST. The fractal dimensions (FD) for FS flocs were highest in the PST effluent (2.7), which indicates a denser floc structure compared to FE (2.61) and crude (2.49).

The initial floc sizes for ALS were generally smaller than FS, with crude samples peaking at 145 μm during the growth phase. The break and regrowth phases were 64 μm and 81 μm , respectively, with floc regrowth of 21. PST samples showed similar trends, with smaller floc regrowth of 9.9 and a peak FD of 2.48. ALS demonstrated its highest FD in the FE sample (2.53), although floc regrowth was limited to 7.5, which may suggest the coagulant's suitability for secondary treatment stages rather than crude wastewater.

PACL exhibited better performance in terms of floc regrowth potential, particularly in PST samples where regrowth reached 30, the highest among the three coagulants. Initial floc sizes in Crude samples were smaller than FS, peaking at approximately 139 μm during growth. The break phase reduced floc sizes to 82 μm , but the regrowth phase reached 84 μm , which indicates a comparatively weaker performance in crude wastewater. In FE samples, PACL formed smaller but more stable flocs, with a regrowth of 11.1 and an FD of 2.59.

Table 4-2: Floc properties (strength, regrowth, and fractal dimension) of wastewater samples treated with FS, ALS, and PACL at three sampling locations (Crude, PST, and FE)

Location	Floc strength	Floc Re-growth	FD
Crude-FS	51.3	24	2.49
Crude-ALS	43.9	21	5.2
Crude-PACL	59.4	3	2.35
PST-FS	48.7	10.4	2.7
PST-ALS	50.2	9.9	2.48
PST-PACL	52.3	30	2.48
FE-FS	39.7	15.4	2.61
FE-ALS	82.1	7.5	2.53
FE-PACL	65.5	11.1	2.59

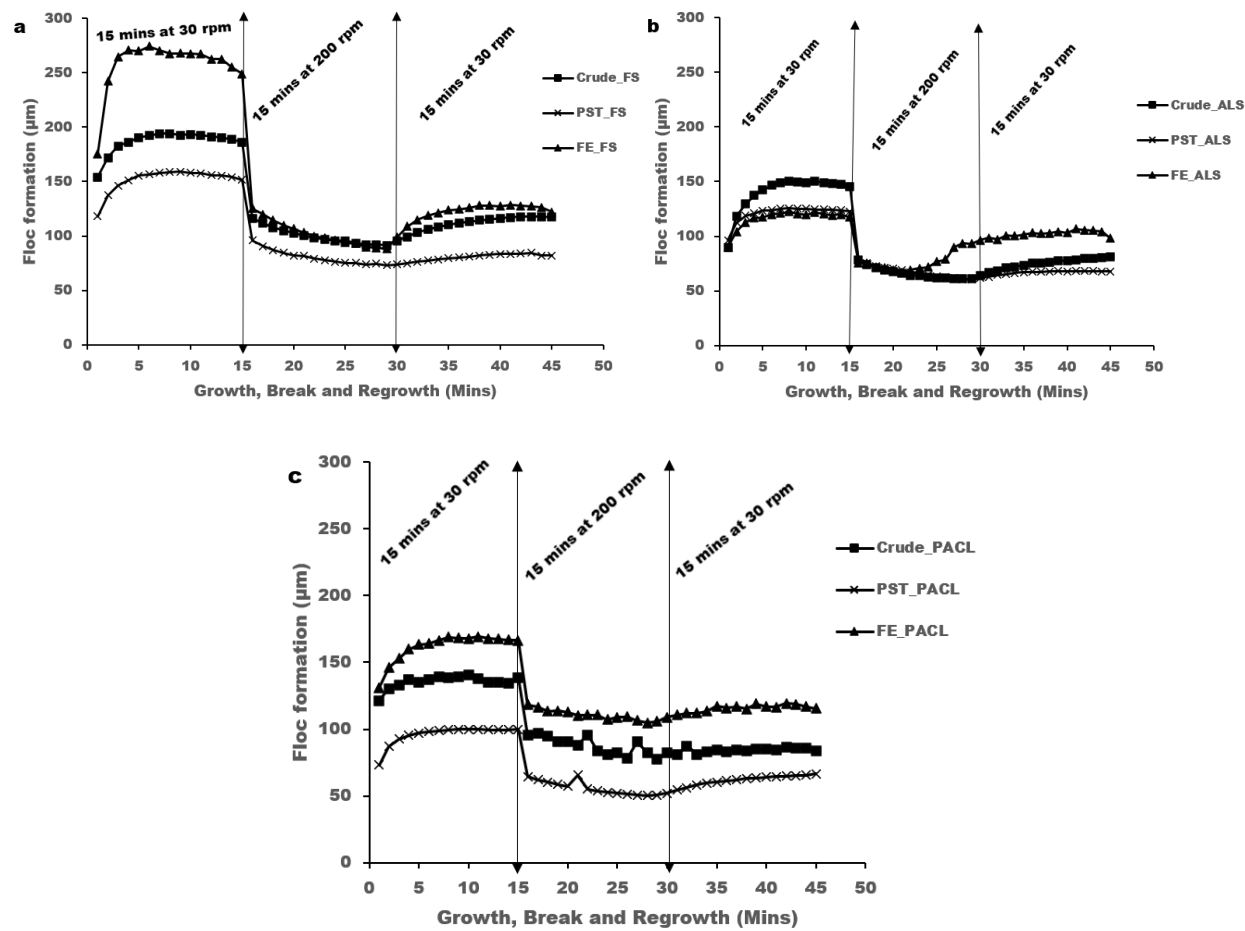


Figure 4-7: Floc formation over time under growth, break, and regrowth conditions for wastewater samples treated with FS (a), ALS (b), and PACL (c) at three sampling locations-crude, PST, and FE

4.3.7 Particle size distribution

The particle size distribution results reveal significant variations in floc formation based on coagulant type, dosage, and sampling location (Figure 4-8). In FE FS samples, the peak floc size increased notably from 10 to 40 minutes, with a gradual broadening of the particle size distribution curve, which suggests a greater range of floc sizes. Similar trends are observed in PST and Crude samples, although with smaller maximum particle sizes compared to FE FS, which corroborate with the fractal dimension (FD) data in Table 1, where FS flocs exhibited a higher FD (2.61) in FE samples and indicate more robust and dense floc structures.

Subsequently, ALS displayed a narrower particle size distribution across all dosages and treatment stages, which indicates uniform floc formation. However, its effectiveness appears to decrease at higher dosages in PST and Crude samples, as reflected by the decline in maximum particle size beyond 25 mg Al/L. This trend aligns with the FD values (5.2 for crude and 2.48 for PST) in Table 4-2, which suggests a decrease in floc density and structural integrity as the particulate-to-coagulant ratio decreases.

Polyaluminum chloride showed the most variability in particle size distribution across the stages. In crude samples, the particle sizes were comparable to FS, but PACL produced broader distributions, with smaller flocs dominated in the PST and FE samples. The FD for PACL flocs was lowest in crude samples (2.35), indicating fewer compact flocs, while the regrowth factor was highest (30) in PST samples Table 1, and suggests a higher propensity for structural recovery after shear forces.

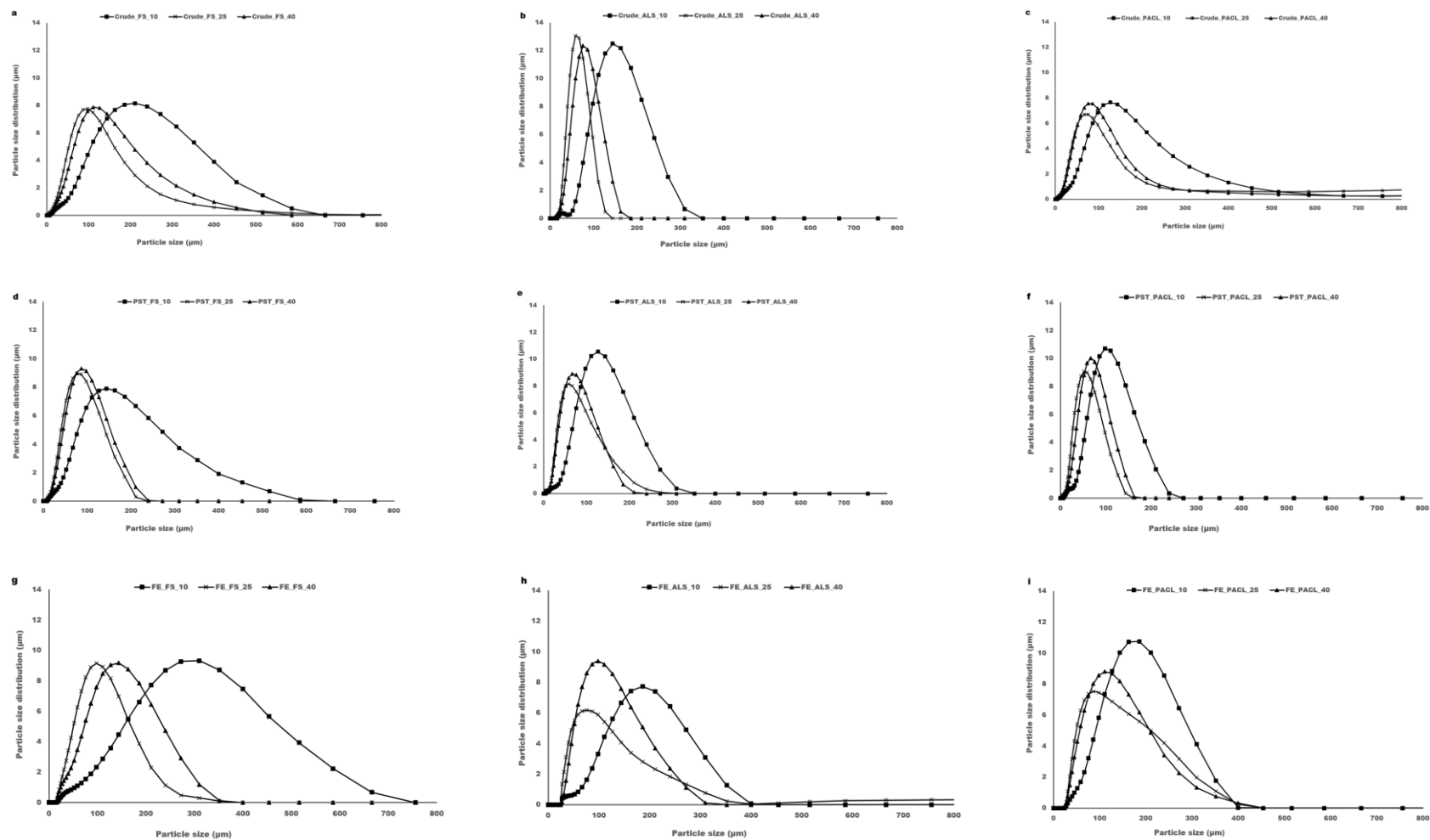


Figure 4-8: Particle size distribution of wastewater samples treated with FS, ALS, and PACL at varying dosages (10, 25, and 40 mg/L) from three locations in the treatment train-Crude (a: FS, b: ALS, c: PACL), PST (d: FS, e: ALS, f: PACL), and FE (g: FS, h: ALS, i: PACL)

4.4 Discussion

The effectiveness of P removal using chemical coagulants such as FS, ALS, and PACL were strongly influenced by the sampling location, which reflects varying wastewater matrix characteristics such as organic matter, suspended solids (SS), pH, and buffering capacity. Across all coagulants, the trend in removal efficiency followed the order: Crude < PST < FE (Figure 4-2a-f).

This improved performance at PST and FE can be attributed to lower concentrations of organic matter and SS due to upstream sedimentation and biological treatment (and the existing phosphorus removal before the final effluent discharge). Such conditions reduce competition for coagulant binding sites and minimise organic interference, thus promoting favourable metal-phosphate complexation and stable floc formation. Despite its higher SS (180 mg/L) and organic content, Crude wastewater maintained relatively stable pH profiles due to its high buffering capacity (Figure 4-4a-c). In contrast, PST (80 mg/L SS) and FE (22 mg/L SS) exhibited greater pH reductions at higher doses of ALS and PACL, leading to over-acidification and reduced phosphate removal (Figure 4-4b-c).

Among the coagulants, FS consistently achieved TP levels below the 0.3 mg/L target across all locations (Figure 4-2a), indicating strong performance even in challenging matrices. This can be attributed to FS's rapid hydrolysis, forming $\text{Fe}(\text{OH})_3$ and FePO_4 precipitates via charge neutralisation and sweep coagulation. However, at high dosages, particularly in FE, pH dropped below 4.5, coinciding with reduced TP removal likely due to increased solubility of ferric-phosphate precipitates at acidic pH (Zhu and Ma, 2020). ALS and PACL both achieved the TP target at PST and FE but failed to do so in Crude, even at 40 mg/L (Figure 4-2b-c), reflecting limitations under high organic and particulate conditions.

pH variations played a critical role in coagulant performance. ALS performed optimally within the pH range of 5.5–7.0, where the formation of $\text{Al}(\text{OH})_3$ flocs facilitates efficient phosphate removal through sweep flocculation, and below this

range, hydrolysis is compromised. A lower pH, Al^{3+} remains in solution, reducing phosphate precipitation, while at higher pH values, soluble $\text{Al}(\text{OH})_4^-$ dominates, limiting coagulation effectiveness (Figure 2-1). In the Crude, although pH remained relatively stable (5.0-6.0), the high organic matter likely interfered with hydrolysis and promoted competitive complexation, as supported by the increase in the Ortho-P/TP ratio at higher ALS dosages. PACL, due to its pre-polymerised structure, showed greater stability in pH, maintaining pH levels between 5.4 and 6.2 at PST and FE. However, in the Crude, its effectiveness was reduced, likely due to interactions with non-phosphorus organic ligands (Niu *et al.*, 2013; He *et al.*, 2021).

Turbidity and TSS trends mirrored P removal outcomes: For Crude, high solids and organics led to more variable turbidity and TSS reductions across all coagulants (Figure 4-5a-c). FS achieved the most consistent reductions, with turbidity below 7 NTU and TSS of 60–70 mg/L at ≥ 15 mg/L dosage. ALS and PACL showed higher TSS residuals in Crude (ALS: 50 mg/L TSS at 30 mg/L; PACL: 59 mg/L at 30 mg/L, dropping at 40 mg/L), indicating reduced aggregation efficiency. In PST and FE, with lower initial SS, all coagulants achieved similar residuals (~20–30 mg/L TSS), highlighting their ability to remove particulate matter effectively when less interference is present (Cui *et al.*, 2020).

Particle size distribution data provided insight into floc formation mechanisms. Although Crude contained more particulate matter, larger flocs formed in FE, especially with FS, suggesting that lower organic interference and more favourable pH conditions in FE promoted stable aggregation. In Crude, the dense particulate environment may have increased collision frequency, causing floc breakage and size limitations. FS produced the largest, most stable flocs across locations, though susceptible to fragmentation under shear. PACL formed broader size distributions, indicating interaction with both colloidal and dissolved particles, but its flocs were more porous. ALS yielded denser, compact flocs but with limited regrowth potential.

These findings align with Jarvis *et al.* (2005), who reported that, although in drinking water application, larger flocs formed in low-DOC systems. In this study,

FS-treated samples achieved floc sizes of 186–250 μm , smaller than those seen in drinking water, reflecting the impact of higher organic loads and more complex wastewater matrices. Additionally, fractal dimension ($\text{FD} > 2.5$) analysis of FS flocs confirmed their dense structure but vulnerability to shear-induced fragmentation.

The effectiveness of the two-point dosing (2PD) strategy, particularly in Crude with FS, highlighted operational benefits. While single-point dosing required 30 mg/L to meet the TP target, 2PD achieved the same performance with 16–17 mg/L (Figure 4-1), indicating improved reagent distribution, enhanced target compound interaction, and reduced chemical consumption (Kulandaivelu *et al.*, 2020). This supports the feasibility of adopting spatially strategic dosing in complex matrices.

The phosphorus fractionation (Figure 4-3) showed that all coagulants removed RP effectively across locations, with improved removal of colloidal and acid-hydrolysable fractions at PST and FE. FS demonstrated strong performance for both reactive and non-reactive forms, while ALS and PACL were less effective in Crude, likely due to interference from organic matter and particulate loads.

4.5 Conclusion

This study systematically evaluated the impact of coagulant selection and dosing location on phosphorus removal efficiency in municipal wastewater treatment. The results demonstrate that coagulant type, pH stability, and the presence of organic and particulate matter significantly influence phosphorus removal, floc formation, and overall treatment performance.

All coagulants demonstrated effective removal of phosphorus across all dosing locations, particularly at PST and FE, where TP concentrations were below the target of 0.3 mg/L at dosages of 5–30 mg/L. Its strong hydrolysis reactions facilitated the formation of dense, stable ferric-phosphate complexes, enhancing phosphorus precipitation and removal. However, excessive FS dosing in FE resulted in pH declines below 5.0, potentially leading to phosphorus re-dissolution. ALS demonstrated effective phosphorus removal at PST and FE but

was less efficient in Crude wastewater, likely due to organic matter interference with aluminium-phosphate complex formation. PACL, while effective at PST and FE, exhibited variability in Crude wastewater, where high organic loads limited its hydrolysis efficiency and phosphorus binding capacity. These findings highlight the importance of selecting the optimal coagulant and dosing location to maximise treatment efficiency while minimising unintended consequences such as excess metal discharge, pH destabilisation, or coagulant wastage.

A key contribution of this research is the demonstration of two-point dosing (2PD_FS) as an effective strategy for phosphorus removal in high-strength wastewater. The results indicate that splitting the FS dosage in Crude significantly improved phosphorus removal, reducing residual TP concentrations to levels comparable to single-point dosing at PST and FE. This finding highlights the potential of adaptive dosing strategies to optimise coagulant utilisation, reduce chemical consumption, and enhance treatment performance. Such strategies offer promising cost-saving and sustainability benefits for wastewater treatment plants aiming to meet increasingly stringent phosphorus discharge limits.

These findings directly affect the design and optimisation of municipal wastewater treatment processes. Implementing coagulant-specific dosing strategies and optimising treatment stages can significantly enhance phosphorus removal efficiency while maintaining cost-effectiveness and regulatory compliance. Given the increasing pressure on wastewater treatment plants to achieve stringent phosphorus limits, this study provides practical guidance on coagulant selection, dosing strategies, and process control measures to balance treatment efficacy with environmental sustainability.

However, certain constraints of this study should be acknowledged. Firstly, the experiments were conducted under controlled laboratory conditions using batch jar tests, which may not fully replicate the complex hydrodynamics and variable loading rates of full-scale treatment plants. Secondly, the study used samples from a single municipal site in Scotland, and while the results provide valuable insights, they may not capture the full diversity of wastewater characteristics found at other locations or in different seasons. Thirdly, although the two-point

dosing strategy demonstrated promise at lab scale, its operational feasibility and optimisation under real plant conditions, where mixing efficiency, retention times, and chemical dosing systems differ, require further investigation. Finally, the focus was more on chemical phosphorus removal; potential interactions with biological processes (e.g., in enhanced biological phosphorus removal systems) and the impacts on downstream sludge handling were not assessed.

4.6 References

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Appendix D

Table D-1: ICP-MS analysis of metal concentrations (Fe, Al, Zn, Ca measured in mg/L) at different coagulant dosages and dosing locations (FE, PST, Crude) for FS, ALS, and PACL

Coagulant	Dosage (mg/L)	Fe_FE	Al_FE	Zn_FE	Ca_FE	Fe_PST	Al_PST	Zn_PST	Ca_PST	Fe_Crude	Al_Crude	Zn_Crude	Ca_Crude
FS	0	-0.2	0	0	38.7	0.3	0	-0.4	41.5	0.1	0	0	25.8
	5	0.5	0	0	37.7	2.3	0	-0.5	38.7	2.6	0	0.1	24.8
	10	0.2	0	0	39.4	2.1	-0.1	-0.5	40.1	3.1	0	0	25.9
	15	0.2	0	0	38	0.7	-0.1	-0.5	38.7	2	0	0	24.1
	30	5.5	0.1	0	38.3	0.4	-0.1	-0.5	39.3	2.2	0	0	25.3
	40	8.2	0	0	38.3	0.6	-0.1	-0.5	39.5	4.6	0	0	25.9
ALS	0	-0.2	0	0	38.7	0.3	0	-0.4	41.5	0.1	0	0	25.8
	5	0	0.3	0	36.5	0.2	1.2	1	35.7	0.2	0.4	0	23.6
	10	-0.1	0.5	0	37.7	0.2	0.5	1.1	36.1	0	0.4	0	23.9
	15	0	1	0	39.6	0	0.5	1.2	36.1	-0.1	0.4	0	24.7
	30	0	12.2	0	38	0.1	0.1	0	37.7	0.5	0.7	0	23.7
	40	0	20.7	0	37.4	0.3	0.1	0	37.4	0.7	5.6	0	24.7
PACL	0	-0.2	0	0	38.7	0.3	0	-0.4	41.5	0.1	0	0	25.8
	5	-0.1	0.3	0	41.1	0.3	0.7	0	38.5	0.3	0.7	0.1	22.7
	10	0	0.6	0.1	39.9	0.1	0	-0.1	37.7	0	0.3	0	22.2
	15	0	0.8	0.1	39.3	0	0	-0.1	38.4	0	0.4	0	23.1
	30	0	14.8	0.1	40.1	0	0	-0.1	39.1	0.4	7.1	0	23
	40	0	26.3	0.1	41.3	0.1	0.2	-0.1	38.4	0.7	18.1	0.2	23.5

Table D-2: Concentrations of chloride and sulphate anions (measured in mg/L) at different sampling locations (FE, PST, Crude) across coagulant types and dosages

Coagulant	Dosage (mg/L)	FE		PST		Crude	
		Chloride	Sulphate	Chloride	Sulphate	Chloride	Sulphate
FS	0	49.2	38	86.6	31.9	175.3	82.6
	5	50.3	61.3	87.8	48.9	181.1	109.4
	10	50.3	84.2	88.2	69.4	177.7	127.2
	15	50	107.3	88.4	93.3	179.2	153
	30	50.4	205.4	87.9	171	180.6	232.2
	40	49.9	260.8	87.8	225.7	180.2	288.3
ALS	0	49.2	38	na	na	na	na
	5	54	72.5	na	na	na	na
	10	54.5	100.3	na	na	na	na
	15	54.8	127	na	na	na	na
	30	54.3	270.3	na	na	na	na
	40	54.9	340.7	na	na	na	na
PACL	0	49.2	38	72.1	33.8	64.5	35.4
	5	68	42.5	87.5	35.1	78.1	35.1
	10	78.1	40.3	98.4	34.9	89.9	35.9
	15	90.7	38.9	109.1	34	101.9	36.1
	30	156.8	38.1	144	30.8	136.9	33.5
	40	156.7	66.6	166.7	30.3	160	31.4

Note: na = Not available

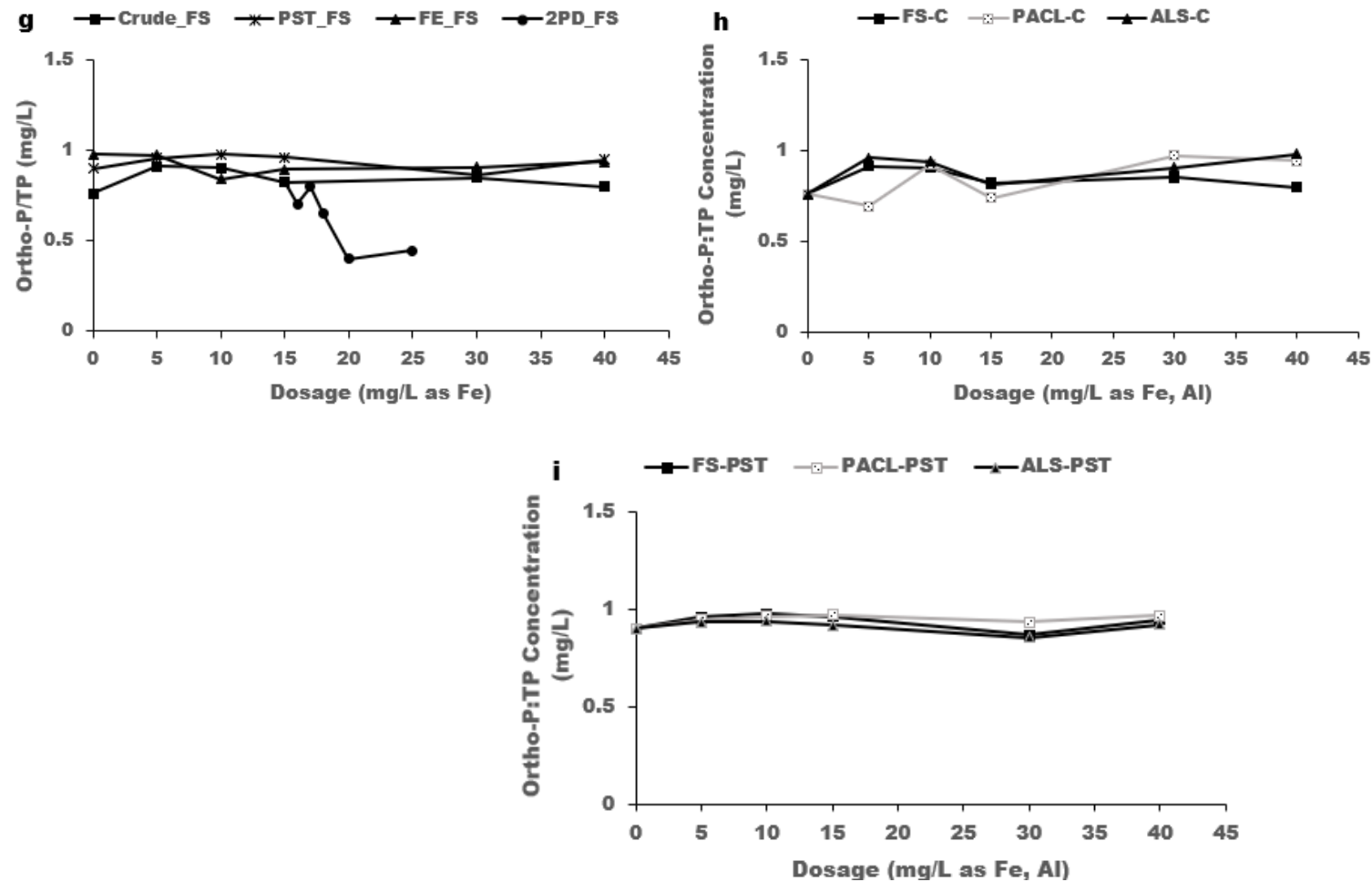


Figure D-1: Effect of coagulant dosage on Ortho-P/TP ratio concentrations at different wastewater treatment stages (Crude, PST, FE) for FS (g), ALS (h), and PACL (i)

Chapter 5

5 Implications of the research work

The overarching aim of this thesis was to understand and critically evaluate the influence of coagulant type, operating pH, and application point within the treatment train on phosphorus removal performance in municipal wastewater treatment for the water industries to develop optimum dosing strategies that maximise P removal efficiency under variable wastewater conditions.

Despite the crucial role of coagulant dosing in achieving low effluent P concentrations, guidelines for selecting appropriate coagulant types and optimal application points across varying operational conditions are limited. This thesis contributes to closing this knowledge gap by providing evidence-based insights into the role of coagulant chemistry, pH control, and dosing location in achieving effective P removal. The research advanced understanding of how coagulant properties (e.g., charge density, hydrolysis behaviour) interact with wastewater characteristics and process conditions to influence treatment outcomes. Through comparative bench-scale experiments, the study established critical parameters for coagulant selection and dosing strategy optimisation. Ultimately, the implications for the sector generated by this thesis's outcomes are presented as answers to the following relevant questions.

5.1 What factors influence chemical selection?

The findings across Chapters 2 to 4 underscore a complex interplay of sustainability, performance, cost, and operational considerations in the selection and application of metal-based coagulants for phosphorus removal from municipal wastewater. Commonly used coagulants such as ferric sulphate (FS), aluminium sulphate (ALS), and polyaluminium chloride (PACL) remain prevalent due to their favourable balance of cost, availability, and well-established supply chains. However, their production processes are energy-intensive and rely on the extraction of non-renewable ores, thereby contributing significantly to the environmental footprint of wastewater treatment operations (van der et al., 2016). As environmental policy increasingly favours decarbonisation and circular

economy approaches (Hermann et al., 2018), these factors call into question the long-term sustainability of conventional coagulants.

Rare earth and zirconium-based coagulants showed promising phosphate binding capabilities under standardised conditions, particularly in laboratory environments. Nonetheless, their scalability is limited by high costs and global supply constraints (Zheng *et al.*, 2022). Additionally, these coagulants often require higher doses to achieve comparable results to more conventional agents, increasing both operational complexity and cost. Dose efficiency becomes an essential metric, not only from a financial standpoint but also in terms of resource conservation and environmental sustainability. In this context, the research highlights pH as a pivotal variable influencing coagulant performance.

Coagulants such as FS and ALS achieved stable phosphorus removal across a near-neutral pH range (6-7), while PACL and rare earth compounds demonstrated diminished performance under acidic or uncontrolled pH conditions. pH adjustment, through sodium hydroxide (NaOH) or hydrochloric acid (HCl), improved coagulant efficacy and facilitated lower chemical dosing. Given that pH adjustment chemicals are generally less expensive than most coagulants, their use in combination with reduced coagulant volumes can result in a more cost-effective treatment strategy (Table 5-1). This is particularly pertinent for expensive formulations such as PACL, cerium sulphate, or zirconium-based coagulants, where pH control can offset material costs by enhancing performance and reducing dosage requirements. Even where pH control increases operational complexity, the benefits, in terms of improved treatment efficiency, reduced environmental burden, and regulatory compliance, may outweigh associated costs.

Dose optimisation trials across wastewater matrices (Crude, PST, FE) at Cranfield and in Scotland confirmed that FS and ALS could achieve residual TP levels below 0.3 mg/L at doses of 5-30 mg/L, aligning with full-scale operational ranges and literature benchmarks (Keeley *et al.*, 2016; Sun *et al.*, 2016). However, more complex influents such as crude wastewater showed greater variability in coagulant demand, particularly for less stable or more expensive

coagulants. These findings suggest that dosing strategies should be site-specific and responsive to influent characteristics such as organic matter, phosphate speciation, and alkalinity. Incorporating real-time control systems equipped with sensors for pH, turbidity, and orthophosphate concentrations could facilitate dynamic dose adjustments, promoting operational resilience and chemical efficiency.

In terms of solid-liquid separation, FS and ALS consistently produced robust, dense flocs conducive to improved sludge dewaterability and clarifier performance. Conversely, PACL and rare earth-based coagulants, especially under suboptimal pH, formed weak or fragile flocs prone to fragmentation and resuspension, contributing to higher total suspended solids (TSS) and compromised effluent quality. Analyses indicated that residual phosphorus following coagulation often existed in particulate form, suggesting that phosphorus had precipitated but was not completely removed via sedimentation. This highlights the potential need for tertiary filtration technologies to capture remaining particulates and improve compliance with discharge standards. As such, floc morphology and mechanical stability should become key screening criteria when selecting coagulants.

The research consistently identified pH and alkalinity as critical to coagulation performance. pH influences metal speciation, solubility, precipitation dynamics, and floc formation. PACL exhibited poor performance below pH 6, whereas FS and ALS maintained efficacy across a broader pH range. Maintaining near-neutral pH between 6 and 7 optimised phosphate precipitation and floc formation (Chowdhury *et al.*, 2013). In low-alkalinity systems, such as the final effluent, coagulants like FS caused significant pH drops, necessitating buffering with NaOH or lime. While this adds operational cost and carbon footprint, it improves phosphorus removal and ensures regulatory compliance.

The decision to implement pH adjustment should be evaluated case-by-case. Factors including effluent quality targets, sludge generation, and chemical costs must be considered. Where feasible, selecting coagulants that perform well under ambient conditions may offer a more sustainable solution. Alternatively, lime-

based buffering, biologically generated alkalinity, or strategic dosing adjustments could reduce reliance on chemical pH control.

Table 5-1: Coagulant and pH adjustment chemical costs per kg used during phosphorus removal experiments

S/N	Coagulant	Cost per mole metal ion (£)	Source
1	Ferric sulphate	44.40	Fisher Scientific
2	Ferric chloride	7.80	
3	Ferrous sulphate	9.17	
4	Ferrous chloride	18.43	
5	Aluminium sulphate	35.80	Sigma-Aldrich
6	Aluminium chloride	6.52	
7	Polyaluminium chloride	4.26	Airedale Chemical
8	Aluminium chlorohydrate	3.27	
9	Cerium sulphate	276.58	Fisher Scientific
10	Cerium chloride	180.22	
11	Lanthanum sulphate	381.11	
12	Lanthanum chloride	168.14	
13	Zirconium sulphate	100.67	
14	Zirconium chloride	89.53	
15	Zinc sulphate	25.90	Thermo Scientific Chemicals
16	Zinc chloride	15.78	
17	Calcium hydroxide	6.65	Sigma-Aldrich
18	Hydrochloric acid (HCl)	34.64	
19	Sodium hydroxide (NaOH)	36.60	

Note: although these are not the actual cost of products for the utilities, the differences between chemicals are relevant.

5.2 How does dosing location influence performance, and are multiple dosing points a more sustainable option?

The study introduces and evaluates the application of two-point dosing (2PD), involving crude wastewater where initial phosphorus concentrations are elevated. While crude wastewater was selected as the primary location for initial dosing trials due to its high influent load, the 2PD strategy is not limited to this point and could also be effectively applied using combinations such as a PST followed by FE. Moreover, it is important to note that the experiments conducted at the FE stage inherently reflected a two-point dosing configuration, as coagulants had already been applied upstream in earlier treatment stages. This approach of splitting coagulant addition across different stages of the treatment train or locations, 2PD was shown to allow the same, best performance but with an overall lower dose while reducing total chemical use, due to more efficient targeting of both particulate and dissolved phosphorus fractions (Chapter 4). The strategy also mitigated pH decline associated with single-point high-dose addition and improved floc formation. While this dosing configuration offers promising operational benefits, its full-scale implementation requires investment in infrastructure upgrades, such as additional dosing lines and automated control systems, alongside a clear understanding of site hydraulics and flow dynamics. This study provides a compelling case for utilities to consider 2PD to optimise treatment efficiency while minimising chemical usage and costs.

5.3 Are the phosphorus residual levels achieved by the coagulants tested sufficient to meet current or emerging discharge regulations for sensitive water bodies, and could these coagulants help future-proof treatment plants against tightening phosphorus limits?

Regulatory compliance is a critical driver for optimising phosphorus removal, and this study's outcomes align with current and future requirements under the EU Urban Wastewater Treatment Directive and UK Environment Agency guidelines. Across all experiments, FS, ALS, and PACL achieved residual TP concentrations below 0.3 mg/L at optimised doses and conditions, and in several instances reached below 0.1 mg/L (Chapters 2 and 3). These levels are well-aligned with

current phosphorus discharge consents in the UK and EU, and approach the thresholds proposed for ultra-sensitive catchments and anticipated ultra-low discharge limits (<0.1 mg/L) under the EU Urban Wastewater Treatment Directive Recast (Water Framework Directive, 2000).

The results from the two-point dosing strategy in Chapter 4 further reinforce the feasibility of meeting these tighter standards through strategic operational enhancements rather than increased chemical use. This future-proofs wastewater treatment systems against tightening environmental regulations and provides a performance-based framework for upgrading existing infrastructure. However, performance stability under dynamic conditions (e.g., wet weather, industrial inflow variability) must be validated through pilot-scale or real-world trials to ensure robust and reliable treatment. These conditions can alter influent composition and pH, potentially affecting coagulant performance and removal efficiency. Notably, this study observed that in most cases, phosphorus was successfully converted into particulate form through coagulation, yet not all particulates were effectively removed by sedimentation. This highlights the importance of evaluating downstream separation technologies, such as tertiary filtration, which may be necessary to consistently achieve low residual phosphorus levels, especially under variable conditions. Incorporating such technologies could bridge the gap between chemical precipitation and regulatory compliance, enhancing treatment resilience and overall process stability.

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Chapter 6

6 Conclusion

This thesis has advanced the understanding of chemical phosphorus removal from municipal wastewater by comprehensively evaluating the influence of coagulant type, pH conditions, and dosing location. The study explored both theoretical and practical aspects of coagulation-based phosphorus removal through a series of integrated laboratory experiments, detailed characterisation analyses, and strategic dosing trials. The overall aim was to determine how coagulant selection and operational parameters affect phosphorus removal efficiency and how these insights can guide sustainable and regulation-compliant treatment strategies. The following conclusions were drawn in response to the specific research objectives.

Objective 1: Impact of coagulant choice on phosphorus removal from wastewater

A wide comparative analysis of 17 coagulants, including ferric, ferrous, aluminium, rare earth, zirconium, zinc, and calcium-based formulations, was conducted under standardised experimental conditions. Ferric sulphate (FS) and polyaluminium chloride (PACL) demonstrated superior performance, achieving residual total phosphorus (TP) concentrations of 0.35 mg/L and 0.15 mg/L, respectively. Aluminium sulphate (ALS) also achieved low residual TP (0.1 mg/L) under controlled pH.

Performance was shown to depend on factors such as charge density, hydrolysis potential, metal speciation, solubility, and hydrophilicity, with the high-valent metal ions like Fe^{3+} and Al^{3+} forming stable hydroxide flocs. In contrast, rare earth coagulants, despite high phosphate-binding affinities, produced fragile flocs that compromised total phosphorus removal. Metal speciation modelling confirmed that hydroxide species (e.g., $\text{Fe}(\text{OH})_3$, $\text{Al}(\text{OH})_3$) dominate under neutral pH and are responsible for enhanced adsorption and floc formation.

Highly soluble coagulants' counterion (e.g., chloride salts - FC, ALC) could cause pH decline, limiting floc formation under uncontrolled pH. In contrast, calcium hydroxide was useful for pH adjustment but required higher doses for effective

phosphorus removal. Floc structure analysis showed that FS and PACL produced dense and shear-resistant flocs, whereas rare earth and zinc coagulants formed weaker aggregates with limited regrowth potential.

Objective 2: To evaluate the influence of pH on coagulant performance and floc properties to identify the mechanisms behind phosphorus removal.

Using final effluent as a uniform matrix, the study evaluated FS, ALS, and PACL under controlled pH ranging from 4 to 8. FS achieved optimal phosphorus removal at pH 6-8 due to hydrolysis and formation of $\text{Fe}(\text{OH})_3$. ALS showed comparable performance at pH 6-7 but decreased efficiency at lower pH. PACL was least effective, especially under acidic conditions, where incomplete hydrolysis and weak floc formation impeded phosphorus removal.

Phosphorus fractionation revealed that FS and ALS effectively converted soluble phosphorus into settleable particulate forms. PACL retained higher levels of particulate phosphorus that remained in suspension, leading to elevated turbidity and TSS. Floc characterisation confirmed that FS formed larger and more compact flocs, but with greater susceptibility to shear. ALS flocs were smaller but structurally stable. PACL formed the weakest flocs, requiring higher doses across all pH levels to achieve similar removal.

Objective 3: To evaluate the influence of dosing location on the effectiveness of ferric sulphate, aluminium sulphate, and PACL for phosphorus removal from municipal wastewater.

The performance of FS, ALS, and PACL was assessed across three dosing locations: crude, PST, and FE. All three coagulants achieved residual TP < 0.3 mg/L at PST and FE locations, supporting regulatory discharge requirements. ALS was most dose-efficient at PST and FE but underperformed in crude wastewater due to high organic loads. FS was more resilient under crude conditions, though it required careful pH monitoring to prevent over-acidification. PACL exhibited variability in crude wastewater and required higher doses for effective removal.

The study demonstrated that dosing location significantly influences removal outcomes due to differences in organic matter, solids content, and alkalinity. FE and PST presented more favourable conditions for coagulant performance. Phosphorus fractionation confirmed that all coagulants removed reactive and particulate phosphorus effectively at downstream locations. However, crude wastewater showed more variability in RP removal.

Floc size and stability were found to vary by both coagulant and location, and the most stable flocs formed at the FE stage, reflecting reduced interference and optimal pH. Importantly, a two-point dosing strategy using FS at the crude stage achieved comparable phosphorus removal to single-point dosing but with reduced chemical usage. This suggests that distributed dosing can enhance interaction with diverse phosphorus fractions while improving cost-efficiency.

Broader Sectoral Implications and Contributions to Practice

This thesis contributes a detailed understanding of how coagulant type, dosing location, pH conditions, and operational strategy interact to influence phosphorus removal. The integration of metal speciation modelling (Chapter 2), detailed floc characterisation (Chapters 3 and 4), and application of innovative dosing strategies (Chapter 4) offers a multidimensional approach to coagulant evaluation. These findings will support more informed decision-making for coagulant choice, dosing system design, and compliance planning in wastewater treatment facilities and bridge the gap between bench-scale experimentation and full-scale application. The work aligns with sectoral priorities such as energy efficiency, chemical use minimisation, and compliance with emerging water quality standards, offering practical tools and insights for utilities, regulators, and technology providers seeking to optimise treatment processes within economic and environmental constraints.

Chapter 7

7 Future work

This research provides a comprehensive evaluation of chemical phosphorus removal from municipal wastewater using a range of coagulants under various dosing strategies, pH conditions, and wastewater matrices. Significant insights were gained regarding floc formation, coagulant behaviour, and treatment performance; however, several important avenues for future research remain to enhance mechanistic understanding, treatment resilience, and scalability. Building on the findings of this study, the following areas are recommended for future research to deepen scientific understanding and improve the practical implementation of phosphorus removal using metal-based coagulants:

1. Further investigation is required to characterise the structural dynamics of flocs formed under varying coagulant types and dosing locations (Crude, PST, FE), particularly in relation to their mechanical integrity under operational hydraulic conditions. While floc strength has been broadly assessed in the literature, limited attention has been given to the resilience of flocs against shear-induced fragmentation and their implications for downstream processes, such as sludge dewatering and tertiary filtration, within the context of municipal wastewater matrices. To address this, future research should implement controlled flocculation-shear experiments using jar tests followed by image-based analysis (e.g., microscopy and fractal dimension quantification) and particle size distribution measurements under variable shear intensities. Subsequent sludge handling assessments, such as dewatering trials and filterability tests, will help determine downstream implications.
2. Experimental validation of metal speciation and phosphate precipitation mechanisms under realistic wastewater conditions remains limited, as most existing studies predominantly rely on theoretical modelling tools such as Hydra Medusa. To bridge this gap, future work should incorporate advanced analytical techniques to characterise both the chemical and physical properties of precipitated solids formed during coagulation. Techniques such as Fourier Transform Infrared Spectroscopy (FTIR) for

identifying bonding groups, X-ray Diffraction (XRD) for determining crystalline phases, and Nuclear Magnetic Resonance (NMR) for analysing the phosphorus coordination environment are essential for elucidating the speciation of metal-phosphate complexes. These methods should be applied to solids collected under both controlled and uncontrolled pH regimes, as well as across different wastewater matrices, to establish correlations between chemical speciation and phosphorus removal efficiency.

In parallel, a deeper understanding of the physicochemical factors limiting effective solid-liquid separation is required, particularly in the context of poorly settling flocs observed with certain coagulants such as PACL under acidic conditions. Comprehensive characterisation of floc properties should therefore include zeta potential measurements to assess surface charge, Atomic Force Microscopy (AFM) to examine surface morphology, and FTIR for surface functional group analysis. Additionally, bench-scale studies should explore the influence of operational variables such as mixing intensity, sedimentation duration, and controlled pH modulation. These experimental efforts will support the optimisation of coagulation processes by identifying the conditions that enhance floc formation, stability, and settleability—ultimately improving treatment efficiency and regulatory compliance under realistic wastewater conditions.

3. Despite the promising phosphorus binding capacities of zirconium- and rare-earth-based coagulants, their practical utility in full-scale wastewater treatment is currently limited by floc instability and fragility. While these coagulants were tested under standardised conditions to enable side-by-side performance comparison, future research should investigate their behaviour under a broader range of operational conditions, including longer settling times, variable shear conditions, and fluctuating influent characteristics. This can be assessed using pilot-scale continuous flow systems with real wastewater, comparing floc development, breakage, and settleability under controlled operational changes. Enhancing floc

structural integrity through co-precipitation with additives can also be explored using bench-scale formulations and performance tests.

4. The influence of dynamic wastewater characteristics on coagulant efficacy, particularly the composition and reactivity of dissolved organic matter (DOM), has not been fully elucidated. This can be addressed by conducting controlled coagulation tests with wastewater samples subjected to seasonal and source variability, while characterising DOM using excitation emission matrix (EEM) fluorescence, FTIR spectroscopy, and Liquid Chromatography Organic Carbon Detection (LC-OCD). The interactions between coagulants and identified DOM fractions can then be evaluated to understand their impact on removal performance and floc quality.
5. Although two-point dosing (2PD) strategies have demonstrated improved phosphorus and COD removal in high-strength influent, optimisation of this approach requires further research. Pilot-scale simulations or advanced jar testing setups with staggered coagulant addition can be used to test different spatial and temporal separations. Real-time monitoring tools like turbidity sensors and online phosphate analysers should be incorporated to develop feedback-based dosing algorithms, and performance stability should be evaluated under simulated diurnal and seasonal variations in influent composition.
6. Comparative studies of drinking water and wastewater matrices using standardised experimental protocols are still limited. Future research should conduct parallel coagulation trials with a jar tester using identical coagulant types, doses, pH ranges, and mixing conditions on both surface water and municipal wastewater. Floc properties and removal efficiencies should be systematically compared using turbidity, particle size analysis, and residual metal/phosphate concentrations to determine how matrix composition influences coagulation dynamics.
7. The recovery and potential reuse of ferric and aluminium-based coagulants have received limited attention in municipal wastewater

contexts. To explore this, batch experiments should be performed to test different regeneration methods (e.g., acid or base leaching, magnetic separation, biological stripping), followed by coagulation tests using the recovered materials. Comparative analysis of removal efficiency, floc characteristics, and economic feasibility should be carried out against conventional coagulants.

8. While bench-scale experimentation provided valuable insights into coagulant behaviour across locations, scaling up to pilot or full-scale systems often introduces complexities, such as increased heterogeneity in flow and pollutant distribution, which may not be fully captured in controlled laboratory experiments. Pilot-scale trials should be implemented at operational treatment sites with automatic dosing systems, continuous flow reactors, and real-time sensors for pH and phosphate. Performance metrics, including effluent quality, sludge volume, and chemical consumption, should be monitored over extended operational periods.
9. A comprehensive life cycle assessment (LCA) and techno-economic analysis (TEA) tailored to ferric sulphate, aluminium sulphate, and PACL under various dosing regimes is currently lacking in the literature. Future work should compile data on coagulant sourcing, transport, dosage, pH control chemicals, sludge handling, and residual treatment. Process modelling software and LCA tools can be used to simulate environmental and economic outcomes under different treatment scenarios, thereby enabling data-driven selection of the most sustainable and cost-effective options.

Appendix E: Ethical approval letter



29 May 2025

Dear Mr Imafidon ,

Reference: CURES/25356/2025

Project ID: 14053

Title: Evaluation of the impact of coagulant choice on phosphorus removal from municipal wastewater

Thank you for your application to the Cranfield University Research Ethics System (CURES).

We are pleased to inform you your project title change request, reference CURES/25356/2025 has been approved.

If you have any queries, please contact CURES Support.

Regards,

CURES Team