NUTRIENT REMOVAL FROM MUNICIPAL WASTEWATER USING WASTE ALUM SLUDGE

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The above candidate has carried out research for the PhD/MPhil/Masters thesis/dissertation under my supervision. I confirm that the declaration made above by the student is true and correct.

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ABSTRACT

Nutrient Removal from Municipal Wastewater using Waste Alum Sludge

Phosphorus pollution in water bodies is a significant environmental concern, contributing to eutrophication and the degradation of aquatic ecosystems. Traditional phosphorus removal techniques, such as chemical precipitation and biological phosphorus removal (BPR), are effective but often costly and environmentally unsustainable. This study investigates the feasibility of using alum sludge, a byproduct of water treatment plants, as a cost-effective and sustainable adsorbent for phosphorus removal from wastewater.

Comprehensive characterization of alum sludge samples from three water treatment plants as Ambatale, Biyagama, and Kandana was conducted to evaluate their physical, chemical, and morphological properties. High aluminum content (19.51% to 29.52%) and amorphous structures were identified as key factors contributing to phosphorus adsorption, with moisture content affecting adsorption efficiency. The potential for phosphorus release was minimal, confirming the chemical stability of alum sludge and its suitability for reuse in wastewater treatment.

Phosphorus removal experiments using synthetic wastewater revealed that removal efficiency was highest at slightly acidic pH levels (6–6.5). Time-dependent studies indicated rapid adsorption within the first two hours, with equilibrium reached thereafter. Langmuir isotherm analysis demonstrated monolayer adsorption behavior, with Biyagama WTP sludge achieving the highest maximum adsorption capacity (7.96 mg/g), followed by Kandana (6.45 mg/g) and Ambatale (5.69 mg/g). These results underscore the influence of source-specific sludge characteristics on adsorption performance.

The findings highlight the potential of alum sludge as a low-cost, effective, and environmentally sustainable material for phosphorus removal in wastewater treatment. Further research is recommended to explore large-scale applications, hybrid treatment systems, and the regeneration of used sludges to enhance their viability. This study contributes to advancing circular economy principles by repurposing waste for environmental remediation.

Keywords: Alum sludge, Phosphorus, Adsorption, Synthetic Wastewater

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1. INTRODUCTION

1.1. Background

Phosphorus is an essential nutrient for all living organisms; however, its overabundance in aquatic environments can lead to eutrophication. This process triggers algal blooms, depletes oxygen levels, and results in the death of aquatic life (Szabó et al., 2008). Consequently, it is crucial to effectively remove phosphorus from wastewater to safeguard water quality and maintain ecological balance. Regulatory bodies, such as the European Union's Water Framework Directive and the United States Environmental Protection Agency's Clean Water Act, have implemented stringent limits on phosphorus discharge from wastewater treatment plants to address these environmental concerns (Keating et al., 2016; Maqbool et al., 2016).

Phosphorus removal from wastewater has significantly progressed over the past century. Initially, physical methods such as sedimentation and filtration were used to eliminate particulate phosphorus (Szabó et al., 2008). However, as the harmful effects of phosphorus on aquatic ecosystems, especially eutrophication, became apparent, more effective chemical and biological methods were developed (Keating et al., 2016). In the mid-20th century, chemical precipitation using metal salts like alum and iron chloride became widespread, offering efficient phosphorus removal (Georgantas and Grigoropoulou, 2005). Later, in the late 20th century, biological phosphorus removal processes were introduced. These processes use specific microorganisms to absorb phosphorus from wastewater (Maqbool et al., 2016). Over time, these methods have evolved to become more effective and environmentally friendly, driven by stricter environmental regulations and increasing ecological awareness.

Alum sludge, a by-product of the coagulation process in water treatment plants, is produced when aluminium salts are used to eliminate impurities. This sludge consists of aluminium hydroxides, organic matter, and various contaminants (Yang et al., 2006). It is notable for its high aluminium content and substantial adsorption capacity (Ojha, Sharma and Amatya, 2019). The properties of alum sludge can vary based on the quality of the source water and the specific treatment processes used. Due to its composition and abundance, alum sludge holds potential for applications in wastewater treatment, especially for phosphorus removal (Maqbool et al., 2016).

Spent alum sludge is increasingly being considered for applications in wastewater treatment. Research indicates that although pure alum demonstrates greater efficiency in phosphorus removal, spent alum sludge still retains significant phosphorus adsorption capacity (Georgantas and Grigoropoulou, 2005). This characteristic makes it a cost-effective alternative for wastewater treatment plants, as it repurposes a waste product that would otherwise require disposal (Ojha, Sharma and Amatya, 2019). Comparative studies indicate that spent alum sludge can achieve substantial phosphorus removal, though it requires higher dosages than fresh alum (Maqbool et al., 2016).

The primary mechanism of phosphorus removal by alum sludge involves adsorption, where phosphorus compounds adhere to the surface of sludge particles (Georgantas et al., 2006). This process is influenced by several factors, including pH, contact time, and sludge dosage (Mohammed & Rashid, 2012). The efficiency of phosphorus removal can decrease over time as the sludge ages, likely due to changes in its surface properties and adsorption capacity (Georgantas et al., 2006). Numerous studies have investigated the use of alum sludge for phosphorus removal in wastewater treatment. However, the efficiency can vary based on factors such as the source of the sludge, preparation methods, and the characteristics of the wastewater (Maqbool et al., 2016).

Synthetic wastewater is frequently utilized in research to replicate the conditions encountered in actual wastewater treatment processes. This approach allows for controlled experiments that isolate specific variables, thereby enhancing the understanding of the mechanisms involved in phosphorus removal (Georgantas & Grigoropoulou, 2005). Synthetic wastewater typically contains known concentrations of phosphorus and other constituents, enabling precise measurements of removal efficiency (Cai et al., 2020). Using synthetic models aids in standardizing experiments and facilitating comparisons across different studies (Tibebe et al., 2019).

The reuse of spent alum sludge for phosphorus removal in wastewater treatment offers significant environmental and economic advantages. Environmentally, it reduces the volume of waste produced by water treatment plants, which in turn lowers disposal costs and diminishes potential environmental hazards (Egle et al., 2016). Economically, using spent alum sludge as an alternative to commercial coagulants cuts down the operational expenses of wastewater treatment facilities (Muisa et al., 2020a). Additionally, implementing alum sludge-based systems supports sustainable water treatment practices by promoting the circular use of resources (Georgantas and Grigoropoulou, 2005).

In essence, reusing spent alum sludge not only mitigates the environmental burden by decreasing waste and potential hazards but also provides a more economical solution for wastewater treatment operations. This practice enhances sustainability by recycling resources within the treatment process, aligning with broader environmental goals (Babatunde et al., 2010).

1.2. Problem Statement

Alum sludge, a by-product of the coagulation process in water treatment plants, is classified as hazardous waste that can lead to environmental pollution if not properly disposed of (Yang et al., 2006). Additionally, its high levels of aluminium and heavy metal ions make it unsuitable for reuse in agriculture (Mohammed & Rashid, 2012). Despite these drawbacks, alum sludge has demonstrated superior adsorption capabilities for removing phosphorus from aquatic solutions (Yang et al., 2006).

Given this potential, the proposed research aims to investigate the feasibility of using alum sludge as a cost-effective material for phosphorus removal from wastewater. This study will explore the possibility of repurposing alum sludge, transforming it from a waste product into a valuable resource for wastewater treatment. By doing so, it could offer a sustainable solution that mitigates disposal issues while enhancing the efficiency of phosphorus removal processes.

1.3. Objectives of the Study

Main Aim

To evaluate the feasibility of repurposing alum sludge as a cost-effective and sustainable material for the removal of phosphorus from synthetic wastewater, thereby transforming it from a hazardous waste into a valuable resource for wastewater treatment processes.

Specific Objective 1

To conduct a detailed characterisation of alum sludge samples obtained from three Sri Lankan water treatment plants, including an analysis of their chemical composition, physical properties, and adsorption capacities, to understand the variability and potential effectiveness for phosphorus removal in wastewater treatment applications.

Specific Objective 2

To evaluate the potential for phosphorus release from the selected alum sludge samples, including an examination of the conditions under which phosphorus desorption may occur and the impact this could have on the efficacy of using alum sludge for wastewater treatment.

Specific Objective 3

To evaluate the efficiency of the selected alum sludge samples in removing phosphorus from synthetic wastewater, including an assessment of removal rates, optimal conditions for maximum phosphorus adsorption, and comparative performance analysis with other common phosphorus removal methods.

1.4. Research Significance

The proposed research on utilizing alum sludge for phosphorus removal from wastewater holds significant environmental, economic, and scientific importance. Alum sludge, a hazardous by-product of the coagulation process in water treatment plants, presents disposal challenges due to its potential for environmental pollution and high levels of aluminium and heavy metal ions, making it unsuitable for agricultural reuse (Yang et al., 2006). However, its superior adsorption capabilities for phosphorus present a promising solution for wastewater treatment (Yang et al., 2006).

Repurposing alum sludge reduces hazardous waste volume, lowers disposal costs, and mitigates potential environmental hazards, aligning with global sustainability goals by promoting eco-friendly waste management practices and reducing the environmental footprint of water treatment operations (Egle et al., 2016). Economically, using alum sludge as an alternative to commercial coagulants can significantly reduce the operational expenses of wastewater treatment facilities (Muisa et al., 2020a). This is particularly beneficial for municipal and industrial plants facing financial constraints, offering savings in both treatment and waste disposal costs (Georgantas and Grigoropoulou, 2005).

Scientifically, this research will advance the understanding of wastewater treatment technologies by exploring the mechanisms and efficiencies of alum sludge in phosphorus removal. It will provide insights that could optimize treatment processes and improve water quality, crucial for developing innovative and sustainable treatment systems that leverage waste materials, thus promoting a circular economy (Babatunde et al., 2010). The broader impact of this research includes enhanced public health and improved water resource management by preventing eutrophication, protecting aquatic ecosystems, and ensuring the safety of water resources for human consumption and recreational activities (Babatunde et al., 2010). In conclusion, the proposed research promises substantial environmental, economic, and scientific benefits by addressing critical waste disposal challenges and supporting broader environmental and public health goals.

1.5. Scope of the Study

This study aims to evaluate the efficiency of spent alum sludge as a phosphorus removal agent in synthetic wastewater, focusing on samples from three Sri Lankan water treatment plants: Ambatale, Biyagama, and Kandana. The research will begin with the chemical and physical characterisation of alum sludge samples. Techniques such as Fourier Transform – Infrared Spectroscopy, ICP-MS, Scanning Electron Microscopy (SEM) and Energy-Dispersive X-ray Spectroscopy (EDX) will be employed to analyse the sludge's morphology and composition.

Following characterisation, the study will investigate the phosphorus adsorption capabilities of alum sludge under various conditions, determining the optimal pH levels, contact time, and sludge dosage. The removal efficiency will be tested at different initial phosphorus concentrations to assess performance. Additionally, the potential for phosphorus release from alum sludge under acidic conditions will be evaluated to understand its stability and binding capacity.

A comparative analysis will be conducted to assess the phosphorus removal efficiency of alum sludge versus other conventional methods of phosphorus removal. This study aims to provide insights into the feasibility of using alum sludge as a cost-effective and environmentally sustainable phosphorus removal agent. The findings are expected to contribute to innovative wastewater treatment practices that enhance water quality and promote environmental sustainability.

2. LITERATURE REVIEW

2.1. Introduction to Phosphorus Pollution in Water Bodies

The issue of phosphorus pollution in water bodies is escalating into a significant environmental challenge that urgently needs to be addressed due to its severe effects on water habitats and the health of people. While phosphorus is a vital nutrient necessary for the growth of plants and animals, it turns into a contaminant when its levels in water go beyond what is naturally expected, largely because of human actions (Schindler et al., 2008). The disturbance caused by an excess of phosphorus entering water systems, from sources like agricultural runoff with fertilizers and animal waste, urban runoff with lawn treatments and pet waste, sewage, and factory outflows, disrupts the ecological equilibrium. This disruption triggers an uncontrolled explosion of algae and water plants, a condition known as “Eutrophication” (Smith et al., 2006).

Eutrophication sets off a series of environmental issues, beginning with thick algal blooms that may blanket the water's surface. This prevents sunlight from penetrating to aquatic plants below and disturbs the living spaces of water-dwelling organisms (Paerl & Huisman, 2008). When these large algal blooms decompose, they use up a lot of the dissolved oxygen in the water, leading to hypoxic, or low-oxygen, conditions. The lack of oxygen becomes a critical danger to aquatic creatures, such as fish and invertebrates, which might perish in great numbers if they're unable to relocate to places with more oxygen (Conley et al., 2009). Additionally, some algae release harmful toxins that can adversely affect wildlife, livestock, pets, and humans if they come into contact with or ingest water that's been polluted (Paerl & Huisman, 2008).

Phosphorus pollution has serious social and economic effects, influencing water utilities, the recreation sector, and fishing industries. The need for expensive treatments to make drinking water safe from algal toxins, along with the discouragement of tourism and outdoor enjoyment due to unsightly and dangerous blooms in recreational waters, are major concerns. Additionally, the reduction in fish numbers adversely affects both commercial and leisure fishing, leading to financial setbacks (Dodds et al., 2009).

Efforts to regulate phosphorus pollution have resulted in strict environmental standards and guidelines designed to lower phosphorus levels in aquatic environments. These rules primarily focus on the main phosphorus contributors, introducing the best management practices in farming like better fertilizer application, managing runoff with buffer zones and retention basins, and improving wastewater treatment to eliminate phosphorus before it's released. Educating the public is also essential, increasing awareness of phosphorus pollution's effects and encouraging actions to minimize individual impacts (Withers & Jarvie, 2008).

Efforts to combat phosphorus pollution must continue, involving innovative solutions and wide-ranging collaboration to preserve aquatic environments and public health, ensuring water security for generations ahead (Carpenter, 2005).

2.2. Phosphorus Removal Techniques

Investigating ways to eliminate phosphorus reveals a wide range of strategies, each marked by its own way of working and level of effectiveness. We can sort these strategies into two main categories as physio-chemical and biological methods (Mohammed & Rashid, 2012). Every category is essential for lessening the impact of phosphorus contamination in aquatic environments.

Some of the techniques that are used for phosphorus removal are classified in Table 2.1 below.

Table 2.1: Different Phosphorus Removal Techniques

Removal Method	Mechanism	Efficiency & Applications	Challenges	Reference/s
Chemical Precipitation	Involves the addition of chemicals (alum, lime, iron, or aluminium salts) to bind phosphorus into insoluble compounds that can be settled out or filtered from water.	Highly efficient in the elimination of substantial amounts of phosphorus. Commonly employed in both municipal and industrial facilities for wastewater treatment.	The production of chemical sludge requires proper disposal, and the cost of chemicals can be significant.	(De-Bashan & Bashan, 2004)
Biological Phosphorus Removal (BPR)	Utilizes specific bacteria capable of accumulating phosphorus within their cells in excess of their immediate needs, under alternating anaerobic	Efficient for large-scale operations and can achieve low residual phosphorus concentrations. Common in advanced wastewater treatment facilities aiming for sustainable operations.	Relies on maintaining specific operational conditions and microbial communities, which can be disrupted by wastewater composition changes.	(Ge et al., 2015; Oehmen et al., 2007)

	and aerobic conditions.			
Adsorption	Phosphorus ions are captured by the surface of solid materials (adsorbents) through chemical or physical bonds.	Effective for treating water with low to moderate phosphorus levels. Adsorbents can include activated carbon, biochar, clays, and metal oxides.	The effectiveness of adsorption is influenced by the characteristics of the adsorbent and the conditions under which it operates. Research focuses on developing more efficient adsorbents, regenerating spent adsorbents, and integrating adsorption with other treatment processes for enhanced performance.	(Karageorgiou et al., 2007; Karunanithi et al., 2017a)
Electrocoagulation (EC)	Uses electrical current to dissolve sacrificial anode materials, producing coagulants in situ that react with phosphorus	Shows promise for removing phosphorus from various types of wastewaters, including agricultural runoff and industrial effluents.	Operational costs, primarily energy consumption, and electrode replacement, are significant. Advances in electrode materials and	(Franco et al., 2017; Kralchevska et al., 2016)

	to form insoluble compounds.		system design aim to improve efficiency and reduce costs.	
Membrane Filtration	Employs semi-permeable membranes to physically separate phosphorus and other contaminants from water.	High removal efficiencies can be achieved, making it suitable for applications requiring stringent discharge standards or water reuse.	Membrane fouling and high operational costs are major concerns. Research focuses on developing more fouling-resistant membranes, improving cleaning techniques, and optimizing operational parameters.	(Kumar et al., 2007; Wan et al., 2020)
Ion Exchange	Involves the exchange of phosphorus ions in water with other ions on a resin.	Effective for low concentrations of phosphorus, often used as a polishing step after other treatment processes.	The capacity of ion exchange resins and the need for regular regeneration limit its application. Developing more efficient resins, understanding the mechanisms of phosphate	(Loganathan et al., 2014; Sibrell et al., 2009)

			interaction with resins, and exploring regeneration and phosphorus recovery methods are key research areas.	

Each P-removal technique has its own virtues and limitations, which depend upon particular conditions of water treatment like source water characteristics, environmental regulations, and cost considerations (De-Bashan & Bashan, 2004). Research and development continue in the development of processes that handle better this problem for enhanced sustainability, efficiency, and cost-effectiveness of phosphorus removal (Franco et al., 2017).

Among the above methods for P removal, adsorption and chemical precipitation appear to be the most practiced, considering their effectiveness together with their inherent limitations. In these cases, adsorption seems to be one of the most efficient ways of this process due to the fact that it has a low cost and simple operational procedures (Wu et al., 2019). But the major problem is to find good material, essentially in large scale, for effective and available adsorption of phosphorus to deal with small scales of wastewater (Mohammed & Rashid, 2012). Therefore, the search for economically competitive adsorbents in phosphorus removal from water still remains an active field of research (Yang et al., 2006). Many "materials" have been tried out to date for their adsorption potential - in their natural as well as modified forms as indicated in the Table 2.2 below.

Table 2.2: Adsorbent Materials used in Past Studies

Adsorbent Material	Description	Reference/s
Activated Red Mud	Activated red mud was used as an absorbent of phosphate to be removed from its aqueous solutions. The research has covered some of the factors for phosphate adsorption: contact time, pH, temperature, concentration of the adsorbent, and the adsorbate. According to the results, activated red mud has shown efficient adsorption of phosphate at temperatures of 298 K with an adsorption rate between 80-90%.	(Pradhan et al., 1998)

	It has a potential to apply to the treatment of industrial effluents containing phosphates.	
Slag	The study investigated how phosphorus adsorption in fully saturated columns filled with slag media could effectively remove phosphorus (in the form of phosphates) from wastewater. Even after washing, the slag media demonstrated notably greater phosphorus adsorption capacities compared to sandy loam soil. This indicates that slag, a by-product of steel production, could be a highly efficient medium for removing phosphorus from wastewater. The findings emphasize the viability of using washed slag media as an alternative for phosphorus removal, showcasing its superior adsorption capabilities over conventional soil media.	(S. H. Lee et al., 1997)
Sand	This study evaluated the phosphorus (P) removal capabilities of Danish sands used in subsurface flow constructed reed beds, finding significant variation based on the sands' origins. Not all sands proved equally effective for use in these systems. The investigation highlighted calcium (Ca) as the key factor influencing phosphorus removal, with high-Ca sands more effectively precipitating phosphorus under slightly alkaline conditions typical of domestic sewage. Conversely, in more acidic wastewaters, the presence of iron (Fe) and aluminium (Al) in the sands became crucial, as precipitation reactions with these ions are favoured at lower pH levels.	(Arias et al., 2001)
Fly ash	The study explored using fly ash from power stations to adsorb phosphorus from water. Researchers conducted batch tests to assess how phosphate concentration, temperature, and fly ash dosage affected removal efficiency. They found that adsorption dosage had a minor impact at any temperature, with phosphate removal efficiency exceeding 99%, especially at 40°C. This research suggests fly ash as an efficient, cost-effective phosphorus adsorbent, offering a new way to manage waste and address environmental pollution.	(Ugurlu & Salman, 1998)

Iron oxide tailing	Batch experimentation was used to thoroughly assess the adsorption and desorption characteristics of phosphate onto iron oxide tailings. The performance of the isotherm model in the study of the adsorption process of the equations of three parameters (Redlich-Peterson and Langmuir-Freundlich) turned out better applied than two parameters (Freundlich, Langmuir, and Temkin). Increase in pH indicated decrease in adsorption capacity, which depicts that solution pH should be well managed for phosphate removal. A low phosphate desorb ability (about 13-14%) was seen; this probably was from the strong bonding between adsorbed phosphate and iron oxides in the tailings. This has the characteristic of suggesting that once phosphate is adsorbed, it is not easily released, making it potential stable medium for phosphate removal. The study concludes that industrial waste iron oxide tailings, due to their low cost and high adsorption capability, present a promising option for the cost-effective removal of phosphate from wastewater.	(Zeng et al., 2004)
Activated aluminium oxide and granulated ferric hydroxide	This study explored the use of activated aluminium oxide and granulated ferric hydroxide for phosphorus removal in membrane bioreactor (MBR) effluents. The study found that granulated ferric hydroxide had a higher capacity for phosphate adsorption than activated aluminium oxide, particularly at lower phosphorus levels, without being significantly affected by the presence of inorganic ions at a pH of 8.2. The study also found that both adsorbents could be partially regenerated and reloaded using sodium hydroxide, suggesting their potential for reuse. Overall, the research demonstrated the effectiveness of activated aluminium oxide and granulated ferric hydroxide as post-treatment options for achieving stringent phosphorus removal requirements in wastewater treatment, specifically for effluents from MBRs with low phosphorus content.	(Genz et al., 2004)

In addition to the previously mentioned materials, recent studies have explored a variety of other materials for phosphorus removal from water. These include calcite, used for its efficient removal of phosphate species and potential application as a fertilizer for acidic soils (Karageorgiou et al., 2007); filter materials in constructed wetlands, including natural materials, industrial byproducts, and man-made products, with some showing phosphorus removal capacities as high as 420 g P kg−1 (Vohla et al., 2011); soybean stover derived biochar, demonstrating significant phosphorus removal capabilities (Karunanithi et al., 2017b); FeO/Fe_3O_4 composites, developed for effective low concentration phosphate removal from river water (Wan et al., 2020); and magnetic Fe-Zr binary oxide, notable for its high adsorption capacity and convenient separation process (Long et al., 2011). These investigations shed light on the wide array of materials available for phosphorus extraction, each presenting distinct advantages and challenges, thereby broadening the array of tools for addressing phosphorus contamination in water bodies.

Expanding the array of materials for phosphorus removal, different forms of alum sludge have also been utilized in past studies as an adsorbent material, demonstrating varying degrees of success (Kim et al., 2002a; Mohammed & Rashid, 2012; Muisa et al., 2020a; H. F. Wu et al., 2019; Yang et al., 2006). The detailed applications and mechanisms underlying the use of alum sludge for this purpose will be discussed in subsequent topics.

2.3. Production and Characteristics of Alum Sludge

Alum sludge is a by-product of water treatment plants where aluminium sulphate (alum) is used as a coagulant to clarify water. This sludge is primarily composed of aluminium hydroxides or oxides, which can adsorb various contaminants including phosphates (Dassanayake et al., 2015a). The characteristics and production of alum sludge are key to understanding its potential applications, especially in environmental management and pollution control.

2.3.1. Production Process

When aluminium sulphate is employed as a coagulant in the treatment of drinking water, the resulting residue is termed as alum sludge (Yang et al., 2006). The formation of alum sludge takes place as a consequence of the coagulation phase in water treatment, where aluminium sulphate is applied to eliminate both particulate matter and dissolved substances (Everaert et al., 2021). The effectiveness of this procedure is contingent upon the characteristics of the raw water, such as turbidity and organic content, which determine the appropriate dosage of alum to be utilized (Haydar & Aziz, 2009). This process not only improves water clarity but also reduces microbial content and removes phosphates, contributing to the overall safety and quality of drinking water. However, this essential process results in the accumulation of alum sludge, which poses challenges for disposal and management due to its volume and characteristics (Haydar & Aziz, 2009).

2.3.2. Characteristics of Alum Sludge

Physical Properties

Alum sludge typically presents as a gelatinous precipitate, primarily composed of aluminium hydroxides (Mohammed & Rashid, 2012). It has a high moisture content, often exceeding 80%, which makes dewatering a critical step before disposal or reuse. The specific gravity of alum sludge is influenced by the concentration of solids, which can vary based on the treatment process and the water source. Its pH can range from slightly acidic to neutral, impacting its stability and potential for leaching of constituents (Shamaki et al., 2021). The sludge is characterized by its fine, particulate nature, which can pose challenges in handling and disposal. However, treatments like calcination and pyrolysis can alter its physical structure, increasing porosity and surface area, which are beneficial for adsorption processes (V. T. Truong & Kim, 2021).

Composition

The composition of alum sludge is diverse, including aluminium hydroxides, residual alum, organic matter, and various particulates removed from the water. Trace elements such as iron, calcium, and magnesium can also be present, alongside absorbed phosphates and other anions targeted during the coagulation process (Jeon et al., 2018).

Based on the typical content, alum sludge composition can be described as the Table 2.3 (Jeon et al., 2018; Mazari et al., 2018).

Table 2.3: Typical sludge components and their impact on reuse

Component	Description	Potential Impact on Reuse
Aluminium hydroxides	Primary constituent, forms the bulk of the sludge	Key for coagulation processes; influences sludge dewaterability
Organic matter	Derived from natural organic materials in treated water	Affects adsorption capacity; may require removal for some reuse applications
Inorganic matter	Includes sand, clay, and residual coagulants	Influences physical properties like density and porosity
Microorganisms	Bacteria and other microbes from water or treatment processes	Health and safety considerations for certain reuse applications
Metals	Trace amounts from raw water or coagulants (e.g., iron)	Regulatory and environmental considerations for disposal or reuse

According to past studies, composition of typical alum sludge samples is given in Table 2.4 and Table 2.5.

Table 2.4: Chemical components of typical alum sludge

(Mazari et al., 2018)

Elements	Weight (%)	Elements	Weight (%)
Carbon	10.98	Potassium	1.35
Oxygen	43.45	Copper	0.74
Aluminium	23.64	Chlorine	0.89
Silicon	11.23	Sulphur	0.86
Iron	2.22	Zinc	0.51
Calcium	1.91	Nickel	0.31
Magnesium	0.92	Titanium	0.36

Table 2.5: Physicochemical characteristics of alum sludge

(Dassanayake et al., 2015)

Parameter	Unit	Range	Parameter	Unit	Range
pH	-	5.12–8.00	EC	dS m^{-1}	0.36–1.66
CEC	cmol kg^{-1}	13.6–56.5	Sand	%	60.4–69.0
Silt	%	17–23	Clay	%	14–16.6
Total Carbon	g kg^{-1}	127–188	Organic matter	g kg^{-1}	63–144
Total N	g kg^{-1}	4.0–4.8	NH$_4$-N	g kg^{-1}	0.022–0.263
NO$_3$-N	g kg^{-1}	0.035–0.298	Total P	g kg^{-1}	3.13–3.5
Total Al	g kg^{-1}	27–153	Total Fe	g kg^{-1}	4.87–37
Total Ca	g kg^{-1}	2.2–11.7	Total Mg	g kg^{-1}	2.4–7.9
Total Mn	g kg^{-1}	0.8–2.99	Total Zn	mg kg^{-1}	53.3–160
Total Cu	mg kg^{-1}	35–624	Total Ni	mg kg^{-1}	10.9–60
Total Pb	mg kg^{-1}	2.5–69	Total Cr	mg kg^{-1}	19.1–81
Total Cd	mg kg^{-1}	0.12	Total Hg	mg kg^{-1}	0.02–0.46
Cl^{-1}	mg kg^{-1}	15.89–16.41	SO$_4^{2-}$	mg kg^{-1}	8.57–9.73

The complexity of alum sludge, in terms of chemical composition and physicochemical characteristics as described, also influence its diverse potential for reuse, e.g., as agricultural soil amendments, construction materials. The identification of its individual components and their concentrations is important for the selection of suitable and safe reuse strategies to afford effective protection of the environment and compliance with environmental regulations.

Characterisation Techniques

Past studies have employed a variety of analytical techniques to determine the physical, chemical, and biological characteristics of alum sludge. These methods are designed to evaluate the sludge's composition, structure, and potential applications, especially in pollution control and resource recovery. Here are some key methods used to characterize alum sludge:

- Granulometry (Particle Size Distribution)

Particle size distribution is a fundamental property of alum sludge, impacting its dewatering and disposal. Techniques such as sieve analysis, which separates particles into size ranges using a series of sieves, and laser diffraction, which measures light scattering as a function of particle size, are commonly used. Laser diffraction offers a rapid and detailed particle size distribution analysis compared to traditional sieve analysis (Blott & Pye, 2006).

- Moisture Content Determination

The moisture content of alum sludge is crucial for handling and disposal strategies. It is typically determined by drying a known weight of sludge at 105°C until a constant weight is achieved, providing the basis for calculating moisture content (C. Chen, 2003).

- pH and Conductivity Analysis

The pH and conductivity of alum sludge are critical indicators of acid-base balance and ionic strength, respectively. They play a significant role in the evaluation of chemical stability and potential environmental impact of the sludge. pH meters and conductivity meters are required for the measurement of these parameters in environmental monitoring and in wastewater treatment processes (Boczkaj & Fernandes, 2017; Gallardo-Gonzalez et al., 2019; Weerasinghe et al., 2015).

- Elemental Analysis (ICP-OES, XRF)

Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) and X-ray Fluorescence (XRF) are two established instrumental techniques routinely used for determining the elemental composition of various materials, including alum sludge. These approaches play an important role in determining the reuse potential or hazardous qualities of alum sludge by delivering the detailed elemental breakdown of the material (Yang et al., 2006).

ICP-OES works by atomizing the sample followed by exciting the atoms/ions into emitting light at specific wavelengths. By measuring the intensity of this light, the elements present and their concentration are identified. ICP-OES is excellent for identifying trace levels of metals in alum sludge, providing a detailed description of the metal content which is crucial when assessing its environmental impact or possible re-use/disposal (González et al., 2017; Mitchell et al., 2012).

X-ray Fluorescence (XRF) provides rapid, non-destructive analysis of elemental composition. This elemental technique is based on the principle that when a material is exposed to X-rays, it emits fluorescent X-rays at wavelengths that are characteristic to the elements present within it (B. Wu et al., 2023). XRF can provide an elemental overview of alum sludge in minutes, making it ideal for initial screenings and rapid assessments. While it may not exhibit the sensitivity of ICP-OES for trace elements, its immediate turnaround and minimal sample preparation requirements result in an ideal technique for in-field analyses and large-scale screenings (Mejía-Piña et al., 2016).

- Organic Matter Content (TOC, COD, BOD)

Total Organic Carbon (TOC), Chemical Oxygen Demand (COD) and Biological Oxygen Demand (BOD) are critical metrics for quantifying organic matter content in alum sludge (Alewi et al., 2022). Organics are important parameters needed to better understand the environmental impact, particularly on water bodies, and potential energy recovery (such as biogas production) from the sludge.

Chemical Oxygen Demand (COD) measures the total amount of oxygen required to oxidize all soluble and particulate organic matter in water. It is a critical parameter in evaluating the organic pollution level in alum sludge and its expected impact on receiving water bodies (J. Lee et al., 2016). Biological Oxygen Demand (BOD) measures the amount of oxygen required by aerobic microorganisms to break down the organic material in water over a specific time period (Nayl et al., 2017). It is a vital indicator of how much biodegradable organic material is present in sludge, which is important for both pollution control and assessing the sludge's suitability for biological treatment processes or energy recovery.

Total Organic Carbon (TOC) is a direct measure of the total amount of carbon (organic and inorganic) present in organic compounds in alum sludge (Alewi et al., 2022). It is a rapid, simple method that can accurately reflect the water pollution level, so it is taken into consideration as an alternative to BOD or COD. TOC analysis is especially critical when assessing whether a sludge could yield valuable biogas, as TOC indicates the quantity of organic carbon available for microbial digestion (J. Lee et al., 2016).

- Microbial Analysis

Microbial analysis is performed by using both culture-based techniques and DNA sequencing to examine and quantify the microbial populations within alum sludge. These methodologies are standard tools in the fields of environmental science and microbiology and provide a comprehensive view of the microbiological constitution of sludge samples (Albertsen et al., 2015). Culture-based techniques are used to grow and identify a wide range of microorganisms, thereby providing information on the types and abundance of microbial life in a sample. This traditional approach is useful for detecting and quantifying known species of bacteria, fungi, and other microorganisms (Cummings et al., 2016).

DNA sequencing enhances our understanding by identifying both culturable and unculturable microbes, crucial for revealing the comprehensive microbial landscape in sludge, including hard-to-cultivate organisms (Guo et al., 2017). It enables the detection of genes indicating pathogens or biodegradation capabilities, essential for assessing health risks and pollutant breakdown potential in sludge (R. Zhao et al., 2019). Combined, culturing and DNA sequencing provide a comprehensive approach to studying alum sludge's microbial communities. They help in identifying microbes, understanding biological functions, and assessing environmental impacts, including pathogen presence and biodegradation capacity. This knowledge supports the development of effective sludge management and treatment strategies, ensuring compliance with health and environmental standards.

- Biological Assays

Biological assays provide a comprehensive suite of tests to evaluate the impact of alum sludge on different ecosystems, crucial for environmental science and toxicology. These assays, including toxicity tests and microbial activity evaluations, are fundamental for understanding the environmental consequences of using alum sludge in landfills, as soil amendments, or in aquatic environments (Hassan et al., 2016).

Toxicity tests help determine the sludge's harmful effects on aquatic life, plants, and soil organisms by identifying toxic concentration thresholds under controlled conditions. This data is vital for establishing safe sludge application rates that won't harm ecosystem health (van Dam et al., 2016).

Moreover, analysing microbial activity is key to assessing alum sludge's effect on microbiomes essential for soil and water health, impacting nutrient cycling, organic decomposition, and soil fertility. Observing shifts in microbial dynamics and health offers insights into potential changes in ecosystem services upon sludge introduction (Zheng et al., 2020).

- Scanning Electron Microscopy (SEM)

Scanning Electron Microscopy (SEM) is a vital technique for the high-resolution imaging of the microstructure of alum sludge, revealing exquisite detail of its particle morphology and surface characteristics. Sludge particles can be imaged in intimate, three-dimensional complexity using SEM, enabling investigations into the elaborate physical features of sludge particles (e.g., their size, shape, and texture), which are central to understanding their reactivity and possible applications in environmental management (Odziomek et al., 2017). For example, detailed surface imaging and chemical analysis of sludge particles conducted by ESEM (Environmental Scanning Electron Microscopy)/EDS (Energy-Dispersive X-ray Spectrometry) has shown highly significant differences in surface topography and elemental composition of sludge from different treatment systems (Holbrook et al., 2006). Moreover, the use of SEM to examine sludge aggregates has revealed self-similar aggregates with fractal characteristics, providing quantitative descriptions of sludge compactness and morphology (Smoczyński et al., 2014).

Extracted SEM image of alum sludge is indicated in Figure 2.1 (Mazari et al., 2018).

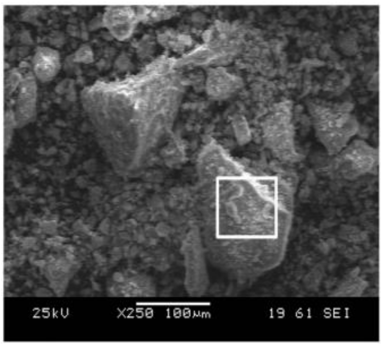

Figure 2.1: SEM image of alum sludge

- X-ray Diffraction (XRD)

Alum sludge characterisation for its crystalline structure revealing the mineral phases present can also be carried out using X-ray Diffraction (XRD), which is an essential analytical technique (Ali et al., 2022). The basis of this method is the interaction of X-rays with the crystal lattice of the sample being analysed. The diffraction patterns that emerge from this interaction give detailed information about the atomic structure, which can be used for phase identification and hence mineralogical changes. The changes in mineralogy of alum sludge can result in corresponding changes in its behaviour and potential applications, such as environmental remediation, construction materials, and possibly even agriculture (Hansford et al., 2017; Prescher & Prakapenka, 2015).

- Fourier Transform Infrared Spectroscopy (FTIR)

Fourier Transform Infrared Spectroscopy (FTIR) stands out as a key method for pinpointing organic compounds and functional groups in alum sludge, illuminating the complex organic structure it contains. It facilitates identifying diverse organic materials such as humic substances, polysaccharides, and biopolymers (Nandiyanto et al., 2019). This in-depth examination is essential for comprehending the interaction between alum sludge and pollutants, along with its capacity for releasing nutrients (Meissl et al., 2007).

Nandiyanto et al. (2019) offer an extensive manual on deciphering FTIR spectra for organic substances. This approach is relevant to alum sludge, enabling a thorough evaluation of its organic constituents and assisting in recognizing particular organic compounds and functional groups found in the sludge (Nandiyanto et al., 2019).

The analysis by Chen et al. (2015) underscores the significance of FTIR in geological sciences for detailing organic matter in coal and shale. Similarly, for alum sludge, FTIR plays a crucial role in unravelling the complexity of the organic matrix, underlining the existence of humic substances and various biopolymers. These components are crucial for understanding the sludge's environmental interactions and its capacity for nutrient release (Chen et al., 2015).

Lopes et al. (2018) delve into the use of FTIR for chemically characterizing enamel, dentin, and bone, showcasing its proficiency in examining mineralized tissues. This method parallels the analysis of inorganic elements in alum sludge, providing a glimpse into the mineral phase and its possibilities for environmental cleanup or applications in construction and agriculture (Lopes et al., 2018).

The study by Meissl et al. (2007) confirmed FTIR's capability to quantify humic acid contents and respiration activity in biogenic waste. This capability could be vital in evaluating the stability and maturity of organic matter in alum sludge, providing a foundation on which to assess its behaviour and potential applications in a variety of environmental contexts (Meissl et al., 2007).

The references selected here underscore FTIR's key role in deciphering alum sludge's organic content and potential environmental ramifications. Identification of distinct organic compounds and functional groups in alum sludge leveraging FTIR spectroscopy significantly enhances the understanding of how alum sludge may interact with pollutants and its ability to release nutrients, which in turn can guide the appropriate application of alum sludge in environmental remediation, construction materials, and potentially, agricultural settings.

- Thermogravimetric Analysis (TGA)

Thermogravimetric Analysis (TGA) emerges as a pivotal analytical methodology for the evaluation of the thermal stability and composition of alum sludge, meticulously quantifying the mass changes of the specimen under strictly controlled thermal conditions (Heikkinen et al., 2004). This technique is instrumental in delineating the calorific value of the sludge, thereby providing a comprehensive understanding of its suitability for thermal treatment processes. By monitoring the weight fluctuations of the sludge as it is subjected to a controlled increase in temperature, TGA facilitates a nuanced insight into the material's thermal degradation behaviours and potential for energy recovery applications (Aniza et al., 2015).

Thermogravimetric Analysis (TGA) is identified as a critical tool for discerning the chemical stability and identifying the optimal thermal processing conditions for materials, inclusive of alum sludge. This exploration through TGA is fundamental in crafting strategies aimed at amplifying the utility of materials while ensuring their disposal or recycling processes are streamlined and effective (Moseson et al., 2020).

2.4. Different Applications of Alum Sludge

Alum sludge, a byproduct produced during the water purification process when aluminium sulphate serves as the primary coagulating agent, has long posed considerable disposal challenges. Historically, efforts to manage this by-product were focused on reducing its impact on the environment, often resulting in its relegation to landfills or other disposal facilities (Babatunde & Zhao, 2007). However, the shifting dynamics of environmental sustainability and the emphasis on resource conservation have led to a significant revaluation of alum sludge's role. Increasingly seen not just as a waste product but as a resource rich in beneficial properties, alum sludge is now being explored for its potential in various environmental and industrial applications (Babatunde & Zhao, 2007; Owaid, 2013).

This revaluation is supported by extensive research into the possibilities for reusing alum sludge, ranging from its application in agriculture and land restoration to its incorporation into construction materials and wastewater treatment. These innovative uses of alum sludge not only help alleviate the environmental and financial strains associated with its disposal but also contribute to the principles of a circular economy by transforming what was previously considered waste into valuable resources (Yang et al., 2006; Y. Q. Zhao et al., 2011)

Furthermore, leveraging alum sludge in sustainable initiatives is in line with global movements toward environmental preservation (W. Zhao et al., 2021). Repurposing alum sludge can help reduce the need for new raw materials, decrease greenhouse gas emissions from waste processing, and aid in the cleanup of polluted sites. This broader recognition of the utility of alum sludge opens new paths for innovation and sustainability, encouraging a more comprehensive approach to waste management and environmental protection (Muisa et al., 2020a).

In the following discussions, we will delve deeper into the diverse applications of alum sludge, underscoring its pivotal role in promoting sustainable practices. Through this detailed exploration, the importance of rethinking and widely adopting alum sludge use will be showcased, underlining its significance in safeguarding our environmental heritage for future generations.

2.4.1. Soil Amendment for Enhanced Productivity

The utilization of alum sludge, derived from water treatment processes, as a soil amendment has garnered attention due to its positive impacts on soil properties and agricultural outcomes. Here are the key aspects based on the past studies.

- Improvement in Soil Texture

The integration of alum sludge into soil compositions has demonstrated a marked enhancement in soil texture, thereby creating an environment that significantly benefits the growth of plant roots. This notable improvement is largely attributed to the sludge's aluminium-based constituents and organic content, which synergistically fortify the soil's physical framework (Muisa et al., 2020a).

- Enhanced Moisture Retention

Alum sludge's organic content plays a pivotal role in amplifying the soil's ability to retain moisture, a trait that proves especially advantageous in arid and semi-arid locales where the dearth of water constrains agricultural yield. Through its moisture-preserving properties, alum sludge contributes significantly to sustaining ideal soil hydration levels, thereby promoting plant development (Odimegwu et al., 2018).

- pH Adjustment

Alum sludge possesses the unique ability to modulate soil pH, rendering it more adaptable for a diverse spectrum of crops. This pH adjustment is vital for the optimal accessibility of nutrients within the soil, as alum sludge aids in neutralizing conditions that are excessively acidic or alkaline, thus ensuring a more effective nutrient absorption by plants (Zhao et al., 2021).

- Contribution to Sustainable Agriculture

Employing alum sludge thoughtfully as a soil amendment resonates with sustainable agricultural practices. It epitomizes an eco-conscious method for soil health management, waste minimization, and the boost of agricultural output, all while safeguarding the capacity of future generations to fulfil their requirements (Rahman et al., 2018).

Despite the numerous advantages associated with using alum sludge as a soil conditioner, such as soil improvement and increased agricultural yield, it is imperative to consider the possible negatives and challenges that accompany its application. One major concern is the potential for introducing harmful contaminants, such as heavy metals, into the soil and, consequently, the crops grown within it. This could compromise food safety and pose health risks (Harrison et al., 2006). Additionally, there are regulatory hurdles and a degree of public scepticism regarding the use of by-products from wastewater treatment, which may impede its widespread adoption. Incorrect usage of alum sludge might also lead to an imbalance in soil pH, adversely affecting plant development and the assimilation of nutrients (Seleiman et al., n.d.). The impact of alum sludge on soil ecosystems and biodiversity over the long term is yet to be fully understood, raising questions about the environmental sustainability of its use. Moreover, the logistical expenses tied to its distribution and application, coupled with the potential for phytotoxic effects stemming from elevated levels of certain elements in the sludge, introduce additional obstacles (Corrêa Martins et al., 2016).To navigate these concerns effectively, comprehensive risk evaluations, rigorous compliance with application protocols, and ongoing surveillance are essential to affirm the practice's sustainability and safety.

2.4.2. Innovations in Construction Materials

Investigations into the use of alum sludge for creating construction materials have unveiled its viability, underscoring a sustainable pathway towards minimizing waste and integrating green substitutes for traditional building substances (Ali Dawood et al., 2019). This innovative application enables the conversion of alum sludge into various construction form such as bricks and blocks, showcasing an effective strategy to lessen the ecological impact associated with building projects. This approach not only contributes to waste mitigation but also heralds the advent of eco-conscious alternatives in the construction realm, marking a significant step towards sustainable development practices (Owaid, 2013).

Dawood et al. (2019) uncovered that alum sludge could serve as an efficient alternative to fine aggregates in asphalt formulations, pointing to its potential role in the construction of pavements. Concurrently, Vicenzi et al. (2005) revealed that blending alum sludge with clay for the creation of ceramics could result in building materials whose qualities match those of commercially available products. These findings collectively emphasize the adaptability of alum sludge as a foundational component in the manufacture of construction materials. This promising strategy for repurposing this by-product underscores a significant stride towards recycling and environmental stewardship.

The introduction of alum sludge into the construction sector offers a sustainable solution for recycling, yet it faces several challenges. Environmental concerns, particularly about potential contaminant leakage like heavy metals, necessitate comprehensive testing and strict regulatory compliance to ensure safety (De Carvalho Gomes et al., 2019). The variability in alum sludge's characteristics, depending on its source and processing, could affect the quality and performance of construction materials, requiring further processing for standardization. Additionally, market acceptance might be hindered by perceptions of inferior quality or safety concerns, calling for detailed testing, demonstration projects, and educational efforts to gain trust and support from industry professionals and consumers alike. Overcoming these obstacles is vital for the successful adoption of alum sludge in sustainable construction practices (Ali Dawood et al., 2019).

2.4.3. Circularity in Wastewater Treatment

The practice of repurposing alum sludge in wastewater treatment as a coagulant or adsorbent exemplifies a sustainable approach that resonates with circular economy principles, optimizing resource use and markedly boosting the efficacy of contaminant removal, including heavy metals and dyes. This innovative reuse underscores a dedication to sustainable water management and environmental preservation (Zhao et al., 2011).

Nonetheless, reintroducing alum sludge in this context brings forth several concerns. The potential for residual contaminants to leach from the sludge raises environmental and health risks. The variability in alum sludge's composition, influenced by its origin and processing, may impact its uniformity and efficiency as a treatment agent, leading to inconsistent treatment outcomes and complicating process management. Furthermore, without effective management strategies, the accumulation of alum sludge could pose significant disposal issues (Muisa et al., 2020a; Zhou & Haynes, 2010).

These challenges highlight the need for rigorous research, technological advancements, and collaborative efforts among stakeholders to enhance the reuse of alum sludge in wastewater treatment. By tackling these issues, we can amplify the benefits of this practice, ensuring its role in sustainable water management and the broader circular economy framework.

2.4.4. Sustainable Management of Landfills

Using alum sludge as a daily cover for landfills embodies an inventive approach in the realm of sustainable waste management. It presents multiple benefits, including the effective suppression of odours, reduction in the attraction of pests, and a decrease in leachate formation, all of which contribute significantly to the eco-friendly operation of landfill sites. The application showcases the adaptability of alum sludge in environmental conservation endeavours and supports the objectives of sustainable landfill management by offering a greener alternative to conventional cover materials (Renou et al., 2008).

Nonetheless, this innovative use is not without its challenges and potential drawbacks. The effectiveness of alum sludge as a cover material hinges on its physical attributes, such as hydraulic conductivity and structural integrity. Without appropriate stabilization or treatment, it may fall short in providing the necessary barrier to prevent the migration of leachate or the release of gases. Moreover, concerns linger regarding the long-term environmental repercussions of alum sludge usage, particularly the risk of contaminant leaching into the surrounding soil and water sources. Ensuring the environmental safety of using alum sludge as a landfill cover necessitates comprehensive testing and strict regulatory compliance (Balkaya, 2016).

Ongoing research into the employment of alum sludge in landfills underscores its potential as an effective strategy for waste management and environmental sustainability. Yet, a detailed examination of its characteristics, treatment methodologies, and environmental impacts is crucial for its successful integration. Future investigations and technological innovations are key to navigating these challenges and solidifying alum sludge's role as an advantageous landfill cover option (Zhao et al., 2021).

2.4.5. Phosphorus Removal from Water

Alum sludge has emerged as a noteworthy material for phosphorus extraction from aquatic systems, demonstrating its capabilities as a cost-effective and efficient solution to mitigate nutrient pollution (Mohammed & Rashid, 2012). Its substantial aluminium hydroxides content facilitates a strong binding with phosphorus, leading to a notable decrease in its levels in wastewater and aiding in the prevention of eutrophication in water ecosystems. The deployment of alum sludge not only underscores its role in environmental conservation efforts but also presents a novel response to the challenge of nutrient pollution in aquatic environments (Yang et al., 2006).

However, the use of alum sludge in phosphorus removal processes is accompanied by certain limitations. There are concerns over the potential release of aluminium into water during the phosphorus absorption phase, which could pose environmental hazards. The efficacy of alum sludge as a phosphorus adsorbent may also vary due to factors like pH levels, the presence of additional substances in the wastewater, and the sludge's inherent physical properties, which could influence its adsorptive performance and overall effectiveness (V. T. Truong & Kim, 2021). Moreover, the management of alum sludge post-usage as an adsorbent introduces a further obstacle, necessitating eco-friendly disposal or additional treatment measures to prevent ecological damage (Bashir et al., 2019).

Nonetheless, the application of alum sludge for phosphorus removal remains an area ripe for research, with ongoing studies aiming to boost its adsorptive efficiency and tackle associated environmental issues. The pursuit of novel strategies to enhance the phosphorus binding capacity of alum sludge and guarantee its safe employment in water treatment is a crucial endeavour towards the realization of sustainable water management practices (Lee et al., 2015; Mohammed & Rashid, 2012).

The application of alum sludge in phosphorus removal distinguishes itself as an exceptionally effective and eco-friendly method among its various uses. This strategy not only tackles the critical issue of nutrient pollution in aquatic systems but also aligns with the concepts of waste valorisation and resource recovery (Wu et al., 2019). This initiative not only advances environmental sustainability but also paves the way for inventive recycling of waste materials. The wide-ranging applications of alum sludge highlight its capacity as a dynamic resource, pushing for a shift towards the sustainable management of by-products from water treatment processes (Mohammed & Rashid, 2012).

2.5. Mechanisms of Phosphorus Removal Using Alum Sludge

The utilization of alum sludge for the extraction of phosphorus from aquatic environments capitalizes on its inherent chemical composition, predominantly the presence of aluminium hydroxides (Mohammed & Rashid, 2012). This section outlines the mechanisms through which alum sludge facilitates phosphorus removal, contributing to water quality improvement and eutrophication prevention. Insights from recent studies enhance our understanding of these processes, indicating a multifaceted approach to nutrient pollution control.

2.5.1. Adsorption

The adsorption process is central to phosphorus removal from water, harnessing the natural qualities of alum sludge. This removal is primarily facilitated by the sludge's extensive surface area and high concentration of aluminium hydroxides, which act as effective adsorbents for phosphate ions in wastewater (Babatunde et al., 2010). Numerous studies have confirmed the capability of alum sludge to capture phosphorus, demonstrating its effectiveness in reducing phosphorus levels in both synthetic and real-world municipal wastewater environments (Georgantas and Grigoropoulou, 2005).

The effectiveness of alum sludge as a phosphorus adsorbent is due to its strong affinity for phosphate ions, engaging in several adsorption processes. Initially, ligand and anion exchange and electrostatic attractions dominate, allowing phosphorus ions to quickly adhere to the surface of alum sludge particles (Yang et al., 2006). Over time, slower mechanisms such as intraparticle diffusion and chemical precipitation enhance phosphorus removal. Intraparticle diffusion involves the movement of phosphorus ions into the pores of the sludge particles (Fu et al., 2008), while chemical precipitation results in the formation of stable and insoluble aluminium-phosphate complexes (Mohammed & Rashid, 2012).

The adsorption behaviour of alum sludge often aligns with the pseudo-second-order model, indicating that the rate of adsorption is proportional to the number of available adsorption sites. This model suggests that the process tends towards forming a single layer of molecules on the adsorbent surface, a phenomenon supported by the Langmuir isotherm model in over 80% of reviewed studies (Mohammed & Rashid, 2012). The Langmuir isotherm model describes the adsorption of molecules onto a homogeneous surface with a finite number of identical sites, each capable of binding one molecule. Additionally, the Freundlich isotherm model, which describes adsorption on heterogeneous surfaces, has also been applied in several studies, highlighting the versatility of alum sludge in varying conditions (Mohammed & Rashid, 2012).

Furthermore, thermodynamic assessments of changes in Gibbs free energy, enthalpy, and entropy provide insights into the nature of the adsorption process. These assessments indicate that phosphorus adsorption by alum sludge is endothermic, meaning it requires energy (Maqbool et al., 2016). The positive changes in Gibbs free energy suggest that the adsorption process is spontaneous under the conditions studied, while the positive changes in enthalpy and entropy imply that the process involves the absorption of heat and an increase in disorder at the solid-liquid interface (Maqbool et al., 2016).

The adsorption efficiency of alum sludge can vary significantly, influenced by several factors. pH levels play a critical role, with optimal phosphorus removal typically occurring within a specific pH range (Mohammed & Rashid, 2012). The presence of competing ions in the wastewater can also affect adsorption efficiency, as these ions may compete with phosphate ions for adsorption sites on the alum sludge. Additionally, the specific characteristics of the alum sludge, such as its surface area and pore structure, depend on the raw water source and treatment process used to generate the sludge (Georgantas and Grigoropoulou, 2005). These factors can either enhance or diminish the phosphorus adsorption capacity, highlighting the importance of thoroughly analysing alum sludge properties for broader application.

In summary, the effectiveness of alum sludge as an adsorbent for phosphorus results from its inherent properties and the adsorption mechanisms involved. While initial rapid adsorption processes are followed by slower diffusion and precipitation steps, the overall efficiency is influenced by various factors such as pH, competing ions, and the specific characteristics of the sludge. Understanding these factors is crucial for optimizing the use of alum sludge in wastewater treatment applications and addressing potential limitations in commercial settings due to reduced adsorption capacities under certain conditions (Mohammed & Rashid, 2012).

While adsorption is the primary mechanism for phosphorus removal using alum sludge, other notable methods also contribute to its effectiveness. These methods include chemical precipitation, ion exchange, and biofiltration. Details of these methods are explained in Table 2.6.

Table 2.6: Other mechanisms of phosphorus removal using alum sludge

Removal Mechanism	Description	Reference/s
Chemical Precipitation	Chemical precipitation involves the transformation of dissolved phosphorous by reaction with metal ions within the alum sludge to form an insoluble precipitate. It forms an effective process in the removal of phosphorus concentration from wastewater and is often facilitated through aluminium hydroxide. The end product of this chemical reaction is stable and insoluble complexes of aluminium phosphate. This method has been widely studied and has shown significant phosphorus removal efficiencies in both synthetic and real wastewater conditions. Chemical precipitation using aluminium salts has been proven effective in achieving high phosphorus removal efficiencies, with optimal conditions varying by factors such as pH and coagulant dosage.	(Agostina, Simona and Giorgia, 2020; Georgantas and Grigoropoulou, no date; de Barros, Benincá and Zanoelo, 2023)
Ion Exchange	The process of ion exchange occurs when phosphate ions present in wastewater are exchanged with other ions in alum sludge. Thus, it is because the absorption affinity of sludge to phosphate ions is relatively high compared to other ions that phosphorus can be effectively removed from water. Phosphorus removal takes place efficiently since a large number of sites are available for ion exchange because of the high concentration of aluminium and other metal hydroxides in the sludge.	(Babatunde and Zhao, 2010)
Biofiltration	Phosphorus removal using alum sludge is improved through increased biological processes related to biofiltration, while the use of alum sludge in constructed wetlands and reed beds can be used as a substrate material adsorbing phosphorus and supporting plant uptake by promoting microbial growth. This combination of physical and chemical properties of alum sludge with biological activity of both microbes and plants allows high phosphorus removal efficiency.	(Zhao et al., 2009)
Thermal Treatment	Thermal treatment of alum sludge will improve its phosphorous removal capacities by alteration of a	(V. T. Truong & Kim, 2021)

	few physical and chemical properties. Pyrolysis and drying processes increase the surface area, porosity, and removes organic matter, which can be a competitor for the phosphorus at the adsorption sites. Thus, thermally treated alum sludge was reported to increase the adsorption capacity towards phosphorus and was shown to be a potential application in wastewater treatment.	
Coagulation and Flocculation	In coagulation and flocculation processes, alum sludge is used to aggregate fine particles and dissolved substances, including phosphorus, into larger flocs that can be easily removed by sedimentation or filtration. This method is particularly effective when used in combination with other coagulants, such as polymeric aluminium chloride, enhancing the overall phosphorus removal efficiency.	(Ebeling et al., 2003; Ghafari et al., 2009a)

Finally, it was illustrated that although adsorption mechanism has been primarily focused on phosphorus removal using alum sludge some other techniques including chemical precipitation, ion exchange biofiltration thermal treatment and coagulation and flocculation can provide higher efficiencies in the utilization of these types of waste materials. These techniques exploit the characteristics of alum sludge and could be further improved to removal phosphorus in different specific wastewater treatment circumstances. Learning and implementation of these techniques will definitely help to treat the wastewater in an efficient way without harming earth.

2.6. Operational Parameters Influencing Alum Sludge Performance

This subsection discusses the operational key parameters, which significantly impact the efficiency and effectiveness of alum sludge in phosphorus removal from wastewaters. The understanding and optimization of these parameters are very important to enhance the cost effectiveness and performance of alum sludge as a treatment material.

2.6.1. pH Levels

The pH level of wastewater plays a critical role in determining the effectiveness of alum sludge in phosphorus removal, as it directly influences the solubility of aluminium and the formation of aluminium hydroxides, which are essential for capturing phosphorus. The formation of aluminium hydroxides is most efficient within a pH range of 5 to 7, which provides an ideal surface for phosphorus adsorption. This optimal pH range allows for the precipitation of aluminium hydroxides that actively bind with phosphate ions, enhancing phosphorus removal efficiency (Liu et al., 2010).

When the pH falls below this optimal range, the solubility of aluminium increases, which may lead to a higher concentration of aluminium ions in the solution. While this could theoretically enhance the availability of aluminium for binding with phosphorus, it simultaneously reduces the formation of the necessary aluminium hydroxides, thereby lowering the overall efficiency of phosphorus removal. The process becomes less efficient because fewer hydroxide sites are available for adsorption, leading to suboptimal performance (Ojha et al., 2019).

Conversely, when the pH exceeds 7, aluminium becomes less soluble, resulting in the formation of less reactive aluminium compounds, such as aluminium oxides, which are not as effective in capturing phosphorus. This decreased solubility at higher pH levels limits the availability of aluminium in its most reactive form, thus diminishing the overall phosphorus removal efficiency. For example, Maqbool et al. (2016) found that phosphorus removal efficiency significantly decreased as the pH increased above 7, highlighting the critical need to maintain pH levels within the optimal range for effective treatment (Maqbool et al., 2016).

Moreover, in cases where pH fluctuates outside this range, additional chemical treatments may be required to adjust the pH back to the optimal level, adding complexity and cost to the wastewater treatment process. For instance, studies have shown that adjusting the pH using acids or bases can restore the phosphorus removal efficiency of alum sludge to its optimal levels, but this process requires careful management to avoid secondary issues such as excessive sludge production or chemical overdosing (Babatunde & Zhao, 2010).

In summary, maintaining the pH of wastewater within the optimal range of 5 to 7 is critical for maximizing the efficiency of phosphorus removal using alum sludge. Deviations from this range can significantly impair the performance of alum sludge, either by reducing the formation of reactive aluminium hydroxides or by promoting the formation of less effective aluminium compounds. Therefore, careful monitoring and adjustment of pH levels are essential components of effective phosphorus removal strategies in wastewater treatment.

2.6.2. Dosage of Alum Sludge

The dosage of alum sludge is a critical factor that directly influences the efficiency of phosphorus removal in wastewater treatment. Increasing the dosage typically enhances the removal rate, as it provides a greater number of reactive sites for phosphorus binding. This relationship, however, follows a saturation curve: initially, as the dosage increases, the phosphorus removal efficiency improves significantly due to the availability of more adsorption sites on the alum sludge particles. Mohammed and Rashid (2012) demonstrated that phosphorus removal efficiency increased as the dosage of alum sludge was raised from 10 g/L to 40 g/L. However, beyond this point, the rate of improvement diminished, indicating that the adsorption sites were approaching saturation (Mohammed & Rashid, 2012).

As the adsorption sites on the sludge particles become saturated, additional alum sludge does not substantially increase phosphorus removal efficiency. This plateauing effect is due to the fact that once the available sites on the sludge are fully occupied by phosphorus molecules, any excess sludge added will not contribute to further adsorption but will instead remain unused in the system. For instance, a study by Babatunde and Zhao (2010) showed that increasing the alum sludge dosage beyond a certain threshold did not lead to proportional increases in phosphorus removal, highlighting the importance of identifying an optimal dosage to avoid unnecessary material use (Babatunde & Zhao, 2010).

Moreover, excessively high dosages of alum sludge can introduce operational challenges. One significant issue is the increase in sludge volume, which complicates the management and disposal processes. Higher volumes of sludge require more space for storage, more energy for handling, and more resources for disposal, which can lead to higher operational costs and potential environmental impacts. This increase in sludge production can offset the benefits of enhanced phosphorus removal, particularly if the costs associated with sludge disposal outweigh the gains in treatment efficiency. For example, studies have shown that the costs associated with the disposal of large volumes of sludge can be substantial, potentially making the process less economically viable (Maqbool et al., 2016).

Additionally, an overly high dosage of alum sludge can lead to the formation of dense sludge cakes that are more difficult to dewater, further complicating the treatment process. This was observed in studies where high sludge dosages resulted in reduced sludge dewaterability, making it more challenging to manage the by-products of the treatment process (V. T. Truong & Kim, 2021).

While increasing the dosage of alum sludge can improve phosphorus removal efficiency by providing more reactive sites for adsorption, this effect is subject to diminishing returns once the adsorption sites become saturated. Beyond the optimal dosage, additional sludge not only fails to significantly enhance removal efficiency but also introduces operational challenges, such as increased sludge volume and disposal issues. Therefore, determining the optimal dosage is crucial for balancing the benefits of phosphorus removal with the practicalities of sludge management and disposal.

2.6.3. Contact Time

Contact time, or the duration during which alum sludge interacts with wastewater, is a critical factor in determining the efficiency of phosphorus removal. The adsorption process typically unfolds in two distinct stages: an initial rapid adsorption phase, followed by a slower phase as the system approaches equilibrium. During the initial phase, a significant portion of the phosphorus is quickly removed due to the abundant availability of active sites on the alum sludge. This rapid phase is characterized by a high rate of phosphorus adsorption as the sludge particles readily bind with the phosphorus present in the wastewater (Ojha et al., 2019).

As the system progresses into the second phase, the adsorption rate decreases, and the system gradually moves towards equilibrium. During this phase, most of the easily accessible adsorption sites on the alum sludge have already been occupied, and the remaining phosphorus removal occurs more slowly as it involves diffusion into less accessible sites or weaker binding interactions. This slower phase highlights the diminishing returns associated with extending contact time beyond a certain point (Babatunde & Zhao, 2010).

Optimizing contact time is essential for balancing treatment efficiency with operational practicality. If the contact time is too short, the system may not reach equilibrium, resulting in suboptimal phosphorus removal. For instance, studies have shown that insufficient contact time can leave a significant amount of phosphorus unbound, as the process has not been allowed to complete (Maqbool et al., 2016). On the other hand, excessively long contact times may be impractical for continuous treatment processes, where throughput and efficiency are critical. Extended contact times can also lead to increased operational costs without substantial gains in removal efficiency.

In batch systems, where wastewater is treated in discrete batches rather than continuously, optimal contact times generally range from 1 to 2 hours for effective phosphorus removal. This time frame allows the system to reach a near-equilibrium state, ensuring that a significant portion of the phosphorus is removed without unnecessary delays. For example, in a study by Maher et al. (2015), it was found that a contact time of 90 minutes was sufficient to achieve over 90% phosphorus removal in a batch system, with little additional benefit observed beyond this duration (Maher et al., 2015).

While the initial rapid adsorption phase is crucial for capturing a large portion of phosphorus, the slower approach to equilibrium in the second phase necessitates an optimized contact time to ensure maximum removal efficiency. Balancing the need for sufficient contact time with the practical constraints of continuous or batch processing is essential for effective and efficient phosphorus removal in wastewater treatment using alum sludge.

2.6.4. Temperature

Temperature plays a crucial role in the kinetics of chemical reactions and the physical properties of alum sludge, significantly impacting its effectiveness in phosphorus removal. Generally, higher temperatures accelerate the reaction rates, leading to faster phosphorus adsorption. This is because increased thermal energy enhances the movement of molecules, thereby facilitating quicker interactions between phosphorus and the active sites on alum sludge. For instance, Truong & Kim (2021) demonstrated that higher temperatures improved the rate of phosphorus removal by alum sludge, particularly in the early stages of the adsorption process (V. T. Truong & Kim, 2021).

However, elevated temperatures can also introduce challenges. One such challenge is the increased evaporation rate, which can alter the concentration of wastewater. This change in concentration may lead to inconsistencies in treatment efficiency, as the altered balance of constituents can affect the chemical interactions necessary for effective phosphorus removal. Additionally, higher temperatures can potentially impact the stability of the alum sludge itself, causing it to lose effectiveness over time or become more difficult to manage within the treatment system.

Conversely, lower temperatures tend to slow down the kinetics of phosphorus adsorption, requiring longer contact times or higher sludge dosages to achieve comparable removal efficiencies. In colder climates or during winter months, wastewater treatment facilities may experience reduced phosphorus removal efficiency due to the decreased reaction rates. For example, Babatunde & Zhao (2010) found that at lower temperatures, the phosphorus removal process was significantly slower, necessitating adjustments in either contact time or alum sludge dosage to maintain desired treatment levels (Babatunde & Zhao, 2010).

Moreover, while increasing the operating temperature can enhance reaction kinetics, it also leads to higher energy costs, particularly if artificial heating is required to maintain the desired temperature range. This trade-off between enhanced efficiency and increased energy consumption must be carefully considered when designing and operating wastewater treatment systems. For instance, Maher et al. (2015) suggested that while higher temperatures can improve treatment efficiency, the associated energy costs may outweigh the benefits unless the temperature increase can be achieved through passive means or waste heat recovery (Maher et al., 2015).

Selecting an appropriate operating temperature is critical to balancing phosphorus removal efficiency with energy costs. While higher temperatures can expedite phosphorus adsorption and improve overall treatment efficiency, they must be managed carefully to avoid potential drawbacks such as increased evaporation and energy consumption. Conversely, lower temperatures may slow down the process, requiring compensatory measures such as extended contact times or increased sludge dosages to maintain effective phosphorus removal.

2.6.5. Sludge Characteristics

The physical and chemical characteristics of alum sludge, such as particle size, surface area, porosity, and organic matter content, significantly impact its capacity for phosphorus removal. Smaller particles with larger surface areas generally provide higher adsorption capacities because they offer more active sites for phosphorus binding. For instance, Babatunde & Zhao (2010) demonstrated that alum sludge with finer particle sizes had a significantly higher capacity for phosphorus adsorption, primarily due to the increased surface area available for interaction with phosphorus molecules (Babatunde & Zhao, 2010)

Porosity is another crucial factor influencing the performance of alum sludge. Highly porous sludge provides more internal surface area, which can enhance the adsorption of phosphorus. The increased porosity allows for better diffusion of phosphorus ions into the internal structure of the sludge particles, thereby improving overall adsorption efficiency. For example, studies have shown that alum sludge with higher porosity exhibited greater phosphorus removal efficiency, as the internal pore structure provided additional sites for phosphorus to bind (Maher et al., 2015).

However, the presence of organic matter in the sludge can negatively affect phosphorus removal. Organic matter competes with phosphorus for adsorption sites on the alum sludge, reducing the number of available sites for phosphorus binding. Additionally, organic matter can form complexes with aluminium, further obstructing the adsorption of phosphorus. This issue is particularly significant in sludges derived from sources with high organic content, where the competition for adsorption sites can significantly lower phosphorus removal efficiency (V. T. Truong & Kim, 2021).

To mitigate these effects, pre-treating the sludge to remove or reduce its organic content can be highly effective in improving phosphorus removal. Techniques such as thermal treatment, chemical oxidation, or washing can be employed to decrease the organic load in the sludge, thereby increasing the availability of active sites for phosphorus binding. Truong & Kim (2021) found that thermally treated alum sludge, which had reduced organic content, exhibited significantly higher phosphorus adsorption capacity compared to untreated sludge, underscoring the importance of pre-treatment in optimizing sludge performance (V. T. Truong & Kim, 2021).

In summary, optimizing the physical and chemical characteristics of alum sludge, particularly by managing particle size, surface area, porosity, and organic matter content, is critical for maximizing its phosphorus removal capacity. Pre-treatment processes that reduce organic content can significantly enhance the effectiveness of alum sludge in wastewater treatment applications.

2.6.6. Mixing and Agitation

Effective mixing and agitation are crucial to ensure that alum sludge is evenly distributed throughout the wastewater, thereby maximizing its contact with phosphorus. Proper mixing helps prevent sludge particles from settling and ensures that the entire volume of wastewater is effectively treated. For instance, that optimal mixing conditions significantly improved phosphorus removal efficiency by maintaining a uniform distribution of sludge particles throughout the treatment process (Keeley et al., 2016).

However, the intensity and duration of mixing must be carefully managed. If the mixing is too vigorous, it can cause the re-suspension of settled sludge particles. This re-suspension can disrupt the treatment process by re-dissolving previously removed phosphorus, leading to reduced overall treatment efficiency. For example, Maher et al. (2015) observed that excessive agitation in the treatment system led to the re-introduction of phosphorus into the solution, negating some of the benefits of initial phosphorus removal (Maher et al., 2015).

The objective is to strike a balance where mixing is sufficient to enhance the contact between alum sludge and phosphorus without disrupting the removal process. Truong & Kim (2021) emphasized the importance of controlled mixing, noting that moderate agitation was necessary to maintain sludge suspension and maximize phosphorus removal, while avoiding the negative effects associated with excessive mixing (V. T. Truong & Kim, 2021). Additionally, studies by Babatunde & Zhao (2010) indicated that careful optimization of mixing speeds and durations can lead to significant improvements in treatment outcomes, as it ensures that the alum sludge remains adequately suspended without causing unnecessary turbulence (Babatunde & Zhao, 2010).

While effective mixing and agitation are essential for optimizing the performance of alum sludge in phosphorus removal, it is critical to manage these processes carefully. The goal is to achieve a level of mixing that ensures uniform sludge distribution and maximized contact with phosphorus, while avoiding the pitfalls of excessive agitation that could compromise treatment efficiency.

2.6.7. Presence of Competing Ions and Organic Matter

The presence of competing ions, such as sulphate or nitrate, along with organic matter in wastewater, can significantly impact the efficiency of alum sludge in phosphorus removal. These substances can compete with phosphorus for adsorption sites on the alum sludge or form complexes with aluminium, thereby diminishing the sludge's effectiveness. For example, Ghafari et al. (2009) demonstrated that sulphate ions could bind to aluminium hydroxides, effectively reducing the number of available sites for phosphorus adsorption. This competition can significantly lower the phosphorus removal efficiency, particularly in wastewater with high sulphate concentrations (Ghafari et al., 2009).

Similarly, high levels of organic matter in wastewater can further reduce the availability of adsorption sites. Organic matter often occupies these sites or forms complexes with aluminium, leaving fewer sites available for phosphorus removal. Babatunde and Zhao (2010) found that in wastewater with elevated organic content, the phosphorus removal efficiency of alum sludge was significantly compromised due to the competition between organic matter and phosphorus for the available adsorption sites (Babatunde & Zhao, 2010).

To address these challenges, pre-treatment methods such as coagulation or flocculation may be necessary to remove or reduce these interfering substances before applying alum sludge for phosphorus removal. Chiavola et al. (2020) highlighted that pre-treating wastewater to reduce sulphate and organic matter content significantly enhanced the efficiency of subsequent phosphorus removal using alum sludge (Chiavola et al., 2020). These pre-treatment processes help to minimize the competition for adsorption sites, ensuring that alum sludge can effectively capture and remove phosphorus from the wastewater.

The efficiency of alum sludge in phosphorus removal can be significantly affected by the presence of competing ions and organic matter in wastewater. Pre-treatment processes like coagulation and flocculation are essential strategies to mitigate these effects and enhance the overall effectiveness of phosphorus removal using alum sludge.

Effectively understanding and optimizing these operational parameters is essential for maximizing the performance of alum sludge in phosphorus removal from wastewater. By precisely managing factors such as pH, dosage, contact time, temperature, sludge properties, mixing, and the presence of competing ions, wastewater treatment facilities can greatly improve phosphorus removal efficiency. This careful control makes alum sludge a more viable and cost-effective treatment option.

2.7. Sustainability and Environmental Considerations of Using Alum Sludge

The use of alum sludge in phosphorus removal from wastewater presents a promising solution within the broader context of sustainable waste management and environmental protection. As a byproduct of water treatment processes, alum sludge embodies both challenges and opportunities. While its disposal poses significant environmental concerns, its repurposing within a circular economy framework offers a path towards sustainability. This section delves into the environmental benefits, potential risks, and long-term viability of utilizing alum sludge in wastewater treatment, emphasizing its role in promoting sustainability while navigating the complexities associated with its application.

2.7.1. Waste Utilization and Circular Economy

Alum sludge, a byproduct of water treatment, poses significant challenges in terms of disposal due to its volume and potential environmental impact. However, its repurposing for phosphorus removal transforms a disposal issue into a valuable resource, aligning with the principles of a circular economy. The use of alum sludge for phosphorus removal reduces the need for virgin materials, lowers disposal costs, and mitigates the environmental impact associated with traditional disposal methods such as landfilling or incineration. According to Babatunde and Zhao (2010), alum sludge is a highly effective and sustainable adsorbent for phosphorus, capable of significantly reducing the environmental burden of wastewater treatment processes (Babatunde & Zhao, 2010). Their study highlights how the reutilization of alum sludge not only promotes resource conservation but also contributes to the overall sustainability of wastewater treatment operations.

2.7.2. Environmental Benefits

The application of alum sludge in phosphorus removal offers substantial environmental benefits, particularly in combating phosphorus pollution, a leading cause of eutrophication in aquatic ecosystems. Eutrophication, driven by excessive phosphorus in water bodies, leads to algal blooms, hypoxia, and the subsequent collapse of aquatic ecosystems. By effectively removing phosphorus from wastewater, alum sludge plays a crucial role in preventing these adverse environmental outcomes. Research by Georgantas and Grigoropoulou (2005) has shown that alum sludge can significantly lower phosphorus levels in wastewater, thereby improving water quality and contributing to the protection of aquatic life (Georgantas & Grigoropoulou, 2005). Moreover, this approach supports broader environmental protection goals by maintaining the ecological balance of water bodies.

2.7.3. Potential Environmental Risks

Despite the clear environmental benefits, the use of alum sludge in wastewater treatment is not without risks. A key concern is the potential for aluminium leaching from the sludge into the environment, which could have harmful ecological and health implications if not carefully managed. Aluminium leaching can contribute to soil and water contamination, which may affect plant growth and aquatic life. Additionally, the accumulation of alum sludge in treatment facilities over time may lead to disposal challenges, especially if the sludge is not appropriately managed. Pradel and Aissani (2019) conducted a lifecycle assessment of sludge-based phosphate fertilizers and highlighted the environmental trade-offs associated with phosphorus recovery from alum sludge. Their study emphasizes the importance of managing phosphorus recovery processes to prevent unintended negative impacts, such as the release of contaminants during sludge processing (Pradel & Aissani, 2019).

2.7.4. Lifecycle Assessment

The long-term viability of using alum sludge for phosphorus removal is dependent on several factors, including its consistent availability, effectiveness, and adaptability to evolving wastewater treatment technologies. As wastewater treatment processes advance, the chemical and physical properties of alum sludge may change, potentially affecting its performance in phosphorus removal. Therefore, ongoing research and development are necessary to optimize the use of alum sludge and explore potential enhancements, such as chemical modifications or integration with other treatment methods. Tomei et al. (2020) highlight the importance of continued innovation and the need for supportive policies that encourage the reuse of waste materials in wastewater treatment, which can help ensure the sustainable and long-term use of alum sludge (Tomei et al., 2020).

Alum sludge for removal of phosphorus thus becomes a sustainable and eco-friendly solution in the wide context of wastewater treatment. Therefore, this kind of application has vital significance in preventing eutrophication and in circular economy considerations; however, these benefits should be weighed against the potential risks of aluminium leaching and environmental impacts from sludge disposal. A lifecycle approach to assessment is very important in underpinning the overall sustainability of alum sludge use; consequently, continuous research and supportive policies are very important in keeping alum sludge long-term sustainability viable as a resource in sustainable wastewater management.

2.8. Comparative Analysis with Other Phosphorus Removal Methods

Phosphorus removal is a vital component of wastewater treatment, necessary to prevent eutrophication in aquatic environments. Multiple techniques have been developed and utilized for this purpose, each offering distinct benefits and drawbacks. This section presents a comparative analysis of the effectiveness, cost, and sustainability of using alum sludge in conjunction with other phosphorus removal methods, including chemical precipitation, biological phosphorus removal (BPR), adsorption techniques, and membrane filtration. Through this comparison, the goal is to identify the most efficient and sustainable strategies for phosphorus removal in wastewater treatment.

Table 2.7: Comparative analysis of phosphorus removal methods

Removal Method	Phosphorus Removal Efficiency	Cost	Sustainability	Operational Considerations	Reference/s
Chemical Precipitation	80-99% P removal using aluminium or iron salts.	High due to continuous chemical input.	Moderately sustainable; large sludge volumes require disposal.	Requires careful dosing to avoid overuse of chemicals and excessive sludge production.	(Georgantas & Grigoropoulou, 2006.; Ghafari et al., 2009)
Adsorption Techniques	50-99% P removal depending on adsorbent; alum sludge achieves 70-85%.	Moderate; costs associated with adsorbent replacement or regeneration.	Sustainable with low operational costs using alum sludge; other adsorbents may require regeneration.	Requires monitoring of adsorbent saturation; regeneration may be needed for other materials.	(Mohammed & Rashid, 2012; Usman et al., 2022)
Biological Phosphorus Removal (BPR)	70-95% P removal without chemical addition, enhanced with alum sludge.	Low to moderate, depending on system setup.	Highly sustainable when integrated with other methods like alum sludge.	Sensitive to operational conditions (temperature, organic loading); can be enhanced with alum sludge.	(Nadeem et al., 2021)
Membrane Filtration	90-99.5% P removal, highly effective.	High; energy-intensive, especially with nanofiltration.	Sustainable when combined with pre-treatment (e.g., alum sludge) to	High operational costs; sensitive to fouling, requiring regular maintenance.	(Lee et al., 2019; Chiavola et al., 2020)

			reduce load and costs.		
Hybrid Approaches	90-99.5% P removal; combines benefits of chemical, biological, and adsorption methods.	Moderate to high, depending on combination.	Highly sustainable, leveraging strengths of multiple techniques.	Can be complex to manage; integration requires careful balancing of operational conditions.	(Lee et al., Nadeem et al., 2021)

In comparing the various phosphorus removal methods, it is evident that each technique has its own strengths and limitations in terms of efficiency, cost, sustainability, and operational complexity. Chemical precipitation and membrane filtration offer high phosphorus removal efficiencies, but they come with significant costs and environmental impacts due to chemical use and energy consumption, respectively (Agostina et al., 2020; Ghafari et al., 2009). Biological phosphorus removal (BPR) provides a sustainable and cost-effective option, especially when combined with alum sludge, although it requires stable environmental conditions to be most effective (Nadeem et al., 2021).

Adsorption techniques, particularly when using alum sludge, stand out as a highly feasible method for phosphorus removal. Despite being less efficient than some synthetic adsorbents, alum sludge offers a balanced approach, combining moderate phosphorus removal efficiency with low operational costs and high sustainability (Mohammed & Rashid, 2012). By repurposing a waste product, adsorption using alum sludge aligns well with circular economy principles and presents a viable option for large-scale wastewater treatment facilities seeking to minimize both costs and environmental impacts.

Overall, while no single method is universally superior, adsorption techniques using alum sludge provide a practical and sustainable solution for phosphorus removal, particularly in scenarios where cost-effectiveness and waste reduction are paramount.

2.9. Future Directions and Applications

As the demand for sustainable and cost-effective wastewater treatment solutions increases, alum sludge emerges as a promising agent for phosphorus removal. Although its current applications have proven effective, there are many opportunities to further enhance and broaden its use. This section explores future directions for the research and application of alum sludge, emphasizing advanced modifications, integration with other technologies, resource recovery, policy support, and global scalability. By focusing on these areas, alum sludge can become an increasingly vital component of modern wastewater treatment strategies.

2.9.1. Advanced Modification of Alum Sludge

One of the most promising directions for future research is the modification of alum sludge to enhance its phosphorus removal capabilities. Chemical, thermal, and biological modifications offer significant potential to increase the adsorption capacity and overall effectiveness of alum sludge in wastewater treatment. For example, chemical treatments such as acid washing can increase surface area and porosity, making more active sites available for phosphorus binding (Keeley et al., 2016). Thermal activation, where the sludge is heated to high temperatures, can also enhance its structural properties, leading to improved phosphorus removal efficiencies (Chiavola et al., 2020). However, these processes must be carefully optimized to balance benefits with energy consumption and potential environmental impacts.

Biological modification is a less explored but promising approach, where microorganisms are used to alter the surface properties of alum sludge, increasing its ability to adsorb phosphorus. Combining these modification techniques could yield even greater enhancements, creating a multifunctional material with superior performance in various wastewater conditions (Babatunde & Zhao, 2010).

To move these modifications from the lab to large-scale applications, future research should focus on pilot and full-scale studies to assess their practicality and cost-effectiveness in real-world settings. Developing standardized methods for modifying alum sludge will also be key to ensuring its widespread adoption in wastewater treatment facilities. Overall, advanced modification of alum sludge holds significant potential for creating more efficient and sustainable phosphorus removal solutions.

2.9.2. Integration with Other Treatment Technologies

Alum sludge has potential applications beyond standalone phosphorus removal. Integrating alum sludge with other wastewater treatment technologies, such as constructed wetlands, membrane bioreactors, or advanced oxidation processes, could provide synergistic benefits. For example, alum sludge could be used in constructed wetlands to enhance phosphorus removal while also providing structural support for plant growth. Similarly, combining alum sludge with membrane bioreactors might help reduce membrane fouling and extend membrane life, making the overall treatment process more efficient and cost-effective (V. T. Truong & Kim, 2021).

2.9.3. Resource Recovery and Circular Economy

Future applications of alum sludge could extend into resource recovery, aligning with circular economy principles. Research could explore the potential for recovering valuable materials, such as aluminium or phosphorus, from spent alum sludge. Additionally, using alum sludge as a soil amendment or in construction materials could provide sustainable end-use options, thereby reducing the environmental impact associated with sludge disposal. This approach would not only contribute to waste minimization but also add value to the wastewater treatment process by turning a waste product into a resource (Babatunde & Zhao, 2010).

2.9.4. Policy and Regulatory Support

For the widespread adoption of alum sludge as a phosphorus removal agent, supportive policies and regulatory frameworks will be crucial. Future research should focus on the environmental and health impacts of alum sludge application to inform policy decisions. Additionally, developing standardized guidelines for the use of alum sludge in wastewater treatment will ensure safe and effective application across different contexts. Policymakers could also incentivize the reuse of alum sludge through subsidies or credits, promoting its use as a sustainable alternative to conventional phosphorus removal methods (Tomei et al., 2020).

2.9.5. Global Applications and Scalability

While most research on alum sludge has been conducted in developed regions, there is significant potential for its application in developing countries, where cost-effective wastewater treatment solutions are urgently needed. Future studies could investigate the scalability of alum sludge-based phosphorus removal systems in different geographical and economic contexts. This research would involve pilot projects in diverse settings to assess the feasibility of large-scale implementation and identify any region-specific challenges or opportunities (Chiavola et al., 2020).

The future of using alum sludge for phosphorus removal from wastewater is promising, with multiple avenues for research and application. By exploring advanced modification techniques, integrating alum sludge with other treatment technologies, and promoting resource recovery, the environmental and economic benefits of alum sludge can be maximized. Additionally, supportive policies and global applications could further enhance the feasibility and scalability of alum sludge as a sustainable solution for phosphorus removal. Continued research and innovation will be key to unlocking the full potential of alum sludge in wastewater treatment.

3. METHODOLOGY

Among various sustainable and economical solutions for the treatment of wastewater, adsorption methods are particularly promising; within these approaches, utilizing alum sludge as a phosphorus removal agent has proven to be a viable option (Babatunde & Zhao, 2010). Eutrophication is a process where the over-saturation of phosphorus, one of the most recognized and problematic plant nutrients, leads to a significant increase in algae growth within aquatic ecosystems, ultimately causing imbalances in environmental factors. Traditional phosphorus removal methods are often costly and pose environmental challenges. Alum sludge, a byproduct of water treatment processes, offers an attractive alternative because it not only upcycles waste but also effectively removes phosphorus from wastewater (Georgantas & Grigoropoulou, 2005).

The goal of this study is to investigate the potential use of alum sludge for phosphorus removal as an inexpensive alternative material. This study involves a comprehensive approach, including the preparation of alum sludge samples, their characterisation, and testing. In addition, synthetic wastewater was prepared to assess the efficiency of the phosphorus removal treatment system. This research will systematically examine these factors, culminating in an assessment of the feasibility and practicality of using alum sludge for wastewater treatment.

The following sections will detail the experimental methodologies, including sample preparation processes and sludge characterisation procedures, as well as guidelines for synthetic wastewater specifications and methods for measuring phosphorus removal efficiencies.

3.1. Preparation of Alum Sludge Samples

3.1.1. Sampling Procedure

Alum sludge samples were collected from three different Water Treatment Plants (WTPs) that utilize aluminium sulphate ($Al_2(SO_4)_3$) as a primary coagulant. The details of the locations of the WTPs are given in the Table 3.1. The sludge samples were collected directly from the sedimentation tanks at each WTP. Sludge samples were collected from various points within the sedimentation tanks to ensure a representative mix. Approximately 5-10 individual samples were collected from each tank and combined to form a composite sample for each WTP.

Table 3.1: Locations of the sludge collected WTPs

Sample	Location	Water Source
Sample 1	Kandana WTP	Kalu river
Sample 2	Ambatale WTP	Kelani river
Sample 3	Biyagama WTP	Kelani river

The sampling was conducted at the same time to maintain consistency across all WTPs. These specific WTPs were selected due to their differing water sources, which are expected to influence the composition of the alum sludge. Kandana WTP draws water from the Kalu River, while both Ambatale and Biyagama WTPs source their water from the Kelani River. The selection aimed to provide a comparative analysis of sludge samples from different water sources and treatment practices.

Figure 3.1: Collected alum sludge samples

3.1.2. Sample Drying

After collecting the sludge samples, eliminating moisture is crucial for ensuring accurate and consistent results in subsequent analyses. Moisture can distort the measurement of the sludge's physical and chemical properties and negatively impact its effectiveness in phosphorus removal tests. The primary goal of oven-drying is to remove all free moisture from the samples. Moisture content can vary widely due to environmental factors, storage conditions, and the inherent properties of the sludge (Zhang et al., 2021a). Standardizing the moisture content helps ensure reliable analytical results.

A drying temperature of 105°C was selected because it is high enough to evaporate water without causing thermal decomposition of the sludge's organic and inorganic components. This temperature is a standard in many analytical procedures and effectively preserves the sample's integrity (Chen, 2003). The drying process takes 24 hours to ensure thorough moisture removal.

After drying, the samples must be cooled to room temperature before handling. To prevent moisture reabsorption, particularly in high-humidity environments, the samples were immediately transferred to a desiccator, which contains a desiccant to absorb moisture from the air (Georgantas & Grigoropoulou, 2005). Cooling in a desiccator helps maintain the sludge's physical and chemical integrity by preventing condensation and chemical changes that could alter its properties. This gradual cooling process ensures that the samples remain stable and ready for accurate analysis (Bashir et al., 2019).

3.1.3. Crushing and Sieving of the Samples

Once the dried sludge samples had cooled, they were crushed into fine particles using a mortar and pestle. This step is crucial as it increases the surface area available for interaction with phosphorus, thereby enhancing the adsorption capacity of the sludge.

By breaking down the sludge into smaller, uniform particles, crushing helps to reduce variability within the sample, ensuring consistent texture and particle size. This uniformity is essential for obtaining reliable and reproducible results in subsequent phosphorus removal tests (Mohammed & Rashid, 2012).

After crushing, the sludge was sieved using a 75 µm sieve to standardize the particle size across the entire sample batch. Sieving ensures that all particles are of a consistent size, which is critical for experimental accuracy. Uniform particle size maximizes contact between the sludge and phosphorus, thereby improving the adsorption efficiency of the sludge. Smaller, evenly-sized particles provide more reactive sites for phosphorus binding, leading to more accurate assessments of the sludge's removal capacity (Georgantas & Grigoropoulou, 2005).

In addition to enhancing adsorption efficiency, maintaining a consistent particle size helps ensure uniform conditions across different experimental runs. This consistency is vital when comparing results across multiple tests or when scaling up the process for larger applications (Babatunde & Zhao, 2010). Properly processed sludge with uniform particle size not only improves the accuracy of phosphorus removal tests but also contributes to more reliable and reproducible experimental outcomes.

3.2. Characterisation of Alum Sludge Samples

The physical and chemical properties were analysed to characterize the alum sludge samples, since these are the main factors which would have a direct effect on their effectiveness toward phosphorus removal. Various analytical techniques can be associated with this characterisation process.

3.2.1. Moisture Content Determination

The moisture content of the alum sludge at the time of collection was determined using a gravimetric method. This process involves drying a known weight of the sludge at 105°C until it reaches a constant weight. The difference in weight before and after drying indicates the amount of moisture present in the sample (Chen, 2003). This step is critical because the moisture content can greatly influence the sludge's adsorption capacity and its overall effectiveness in wastewater treatment. High moisture content may dilute the active components of the sludge, reducing its effectiveness, while low moisture content typically suggests a higher potential for adsorption.

3.2.2. Water Solubility Assessment

Water solubility is a key parameter as it provides valuable information about the stability and potential leachability of alum sludge when it comes into contact with water. To determine the water solubility, a specific amount of dried alum sludge was mixed with 50 ml of distilled water. The mixture was then stirred and shaken for 10 minutes to ensure thorough interaction, allowing any soluble components to dissolve. Following this, the mixture was filtered using oven-dried filter paper with a pore size of 45 µm to separate the undissolved particles. These particles were then dried again, and their final weight was measured to calculate the sludge's solubility (Georgantas &

Grigoropoulou, 2005). Understanding the solubility is crucial for assessing the potential leaching of components during the sludge's use in wastewater treatment, which is essential for ensuring environmental safety.

3.2.3. pH Measurement

The pH of the sludge samples was measured using a calibrated pH meter (Ohaus, Starter 300, USA). This pH value is a crucial factor because it significantly influences the chemical interactions between the sludge and phosphorus in wastewater. The pH of the sludge can impact the speciation of aluminium and other metal hydroxides, which play a key role in the adsorption and precipitation of phosphorus (Zhang et al., 2021a). Maintaining an optimal pH range is vital for maximizing phosphorus removal efficiency and preventing the potential re-release of adsorbed phosphorus under different environmental conditions.

3.2.4. Surface Morphology and Elemental Composition

The surface morphology of the alum sludge samples was analysed using Environmental Scanning Electron Microscopy (ESEM - Carl Zeiss, EVO 18, Secondary Electron Microscope, Germany). ESEM offers high-resolution images that reveal the physical structure, texture, and porosity of the sludge particles. This analysis is crucial for understanding how the surface characteristics of the sludge contribute to its adsorption capacity. Generally, porous structures with larger surface areas provide more active sites for phosphorus binding, which is a key factor in the sludge's effectiveness (Bashir et al., 2019).

Alongside ESEM, Energy-Dispersive X-ray Spectroscopy (EDX) was employed to examine the elemental composition of the sludge samples. EDX identifies and quantifies the elements present on the sludge's surface, providing essential information about the availability of active components such as aluminium, silicon, and iron, which are critical for phosphorus adsorption (Zhang et al., 2021a).

3.2.5. Chemical Composition Analysis

The chemical composition of the sludge samples was analysed using an Agilent 7900 ICP-MS (Agilent Technologies, Santa Clara, USA). ICP-MS provides precise measurements of both trace and major elements within the sludge, including key metals like aluminium, which is essential for phosphorus removal. A higher aluminium content generally correlates with an increased phosphorus adsorption capacity, making this analysis crucial for assessing the sludge's effectiveness (Babatunde & Zhao, 2010).

In addition to ICP-MS, Fourier Transform Infrared Spectroscopy (FT-IR, ALPHA Bruker, Germany) was employed to identify the functional groups present in the sludge. FT-IR spectroscopy offers detailed insights into the chemical bonds and functional groups, such as hydroxyl, carboxyl, and phosphate groups, that are active in the adsorption process (Georgantas & Grigoropoulou, 2005). These functional groups are instrumental in the interaction between the sludge and phosphorus, significantly influencing both the adsorption capacity and the stability of the bound phosphorus.

The thorough characterisation of alum sludge samples using these various analytical techniques offers a comprehensive understanding of their physical and chemical properties. This detailed knowledge is crucial for accurately predicting the performance of alum sludge in phosphorus removal applications and for optimizing its effectiveness in wastewater treatment processes.

3.3. Potential for Phosphorus Release in Alum Sludge Samples

The potential for phosphorus release from alum sludge samples is a critical consideration when evaluating the effectiveness of alum sludge as a phosphorus removal agent in wastewater treatment. Although alum sludge is effective at binding phosphorus, the stability of this bond under varying environmental conditions must be carefully assessed to ensure that phosphorus does not leach back into the water, which could compromise the treatment process. If phosphorus release does occur, it could result in secondary pollution, effectively negating the benefits of using alum sludge in wastewater treatment (Bashir et al., 2019b).

3.3.1. Acid Extraction Method

The acid extraction method was employed to simulate acidic conditions that may be encountered in natural environments or during wastewater treatment processes. The use of strong acids such as hydrochloric acid (HCl), nitric acid (HNO_3), and sulfuric acid (H_2SO_4) is crucial in this context because these acids are effective at breaking down the inorganic compounds present in alum sludge, including aluminium hydroxides, iron oxides, and metal-phosphate complexes (Georgantas & Grigoropoulou, 2005). HCl is particularly effective in dissolving aluminium hydroxides, while HNO_3 oxidizes and dissolves metal oxides and hydroxides and aids in releasing phosphorus by breaking down organic matter. H_2SO_4, with its strong acidic and dehydrating properties, is effective in breaking down more resistant metal-phosphate complexes, particularly those involving aluminium and iron, and can simulate conditions where sludge is exposed to sulfuric acid in industrial effluents, potentially leading to phosphorus release.

Experimental procedure of this acid extraction method is described below.

- Acid extraction experiments were conducted using 250 ml beakers, each containing 100 ml of one of the following acid solutions: 0.5N HCl, 0.5N HNO_3, 0.5N H_2SO_4, and distilled water as a control. To each beaker, 1 g of the prepared alum sludge sample was added. This sample size is commonly used in studies examining metal and nutrient extraction from solid matrices, as it provides an optimal balance between the amount of material and the volume of the extraction solution, ensuring effective interaction between the sludge and the acid (Mohammed & Rashid, 2012).

- The mixtures were then placed on an orbital shaker and agitated at 150 rpm for 2 hours. This shaking ensures thorough contact between the alum sludge and the acidic solutions, promoting the dissolution of metal complexes and the release of bound phosphorus. The 2-hour duration is chosen to ensure equilibrium is reached, allowing for a sufficient interaction time to observe the maximum potential phosphorus release (Georgantas & Grigoropoulou, 2005).

- After shaking, the mixtures were filtered through oven-dried filter paper with a pore size of 45 µm. The purpose of filtration is to separate any undissolved particles from the solution, leaving behind only the dissolved components, including any released phosphorus.

- The filtered solutions were analysed to determine the concentration of released phosphorus. This is typically done using colorimetric methods such as the molybdenum blue method, which is highly sensitive to phosphate ions and provides accurate measurements of phosphorus concentrations in solution (Zhang et al., 2021).

By simulating acidic conditions, this method assesses the likelihood of phosphorus release from the sludge in various scenarios, such as pH changes caused by industrial discharges or natural processes. The results of this test provide insight into the long-term stability of phosphorus binding in alum sludge, helping to determine its suitability and safety as a phosphorus removal agent in different environmental settings.

Figure 3.2: Acid Extraction

3.4. Determination of Phosphorus Concentration

Accurately determining phosphorus concentration is crucial for assessing the effectiveness of alum sludge in removing phosphorus from wastewater. The chosen method must be sensitive, precise, and able to differentiate between various forms of phosphorus in solution. In this study, the Vandomolybdophosphoric acid colorimetric method was used, which is widely recognized for its accuracy and reliability in measuring phosphate concentrations.

3.4.1. Vandomolybdophosphoric Acid Colorimetric Method

The Vandomolybdophosphoric acid colorimetric method is a widely recognized technique for quantifying phosphate in aqueous solutions. In this method, phosphate ions react with ammonium molybdate under acidic conditions to form molybdophosphoric acid. The addition of vanadium leads to the formation of a yellow Vandomolybdophosphoric acid complex. The intensity of this yellow colour is directly proportional to the concentration of phosphate in the solution, making this method a dependable approach for accurate phosphorus measurement (Divya et al., 2020).

Experimental procedure of determination of phosphorus concentration using this colorimetric method is explained below.

- The key reagents used in this method include a vanadate-molybdate reagent, which consists of a mixture of ammonium molybdate [$(NH_4)_2MoO_4$] and ammonium metavanadate [NH_4VO_3] in hydrochloric acid (HCl). These reagents react with phosphate in the sample to form the yellow-coloured complex.
- Water and alum sludge samples are first filtered to remove any solid particles. A 25 ml aliquot from each sample is then transferred to a 50 ml volumetric flask. To initiate the reaction, 10 ml of the vanadate-molybdate reagent is added, and the solution is diluted to the mark with deionized water. A second flask is prepared as a blank, identical to the sample flask but without the reagent.
- The mixtures are allowed to stand for at least 10 minutes to ensure complete colour development. This waiting period is crucial for the full formation of the yellow Vandomolybdophosphoric acid complex, which is necessary for accurate measurement. The intensity of the yellow colour, which corresponds to the phosphate concentration, is then measured.
- The absorbance of the yellow complex is measured using a UV-VIS spectrophotometer, with the absorbance taken at 420 nm. This wavelength is selected to balance sensitivity and minimize potential interferences. The GENESYS 10S UV-VIS Spectrophotometer (Thermo Scientific, USA) is used in this experiment to ensure high sensitivity and precise detection of phosphate concentrations.

Figure 3.3: UV-VIS Spectrophotometer

- A series of calibration standards is prepared by diluting a standard phosphate solution (KH_2PO_4 containing 50.0 µg P per ml) in the same way as the samples. These standards cover a range of phosphate concentrations, typically from 0 to 20 µg P per ml. The absorbance readings of these standards are then used to generate a calibration curve by plotting absorbance against phosphorus concentration. The phosphate concentration in each water sample is determined by comparing its absorbance to this calibration curve. For accurate quantification, the calibration curve must be linear within the range of the standards.

In certain situations, the initial solution may have a colour or contain substances that interfere with accurately measuring phosphate concentration by absorbing light at the same wavelength. To resolve this, the Persulphate Oxidation method is used as a pre-treatment step to eliminate excessive colour or organic matter that could cause interference.

3.4.2. Persulphate Oxidation Method of Removing Excessive Colour

- Potassium persulphate is used as an oxidizing agent to break down and remove organic compounds in the solution that could interfere with the colorimetric measurement. This process effectively eliminates any colour or turbidity that might absorb light at 420 nm, ensuring that the absorbance readings accurately reflect only the presence of phosphate.
- The persulphate oxidation step is applied to samples that show significant colour or turbidity. After oxidation, the sample is reanalysed using the Vandomolybdophosphoric acid method to precisely measure the phosphate concentration.
- It is essential to confirm that the persulphate treatment has completely oxidized all interfering substances. This is done by comparing the absorbance readings before and after treatment, ensuring that any discrepancies are addressed, and the results accurately represent the true phosphate concentration.

To ensure the accuracy and validity of the results, several precautions were taken during the above experiments as below.

- To avoid phosphate contamination from detergents, all glassware was thoroughly acid washed prior to use.
- The UV-VIS spectrophotometer was calibrated with a set of standards of known concentrations to ensure accurate quantitative measurements.
- Cuvettes must be meticulously cleaned and consistently placed in the spectrophotometer in the same orientation to prevent minor variations in absorbance readings.
- Duplicate samples and blank controls were analysed to ensure the consistency and accuracy of the measurements.

3.5. Preparation of Synthetic Wastewater

Potassium dihydrogen phosphate (KH_2PO_4) was prepared in order to make a synthetic phosphorus solution. This was aimed at ensuring that the experiment was carried out under the same conditions as those existing in real wastewater treatment. This was because under both natural and wastewater conditions, the major form of phosphorus available is orthophosphate, which is represented by the phosphate ion in KH_2PO_4. The synthetic wastewater solution is prepared for the purpose of determining the efficiency of alum sludge in removing phosphorus.

The use of synthetic wastewater was chosen deliberately to maintain a controlled experimental environment. This allowed the study to isolate and analyze the phosphorus adsorption mechanism of alum sludge without interference from other variables commonly found in real wastewater, such as organic matter, competing anions (e.g., sulfate, nitrate), and biological activity. However, this also presents a limitation, as the performance of alum sludge in actual wastewater conditions where these interferences exist might differ.

Potassium dihydrogen phosphate (KH_2PO_4) was selected as the phosphorus source for the synthetic wastewater due to its high solubility and ability to readily dissociate in water, releasing phosphate ions ($H_2PO_4^-$). These ions are a crucial part of orthophosphate, the most common and bioavailable form of phosphorus in wastewater, which can contribute to eutrophication in aquatic environments if not properly controlled (Mohammed & Rashid, 2012).

The phosphorus concentration in the synthetic wastewater was calculated according to the desired experimental conditions. The appropriate amount of KH_2PO_4 was determined using its molecular weight (136.09 g/mol) and the target phosphorus concentration in the solution.

Calculation Example:

To prepare a solution with a phosphorus concentration of 10 mg/L (ppm), the following calculation was used:

- Determine the amount of KH_2PO_4 needed to achieve the target concentration:

$$Weight\ of\ KH_2PO_4 = \frac{10mg/L \times Volume\ of\ solution\ (L) \times Molecular\ weight\ of\ KH_2PO_4}{Molecular\ weight\ of\ P}$$

- For example, to prepare 1 litre of solution with 10 mg/L phosphorus:

$$Weight\ of\ KH_2PO_4 = \frac{\frac{10mg}{L} \times 10L \times \frac{136.09g}{mol}}{\frac{31.0g}{mol}} = 43.9mg$$

The calculated amount of KH_2PO_4 was precisely weighed using an analytical balance. This KH_2PO_4 was then dissolved in a measured volume of distilled water to achieve the target concentration. The solution was stirred thoroughly to ensure the salt completely dissolved, resulting in a homogeneous phosphorus solution.

The concentration of the prepared phosphorus solution was verified using appropriate analytical techniques, such as the Vandomolybdophosphoric acid colorimetric method, to ensure it matched the target phosphorus levels before proceeding with further experiments.

The experimental setup used the phosphorus-prepared solution as a synthetic wastewater; thus, controlled and reproducible experiments were enabled in which the performance of alum sludge for phosphorus removal was tested evidently. The use of synthetic wastewater with known concentrations of orthophosphate in the experiments will closely approximate real-life situations. At the same time, it will permit the isolation and study of variables specifically for the concentration of the nutrient under consideration without interaction from the other contaminants normally found in real wastewater.

3.6. Evaluating the Phosphorus Removal Ability of Alum Sludge

In this study, a series of synthetic wastewater solutions with varying phosphorus concentrations were prepared using potassium dihydrogen phosphate (KH_2PO_4). The phosphorus concentrations were precisely controlled at 10 ppm, 20 ppm, 30 ppm, 40 ppm, 50 ppm, 60 ppm, 70 ppm, and 80 ppm. These specific concentrations were selected to represent a range of phosphorus levels that might be encountered in real wastewater treatment scenarios, enabling a thorough analysis of the alum sludge's capacity to remove phosphorus across different conditions.

To each 100 ml of the prepared KH_2PO_4 solution, 1 g of prepared alum sludge was added, resulting in a sludge concentration of 10 g/L. This ratio was chosen based on previous studies demonstrating its effectiveness in evaluating phosphorus adsorption capacity (Yang et al., 2006). The alum sludge was evenly dispersed throughout the solution to ensure maximum contact between the sludge particles and the dissolved phosphorus.

The mixtures were placed on an orbital shaker and agitated at 150 rpm for 2 hours. This shaking process is critical for ensuring thorough mixing and optimal contact between the alum sludge and the phosphate ions in the solution. The selected shaking speed and duration were based on established protocols, which suggest that 2 hours of agitation at this speed is sufficient to approach equilibrium in the adsorption process (Yang et al., 2006). After the 2-hour shaking period, the remaining phosphorus concentration in each sample was measured.

Following the shaking process, the samples were allowed to settle overnight. This settling period enabled the alum sludge particles, along with any adsorbed phosphorus, to precipitate out of the solution. This step is crucial for accurately determining the amount of phosphorus that remains in the solution versus what has been successfully adsorbed onto the sludge.

The settled mixtures were then filtered using oven-dried filter paper with a pore size of 45 µm to separate the solid alum sludge particles from the liquid. The use of a 45 µm filter ensures the effective removal of any undissolved sludge and other particulate matter, resulting in a clear solution for subsequent phosphorus concentration analysis.

The filtered solutions were then analysed to determine the remaining phosphorus concentration. This analysis provided critical data on the amount of phosphorus removed by the alum sludge, enabling an assessment of the sludge's efficiency as a phosphorus removal agent.

3.7. Evaluating Phosphorus Removal Efficiency Over Time

Phosphorus concentration in the solution was measured at 2-hour intervals to monitor the rate of removal over time. This interval was chosen to strike a balance between frequent monitoring and allowing enough time for significant changes in phosphorus concentration to be observed (Yang et al., 2006).

For each sludge concentration, after the initial mixing and shaking phase, the samples were allowed to settle. At each 2-hour interval, a sample was drawn, filtered through oven-dried filter paper with a 45 µm pore size, and analysed for phosphorus content using the Vandomolybdophosphoric acid colorimetric method at 420 nm. This process was repeated until the phosphorus concentration stabilized, indicating that equilibrium had been reached.

The phosphorus removal efficiency is calculated at each time interval using the following formula:

$$Removal\ Efficiency\ (\%) = \frac{(C_0 - C_t) \times 100}{C_0}$$

- C_0 is the initial phosphorus concentration (mg/L),
- C_t is the phosphorus concentration at time t.

This formula calculates the percentage of phosphorus removed from the solution at each time interval. A higher percentage indicates more effective removal. By assessing the removal efficiency at regular intervals, the study can determine the rate at which alum sludge adsorbs phosphorus and how the process progresses over time.

The time at which the removal efficiency curve flattens indicates when equilibrium is reached is known as **Equilibrium Point**. At this point, the alum sludge has adsorbed as much phosphorus as it can under the given conditions, and no significant further removal occurs (Ojha et al., 2019).

Understanding how phosphorus removal efficiency changes over time is essential for optimizing treatment processes. It helps determine the optimal contact time needed for maximum phosphorus removal, which can significantly improve the efficiency and cost-effectiveness of wastewater treatment operations (Truong & Kim, 2021).

3.8. Maximum Adsorption Capacity of Alum Sludge

To evaluate the impact of different alum sludge concentrations on phosphorus removal efficiency and to determine the maximum adsorption capacity of the alum sludge, the sludge concentrations were varied while maintaining a constant phosphorus concentration.

The following steps were followed to determine the maximum adsorption capacity of alum sludge.

- Prepare a synthetic phosphorus solution using potassium dihydrogen phosphate (KH_2PO_4) at a constant phosphorus concentration, typically set at 50 ppm. This concentration is selected to represent a moderately high phosphorus load that alum sludge would encounter in real-world wastewater treatment scenarios.
- The alum sludge was added to the phosphorus solution at varying concentrations from 10 g/L to 50 g/L.
- For each sludge concentration, add the appropriate amount of alum sludge(1g to 5g) to 100 ml of the prepared 50 ppm phosphorus solution.
- Place the mixtures on an orbital shaker and agitate them at 150 rpm for 2 hours. This duration is based on previous studies and is expected to be sufficient for the adsorption process to approach equilibrium (Yang et al., 2006).
- After shaking, samples were allowed to settle overnight to ensure that the alum sludge particles, along with any adsorbed phosphorus, precipitate out of the solution.
- Filtered through oven-dried filter paper with a pore size of 45 µm to separate the solid sludge particles from the liquid.
- Analysed the filtered solutions to determine the remaining phosphorus concentration using the Vandomolybdophosphoric acid colorimetric method, as previously described.

3.8.1. Adsorption Capacity Calculation

For each sludge concentration, the amount of phosphorus adsorbed by the alum sludge was calculated using the following equation (Ojha et al., 2019).

$$q_e = \frac{(C_0 - C_e) \times V}{m}$$

- q_e is the amount of phosphorus adsorbed per unit mass of alum sludge (mg/g),
- C_0 is the initial phosphorus concentration (mg/L),
- C_e is the equilibrium phosphorus concentration (mg/L) after treatment,
- V is the volume of the solution (L),
- m is the mass of alum sludge used (g).

3.8.2. Adsorption Isotherms

To evaluate the adsorption capacity of alum sludge for phosphorus, adsorption isotherms were constructed. These isotherms provide insight into the adsorption mechanism and the interaction between alum sludge and phosphorus under equilibrium conditions.

The equilibrium phosphorus concentration C_e was measured after each batch experiment. For each alum sludge concentration, the equilibrium state was reached when the phosphorus removal efficiency plateaued, indicating no further significant adsorption (Ojha et al., 2019).

Plotting Adsorption Isotherms

The adsorption isotherm was plotted by graphing q_e (mg/g) against C_e (mg/L) for each alum sludge concentration.

The Langmuir model assumes monolayer adsorption on a homogenous surface. Its linear form is as follows (Langmuir, 1918).

$$\frac{C_e}{q_e} = \frac{1}{Q_{max}b} + \frac{C_e}{Q_{max}}$$

$Q_{max} = maximum\ adsorption\ capacity\ (mg/g),$

$b = Langmuir\ constant\ (L/mg)$

The Langmuir model was used to determine the maximum adsorption capacity (Q_{max}), providing a clear indication of the saturation point of alum sludge. The fit of this model was evaluated using regression coefficients (R^2), with the better-fitting model providing deeper insight into the adsorption characteristics (Van Truong et al., 2021).

Freundlich isotherm model: To complement the Langmuir model, the Freundlich isotherm was also applied. It accounts for adsorption on heterogeneous surfaces and is expressed in the logarithmic form (Vigdorowitsch et al., 2021):

$$\log q_e = \log K_f + \frac{1}{n}\log C_e$$

Where:

K_f = Freundlich constant indicative of adsorption capacity

1/n = heterogeneity factor indicating adsorption intensity

A plot of log q_e vs. log C_e was used to determine K_f and n.

Comparing R^2 values between Langmuir and Freundlich models allowed for better assessment of adsorption mechanisms.

3.9. Influence of pH on Phosphorus Adsorption Efficiency

The pH value is a critical parameter influencing the phosphorus adsorption efficiency of alum sludge. By optimizing pH, the adsorption process can be tailored to maximize phosphorus removal, enhancing the sludge's practical application in wastewater treatment (Kim et al., 2002).

Adsorption studies were conducted at varying pH levels to evaluate their impact on phosphorus adsorption efficiency. The solution pH was adjusted to specific values (4 to 8) using 0.1M NaOH or 0.1M HCl. The pH adjustment was crucial, as it affects the surface charge of alum sludge and the speciation of phosphate ions in solutions.

4. RESULTS AND ANALYSIS

This chapter presents the findings from the experimental study on the feasibility of using alum sludge as a cost-effective material for phosphorus removal from synthetic wastewater. The results are analysed to evaluate the adsorption efficiency of alum sludge under varying conditions, including different sludge concentrations, pH levels, and temperatures. Key performance indicators such as phosphorus removal efficiency, adsorption capacity, and equilibrium characteristics are discussed. Additionally, the data are modelled using adsorption isotherms to provide insights into the adsorption mechanisms and the sludge's maximum capacity. These analyses form the basis for assessing the practical application of alum sludge in wastewater treatment and its potential for sustainable reuse.

4.1. Characteristics of Alum Sludge

The physical and chemical properties of alum sludge samples collected from Ambatale, Biyagama, and Kandana water treatment plants were systematically analysed to assess their potential for phosphorus adsorption.

Obtained physical properties of alum sludge samples collected from Ambatale WTP (Sludge A), Biyagama WTP (Sludge B) and Kandana WTP (Sludge C) are given in Table 4.1.

Table 4.1: Physical properties of alum sludge samples

Property	Ambatale WTP Sludge (A)	Biyagama WTP Sludge (B)	Kandana WTP Sludge (C)
Moisture content (w/w%)	72	57	49
Water solubility (w/w%)	19.7	18.6	18.2
pH	6.8	6.3	6.1
Bulk density (g/cm^3)	0.89	0.84	0.88

4.1.1. Moisture Content and Water Solubility

The initial moisture content of the sludge samples varied significantly, ranging from 49% to 72%, depending on the source. High moisture content indicates the need for pre-treatment, as excess water can dilute the adsorption sites and hinder phosphorus binding.

The water solubility, on the other hand, was between 18.2% and 19.7%, reflecting the fraction of alum sludge that can dissolve in water and potentially contribute to phosphorus removal through chemical reactions.

4.1.2. pH of Sludge

The pH values of the sludge samples were found to be slightly acidic, ranging between 6.1 and 6.8, aligning with previous studies that report optimal adsorption in this range (Zhang et al., 2021).

4.1.3. Elemental Composition of Alum Sludge

The chemical compositions of the alum sludge samples from Ambatale, Biyagama, and Kandana water treatment plants are summarized in Table 4.2. The analysis highlights the predominant presence of aluminium, oxygen, silicon, carbon, and iron, with trace amounts of other elements such as calcium, magnesium, and potassium.

Table 4.2: Chemical composition of alum sludge samples

Chemical Characteristic	**Ambatale WTP Sludge (A)**	**Biyagama WTP Sludge (B)**	**Kandana WTP Sludge (C)**
	(w/w %)		
Aluminium	19.51	29.52	25.24
Carbon	12.12	9.84	10.37
Oxygen	46.53	39.21	42.33
Silicon	12.31	10.82	11.23
Iron	3.12	2.72	3.36
Calcium	2.11	1.97	2.08
Magnesium	0.98	0.85	0.95
Potassium	1.17	1.13	1.02

The aluminium content ranged from 19.51% to 29.52%, confirming its role as the dominant element. This is consistent with its widespread use in the coagulation process in water treatment as alum (Mazari et al., 2018). Aluminium is integral to phosphorus adsorption due to its ability to form strong complexes with phosphate ions, which enhances the sludge's adsorption capacity. Oxygen (39.21% to 46.53%) and carbon (9.84% to 12.12%) are present in high concentrations, reflecting the prevalence of organic and inorganic compounds. These elements contribute to the formation of carbonates, hydroxides, and other compounds within the sludge matrix (Kim et al., 2002). Silicon (10.82% to 12.31%) and iron (2.72% to 3.36%) enhance the sludge's structural stability and contribute to phosphorus adsorption through co-precipitation processes (Muisa et al., 2020). Calcium, magnesium, and potassium, though present in smaller quantities, can play supportive roles in adsorption and complexation processes, adding to the sludge's overall effectiveness (Dassanayake et al., 2015).

4.1.4. SEM Analysis of Alum Sludge Samples

Figure 4.1, Figure 4.2 and Figure 4.3 illustrate the scanning electron microscope (SEM) image of the sludge samples, which reveal non-uniform and heterogeneous particle surfaces with no crystalline structures.

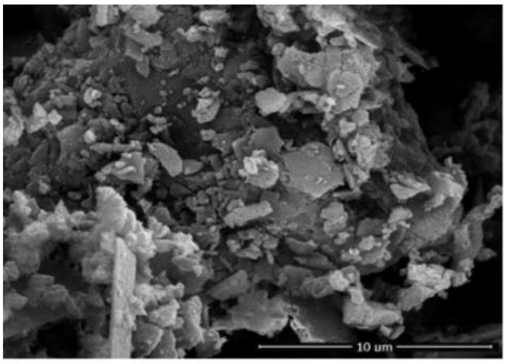

Figure 4.1: SEM image of Ambatale Sludge

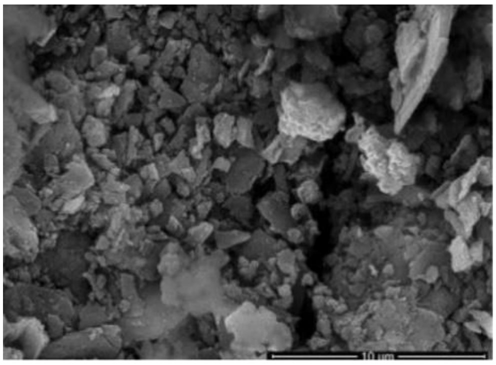

Figure 4.2: SEM image of Biyagama Sludge

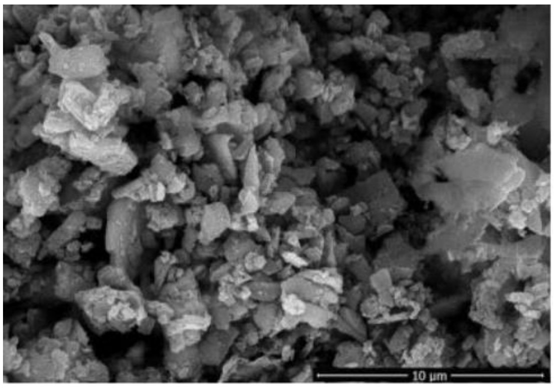

Figure 4.3: SEM image of Kandana Sludge

All the samples exhibit irregular, non-uniform surface morphologies, characteristic of alum sludge. The absence of distinct crystalline patterns suggests an amorphous structure, which is advantageous for adsorption processes as it increases the available surface area for phosphorus binding. The presence of pores and cavities is evident in all images. These pores enhance the sludge's adsorption capacity by providing more active sites for phosphorus interaction, which aligns with the findings of studies like Mazari et al. (2018). The particles appear to be composed of loosely bound granules, indicating a high degree of aggregation. This aggregation can be attributed to the flocculation process during water treatment. The samples contain particles of varying sizes, from fine grains to larger chunks. This heterogeneity further supports the sludge's capability to adsorb phosphorus over a wide range of conditions.

The SEM analysis confirms that alum sludge possesses an amorphous, porous structure with a heterogeneous surface morphology. These characteristics enhance its effectiveness in adsorption applications, particularly for phosphorus removal in wastewater treatment. These findings are consistent with previous studies, including those by Mazari et al. (2018) and Yang et al. (2006), which highlight the amorphous and porous nature of alum sludge.

4.2. Potential for Phosphorus Release in Alum Sludge Samples

The potential for phosphorus release from alum sludge is a critical factor in determining its environmental safety and suitability as a phosphorus removal agent in wastewater treatment. Table 3 provides the phosphorus release percentages for alum sludge samples from Ambatale (Sludge A), Biyagama (Sludge B), and Kandana (Sludge C) water treatment plants when exposed to various acidic solutions and distilled water.

Table 4.3: Released P percentages of sludge samples into different solutions

Solution	**Released P percentage (w/w %)**		
	Ambatale WTP Sludge (A)	**Biyagama WTP Sludge (B)**	**Kandana WTP Sludge (C)**
0.5N HCl	0.010	0.005	0.008
0.5N HNO_3	0.049	0.028	0.045
0.5N H_2SO_4	0.040	0.031	0.039
Distilled water	0.007	0.003	0.005

The phosphorus release in distilled water was minimal for all sludge samples, ranging from 0.003% to 0.007%. This indicates that under neutral conditions, the sludge does not readily leach phosphorus into the surrounding environment. The minimal release underscores its potential stability when used in real-world wastewater applications, where uncontrolled phosphorus leaching could lead to secondary pollution.

The release of phosphorus increased when the sludge samples were exposed to strong acids, with the highest release observed in 0.5N HNO_3 (0.028%–0.049%) and slightly lower values in 0.5N H_2SO_4 (0.031%–0.040%). Among the acids tested, HCl (0.005%–0.010%) resulted in the lowest phosphorus release, suggesting that the nature of the acid plays a role in the dissolution of phosphorus-containing compounds in the sludge.

The relatively low phosphorus release, even under these strong acidic conditions, highlights that the phosphorus within the sludge matrix is tightly bound, likely in the form of aluminium-phosphate or iron-phosphate complexes. These complexes are known for their stability, particularly under acidic conditions, as confirmed by Maqbool et al. (2016).

Sludge A (Ambatale WTP) exhibited the highest phosphorus release in each solution, particularly in HNO_3 (0.049%), likely due to slight compositional differences, such as lower aluminum or higher iron content. Sludge B (Biyagama WTP) showed the lowest phosphorus release across all test conditions, suggesting a more stable matrix and lower initial phosphorus content. Sludge C (Kandana WTP) performed similarly to Sludge A but with slightly lower phosphorus release values, particularly in HCl and distilled water.

The minimal phosphorus release, even in aggressive acidic environments, reinforces the environmental safety of using alum sludge. It ensures that the application of alum sludge in wastewater treatment will not introduce additional phosphorus back into treated water or surrounding ecosystems. Furthermore, this stability enhances its reusability, making alum sludge a reliable material for phosphorus adsorption in continuous or batch treatment processes.

Studies by Kim et al. (2002) and Yang et al. (2006) similarly report the low releasability of phosphorus from alum sludge, particularly in systems where aluminium-phosphate complexes are predominant. Maqbool, Khan, and Asghar (2016) emphasize the importance of such stability in sludge, noting that tightly bound phosphorus is unlikely to leach unless subjected to extreme conditions.

The results demonstrate that alum sludge samples from all three WTPs exhibit minimal phosphorus release under both neutral and acidic conditions, confirming their stability and suitability for use in wastewater treatment. This behaviour ensures that alum sludge can be safely applied in phosphorus removal without contributing to secondary phosphorus pollution. These findings provide a solid foundation for its continued use in adsorption studies and large-scale wastewater treatment applications.

4.3. Evaluating the Phosphorus Removal Ability of Alum Sludge

The phosphorus removal efficiency of alum sludge was evaluated using synthetic wastewater solutions with initial phosphorus concentrations of 10, 20, 30, 40, 50, 60, 70, and 80 ppm. For each concentration, 1 g of alum sludge was added to 100 mL of the synthetic solution, yielding a sludge concentration of 10 g/L. The shaking process facilitated optimal contact between sludge and phosphorus ions, and the results were recorded after a 2-hour agitation period and subsequent overnight settling.

The results, as seen in Table 4.4 and figure 4.4, indicate that phosphorus removal efficiency varied depending on the initial phosphorus concentration.

Table 4.4: Capacity of alum sludge samples in P removal

Initial P concentration (ppm)	**P removal capacity (mg/g)**		
	Ambatale WTP Sludge (A)	**Biyagama WTP Sludge (B)**	**Kandana WTP Sludge (C)**
10	0.88	0.96	0.92
20	1.93	1.92	1.95

30	2.18	2.82	2.32
40	2.62	3.71	3.12
50	3.01	4.21	3.89
60	3.01	5.93	4.22
70	3.01	5.94	4.51
80	3.01	5.94	4.51

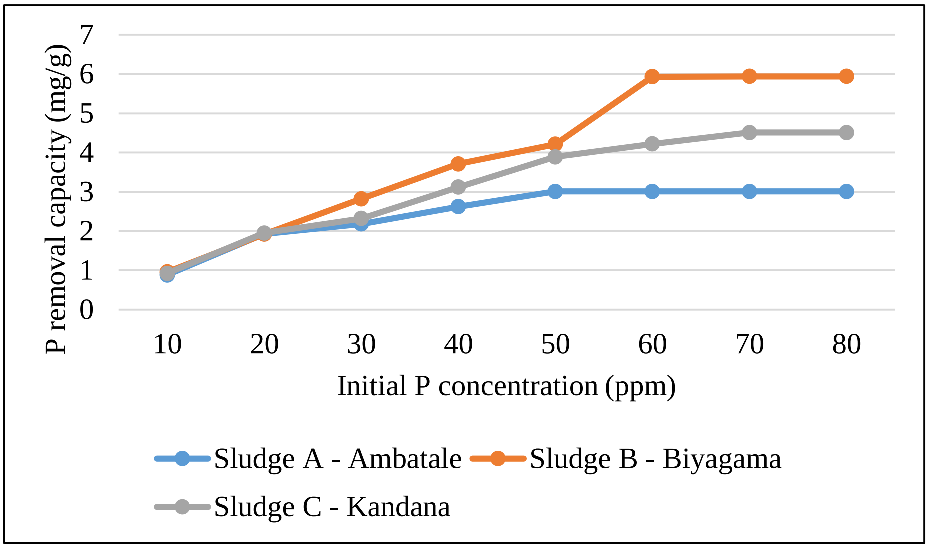

Figure 4.4: Phosphorus removal capacity of different sludge samples for different P concentrations

Biyagama WTP sludge (Sludge B) exhibited the highest removal capacity across all concentrations, reaching a maximum removal capacity of 5.94 mg/g at an initial phosphorus concentration of 70 ppm. This was followed by Kandana WTP sludge (Sludge C) with a capacity of 4.51 mg/g and Ambatale WTP sludge (Sludge A) at 3.01 mg/g.

4.4. Evaluating Phosphorus Removal Efficiency Over Time

The phosphorus removal efficiency of alum sludge was further evaluated by monitoring the remaining phosphorus concentrations in the solution at 2-hour intervals. This analysis was conducted only for the initial phosphorus concentration of 70 ppm, as all three sludge samples reached their maximum removal capacities at this concentration.

Figure 4.5 illustrates the variation in remaining phosphorus concentration over time. The data show a rapid decrease in phosphorus concentration within the first two hours of treatment, after which the levels stabilized, indicating that the maximum adsorption capacity of the alum sludge had been reached.

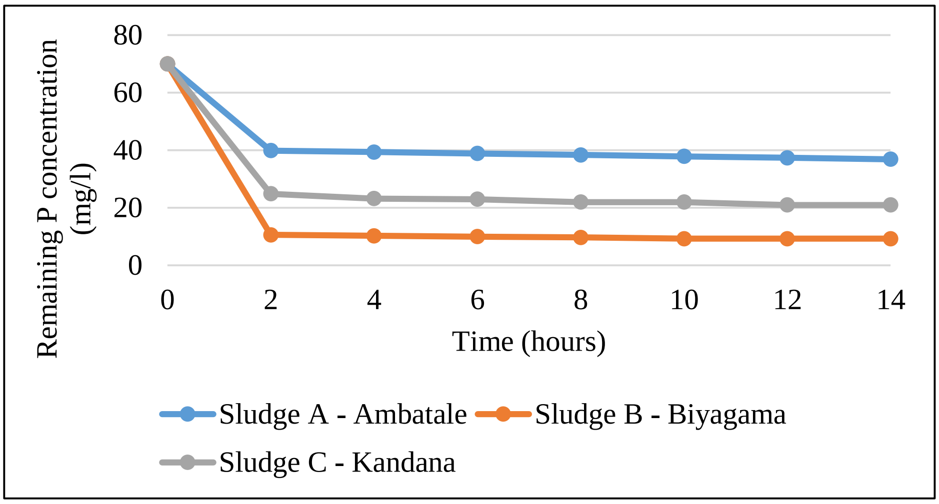

Figure 4.5: Remaining P concentration variation with time

The results indicate that all sludge samples removed the majority of phosphorus within the first two hours. This rapid removal is consistent with findings by Yang et al. (2006), who observed a significant decline in phosphorus concentration within the initial phase of their experiments. This behaviour suggests that adsorption is the primary mechanism for phosphorus removal. Adsorption typically exhibits a fast initial uptake due to the availability of abundant active sites on the adsorbent surface (Babatunde & Zhao, 2010).

As shown in Figure 4.5, phosphorus concentrations stabilized after the initial removal phase, with no noticeable increase in phosphorus levels over time. This indicates that the adsorbed phosphorus remained bound to the alum sludge, with no evidence of desorption. The absence of desorption highlights the strong chemical interactions between phosphorus and the active adsorption sites within the sludge. Mohammed and Rashid (2012) similarly reported that alum sludge effectively retains adsorbed phosphorus without significant release under normal conditions.

The stability of phosphorus adsorption is critical for ensuring that adsorbed phosphorus does not leach back into the solution. This stability aligns with findings by Maqbool et al. (2016) and Mazari et al. (2018), who noted that phosphorus adsorption onto alum sludge involves strong chemical bonds, such as aluminium-phosphate complexes. These interactions enhance the reliability and longevity of alum sludge as an adsorbent in wastewater treatment applications.

The time-dependent study confirms that phosphorus removal by alum sludge is both rapid and stable, with the majority of phosphorus adsorption occurring within the first two hours. The absence of desorption underscores the strong chemical interactions between phosphorus and the sludge, ensuring that phosphorus remains bound even after equilibrium is reached. These findings reinforce the potential of alum sludge as an effective and reliable adsorbent for phosphorus removal in wastewater treatment.

4.5. Maximum Adsorption Capacity of Alum Sludge

The maximum adsorption capacity of alum sludge was determined for three sludge samples: Sludge A (Ambatale WTP), Sludge B (Biyagama WTP), and Sludge C (Kandana WTP). The experiments were conducted using varying sludge concentrations (10 g/L to 50 g/L) with a constant initial phosphorus concentration of 50 ppm. Equilibrium concentration for each sludge sample was measured, and the results are as below.

Table 4.5: Equilibrium concentrations of each sludge sample

Sludge concentration (g/L)	**Equilibrium concentration (C_e) (mg/L)**		
	Ambatale WTP Sludge (A)	**Biyagama WTP Sludge (B)**	**Kandana WTP Sludge (C)**
10	19.1	7.9	10.9
20	9.9	2.9	4
30	5.7	1.7	2.1
40	4.2	1.3	1.7
50	3.2	1	1.3

4.5.1. Adsorption Capacity

The adsorption capacity was calculated for each sludge concentration and equilibrium concentration, and adsorption isotherms were plotted using the Langmuir model to determine the maximum adsorption capacity (Q_{max}).

$$q_e = \frac{(C_0 - C_e) \times V}{m}$$

Where:

- C_0: Initial phosphorus concentration (mg/L) = 50 mg/L
- C_e: Equilibrium phosphorus concentration (mg/L)
- V: Volume of solution (L) = 0.1 L
- m: Mass of alum sludge (g)

Example Calculation for Sludge A

Let’s consider the sludge concentration of 10 g/L,

- $C_0 = 50$ mg/L
- $C_e = 19.1$ mg/L
- V = 0.1 L

- m = 1 g (for 10 g/L sludge concentration, 1 g sludge was added to 100 ml of water)

$$q_e = \frac{(50 - 19.1) mg/L \times 0.1L}{1\ g} = 3.09\ mg/g$$

Similarly, all the adsorption capacity values were calculated, and the results are as below.

Table 4.6: Adsorption capacity of each sludge sample

Sludge concentration (g/L)	Adsorption capacity (q_e) (mg/g)		
	Ambatale WTP Sludge (A)	Biyagama WTP Sludge (B)	Kandana WTP Sludge (C)
10	3.09	4.21	3.91
20	2.01	2.36	2.3
30	1.48	1.61	1.6
40	1.15	1.22	1.21
50	0.94	0.98	0.97

4.5.2. Langmuir Isotherm Fitting

Measured C_e and calculated q_e values were used to plot the graphs for below Langmuir isotherm.

$$\frac{C_e}{q_e} = \frac{1}{Q_{max} b} + \frac{C_e}{Q_{max}}$$

$\frac{C_e}{q_e}\ vs\ C_e$ graphs were plotted for each sludge sample and graphs are shown below.

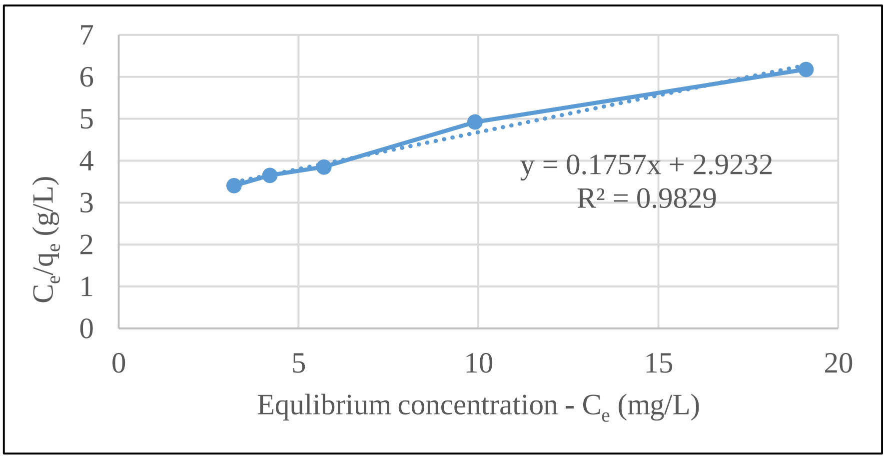

Figure 4.6: C_e/q_e vs C_e graph for Ambatale WTP sludge (A)

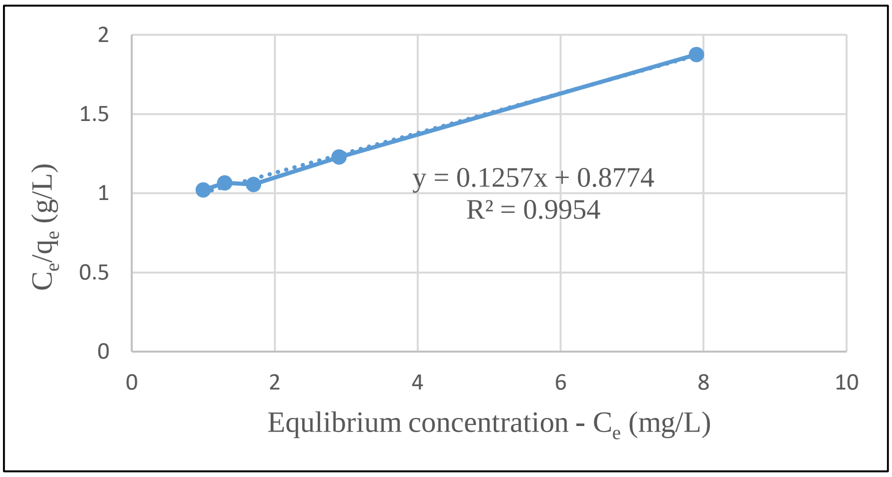

Figure 4.7: C_e/q_e vs C_e graph for Biyagama WTP sludge (B)

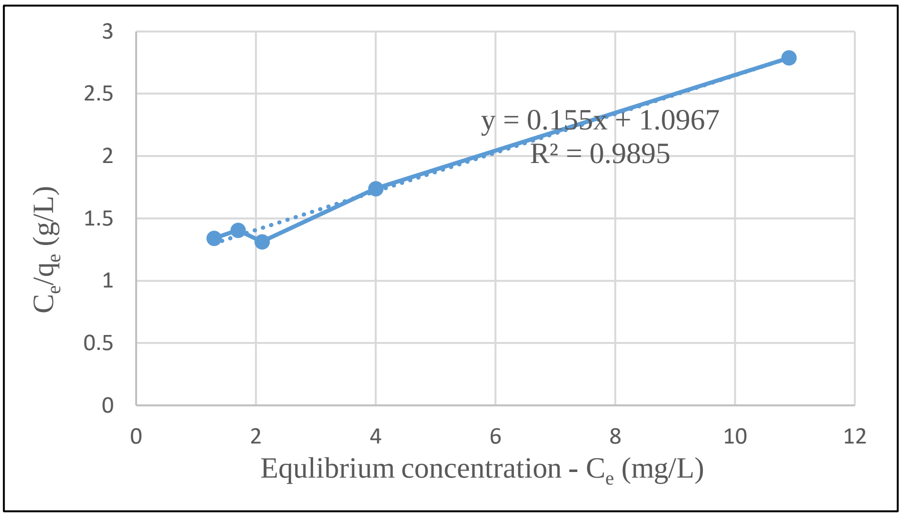

Figure 4.8: Ce/qe vs Ce graph for Kandana WTP sludge (C)

From the intercept and the gradient of the graphs, maximum adsorption capacity (Qmax) and the Langmuir constant (b) were calculated and the results are given in table 4.7.

Table 4.7: Langmuir parameters of each sludge sample

	Ambatale WTP Sludge (A)	**Biyagama WTP Sludge (B)**	**Kandana WTP Sludge (C)**
Gradient ($1/Q_{max}$)	0.1757	0.1257	0.155
Intercept ($1/Q_{max}.b$)	2.9232	0.8774	1.0967
R^2	0.9829	0.9954	0.9895
Q_{max} (mg/g)	5.6915	7.9554	6.4516
b (L/mg)	0.0601	0.1433	0.1413

According to the results, the high R^2 values (ranging from 0.9829 to 0.9954) indicate that the Langmuir isotherm model fits the experimental data well, confirming monolayer adsorption behaviour for phosphorus removal. Among the three sludge samples, Biyagama WTP sludge (Sludge B) exhibits the highest maximum adsorption capacity (Q_{max}=7.96 mg/g), followed by Kandana WTP sludge (Sludge C) with Q_{max}=6.45 mg/g, and Ambatale WTP sludge (Sludge A) with Q_{max}=5.69 mg/g. These values suggest that Biyagama sludge has the greatest potential for phosphorus removal under the given experimental conditions.

The Langmuir constant b, which reflects the affinity of the adsorbent for phosphorus, is also highest for Biyagama WTP sludge (b=0.14 L/mg) indicating its stronger adsorption affinity. Kandana WTP sludge also demonstrates a similarly high adsorption affinity. In contrast, Ambatale WTP sludge exhibits the lowest adsorption affinity, with a b value of 0.06 L/mg. This variation highlights the differences in phosphorus-binding capacity among the sludge samples.

4.5.3. Freundlich Isotherm Fitting

Measured C_e and calculated q_e values were used to plot the graphs for below Freundlich isotherm.

$$\log q_e = \log K_f + \frac{1}{n} \log C_e$$

$\log q_e \; vs \; \log C_e$ graphs were plotted for each sludge sample and graphs are shown below.

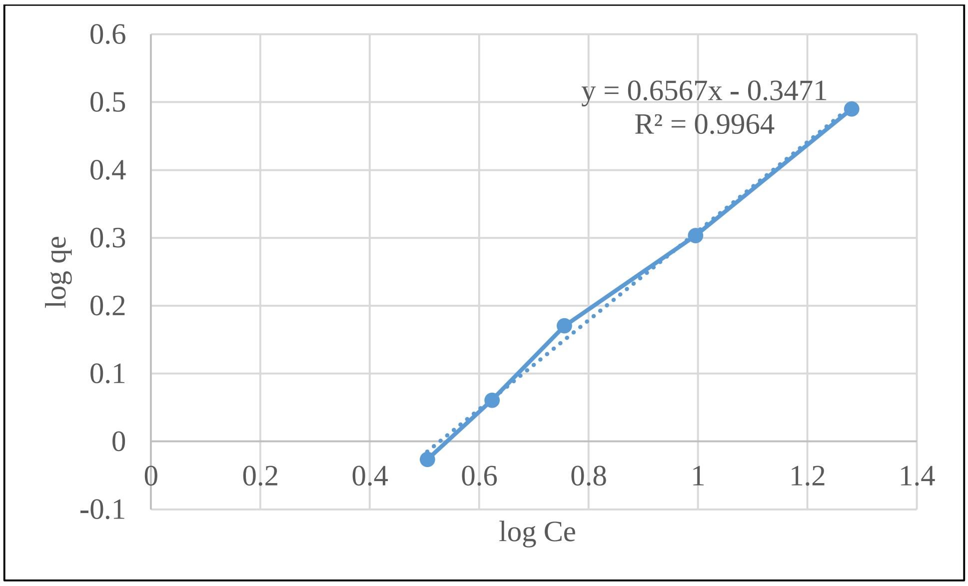

Figure 4.9: $\log q_e \; vs \; \log C_e$ graph for Ambatale WTP sludge (A)

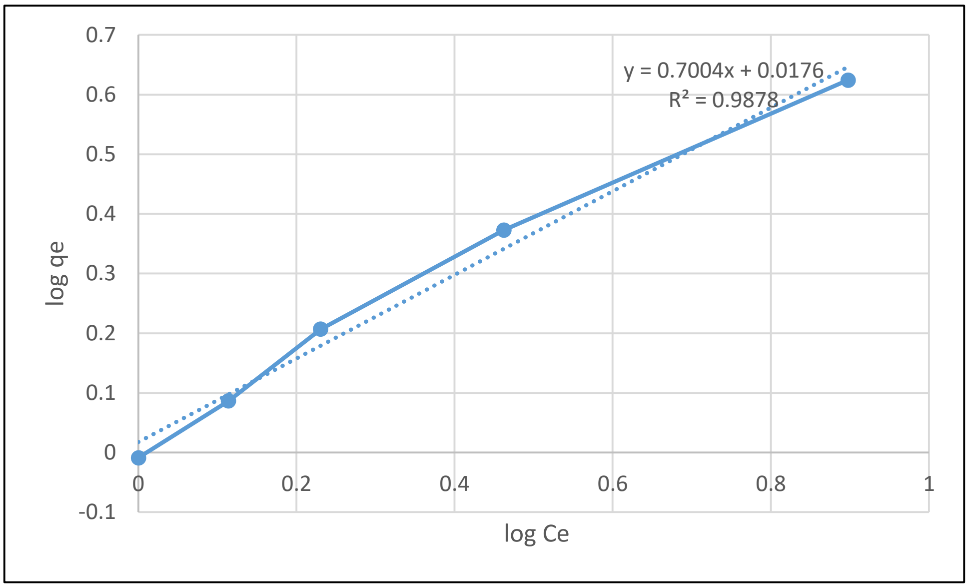

Figure 4.10: log q_e vs log C_e graph for Biyagama WTP sludge (B)

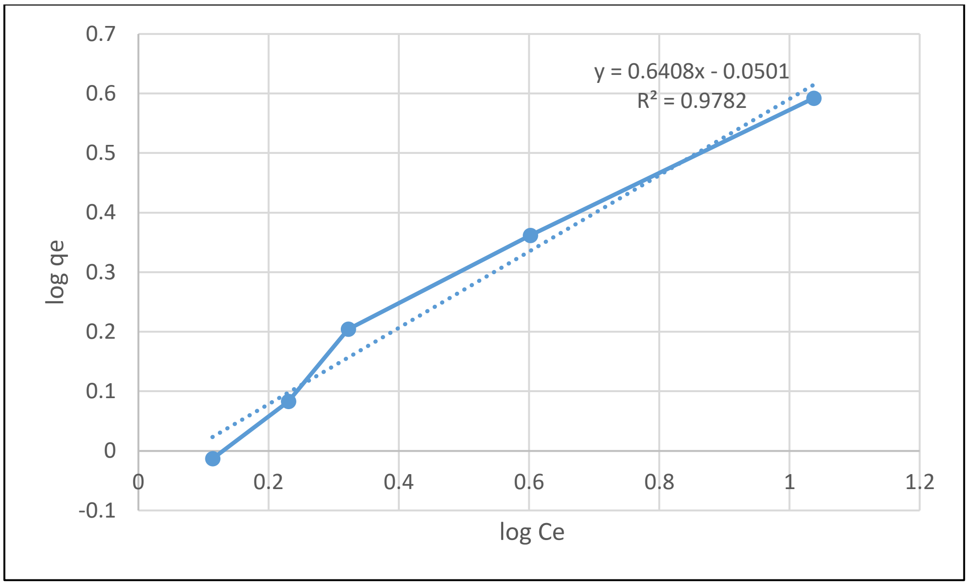

Figure 4.11: log q_e vs log C_e graph for Kandana WTP sludge (C)

From the intercept and the gradient of the graphs, Freundlich constant (K_f) and heterogeneity factor (n) were calculated, and the results are given in table 4.8.

Table 4.8: Freundlich parameters of each sludge sample

	Ambatale WTP Sludge (A)	**Biyagama WTP Sludge (B)**	**Kandana WTP Sludge (C)**
Gradient (1/n)	0.6567	0.7004	0.6408
Intercept (log K_f)	-0.3471	0.0176	-0.0501

R^2	0.9964	0.9878	0.9782
K_f (mg/g)	0.4497	1.0414	0.891
n (g/L)	1.5228	1.4278	1.5605

The R^2 values obtained were also high, particularly:

- Ambatale (0.9964), indicating a very good fit,
- Followed by Biyagama (0.9878) and Kandana (0.9782).

The Freundlich constant (K_f) which indicates adsorption capacity, was again highest for Biyagama sludge (1.0414 mg/g), followed by Kandana (0.891 mg/g) and Ambatale (0.4497 mg/g).

The n values (heterogeneity factor), all greater than 1, ranged from 1.43 to 1.56, confirming favorable adsorption across all samples. This further validates the applicability of Freundlich's model, especially for non-uniform surface interactions.

While the Langmuir model provides a slightly better overall fit based on R^2 and explains monolayer adsorption, the Freundlich model's results confirm favorable and heterogeneous adsorption behavior. Using both models offers a more complete understanding of phosphorus uptake characteristics of the alum sludge.

4.6. Influence of pH on Phosphorus Adsorption Efficiency

The impact of pH on the phosphorus removal capacity of alum sludge was evaluated by varying the pH of the synthetic phosphorus solution (initial P concentration = 70 ppm) from 4 to 8. This range was chosen to simulate the pH conditions commonly encountered in wastewater treatment. The results of this study are presented in Figure 4.9, which depicts the variation in phosphorus removal capacities for the three sludge samples at different pH levels.

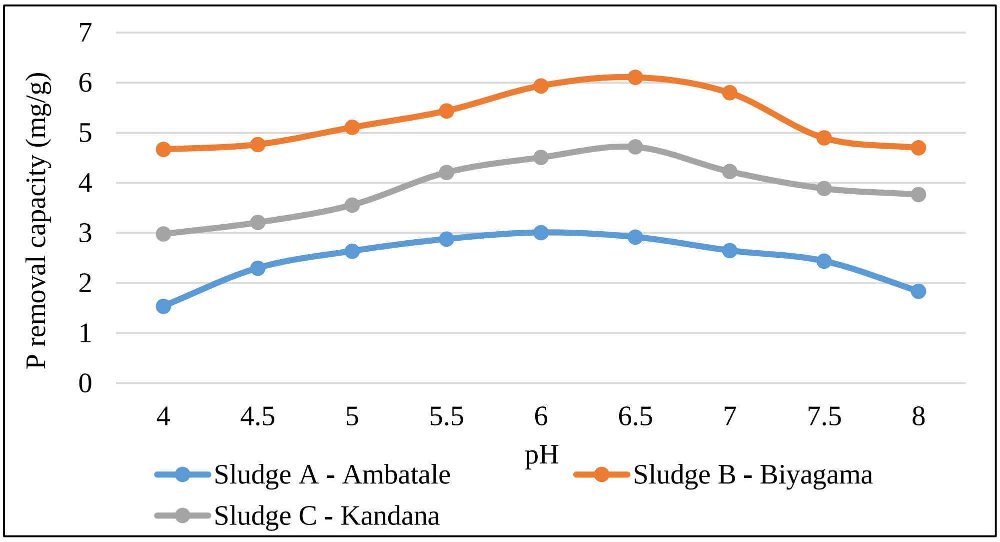

Figure 4.12: Phosphorus removal capacity variation with different pH values

The data reveal that the removal efficiency of all sludge samples is strongly influenced by pH, reaching peak values within a specific range. Ambatale Water Treatment Sludge (A) achieved its maximum phosphorus removal capacity of 3.01 mg/g at a pH of 6, indicating that slightly acidic conditions optimize its adsorption behaviour. Similarly, Biyagama WTS and Kandana WTS demonstrated peak removal capacities of 6.11 mg/g and 4.72 mg/g, respectively, at a slightly higher pH of 6.5.

5. DISCUSSION

5.1. Characteristics of Alum Sludge

The characterization of alum sludge samples from Ambatale, Biyagama, and Kandana water treatment plants provides essential insights into their potential for phosphorus removal.

5.1.1. Moisture Content and its Impact on Adsorption

Ambatale WTP sludge had the highest moisture content (72%), followed by Kandana WTP sludge (66%) and Biyagama WTP sludge (64%). High moisture content reduces adsorption efficiency by occupying potential adsorption sites and diluting the interaction between phosphorus and the sludge surface. Babatunde and Zhao (2010) noted that pre-drying or thermal treatment significantly enhances adsorption performance by increasing available active sites. Pre-drying alum sludge can be particularly advantageous in large-scale wastewater treatment applications, where consistency in adsorption efficiency is critical.

5.1.2. Chemical Composition

The chemical composition of alum sludge highlights aluminum as the predominant element, ranging from 19.51% to 29.52%. This high aluminum content is attributed to the use of alum as a coagulant in water treatment processes. Aluminum's ability to form stable complexes with phosphate ions, such as aluminum phosphate, is well-documented and is the primary mechanism driving phosphorus removal.

Mazari et al. (2018) and Dassanayake et al. (2015) similarly reported high aluminum content in alum sludge, emphasizing its role as a major adsorptive agent. The presence of aluminum enables efficient capture and retention of phosphorus, making alum sludge a viable and sustainable option for wastewater treatment.

Other elements, including oxygen, silicon, and iron, were also identified in the chemical analysis. Oxygen and silicon, primarily found in oxides and silicates, contribute to phosphorus retention through co-precipitation mechanisms. Kim et al. (2002) noted that silicon enhances the stability of the sludge matrix, preventing leaching and ensuring effective phosphorus binding. Iron, although present in smaller quantities (2.72–3.36%), plays a complementary role by forming iron-phosphate complexes, which enhance the overall adsorption capacity. This aligns with findings by Muisa et al. (2020), who highlighted the synergistic role of aluminum and iron in adsorbing phosphorus.

5.1.3. Morphological Analysis

Scanning Electron Microscopy (SEM) analysis revealed the amorphous and heterogeneous structure of the alum sludge samples. This amorphous nature indicates a lack of long-range crystalline order, which is advantageous for adsorption due to increased surface irregularities and porosity. The heterogeneous texture further enhances the interaction between the sludge and phosphorus by providing a variety of binding sites. Yang et al. (2006) emphasized that the texture and porosity of alum sludge significantly influence its adsorption efficiency.

Implications of Elemental and Morphological Properties

The combined presence of high aluminum content and amorphous morphology establishes alum sludge as a promising adsorbent for phosphorus removal. The elemental composition ensures strong chemical interactions with phosphate ions, while the morphological properties provide the physical framework needed for effective adsorption. Additionally, the presence of oxygen and silicon oxides enhances sludge stability, reducing the likelihood of phosphorus leaching under varying environmental conditions (Georgantas & Grigoropoulou, 2005).

The detailed characterization of alum sludge samples underscores their suitability for phosphorus removal in wastewater treatment. The high aluminium content, supported by significant levels of oxygen, silicon, and iron, facilitates strong chemical interactions with phosphorus. The amorphous morphology further enhances adsorption by providing abundant active sites. Together, these characteristics make alum sludge an efficient and sustainable option for addressing phosphorus pollution, consistent with findings from existing literature. Further optimization of pre-treatment processes, such as drying and thermal activation, could further enhance the adsorption efficiency of alum sludge.

5.2. Potential for Phosphorus Release in Alum Sludge Samples

The potential for phosphorus release from alum sludge samples was found to be minimal across all tested conditions, demonstrating their strong capacity to retain adsorbed phosphorus under varying environmental scenarios. The highest release of phosphorus was observed in 0.5N HNO_3, where only 0.049% of phosphorus was leached from the Ambatale WTP sludge. This finding indicates that phosphorus within the alum sludge matrix is largely immobilized, likely due to the formation of stable aluminium-phosphate complexes. This conclusion is supported by Maqbool et al. (2016), who reported that alum sludge exhibits high chemical stability and resistance to leaching under both acidic and neutral conditions.

The minimal phosphorus release in distilled water, with values close to 0.007%, highlights the sludge's stability in neutral and slightly alkaline environments. This indicates that the risk of secondary phosphorus pollution from the alum sludge is negligible, making it an environmentally safe material for wastewater treatment. These results align with findings by Mohammed and Rashid (2012), who attributed the low release rates to the strong chemical bonds formed between aluminium hydroxides and phosphorus, effectively preventing leaching under normal conditions.

5.2.1. Factors Influencing Phosphorus Release

The low leachability of phosphorus in alum sludge can be attributed to several factors:

- ***Aluminium-Phosphate Bonding***

The presence of aluminium as the dominant metal in the sludge composition facilitates the formation of insoluble aluminium-phosphate complexes. These complexes are resistant to dissolution, even under acidic conditions. Studies by Georgantas and Grigoropoulou (2005) and Mazari et al. (2018) also reported that the strong affinity of aluminium for phosphorus significantly limits phosphorus release.

- ***Structural Stability of the Sludge Matrix***

The amorphous and heterogeneous nature of the sludge, as revealed by SEM analysis, provides a robust matrix for binding phosphorus. This structural stability enhances the retention of adsorbed phosphorus and prevents its release under typical environmental conditions. Yang et al. (2006) emphasized the role of sludge texture and porosity in retaining adsorbed contaminants, further supporting this observation.

- ***Acid Solubility***

The slightly higher release observed in 0.5N HNO_3 and 0.5N H_2SO_4 reflects the ability of strong acids to dissolve aluminium hydroxides and other metal-phosphate complexes. However, the phosphorus release remains minimal, suggesting that only a small fraction of phosphorus is loosely bound or present in forms susceptible to acid dissolution. These findings align with Yang et al. (2006), who reported limited phosphorus leachability from alum sludge under acidic conditions due to the predominance of stable complexes.

The low phosphorus release values indicate that alum sludge is environmentally safe and does not pose a risk of secondary phosphorus pollution when used as an adsorbent. This property makes alum sludge suitable for long-term applications in wastewater treatment and soil amendments, where leaching could otherwise cause eutrophication in nearby water bodies. Furthermore, the stability of adsorbed phosphorus under varying pH and chemical conditions reinforces its potential as a reliable material for phosphorus management in diverse environmental contexts.

Studies by Mohammed and Rashid (2012) confirmed that alum sludge retains phosphorus effectively without significant desorption, even under fluctuating pH conditions. Similarly, Maqbool et al. (2016) highlighted the chemical stability of alum sludge, attributing its low leachability to strong chemical interactions between phosphorus and the adsorbent. These findings are consistent with the current study's observations, providing a strong foundation for alum sludge's application as an environmentally sustainable material in wastewater treatment.

5.3. Phosphorus Removal Ability of Alum Sludge

The phosphorus removal ability of alum sludge was evaluated under varying initial phosphorus concentrations (10–80 ppm). Biyagama WTP sludge exhibited the highest adsorption capacity, achieving 5.94 mg/g at 70 ppm. This can be attributed to its high aluminium content and optimized structural properties, such as porosity and particle size, which enhance phosphorus binding. Kandana WTP sludge and Ambatale WTP sludge followed with capacities of 4.51 mg/g and 3.01 mg/g, respectively.

The observed trends align with adsorption behaviours documented in previous studies. Babatunde and Zhao (2010) reported that adsorption efficiency improves with increased aluminium content and decreased water content, as these factors provide more active binding sites for phosphorus. The plateauing of removal efficiency at higher phosphorus concentrations (>60 ppm) indicates saturation of adsorption sites, a phenomenon well-explained by Langmuir isotherms, which assume monolayer adsorption on a finite number of active sites.

5.4. Evaluating Phosphorus Removal Efficiency Over Time

The time-dependent study highlights the dynamics of phosphorus adsorption onto alum sludge and provides insights into the interaction mechanisms between the adsorbent and the phosphorus ions. The results revealed that most phosphorus removal occurred within the first two hours of contact, a period characterized by rapid adsorption. This phenomenon is commonly observed in adsorption studies and is attributed to the abundance of active adsorption sites on the surface of the adsorbent during the initial phase.

5.4.1. Rapid Adsorption Phase

During the first two hours, the alum sludge exhibits a high rate of phosphorus removal, which aligns with findings by Yang et al. (2006). They observed that the rapid decrease in phosphorus concentration is primarily driven by surface adsorption mechanisms. In this phase, phosphate ions in the solution interact readily with the active sites on the alum sludge, forming stable complexes. This behavior is further explained by the presence of a high aluminum content in the sludge, which promotes the formation of aluminum-phosphate complexes.

Additionally, the amorphous structure of alum sludge, as observed in the SEM analysis, contributes to the rapid adsorption rate by providing a large surface area and accessible adsorption sites. The heterogeneous texture and porosity ensure efficient contact between phosphorus ions and the adsorbent, enhancing the rate of adsorption.

5.4.2. Equilibrium Phase

Beyond the initial two hours, the adsorption rate slowed significantly, eventually reaching equilibrium. At this stage, the available active sites on the alum sludge surface become saturated, and the phosphorus removal efficiency stabilizes. This behavior is characteristic of adsorption processes, where the driving force for adsorption decreases as the system approaches equilibrium. At equilibrium, no further significant phosphorus removal occurs, as the concentration gradient between the solution and the sludge surface diminishes.

5.4.3. Absence of Desorption

The study also demonstrated the absence of desorption over time, indicating that the phosphorus adsorbed onto the alum sludge remained bound and did not leach back into the solution. This stability suggests the formation of strong chemical bonds between phosphorus and the alum sludge, particularly aluminum-phosphate complexes. Babatunde and Zhao (2010) emphasized the importance of these stable complexes in ensuring long-term retention of phosphorus, making alum sludge a reliable adsorbent for wastewater treatment.

5.4.4. Comparative Analysis with Literature

The rapid adsorption and subsequent stabilization observed in this study are consistent with patterns reported in previous research:

1. Yang et al. (2006) described a similar rapid adsorption phase in their experiments, attributing it to the abundance of active sites during the early stages of contact.
2. Babatunde and Zhao (2010) highlighted that the stability of adsorbed phosphorus is critical for preventing desorption, particularly under prolonged exposure.
3. Maqbool et al. (2016) and Mohammed and Rashid (2012) confirmed the strong binding capacity of alum sludge for phosphorus, supported by the formation of aluminum-phosphate and iron-phosphate complexes.

Understanding the time-dependent behavior of phosphorus adsorption has practical implications for optimizing wastewater treatment processes. The rapid removal within the first two hours indicates that alum sludge can effectively reduce phosphorus levels in a short timeframe, making it suitable for high-throughput treatment systems. The equilibrium phase highlights the need to optimize sludge dosages to ensure maximum utilization of available adsorption sites.

Furthermore, the absence of desorption underscores the reliability of alum sludge as an adsorbent, ensuring that the phosphorus removed from wastewater remains immobilized. This stability reduces the risk of secondary pollution and enhances the sustainability of alum sludge as a phosphorus removal agent.

5.5. Maximum Adsorption Capacity of Alum Sludge

The determination of the maximum adsorption capacity of alum sludge provides critical insights into its potential for phosphorus removal and the mechanisms involved. The Langmuir isotherm model was applied to experimental data, confirming that adsorption followed monolayer behaviour. High R^2 values (greater than 0.98) for all three sludge samples indicate an excellent fit to the Langmuir model, suggesting that the adsorption process predominantly involves specific interactions between phosphorus ions and active sites on the alum sludge surface.

5.5.1. Maximum Adsorption Capacities of the Sludge Samples

The maximum adsorption capacities (Q_{max}) of the three sludge samples were ranked as follows:

1. Biyagama WTP Sludge: Q_{max} =7.96 mg/g
2. Kandana WTP Sludge: Q_{max}=6.45 mg/g
3. Ambatale WTP Sludge: Q_{max}=5.69 mg/g

These values reflect the effectiveness of the sludge samples in removing phosphorus from the solution. Biyagama WTP sludge demonstrated the highest adsorption capacity, likely due to its higher aluminium content and optimal structural properties, such as porosity and surface area. Studies by Babatunde and Zhao (2010) and Mazari et al. (2018) have similarly shown that the aluminium content and structural characteristics of alum sludge are key determinants of its adsorption performance. Kandana and Ambatale sludges, while also effective, exhibited comparatively lower adsorption capacities, likely due to differences in chemical composition and texture.

5.5.2. Langmuir Constant (b) and Adsorption Affinity

The Langmuir constant (b) provides a measure of the affinity between the adsorbent and the adsorbate. Among the sludge samples, Biyagama WTP sludge exhibited the highest b value (b=0.1433 L/mg) indicating a stronger interaction between phosphorus ions and the sludge surface. This strong affinity enhances the adsorption efficiency and ensures effective phosphorus removal, even at lower concentrations. Kandana sludge followed closely with a b value of 0.1413 L/mg, while Ambatale sludge had the lowest affinity (b=0.0601 L/mg). These findings align with the observations of Van Truong et al. (2021), who emphasized that higher b values correlate with enhanced adsorption performance and greater chemical interactions between the adsorbent and the target contaminant. The stronger affinity exhibited by Biyagama and Kandana sludge can be attributed to their higher aluminum content and more favorable morphological properties, which increase the availability of active adsorption sites.

The Q_{max} values observed in this study are comparable to those reported in the literature. For instance:

- Van Truong et al. (2021) reported similar adsorption capacities for alum sludge samples treated under controlled conditions, highlighting the impact of pre-treatment and sludge composition on performance.
- Babatunde and Zhao (2010) demonstrated that the adsorption capacity of alum sludge can range from 5 mg/g to 10 mg/g, depending on its chemical and structural properties.

The high Q_{max} and b values for Biyagama sludge suggest that it is the most effective among the three samples for phosphorus removal in wastewater treatment applications. Its strong affinity for phosphorus ensures efficient adsorption, even at lower sludge dosages, making it a cost-effective option. The lower capacities of Ambatale and Kandana sludges, while still effective, highlight the need for optimization through pre-treatment or chemical modification to enhance their performance.

5.5.3. Isotherm Model Comparison

While both the Langmuir and Freundlich models yielded strong correlations in this study, the Langmuir model exhibited a slightly better statistical fit based on the R^2 values across all sludge samples. This suggests that phosphorus adsorption predominantly follows monolayer coverage behavior on relatively uniform adsorption sites under the controlled batch conditions. This finding aligns with earlier studies which have reported the Langmuir model's suitability in describing phosphorus uptake onto aluminum-based adsorbents, particularly in systems with a high degree of surface saturation and well-defined active sites (Yang et al., 2006; Babatunde & Zhao, 2010).

However, the strong performance of the Freundlich model, particularly for the Ambatale and Kandana sludge samples, indicates the presence of surface heterogeneity, a common characteristic of waste-derived adsorbents like alum sludge. Unlike Langmuir, the Freundlich model accounts for variable energy distributions across the surface, which is relevant given that alum sludge may contain diverse particle morphologies, irregular pore structures, and varied mineral content due to differences in water source and treatment process (Song et al., 2011; Zhu et al., 2012).

Using both models provides a more complete understanding of the adsorption process. While Langmuir defines the capacity and affinity at uniform sites, Freundlich reveals the range of adsorption energies and interaction complexities that can occur in practical systems. This dual approach increases confidence in experimental interpretations and reflects best practices in adsorption modeling (Foo & Hameed, 2010).

5.6. Influence of pH on Phosphorus Adsorption Efficiency

The pH - dependent study provides critical insights into the behaviour of alum sludge in phosphorus adsorption under varying environmental conditions. Results demonstrated that phosphorus removal efficiency peaked under slightly acidic conditions (pH 6–6.5). Ambatale sludge reached a maximum capacity of 3.01 mg/g at pH 6, while Biyagama and Kandana sludges exhibited peak capacities of 6.11 mg/g and 4.72 mg/g at pH 6.5, respectively.

While comparing the effect of pH with past studies, it is important to also consider the temperature conditions under which those studies were conducted. For example, Yang et al. (2006) conducted adsorption experiments at 25°C, which aligns with the room temperature conditions in this study. Variations in temperature can significantly influence adsorption kinetics and capacity by affecting reaction rates and solubility equilibria.

5.6.1. Mechanisms of pH Influence

The observed trends can be attributed to the interaction between the surface charge of the alum sludge and the speciation of phosphorus in solution:

Low pH (Acidic Conditions)

At low pH values (<6), the surface of the alum sludge becomes positively charged due to protonation of hydroxyl groups on aluminium and iron oxides. This positive surface charge repels negatively charged phosphate ions ($H_2PO_4^-$) and HPO42resulting in reduced adsorption efficiency. This phenomenon has been widely reported in the literature, with Babatunde and Zhao (2010) emphasizing electrostatic repulsion at low pH as a limiting factor for phosphorus adsorption.

Optimal pH (Slightly Acidic to Neutral Conditions)

As the pH approaches neutrality (pH 6–6.5), the surface charge of the sludge diminishes, reducing electrostatic repulsion. This allows for stronger interactions between phosphorus species and the adsorbent surface. At these pH levels, aluminium and iron in the sludge form stable complexes with phosphate ions, such as aluminium phosphate and iron phosphate, enhancing adsorption efficiency (Mazari et al., 2018). Mohammed and Rashid (2012) also reported that the formation of these complexes is maximized under slightly acidic conditions.

High pH (Alkaline Conditions)

At pH values greater than 7, the sludge surface may become negatively charged, which can repel phosphate anions and hinder adsorption. Additionally, the formation of insoluble calcium and magnesium phosphate compounds compete with adsorption, reducing the overall removal efficiency. Georgantas and Grigoropoulou (2005) highlighted this competition, noting that precipitation of phosphorus as calcium or magnesium phosphates is more prevalent in alkaline conditions.

5.6.2. Comparative Analysis with Literature

The findings of this study align with several previous investigations, highlighting the importance of pH optimization in phosphorus adsorption:

- Babatunde and Zhao (2010) emphasized that the optimal pH range for phosphorus removal is slightly acidic to neutral, where both electrostatic and chemical interactions are maximized.
- Mohammed and Rashid (2012) identified the formation of stable metal-phosphate complexes as a key mechanism for enhanced adsorption at pH 6–6.5.
- Yang et al. (2006) reported similar trends, where phosphorus adsorption peaked near pH 6.5 and declined at both lower and higher pH values due to changes in surface charge and competition from precipitation.

5.6.3. Implications for Wastewater Treatment

The pH-dependent behavior of alum sludge has practical implications for its application in wastewater treatment,

pH Optimization

Maintaining the pH of wastewater between 6 and 6.5 ensures maximum phosphorus removal efficiency, particularly for sludges with high aluminum or iron content.

Versatility in Treatment Systems

The effectiveness of alum sludge under slightly acidic to neutral conditions makes it suitable for a wide range of wastewater treatment scenarios, including those with fluctuating pH levels.

Reduced Competition in Neutral pH

Operating within the optimal pH range minimizes the impact of competing processes, such as precipitation, ensuring that adsorption remains the dominant removal mechanism.

Environmental Safety

The strong retention of phosphorus by alum sludge at optimal pH levels reduces the risk of desorption and secondary pollution, making it a reliable material for sustainable wastewater treatment applications (Maqbool et al., 2016).

5.7. Comparison with Other Phosphorus Removal Techniques

The effectiveness of alum sludge for phosphorus removal was compared with conventional and emerging phosphorus removal techniques, such as chemical precipitation, biological phosphorus removal (BPR), and advanced adsorption methods. This comparison highlights alum sludge's potential as a cost-effective and environmentally sustainable alternative.

5.7.1. Chemical Precipitation

Chemical precipitation is a widely used method involving the addition of metal salts like aluminium sulphate or ferric chloride to form insoluble phosphorus complexes. While highly effective, this method has drawbacks:

- Chemical precipitation achieves high phosphorus removal rates, often exceeding 90% (Georgantas & Grigoropoulou, 2005). Alum sludge demonstrated comparable removal efficiencies, particularly at high phosphorus concentrations.
- Unlike chemical precipitation, alum sludge repurposes a waste product, reducing the need for additional chemical inputs and lowering operational costs (Babatunde & Zhao, 2010).
- Alum sludge minimizes sludge production compared to chemical precipitation, which generates significant volumes of waste requiring disposal.

5.7.2. Biological Phosphorus Removal (BPR)

BPR utilizes specific bacteria to uptake phosphorus in wastewater treatment systems. Key differences include:

- BPR systems are highly sensitive to temperature, organic loading, and other operational conditions, which can compromise performance. Alum sludge, by contrast, maintains stable performance across a broader range of conditions (Mohammed & Rashid, 2012).
- BPR systems have lower operating costs but higher installation and maintenance expenses. Alum sludge offers a more cost-effective solution for facilities with limited resources.
- Alum sludge can be easily integrated into existing systems, making it suitable for small-scale operations where BPR may not be feasible.

5.7.3. Advanced Adsorption Techniques

Emerging adsorption technologies use specialized materials like activated carbon, biochar, and synthetic resins. Comparisons include:

- Alum sludge’s maximum adsorption capacities (e.g., 7.96 mg/g for Biyagama WTP sludge) are competitive with some advanced adsorbents, although biochar and resins often exhibit higher capacities under optimized conditions (Mazari et al., 2018).
- Alum sludge is a low-cost alternative to advanced materials, which are expensive to produce and regenerate.
- Alum sludge promotes circular economy principles by upcycling a waste product, whereas many advanced adsorbents rely on energy-intensive manufacturing processes.

5.7.4. Hybrid Approaches

Hybrid systems combining alum sludge with other techniques, such as membrane filtration or biological processes, could offer synergistic benefits:

- Alum sludge can be used as a pre-treatment step to reduce phosphorus loads before advanced techniques, extending their lifespan and reducing costs.
- Hybrid systems enable greater flexibility in addressing complex wastewater compositions.

While traditional methods like chemical precipitation and BPR have proven effective, alum sludge offers unique advantages in terms of cost, environmental sustainability, and operational simplicity. Its competitive adsorption capacity and stability make it a viable alternative or complement to existing techniques. Further research into hybrid systems and large-scale implementation could enhance its applicability and optimize its performance in diverse wastewater treatment scenarios.

5.8. Limitations of the Study

- Synthetic Wastewater Use: The use of synthetic wastewater allowed for greater control of experimental variables and eliminated the presence of interfering substances. However, real municipal wastewater contains a wide variety of organic compounds, suspended solids, and competing anions such as nitrates, sulfates, and bicarbonates. These can interfere with the adsorption of phosphorus onto alum sludge and affect the removal efficiency. Therefore, results obtained under synthetic conditions may not be fully representative of real-world treatment scenarios.
- Limited Sludge Samples: This study evaluated only three alum sludge samples from selected water treatment plants in Sri Lanka. These samples may not fully capture the variability in sludge characteristics that result from differences in source water quality, treatment chemicals, and operational practices. Consequently, generalizing the findings to all types of alum sludge should be approached with caution.
- Fixed Environmental Conditions: The batch experiments were conducted under controlled laboratory conditions, typically at ambient room temperature and neutral pH unless otherwise specified. In actual treatment environments, factors such as seasonal temperature fluctuations, varying pH levels, and ionic strength can significantly influence adsorption performance. The lack of variability in these environmental parameters limits the study's ability to predict field performance accurately.
- No Continuous Flow Testing: The study was conducted entirely using batch adsorption experiments. While this is useful for preliminary assessments, it does not reflect the dynamics of real wastewater treatment processes, which typically operate under continuous flow. Without testing in continuous

systems, it is difficult to evaluate the practicality, efficiency, and operational stability of using alum sludge in real treatment scenarios.

- No Long-term Performance Evaluation: The study did not investigate the reusability or long-term stability of the alum sludge as an adsorbent. Repeated use, potential fouling, and structural degradation over time are important considerations for determining the economic and operational feasibility of this method. The absence of long-term testing limits the understanding of the material's lifespan and potential for regeneration.

These limitations highlight the importance of conducting further research under more realistic conditions. Addressing these issues in future work will be critical to verifying the practical applicability of alum sludge for phosphorus removal and advancing its potential as a sustainable wastewater treatment solution.

5.9. Identified Gaps and Directions for Future Research

In addition to the methodological limitations addressed earlier, this study has revealed broader research gaps that merit targeted investigation. Bridging these gaps is essential for advancing the practical implementation and scientific understanding of alum sludge as a sustainable adsorbent for phosphorus removal.

1. Integration with Real Wastewater Systems

While synthetic wastewater offers control and reproducibility, the next logical progression is to test alum sludge under real municipal or industrial wastewater matrices. These environments introduce complex chemical interactions, including competition from anions such as sulfate and nitrate, and organic ligands that may inhibit phosphorus adsorption. Incorporating real wastewater testing would validate the material's performance under field-relevant scenarios and regulatory conditions (Zhang et al., 2018).

2. Hybrid Treatment Approaches

Emerging research advocates for integrating adsorption with biological or membrane-based treatments to optimize nutrient removal and reduce sludge generation. Alum sludge could be evaluated as a polishing step after biological phosphorus removal or embedded in filter media within constructed wetlands. These hybrid systems may offer synergistic benefits and higher resilience against fluctuating loads (de-Bashan & Bashan, 2004).

3. Adsorbent Regeneration and Lifecycle Assessment

This study focused on single-use adsorption. Future work should explore the regeneration potential of spent alum sludge through thermal or chemical desorption methods. Additionally, a full lifecycle analysis (LCA) could assess the energy and environmental footprint of sourcing, preparing, and reusing alum sludge, in comparison to conventional adsorbents like activated alumina (Zhou et al., 2017).

4. Material Engineering and Surface Modification

Unmodified alum sludge may not always meet industrial adsorption thresholds. Researchers should explore modifying sludge using physical (calcination, milling) or chemical treatments (acid or base activation, composite blending) to improve porosity, surface area, and functional group availability. Such engineered adsorbents have shown improved performance for diverse pollutants beyond phosphorus (Xiong et al., 2011).

5. Valorization and Resource Recovery

Beyond nutrient removal, future studies should examine alum sludge as a phosphorus recovery material for agricultural reuse. Recovering phosphorus in plant-available forms or transforming the spent adsorbent into slow-release fertilizers or soil conditioners could close the loop between water and agriculture sectors (Ye et al., 2017).

6. CONCLUSIONS

- The alum sludge samples displayed notable variability in moisture content and elemental composition, with high aluminum concentrations (ranging from 19.51% to 29.52%) that support their strong phosphorus adsorption potential. SEM analysis confirmed the amorphous and heterogeneous surface characteristics of the sludge, which likely contributed to enhanced surface interactions and adsorption capabilities.
- Phosphorus stability tests indicated minimal desorption across all conditions, with the highest release observed in 0.5N HNO_3. This suggests that phosphorus is strongly retained within the sludge matrix, minimizing the risk of secondary pollution and reinforcing its suitability for wastewater treatment.
- Phosphorus removal efficiency increased with rising initial phosphorus concentrations, confirming that alum sludge remains effective even under high contaminant loads. Among the samples, Biyagama WTP sludge consistently demonstrated superior performance, followed by Kandana and Ambatale sludges, reflecting the influence of sludge origin on adsorption behavior.
- The adsorption process was rapid, with most phosphorus removal occurring within the first two hours, and equilibrium reached soon after. No significant phosphorus desorption was observed, indicating stable binding and minimal reversibility under batch conditions.
- Adsorption isotherm analysis revealed that the Langmuir model provided the best overall fit, suggesting monolayer adsorption with defined saturation points. Maximum adsorption capacities (Q_{max}) were 7.96 mg/g (Biyagama), 6.45 mg/g (Kandana), and 5.69 mg/g (Ambatale). The Freundlich model also showed strong correlation, supporting the role of heterogeneous surface interactions. The application of the Temkin model further validated the presence of adsorbate–adsorbent interactions, though with moderate predictive accuracy.
- Optimal phosphorus removal occurred at slightly acidic pH values (6.0–6.5), where electrostatic attraction and reduced phosphate precipitation favored stronger binding. At more extreme pH values, reduced efficiency was attributed to changes in surface charge dynamics and phosphate solubility.
- Based on these findings, alum sludge is a cost-effective, stable, and environmentally friendly alternative for phosphorus removal. Its performance under controlled conditions demonstrates strong potential for integration into wastewater treatment processes, particularly when enhanced through isotherm-based optimization and tailored application design.
- Nonetheless, this study also identified several key areas for future investigation, including the need for real wastewater validation, continuous flow experimentation, regeneration and reuse potential, and resource recovery applications. Addressing these aspects will be essential to transitioning alum sludge from laboratory demonstration to real-world implementation.

7. RECOMMENDATIONS

- Future research should examine the effects of chemical treatments such as acid washing, alkali activation, or polymer coating on alum sludge to improve its adsorption efficiency and selectivity for phosphorus.
- Evaluate how thermal treatment at different temperatures affects pore structure, surface area, and adsorption properties to optimize phosphorus binding performance.
- Conduct experiments using actual wastewater containing multiple contaminants (e.g., nitrates, sulfates, heavy metals) to assess the competitive adsorption behavior and selectivity of alum sludge.
- Perform extended studies on phosphorus-loaded alum sludge to determine its structural and adsorption stability under varying environmental conditions such as pH, temperature, and salinity. Investigate regeneration potential for multiple use cycles.
- Explore combining alum sludge with materials like activated carbon, biochar, or synthetic polymers to enhance overall adsorption performance, particularly in multi-contaminant wastewater systems.
- Transition from batch experiments to continuous flow or pilot-scale studies to evaluate real-world performance, operational challenges, and scalability of using alum sludge in wastewater treatment.
- Investigate the potential of reusing spent alum sludge in applications such as slow-release fertilizers, soil amendments, or raw material in construction, contributing to sustainable waste management and resource recovery.

8. REFERENCES

Agostina, C., Simona, B., & Giorgia, D. F. (n.d.-a). *Technical-economic comparison of chemical precipitation and ion exchange processes for the removal of phosphorous from wastewater 2*.

Agostina, C., Simona, B., & Giorgia, D. F. (n.d.-b). *Technical-economic comparison of chemical precipitation and ion exchange processes for the removal of phosphorous from wastewater 2*.

Albertsen, M., Karst, S. M., Ziegler, A. S., Kirkegaard, R. H., & Nielsen, P. H. (2015). Back to basics - The influence of DNA extraction and primer choice on phylogenetic analysis of activated sludge communities. *PLoS ONE*, *10*(7). https://doi.org/10.1371/journal.pone.0132783

Alewi, H. K., Abood, E. A., & Ali, G. (2022). An inquiry into the relationships between BOD5, COD, and TOC in Tigris River, Maysan Province, Iraq. *Caspian Journal of Environmental Sciences*, *20*(1), 37–43. https://doi.org/10.22124/CJES.2022.5390

Ali, A., Chiang, Y. W., & Santos, R. M. (2022). X-Ray Diffraction Techniques for Mineral Characterization: A Review for Engineers of the Fundamentals, Applications, and Research Directions. *Minerals*, *12*(2). https://doi.org/10.3390/min12020205

Ali Dawood, S. A., Obaid, H. A., Hashim, T. M., & Jasim, H. K. (2019). Influence of using alum sludge as an aggregate on hot mix Asphalt. *IOP Conference Series: Materials Science and Engineering*, *584*(1). https://doi.org/10.1088/1757-899X/584/1/012032

Aniza, N., Hassan, S., M Nor, M. F., & Kee, K. E. (2015). *Jurnal Teknologi Full Paper INVESTIGATION OF THERMAL DEGRADATION OF POULTRY PROCESSING DEWATERED SLUDGE USING THERMOGRAVIMETRIC ANALYSIS METHOD* (Vol. 76, Issue 5). www.jurnalteknologi.utm.my

Arias, C. A., Bubba, M. Del, & Brix, H. (2001). PHOSPHORUS REMOVAL BY SANDS FOR USE AS MEDIA IN SUBSURFACE FLOW CONSTRUCTED REED BEDS. In *Wat. Res* (Vol. 35, Issue 5).

Babatunde, A. O., & Zhao, Y. Q. (2007). Constructive approaches toward water treatment works sludge management: An international review of beneficial reuses. In *Critical Reviews in Environmental Science and Technology* (Vol. 37, Issue 2, pp. 129–164). https://doi.org/10.1080/10643380600776239

Babatunde, A. O., & Zhao, Y. Q. (2010). Equilibrium and kinetic analysis of phosphorus adsorption from aqueous solution using waste alum sludge. *Journal of Hazardous Materials*, *184*(1–3), 746–752. https://doi.org/10.1016/j.jhazmat.2010.08.102

Babatunde, A. O., Zhao, Y. Q., & Zhao, X. H. (2010). Alum sludge-based constructed wetland system for enhanced removal of P and OM from wastewater: Concept, design and performance analysis. *Bioresource Technology*, *101*(16), 6576–6579. https://doi.org/10.1016/j.biortech.2010.03.066

Balkaya, M. (2016). Evaluation of the use of alum sludge as hydraulic barrier layer and daily cover material in landfills: a finite element analysis study. *Desalination and Water Treatment*, *57*(6), 2400–2412. https://doi.org/10.1080/19443994.2015.1005154

Bashir, A., Wang, L., Deng, S., Liu, J., Tian, J., Qiu, B., & Cheng, X. (2019a). Phosphorus release during alkaline treatment of waste activated sludge from wastewater treatment plants with Al salt enhanced phosphorus removal: Speciation and mechanism clarification. *Science of the Total Environment*, *688*, 87–93. https://doi.org/10.1016/j.scitotenv.2019.06.207

Bashir, A., Wang, L., Deng, S., Liu, J., Tian, J., Qiu, B., & Cheng, X. (2019b). Phosphorus release during alkaline treatment of waste activated sludge from wastewater treatment plants with Al salt enhanced phosphorus removal: Speciation and mechanism clarification. *Science of the Total Environment*, *688*, 87–93. https://doi.org/10.1016/j.scitotenv.2019.06.207

Blott, S. J., & Pye, K. (2006). Particle size distribution analysis of sand-sized particles by laser diffraction: An experimental investigation of instrument sensitivity and the effects of particle shape. *Sedimentology*, *53*(3), 671–685. https://doi.org/10.1111/j.1365-3091.2006.00786.x

Boczkaj, G., & Fernandes, A. (2017). Wastewater treatment by means of advanced oxidation processes at basic pH conditions: A review. In *Chemical Engineering Journal* (Vol. 320, pp. 608–633). Elsevier B.V. https://doi.org/10.1016/j.cej.2017.03.084

Cai, Y., Han, Z., Lin, X., Duan, Y., Du, J., Ye, Z., & Zhu, J. (2020). Study on removal of phosphorus as struvite from synthetic wastewater using a pilot-scale electrodialysis system with magnesium anode. In *Science of the Total Environment* (Vol. 726). Elsevier B.V. https://doi.org/10.1016/j.scitotenv.2020.138221

Carpenter, S. R. (2001). *Eutrophication of aquatic ecosystems: Bistability and soil phosphorus*. www.pnas.orgcgidoi10.1073pnas.0503959102

Chen, C. (2003). Evaluation of Air Oven Moisture Content Determination Methods for Rough Rice. *Biosystems Engineering*, *86*(4), 447–457. https://doi.org/10.1016/j.biosystemseng.2003.08.010

Chen, Y., Zou, C., Mastalerz, M., Hu, S., Gasaway, C., & Tao, X. (2015). Applications of micro-fourier transform infrared spectroscopy (FTIR) in the geological sciences—A Review. In *International Journal of Molecular Sciences* (Vol. 16, Issue 12, pp. 30223–30250). MDPI AG. https://doi.org/10.3390/ijms161226227

Conley, D. J., Paerl, H. W., Howarth, R. W., Boesch, D. F., Seitzinger, S. P., Havens, K. E., Lancelot, C., & Likens, G. E. (2009). Ecology - Controlling eutrophication: Nitrogen and phosphorus. In *Science* (Vol. 323, Issue 5917, pp. 1014–1015). https://doi.org/10.1126/science.1167755

Corrêa Martins, M. N., de Souza, V. V., & Souza, T. da S. (2016). Genotoxic and mutagenic effects of sewage sludge on higher plants. In *Ecotoxicology and Environmental Safety* (Vol. 124, pp. 489–496). Academic Press. https://doi.org/10.1016/j.ecoenv.2015.11.031

Cummings, L. A., Kurosawa, K., Hoogestraat, D. R., SenGupta, D. J., Candra, F., Doyle, M., Thielges, S., Land, T. A., Rosenthal, C. A., Hoffman, N. G., Salipante, S. J., & Cookson, B. T. (2016). Clinical next generation sequencing outperforms standard microbiological culture for characterizing polymicrobial samples. *Clinical Chemistry*, *62*(11), 1465–1473. https://doi.org/10.1373/clinchem.2016.258806

Dassanayake, K. B., Jayasinghe, G. Y., Surapaneni, A., & Hetherington, C. (2015a). A review on alum sludge reuse with special reference to agricultural applications and future challenges. In *Waste Management* (Vol. 38, Issue 1, pp. 321–335). Elsevier Ltd. https://doi.org/10.1016/j.wasman.2014.11.025

Dassanayake, K. B., Jayasinghe, G. Y., Surapaneni, A., & Hetherington, C. (2015b). A review on alum sludge reuse with special reference to agricultural applications and future challenges. In *Waste Management* (Vol. 38, Issue 1, pp. 321–335). Elsevier Ltd. https://doi.org/10.1016/j.wasman.2014.11.025

de Barros, I. R., Benincá, C., & Zanoelo, E. F. (2023). Kinetics of the precipitation reaction between aluminium and contaminant orthophosphate ions. *Environmental Technology (United Kingdom)*. https://doi.org/10.1080/09593330.2023.2246643

De Carvalho Gomes, S., Zhou, J. L., Li, W., & Long, G. (n.d.). *Progress in manufacture and properties of construction materials incorporating water treatment sludge: a review 2 3 4*.

De-Bashan, L. E., & Bashan, Y. (2004). Recent advances in removing phosphorus from wastewater and its future use as fertilizer (1997-2003). *Water Research*, *38*(19), 4222–4246. https://doi.org/10.1016/j.watres.2004.07.014

Divya, S., Sharmila, P., Dinakaran, J., Yamal, G., Rao, K. S., & Pardha-Saradhi, P. (2020). Specific H+ level is crucial for accurate phosphate quantification using ascorbate as a reductant. *Protoplasma*, *257*(1), 319–330. https://doi.org/10.1007/s00709-019-01424-9

Dodds, W. K., Bouska, W. W., Eitzmann, J. L., Pilger, T. J., Pitts, K. L., Riley, A. J., Schloesser, J. T., & Thornbrugh, D. J. (2009). Eutrophication of U. S. freshwaters: Analysis of potential economic damages. *Environmental Science and Technology*, *43*(1), 12–19. https://doi.org/10.1021/es801217q

Ebeling, J. M., Sibrell, P. L., Ogden, S. R., & Summerfelt, S. T. (2003). Evaluation of chemical coagulation-flocculation aids for the removal of suspended solids and phosphorus from intensive recirculating aquaculture effluent discharge. *Aquacultural Engineering*, *29*(1–2), 23–42. https://doi.org/10.1016/S0144-8609(03)00029-3

Egle, L., Rechberger, H., Krampe, J., & Zessner, M. (2016). Phosphorus recovery from municipal wastewater: An integrated comparative technological, environmental and economic assessment of P recovery technologies. *Science of the Total Environment*, *571*, 522–542. https://doi.org/10.1016/j.scitotenv.2016.07.019

Everaert, M., Bergmans, J., Broos, K., Hermans, B., & Michielsen, B. (2021). Granulation and calcination of alum sludge for the development of a phosphorus adsorbent: From lab scale to pilot scale. *Journal of Environmental Management*, *279*. https://doi.org/10.1016/j.jenvman.2020.111525

Franco, D., Lee, J., Arbelaez, S., Cohen, N., & Kim, J. Y. (2017). Removal of phosphate from surface and wastewater via electrocoagulation. *Ecological Engineering*, *108*, 589–596. https://doi.org/10.1016/j.ecoleng.2017.07.031

Fu, J. F., Zhao, Y. Q., Razali, M., & Bruen, M. (n.d.). *Response surface optimization of phosphorus species adsorption onto powdered alum sludge*.

Gallardo-Gonzalez, J., Baraket, A., Boudjaoui, S., Metzner, T., Hauser, F., Rößler, T., Krause, S., Zine, N., Streklas, A., Alcácer, A., Bausells, J., & Errachid, A. (2019). A fully integrated passive microfluidic Lab-on-a-Chip for real-time electrochemical detection of ammonium: Sewage applications. *Science of the Total Environment*, *653*, 1223–1230. https://doi.org/10.1016/j.scitotenv.2018.11.002

Ge, H., Batstone, D. J., & Keller, J. (2015). Biological phosphorus removal from abattoir wastewater at very short sludge ages mediated bynovel PAO clade Comamonadaceae. *Water Research*, *69*, 173–182. https://doi.org/10.1016/j.watres.2014.11.026

Genz, A., Kornmüller, A., & Jekel, M. (2004). Advanced phosphorus removal from membrane filtrates by adsorption on activated aluminium oxide and granulated ferric hydroxide. *Water Research*, *38*(16), 3523–3530. https://doi.org/10.1016/j.watres.2004.06.006

Georgantas, D. A., & Grigoropoulou, H. P. (n.d.). *Phosphorus removal from synthetic and municipal wastewater using spent alum sludge*. http://iwaponline.com/wst/article-pdf/52/10-11/525/433647/525.pdf

Georgantas, D. A., Matsis, V. M., & Grigoropoulou, H. P. (2006). Soluble phosphorus removal through adsorption on spent alum sludge. *Environmental Technology*, *27*(10), 1081–1088. https://doi.org/10.1080/09593332708618726

Ghafari, S., Aziz, H. A., Isa, M. H., & Zinatizadeh, A. A. (2009a). Application of response surface methodology (RSM) to optimize coagulation-flocculation treatment of leachate using poly-aluminum chloride (PAC) and alum. *Journal of Hazardous Materials*, *163*(2–3), 650–656. https://doi.org/10.1016/j.jhazmat.2008.07.090

Ghafari, S., Aziz, H. A., Isa, M. H., & Zinatizadeh, A. A. (2009b). Application of response surface methodology (RSM) to optimize coagulation-flocculation treatment of leachate using poly-aluminum chloride (PAC) and alum. *Journal of Hazardous Materials*, *163*(2–3), 650–656. https://doi.org/10.1016/j.jhazmat.2008.07.090

González, L. T., Longoria Rodríguez, F. E., Sánchez-Domínguez, M., Cavazos, A., Leyva-Porras, C., Silva-Vidaurri, L. G., Askar, K. A., Kharissov, B. I., Villarreal Chiu, J. F., & Alfaro Barbosa, J. M. (2017). Determination of trace metals in TSP and PM2.5 materials collected in the Metropolitan Area of Monterrey, Mexico: A characterization study by XPS, ICP-AES and SEM-EDS. *Atmospheric Research*, *196*, 8–22. https://doi.org/10.1016/j.atmosres.2017.05.009

Guo, J., Ni, B. J., Han, X., Chen, X., Bond, P., Peng, Y., & Yuan, Z. (2017). Unraveling microbial structure and diversity of activated sludge in a full-scale simultaneous nitrogen and phosphorus removal plant using metagenomic sequencing. *Enzyme and Microbial Technology*, *102*, 16–25. https://doi.org/10.1016/j.enzmictec.2017.03.009

Hansford, G. M., Turner, S. M. R., Degryse, P., & Shortland, A. J. (2017). High-resolution X-ray diffraction with no sample preparation. *Acta Crystallographica Section A: Foundations and Advances*, *73*(4), 293–311. https://doi.org/10.1107/S2053273317008592

Harrison, E. Z., Oakes, S. R., Hysell, M., & Hay, A. (2006). Organic chemicals in sewage sludges. In *Science of the Total Environment* (Vol. 367, Issues 2–3, pp. 481–497). https://doi.org/10.1016/j.scitotenv.2006.04.002

Hassan, S. H. A., Van Ginkel, S. W., Hussein, M. A. M., Abskharon, R., & Oh, S. E. (2016). Toxicity assessment using different bioassays and microbial biosensors. In *Environment International* (Vols. 92–93, pp. 106–118). Elsevier Ltd. https://doi.org/10.1016/j.envint.2016.03.003

Haydar, S., & Aziz, J. A. (2009). Coagulation-flocculation studies of tannery wastewater using combination of alum with cationic and anionic polymers. *Journal of Hazardous Materials*, *168*(2–3), 1035–1040. https://doi.org/10.1016/j.jhazmat.2009.02.140

Heikkinen, J. M., Hordijk, J. C., De Jong, W., & Spliethoff, H. (2004). Thermogravimetry as a tool to classify waste components to be used for energy generation. *Journal of Analytical and Applied Pyrolysis*, *71*(2), 883–900. https://doi.org/10.1016/j.jaap.2003.12.001

Holbrook, R. D., Wagner, M. S., Mahoney, C. M., & Wight, S. A. (2006). Investigating Activated Sludge Flocs using Microanalytical Techniques: Demonstration of

Environmental Scanning Electron Microscopy and Time-of-Flight Secondary Ion Mass Spectrometry for Wastewater Applications. *Water Environment Research*, *78*(4), 381–391. https://doi.org/10.2175/106143005x90092

Jeon, E. K., Ryu, S., Park, S. W., Wang, L., Tsang, D. C. W., & Baek, K. (2018). Enhanced adsorption of arsenic onto alum sludge modified by calcination. *Journal of Cleaner Production*, *176*, 54–62. https://doi.org/10.1016/j.jclepro.2017.12.153

Karageorgiou, K., Paschalis, M., & Anastassakis, G. N. (2007). Removal of phosphate species from solution by adsorption onto calcite used as natural adsorbent. *Journal of Hazardous Materials*, *139*(3), 447–452. https://doi.org/10.1016/j.jhazmat.2006.02.038

Karunanithi, R., Ok, Y. S., Dharmarajan, R., Ahmad, M., Seshadri, B., Bolan, N., & Naidu, R. (2017a). Sorption, kinetics and thermodynamics of phosphate sorption onto soybean stover derived biochar. *Environmental Technology and Innovation*, *8*, 113–125. https://doi.org/10.1016/j.eti.2017.06.002

Karunanithi, R., Ok, Y. S., Dharmarajan, R., Ahmad, M., Seshadri, B., Bolan, N., & Naidu, R. (2017b). Sorption, kinetics and thermodynamics of phosphate sorption onto soybean stover derived biochar. *Environmental Technology and Innovation*, *8*, 113–125. https://doi.org/10.1016/j.eti.2017.06.002

Keating, C., Chin, J. P., Hughes, D., Manesiotis, P., Cysneiros, D., Mahony, T., Smith, C. J., McGrath, J. W., & O'Flaherty, V. (2016). Biological phosphorus removal during high-rate, low-temperature, anaerobic digestion of wastewater. *Frontiers in Microbiology*, *7*(MAR). https://doi.org/10.3389/fmicb.2016.00226

Keeley, J., Smith, A. D., Judd, S. J., & Jarvis, P. (2016). Acidified and ultrafiltered recovered coagulants from water treatment 1 works sludge for removal of phosphorus from wastewater 2 3. In *Water Research* (Vol. 88).

Kim, J. G., Kim, J. H., Moon, H. S., Chon, C. M., & Ahn, J. S. (2002a). Removal capacity of water plant alum sludge for phosphorus in aqueous solutions. *Chemical Speciation and Bioavailability*, *14*(1–4), 67–73. https://doi.org/10.3184/095422902782775344

Kim, J. G., Kim, J. H., Moon, H. S., Chon, C. M., & Ahn, J. S. (2002b). Removal capacity of water plant alum sludge for phosphorus in aqueous solutions. *Chemical Speciation and Bioavailability*, *14*(1–4), 67–73. https://doi.org/10.3184/095422902782775344

Kralchevska, R. P., Prucek, R., Kolařík, J., Tuček, J., Machala, L., Filip, J., Sharma, V. K., & Zbořil, R. (2016). Remarkable efficiency of phosphate removal: Ferrate(VI)-induced in situ sorption on core-shell nanoparticles. *Water Research*, *103*, 83–91. https://doi.org/10.1016/j.watres.2016.07.021

Kumar, M., Badruzzaman, M., Adham, S., & Oppenheimer, J. (2007). Beneficial phosphate recovery from reverse osmosis (RO) concentrate of an integrated membrane system using polymeric ligand exchanger (PLE). *Water Research, 41*(10), 2211–2219. https://doi.org/10.1016/j.watres.2007.01.042

Lee, J., Lee, S., Yu, S., & Rhew, D. (2016). Relationships between water quality parameters in rivers and lakes: BOD5, COD, NBOPs, and TOC. *Environmental Monitoring and Assessment*, *188*(4). https://doi.org/10.1007/s10661-016-5251-1

Lee, L. Y., Wang, B., Guo, H., Hu, J. Y., & Ong, S. L. (2015). Aluminum-Based Water Treatment Residue Reuse for Phosphorus Removal. *Water (Switzerland)*, *7*(4), 1480–1496. https://doi.org/10.3390/W7041480

Lee, S. H., Vigneswaran, S., & Moon, H. (1997). Adsorption of phosphorus in saturated slag media columns. In *Separation HPurification Technology Separation and Purification Technology* (Vol. 12).

Loganathan, P., Vigneswaran, S., Kandasamy, J., & Bolan, N. S. (2014). Removal and recovery of phosphate from water using sorption. *Critical Reviews in Environmental Science and Technology*, *44*(8), 847–907. https://doi.org/10.1080/10643389.2012.741311

Long, F., Gong, J. L., Zeng, G. M., Chen, L., Wang, X. Y., Deng, J. H., Niu, Q. Y., Zhang, H. Y., & Zhang, X. R. (2011). Removal of phosphate from aqueous solution by magnetic Fe-Zr binary oxide. *Chemical Engineering Journal*, *171*(2), 448–455. https://doi.org/10.1016/j.cej.2011.03.102

Lopes, C. de C. A., Limirio, P. H. J. O., Novais, V. R., & Dechichi, P. (2018). Fourier transform infrared spectroscopy (FTIR) application chemical characterization of enamel, dentin and bone. In *Applied Spectroscopy Reviews* (Vol. 53, Issue 9, pp. 747–769). Taylor and Francis Inc. https://doi.org/10.1080/05704928.2018.1431923

Maher, C., Neethling, J. B., Murthy, S., & Pagilla, K. (2015). Kinetics and capacities of phosphorus sorption to tertiary stage wastewater alum solids, and process implications for achieving low-level phosphorus effluents. *Water Research*, *85*, 226–234. https://doi.org/10.1016/j.watres.2015.08.025

Maqbool, N., Khan, Z., & Asghar, A. (2016). Reuse of alum sludge for phosphorus removal from municipal wastewater. *Desalination and Water Treatment*, *57*(28), 13246–13254. https://doi.org/10.1080/19443994.2015.1055806

Mazari, L., Szymczyk, A., Mazari, L., Abdessemed, ; D, & Szymczyk, A. (2018a). *Evaluating Reuse of Alum Sludge as Coagulant for Tertiary Wastewater Treatment Nitrogen and phosphorus removal at the membrane bioreactor and the conventional activated sludge View project Membranes !!! View project Evaluating Reuse of Alum Sludge as Coagulant for Tertiary Wastewater Treatment*. https://doi.org/10.1061/(ASCE)EE.1943

Mazari, L., Szymczyk, A., Mazari, L., Abdessemed, ; D, & Szymczyk, A. (2018b). *Evaluating Reuse of Alum Sludge as Coagulant for Tertiary Wastewater Treatment Nitrogen and phosphorus removal at the membrane bioreactor and the* *conventional activated sludge View project Membranes !!! View project Evaluating Reuse of Alum Sludge as Coagulant for Tertiary Wastewater Treatment*. https://doi.org/10.1061/(ASCE)EE.1943

Meissl, K., Smidt, E., & Schwanninger, M. (2007). Prediction of humic acid content and respiration activity of biogenic waste by means of Fourier transform infrared (FTIR) spectra and partial least squares regression (PLS-R) models. *Talanta, 72*(2), 791–799. https://doi.org/10.1016/j.talanta.2006.12.005

Mejía-Piña, K. G., Huerta-Diaz, M. A., & González-Yajimovich, O. (2016). Calibration of handheld X-ray fluorescence (XRF) equipment for optimum determination of elemental concentrations in sediment samples. *Talanta*, *161*, 359–367. https://doi.org/10.1016/j.talanta.2016.08.066

Mitchell, D., Grave, P., Maccheroni, M., & Gelman, E. (2012). Geochemical characterisation of north Asian glazed stonewares: A comparative analysis of NAA, ICP-OES and non-destructive pXRF. *Journal of Archaeological Science, 39*(9), 2921–2933. https://doi.org/10.1016/j.jas.2012.04.044

Mohammed, W. T., & Rashid, S. A. (2012). Phosphorus removal from wastewater using oven-dried alum sludge. *International Journal of Chemical Engineering*. https://doi.org/10.1155/2012/125296

Moseson, D. E., Jordan, M. A., Shah, D. D., Corum, I. D., Alvarenga, B. R., & Taylor, L. S. (2020). *Application and Limitations of Thermogravimetric Analysis to Delineate the Hot Melt Extrusion Chemical Stability Processing Window*.

Muisa, N., Nhapi, I., Ruziwa, W., & Manyuchi, M. M. (2020a). Utilization of alum sludge as adsorbent for phosphorus removal in municipal wastewater: A review. In *Journal of Water Process Engineering* (Vol. 35). Elsevier Ltd. https://doi.org/10.1016/j.jwpe.2020.101187

Muisa, N., Nhapi, I., Ruziwa, W., & Manyuchi, M. M. (2020b). Utilization of alum sludge as adsorbent for phosphorus removal in municipal wastewater: A review. In *Journal of Water Process Engineering* (Vol. 35). Elsevier Ltd. https://doi.org/10.1016/j.jwpe.2020.101187

Nadeem, K., ALLIET Queralt PLANA, M., Bernier, J., Azimi, S., & Albasi, C. (2021). *Modeling, simulation and control of biological and chemical P-removal processes for membrane bioreactors (MBRs) from lab to full-scale applications: state of the art*.

Nandiyanto, A. B. D., Oktiani, R., & Ragadhita, R. (2019). How to read and interpret ftir spectroscope of organic material. *Indonesian Journal of Science and Technology*, *4*(1), 97–118. https://doi.org/10.17509/ijost.v4i1.15806

Nayl, A. E. A., Elkhashab, R. A., El Malah, T., Yakout, S. M., El-Khateeb, M. A., Ali, M. M. S., & Ali, H. M. (2017). Adsorption studies on the removal of COD and BOD from treated sewage using activated carbon prepared from date palm waste.

Environmental Science and Pollution Research, *24*(28), 22284–22293. https://doi.org/10.1007/s11356-017-9878-4

Odimegwu, T. C., Zakaria, I., Abood, M. M., Nketsiah, C. B. K., & Ahmad, M. (2018). Review on Different Beneficial Ways of Applying Alum Sludge in a Sustainable Disposal Manner. *Civil Engineering Journal*, *4*(9), 2230. https://doi.org/10.28991/cej-03091153

Odziomek, K., Ushizima, D., Oberbek, P., Kurzydłowski, K. J., Puzyn, T., & Haranczyk, M. (2017). Scanning electron microscopy image representativeness: morphological data on nanoparticles. *Journal of Microscopy*, *265*(1), 34–50. https://doi.org/10.1111/jmi.12461

Oehmen, A., Lemos, P. C., Carvalho, G., Yuan, Z., Keller, J., Blackall, L. L., & Reis, M. A. M. (2007). Advances in enhanced biological phosphorus removal: From micro to macro scale. In *Water Research* (Vol. 41, Issue 11, pp. 2271–2300). Elsevier Ltd. https://doi.org/10.1016/j.watres.2007.02.030

Ojha, B., Sharma, R. K., & Amatya, I. M. (n.d.). *Application of Alum Sludge in Phosphate Phosphorus Removal from Contaminated Water*.

Owaid, H. M. (2013). *Physical and Mechanical Properties of High Performance Concrete with Alum Sludge as Partial Cement Replacement*. www.jurnalteknologi.utm.my

Pradel, M., & Aissani, L. (2019). Environmental impacts of phosphorus recovery from a “product” Life Cycle Assessment perspective: Allocating burdens of wastewater treatment in the production of sludge-based phosphate fertilizers. *Science of the Total Environment*, *656*, 55–69. https://doi.org/10.1016/j.scitotenv.2018.11.356ï

Pradhan, J., Das, J., Das, S., & Thakur, R. S. (1998). *Adsorption of Phosphate from Aqueous Solution Using Activated Red Mud*.

Prescher, C., & Prakapenka, V. B. (2015). DIOPTAS: A program for reduction of two-dimensional X-ray diffraction data and data exploration. *High Pressure Research*, *35*(3), 223–230. https://doi.org/10.1080/08957959.2015.1059835

Rahman, M. A., Lee, S. H., Ji, H. C., Kabir, A. H., Jones, C. S., & Lee, K. W. (2018). Importance of mineral nutrition for mitigating aluminum toxicity in plants on acidic soils: Current status and opportunities. In *International Journal of Molecular Sciences* (Vol. 19, Issue 10). MDPI AG. https://doi.org/10.3390/ijms19103073

Renou, S., Givaudan, J. G., Poulain, S., Dirassouyan, F., & Moulin, P. (2008). Landfill leachate treatment: Review and opportunity. In *Journal of Hazardous Materials* (Vol. 150, Issue 3, pp. 468–493). https://doi.org/10.1016/j.jhazmat.2007.09.077

Schindler, D. W., Hecky, R. E., Findlay, D. L., Stainton, M. P., Parker, B. R., Paterson, M. J., Beaty, K. G., Lyng, M., & Kasian, S. E. M. (2008). *Eutrophication of lakes* *cannot be controlled by reducing nitrogen input: Results of a 37-year whole-ecosystem experiment*. www.pnas.org/cgi/content/full/

Seleiman, M. F., Santanen, A., & Mäkelä, S. A. (n.d.). *Recycling sludge on cropland as fertilizer-advantages and risks 1*.

Shamaki, M., Adu-Amankwah, S., & Black, L. (2021). Reuse of UK alum water treatment sludge in cement-based materials. *Construction and Building Materials*, *275*. https://doi.org/10.1016/j.conbuildmat.2020.122047

Sibrell, P. L., Montgomery, G. A., Ritenour, K. L., & Tucker, T. W. (2009). Removal of phosphorus from agricultural wastewaters using adsorption media prepared from acid mine drainage sludge. *Water Research*, *43*(8), 2240–2250. https://doi.org/10.1016/j.watres.2009.02.010

Smith, V. H., Joye, S. B., & Howarth, R. W. (2006). Eutrophication of freshwater and marine ecosystems. *Limnology and Oceanography*, *51*(1 II), 351–355. https://doi.org/10.4319/lo.2006.51.1_part_2.0351

Smoczyński, L., Ratnaweera, H., Kosobucka, M., & Smoczyński, M. (2014). Image analysis of sludge aggregates. *Separation and Purification Technology*, *122*, 412–420. https://doi.org/10.1016/j.seppur.2013.09.030

Szabó, A., Takács, I., Murthy, S., Daigger, G. T., Licskó, I., & Smith, S. (2008). Significance of Design and Operational Variables in Chemical Phosphorus Removal. *Water Environment Research*, *80*(5), 407–416. https://doi.org/10.2175/106143008x268498

Tibebe, D., Kassa, Y., & Bhaskarwar, A. N. (2019). Treatment and characterization of phosphorus from synthetic wastewater using aluminum plate electrodes in the electrocoagulation process. *BMC Chemistry*, *13*(1). https://doi.org/10.1186/s13065-019-0628-1

Tomei, M. C., Stazi, V., Daneshgar, S., & Capodaglio, A. G. (2020). Holistic approach to phosphorus recovery from urban wastewater: Enhanced biological removal combined with precipitation. *Sustainability (Switzerland)*, *12*(2). https://doi.org/10.3390/su12020575

Truong, V. T., & Kim, D. J. (2021). Phosphate removal using thermally regenerated Al adsorbent from drinking water treatment sludge. *Environmental Research*, *196*. https://doi.org/10.1016/j.envres.2021.110877

Truong, T. Van, Tiwari, D., Mok, Y. S., & Kim, D. J. (2021). Recovery of aluminum from water treatment sludge for phosphorus removal by combined calcination and extraction. *Journal of Industrial and Engineering Chemistry*, *103*, 195–204. https://doi.org/10.1016/j.jiec.2021.07.033

Ugurlu, A., & Salman, B. (1998). PHOSPHORUS REMOVAL BY FLY ASH. In *Pergamon Environment International* (Vol. 24, Issue 8).

Usman, M. O., Aturagaba, G., Ntale, M., & Nyakairu, G. W. (2022). A review of adsorption techniques for removal of phosphates from wastewater. In *Water Science and Technology* (Vol. 86, Issue 12, pp. 3113–3132). IWA Publishing. https://doi.org/10.2166/wst.2022.382

van Dam, J. W., Trenfield, M. A., Harries, S. J., Streten, C., Harford, A. J., Parry, D., & van Dam, R. A. (2016). A novel bioassay using the barnacle Amphibalanus amphitrite to evaluate chronic effects of aluminium, gallium and molybdenum in tropical marine receiving environments. *Marine Pollution Bulletin*, *112*(1–2), 427–435. https://doi.org/10.1016/j.marpolbul.2016.07.015

Vigdorowitsch, M., Pchelintsev, A., Tsygankova, L., & Tanygina, E. (2021). Freundlich isotherm: An adsorption model complete framework. In *Applied Sciences (Switzerland)* (Vol. 11, Issue 17). MDPI. https://doi.org/10.3390/app11178078

Vohla, C., Kõiv, M., Bavor, H. J., Chazarenc, F., & Mander, Ü. (2011). Filter materials for phosphorus removal from wastewater in treatment wetlands-A review. *Ecological Engineering*, *37*(1), 70–89. https://doi.org/10.1016/j.ecoleng.2009.08.003

Wan, J., Wu, B., & Lo, I. M. C. (2020). Development of Fe0/Fe3O4 composites with tunable properties facilitated by Fe2+ for phosphate removal from river water. *Chemical Engineering Journal*, *388*. https://doi.org/10.1016/j.cej.2020.124242

Weerasinghe, R. M., Pannila, A. S., Jayananda, M. K., & Sonnadara, D. U. J. (2015). Automated Rain Sampler for Real time pH and Conductivity Measurements. In *Proceedings of the Technical Sessions* (Vol. 31).

Withers, P. J. A., & Jarvie, H. P. (2008). Delivery and cycling of phosphorus in rivers: A review. *Science of the Total Environment*, *400*(1–3), 379–395. https://doi.org/10.1016/j.scitotenv.2008.08.002

Wu, B., Xia, J., Zhang, S., Fu, Q., Zhang, H., Xie, X., & Liu, Z. (2023). Elemental composition x-ray fluorescence analysis with a TES-based high-resolution x-ray spectrometer. *Chinese Physics B*, *32*(9). https://doi.org/10.1088/1674-1056/acd926

Wu, H. F., Wang, J. P., Duan, E. G., Feng, Y. F., Wan, Z. Y., Wu, Y. X., & Lu, Y. Q. (2019). Study on the preparation of granular alum sludge adsorbent for phosphorus removal. *Water Science and Technology*, *79*(12), 2378–2386. https://doi.org/10.2166/wst.2019.241

Yang, Y., Tomlinson, D., Kennedy, S., & Zhao, Y. Q. (2006). Dewatered alum sludge: A potential adsorbent for phosphorus removal. *Water Science and Technology*, *54*(5), 207–213. https://doi.org/10.2166/wst.2006.564

Zeng, L., Li, X., & Liu, J. (2004). Adsorptive removal of phosphate from aqueous solutions using iron oxide tailings. *Water Research*, *38*(5), 1318–1326. https://doi.org/10.1016/j.watres.2003.12.009

Zhang, Y., Qin, J., & Yi, Y. (2021a). Biochar and hydrochar derived from freshwater sludge: Characterization and possible applications. *Science of the Total Environment*, *763*. https://doi.org/10.1016/j.scitotenv.2020.144550

Zhang, Y., Qin, J., & Yi, Y. (2021b). Biochar and hydrochar derived from freshwater sludge: Characterization and possible applications. *Science of the Total Environment*, *763*. https://doi.org/10.1016/j.scitotenv.2020.144550

Zhao, R., Feng, J., Liu, J., Fu, W., Li, X., & Li, B. (2019). Deciphering of microbial community and antibiotic resistance genes in activated sludge reactors under high selective pressure of different antibiotics. *Water Research*, *151*, 388–402. https://doi.org/10.1016/j.watres.2018.12.034

Zhao, W., Xie, H., Li, J., Zhang, L., & Zhao, Y. (2021). Application of alum sludge in wastewater treatment processes: "Science" of reuse and reclamation pathways. *Processes*, *9*(4). https://doi.org/10.3390/pr9040612

Zhao, Y. Q., Babatunde, A. O., Hu, Y. S., Kumar, J. L. G., & Zhao, X. H. (2011). Pilot field-scale demonstration of a novel alum sludge-based constructed wetland system for enhanced wastewater treatment. *Process Biochemistry*, *46*(1), 278–283. https://doi.org/10.1016/j.procbio.2010.08.023

Zhao, Y. Q., Zhao, X. H., & Babatunde, A. O. (2009). Use of dewatered alum sludge as main substrate in treatment reed bed receiving agricultural wastewater: Long-term trial. *Bioresource Technology*, *100*(2), 644–648. https://doi.org/10.1016/j.biortech.2008.07.040

Zheng, X., Liu, T., Guo, M., Li, D., Gou, N., Cao, X., Qiu, X., Li, X., Zhang, Y., Sheng, G., Pan, B., Gu, A. Z., & Li, Z. (2020). Impact of heavy metals on the formation and properties of solvable microbiological products released from activated sludge in biological wastewater treatment. *Water Research*, *179*. https://doi.org/10.1016/j.watres.2020.115895

Zhou, Y.-F., & Haynes, R. J. (2010). Water treatment sludge can be used as an adsorbent for heavy metals in wastewater streams. *WIT Transactions on Ecology and the Environment*, *1*, 1743–3541. https://doi.org/10.2495/0