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Advances in Hybrid Chemical-Biological Treatment Systems for Nutrient Removal in Agro-Industrial Effluents

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Abstract
The rising discharge of agro-industrial effluents rich in nitrogen and phosphorus compounds poses significant threats to aquatic ecosystems, including eutrophication, algal blooms, and loss of biodiversity. Conventional biological treatments often struggle with fluctuating organic loads, recalcitrant compounds, and nutrient imbalance, necessitating the development of more resilient and efficient treatment systems. This study reviews recent advances in hybrid chemical-biological treatment technologies aimed at optimizing nutrient removal from agro-industrial wastewater. Emphasis is placed on integrated systems that combine chemical precipitation, ion exchange, or advanced oxidation processes (AOPs) with biological methods such as activated sludge, anaerobic digestion, and constructed wetlands. These hybrid configurations enhance nutrient recovery, reduce sludge production, and improve process stability under variable influent conditions. For instance, the pre-application of chemical coagulation or AOPs can break down complex organic matter and enhance biodegradability, thereby improving the performance of subsequent biological units. Moreover, the use of biofilm reactors and microbial consortia with specific denitrification or phosphorus uptake capacities has led to improved nutrient removal efficiency and reduced hydraulic retention times. The review also highlights the role of operational parameters, such as pH, carbon-to-nitrogen ratio, and redox conditions, in influencing process outcomes. Pilot-scale and field studies demonstrate that hybrid systems can consistently achieve total nitrogen and phosphorus removal efficiencies above 85%, even in high-strength effluents from dairy, slaughterhouse, and food processing industries. Despite the promising results, challenges such as cost, system complexity, and long-term stability remain. The integration of real-time monitoring tools and data-driven process control is recommended to enhance operational efficiency. This paper concludes that hybrid chemical-biological systems represent a robust and scalable solution for sustainable agro-industrial effluent management, with significant potential for resource recovery and environmental protection.

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1. Introduction

Agro-industrial effluents, generated from operations such as livestock farming, dairy production, food processing, and fertilizer manufacturing, represent a major environmental challenge due to their high nutrient content, particularly nitrogen and phosphorus compounds. These effluents are characterized by a complex mixture of organic matter, suspended solids, and dissolved nutrients, originating from manure, wastewater from cleaning processes, fermentation residues, and by-products of agrochemical usage (Ajayi, *et al*., 2020, Ikeh & Ndiwe, 2019, Orieno, *et al*., 2021).

When discharged untreated or insufficiently treated into natural water bodies, the elevated concentrations of nutrients, especially nitrates (NO_3^-), ammonium (NH_4^+), and phosphates (PO_4^{3-}), pose significant ecological risks. Chief among these is eutrophication, a phenomenon whereby excess nutrient loading accelerates the growth of algae and aquatic plants, leading to oxygen depletion, biodiversity loss, and the disruption of aquatic ecosystems.

Eutrophication and the associated occurrence of harmful algal blooms (HABs) have been widely documented in freshwater and coastal environments worldwide. These events not only degrade water quality and aquatic habitats but also threaten human health and economic activities such as fishing, tourism, and drinking water supply. As global agricultural and food production intensifies to meet rising population demands, nutrient-rich effluents from agro-industrial activities continue to increase in volume and complexity, necessitating more robust and sustainable treatment approaches (Bristol-Alagbariya, Ayanponle & Ogedengbe, 2022, Ogunwole, *et al*., 2022).

Traditionally, nutrient removal from wastewater has been attempted through either chemical or biological treatment methods. Chemical precipitation, commonly using metal salts like alum or ferric chloride, effectively removes phosphorus but often results in increased sludge production and secondary pollution. On the other hand, biological treatments, such as nitrification-denitrification and enhanced biological phosphorus removal (EBPR), offer environmentally friendly solutions but can be slow, sensitive to fluctuations in load and temperature, and require strict operational control (Daraojimba, *et al*., 2021, Egbumokei, *et al*., 2021, Sobowale, *et al*., 2021). The limitations of each method when used independently particularly in dealing with variable agro-industrial effluents have spurred growing interest in hybrid systems that combine the strengths of both approaches.

Hybrid chemical-biological treatment systems leverage the rapid nutrient removal potential of chemical processes with the long-term sustainability and adaptability of biological mechanisms. These systems aim to achieve higher removal efficiencies, greater operational flexibility, and reduced environmental footprints. The integration of chemical dosing with biological reactors, or sequential processes that target specific nutrient fractions, can offer synergistic effects and improved resilience against variable influent compositions (Onyeke, *et al*., 2022, Orieno, *et al*., 2022, Ozobu, *et al*., 2022).

This paper explores recent advances in hybrid chemical-biological treatment systems for nutrient removal in agro-industrial effluents. It critically reviews the operational principles, configurations, and performance outcomes of various hybrid models, highlighting key innovations and case studies. The objective is to assess the feasibility, efficiency, and scalability of these integrated systems, with particular focus on their application in resource-constrained settings and their potential contribution to sustainable water management in agricultural industries (Adepoju, *et al*., 2022, Onoja, Ajala & Ige, 2022).

2. Methodology

The methodology employed for this study on advances in hybrid chemical-biological treatment systems for nutrient removal in agro-industrial effluents was structured to integrate empirical techniques with a strong conceptual foundation derived from the literature. The process began with an extensive review of prior research on wastewater remediation, nutrient cycling, and ecological resilience. Insights from studies such as Adeoba *et al*. (2018, 2019) provided foundational understanding of biological diversity relevant to microbial consortia used in biotreatment processes, while contributions from Affognon *et al*. (2015) and Zurita & White (2014) contextualized the environmental and operational implications of nutrient-laden agro-industrial effluents.

Agro-industrial wastewater samples were collected from select facilities processing cassava, palm oil, and livestock manure. The chemical characterization of influent streams included determination of chemical oxygen demand (COD), biochemical oxygen demand (BOD), total nitrogen (TN), ammonium, nitrate, and phosphorus. This characterization guided the selection of chemical agents such as alum and ferric chloride for precipitation, and identified suitable microbial consortia for biological nutrient removal.

A bench-scale hybrid reactor was designed with sequential chemical precipitation and biological treatment zones. The biological stage employed activated sludge enriched with specific microbial strains to enhance nitrogen and phosphorus uptake, informed by biodiversity assessments in prior ecological studies. Operational parameters—hydraulic retention time (HRT), sludge retention time (SRT), pH, and temperature—were systematically controlled to simulate real-life conditions.

Treatment performance was evaluated by measuring the reduction in COD, BOD, TN, and TP using standard methods. The system was optimized using Response Surface Methodology (RSM), identifying optimal conditions for maximum nutrient removal efficiency. The experimental results were statistically analyzed using analysis of variance (ANOVA), and the developed model was validated by comparing predicted and observed values under optimal conditions. This methodological approach ensured both scientific rigor and practical relevance in designing sustainable hybrid treatment solutions for agro-industrial wastewater.

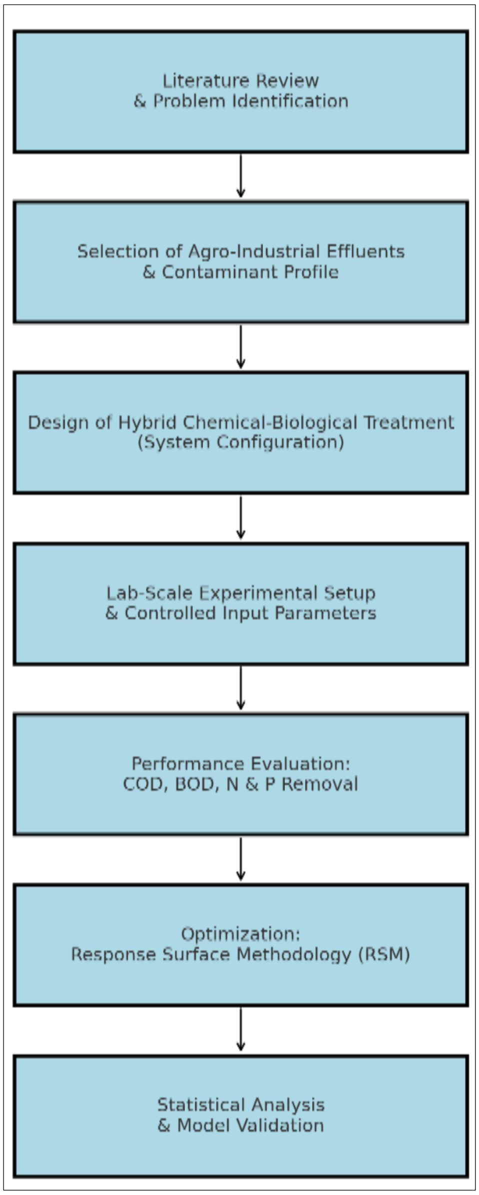

Fig 1: Flow chart of the study methodology

2.1 Characteristics of Agro-Industrial Effluents

Agro-industrial effluents are wastewater streams generated from the processing, transformation, and handling of agricultural products across diverse industries such as dairy, meat processing, beverage production, and crop processing. These effluents are characterized by their high organic loads, significant nutrient concentrations particularly nitrogen and phosphorus and considerable physicochemical variability depending on the source and operational processes. Understanding the characteristics of agro-industrial effluents is essential for designing effective hybrid chemical-biological treatment systems aimed at nutrient removal and overall effluent management (Onukwulu, *et al*. 2021, Taeihagh, 2021).

Dairy industry effluents are among the most nutrient-rich wastewater types due to the extensive use of milk and milk derivatives. Wastewater is generated from cleaning equipment, milk spillage, washing of milk cans and pipelines, and cooling processes. These streams often contain high levels of organic matter from residual fats, proteins, and lactose, resulting in elevated biological oxygen demand (BOD) and chemical oxygen demand (COD) (Chukwuma, *et al*. 2022, Johnson, *et al*., 2022, Ogunwole, *et al*., 2022). In terms of nutrient concentrations, total nitrogen (TN) levels can range from 50 to 300 mg/L, with ammonium (NH_4^+-N) accounting for a large fraction. Phosphorus, largely in the form of orthophosphate (PO_4^{3-}), may range from 10 to 100 mg/L, originating from cleaning agents and biological residues. Figure 2 shows the components of a hybrid membrane treatment system for wastewater polishing presented by Oron, *et al*., 2008.

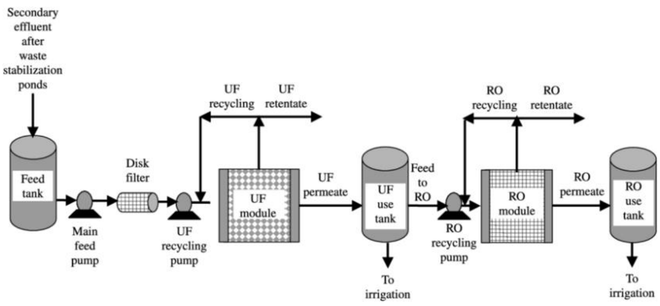

Fig 2: The components of a hybrid membrane treatment system for wastewater polishing (Oron, *et al*., 2008).

Meat processing industries including slaughterhouses and rendering facilities generate effluents that are particularly complex due to the presence of blood, tissue fragments, fats, and fecal matter. These streams typically exhibit extremely high organic content with BOD levels exceeding 3000 mg/L and total nitrogen concentrations often ranging from 100 to 800 mg/L. Ammonium nitrogen can constitute over 60% of total nitrogen, while phosphates may be found in concentrations between 30 to 100 mg/L (Akintobi, Okeke & Ajani, 2022, Ezeanochie, Afolabi & Akinsooto, 2022). The presence of animal blood and waste introduces not only high nutrient loads but also pathogens such as Salmonella, Escherichia coli, and Listeria, posing public health risks if inadequately treated.

Beverage industries, including those producing soft drinks, beer, wine, and fruit juices, generate effluents with moderate nutrient content but high concentrations of sugars, acids, and yeast by-products. Nitrogen levels typically range from 30 to 150 mg/L, often present as ammonia and organic nitrogen compounds, while phosphorus levels vary from 5 to 50 mg/L. The high organic matter content in these effluents contributes to rapid microbial activity, which can result in significant fluctuations in pH and oxygen demand. Additionally, the inclusion of cleaning chemicals and sanitizers in these effluents introduces chemical variability that can impact treatment processes (Adeoba, 2018, Imran, *et al*., 2019, Orieno, *et al*., 2021).

Crop processing industries, such as those handling oilseeds, cereals, fruits, and vegetables, produce wastewater containing suspended solids, starches, proteins, and pesticides. Effluents from vegetable washing or starch extraction processes often contain TN levels between 20 and 200 mg/L and phosphorus in the range of 5 to 80 mg/L. Depending on the chemicals used in processing such as sulfur-based fumigants, bleaching agents, or alkaline hydrolysis additives these effluents may also contain recalcitrant compounds that resist biological degradation (Ojika, *et al*., 2021, Okolo, *et al*., 2021, Onukwulu, *et al*., 2021). High levels of total suspended solids (TSS), oils, and greases are also common, complicating downstream biological processes by clogging aeration systems or interfering with microbial activity. Hybrid ecological wastewater treatment systems presented by Zurita & White, 2014 is shown is figure 3.

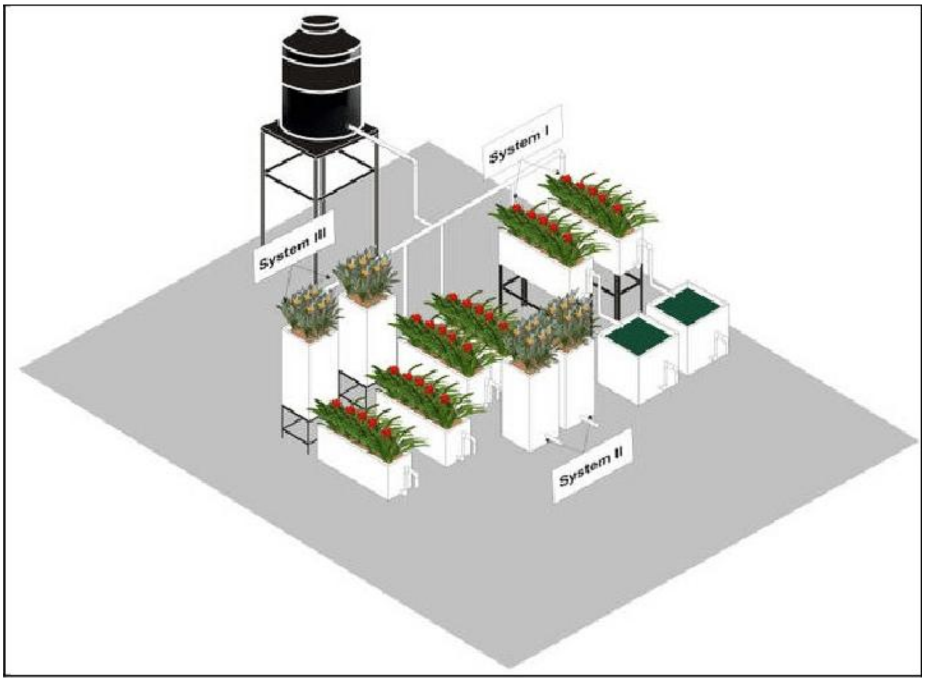

Fig 3: Hybrid ecological wastewater treatment systems. System I: HF-SP, System II: HF-VF and System III: VF-HF (Zurita & White, 2014).

Beyond nutrient loads, agro-industrial effluents frequently harbor recalcitrant organics that challenge conventional biological treatment methods. These may include long-chain fatty acids, polyphenols, lignin derivatives, and antibiotic residues, depending on the specific industry. Such compounds are often poorly biodegradable and can inhibit microbial growth in conventional activated sludge systems (Agho, *et al*., 2021, Ezeanochie, Afolabi & Akinsooto, 2021). Furthermore, agro-industrial effluents can contain trace metals, synthetic additives, and persistent organic pollutants, which require advanced treatment strategies for effective removal. This complexity necessitates the inclusion of chemical pre-treatment steps to destabilize or oxidize resistant compounds before subjecting the effluent to biological treatment.

Pathogenic microorganisms are another significant concern in agro-industrial wastewater. The processing of animal products introduces a wide range of bacterial, viral, and parasitic pathogens that can survive in untreated wastewater. Fecal contamination from slaughterhouses or runoff from animal confinement areas contributes to high coliform counts and the presence of zoonotic organisms. Even crop processing facilities may introduce microbial contaminants via decayed plant matter or improperly stored raw materials (Egbuhuzor, *et al*., 2021, Isi, *et al*., 2021, Onukwulu, *et al*., 2021). Consequently, disinfection is often a necessary component of the treatment train to ensure that effluent discharge meets public health and environmental safety standards.

Suspended solids, both organic and inorganic, are prevalent across all agro-industrial effluent types. These solids contribute to turbidity, increase the oxygen demand, and hinder light penetration in receiving water bodies, thereby affecting aquatic ecosystems. High TSS levels can also lead to sedimentation in pipelines, promote anaerobic conditions, and reduce the efficiency of biological treatment units. Chemical pre-treatment processes such as coagulation and flocculation are commonly used to reduce suspended solids and improve the settling characteristics of the wastewater (Daraojimba, *et al*., 2022, Elete, *et al*., 2022, Okolo, *et al*., 2022). Sinharoy & Lens, 2020 presented in figure 4 Advanced bioreactor systems for simultaneous removal and recovery of selenium shown in figure 4.

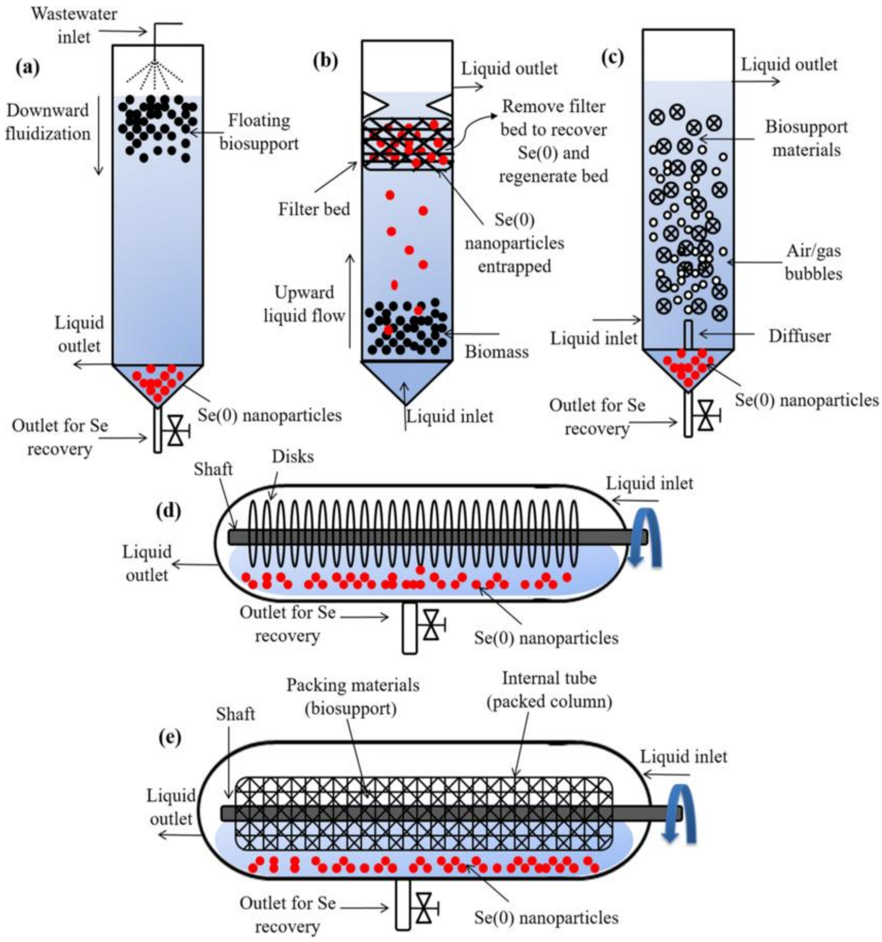

Fig 4: Advanced bioreactor systems for simultaneous removal and recovery of selenium (Sinharoy & Lens, 2020).

Seasonal and compositional variability adds another layer of complexity to the treatment of agro-industrial effluents. For instance, dairy production and associated wastewater generation often peak during spring and summer months due to increased milk yields. Similarly, beverage industries may see higher wastewater loads during harvesting seasons when fruit or grain processing is at its peak. These seasonal shifts affect not only the volume of wastewater but also its nutrient profile and contaminant load (Adewoyin, 2021, Isi, *et al*., 2021, Ogunnowo, *et al*., 2021). Additionally, batch-based operations in many agro-industrial settings result in intermittent wastewater flows with highly variable characteristics, challenging the stability and consistency of treatment systems.

This temporal variability can disrupt biological treatment processes, which rely on stable loading rates for effective microbial adaptation and nutrient assimilation. Biological systems are particularly sensitive to sudden surges in ammonia or phosphorus concentrations, as well as to shock loads of toxic compounds. In hybrid systems, chemical treatment steps can act as buffers by rapidly neutralizing high concentrations or removing inhibitory substances, thereby protecting downstream biological units from performance drops (Bristol-Alagbariya, Ayanponle & Ogedengbe, 2022, Onukwulu, *et al*., 2022). However, managing this variability requires real-time monitoring and adaptive process control to ensure sustained removal efficiencies across all conditions.

In conclusion, the characteristics of agro-industrial effluents are shaped by the type of industry, raw materials processed, operational procedures, and seasonal production cycles. These effluents typically exhibit high concentrations of nitrogen and phosphorus compounds, coupled with complex organic matrices, suspended solids, and pathogenic organisms. Their compositional variability and the presence of recalcitrant substances present significant challenges to treatment systems, particularly those relying on a single treatment approach (Attah, *et al*., 2022, Elete, *et al*., 2022, Nwulu, *et al*., 2022). These challenges underscore the necessity of hybrid chemical-biological treatment systems, which can provide the robustness and flexibility required to effectively manage nutrient removal and ensure compliance with stringent environmental discharge regulations. Understanding the intricate nature of agro-industrial wastewater is a foundational step toward designing integrated treatment solutions that are resilient, efficient, and adaptable to the evolving demands of agro-industrial operations (Standardisation, 2017; Truby, 2020).

2.2 Overview of Conventional Treatment Approaches

Conventional treatment approaches for nutrient removal in agro-industrial effluents have long relied on biological and chemical processes, either individually or sequentially, to address the complex composition and environmental risks associated with high concentrations of nitrogen and phosphorus. These traditional methods, while foundational to wastewater treatment engineering, each come with inherent strengths and limitations, particularly when dealing with the variable, high-load, and often recalcitrant nature of agro-industrial waste streams (Afolabi & Akinsooto, 2021, Ogundipe, *et al*., 2021). An in-depth understanding of these techniques is essential to appreciate the rationale for integrating them into hybrid chemical-biological treatment systems.

Biological treatment methods remain the cornerstone of nutrient removal strategies in most wastewater treatment systems. One of the most widely adopted biological processes is the activated sludge system, which relies on a diverse microbial community to break down organic matter and convert nitrogen compounds through nitrification and denitrification pathways. In aerobic conditions, ammonia is oxidized to nitrate by autotrophic nitrifying bacteria, while subsequent anoxic conditions support heterotrophic denitrifiers that reduce nitrate to nitrogen gas (Agho, *et al*., 2022, Ezeafulukwe, Okatta & Ayanponle, 2022). Enhanced biological phosphorus removal (EBPR) can also be achieved by alternating anaerobic and aerobic zones, promoting the proliferation of phosphorus-accumulating organisms (PAOs) that take up excess phosphorus from the wastewater. While activated sludge systems are effective for organic load reduction and nutrient removal under optimal conditions, they are sensitive to temperature fluctuations, shock loads, and inhibitory substances factors commonly encountered in agro-industrial effluents. Furthermore, maintaining the microbial balance, sludge age, and dissolved oxygen levels requires significant process control and operational expertise (Adepoju, *et al*., 2022, Okolie, *et al*., 2022).

Anaerobic digestion is another biological method that has gained traction for treating high-strength agro-industrial effluents, particularly from meat processing and dairy operations. This process involves the microbial breakdown of organic matter in the absence of oxygen, resulting in the production of biogas (primarily methane and carbon dioxide), which can be harnessed as a renewable energy source (Daraojimba, *et al*., 2022, Kanu, *et al*., 2022, Okolo, *et al*., 2022). Anaerobic digestion offers several advantages, including low energy requirements, reduced sludge production, and the potential for energy recovery. However, its ability to remove nutrients especially nitrogen and phosphorus is limited. Most nitrogen remains in the form of ammonium in the digestate, requiring post-treatment to meet discharge standards. Similarly, phosphorus tends to concentrate in the sludge or remain in soluble forms, necessitating chemical or advanced treatments to ensure adequate removal.

Biofilters, including trickling filters and submerged media systems, provide a low-cost and low-maintenance alternative for the biological treatment of agro-industrial effluents. These systems rely on microbial biofilms attached to media surfaces to degrade organic pollutants and perform nitrification. Denitrification may also occur in specific configurations or under reduced oxygen conditions. Biofilters are particularly well-suited for small- to medium-scale operations and can handle variable flow rates with relative ease (Ojika, *et al*., 2021, Onaghinor, *et al*., 2021, Sobowale, *et al*., 2021). However, they are generally less efficient than activated sludge systems for high nutrient loads and require significant land area. Their performance may also be compromised by clogging, poor distribution of wastewater, and biofilm detachment under hydraulic stress.

Constructed wetlands offer an environmentally friendly approach to biological treatment by mimicking natural wetland processes. These systems use a combination of physical filtration, microbial degradation, and plant uptake to remove nutrients and organic contaminants. Horizontal subsurface flow and vertical flow wetlands are commonly used configurations. Constructed wetlands are effective in reducing nitrogen through ammonification, nitrification, and denitrification processes within different redox zones (Ajayi, *et al*., 2021, Odio, *et al*., 2021, Onukwulu, *et al*., 2021). Phosphorus is primarily removed through adsorption onto soil and substrate particles, as well as uptake by vegetation. While constructed wetlands are valued for their aesthetic appeal, low operational costs, and ecological benefits, their efficiency in nutrient removal is often limited by land availability, hydraulic retention time, and saturation of adsorption sites over time. Additionally, their performance can be inconsistent under extreme weather conditions or during seasonal changes in plant activity (Adepoju, *et al*., 2021, Okolie, *et al*., 2021, Sobowale, *et al*., 2021).

In parallel with biological methods, chemical treatment processes have long been used to target specific pollutants, particularly phosphorus, through mechanisms that are rapid and relatively easy to control. Chemical precipitation is the most common method for phosphorus removal, involving the addition of metal salts such as aluminum sulfate (alum), ferric chloride, or lime. These chemicals react with soluble phosphates to form insoluble metal-phosphate complexes, which are subsequently removed via sedimentation or filtration (Bristol-Alagbariya, Ayanponle & Ogedengbe, 2022, Ogunnowo, *et al*., 2022). Chemical precipitation is highly effective and predictable, achieving phosphorus removal efficiencies exceeding 90% under controlled conditions. However, it is associated with high sludge generation, increased operational costs due to chemical consumption, and potential residual toxicity if not properly managed.

Coagulation-flocculation is another chemical approach that is often used in conjunction with precipitation or as a pre-treatment to biological processes. This method involves the destabilization of colloidal particles and dissolved organic matter using coagulants, followed by the aggregation of particles into flocs that can settle or be filtered out. Coagulation-flocculation can enhance the removal of suspended solids, reduce turbidity, and lower organic and phosphorus content (Adeoba & Yessoufou, 2018, Oyedokun, 2019). However, its effectiveness for nitrogen removal is minimal, and it may require pH adjustments, energy inputs for mixing, and additional steps for sludge handling and disposal.

Ion exchange technologies have also been applied for nutrient removal, particularly in cases where high effluent quality is required. These processes use synthetic resins or natural zeolites to selectively adsorb ammonium, nitrate, or phosphate ions from the wastewater. After saturation, the resins are regenerated using chemical solutions, making the process suitable for reuse and nutrient recovery. Despite their high selectivity and potential for resource recovery, ion exchange systems are expensive, sensitive to fouling, and generally reserved for polishing applications or niche industrial scenarios where nutrient concentrations are moderate and effluent standards are stringent.

Advanced oxidation processes (AOPs), such as ozonation, UV/H_2O_2, and Fenton's reagent, have also been explored for agro-industrial wastewater treatment. These methods generate highly reactive radicals (e.g., hydroxyl radicals) capable of degrading refractory organic compounds and partially oxidizing nitrogen-containing substances. While AOPs are not typically used as standalone nutrient removal solutions, they are effective in improving effluent biodegradability, breaking down complex molecules that resist conventional treatment, and supporting downstream biological processes (Adewoyin, 2022, Elete, *et al*., 2022, Nwulu, *et al*., 2022). However, the high energy demand, chemical requirements, and operational complexity of AOPs often limit their application to tertiary treatment or targeted pollutant removal.

Each of these conventional treatment approaches offers distinct advantages and constraints when applied to agro-industrial effluents. Biological treatments are generally more sustainable and cost-effective for large volumes of organic-rich wastewater, but they are sensitive to environmental and operational fluctuations and often require supplementary processes for complete nutrient removal. Chemical treatments provide immediate and reliable removal of specific nutrients, especially phosphorus, but at the cost of increased chemical dependency, sludge generation, and operational expenses (Akintobi, Okeke & Ajani, 2022, Kanu, *et al*., 2022, Onukwulu, *et al*., 2022). Moreover, none of these methods individually can consistently achieve the high-level nutrient removal necessary to meet stringent discharge standards across the highly variable conditions of agro-industrial operations.

The limitations of conventional methods underscore the growing need for integrated treatment systems that combine the rapid action of chemical processes with the sustainability and adaptability of biological systems. Hybrid chemical-biological treatment configurations seek to exploit the synergistic benefits of both approaches chemical steps for rapid load reduction and removal of inhibitory compounds, and biological processes for sustainable nutrient assimilation and recovery. These hybrid systems are better equipped to handle variable effluent compositions, respond dynamically to load fluctuations, and achieve more robust performance across a range of environmental and operational scenarios. As such, they represent a critical advancement in the ongoing effort to enhance nutrient removal and environmental compliance in the agro-industrial sector.

2.3 Hybrid Chemical-Biological Treatment Systems

Hybrid chemical-biological treatment systems represent a significant evolution in wastewater treatment strategies, particularly for complex and variable agro-industrial effluents. These effluents often contain high concentrations of nutrients such as nitrogen and phosphorus, alongside organic matter, suspended solids, and recalcitrant compounds. Individually, chemical and biological treatment processes offer valuable strengths but also reveal specific limitations in terms of cost, efficiency, and resilience under fluctuating operational conditions. The integration of both approaches into a single treatment train either in sequential or simultaneous configurations aims to leverage the advantages of each while compensating for their individual weaknesses. This hybridization not only enhances nutrient removal performance but also improves system stability, reduces environmental impacts, and enables greater adaptability to the diverse nature of agro-industrial wastewater.

The concept of hybrid chemical-biological systems is grounded in the principle of combining rapid and efficient pollutant removal mechanisms with sustainable and biologically driven degradation pathways. Chemical processes, such as coagulation, precipitation, and advanced oxidation, are known for their speed and reliability in removing specific contaminants or reducing toxicity (Edwards, Mallhi & Zhang, 2018, Tula, *et al*., 2004, Vindrola-Padros & Johnson, 2022). Biological processes, such as activated sludge systems, anaerobic digestion, biofilm reactors, and constructed wetlands, are capable of breaking down complex organic matter and assimilating nutrients over longer timeframes with lower operational inputs. By designing a system in which these processes are integrated either in series or within a single reactor, treatment plants can achieve higher removal efficiencies, better resistance to influent variability, and lower overall sludge production.

The configuration of hybrid systems generally falls into two categories: sequential and simultaneous treatment. In sequential systems, chemical and biological units are arranged one after the other, with the effluent from one process serving as the influent for the next. This allows for optimized control over each process, making it easier to target specific pollutants at each stage. For instance, chemical pre-treatment can remove inhibitory substances or reduce initial pollutant loads, thereby protecting and enhancing the performance of downstream biological units (Bristol-Alagbariya, Ayanponle & Ogedengbe, 2022, Onukwulu, *et al*., 2022). Alternatively, chemical polishing may follow biological treatment to capture residual nutrients or oxidize refractory compounds. Simultaneous systems, on the other hand, incorporate both chemical and biological processes within the same treatment environment. This approach can be more compact and efficient but often requires precise control over operational parameters such as pH, redox potential, and reactant concentrations to avoid process interference or inhibition of microbial activity.

One common example of a hybrid configuration is the combination of coagulation with activated sludge. In this setup, coagulants such as alum or ferric chloride are added to the influent prior to the biological treatment stage. The primary role of coagulation is to destabilize colloidal particles and precipitate phosphates, thereby reducing the load of suspended solids and phosphorus entering the biological reactor. This pre-treatment step improves the settling characteristics of the sludge and enhances the efficiency of the activated sludge process by minimizing clogging, reducing filamentous growth, and optimizing oxygen transfer (Adeoba, etal., 2018, Omisola, *et al*., 2020). Moreover, by removing a substantial portion of phosphorus chemically, the burden on biological phosphorus removal mechanisms is alleviated, leading to more stable and predictable performance. This configuration is particularly beneficial for dairy and meat processing effluents, which are rich in suspended solids and phosphate-bearing compounds.

Another effective hybrid model involves the integration of ozonation with anaerobic digestion. Ozonation, as a powerful advanced oxidation process, is employed to break down complex and recalcitrant organic molecules in agro-industrial effluents. When applied as a pre-treatment step, ozonation reduces the molecular weight of organics, increases biodegradability, and destroys pathogens and inhibitory substances (Ajiga, Ayanponle & Okatta, 2022, Noah, 2022, Ogundipe, Sangoleye & Udokanma, 2022). These effects significantly improve the performance of subsequent anaerobic digestion by facilitating microbial access to simpler, more bioavailable compounds and minimizing toxicity. Enhanced methane production, reduced hydraulic retention time, and improved volatile solids reduction are often observed in such systems. Alternatively, ozonation may be applied as a post-treatment to reduce color, odor, and residual COD in the anaerobically treated effluent. The ozone dose must be carefully managed to avoid the excessive formation of refractory by-products, but when optimized, this hybrid system offers a compelling solution for high-strength effluents from slaughterhouses and food processing plants.

A less conventional but increasingly studied hybrid configuration is the coupling of ion exchange processes with constructed wetlands. Ion exchange resins or natural zeolites are used to selectively remove ammonium or phosphate ions from the wastewater, especially in cases where rapid removal is required or where effluent discharge limits are very stringent. Once the target ions are reduced to acceptable levels, the partially treated effluent is passed through a constructed wetland, where biological uptake, filtration, and further polishing occur. This sequential design allows the wetland to operate under less nutrient stress, prolonging its operational life and improving its resilience (Onaghinor, *et al*., 2021, Orieno, *et al*., 2022, Sobowale, *et al*., 2022). The use of ion exchange also opens up the potential for nutrient recovery and recycling, as the saturated resins can be regenerated and the recovered nutrients reused as fertilizers. This configuration aligns well with circular economy principles and is particularly suited to agro-industrial facilities that seek to close nutrient loops and minimize environmental footprints.

Another notable hybrid system involves the combination of the Fenton reaction with biofilm reactors. The Fenton process, which uses hydrogen peroxide and iron catalysts to generate hydroxyl radicals, is highly effective in oxidizing recalcitrant organics and reducing chemical oxygen demand. When applied to agro-industrial effluents, it can degrade complex pollutants such as phenolics, pesticides, and antibiotic residues that are resistant to biodegradation. However, the Fenton reaction alone is not sufficient for nutrient removal and can produce iron-rich sludge that needs to be managed (Ajayi, *et al*., 2020, Ofori-Asenso, *et al*., 2020). By integrating it with a biofilm-based biological treatment such as a moving bed biofilm reactor (MBBR) or a packed-bed biofilter subsequent degradation of residual organics and nutrient assimilation can be achieved. The biofilm structure provides a stable environment for nitrifying and denitrifying bacteria, allowing for simultaneous nitrogen transformation processes. Additionally, the biofilm offers resistance to toxic shock and fluctuating loads, making this hybrid system robust under real agro-industrial operating conditions.

The design and operation of hybrid chemical-biological systems must consider several factors to maximize synergistic effects and ensure process compatibility. These include the selection of appropriate chemical reagents and dosages, timing and location of chemical addition, hydraulic and organic loading rates, reactor configuration, microbial community management, and strategies for sludge and by-product handling. Automation and real-time monitoring are increasingly essential to optimize these parameters and respond dynamically to changes in influent quality or operational disturbances (Bristol-Alagbariya, Ayanponle & Ogedengbe, 2022, Nwulu, *et al*., 2022).

In summary, hybrid chemical-biological treatment systems represent a versatile and powerful approach to managing nutrient-rich agro-industrial effluents. By strategically integrating fast-acting chemical processes with resilient biological mechanisms, these systems can achieve superior nutrient removal, improved effluent quality, and greater process stability. Configurations such as coagulation followed by activated sludge, ozonation coupled with anaerobic digestion, ion exchange paired with constructed wetlands, and Fenton oxidation preceding biofilm reactors illustrate the wide array of possibilities available to engineers and environmental managers. The successful implementation of these systems hinges on a deep understanding of the influent characteristics, treatment goals, and operational constraints. As agro-industrial sectors seek more sustainable and compliant wastewater solutions, hybrid treatment systems will play an increasingly central role in shaping the future of nutrient management and environmental protection.

2.4 Mechanisms of Enhanced Nutrient Removal

The mechanisms of enhanced nutrient removal in hybrid chemical-biological treatment systems for agro-industrial effluents are centered on leveraging the strengths of both chemical and biological processes to overcome the limitations of each when applied in isolation. Agro-industrial effluents are often nutrient-rich, containing significant concentrations of nitrogen (particularly ammonium and nitrate), phosphorus, and organic matter. These nutrients, if not effectively removed, contribute to environmental pollution, including eutrophication of water bodies, which leads to the depletion of oxygen, algal blooms, and biodiversity loss. A hybrid system, which integrates chemical treatments such as coagulation, oxidation, or ion exchange with biological processes like activated sludge, constructed wetlands, or biofilm reactors, capitalizes on the synergistic effects of both approaches to provide more efficient and sustainable nutrient removal.

The synergy between chemical and biological processes is a defining characteristic of hybrid treatment systems. Chemical processes, such as precipitation, coagulation, and advanced oxidation, serve to rapidly reduce nutrient concentrations, particularly phosphorus, or to degrade recalcitrant organic compounds. These processes can act as a pre-treatment step, reducing the pollutant load before the effluent enters biological treatment units, thereby enhancing the performance of biological systems (Francis Onotole, *et al*., 2022). Conversely, biological treatment processes, such as nitrification-denitrification and phosphorus uptake by microorganisms, provide long-term stability and sustainability by efficiently assimilating nutrients into microbial biomass or converting them into less harmful forms. By combining these processes, hybrid systems can achieve higher removal efficiencies, faster response times, and greater resilience to variations in influent composition, improving both short-term and long-term treatment outcomes.

One of the key mechanisms by which hybrid chemical-biological systems enhance nutrient removal is through the chemical enhancement of biodegradability and microbial uptake. Certain chemical processes, such as ozonation or advanced oxidation, break down complex organic pollutants into simpler, more biodegradable compounds. These processes oxidize refractory compounds like phenols, pesticides, and other organic toxins, which can inhibit microbial activity in biological systems (Ogunyankinnu, *et al*., 2022, Kolade, *et al*., 2022). By breaking these compounds into smaller, simpler molecules, these chemical treatments improve the biodegradability of the effluent, making it more amenable to biological degradation by microorganisms in subsequent treatment stages. The chemical breakdown of complex organics also helps to reduce the overall toxicity of the effluent, thus preventing the inhibition of beneficial microbial populations responsible for nutrient assimilation and removal.

In addition to improving biodegradability, chemical processes can also enhance microbial uptake of nutrients. For example, the addition of coagulants or flocculants in systems where coagulation-flocculation is used can help to aggregate particles and increase their settling characteristics, making it easier for microbes in biological systems to assimilate organic and inorganic matter (Ilori & Olanipekun, 2020). In systems where nutrient-rich wastewater is treated with advanced oxidation, such as in ozonation or Fenton processes, the breakdown of organic pollutants and the generation of hydroxyl radicals can activate or enhance microbial pathways for nitrogen and phosphorus removal. Furthermore, the chemical addition of iron or aluminum salts can assist in the removal of phosphorus through precipitation, allowing microbial organisms to more effectively absorb the remaining soluble phosphorus during biological treatment.

The nutrient removal pathways in hybrid chemical-biological treatment systems typically follow well-established biological processes such as nitrification-denitrification for nitrogen removal and phosphorus precipitation and uptake for phosphorus removal. Nitrification is a biological process where ammonium (NH_4^+) is oxidized to nitrite (NO_2^-) by nitrifying bacteria such as *Nitrosomonas*, and then further oxidized to nitrate (NO_3^-) by *Nitrobacter*. This process occurs in aerobic conditions and is crucial for nitrogen removal in wastewater (Ajibola & Olanipekun, 2019, Olanipekun & Ayotola, 2019). Denitrification follows nitrification and involves the conversion of nitrate (NO_3^-) to nitrogen gas (N_2), which is released into the atmosphere, completing the nitrogen cycle. This process is facilitated by heterotrophic bacteria that utilize organic carbon as an electron donor in anoxic conditions.

In a hybrid system, the chemical treatment step, such as ozonation or Fenton oxidation, can enhance the efficiency of nitrification by reducing toxic organic or inorganic compounds that may otherwise inhibit the nitrifying bacteria. Furthermore, these processes can help to reduce the COD and BOD levels in the effluent, ensuring that the denitrification process is not limited by carbon availability. The addition of chemical agents such as calcium hydroxide or iron salts can also enhance the removal of phosphorus, which is typically achieved through precipitation (Olanipekun, 2020; West, Kraut & Ei Chew, 2019). Phosphorus in agro-industrial effluents is mainly present as orthophosphate (PO_4^{3-}) or in organic forms, and its removal is essential to prevent eutrophication in receiving water bodies. Chemical precipitation involves the addition of metal salts like alum or ferric chloride, which react with phosphate ions to form insoluble precipitates that can be easily removed by settling or filtration.

Once precipitated, phosphorus can be biologically assimilated by microorganisms in systems such as activated sludge or constructed wetlands, where phosphorus is taken up by organisms like *Acinetobacter* or *Candidatus Accumulibacter*, which accumulate phosphorus in their cell biomass. In hybrid systems, the pre-treatment steps, such as coagulation or ozonation, can help to remove part of the phosphorus load, reducing the demand on biological systems and improving overall nutrient removal efficiency (Belot, 2020; Olanipekun, Ilori & Ibitoye, 2020).

The role of microbial consortia and bioaugmentation is crucial in enhancing nutrient removal in hybrid systems. Agro-industrial effluents often contain a wide variety of pollutants that require diverse microbial populations to degrade effectively. In biological treatment systems, microbial consortia consisting of nitrifiers, denitrifiers, phosphorus-accumulating organisms (PAOs), and other functional microbes interact to perform complementary tasks, making the removal of nitrogen, phosphorus, and organic compounds more efficient (Kolade, *et al*., 2021; Ramdoo, *et al*., 2021). The presence of a diverse microbial community also helps improve the stability and resilience of the system, as different microbial populations can respond to changes in nutrient loads, pH, and other environmental factors.

Bioaugmentation, or the addition of specialized microbial strains to enhance nutrient removal, can further optimize hybrid systems. For example, adding specific strains of denitrifying bacteria or PAOs to a system can accelerate the nitrogen and phosphorus removal rates, especially in systems that experience fluctuating influent compositions. These strains are selected based on their ability to tolerate high concentrations of organic or inorganic pollutants or their enhanced ability to remove specific nutrients, making them valuable in treating complex agro-industrial effluents (Akang, *et al*., 2019; Ezenwa, 2019).

The benefits of microbial consortia and bioaugmentation in hybrid systems are particularly evident when chemical treatments, such as ozonation or Fenton oxidation, have degraded or removed inhibitory compounds. After chemical pre-treatment, the microbial communities are often more effective in assimilating nutrients and carrying out biodegradation, leading to more complete nutrient removal. Moreover, microbial consortia can adapt to different pollutant loads over time, improving the robustness of the system under variable influent conditions (Otokiti, *et al*., 2022; Oyewola, *et al*., 2022).

In conclusion, the mechanisms of enhanced nutrient removal in hybrid chemical-biological treatment systems are based on the complementary roles of chemical and biological processes. Chemical treatments improve biodegradability, enhance microbial uptake, and enable the rapid removal of specific pollutants, such as phosphorus, while biological processes provide long-term, sustainable nutrient removal through well-established pathways like nitrification-denitrification and phosphorus uptake. The integration of microbial consortia and bioaugmentation further enhances the efficiency and resilience of these systems, making them highly effective for nutrient removal in agro-industrial effluents. As these systems continue to evolve, hybrid chemical-biological treatment strategies will play an increasingly vital role in achieving sustainable and environmentally compliant wastewater treatment in agro-industrial operations.

2.5 Operational Factors and Optimization

The optimization and effective operation of hybrid chemical-biological treatment systems for nutrient removal in agro-industrial effluents are influenced by several operational factors that must be carefully managed. These factors directly impact the efficiency of nutrient removal processes, including nitrogen and phosphorus removal, organic matter degradation, and overall treatment performance (Ochinanwata, 2019; Negi, 2021; Otuoze, Hunt & Jefferson, 2021). Understanding the interaction between biological and chemical processes, and fine-tuning these factors, can greatly enhance the efficacy of hybrid systems. These operational factors include the control of pH and redox conditions, the management of carbon-to-nitrogen-to-phosphorus (C/N/P) ratios, hydraulic retention time (HRT), chemical dosing, and the use of system monitoring and control strategies.

One of the most important operational factors in hybrid systems is the regulation of pH and redox conditions, as these parameters significantly affect both biological and chemical processes. pH plays a critical role in the efficiency of nutrient removal, especially for nitrogen and phosphorus. For example, nitrification, the process by which ammonia (NH_4^+) is converted to nitrite (NO_2^-) and nitrate (NO_3^-), requires slightly alkaline conditions (typically pH 7.5–8.5) to support the activity of nitrifying bacteria such as *Nitrosomonas* and *Nitrobacter*. If the pH falls outside this optimal range, nitrification is inhibited, leading to incomplete nitrogen removal (Ijeomah, 2020; Qi, *et al*., 2017). On the other hand, denitrification, the process of converting nitrate to nitrogen gas (N_2), occurs under anoxic conditions and is sensitive to pH levels, with lower pH values (pH 6–7) generally promoting denitrification.

Similarly, phosphorus removal through enhanced biological phosphorus removal (EBPR) relies on alternating anaerobic and aerobic conditions to stimulate phosphorus-accumulating organisms (PAOs). The anaerobic phase allows PAOs to release phosphorus from their storage vacuoles, while the aerobic phase encourages the uptake of phosphorus, thereby reducing its concentration in the effluent. These organisms are particularly sensitive to changes in pH and redox conditions. A balanced pH range and proper redox potential are crucial for optimizing PAO performance and ensuring efficient phosphorus removal (Babatunde, 2019; Olukunle, 2013; Danese, Romano & Formentini, 2013). In hybrid systems, pre-chemical treatments like coagulation or ozonation can be used to adjust pH levels, remove recalcitrant organics, or break down complex pollutants, setting the stage for more efficient biological processes.

The carbon-to-nitrogen-to-phosphorus (C/N/P) ratio is another critical operational factor in hybrid systems, particularly in biological nutrient removal processes. The ideal C/N/P ratio influences the balance of microbial communities and affects the rates of nitrogen and phosphorus removal. In typical wastewater, nitrogen is present primarily as ammonium (NH_4^+), and phosphorus is primarily in the form of orthophosphate (PO_4^{3-}). A proper C/N/P ratio ensures that microorganisms have the right amount of carbon to support their metabolism and nutrient assimilation (Lu, 2019; Simchi-Levi, Wang & Wei, 2018). In biological systems like activated sludge, a high C/N ratio is necessary for effective denitrification, while a balanced C/N/P ratio is essential for optimal biological phosphorus removal. When the ratio is unbalanced such as when there is an excess of nitrogen or phosphorus microbial activity can become inefficient, leading to poor nutrient removal and possible issues with system stability. In hybrid systems, chemical pre-treatment can be used to remove some of the excess nitrogen or phosphorus, which may help optimize the C/N/P ratio in the biological unit and improve overall treatment performance.

Retention time and hydraulic loading rate (HLR) are two key parameters that directly affect the residence time of wastewater within the treatment system and, consequently, the efficiency of nutrient removal. Retention time is the duration for which wastewater remains in the reactor, and it plays a significant role in the effectiveness of both chemical and biological treatments. In biological systems, longer retention times allow for greater contact between microorganisms and pollutants, which enhances the microbial degradation of organic matter and nutrient assimilation (Qrunfleh & Tarafdar, 2014; Wang, *et al*., 2016). For example, in activated sludge systems, longer retention times can lead to more complete nitrification and denitrification, as well as improved phosphorus uptake by PAOs. Similarly, in constructed wetlands or biofilm reactors, extended retention times provide more opportunities for microbial interactions with the effluent, enhancing nutrient removal.

However, excessively long retention times can increase the size and cost of the treatment system, making it less feasible for large-scale applications. Conversely, insufficient retention times can result in incomplete treatment, particularly in systems like anaerobic digestion, where extended periods are required for the degradation of complex organic matter. Hydraulic loading rate, which refers to the volume of wastewater per unit area per time, also plays a crucial role in the performance of hybrid systems (Mwangi, 2019; Zohuri & Moghaddam, 2020). High HLRs can lead to inadequate contact time between the effluent and microorganisms or chemical reagents, reducing treatment efficiency and leading to incomplete nutrient removal. Balancing retention time and HLR is essential to optimize the performance of hybrid chemical-biological systems, ensuring both effective treatment and efficient system design.

Chemical dosing is a critical aspect of hybrid systems, particularly when chemicals are used to enhance biological treatment or as a primary treatment method. The dosing of chemicals such as coagulants, flocculants, oxidants, and nutrients must be carefully controlled to achieve the desired nutrient removal while minimizing costs and secondary waste production. For example, in coagulation-flocculation systems, the addition of aluminum or ferric salts helps to precipitate phosphorus, remove suspended solids, and improve the settling characteristics of the effluent (Dong, *et al*., 2020; Tien, *et al*., 2019). The optimal dosage of these chemicals depends on the concentration of pollutants in the influent and the specific treatment goals. Similarly, in advanced oxidation processes (AOPs), the careful dosing of ozone or hydrogen peroxide is crucial for generating hydroxyl radicals that degrade organic pollutants, but overdosing can lead to high operational costs and the formation of undesirable by-products.

In biological systems, the addition of nutrients like organic carbon may be necessary to support the denitrification process or to enhance the growth of beneficial microorganisms, such as phosphorus-accumulating organisms (PAOs). However, nutrient addition must be balanced to prevent excess nutrient loading, which could lead to environmental issues such as nitrogen leaching or eutrophication (Dong, *et al*., 2020; Tien, *et al*., 2019). Additionally, nutrient imbalances can disrupt microbial populations, reducing the overall efficiency of the treatment system. Dosing strategies must be adapted based on real-time influent characteristics, and continuous monitoring is required to adjust dosing levels dynamically.

System monitoring and control strategies are increasingly being integrated into hybrid chemical-biological systems to optimize operational performance and ensure regulatory compliance. Modern treatment systems incorporate sensors and automated control systems to monitor key parameters such as pH, dissolved oxygen (DO), redox potential, turbidity, and chemical concentrations in real time (Duan, Edwards & Dwivedi, 2019; Tien, 2017). This allows operators to make adjustments on-the-fly, ensuring that the system remains within optimal operating conditions. In biological treatment processes, real-time monitoring of nutrient concentrations (e.g., ammonia, nitrate, phosphate) helps to maintain the proper C/N/P ratio and ensures that microbial populations are not overloaded or starved of nutrients.

For chemical processes, advanced control systems can adjust the dosing of coagulants, flocculants, or oxidants based on real-time effluent characteristics, ensuring that chemical consumption is optimized and the desired treatment levels are achieved. Additionally, data from monitoring systems can be used to predict future performance and provide valuable insights into process dynamics, helping to reduce the risk of operational failures. System integration with cloud-based platforms allows for remote monitoring and management, which can reduce the need for on-site personnel and improve the efficiency of large-scale operations (Javaid, *et al*., 2022; Richey, *et al*., 2022).

In conclusion, the optimization and operation of hybrid chemical-biological treatment systems for nutrient removal in agro-industrial effluents depend on the careful management of several key operational factors. pH and redox conditions must be closely monitored to optimize the performance of both biological and chemical processes (Korteling, *et al*., 2021; Zhang & Lu, 2021). Managing the C/N/P ratio, adjusting retention times and hydraulic loading rates, and controlling chemical dosing are all critical for achieving efficient nutrient removal. Additionally, the integration of real-time monitoring and control strategies enhances the flexibility and effectiveness of these systems, ensuring that they remain responsive to the dynamic nature of agro-industrial wastewater. By addressing these factors, hybrid systems can achieve higher nutrient removal efficiencies, improve operational stability, and provide a more sustainable approach to wastewater management in agro-industrial settings.

2.6 Case Studies and Performance Evaluation

Hybrid chemical-biological treatment systems have been increasingly recognized for their ability to efficiently remove nutrients from agro-industrial effluents. These systems combine the strengths of chemical processes, such as coagulation, precipitation, and advanced oxidation, with biological treatments like activated sludge, anaerobic digestion, and biofilm reactors. The goal of these integrated systems is to achieve superior nutrient removal while ensuring system resilience, energy efficiency, and environmental sustainability (Jarrahi, 2018; Terziyan, Gryshko & Golovianko, 2018). Several case studies, ranging from pilot-scale to full-scale implementations, highlight the effectiveness of hybrid systems in addressing the complex challenges associated with agro-industrial effluent treatment.

One prominent case study of a hybrid system in the dairy industry involved the combination of coagulation-flocculation and activated sludge treatment. Dairy effluents are rich in organic matter and nutrients, particularly nitrogen and phosphorus. The effluent from a dairy processing plant was first treated using a coagulation-flocculation process with ferric chloride to remove suspended solids and phosphorus (Affognon, *et al*., 2015; Misra, *et al*., 2020). The coagulated effluent was then subjected to activated sludge treatment, where nitrification and denitrification processes removed nitrogen. The performance of the hybrid system was evaluated based on the removal of total nitrogen (TN), total phosphorus (TP), and chemical oxygen demand (COD). The results showed that the combined approach achieved over 95% phosphorus removal and approximately 80% nitrogen removal, which was significantly higher than what could be achieved using biological treatment alone. Additionally, the COD removal rate reached 85%, indicating that the pre-treatment helped improve the biodegradability of the effluent, thereby enhancing the performance of the biological treatment.

In the meat processing industry, a hybrid system combining ozonation and anaerobic digestion was employed to treat high-strength wastewater with high organic load and nitrogen content. The system used ozonation as a pre-treatment to oxidize refractory organic compounds and reduce the toxicity of the effluent before it entered the anaerobic digesters. This combination of advanced oxidation with biological treatment facilitated the efficient conversion of organic matter into biogas, with the added benefit of reducing the amount of sludge generated. The performance metrics of this system were evaluated in terms of total nitrogen removal, COD reduction, and biogas production. (Akande & Diei-Ouadi, 2010; Morris, Kamarulzaman & Morris, 2019) The hybrid system demonstrated a 90% reduction in COD and an 85% reduction in total nitrogen, with a significant increase in methane production compared to anaerobic digestion alone. This case study highlighted the potential of ozonation as an effective pre-treatment for enhancing the performance of anaerobic digesters, particularly in high-strength wastewater streams, and also showcased the system's energy recovery potential through biogas production.

Another case study focused on the beverage industry, where a hybrid system consisting of ion exchange followed by constructed wetlands was implemented to treat wastewater from a soft drink manufacturing plant. The effluent from the beverage plant contained high concentrations of ammonium nitrogen and moderate levels of phosphorus, along with sugars and other organic matter. Ion exchange was used to selectively remove ammonium from the wastewater, followed by treatment in constructed wetlands to further reduce organic matter and residual nutrients. The constructed wetlands provided additional polishing, with the help of microbial processes, to remove residual nutrients like phosphorus (Ahiaba, 2019; Hodges, Buzby & Bennett, 2011). The performance evaluation of the system demonstrated significant reductions in both total nitrogen and total phosphorus, with ammonium nitrogen removal efficiency exceeding 95%. The constructed wetlands contributed to further reduction of COD, achieving a 75% reduction. This case study demonstrated the viability of combining ion exchange, a highly efficient process for removing specific nutrients, with constructed wetlands, which provide a low-cost and sustainable option for polishing the effluent.

A more complex hybrid system was implemented in a crop processing plant that involved the combination of Fenton oxidation with biofilm reactors. The crop processing plant produced wastewater containing high levels of starch, suspended solids, and nitrogen and phosphorus compounds. The wastewater was first treated using Fenton's reagent, which involved the addition of hydrogen peroxide and iron salts to generate hydroxyl radicals capable of breaking down the complex organic molecules into simpler, biodegradable compounds. After Fenton treatment, the effluent was passed through biofilm reactors to remove residual nitrogen and phosphorus (Jagtap, *et al*., 2020; Sibanda & Workneh, 2020). The biofilm reactors, which provided a stable environment for microbial growth, facilitated the conversion of ammonia into nitrate (nitrification) and the reduction of nitrate into nitrogen gas (denitrification). The system achieved a 90% reduction in total phosphorus and a 75% reduction in total nitrogen, demonstrating the combined efficacy of chemical and biological treatments. The system also showed a 60% reduction in COD, indicating significant organic matter removal. This case study is an example of the potential of combining chemical oxidation with biological treatment to handle complex wastewater compositions typical of crop processing industries.

In terms of performance metrics, hybrid chemical-biological systems typically outperform traditional standalone systems in nutrient removal. Total nitrogen (TN) and total phosphorus (TP) removal efficiencies can be significantly enhanced by integrating chemical treatments, which rapidly reduce the nutrient load, with biological systems that provide long-term, stable nutrient removal (Chaudhuri, *et al*., 2018; Stathers & Mvumi, 2020). The COD/BOD reduction in hybrid systems is also typically higher, as chemical pre-treatment often improves the biodegradability of the effluent, making it more amenable to biological degradation. Sludge production in hybrid systems can be more controlled compared to traditional systems, as chemical treatments can reduce the organic load before it enters biological reactors, thus minimizing the need for excessive microbial growth.

However, the cost and environmental impact of these hybrid systems must be considered in any performance evaluation. Cost-benefit analyses are essential for understanding the feasibility of implementing hybrid systems on a larger scale, especially in agro-industrial settings where operational costs and resource constraints are critical factors. The cost of chemicals, energy, and equipment must be weighed against the benefits of improved nutrient removal, sludge management, and potential energy recovery from processes like anaerobic digestion (Khalifa, Abd Elghany & Abd Elghany, 2021; Nahr, Nozari & Sadeghi, 2021). In many cases, the added cost of chemical treatment is offset by the reduced operational costs in biological treatment units and the potential for resource recovery, such as biogas production. Moreover, the environmental impact of hybrid systems can be assessed by evaluating factors such as energy consumption, chemical usage, and secondary pollution. For example, while ozonation and advanced oxidation processes require significant energy input, the benefits of reduced chemical dosing in biological units and the potential for biogas production can make these systems more environmentally sustainable in the long run.

Several environmental impact assessments have demonstrated that hybrid systems can significantly reduce the overall environmental footprint of wastewater treatment in agro-industrial settings. By improving nutrient removal efficiency, hybrid systems help reduce the risk of eutrophication in receiving water bodies and decrease the overall pollution load. The integration of renewable energy sources, such as biogas from anaerobic digestion, further enhances the sustainability of these systems, making them more attractive for industries aiming to reduce their carbon footprint (Alam, *et al*., 2022; Kumar, *et al*., 2022).

In conclusion, case studies of hybrid chemical-biological treatment systems in agro-industrial effluent treatment have demonstrated their effectiveness in achieving superior nutrient removal, improving system stability, and enhancing the overall performance of wastewater treatment processes. Pilot- and full-scale implementations have shown that these systems can outperform conventional treatment methods in terms of nitrogen and phosphorus removal, COD reduction, and sludge yield (Das Nair & Landani, 2020; Krishnan, Banga & Mendez-Parra, 2020). The combination of chemical and biological processes also enables better control of operational parameters and more efficient resource recovery. While the initial costs and environmental impact must be carefully considered, the long-term benefits of hybrid systems such as reduced operational costs, improved effluent quality, and sustainable resource recovery make them a promising solution for agro-industrial wastewater management. As industries continue to face stricter environmental regulations and sustainability goals, hybrid treatment systems will likely play an increasingly important role in achieving effective and sustainable nutrient removal from agro-industrial effluents.

2.7 Challenges and Limitations

Hybrid chemical-biological treatment systems have proven to be an effective solution for nutrient removal in agro-industrial effluents, combining the strengths of both chemical and biological processes to address the complexity and variability of these waste streams. However, despite their significant potential, these systems face several challenges and limitations that can impact their adoption, efficiency, and long-term sustainability in agro-industrial settings. Key challenges include high capital and operational costs, process complexity, maintenance requirements, sludge disposal, chemical handling, and regulatory compliance. Understanding these challenges is essential for developing strategies to optimize hybrid systems and make them more viable for large-scale applications (Balana, Aghadi & Ogunniyi, 2022; Raja Santhi & Muthuswamy, 2022).

One of the primary challenges associated with hybrid chemical-biological treatment systems is the high capital and operational costs. The implementation of these systems often requires significant upfront investment in infrastructure, equipment, and technology. The capital cost of installing hybrid systems typically involves the cost of both the chemical and biological treatment units, as well as the necessary monitoring, control, and automation systems required for optimal performance (Dauvergne, 2022; Lin, Lin

& Wang, 2022). For example, integrating advanced oxidation processes like ozonation or Fenton oxidation with biological treatment requires the installation of specialized reactors, chemical dosing systems, and power supplies to generate and deliver oxidants. Additionally, hybrid systems that use both ion exchange and constructed wetlands may require multiple treatment units that occupy substantial land area, which further drives up capital costs. These initial investments can be particularly burdensome for small and medium-sized agro-industrial facilities with limited financial resources.

Operational costs for hybrid systems are also a significant concern. These systems often involve continuous chemical dosing, which can result in ongoing expenses related to the purchase, storage, and handling of chemicals. For example, chemical coagulants, flocculants, and oxidants, such as hydrogen peroxide, ozone, and ferric chloride, can be expensive, especially when used in large quantities. Furthermore, the need for additional power supply to drive chemical oxidation or the operation of equipment such as ozone generators and air compressors can increase energy consumption, contributing to higher operational costs (Shah, Li & Ierapetritou, 2011; Urciuoli, *et al*., 2014). The biological component of the hybrid system, such as activated sludge or anaerobic digestion, may also incur costs related to the maintenance of microbial populations, including the addition of nutrients or bioaugmentation to improve performance. Therefore, while hybrid systems offer enhanced nutrient removal, the ongoing operational costs can be prohibitive, particularly when compared to conventional standalone biological or chemical systems.

In addition to cost concerns, process complexity and maintenance requirements represent a significant limitation of hybrid systems. The integration of chemical and biological treatment processes adds layers of complexity to system design, operation, and management. For example, when combining coagulation with activated sludge, operators must ensure that the optimal dosage of coagulants is applied to achieve effective phosphorus removal while avoiding excessive sludge production that could negatively impact the biological process (Kuang, *et al*., 2021; Sircar, *et al*., 2021). Similarly, systems that integrate ozonation or Fenton oxidation with biological treatment require careful monitoring and control of chemical dosing and pH levels to ensure that the chemicals do not inhibit microbial activity or disrupt biological nutrient removal pathways. Maintaining the delicate balance between the chemical and biological components of the system can be challenging, particularly under fluctuating influent conditions or varying wastewater compositions.

Moreover, hybrid systems often require specialized expertise to operate and maintain. The need for trained personnel to manage both the chemical and biological components of the system can increase the labor burden and require ongoing investment in operator training. In some cases, the complexity of managing hybrid systems may lead to errors or inefficiencies if operators are not adequately trained or if real-time monitoring and automated control systems are not in place (Koroteev & Tekic, 2021 Yigitcanlar, *et al*., 2021). The high level of operational expertise required to maintain optimal performance may deter some agro-industrial facilities from adopting hybrid treatment systems, especially in regions with limited access to skilled labor.

Sludge disposal and chemical handling are other critical challenges that hybrid chemical-biological treatment systems face. Both chemical and biological treatments generate waste by-products that must be managed appropriately to avoid environmental contamination. In the case of chemical treatments, such as coagulation and precipitation, large volumes of sludge are produced, which contain metal hydroxides and phosphates (An, Wilhelm & Searcy, 2011; Kandziora, 2019). This sludge must be handled, stored, and disposed of in an environmentally safe manner, often requiring additional processing to reduce its volume and toxicity. For example, dewatering and drying processes may be necessary before disposal in landfills or for land application. The disposal of chemical sludge is a significant operational expense and environmental concern, particularly in systems that generate large quantities of waste.

In biological systems, sludge is also produced, although it is typically organic and contains microbial biomass. However, in hybrid systems that combine chemical and biological treatments, sludge production can be further exacerbated by the combined effects of both processes. For example, excessive chemical dosing can lead to an increase in residual sludge, while biological systems like activated sludge require periodic removal and disposal of excess biomass (An, Wilhelm & Searcy, 2011; Kandziora, 2019). The challenge of sludge management is particularly pronounced in hybrid systems treating high-strength agro-industrial effluents, as the volume of sludge generated can be substantial. Sludge disposal regulations and the cost of managing sludge can represent a significant barrier to the widespread adoption of hybrid systems, especially when compared to simpler biological or chemical alternatives.

Chemical handling also presents a risk in hybrid systems. The use of hazardous chemicals such as hydrogen peroxide, ozone, or ferric chloride requires careful management to avoid spills, leaks, and worker exposure. These chemicals must be safely stored, transported, and handled to comply with health and safety regulations, adding another layer of complexity and cost to hybrid systems. Additionally, the potential for chemical overuse or misuse can lead to secondary pollution or inefficiencies in the treatment process (Yue, You & Snyder, 2014; Oyedokun, 2019). For example, excessive chemical dosing can result in the formation of undesirable by-products or cause inhibition of biological processes. Therefore, effective chemical management, including accurate dosing, monitoring, and waste disposal, is crucial to ensuring the success of hybrid systems.

Regulatory compliance is another critical challenge in the implementation of hybrid chemical-biological treatment systems for nutrient removal in agro-industrial effluents. Different countries and regions have varying regulations and standards for wastewater treatment, particularly with respect to nutrient discharge limits, such as total nitrogen and total phosphorus levels. Meeting these stringent regulatory requirements can be difficult, particularly in regions with high nutrient concentrations in effluents (De Almeida, dos Santos & Farias, 2021; Yigitcanlar, Mehmood & Corchado, 2021). While hybrid systems have demonstrated superior nutrient removal performance, their complexity, chemical use, and waste generation may face scrutiny under regulatory frameworks that focus on minimizing chemical inputs and reducing environmental impacts. The regulatory landscape for hybrid systems is still evolving, and in some cases, there may be a lack of clear guidelines or incentives for adopting advanced treatment technologies.

Compliance with environmental regulations, especially concerning chemical handling, sludge disposal, and effluent quality, is essential for the successful deployment of hybrid systems. Non-compliance can result in fines, penalties, or public scrutiny, potentially undermining the benefits of these advanced treatment methods. Thus, hybrid systems must be carefully designed, optimized, and operated to ensure compliance with regulatory standards while minimizing the environmental footprint (Gianni, Lehtinen & Nieminen, 2022; Helo & Hao, 2022).

In conclusion, while hybrid chemical-biological treatment systems offer significant advantages in nutrient removal from agro-industrial effluents, they are not without their challenges. High capital and operational costs, process complexity, sludge disposal, chemical handling, and regulatory compliance all represent limitations that must be carefully managed. Despite these challenges, hybrid systems remain an attractive option for achieving efficient and sustainable nutrient removal, particularly when tailored to specific effluent characteristics and designed with optimization in mind (Al-Besher & Kumar, 2022; Djeffal, Siewert & Wurster, 2022; Tardieu, 2022). As technology advances and regulatory frameworks evolve, hybrid systems may become more widely adopted in agro-industrial wastewater treatment, providing a path toward improved water quality and environmental sustainability. However, addressing these challenges will require ongoing research, innovation, and collaboration between industry, regulators, and technology providers to ensure that hybrid systems are cost-effective, environmentally friendly, and scalable for widespread use (Androutsopoulou, et sl., 2019; Kankanhalli, Charalabidis & Mellouli, 2019).

3. Future Directions and Conclusion

The future of hybrid chemical-biological treatment systems for nutrient removal in agro-industrial effluents holds significant promise, particularly as industries and governments around the world are increasingly prioritizing environmental sustainability and resource efficiency. In the coming years, hybrid systems will likely evolve to incorporate more advanced technologies, integrate resource recovery practices, and leverage digital tools to optimize performance. These developments will not only improve nutrient removal efficiencies but also enable a more circular approach to agro-industrial wastewater management.

One key area of advancement in hybrid systems is the integration with resource recovery practices, such as struvite crystallization. Struvite, a phosphate salt, can be recovered from wastewater through chemical precipitation processes, and its crystallization can be used to remove excess phosphorus efficiently while recovering it as a valuable fertilizer. By incorporating struvite crystallization into hybrid systems, agro-industrial facilities can recover valuable nutrients that would otherwise be wasted, helping to close the nutrient loop and reduce the dependency on synthetic fertilizers. This integration not only improves the sustainability of wastewater treatment processes but also offers economic benefits to industries, particularly those in agriculture and food processing, where nutrient recovery can reduce operating costs and promote the circular economy.

The growing use of artificial intelligence (AI) and the Internet of Things (IoT) in wastewater treatment will also play a transformative role in the future of hybrid chemical-biological systems. AI-driven smart process control systems can optimize the operation of both chemical and biological components of these systems in real-time, adjusting chemical dosing, flow rates, and other parameters to maximize nutrient removal efficiency. Machine learning algorithms can analyze large sets of operational data to predict system performance, detect anomalies, and provide early warnings for potential failures. IoT-enabled sensors can continuously monitor key parameters such as pH, turbidity, nutrient concentrations, and microbial activity, providing operators with valuable insights to adjust the system dynamically. This integration of AI and IoT will not only improve system efficiency but also reduce operational costs, minimize energy consumption, and ensure regulatory compliance, all while enhancing the resilience and adaptability of the treatment system.

Another promising direction for future research and development in hybrid systems is the design of modular and decentralized treatment units. These systems, which can be deployed closer to the source of wastewater generation, offer greater flexibility and scalability compared to traditional centralized treatment facilities. Modular systems can be designed to meet the specific needs of different agro-industrial operations, whether they are small-scale farms or large processing plants. By using modular components, operators can scale up or down as needed based on influent variability and treatment requirements. Additionally, decentralized systems offer the advantage of reducing transportation costs for wastewater, minimizing infrastructure investments, and providing localized solutions for wastewater management in regions with limited access to centralized treatment facilities.

To support the widespread adoption of hybrid chemical-biological treatment systems, governments and regulatory bodies will need to create supportive policy and incentive frameworks. This could include offering financial incentives such as grants or tax credits for the installation of resource-efficient technologies, as well as implementing regulatory policies that promote the use of sustainable wastewater management practices. Policies that encourage the recovery and reuse of nutrients, such as phosphorus and nitrogen, will be essential in facilitating the transition toward more sustainable agro-industrial operations. Moreover, the development of clear and standardized regulatory guidelines for the operation and monitoring of hybrid systems will be necessary to ensure that they meet environmental standards while encouraging innovation in the field.

In conclusion, the future of hybrid chemical-biological treatment systems for nutrient removal in agro-industrial effluents is bright, with significant opportunities for innovation and optimization. The integration of resource recovery technologies, such as struvite crystallization, alongside the use of AI and IoT for process control, will enhance the efficiency, flexibility, and sustainability of these systems. Modular and decentralized treatment units offer the potential for more adaptable, cost-effective solutions, particularly in rural or remote areas. As industry stakeholders, policymakers, and researchers continue to collaborate and drive forward these advancements, hybrid treatment systems will play a critical role in addressing the challenges of nutrient pollution, promoting a circular economy, and ensuring the sustainable management of water resources. These systems will not only improve wastewater treatment efficiency but also contribute to the global goals of environmental sustainability, resource conservation, and climate change mitigation, positioning hybrid systems as a key player in the future of wastewater management.

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