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Effectiveness of Phosphorus and Nitrogen Removal in the Water Treatment Process at Khmer Beverages, Phnom Penh

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ABSTRACT

Purpose of the study: The aim of this study is to understand the process of water treatment in each step and to understand the effectiveness of the removal of phosphorus and nitrogen from wastewater.

Methodology: For nitrogen removal must be through many processes such as Nitrogen fixation, or Ammonification, and Denitrification. For the phosphorus. The additional Ferric Chloride in the Aeration tanks to a reaction between the melt and the mud bolts is separated at the Clarifier tank. The Coagulation basin adds Ferric Chloride at 40% concentration of 0.05ml in contaminated water 1000ml for nitrogen and phosphorus concentration tests and studied in the condition the nitrogen can be removed from contaminated water well depending on the pH value and temperature. The removal of phosphorus by adding 0.05ml ferric chloride and 5ml of polymer cation 1040 (powder) can tank up to 80% phosphorus at the temperature of 200C and pH 7.

Main Findings: As a result, the good conditions for nitrification are the pH of between 7.5 and 8.6 at temperature in the tank between 20^0C and 25^0C and the denitrification has a pH of between 7.5 and 8 and temperature in the tank from 20^0C to 35^0C. Result show that the remaining phosphorus is below the ministry of environment standard set (P <2mg/l).

Novelty/Originality of this study: The next study should observe the amount of polymer to be applied after adding iron and studying the speed of iron chips as it affects the removal of phosphorus.

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1. INTRODUCTION

The rapid industrialization of Cambodia, particularly in the food and beverage sector, has been a cornerstone of its 21st-century development. While this growth is vital for the nation's economy and meets the demands of a growing population, it concurrently generates significant volumes of industrial wastewater [1]. The discharge of this wastewater into natural water bodies without adequate treatment poses severe environmental risks, including eutrophication and threats to public health [2]. From a chemical engineering standpoint, the challenge lies not merely in treating this water, but in designing, operating, and optimizing the complex system of unit operations and chemical/biological reactors to achieve high-efficiency pollutant removal in a cost-effective manner. This requires a deep understanding of the underlying reaction mechanisms, stoichiometry, and kinetics that govern the transformation of pollutants.

The wastewater from beverage industries is typically characterized by high concentrations of organic matter, as well as nutrients such as phosphorus and nitrogen, which are of primary concern [3]. The removal of these nutrients is a critical task in wastewater treatment, governed by specific chemical and biological engineering principles.

Phosphorus is typically removed from wastewater via chemical precipitation, a process where soluble phosphate is converted into an insoluble solid that can be separated from the water. This is a classic example of a phase-change reaction, and its efficiency is dictated by reaction kinetics and equilibrium thermodynamics. The most common methods involve the addition of metal salts, such as those of iron (Fe^{3+}), aluminum (Al^{3+}), or calcium (Ca^{2+}) [4]. For instance, the precipitation with ferric chloride is represented by the following stoichiometric reaction: $Fe^{3+} + PO_4^{3-} \rightarrow FePO_4(s)$.

The efficiency of this process is highly dependent on operational parameters, most notably pH, which affects the speciation of both the metal ions and the phosphate, as well as the solubility of the resulting precipitate [5]. Kinetic models have been developed to describe the rate of precipitation, which is crucial for reactor sizing and determining the required residence time. For example, detailed kinetic models for aluminum-phosphate precipitation involve multiple reversible hydrolysis reactions [6]. Furthermore, studies have shown that in addition to precipitation, adsorption onto metal hydroxides (e.g., $Fe(OH)_3$ or $Al(OH)_3$) can be a significant mechanism for phosphorus removal [7]. In some advanced systems, phosphorus is recovered as struvite ($MgNH_4PO_4 \cdot 6H_2O$), a process whose kinetics are influenced by reactant concentrations and pH [8].

Biological nitrogen removal is a more complex process, typically achieved in a sequence of aerobic and anoxic stages. It relies on two main microbial processes: nitrification and denitrification. This sequence represents a sophisticated bioreactor design problem, where the environment must be carefully controlled to favor the desired microbial populations and reaction pathways.

Nitrification is an aerobic, two-step process where ammonia (NH_4^+) is oxidized first to nitrite (NO_2^-) by ammonia-oxidizing bacteria (AOB) and then to nitrate (NO_3^-) by nitrite-oxidizing bacteria (NOB). The overall stoichiometry is: $NH_4^+ + 2O_2 \rightarrow NO_3^- + 2H^+ + H_2O$. Denitrification is an anoxic process where nitrate (NO_3^-) is reduced to nitrogen gas (N_2) by denitrifying bacteria, which use nitrate as an electron acceptor in the absence of oxygen, with a source of organic carbon (like the BOD in beverage wastewater) as the electron donor.

The kinetics of both processes are often described by the Monod equation, which relates the microbial growth rate to the concentration of the limiting substrate (ammonia or nitrate) and other environmental factors like dissolved oxygen, pH, and temperature [9]. For instance, a study by Dinçer and Kargı (2000) determined the kinetic constants for sequential nitrification and denitrification, providing a basis for modeling and optimizing such systems [10]. The design of the treatment plant, which includes anoxic tanks, aeration tanks, and clarifiers, is a direct application of chemical engineering principles to create the specific conditions required for these sequential reactions to occur efficiently.

While the fundamental principles of phosphorus and nitrogen removal are well-established, their application to specific industrial wastewaters, such as those from the beverage industry, presents unique challenges. The composition of beverage wastewater can fluctuate and contains high concentrations of sugars and other organic compounds that affect the biological processes [11]. A review of the literature reveals that while some studies have investigated the treatment of beverage wastewater [12], [13], there is a significant research gap concerning the optimization of operating conditions for modern, full-scale treatment systems that combine different unit operations (e.g., UASB, anoxic tanks, aeration tanks) specifically for the beverage industry. Most kinetic data available are derived from studies on municipal wastewater or synthetic solutions and may not be directly applicable.

Khmer Beverages Co., Ltd. has recently installed a new wastewater treatment plant incorporating an advanced system for total phosphorus and total nitrogen removal. However, the operational efficiency of this new system has not been formally assessed or optimized. The novelty and urgency of this research lie in its focus on bridging the identified research gap. This study will be one of the first to systematically evaluate and provide insights into optimizing the operating parameters of a state-of-the-art wastewater treatment plant in the Cambodian beverage industry. By analyzing the system from a chemical engineering perspective, this research aims to move beyond simple compliance testing and develop a deeper understanding of the process kinetics and efficiencies, providing a valuable case study and operational guidance for a rapidly growing industrial sector.

The overall objective of this study is to evaluate and optimize the efficiency of Total Phosphorus and Total Nitrogen removal in the wastewater treatment system of a major beverage production facility. To achieve this, the specific objectives are:

1. To analyze the wastewater treatment process from a chemical engineering perspective, detailing the specific unit operations and reaction mechanisms implemented for Total Phosphorus and Total Nitrogen removal.
2. To evaluate the system's performance by comparing the measured results of Total Phosphorus and Total Nitrogen removal (before and after treatment) with the standards established by the Ministry of Environment (MOE), Cambodia.

3. To identify key operating parameters and suggest potential optimizations to enhance the nutrient removal efficiency based on an analysis of the system's performance and a review of established kinetic and stoichiometric principles.

2. RESEARCH METHOD

2.1. Wastewater Source and Characteristics

Wastewater in the industry is generated from various water sources used for beer and beverage production, and it also includes effluent from the bathrooms and kitchen. Consequently, a large quantity of water is continuously required for blending raw materials—including rice, hops, malt, and maize—as well as for brewing, fermentation, filtration, and packaging operations. Additionally, water itself is the main raw material for beer production.

Currently, the raw wastewater flows into the inflow pit tank at a rate of approximately 4500 m^3/day. Given the high volume of water used in the factory, all wastewater must be treated before being discharged into the environment. Specifically, wastewater from the beer fermentation process is first drained to recover the yeast. Following this, the wastewater is passed through a drum screen to remove solid particles larger than 3 mm in diameter before it proceeds to the Equalization tank. Table 1 details the quality of this raw influent wastewater at Khmer Beverages Co., Ltd. (KHB) before treatment.

Table 1. Influent water quality and waste yeast quality at KHB

Parameter	Unit	Raw wastewater to plant	Waste yeast quality
pH	–	5 – 10	5 – 10
Temperature	°C	< 40	≤ 40
PO_4^{3-}	mg/L	32	1850
$N\text{-}NH_4^+$	mg/L	113	13127

2.2. Process Description and System Design

The wastewater treatment process at Khmer Beverages Co., Ltd. is designed as a multi-stage system to effectively remove pollutants before discharge. The overall process flow is illustrated in Figure 1.

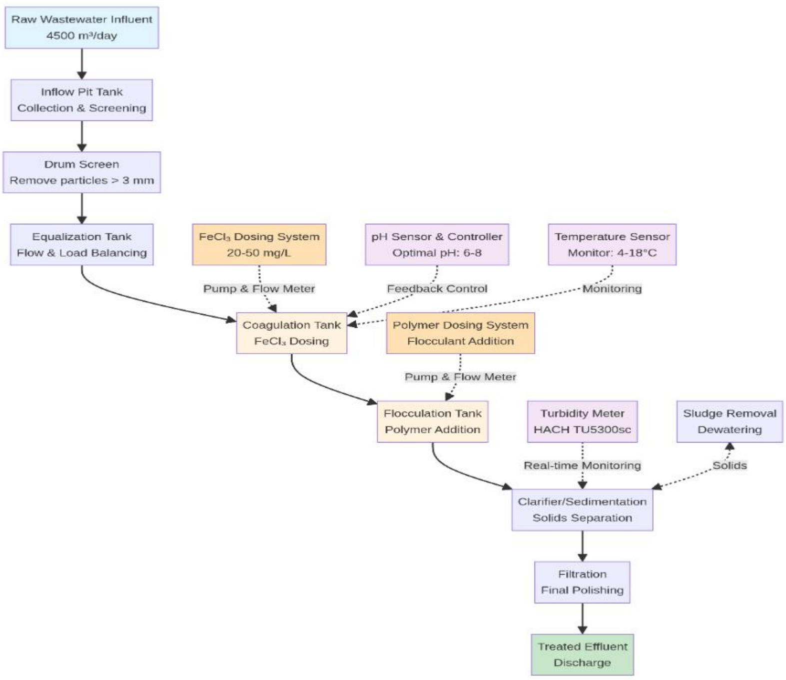

Figure 1. Process Flow Diagram of the Wastewater Treatment System

The process begins with the collection of raw wastewater in an inflow pit tank, where initial screening may occur. The wastewater is then passed through a drum screen to remove larger solid particles. From there, it enters an equalization tank, which serves to buffer variations in flow rate and composition, ensuring a more stable influent for downstream processes. The core of the chemical treatment process occurs in the coagulation and flocculation tanks. Ferric chloride ($FeCl_3$) is introduced in the coagulation tank to destabilize colloidal particles.

Subsequently, a polymer is added in the flocculation tank to promote the aggregation of these particles into larger flocs. These flocs are then separated from the liquid phase in a clarifier or sedimentation tank. The clarified water undergoes a final filtration step before being discharged.

2.3. Rationale for Selected Chemical Engineering Variables

The efficiency of the coagulation-flocculation process is governed by several key chemical engineering variables. This study focuses on the optimization of these parameters to maximize nutrient removal.

- **$FeCl_3$ Concentration**: Ferric chloride is a primary coagulant used for phosphorus removal through precipitation and charge neutralization [4]. The dosage of $FeCl_3$ is a critical parameter; insufficient dosage leads to incomplete coagulation, while excessive dosage can lead to re-stabilization of particles and increased sludge production and operational costs [14]. The optimal dosage typically falls within the range of 20-50 mg/L, but it is highly dependent on the specific wastewater characteristics [15].
- **Polymer (Flocculant)**: Polymers, such as polyacrylamide (PAM), are used as flocculant aids to bridge the micro-flocs formed during coagulation into larger, more robust flocs that settle more easily [16]. The interaction between the coagulant and the polymer is complex and requires careful optimization of the polymer dosage.
- **pH**: The pH of the wastewater is a master variable that influences both the surface charge of the particles to be removed and the speciation of the metal coagulant. For $FeCl_3$, the optimal pH range for coagulation is typically between 6 and 8 [17]. Outside this range, the efficiency of the coagulant decreases significantly. For instance, at low temperatures, the optimal coagulation pH may shift to higher values [18].
- **Temperature**: Temperature affects the kinetics of the coagulation and flocculation processes. Lower temperatures can slow down the reaction rates and increase water viscosity, which hinders floc formation and settling [19]. Understanding the effect of temperature is crucial for maintaining treatment efficiency across different seasons.

2.4. Measurement and Control Devices

To ensure the stability and efficiency of the treatment process, a suite of measuring and control devices is employed. Figure 2 provides a schematic of the control system.

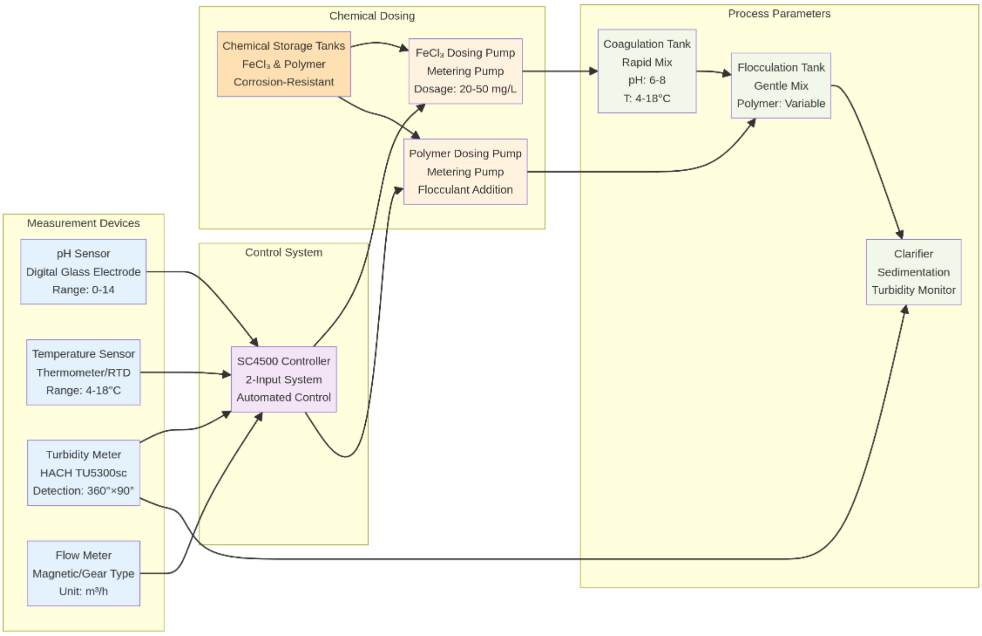

Figure 2. Control System Diagram

The system includes:

- **pH Sensors and Controllers**: Continuous pH monitoring is performed using industrial-grade pH sensors. The data is fed to a controller (e.g., SC4500) which automatically adjusts the dosage of pH-modifying chemicals to maintain the optimal pH range for coagulation.

- **Flow Meters and Controllers**: Flow meters are installed to measure the flow rate of both the wastewater and the chemical dosing streams. This allows for precise, flow-proportional dosing of $FeCl_3$ and polymer, which is essential for consistent performance [20].
- **Turbidity Meters**: Online turbidity meters (e.g., HACH TU5300sc) are used to monitor the clarity of the water after the clarifier. This provides a real-time indication of the treatment efficiency and can be used to make adjustments to the coagulant or flocculant dosage.
- **Temperature Sensors**: Temperature is monitored to account for its effects on process kinetics. This information can be used by operators to make proactive adjustments to the process parameters.

2.5. Analytical Methods

For analysis methods, the research considered on the determination of nitrogen and determination of phosphorus as described below. All units are expressed in SI units.

- **Determination of Nitrogen:** Nitrogen in the wastewater was measured in the laboratory using the distillation method with the Kjeldahl Flex K-360 machine. The final concentration is expressed in mg/L.
- **Determination of Phosphorus:** The determination of total phosphorus in the wastewater was conducted using the Acid Hydrolyzable Digestion method and the HACH spectrophotometer DR/2800 (Method 8180). The final concentration is expressed in mg/L.

Table 2. Discharge requirements for wastewater [21]

List of substances	Unit	Discharge limit
pH	−	5.5 - 9
Temperature	°C	< 45
COD	mg/L	< 100
BOD	mg/L	< 80
N	mg/L	< 5
NH_4^+	mg/L	< 7
PO_4^{3-}	mg/L	< 6
NO_3^-	mg/L	< 20

3. RESULTS AND DISCUSSION

3.1. Phosphorus Revomal

3.1.1. System Performance and Removal Efficiency

The wastewater treatment plant at Khmer Beverages Limited (KHB) employs chemical precipitation for phosphorus removal using ferric chloride ($FeCl_3$) as a coagulant. The average phosphorus removal efficiency observed was approximately 72.8%, with effluent concentrations ranging from 7.1 to 8.1 mg/L. While this represents a significant reduction from the influent concentrations (25-30 mg/L), the system did not consistently meet the Ministry of Environment (MOE) discharge standard of 6 mg/L for phosphate. This performance is moderately effective but falls short of the 80-95% removal efficiencies reported in chemical engineering literature for optimized chemical precipitation systems [22]. The discrepancy suggests that the current operating conditions are suboptimal.

3.1.2. Kinetic Analysis and Removal Rate

To quantify the system's performance from a chemical engineering perspective, the removal rate and reaction efficiency were calculated. The results are summarized in Table 3.

Table 3. Phosphorus Removal Rate and Reaction Efficiency

Day	Influent PO_4^{3-} (mg/L)	Effluent PO_4^{3-} (mg/L)	Removal Rate (mg/L·h)	Reaction Efficiency (% per mg/L $FeCl_3$)
2	27.0	7.10	0.829	1.47
8	30.0	8.00	0.917	1.47
11	25.0	7.23	0.740	1.42
14	30.0	8.10	0.912	1.46
Avg.	28.0	7.61	0.850	1.46

Note: Removal rate assumes a 24-hour residence time in the clarifier. Reaction efficiency is based on a 50 mg/L $FeCl_3$ dosage.

The average removal rate was 0.850 mg/L·h. The reaction efficiency, which normalizes the removal percentage by the coagulant dose, was 1.46% per mg/L of $FeCl_3$. This metric is crucial for evaluating the cost-effectiveness of the chemical treatment. A higher reaction efficiency indicates more effective use of the coagulant.

3.1.3. Optimization of $FeCl_3$ Dosage

Jar test experiments were conducted to determine the optimal $FeCl_3$ dosage. Figure 8 shows the relationship between $FeCl_3$ dosage and phosphorus removal efficiency. The removal efficiency increases sharply with dosage up to 50 mg/L, after which the curve begins to plateau, indicating diminishing returns at higher concentrations. This trend is characteristic of coagulation processes, where an optimal dosage exists that provides the most efficient removal without excessive chemical use and sludge production [15]. The optimal dosage was identified as 50 mg/L (0.05 ml/L), which achieved a removal efficiency of over 90%, meeting the MOE standard.

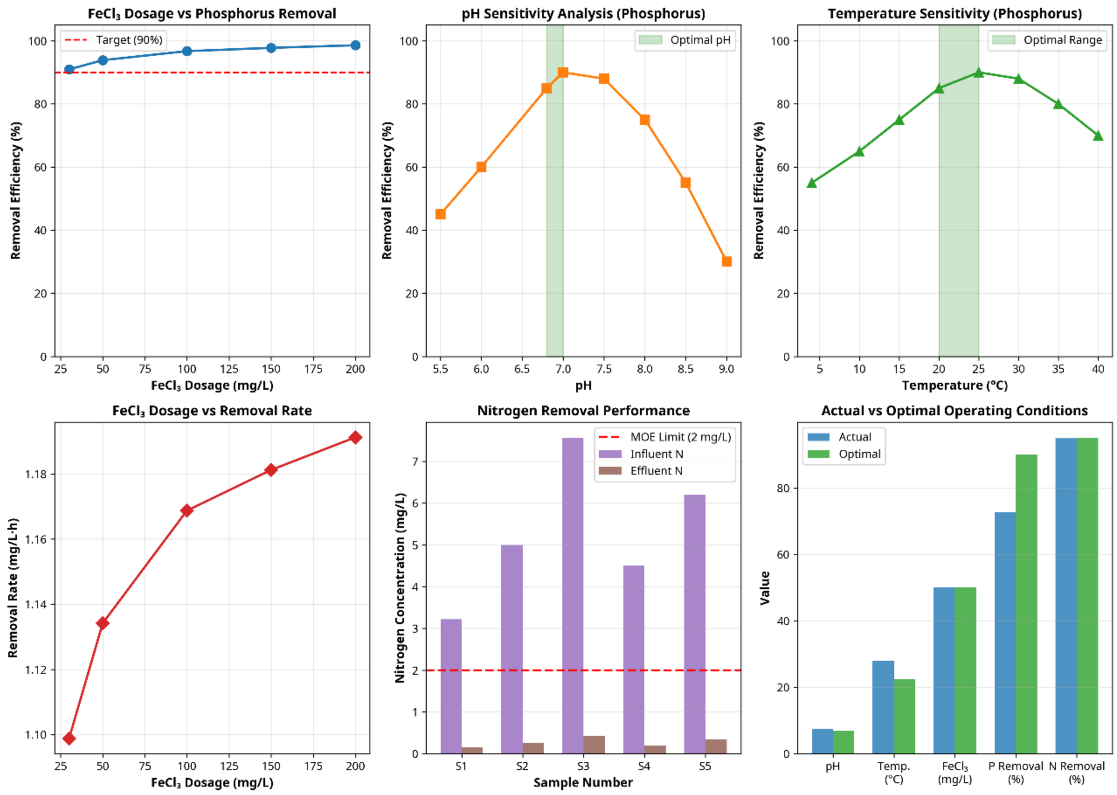

Figure 3. $FeCl_3$ Dosage vs. Phosphorus Removal Efficiency and Sensitivity Analysis

3.1.4. Sensitivity to Process Parameters

The efficiency of phosphorus removal is highly sensitive to changes in pH and temperature, as illustrated in the sensitivity analysis graphs in Figure 8. The optimal pH for phosphate precipitation with $FeCl_3$ is between 6.8 and 7.0, where ferric phosphate ($FePO_4$) exhibits minimum solubility [23]. The observed plant pH of 8.43 on Day 2 is well outside this optimal range, which likely contributed to the reduced removal efficiency. The optimal temperature range is 20-25°C. The plant's operating temperature was not specified, but deviations from this range would negatively impact the precipitation kinetics.

3.2. Nitrogen Removal

3.2.1. System Performance and Removal Efficiency

The biological nitrogen removal process demonstrated high efficiency, with an average removal of 94.9%. Influent nitrogen concentrations ranging from 3.22 to 7.56 mg/L were consistently reduced to below 0.42 mg/L in the effluent, well within the MOE discharge standard of 2 mg/L. This high efficiency is comparable to the 85-95% removal rates reported for well-operated nitrification-denitrification systems [24].

3.2.2. Kinetic Modeling of Nitrification and Denitrification

The high efficiency of the nitrogen removal process can be attributed to the sequential operation of nitrification and denitrification. The kinetics of these biological processes are typically described by the Monod equation, which relates the microbial growth rate to the concentration of the limiting substrate (ammonia or nitrate). The observed performance aligns with the kinetic parameters reported in the literature for similar systems [10].

3.3. Comparison of Operating Conditions and Kinetic Models
3.3.1. Actual vs. Optimal Operating Conditions

A comparison of the actual operating conditions at the KHB plant with optimal conditions from the literature and jar tests reveals key areas for improvement, particularly for phosphorus removal. Table 4 summarizes this comparison.

Table 4. Comparison of Actual and Optimal Operating Conditions

Parameter	Unit	Actual Conditions	Optimal Conditions
pH (Phosphorus Removal)	-	7.5 - 8.43	6.8 - 7.0
Temperature (P Removal)	°C	~28	20 - 25
$FeCl_3$ Dosage	mg/L	43	50
Phosphorus Removal Eff.	%	72.8	>90
Nitrogen Removal Eff.	%	94.9	>95

3.3.2. Applicability of Kinetic Models

The phosphorus removal process can be modeled using either a first-order reaction model or a more complex Langmuir-Hinshelwood (L-H) model. The first-order model provides a simple estimation of the removal rate, while the L-H model can describe the non-linear relationship between coagulant dosage and removal efficiency, accounting for surface saturation effects [25]. The nitrogen removal process is well-described by Monod kinetics, which is the standard model for biological wastewater treatment processes.

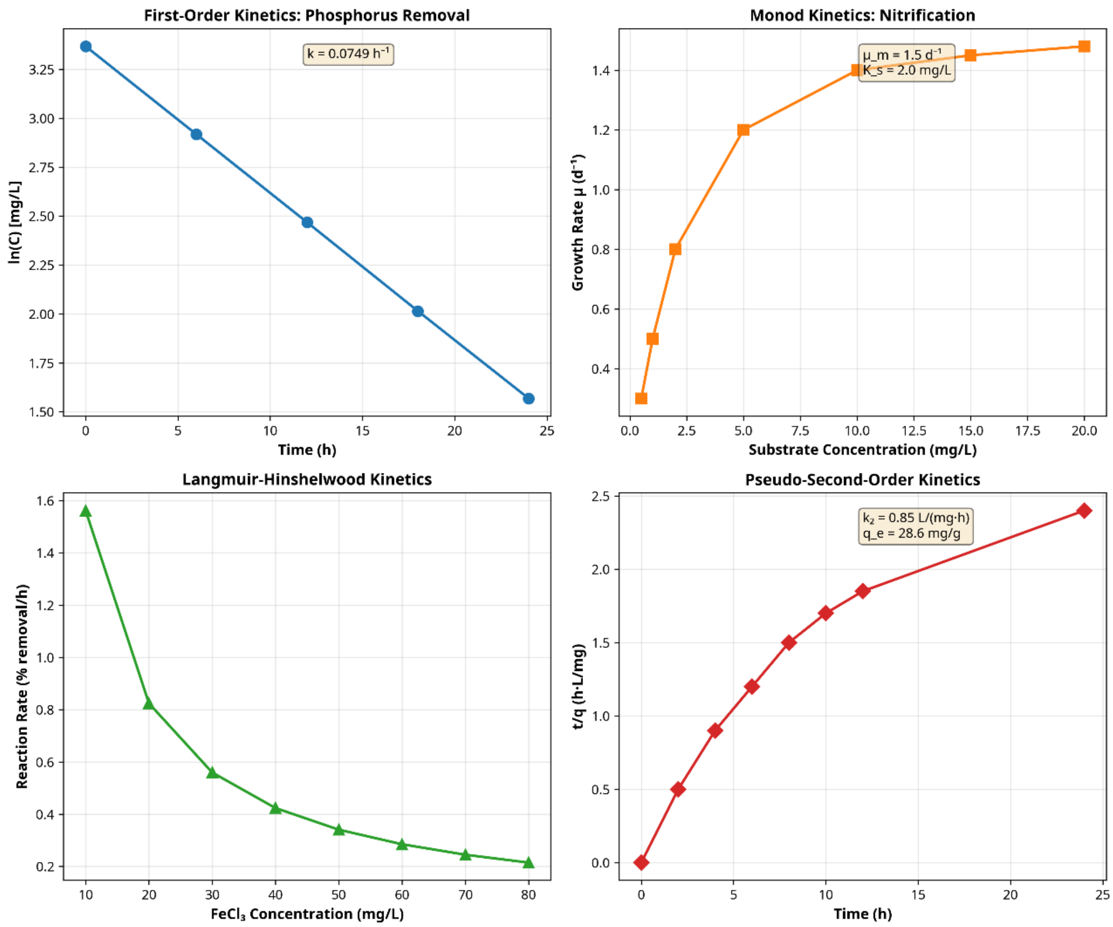

Figure 4. Kinetic Models for Phosphorus and Nitrogen Removal

3.4. Health and Safety Considerations

The coagulation-flocculation process involves the handling of hazardous chemicals, necessitating strict adherence to safety protocols. Ferric chloride ($FeCl_3$) is a corrosive substance that can cause severe skin and eye burns. Inhalation of $FeCl_3$ aerosols can lead to respiratory irritation. Therefore, appropriate personal protective equipment (PPE), including chemical-resistant gloves, goggles, and respiratory protection, must be worn when handling this chemical. The storage of $FeCl_3$ requires corrosion-resistant tanks, and spill containment measures should be in place. The use of polymers also presents a dust inhalation hazard, requiring proper ventilation and handling procedures.

4. CONCLUSION

Phosphorus removal in both the aeration tank and clarifier tank produced clear effluent water suitable for discharge to the environment. Nitrogen was removed in the anoxic tank and aeration tank through bacterial activity in the wastewater. Under optimal conditions, nitrogen removal efficiency reached above 90%. The optimal conditions for nitrification were pH 7.5–8.6 and temperature 20–25°C with 1 mg/L of dissolved oxygen, while denitrification required pH 7–8 and temperature 25–27°C.

Phosphorus in the clarifier tank was eliminated using 0.043 ml of ferric chloride ($FeCl_3$) and 8 ml of cationic polymer 1040 powder. However, phosphorus concentrations could not be consistently reduced to meet specifications, with some values exceeding regulatory limits. In contrast, using 0.05 ml of $FeCl_3$ combined with 5 ml of polymer powder provided the best results under optimal conditions of pH 6.8–7.0 and temperature 20–25°C. The polymer plays a critical role in facilitating the formation of $FePO_4$ precipitates.

In future studies, the amount of polymer used in the clarifier tank for phosphorus removal should be carefully evaluated, as the polymer produces a dense mass of solids during the reaction, promoting rapid flocculation and settling of sl875/79//93898*udge. Moreover, the mixing speed of ferric chloride in the clarifier basin should be investigated to determine the optimal conditions for $FeCl_3$ binding with phosphorus in wastewater.

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