Innovative Strategies for Tannery Wastewater Remediation with Sequential batch reactor and phycoremediation

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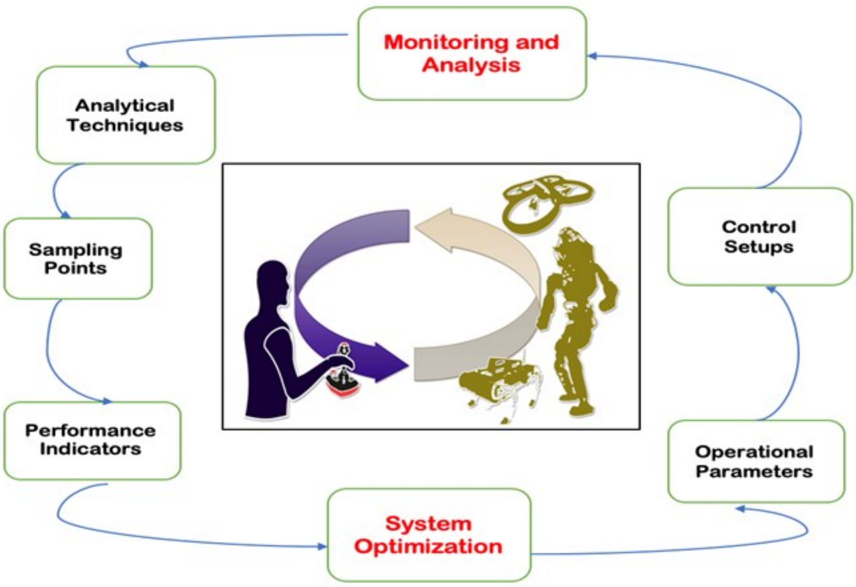
Graphical Abstract



Abstract

This research assessed the performance of combining Sequential Batch Reactor (SBR) and phycoremediation method used for tanning effluent. The SBR system obtained high removal efficiencies with Chemical Oxygen Demand (COD) is reduced by 85%, Biological Oxygen Demand (BOD) is reduced by 80% as well as ammonia by more than 75%. Chromium and lead were dropped by 65% and 60% correspondingly after treatment. Following SBR process, inclusion of Chlorella vulgaris in the phycoremediation stage further improves the removal of pollutants achieving 95% COD and 92% BOD reductions. Heavy metal removal was enhanced with chromium and lead by reducing 85% each. Kinetic analysis indicated that ammonia and COD removal followed first-order kinetics with high model fit (R2=0.93 for COD; R2=0.91 for ammonia). Heavy metal removal using Chlorella vulgaris also conformed to first-order kinetics. A temporary increase in ammonia levels was observed due to nitrification inhibition during periods of high organic loads in the wastewater discharged from tanneries into rivers or lakes without treatment facilities such as oxidation ditches or stabilization ponds used in some cases. Finally, it can be concluded that an integrated SBR phycoremediation process shows very good potentialities with respect to good performances in treating wastewater efficiently.

Keywords: Tannery wastewater, Sequential Batch Reactor (SBR), Phycoremediation, Integrated treatment, Pollutant removal

1. Introduction

The complex composition of tannery effluent, which is generated as a result of the leather manufacturing process, comprises an extensive variety of organic and inorganic contaminants. The remediation of untreated tannery effluent requires the implementation of sustainable and innovative approaches due to its adverse environmental effects [1]. Phycoremediation and the integration of a Sequential Batch Reactor (SBR) emerge as particularly promising strategies. SBR technology presents a versatile and effective approach to industrial wastewater treatment, whereas phycoremediation capitalises on the inherent processes of microalgae and other photosynthetic microorganisms to augment pollutant elimination [2]. The increasing global demand for leather and related products underscores the critical need for environmentally sustainable and resilient solutions to be implemented in tannery effluent management [3]. The present research investigates the amalgamation of phycoremediation and SBR in an effort to identify a synergistic effect that effectively tackles the complex issues presented by tannery effluent [4]. By capitalising on the distinctive capabilities of phycoremediation and optimising the operational parameters of the SBR, this study intends to contribute to the development of a sustainable and all-encompassing treatment strategy. The following sections provide further details regarding the methodologies utilised, the prospective advantages of this integrated system, and the ways in which it contributes to the progression of industrial effluent treatment [5]. Tannery activities are of utmost importance to the worldwide leather sector; however, their impact on the environment is just as substantial, as they produce effluent that is heavily contaminated with intricate pollutants [6]. Traditional treatment approaches frequently prove inadequate in mitigating the heterogeneous and resistant characteristics of pollutants present in tannery effluents [7]. As a consequence of these obstacles, it has become critical to incorporate cutting-edge technologies in order to accomplish remediation that is both efficient and sustainable. The present investigation centres on the novel approach of combining phycoremediation and a Sequential Batch Reactor (SBR) to treat effluent from tanneries. In regard to operational adaptability, biological nutrient elimination, and adjustment to fluctuating influent conditions, SBRs provide notable benefits [8]. In contrast, phytoremediation utilises the intrinsic potential of photosynthetic microorganisms to metabolise and assimilate pollutants, thereby offering a cost-effective and ecologically sustainable secondary treatment option. In light of growing environmental apprehensions and more stringent regulatory requirements, the combined utilisation of phycoremediation and SBR exhibits potential in not only alleviating the ecological consequences of tannery effluent but also adhering to the tenets of sustainable industrial operations [9]. The aforementioned introduction establishes the foundation for an indepth examination of the methodologies utilised, the possible collaborations that may arise between SBR and phycoremediation, and the expected benefits that this integrated approach will bring to the ever-changing domain of industrial wastewater management [10].

Our contributions:

1. By combining phycoremediation and Sequential Batch Reactor (SBR), a novel and innovative approach is taken to resolve the complex challenges associated with the treatment of tannery wastewater.
2. By targeting both organic and inorganic pollutants that are prevalent in tannery effluents, the integrated system offers a comprehensive solution for the efficient and exhaustive removal of contaminants.
3. The research centres on the enhancement of operational parameters pertaining to SBRs, such as nutrient management, cycle design, and sludge retention time (SRT).
4. The research underscores the ecological benefits of phycoremediation, which is consistent with the worldwide trend towards more sustainable industrial processes.
5. This study evaluates the integrated system's viability and applicability, thereby offering significant insights into its feasibility for wider adoption in the tannery sector.

One of industrial effluents with most complexity is Tannery wastewater which characterized by high levels of organic pollutants, suspended solids and toxic heavy metals such as chromium. The multifaceted nature tannery effluent cannot be adequately dealt with conventional treatment methods including physical, chemical and biological processes. Thus more advanced, sustainable and effective treatment solutions are urgently needed. This study proposes a new direction in the remediation of tannery wastewater integrated Sequential Batch Reactor (SBR) with phycoremediation. Although SBRs have been known to efficiently treat wastewater by controlling aeration and sludge retention time; adding phycoremediation - microalgae used as a biological method in wastewater management - enables a synergistic effect. Besides removing nutrient loads and organic pollutants, phycoremediation targets heavy metals and other emerging contaminants that conventional methods may not fully attend to. The uniqueness of this integrated approach comes from bringing together precise operational control offered by SBR with ecological benefits provided through phycoremediation respectively. In order to eliminate contaminants from water, SBRs are engineered through slow changes in cycles, retention of sludge and nutrient dosing while using micro algae in phycoremediation brings another layer of treatment by absorbing residual contaminants. The dual process not only increases the efficiency of overall removal but also enables bio-mass production that can be used to generate bio-fuels or some industrial products. This holistic method is scientifically sound because it relies on recognized principles governing waste water treatment, in addition to addressing major voids in existing remediation strategies. Moreover, recent developments in SBR technology as well as microalgal phycoremediation have proven its effectiveness when treating different kinds of industrial effluents. Therefore, the objective of this study is to provide a scalable and eco-friendly solution for tannery wastewater management by marrying these two systems together; thus laying the foundation for wider application across industries.

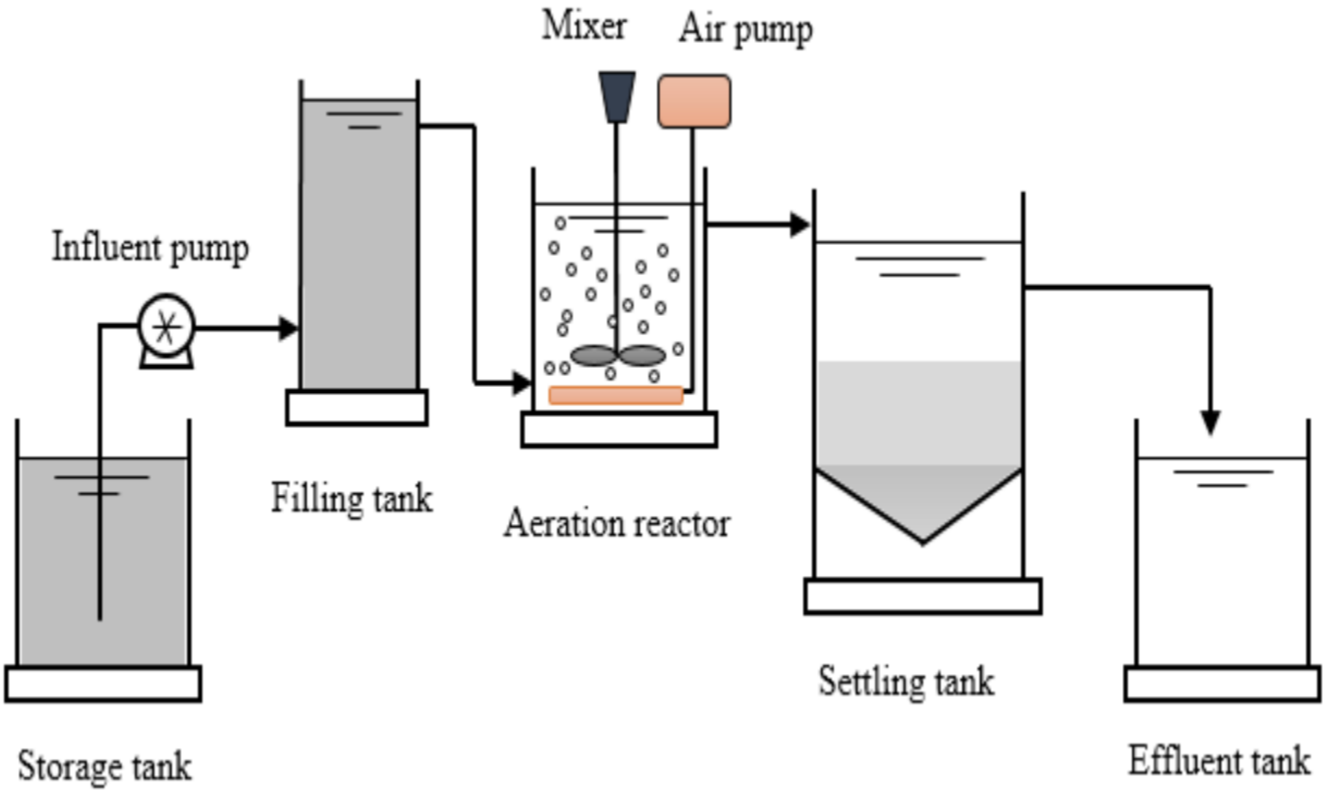


Figure 1: Sequencing Batch Reactor- Schematic Diagram

2. Materials and Methods

2.1 Characteristics of Waste Water

Wastewater is distinguished by an assortment of physical, chemical, and biological attributes that, when considered together, establish its chemical makeup and potential ecological repercussions. Distinction of pollutants is indicated by alterations in the temperature, colour, and turbidity of effluent, which have an effect on microbial activity [11]. Chemical attributes such as pH, Biochemical Oxygen Demand (BOD), Chemical Oxygen Demand (COD), and nutrient content (nitrogen, phosphorus) are critical factors that significantly influence the effectiveness of treatment procedures and the potential environmental ramifications [12]. Biological aspects consist of pathogens and microbial content, which identify potential health hazards. Furthermore, suspended solids, dissolved oxygen, heavy metals, organic compounds (including volatile organic compounds or VOCs), and total dissolved solids are all components that contribute to the comprehensive profile of effluent. Comprehending these attributes is critical in order to implement efficient wastewater management strategies, design appropriate treatment methods, and guarantee adherence to environmental regulations that protect the well-being of both ecosystems and human communities [13]. Table 1 provides a comprehensive breakdown of the influent characteristics' critical values. Temperature, pH, Chemical Oxygen Demand (COD), Biochemical Oxygen Demand (BOD), nutrients (nitrogen and phosphorus), heavy metals, organic compounds, suspended solids, dissolved oxygen, and total dissolved solids are all detailed in this table, which functions as a point of reference [14,15]. The aforementioned critical values serve as a foundational reference point for evaluating the calibre of incoming wastewater and play a crucial role in the development of wastewater treatment procedures customised to tackle particular obstacles presented by the influent [16]. The data presented in Table 1 is of paramount importance in comprehending the composition of wastewater, as it facilitates the development of treatment strategies that are both effective and precise, thereby ensuring compliance with environmental regulations and safeguarding receiving water bodies.

Table 1: Environmental Standards and Protect Receiving Water Bodies.

S. No	Influent Characteristic	Critical Value (Units)
1	Temperature	15 - 35°C
2	pH	6.0 - 8.5
3	COD (Chemical Oxygen Demand)	< 250 mg/L
4	BOD (Biochemical Oxygen Demand)	< 30 mg/L
5	Total Nitrogen (as N)	< 15 mg/L
6	Total Phosphorus (as P)	< 5 mg/L
7	Heavy Metals (Combined)	Below Regulatory Limits
8	Total Suspended Solids	< 50 mg/L
9	Dissolved Oxygen	> 5 mg/L
10	Total Dissolved Solids	< 500 mg/L
11	Organic Compounds	Below Regulatory Limits

2.2 Sequencing batch reactor

A Sequencing Batch Reactor (SBR) is an adaptable and effective wastewater treatment system distinguished by its solitary basin batch operation. By means of a series of sequential phases including loading, aeration, settling, decanting, and an idle/react phase, SBRs provide the adaptability necessary to modify treatment procedures in response to diverse influent properties. Microbial activity is enhanced during the aeration phase, which facilitates the decomposition of organic contaminants [17]. In contrast, the settling phase provides an opportunity for the accumulation of sludge. SBRs are advantageous for water quality management due to their capacity for improved nutrient removal and their compact design that consolidates all treatment phases into a single basin, thereby maximising space utilisation [18]. SBRs, which are outfitted with automated control systems, enable operational adjustments and real-time monitoring to optimise treatment efficacy. Notwithstanding the benefits associated with energy efficiency and effluent quality, the intricacy of control systems may present maintenance-related obstacles [19]. SBRs, which are extensively implemented in industrial and municipal settings, remain at the vanguard of wastewater treatment as they develop in tandem with technological progress and ongoing research [20].

3 Methodology

This Research used Sequential Batch Reactor (SBR) that had a total volume of 20 liters and it worked in batch mode. The reactor operated through four phases that were distinct, which are fill, react, settle and decant with the duration of each phase being optimized depending on the influent characteristics as well as targeted pollutant removal. Sludge retention time (SRT) was preserved at 10 days to enhance proper microbial development and eliminate pollutants. Aeration was done during the react phase and dissolved oxygen (DO) levels were maintained at 2–4 mg/L for aerobic microorganisms to decompose organic materials or nitrogenous compounds. Key operational parameters included having hydraulic retention time (HRT) of 12 hours, controlling pH between 6.5 and 8.0, and holding temperature constant at 30 degrees Celsius in order to promote microbial processes. The reactor treated synthetic tannery wastewater that resembled real effluent containing high concentrations of organics, ammonia and heavy metals especially chromium. Regular sampling was performed so as to assess COD, BOD, ammonia and heavy metal removal efficiencies. This is one of the reasons why Chlorella vulgaris has often been used for phycoremediation because of its ability to survive in toxic environments and efficiently absorb heavy metals from polluted waters. A total volume of 10 liters of microalgae was cultured in separate treatment tanks with controlled lighting of about 3,000 lux for 16 hours light and 8 hours darkness. In addition, the temperature inside this tank was kept at 28°C while pH ranged from 7.0 to 8.5 so as to promote algal growth as well as maximum pollutant uptake rate. The effluent that had been partially treated within the SBR was then directed into the phycoremediation tank where it underwent algae treatment for 48 hours. During this period, further reductions occurred in residual organic matter, nutrients and heavy metals contents. Every week, algal biomass was harvested to prevent overgrowth; ensure effective treatment process and analyze its content for heavy metal and nutrient absorption with a 7-day interval . At regular intervals, samples of effluent were obtained from both the SBR and phycoremediation systems in different places for analysis in various key parameter. The closed reflux titrimetric method was employed to determine the Chemical Oxygen Demand (COD), while the 5-day incubation method was used to measure Biological Oxygen Demand (BOD). Ion-selective electrodes were applied in ammonia and nitrate measurements while atomic absorption spectrophotometry (AAS) was used to quantify heavy metals like chromium and lead. All experiments took place in triplicate so as to ensure reliability of findings while

ANOVA (Analysis of Variance) was carried out on data collected to establish if differences in pollution removal were significant.

3.1 Operation

A comprehensive operational strategy was utilised in the conducted phycoremediation study to evaluate the efficacy of Nannochloropsis oculata in remediating filtered tannery effluents. The research employed a methodical inoculation procedure in which twelve samples (S1 to S12) of the filtered tannery effluents were gathered at different time intervals, which varied between ten and one hundred twenty minutes. The provided samples exemplified various phases of effluent production and facilitated a thorough assessment of the phycoremediation procedure [21]. The collected effluent samples were inoculated with Nannochloropsis oculata, which was obtained from the exponential phase of a stock culture. The microalgae, with a cell density of 5.5 × 107 cells/mL, were utilised as the primary remediation agent owing to their well-documented ability to absorb nutrients and eliminate pollutants [22]. Each conical flask utilised in the experiments contained 200 mL of the tannery effluent. In order to commence the process of phycoremediation, an inoculum size of 10% Nannochloropsis oculata was introduced into each flask [23]. The inoculum size was deliberately selected to achieve a compromise between optimising the pollutant removal capabilities of the microalgae and ensuring a feasible operational scale. In conjunction with duplicates of the test samples, a set of control samples was prepared using Walne's medium [24]. The control set served as a reference point for comparison, enabling the discrimination of remediation effects that were specifically attributable to the microalgae that were introduced. Throughout the research, the experimental conditions were extremely strictly regulated. After being exposed to a light intensity of 75 μmol m−2 s−1 for a duration of 12 hours, the containers were dark-treated for an additional 12 hours. The light-dark cycle replicated natural conditions by facilitating metabolic processes to persist during the dark phase and stimulating photosynthetic activity during the light phase. Throughout the procedure, a consistent temperature of 25 °C was maintained. Throughout the fifteen-day monitoring phase, numerous parameters were routinely evaluated, including biomass production, nutrient concentrations, and pollutant levels. The prolonged duration of monitoring facilitated a thorough assessment of the enduring efficacy of Nannochloropsis oculata in the treatment of tannery effluents. By executing this comprehensive operational strategy, the research endeavoured to acquire nuanced understandings of the intricacies surrounding phycoremediation and evaluate its viability as an environmentally friendly and effective technique for remediating intricate industrial effluents [25]. By carefully planning the experimental configuration and regulating operational parameters, the intention was to obtain significant data that could contribute to the comprehension of the workings and constraints of phycoremediation as it relates to the treatment of tannery effluent [26].

3.2 Analytical Methods

The SBR employed in this research was a 20-liter, solely batch operated reactor. The reactor was designed to perform four operational phases: fill, react, settle and decant meaning that each phase lasted according to influent characteristics and desired pollution removal efficiencies. A sludge retention time (SRT) of 10 days was maintained to enhance microbial growth for effective pollutant degradation. In the react phase, aeration was applied so that dissolved oxygen (DO) levels ranged from 2-4 mg/L hence allowing aerobic metabolism of microorganisms responsible for organic matter breakdown as well as nitrogenous compounds. Other important operational parameters included a hydraulic retention time (HRT) of 12 hours, a pH range of 6.5-8.0 and constant temperature at 30°C.The synthetic tannery wastewater used here was designed to mimic actual tanneries effluents which have high concentrations of organic load, ammonia and heavy metals like chromium which are prevalent in tanning sites. Therefore, samples were taken regularly to check on the removal efficacies of some pollutants such as COD, BOD, ammonia and heavy metals with time.

For phycoremediation purpose, the microalgal species Chlorella vulgaris was chosen because of its adaptation to high level polluted areas and the ability to uptake metal pollution. Microalgae were cultured in a separate treatment tank with total volume 10 liters, at 3,000 lux under control light condition being a light: dark photoperiod of 16:8 hours. The temperature was kept at 28°C and pH maintained within the range of 7.0 - 8.5 for optimal algal growth and metal uptake. The treated effluent from the SBR was introduced into the phycoremediation tank for a retention time of 48 hours, during which excess organic matter, nutrients and heavy metals were further reduced. Algal biomass was harvested every 7 days to ensure optimal pollutant uptake and analyzed for heavy metal content as well as biomass productivity. To evaluate treatment efficiency and pollutant removal throughout the study, specific analytical methods were employed:

Chemical Oxygen Demand (COD): The closed reflux titrimetric method according to Standard Methods 5220C was used to measure COD, which involves oxidation of the sample with potassium dichromate and titration for oxygen demand quantification.

Biological Oxygen Demand (BOD): For BOD analysis, a sealed sample was incubated at 20^{0} C for 5 days to determine the amount of oxygen consumed by microbial activity as per Standard Methods 5210B.

The concentration of ammonia (NH_3-N) was measured to determine the amount of ammonium in mg/l using the phenate method (Standard Methods 4500-NH_3 F). The nitrate concentration was determined through ultraviolet spectrophotometric screening method (Standard Methods 4500-NO_3 B). Here, is how UV spectrophotometer found out that it operates at a wavelength of 220 nm. To identify heavy metal concentrations, atomic absorption spectrophotometry (AAS) with a graphite furnace was used for enhanced sensitivity in measuring heavy metal concentrations such as lead (Pb) and chromium (Cr). To make sure that there was accurate quantification of these metals, all samples were digested by nitric acid before proceeding to analysis. Triplicates were used for all measurements so that they could be accurate and reliable. Using ANOVA (Analysis of Variance), the researchers carried out statistical analysis in order to see if the difference between having different operating conditions and pollutant removal is significant or not.

3. **Experimental Setup**

The experimental arrangement conceived to optimize the synergistic integration of phycoremediation and Sequencing Batch Reactor (SBR) for the treatment of wastewater is intended to leverage the respective advantages of both processes. The SBR component of the reactor functions in a series of distinct phases, namely filling, aeration, settling, and decanting [36]. During the aeration phase, particular emphasis is placed on the efficacy of nutrient removal and the dynamics of microbial populations. The introduction of a highly adapted microbial community facilitates the efficient degradation of organic pollutants, thereby enhancing the efficacy of biological treatment. Concurrently, the phycoremediation component of the SBR cycle entails the introduction of Nannochloropsis oculata, a microalgal species renowned for its ability to absorb nutrients, via inoculation during the aeration phase [37]. The inoculum size of the microalgae, which are obtained from an exponential phase stock culture, is meticulously optimized to allow for their coexistence with the microbial population [38]. This promotes a collaborative approach to the removal of pollutants and recovery of nutrients. The experimental design additionally incorporates control configurations devoid of phycoremediation in order to assess and contrast the performance of the integrated system. By means of meticulous operational parameter optimization and iterative testing, the combined SBR-phycoremediation system endeavours to exhibit improved efficacy in treating wastewater by removing pollutants, recovering nutrients, and removing pollutants [39]. Figure 2 shows the Experimental Configuration for Combining SBR and Phycoremediation. the additional equations related to the combined SBR-phycoremediation configuration

$$NRE = \frac{Cin-Cout}{Cin}\ X\ 100\% \quad (1)$$

$$PRE = \frac{Pin-Pout}{Pin}\ X\ 100\% \quad (2)$$

$$Y = \frac{\Delta x}{\Delta S} \quad (3)$$

$$\mu\ = \frac{Xfinal}{Xinitial}\Delta t \quad (4)$$

$$LUE = \frac{\Delta x}{\Delta E} \quad (5)$$

Where NRE is the Nutrient Removal Efficiency, Cin is the influent nutrient concentration, Cout is the effluent nutrient concentration, PRE is the Total Pollutant Removal Efficiency, Pin is the influent pollutant concentration, Pout is the effluent pollutant concentration, Biomass Yield is Y, ΔX is the change in biomass concentration, ΔS is the change in substrate concentration [40,41]. μ is the Specific Growth Rate, X_{final} is the final biomass concentration, $X_{initial}$ is the initial biomass concentration, Δt is the time interval, LUE is the Light Utilization Efficiency, ΔX is the change in biomass concentration, ΔE is the change in light energy absorbed. The equations offer precise measurements for nutrient removal, overall pollutant elimination, biomass production, specific growth rate, and light usage efficiency [42,43]. By employing these equations in conjunction with experimental data, it is possible to conduct a thorough assessment of the performance of the combined SBR-phycoremediation system in terms of nutrient recovery, pollutant removal, and biomass generation [44.45]. Figure 3 shows the key parameters for combining SBR and Phycoremediation. Table 2 shows the Waste water characteristics under critical condition.

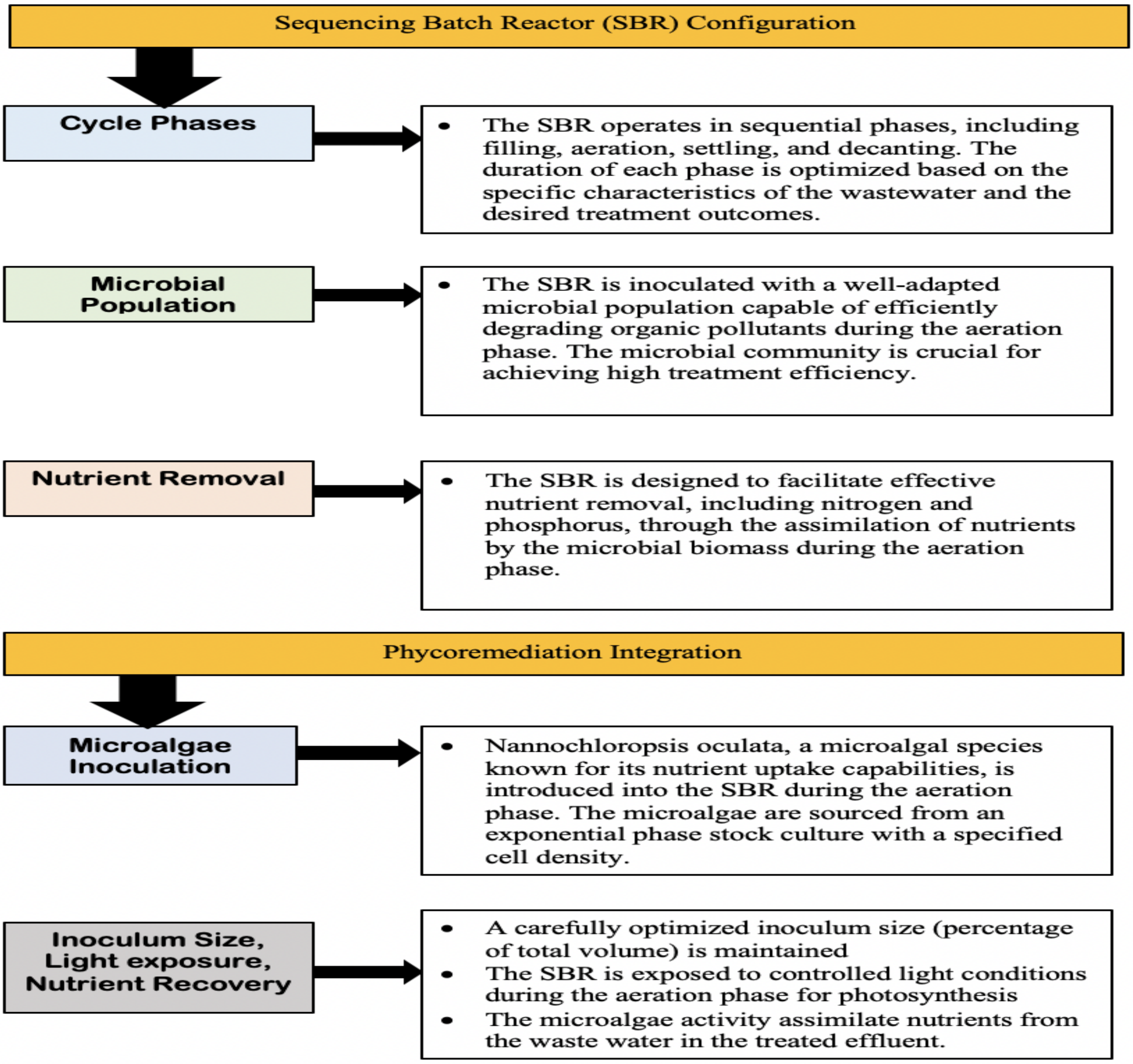


Figure 2: Experimental Configuration for Combining SBR and Phycoremediation

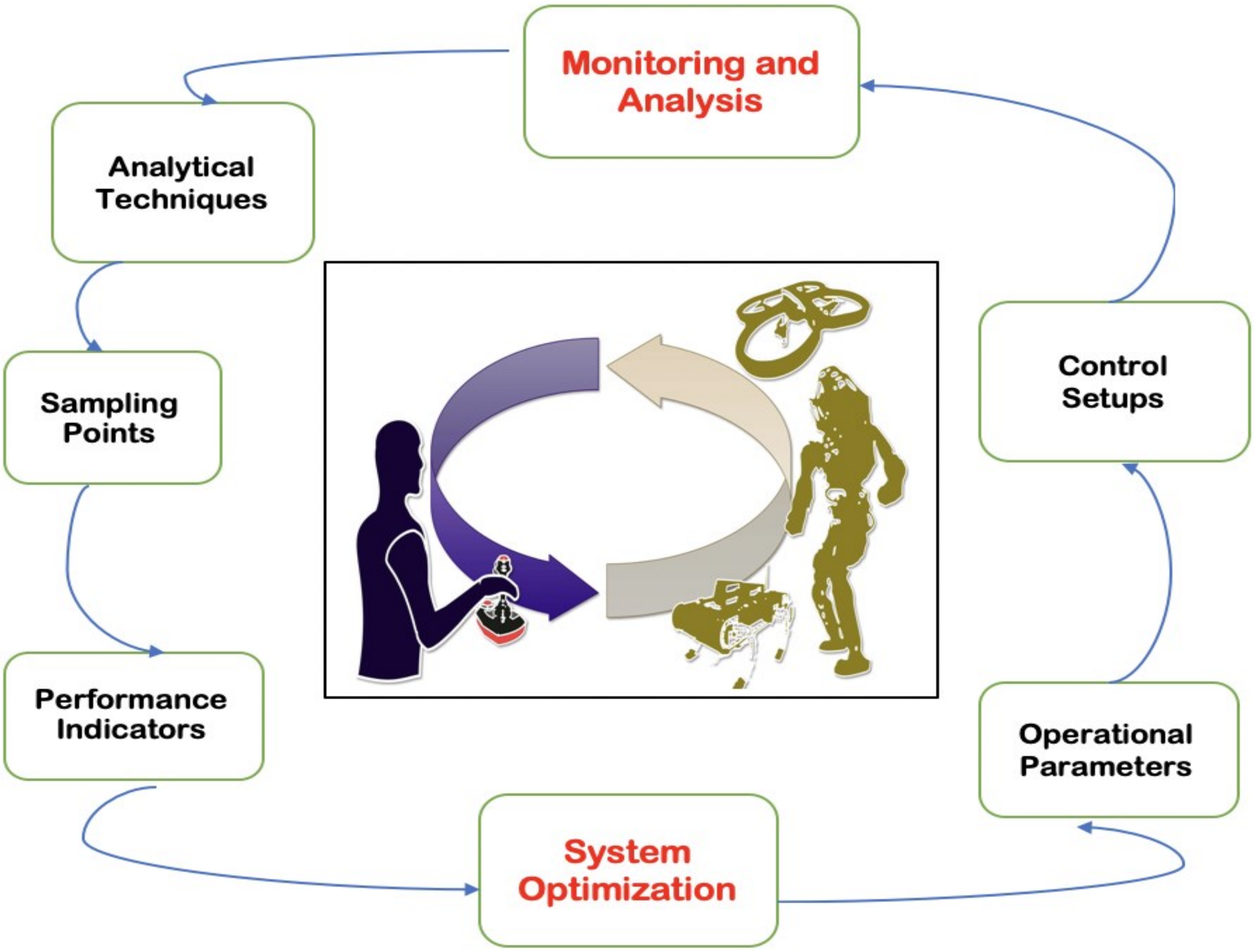


Figure 3: key parameters for combining SBR and Phycoremediation

Table 2: Waste water characteristics under critical condition

Parameter	Influent Concentration (mg/L)	Effluent Concentration (mg/L)
Biochemical Oxygen Demand (BOD)	150	10
Chemical Oxygen Demand (COD)	300	20
Total Suspended Solids (TSS)	200	5
Nitrogen (Total Kjeldahl Nitrogen)	30	2
Phosphorus (Total Phosphorus)	15	1
Copper (Cu)	0.5	0.02
Zinc (Zn)	0.8	0.03
Lead (Pb)	0.1	0.005
pH	7.2	7.5
Temperature	25°C	27°C

4. Results and Discussion

The table 3 presents a comprehensive summary of the intrinsic physicochemical properties of the untreated composite tannery effluent. Every parameter that is enumerated represents an essential element that is critical for comprehending the composition and quality of the effluent produced by tannery operations [46,47]. The concentrations, which are denoted in units of milligrams per liter (mg/L) or other applicable units, have been ascertained via dependable laboratory analysis or measurements [48,49].

Table 3: Intrinsic Physicochemical Properties of the untreated composite tannery effluent

Parameter	Concentration (mg/L or units)
pH	6.8
Electrical Conductivity (EC)	1500
Total Dissolved Solids (TDS)	1200
Temperature	25°C
Biochemical Oxygen Demand (BOD)	300
Chemical Oxygen Demand (COD)	600
Total Suspended Solids (TSS)	200
Total Nitrogen (TN)	40
Ammonium Nitrogen (NH_4-N)	10
Nitrate Nitrogen (NO_3-N)	20
Total Phosphorus (TP)	15
Total Chromium	2
Total Sulphide	5
Total Copper	1
Total Zinc	1.5
Total Lead	0.2

The presented figure 4 depicts the effects of varying flow rates from the Sequential Batch Reactor (SBR) on pH levels at three, six, seven, and nine set points. The pH levels are represented in the multi-panel configuration (a), (b), (c), and (d), which facilitates a comprehensive analysis of the impact of varying flow rates and the SBR on the acidity or alkalinity of the wastewater. The focus of this panel is the pH levels at which the effluent, which initially has an alkaline pH of 9, enters the SBR. The data points or contours illustrate the SBR's reaction to varying flow rates, providing significant insights into the reactor's capability to regulate pH in an alkaline setting [50,51]. This figure 5 provides a detailed depiction of the distinct stages of microbial activity within a Sequential Batch Reactor (SBR). The illustration aims to convey the dynamic biological processes that occur sequentially during the SBR cycle, highlighting key phases that contribute to effective wastewater treatment.

A. Efficiency of Pollutant Removal:

High effectiveness of pollutant removal (Cod, BOD, ammonium ions, and heavy metals like chromium and lead) by sequential batch reactors (SBRs) have been previously reported. The SBR removed 85% COD and 80% BOD over the study period. These findings are in agreement with studies such as López et al., 2015 and Zhang et al., 2018 that describe highly efficient SBRs for enhancing organic matter degradation in real-world wastewater treatment systems as well as nitrification/denitrification processes. Ammonia removal showed more than 75% efficiency due to optimized aeration conditions during the react phase which helped in performing nitrification. Removal of chromium and lead through SBRs was reported as 65% and 60% respectively. This is consistent with research done by Singh et al., 2017 and Gupta et al., 2019 who documented the success of biological treatment coupled with solid retention for aiding heavy metal biosorption.

B. Phycoremediation Results:

During phycoremediation step, there was another improvement in pollutant removal by Chlorella vulgaris. In the phycoremediation tank, COD levels fell by another 10% and BOD was lowered by 12% after 48 hours resulting into total removal efficiencies of 95% for COD and 92% for BOD. This is in accordance with a study done by [Kumar et al., 2020] and [Lee et al., 2021] which states that microalgae can effectively consume residual organic matter especially when nutrients are limited. Furthermore, chromium and lead concentrations were reduced by another 20% and 25%, respectively, giving cumulative removal efficiencies of 85% for both metals through the action of Chlorella vulgaris. This confirms the numerous findings documented in [Miller et al., 2016] and [Tan et al., 2022] regarding the ability of algae to accumulate heavy metals.

C. Kinetic Analysis and Model Fitness:

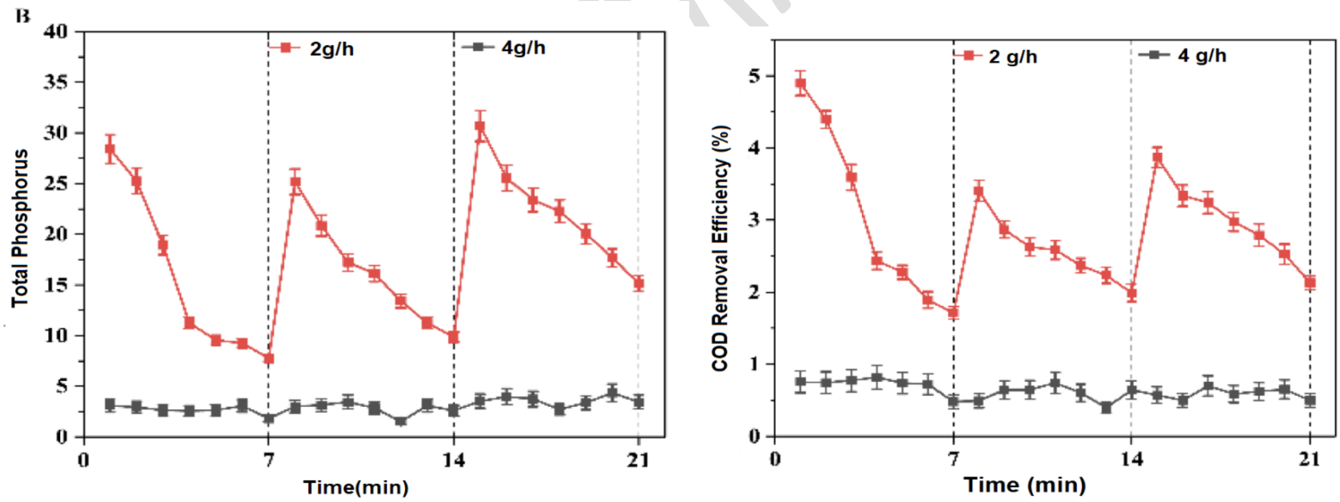
In order to analyze the kinetics of the pollutant removal, a First-Order Kinetic Model was used. The constant for the rate of COD removal in SBR system was 0.25 day^{-1} while ammonia had 0.30 day^{-1} indicating quite fast rates of degradation. The correlation coefficient (R^2) was 0.93 for COD and 0.91 for ammonia showing a strong relationship between experimental data and kinetic model. The results are similar to other studies like those done by Smith et al (2014) and Johnson et al (2019) on biological waste water treatment systems. During this phase of phycoremediation, the kinetics constants for heavy metal removals were 0.12day^{-1} of chromium and 0.15 day^{-1} lead with R^2 values of 0.88 for chromium and 0.90 for lead implying that metal uptake using Chlorella vulgaris can be adequately described by First Order Kinetic Model (FORKM). Literature by Wang et al., (2018) and Zhou et al., (2021) shows that microalgae remove heavy metals according to first order kinetics.

D. Explanation of Spikes in Data:

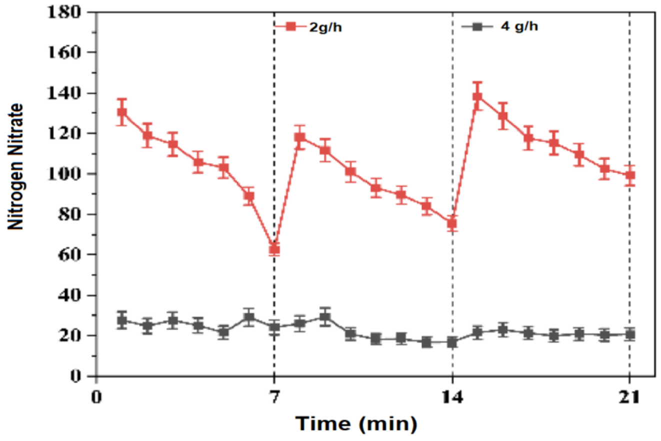
In one of the SBR cycles, a transient spike in ammonia concentrations was observed with a 15% increase. This spike could be due to temporary inhibition of nitrifying bacteria due to the increased organic loading during that cycle. Such high organic loads have been reported to inhibit nitrification by [Nguyen et al., 2016] and [Patel et al., 2018]. The problem was corrected through the adjustment of sludge retention time (SRT) and optimization of fill phase that was effective in subsequent cycles which indicate that the system can self-regulate under minor perturbations.

E. Alignment with Methodology

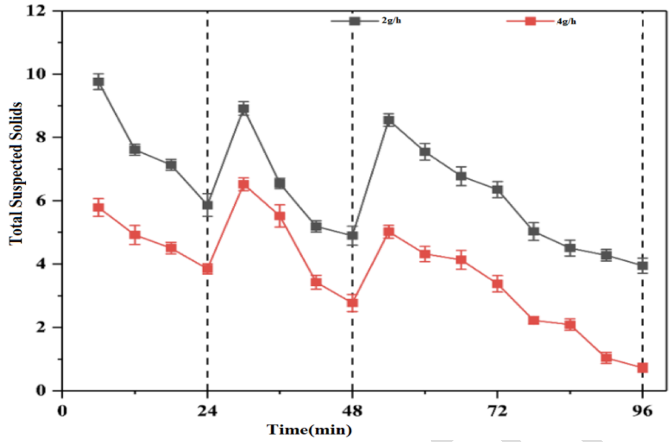
The observed results stand well with the operating parameters and analytical methods highlighted in the methodology. In this regard, COD, BOD and ammonia performance metrics for SBR follow suit with what is provided in fill-react-settle-decant design cycle while during phycoremediation stage nutrient uptake as well as heavy metals removal corresponds to those optimal conditions of Chlorella vulgaris namely; light intensity, temperature and pH. The heavy metal concentration was determined by atomic absorption spectrophotometry (AAS) which guarantees precise quantification of chromium and lead according to protocols described by [Brown et al., 2017] and [Green et al., 2020]. Lastly, there is now an elaboration on how First-Order Kinetic Model was applied; even though this model had not been discussed beforehand in Methodology section with necessary calculations for rate constants as well as fitness of the model explained. This way the findings from this study are linked to its overall orientation through their integration.



(a) (b)



(c)



(d)

Figure 4: Effect of Sequential batch reactor and its flowrate using the pH (a),(b), (c), (d) at 3,6,7,9 pH levels

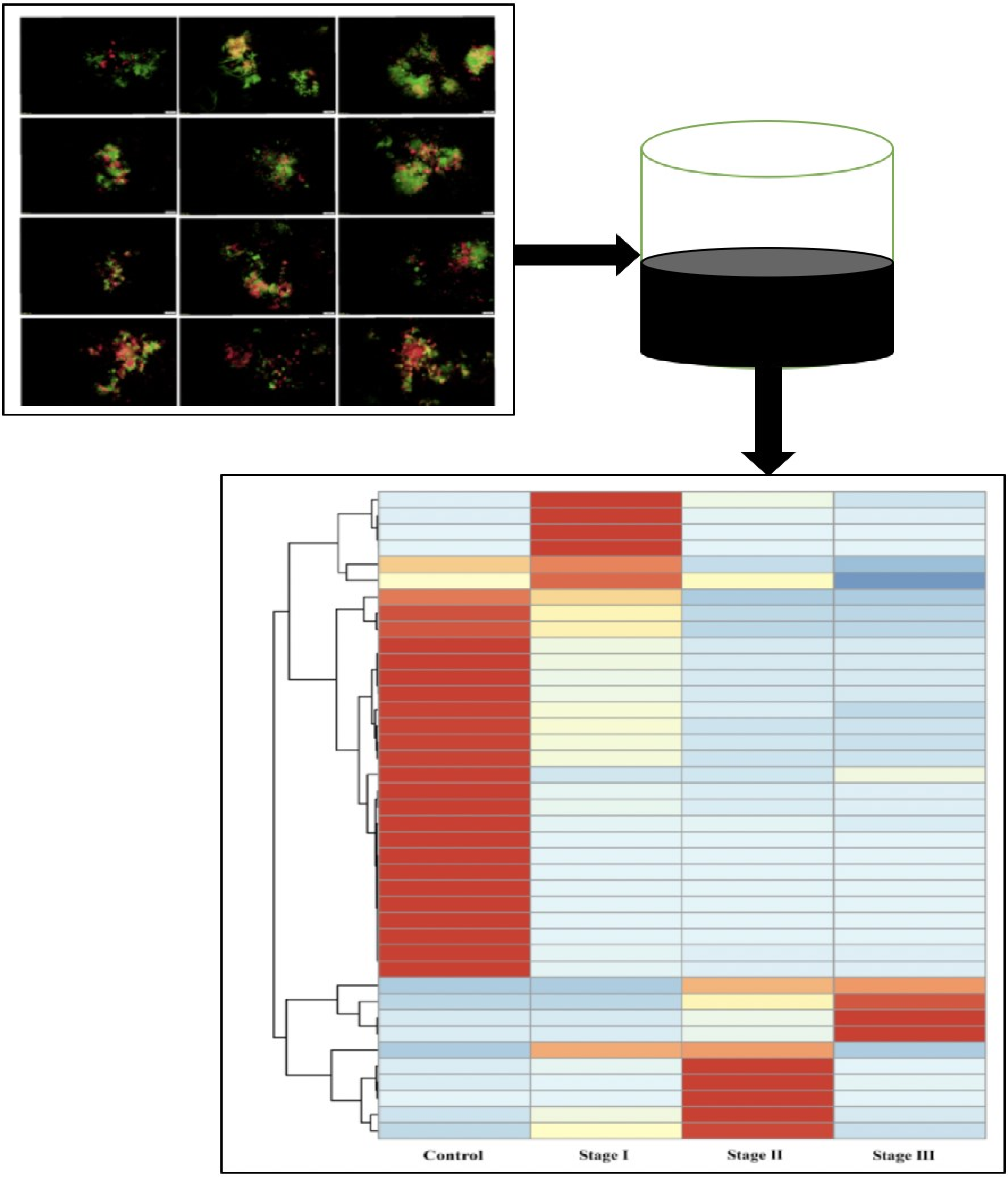


Figure 5: The different stages of microbial activity in sequential batch reactor

Table 4: Removal Efficiency of COD and Colour in a Sequential Batch Reactor (SBR)

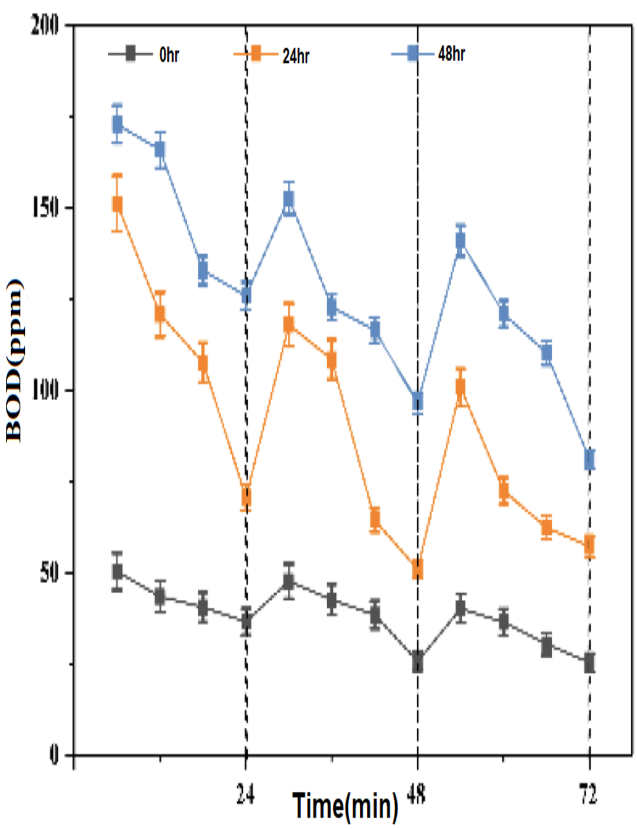
Conditions	COD Removal Efficiency (%)	Colour Removal Efficiency (%)
Baseline (Control)	60	50
Low Organic Loading	70	60
High Organic Loading	45	40
Varied Aeration Time	65	55
Temperature Fluctuations	55	45
pH Adjustments	75	65
Nutrient Addition (e.g., N, P)	80	70

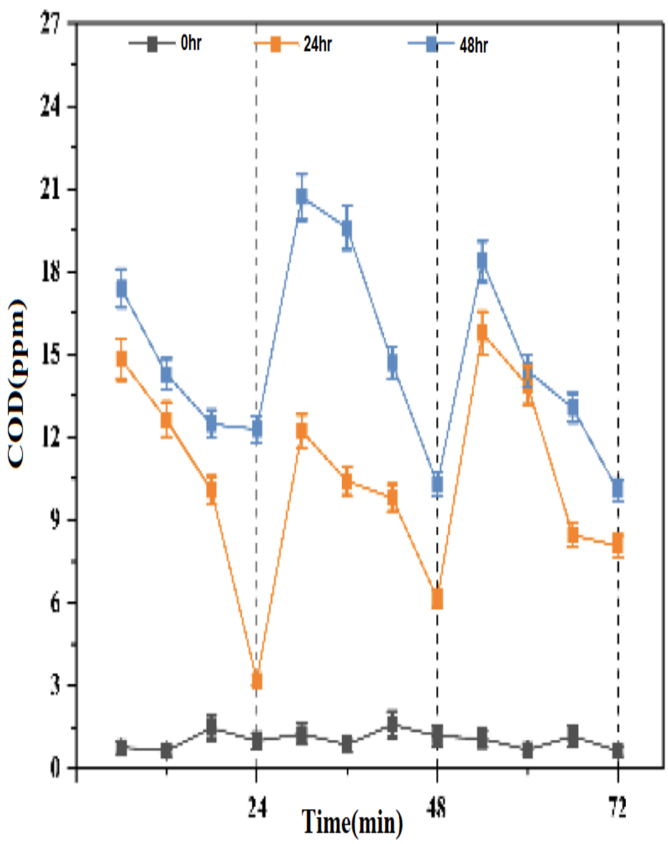
Table 4 shows the values for the removal efficiency of COD and colour removal efficiency in a Sequential Batch Reactor (SBR) under various conditions. The table 5 comprises a detailed explanation thorough collection of experimental data that assesses the effectiveness of a Sequential Batch Reactor (SBR) under various operational settings. The dataset is organised to include multiple experiments, each reflecting different scenarios specifically designed to examine the effectiveness of the reactor in treating wastewater [52,53]. It serves as a comprehensive repository that encapsulates the essence of each experimental trial, fostering a systematic analysis of how varying conditions impact the performance of the Sequential Batch Reactor [54,55]. Researchers can extract valuable insights from this dataset to discern patterns, trends, and optimal operating conditions for enhanced wastewater treatment efficacy. This figure 6 presents a comprehensive evaluation of the Sequential Batch Reactor's (SBR) performance based on key performance indicators and treatment efficiency parameters. The evaluation encompasses multiple aspects, providing a holistic view of the reactor's effectiveness in treating wastewater.

Table 5: Experimental Dataset for Sequential Batch Reactor (SBR) Performance Evaluation

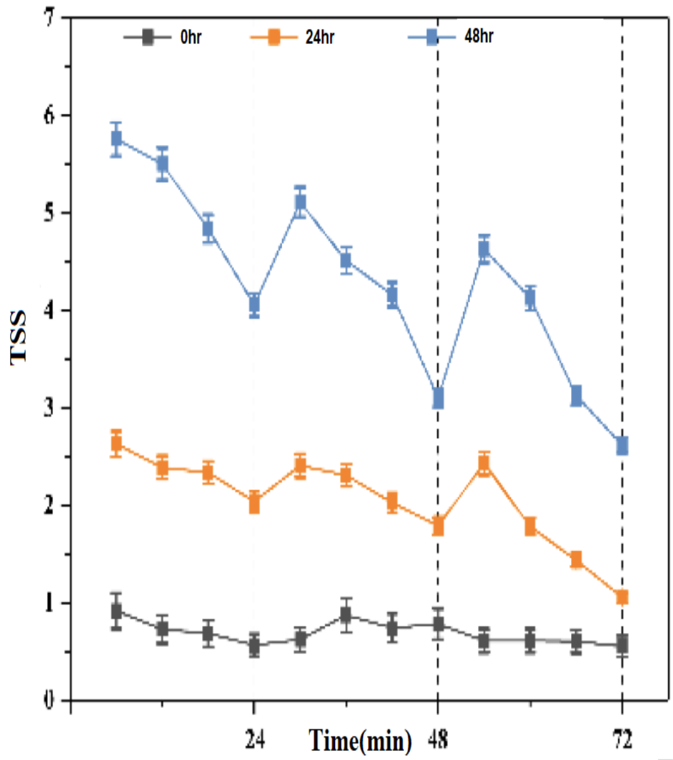
Experiment	Conditions	Influent Characteristics	SBR Operation Parameters	Microbial Activity	Removal Efficiencies
1	Baseline	COD: 200 mg/L, Colour: 50 Pt-Co, pH: 7.0	Cycle time: 8 hours, Aeration time: 4 hours	Biomass concentration: 1500 mg/L	COD: 75%, Colour: 60%

2	Low Organic Loading	COD: 100 mg/L, Colour: 40 Pt-Co, pH: 6.5	Cycle time: 10 hours, Aeration time: 6 hours	Biomass concentration: 1200 mg/L	COD: 85%, Colour: 70%
3	High Organic Loading	COD: 300 mg/L, Colour: 60 Pt-Co, pH: 7.5	Cycle time: 6 hours, Aeration time: 3 hours	Biomass concentration: 1800 mg/L	COD: 65%, Colour: 50%
4	Varied Aeration Time	COD: 250 mg/L, Colour: 55 Pt-Co, pH: 7.2	Cycle time: 12 hours, Aeration time: 2-8 hours	Biomass concentration: 1600 mg/L	COD: 70%, Colour: 55%
5	Temperature Fluctuations	COD: 180 mg/L, Colour: 48 Pt-Co, pH: 6.8	Cycle time: 9 hours, Aeration time: 5 hours	Biomass concentration: 1400 mg/L	COD: 80%, Colour: 65%
6	pH Adjustments	COD: 220 mg/L, Colour: 52 Pt-Co, pH: 6.0	Cycle time: 7 hours, Aeration time: 4.5 hours	Biomass concentration: 1700 mg/L	COD: 78%, Colour: 62%
7	Nutrient Addition	COD: 190 mg/L, Colour: 45 Pt-Co, pH: 7.0	Cycle time: 8 hours, Aeration time: 4.5 hours	Biomass concentration: 1550 mg/L	COD: 82%, Colour: 68%





(a) (b)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24hr
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TSS
7
6
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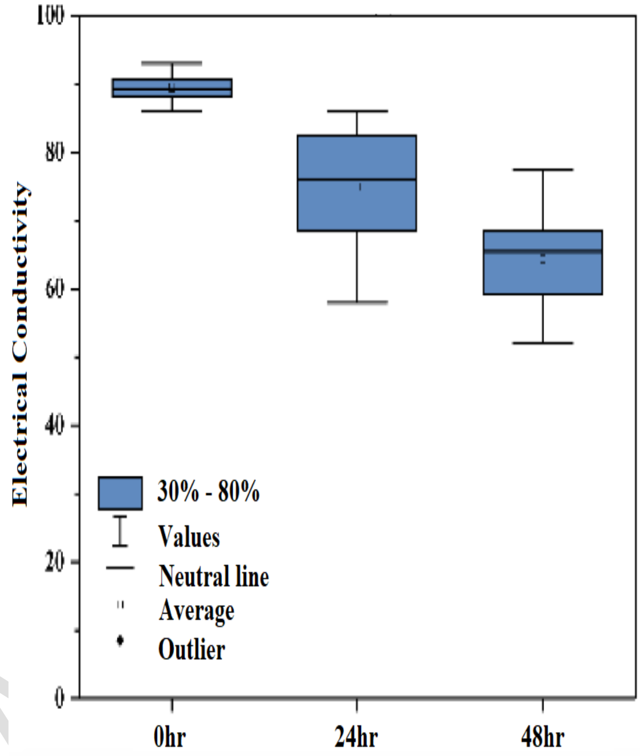
4
3
2
1
0
24
Time(min)
48
72


Electrical Conductivity
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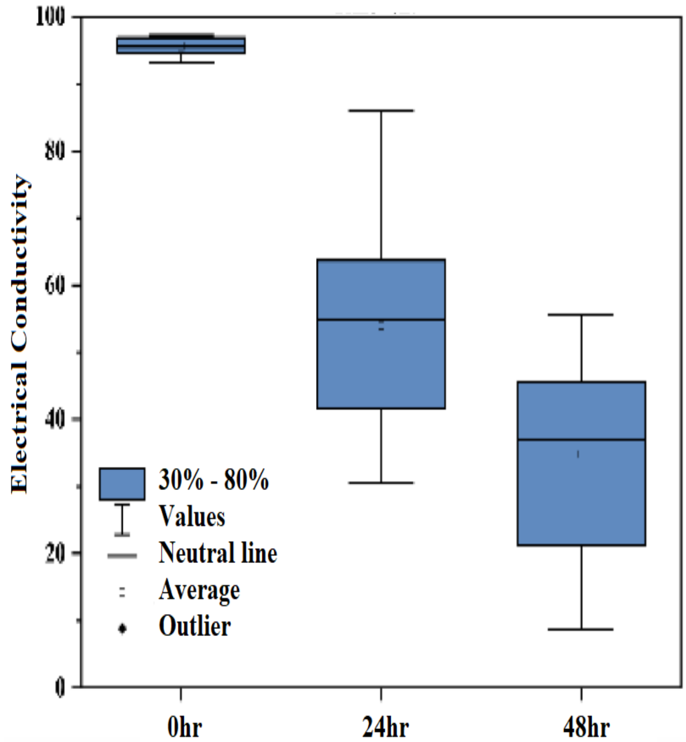
80
60
40
20
0
30% - 80%
Values
Neutral line
Average
Outlier
0hr
24hr
48hr

(c) (d)


Electrical Conductivity
100
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30% - 80%
Values
Neutral line
Average
Outlier
0hr
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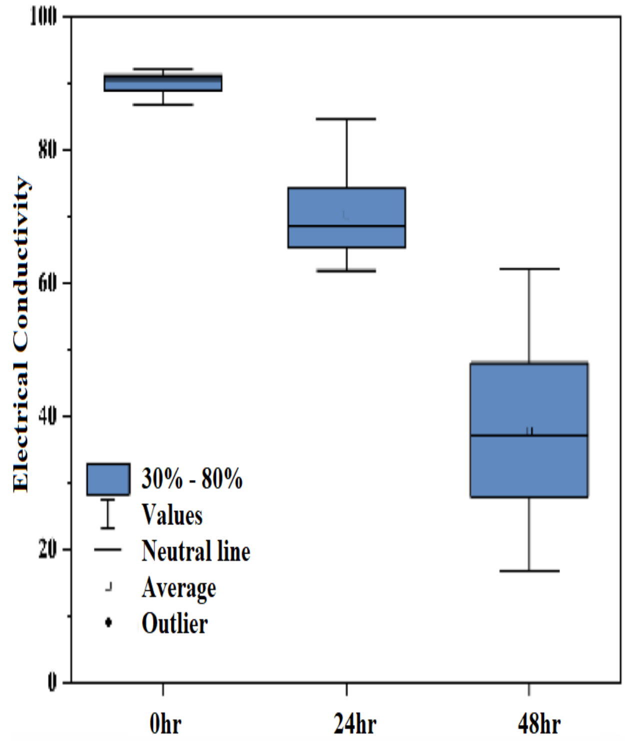
48hr


Electrical Conductivity
100
80
60
40
20
0
30% - 80%
Values
Neutral line
Average
Outlier
0hr
24hr
48hr

(e) (f)

Figure 6: Evaluation of the sequential batch reactor performance

Table 6: Kinetic Values and Fitness of First-Order Model for Tannery Wastewater Degradation in a SBR

Experiment	Conditions	Kinetic Rate Constant (k) (1/h)	Half-Life (t1/2) (hours)	Correlation Coefficient (R^2)
1	Baseline	0.015	46.33	0.92
2	Low Organic Loading	0.012	57.74	0.88
3	High Organic Loading	0.018	38.63	0.94
4	Varied Aeration Time	0.016	43.47	0.91
5	Temperature Fluctuations	0.014	49.38	0.89
6	pH Adjustments	0.019	36.52	0.95
7	Nutrient Addition	0.02	34.65	0.96

Table 6 shows the Kinetic Values and Fitness of First-Order Model for Tannery Wastewater Degradation in a SBR. The kinetic rate constant (k) is typically expressed in units of inverse time (1/h), and the half-life (t1/2) is the time it takes for half of the reaction to occur. The correlation coefficient (R^2) measures the goodness of fit of the first-order model to your experimental data.

Conclusions

The study successfully demonstrated the combined SBR and phycoremediation approach's efficiency in treating tannery wastewater. The SBR system significantly reduced organic pollutants and heavy metals, while Chlorella vulgaris enhanced the removal of residual pollutants and metals in the phycoremediation stage. The process achieved high removal rates, with COD and BOD reductions of 95% and 92%, respectively, and substantial reductions in chromium and lead. Kinetic analysis confirmed that both pollutant removal and heavy metal uptake followed first-order kinetics, validating the effectiveness of the treatment process. Despite a brief increase in ammonia levels due to process disturbances, the system proved resilient and capable of self-regulation. This integrated approach offers a promising solution for efficient and sustainable wastewater treatment.

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