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Equilibrium of Ammonia (NH_3) and Ammonium (NH_4^+) during Microalgae Harvesting using Electrocoagulation

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ABSTRACT

Harvesting microalgae is an important process in gaining biomass while the remaining water is still rich in nutrients. These nutrients, mainly nitrogen and phosphorous, could cause eutrophication of water bodies (rivers, lakes, and oceans) and ecosystem degradation if discharged directly without proper treatment. Electrocoagulation (EC) is one of the harvesting methods and has several advantages: ease of operation, fast harvesting, adaptability, environmental friendliness, and low footprint. However, EC method for harvesting microalgae has the potential in producing ammonia, which is undesirable due to its threat to the environment. The purpose of this study is to establish the equilibrium of ammonium (NH_4^+) and ammonia (NH_3) during *Dunaliella salina* harvesting. The harvesting was conducted using EC with a variation of 20 volts, 30 min, and 400 rpm. The result shows that the harvesting efficiency can reach 93.72% after 5 min of processing, decreasing the concentration of inorganic nitrogen compounds in total ammonia nitrogen (TAN) to 98.80%.

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1. INTRODUCTION

Climate change mitigation, environmental deterioration, and energy scarcity are society's greatest concerns in the 21st century [1]. Biofuels derived from microalgae have become one of the most popular used renewable energy sources. Currently, the focus of efforts to reduce climate-altering CO_2 emissions is shifting from fossil fuels to ones based on biological materials [2]. Microalgae are a biological resource that can be used for many things, such as making food, medicine, animal feed, biofertilizers, cosmetics, fuels, treating wastewater, and making bioplastics [3].

Microalgae produce wastewater containing additional nutrients such as nitrogen and phosphorus immediately after harvest. If these pollutants are not handled carefully, they can cause eutrophication of water bodies (like rivers, lakes, and oceans) and damage to ecosystems [4, 5]. One of the things that contributes to ecosystem degradation is water pollution. Therefore, appropriate solutions are needed to reduce the impact of environmental damage as soon as possible. The harmful effects of ammonia nitrogen on the aquatic environment are attracting global attention [6]. Untreated microalgae effluent containing nutrients (nitrogen and phosphorus) has the potential to pollute aquatic bodies. Instead of treating microalgae effluent before disposal, water dilution may be used [7], but water is a scarce resource [8].

The hardest part of any microalgae-based activity is harvesting the algae. Consquently, the harvesting process is an interesting subject to study so that it can be used in the field. Centrifugation and membrane filtration are the usual methods for large-scale harvesting cultures of microalgae [9]. However, require complex maintenance. Therefore, new methods must be developed to make maintenance easier and lower harvesting costs without slowing down harvesting or making the biomass less pure [10]. EC is a microalgae harvesting method that needs to be explored because of its ease of operation, fast harvesting, adaptability, environmental friendliness, and low footprint [11]. When compared to centrifugation alone, the usage of EC can save up to 89% of energy [12].

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After harvesting microalgae using EC, wastewater with extra nutrients such as nitrogen will be produced. The wastewater contains ammonium and ammonia, which can be quantified as total ammonia nitrogen [13]. In wastewater, ammonium and ammonia are all in equilibrium. Their relative concentrations depend on pH and temperature, at high pH and temperature values promoting the production of ammonia molecules [14].

Producing microalgae and harvesting employing EC (Al electrodes) can remove 75% of the total nitrogen in 5 hours [15]. Similar results were obtained by Liu and Liu [16], which integrated *Chlorella vulgaris* cultivation and EC pretreatment with iron electrodes that removed 88% of total nitrogen from anaerobic digestion wastewater in 40 min. The anode chamber of the biocathode-coupled electrocoagulation cell (bio-ECC) achieved nitrogen removal rates of 7.28 $mg.L^{-1}.h^{-1}$, while the cathode chamber achieved nitrogen removal rates of 6.77 $mg.L^{-1}.h^{-1}$ [17]. However, the previous studies focused on the decrease in nitrogen (NH_4^+-N and total nitrogen), neglecting the equilibrium between ammonium and ammonia. Actually, ammonia production is undesirable due to its toxicity to aquatic biota [6]. According to Meetiyagoda and Fujino [18], wastewater from microalgae harvesting should be introduced into water budies because of contaminants. The novelty of this research includes a high microalgae harvesting efficiency, a quick harvesting time, and a non-toxic microalgae culture wastewater effluent for aquatic biota.The purpose of this research is to investigate the equilibrium between ammonium and ammonia during microalgae harvesting. This study harvested *D. salina* utilizing EC with a voltage of 20 volts, a duration of 30 min, using stainless steel and iron electrodes.

2. MATERIALS AND METHODS

2. 1. The Substrate of *D. salina* This research was conducted using an experimental laboratory method. Cultures of *D. salina* were obtained from UgoPlankton, Jepara Regency and cultured at UPT C-BIORE Laboratory, Diponegoro University, Semarang, Indonesia. Testing of the total ammonia nitrogen, pH, and temperature was carried out at the Environmental Laboratory, Faculty of Engineering, Diponegoro University and UPT Laboratory C-BIORE. The sampling method used was SNI 6989.59:2008 [19]. The parameters observed were pH, temperature (°C), ammonia, ammonium, and total ammonia nitrogen.

2. 2. EC Experiment The harvesting of *D. salina* using EC wais carried out under fixed conditions, which means researchers did not modify any parameters, including pH, initial concentration, room temperature, etc. The stirring speed and substrate volume refer to previous research conducted by Lucakova et al. [20] with a stirring speed of 400 rpm using a magnetic stirrer and a culture volume of 500 mL. The operational details of the research are shown in Table 1. The stainless steel cathode and iron anode are completely submerged in *D. salina* culture. Coating the cathode with a circular insulator (0.5 cm) and inserting it into the anode prevents the cathode and anode from binding together. The experiment was conducted utilizing direct current (DC) electricity with a constant voltage of 20 volts. Using an AC-DC adapter, a 220 volt AC supply was transformed into DC (Sunshine 30V 5A, P-3005D, China). Electrocoagulation times ranging from 0 to 30 min were varied to assess the harvesting efficiency and TAN from the culture of *D. salina.* The settling time was set for 60 min. At a depth of 2 cm, samples were taken from the supernatant to check the optical density (OD), the harvesting efficiency of *D. salina* (%), the total alkalinity (TAN), pH, and temperature.

2. 3. Sample Analysis and Concentration Calculation The pH and temperature measurement refers to standard methods for the examination of water and wastewater [21]. pH was measured using a pH meter WalkLAB TL9000 (TransInstruments, Singapore). TAN analysis was performed using the phenate method [20] by adding 1 mL of phenol, 1 mL of sodium nitroprusside,

TABLE 1. Details of harvesting operations *D. salina* using EC

Indicator	Unit	Note
Temperature	°C	The temperature according to laboratory conditions
pH	-	pH according to the conditions of the microalgae to be harvested (initial pH is 8.72)
Glass beaker volume	mL	600
Types of microalgae	-	*D. salina*
Microalgae culture vol	mL	500
Stirrer/magnet	mm	25 x 8
Anode material	-	stainless steel 304
Anode shape/geometry	-	spiral/ helix
Anode length	cm	10
Anode diameter	cm	5
Cathode material	-	iron S45C
Cathode shape/geometry	-	solid
Cathode length	cm	10
Cathode diameter	cm	2
Stirring speed	rpm	400
Settling time	min	60

and 2.5 mL of oxidizing solution to 25 mL of sample in a 50 mL Erlenmeyer flask. Plastic or paraffin wrap covered the sample.

The color requires at least an hour to develop at room temperature (22-27°C) and under dark , and it is stable for 24 hours. Spectrophotometric measurement of color absorption was at 640 nm wavelength (UV-Vis Genesys 150 Spectrophotometer, Thermo Scientific, USA). The stock ammonia solution was diluted to create standard and blank solutions. A standard curve plotted standard absorbance versus standard ammonia concentration. Sample absorbance was compared to a standard curve to calculate concentration. Ammonium concentration was then calculated using equation (2) [22]. Removal efficiency was calculated using equation (3). A spectrophotometer (Spectroquant®Prove 100, Merck KGaA, Darmstadt, Germany) adjusted to a wavelength of 442 nm was used to measure the optical density (OD) of *D. salina* culture, which allowed for the calculation of the percentage of harvesting efficiency (%).

Lie and Liu [23] stated that optical density is an accurate and efficient approach for measuring microalgal biomass (OD). A spectrophotometer was utilized to scan the maximum wavelength automatically [24].

$$Ammonia = \frac{\text{TAN X } 10^{pH}}{e^{\left(\frac{6344}{273+oC}\right)} + 10^{pH}} \quad (1)$$

where Ammonia is the concentration of ammonia as nitrogen (mg/L), TAN is the concentration of total ammonia nitrogen (mg/L), pH and temperature (°C).
Ammonium calculation:

$$\text{Ammonium} = \text{TAN} - \text{ammonia} \quad (2)$$

where: Ammonium is the concentration of ammonium as nitrogen (mg/L), Ammonia is the concentration of ammonia as nitrogen (mg/L), TAN is the concentration of total ammonia nitrogen (mg/L).

$$\text{Removal efficiency (\%)} = [1-(X_{out}/X_{in})]*100 \quad (3)$$

Where: Removal efficiency is the removal efficiency of *D. salina* culture (%), X_{in} is the initial concentration (mg/L), X_{out} is the final concentration (mg/L).

The statistical significance of the research findings was determined using analysis of variance (ANOVA) (Origin 2022 software) at a 95% confidence level (p value 0.05).

3. RESULT AND DISCUSSION

3. 1. Harvesting Efficiency of *D. salina* Culture

The harvesting efficiency of *D. salina* was evaluated based on differences in optical density (OD) at wavelength 442 nm between the initial and harvested samples. This comparison was made in order to determine how successfully the microalgae were harvested [25].

What stands out in Figure 1 is the harvesting efficiency of *D. salina* culture in 2 min of 56.33%. It is interesting to observe that the harvesting efficiency can reach 93.72% after 5 min of electrocoagulation. The harvesting efficiency reaches a maximum of 98.43% when the electrolysis time is as long as 30 min. In applying electrocoagulation to harvest *D.* salina, Fe^{3+} ions react with *D. salina* and cause coagulation [26]. This harvesting efficiency value is higher than the research conducted by Lucakova et al. [27], where the harvesting efficiency of *Chlorella vulgaris* is 85%. Parmentier [28] harvested *Chlorella* in continuous mode using an electrocoagulation-flotation tubular reactor and successfully harvested 88%. The harvesting efficiency of this study is higher than that of Mixson et al. [29], who applied EC using Al anodes for harvesting *D. viridis*. After 24 hours of EC, more than 95% of the biomass was harvested. The analysis of variance and harvesting time of *D. salina* using EC had no significant effect on harvesting efficiency; at the 0.05 level, the slope was significantly different from zero. This shows that harvesting for more than 5 min does not significantly increase the efficiency of the harvest.

The type of algae can affect the harvesting process due to autoflocculation [30]. *Scenedesmus quadricauda* produces extracellular polymeric substances (EPS) that stimulate efficient self-flocculation. If the pH drops, the negatively charged functional groups in EPS or microalgae cell walls will accept protons. The surface charge of the cell would then be neutralized in the culture media to produce a floc [31].

3. 2. pH Figure 2 shows the change in the pH value of *D. salina* culture during harvesting using the EC. The pH value of *D. salina* culture wastewater was as required in government regulation. Government regulations are decisions made by the government in the form of regulations that apply to all regions of the country. We

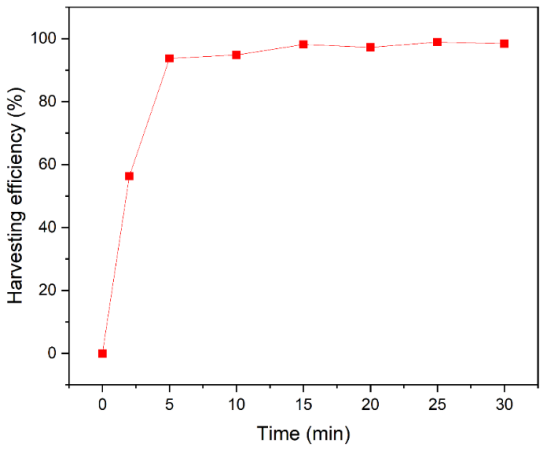


Figure 1. Graphics of harvesting efficiency (%) of *D. salina* culture when harvested using EC for 30 min

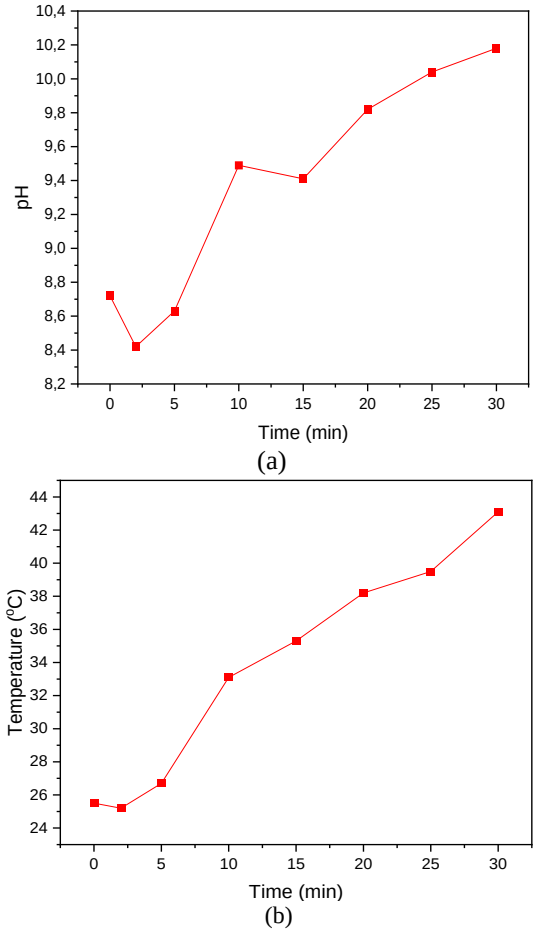


Figure 2. Graph of *D. salina* culture pH and temperature when harvested using EC for 30 min

used Government Regulation Number 22 of 2021 concerning the Implementation of Environmental Protection and Management of Class II Rivers, which states that a safe pH for the environment is between 6-9.

What stands out in Figure 2 is that the initial pH of *D. salina culture* was 8.72; after EC was carried out in an effort to harvest microalgae, the pH decreased in 2 min and 5 min by 8.42 and 8.63, respectively. However, at 10 min, the pH increased to 9.49, and at 30 min the pH increased to 10.18. The analysis of variance and harvesting time of *D. salina* using EC has a significant effect on temperature increase; at the 0.05 level, the slope is significantly different from zero. Based on this study, the pH of *D. salina* culture wastewater was safe for the environment when the harvesting process was carried out for 5 min.

As a result of oxidation processes at the anode, Fe^{2+} ions will be produced if iron is used [32], as in the reaction Equation (4). Meanwhile, a reduction of water at the cathode creates hydroxide ions and H_2 gas (5).

$$Fe \rightarrow Fe^{2+} + 2e^- \quad (4)$$

$$2\ H_2O + 2e^- \rightarrow 2\ OH^- + H_2 \quad (5)$$

The pH of a solution increases as a result of the hydroxide ions produced through Equation (5). The longer the electrolysis process is conducted, the more OH^- ions are produced at the cathode, resulting in a higher pH of the solution [33]. In this study, the pH during the harvesting of microalgae was alkaline. At this pH, it has the potential to shift ammonium equilibrium to ammonia, which is toxic to aquatic biota (Equation (6)) [34].

$$NH_4^+ + OH^- \leftrightarrow NH_3.H_2O \leftrightarrow NH_3 + H_2O \quad (6)$$

3. 3. Temperature Temperature measurements were carried out in situ in the laboratory at around 8 AM and 4 PM. Temperature affects certain chemical and biological reactions that occur in water and the organisms that live in it [35]. Temperature also affects other water quality indicators, such as dissolved oxygen (DO) and the power of hydrogen (pH) [36].

Figure 2 shows the change in *D. salina* culture temperature during harvesting using the EC process for 30 min. The temperature value of *D. salina* culture wastewater, as required in government regulation number 22 of 2021 concerning the Implementation of Environmental Protection and Management of class II rivers, is three deviations from the room temperature of the study site. During the research, the laboratory room temperature was 26°C, so the maximum temperature required was 29°C (26°C+3°C = 29°C).

What stands out in Figure 2 is that the initial *D. salina* culture temperature was 25.5°C; after EC was carried out in an effort to harvest microalgae, the temperature increased to 26.7°C at 5 min. The temperature s increased to 33.1°C at 10 min and 43.1°C at 30 min. Based on the ANOVA test, the harvesting time of *D. salina* using EC had a significant effect on the temperature increase; at the 0.05 level, the slope was significantly different from zero.

In this study, the wastewater temperature exceeds the limits of standards after the harvesting of *D. salina* for 30 min. The temperature of wastewater is safe for water bodies when the harvesting process using EC is carried out for 5 min. This increase in temperature has the potential to shift the balance of NH_4^+ to NH_3 [14], which is toxic to aquatic biota.

3. 4. Removal Efficiency of Total Ammonia Nitrogen (TAN) Total Ammonia Nitrogen (TAN) is the sum of ammonium and ammonia present in the water sample [13]. Figure 3(a) shows the TAN removal (%) and TAN concentration on *D. salina* culture during harvesting using EC for 30 min. Although the concentration of TAN is not required in government regulation number 22 of 2021 regarding the

Implementation of Environmental Protection and Management, TAN needs to be analyzed because it can be used to determine the concentration of ammonium and ammonia. Ammonia has attracted high global attention because its presence in surface water has a highly toxic effect on aquatic biota [6]. *D. salina* culture wastewater containing TAN has the potential to contaminate water bodies if disposed of directly without treatment. In addition to treating *D. salina* culture wastewater, efforts that can be made when disposing of microalgae culture wastewater include dilution by water [7], but water is a scarce resource [8].

What stands out in Figure 3 is that the concentration of TAN in the initial *D. salina culture* was 0.98 mg/L; after EC was carried out in an effort to harvest microalgae, TAN decreased to 0.87mg/L in the 2nd min. The concentration of TAN decreased continuously at 5, 10, 15, 20, 25, and 30 min, respectively, by 0.70 mg/L, 0.63 mg/L, 0.61 mg/L, 0.50 mg/L, 0.46 mg/L, and 0.27 mg/L. Based on the ANOVA test, the harvesting time of *D. salina* using EC had a significant effect on the decrease in TAN; at the 0.05 level, the slope was significantly different from zero.

In this study, maximum TAN removal of 72.49% resulted from the EC process for 30 min, 20 volts of electric power, stainless steel and iron electrodes. TAN removal was as low as 11.25% when using an electrolysis time of 2 min. This TAN removal is slightly lower than the results of a study conducted by Saavedra et al. [15], where the process of cultivating microalgae and harvesting using EC (Al electrodes) can remove 75% of total nitrogen and 5 hours of electrolysis time. Similar results were found by Liu and Liu [16], who integrated *Chlorella vulgaris* cultivation and EC pretreatment with iron electrodes capable of removing 88% of total nitrogen from anaerobic digestion wastewater for 40 min. Although the results of this study are lower, the TAN process only takes 2 min, while the study of Saavedra et al. [15] takes 5 hours and Liu and Liu [16] had 40 min of treatment.

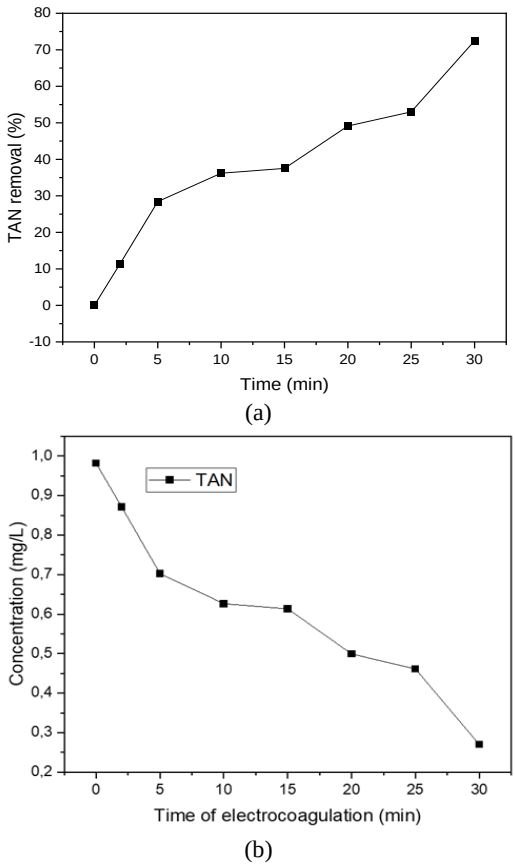


Figure 3. Graph of (a) TAN removal (%) and (b) TAN concentration of *D. salina* culture when harvested using EC

3. 5. The Equilibrium of Ammonia and Ammonium

Ammonia is an inorganic non-metallic component present in water [37]. The results of changes in ammonia and ammonium concentrations on *D. salina* culture during harvesting using the EC process for 30 min are shown in Figure 4. The ammonia concentration required in government regulation number 22 of 2021 for the Implementation of Environmental Protection and Management of Class II rivers is 0.2 mg/ L.

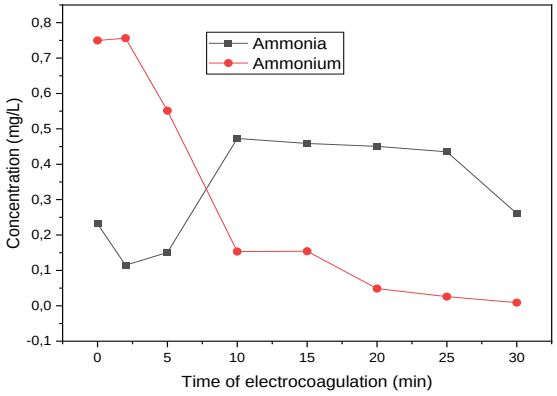
What stands out in Figure 4 is that the ammonia concentration in the initial *D. salina* culture was 0.23 mg/L, and ammonia decreased to 0.15 mg/L after EC for 5 min. Ammonia concentration for 10 min, 15 min, 20 min, and 25 min increased to 0.47 mg/L, 0.46 mg/L, 0.45 mg/L, and 0.44 mg/L, respectively. In this study, the concentration of ammonia in wastewater after harvesting *D. salina* for 30 min exceeds the limits of standards. Based on the ANOVA test, the harvesting time of *D. salina* using EC had no significant effect on the reduction of ammonia; at the 0.05 level, the slope was not significantly different from zero.

Temperature and pH might have had an effect on the amount of ammonia. The increase in ammonia may be due to the effect of increasing temperature and pH when harvesting using EC. When the pH increases, the reaction equilibrium tends to form NH_3 [14], as shown in Equation (6).

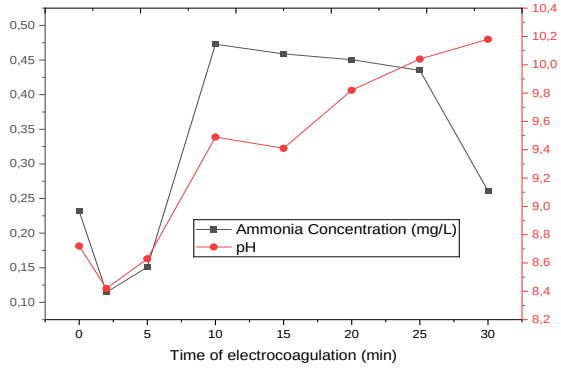
According to the equilibrium reaction, if the pH is high, the reaction equilibrium will shift toward NH_3. This is in accordance with the findings of Liu and Liu [16], which state that, when the pH of the solution is basic, the reaction equilibrium will shift to the right, thus inducing the formation of ammonia. Hydrogen and oxygen gases increase when water is electrolyzed, and nitrate is converted to nitrogen gas, but NH_3 is usually formed as well [38]. Othmani et al. [34] state that the pH of the solution increases after the EC process. The wastewater pH and temperature influence the relative concentrations of ammonia gas and ammonium ions [40].

The initial ammonium concentration of *the D. salina culture* was 0.75mg/L. After EC was carried out in an effort to harvest microalgae, ammonium decreased to 0.55mg/L at 5 min. Ammonium concentration decreased by 0.15 mg/L, 0.05 mg/L, 0.03 mg/L, and 0.01 mg/L after 10, 15, 20, 25, and 30 min, respectively. In this study, the maximum ammonium removal of 98.80 % resulted from the EC treatment for 30 min, 20 volts, stainless steel electrodes and iron. Wastewater treatment using electrochemistry previously reported was able to convert NH_4^+ into NO_3 and N_2 gas through the oxidation process [41]. Based on the ANOVA test, the harvesting time of *D. salina* using EC had a significant effect on ammonium reduction; at the 0.05 level, the slope was significantly different from zero.

Overall, the harvesting time of *D. salina* using EC had no significant effect on the reduction of ammonia but had a significant effect on the reduction of ammonium. Based on this study, it can be concluded that pH harvesting of *D. salina* using EC for 30 min actually increased the concentration of ammonia, which is toxic to aquatic biota. Overall, there was a decrease in the concentration of inorganic nitrogen compounds in the form of TAN. This was due to there being a general decrease in the concentration of ammonium.



(a)



(b)

Figure 4. Equilibrium graph (a) concentrations of ammonia and ammonium; (b) pH and concentration of ammonia in *D. salina* culture when harvested using EC for 30 min

4. CONCLUSION

The harvesting efficiency reached 93.72 % after 5 min of electrocoagulation, which is a remarkable result. When the electrolysis time is as long as 30 min, the harvesting efficiency reaches its most significant point, which is 98.43%. *D. salina* culture wastewater that complies with regulatory standards in terms of temperature and pH may only be harvested for a maximum of 5 min. Overall, inorganic nitrogen compounds in the form of TAN decreased, which was dominated by a decrease in ammonium. Harvesting *D. salina* using EC was found to increase the concentration of ammonia, which is toxic to aquatic biota. Therefore, additional wastewater treatment is required so that the wastewater from microalgae harvesting is non-toxic to aquatic biota. In addition to the treatment of microalgae culture wastewater, efforts that can be made when disposing of microalgae culture wastewater are by reusing microalgae culture wastewater as a culture medium for these microalgae or other species.

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Persian Abstract

چکیده

برداشت ریزجلبک ها یک فرآیند مهم در به دست آوردن زیست توده است در حالی که آب باقیمانده هنوز غنی از مواد مغذی است. این مواد مغذی، عمدتاً نیتروژن و فسفر، در صورت تخلیه مستقیم و بدون تصفیه مناسب، می‌توانند باعث اتروفیکاسیون بدنه‌های آبی (رودخانه‌ها، دریاچه‌ها و اقیانوس‌ها) و تخریب اکوسیستم شوند. انعقاد الکتریکی (EC)یکی از روش‌های برداشت است و دارای چندین مزیت است: سهولت در عملیات، برداشت سریع، سازگاری، سازگاری با محیط زیست و ردپای کم. با این حال، روش EC برای برداشت ریزجلبک‌ها پتانسیل تولید آمونیاک را دارد که به دلیل تهدید محیط زیست نامطلوب است. هدف از این مطالعه ایجاد تعادل آمونیوم (NH_4^+)و آمونیاک (NH_3)در طول برداشت *Dunaliella salina* است. برداشت با استفاده از EC با تغییرات ۲۰ ولت، ۳۰ دقیقه و ۴۰۰ دور در دقیقه انجام شد. نتیجه نشان می دهد که راندمان برداشت می تواند پس از ۵ دقیقه پردازش به ۹۳.۷۲ درصد برسد و غلظت ترکیبات نیتروژن معدنی در نیتروژن کل آمونیاک (TAN)را به ۹۸.۸۰ درصد کاهش دهد.