Jurnal Presipitasi
Media Komunikasi dan Pengembangan Teknik Lingkungan
e-ISSN: 2550-0023

Vol 20, No 1, 2023, 44-52
Article available at homepage presipitasi

Original Research Article

Nutrient Recovery from Agricultural Waste Water Using Electrocoagulation Process, A Case Study of Thekelan, Semarang, Indonesia

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Abstract

Eutrophication is a natural phenomenon in aquatic ecosystems that causes algae and other aquatic plants to overproduce. This process can benefit the ecology in tiny amounts, but too many nutrients can generate hazardous algal blooms and kill fish and other aquatic life. To prevent eutrophication and sustain aquatic ecosystems, agricultural waste water like microalgae production wastewater must be treated. The goal of the project is to get nitrogen and phosphorus out of the wastewater from growing microalgae, which is an agricultural waste water. One way to recover nutrients from wastewater is electrocoagulation. This procedure uses an electric current to create microscopic gas bubbles that collect and remove pollutants from wastewater. According to this study, electrocoagulation reduces phosphate and nitrate in microalgae culture wastewater. Phosphate concentration dropped by 90.20% in the 15^{th} minute, while nitrate concentration dropped by 36.19% in the 30^{th} minute. These reductions may be caused by struvite formation and nitrate conversion to nitrogen gas. This study demonstrates that electrocoagulation is a potential technology for recovering nutrients from agricultural waste water and reducing aquatic ecosystem eutrophication.

Keywords: Wastewater; suds; recovery nutrient; nitrate; phosphate

1. Introduction

Ivarez-González et al. (2022) state that the development of sustainable agriculture necessitates the development of alternatives to the inorganic fertilizers that are now in widespread use. In 2019, FAO reported that chemical fertilizers consumed 62.7 kilogram of nitrogen (N) per hectare of agricultural land (FAO, 2021). Mohsin et al. (2021) estimate that forty percent of the nitrogen in fertilizer gets lost and enters water bodies. Therefore, the nitrogen content in water bodies is high, which has a detrimental effect on the structure of aquatic ecosystems. If utilized in high quantities, the nitrogen and phosphorus content of agricultural waste can promote eutrophication in aquatic habitats (Balasuriya et al., 2022). This can lead to eutrophication in both freshwater and marine habitats (Huang et al., 2017). In addition to nitrogen, phosphorus (P) is an essential ingredient for plant development; yet, agricultural land may promote eutrophication by releasing P into water bodies. Phosphorus is a non-renewable element; hence phosphorus recovery is essential prior to its release into water bodies in addition to its processing. Not only does the paradigm for processing agricultural waste decrease contaminants to the acceptable levels, but it also recovers any remaining nutrients. Phosphorus-containing effluent from agriculture can be recovered. Microalgae may be utilized to recover phosphorus as biomass. For metabolic activities, microalgae use phosphorus and nitrogen (Günther et al., 2018).

The results of nutrient recovery are often employed as fertilizer in agriculture. Another possibility is the recovery of nutrients for more advantageous plant growth (Saliu and Oladoja, 2021). In addition to creating useful biomass and improving water quality, effective agricultural wastewater treatment employing microalgae can prevent eutrophication of wastewater and its detrimental effects on fisheries, agriculture, aquaculture, tourism, and public health. This microalgae's role is to photosynthesize in order to generate oxygen, which is then used by bacteria to oxidize waste (Yure et al., 2022).

Continuous recovery of phosphorus as high-quality calcium phosphate from an anaerobic membrane bioreactor (Damodara Kannan et al., 2023). The product of recovery will be utilized as fertilizer or as raw materials for the fertilizer industry. Utilizing microalgae, wastewater from agricultural businesses such as instant coffee processing, dairy products, and cassava flour and starch was collected (Melo et al., 2022). Nitrogen (N) and phosphorus (P) were recovered by Kékedy-Nagy et al. (2022) from chicken wastewater and urban wastewater from different WWTP facilities. Electrocoagulation is an efficient and approved method for treating and characterizing wastewater (Tibebe et al., 2022).

Producing agricultural wastewater recovery products in the form of fertilizers (Yang et al., 2022). The resultant liquid comprises 89.75% $(NH_4)_2HPO_4$ and 10.25% $NH_4H_2PO_4$, while the solid is a combination of $MgKPO_4$, $MgNH_4PO_4$, $MgNaPO_4$, $MgCO_3 (OH)_2$, and $Mg_3(PO_4)_2$, which are rich in P, K, and Mg and contain 73.75 % K, 92.96% P, and an extra 2.73 % N. Both have the potential to be utilized in agriculture, horticulture, and landscaping (Yadav et al., 2022) for the production of KNO_3 compounds by recovering nitrogen and potassium. Potassium nitrate (KNO_3) is preferred over potassium chloride (KCl) because it interacts favorably with chloride-sensitive plants. According to Teoh et al., (2022), fish culture wastewater includes at least five times the amount of ammonia, phosphate, and potassium prior to treatment. This retainer can serve as the primary nutrient in liquid fertilizer. Cermasite fertilizer, which contains N and P, is another form of fertilizer derived from the recovery of nutrients from waste. Utilizing this fertilizer in plant cultivation closes the nitrogen and phosphorus cycles. In addition to promoting germination, growth, and development of Impatiens commelinoides species, the fertilizer may recover N and P from wastewater. Ramaswamy et al., (2022) generates struvite as a byproduct (magnesium ammonium phosphate). To the best of our knowledge, there has been little study on nutrient recovery from microalgae production effluent until recently. Microalgae harvesting wastewater still contains nutrients that can be recovered into useful products. In addition, the wastewater meets the quality standards required by law.

The objective of this work is to recover nitrogen and phosphate from microalgae production effluent. We apply a sequence of electrocoagulation to recover nutrients at various electrocoagulation times. Mains voltage and electrolysis time are important operating parameters in the EC process (Lucakova et al., 2022).

2. Methods

The research study was conducted in the Environmental Laboratory at the Department of Environmental Engineering at Diponegoro University. We used an electrocoagulation reactor to treat microalgae culture wastewater from the Pure Laboratory (Pudakpayung, banyumanik, Semarang, Indonesia, 7°06'03.0"S 110°24'07.3"E). The electrodes used in the reactor were made of stainless steel and iron, and the reactor was set to a voltage, current of 20 volts, and 500 mL of microalgae production effluent. The experiment involved varying the electrolysis time between 0 and 30 minutes. We measured various characteristics of the wastewater before and after treatment, including conductivity, total dissolved solids (TDS), pH, temperature, nitrate, and phosphate concentration. The sample analysis was carried out using the Standard Method for Examination of Water and Wastewater (APHA, 2017), and we used pro-analyst reagents from Merck (Germany). The conductivity was measured using a conductivity meter that was calibrated using a 0.01 M KCl solution. The results of the analysis were checked for accuracy using the relative percent difference (RPD) method.

$$RPD = \frac{(X_1 - X_2)}{(X_1 + X_2)/2} \ x \ 100\% \qquad (1)$$

X1 is the conductivity value when measuring the first sample and X2 is the conductivity value when measuring the second sample. Analysis and calculation of research data in tables and figures using excel and origin software.

3. Result and Discussion

3.1. Temperature and pH

Based on the data provided, it appears that Figure 1 (a) and (b) show the changes in pH and temperature of the microalgae culture wastewater during the nutrient recovery process. The initial wastewater temperature was 25.5°C, but it increased to 43.1°C after 30 minutes of electrolysis. The temperature of the wastewater at the 5th and 10th minutes were 26.7 and 33.1°C, respectively. The temperature increased to 35.3, 38.2, and 39.5°C at the 15th, 20th, and 25th minutes, respectively.

Flocculation is the process by which particles in a liquid solution come together to form larger, more easily settleable clusters called flocs. Temperature can have a significant effect on floc formation, with higher temperatures generally leading to faster floc formation and lower temperatures leading to slower floc formation. However, the effect of temperature on floc formation is not always well understood, and some researchers may not consider it when conducting studies on flocculation. This is because the effect of temperature can be complex and may vary depending on the specific conditions of the flocculation process, such as the types and concentrations of the particles being flocculated and the type of flocculant being used. Additionally, some researchers may choose to fix the temperature of their experiments at a certain value in order to control for its effect and better isolate the effects of other variables (Liu et al., 2021).

The pH value of a solution can affect the behavior of dissolved ions and can have a significant impact on the effectiveness of the nutrient recovery process. In the context of the Fe^{3+} conversion process, a pH value that is too high or too low can prevent the formation of Fe^{3+} ions, which are necessary for the coagulation mechanism to take place (Harif and Adin, 2011). The pH of a solution is a measure of its acidity or basicity. A solution with a pH of 7 is considered neutral, while a solution with a pH below 7 is considered acidic and a solution with a pH above 7 is considered basic. The concentration of hydrogen ions in a solution determines its pH, and this concentration is influenced by the presence of other dissolved species in the solution. At low pH, there are more hydrogen ions present in the solution, and these ions can interact with other dissolved species, such as cations (positively charged ions) and anions (negatively charged ions). This can cause the cations to dominate the solution, making it more positively charged overall. At high pH, there are fewer hydrogen ions present, so the anions are more likely to dominate the solution and make it more negatively charged overall.

According to Figure 1(a), the starting pH was 8.54 and climbed steadily to 9.98 in 30 seconds. At 5 minutes and 10 minutes, the pH of the effluent was 8.45 and 9.0, respectively. The pH was 9.22, 9.62, and 9.84 after 15, 20, and 25 minutes, respectively. This shows that the pH of the environment is alkaline. This research aims to produce positively charged dissolved organisms in order to bind negatively charged contaminants. Nasrullah et al. (2019) showed that it was simpler to create larger Fe flocs in acidic circumstances compared to neutral or alkaline environments. The conclusion of the research results of the nutrient recovery process in microalgae culture wastewater using electrocoagulation is that it might increase the pH value, which could lead to the formation of smaller Fe flocs.

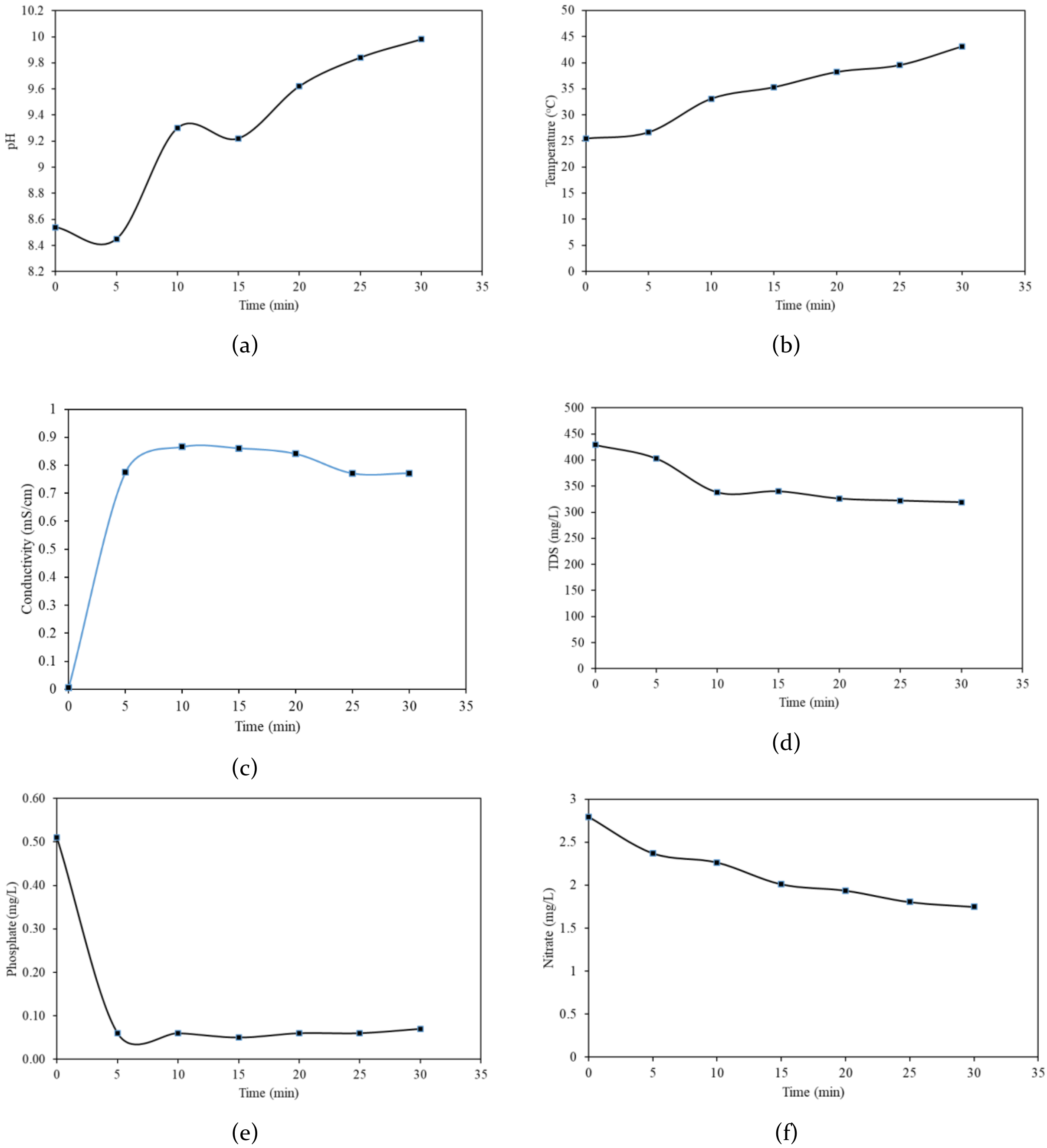

Figure 1. Shows the pH, temperature, conductivity, TDS, phosphate, and nitrate levels of waste water from microalgae cultures during the electrocoagulation nutrient recovery process

3.2. Conductivity and TDS

The conductivity of a solution is a measure of its ability to conduct electricity. In general, the higher the conductivity of a solution, the better it is at conducting electricity. In the case of wastewater, the conductivity can affect the size of the floc, which is the clumps of particles that form as a result of the wastewater treatment process. The floc size of a solution with a conductivity of 8 mS/cm is greater than that of a solution with a conductivity of 1 mS/cm (Harif and Adin, 2007). Figures 1 (c) and (d) show the conductivity and TDS values of microalgae culture wastewater during the nutrient recovery process using electrocoagulation.

According to research data, the conductivity of the wastewater increases over time, starting at 0.006 mS/cm and increasing to 0.772 ms/cm in the 30th minute. This indicates that the wastewater is becoming more conductive as the treatment process progresses. It is also mentioned that the conductivity of the wastewater at the 5th and 10th minutes was 0.776 mS/cm and 0.866 mS/cm, respectively. This indicates that the conductivity of the wastewater is increasing at a faster rate in the first 10 minutes of the treatment process compared to the subsequent 15 minutes. In summary, the conductivity of wastewater can affect the size of the floc formed during the wastewater treatment process. In the case described in the question, the conductivity of the wastewater increases over time, indicating that the wastewater is becoming more conductive. This may result in larger floc sizes.

Total dissolved solids (TDS) is a measure of the concentration of dissolved inorganic and organic substances in water (Maliki et al., 2020; Rusydi, 2018). It is often used as a water quality parameter, as high TDS levels can indicate the presence of potentially harmful contaminants, such as heavy metals, salts, and industrial pollutants. TDS is typically measured in units of milligrams per liter (mg/L) or parts per million (ppm). Water with a low TDS level is considered to be purer and of better quality than water with a high TDS level. In general, water with a TDS level of less than 500 mg/L is considered to be of good quality, while water with a TDS level above 1000 mg/L may taste salty or have an unpleasant odor.

High TDS levels in wastewater can cause a decrease in acceptance of the water. Research by Maliki et al. (2020) showed that the use of electrocoagulation can decrease TDS levels by up to 25.64% from the initial value. This decrease is lower than the results of the study by Bagastyo et al. (Bagastyo et al., 2022), where TDS levels can drop by up to 49% through the same process. TDS levels tend to decrease during the electrocoagulation process, although initial readings are not always consistent due to settling and sedimentation (Idusuyi et al., 2022). Other research has also shown that the longer the electrocoagulation time, the higher the TDS decrease rate (El-Ezaby et al., 2021). Therefore, it is important to optimize the electrocoagulation time to achieve effective results in reducing TDS levels in wastewater.

3.3. Phosphate and Nitrate

Figure 1 (e) and (f) show the concentrations of phosphate and nitrate in microalgae culture wastewater during the nutrient recovery process using electrocoagulation. Electrocoagulation is a process that uses an electric current to coagulate the dissolved particles in wastewater, reducing the concentrations of phosphate and nitrate. This can help to reduce the levels of nutrients in wastewater so that it can be safely discharged into the environment without harming ecosystems.

In this study, the initial concentration of phosphate in the wastewater was 0.51 mg/L, and after treatment with electrocoagulation it was reduced to 0.07 mg/L (Table 1). The concentration of phosphate in the wastewater at minutes 5 and 10 does not change and keeps in 0.06 mg/l. At minutes 15, 20, and 25, the concentration of phosphate was 0.05 mg/L, 0.06 mg/L, and 0.07 mg/L, respectively. The maximum percentage reduction in phosphate concentration was 90.20% at minute 15.

Table 1. Characteristic of wastewater from microalgae harvesting

No	Parameters	Unit	0	5	10	15	20	25	30	Standard
1	pH	-	8.54	8.45	9.3	9.22	9.62	9.84	9.98	6-9
2	Suhu	(°C)	25.5	26.7	33.1	35.3	38.2	39.5	43.1	deviation 3
3	TDS	mg/L	429	403	338	340	326	322	319	1000
4	Nitrate	mg/L	11.61	7.53	9.60497	8.08352	7.95711	7.82619	7.41084	10
5	Fosfat	mg/L	0.51	0.06	0.06	0.05	0.06	0.06	0.07	0,2

Based on the results of physical observations, the nutrient recovery process produces a brown precipitate (Figure 2). The decrease in phosphate concentration is probably due to the formation of struvite ($MgNH_4PO_4 \cdot 6H_2O$). This is supported by the research of Thi Thuy Trang et al. (2018) which states that the way to recover phosphate is through the formation of struvite. The results of this study are higher than the research conducted by Tchamango et al. (2010), where phosphate recovery, nitrogen content reduction, and turbidity were 89.81% and 100%, respectively. Phosphate recovery was up to 100% (reduced from 1.33 mg/L to 0.006 mg/L) when a combination of electrocoagulation and mechanically activated calcite was used, and 98% of the phosphate (reduced from 3.86 mg/L to 0.075 mg/L) was able to be recovered from rainfall runoff from fertilizer companies (Li et al., 2023).

Electrocoagulation is an effective technique for the treatment and characterization of wastewater (Tibebe et al., 2022). The electrochemical process is one method that is used for the removal of nitrate from water. It uses an electric current to oxidize the nitrate ions, converting them into nitrogen gas. In this study, the initial concentration of nitrate in the wastewater was 11.61 mg/L, and after treatment it was reduced to 7.41 mg/L. The concentration of nitrate in the wastewater at minutes 5 and 10 was 7.53 mg/L and 9.60 mg/L, respectively. At minutes 15, 20, and 25, the concentration of nitrate was 8.08 mg/L, 7.96 mg/L, and 7.83 mg/L, respectively. The maximum percentage reduction in nitrate concentration was 36.19% at minute 30. This decrease is likely due to the conversion of nitrate to nitrogen gas. Hydrogen and oxygen gas are produced when water undergoes electrolysis, and the nitrate ions are converted into nitrogen gas (Mook et al., 2012). Additionally, the longer the electrocoagulation time, the more Fe^{3+} are released from the electrodes. These ions serve as coagulants that destabilize negatively charged colloids. This process forms flocs and leads to sedimentation.

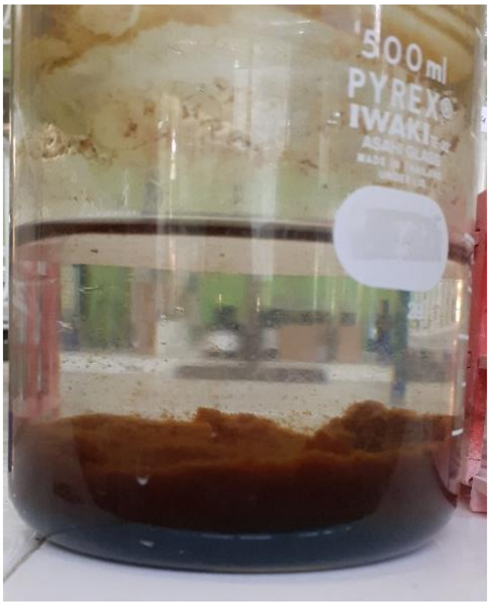

Figure 2. Shows the results of electrocoagulation of wastewater harvesting microalgae.

The formation of flocs, which are clumps of particles in water, can help to reduce the concentration of nitrate in wastewater (Mulwandari, 2019) through a process called electrocoagulation (Al-Marri et al., 2020). A statistical method called Central Composite Design (CCD) to optimize the removal of nitrate using electrocoagulation. CCD is a method that is used to optimize a process or product by studying the effects of several input variables on the output. In this case, the output was the nitrate parameter. The best removal of nitrate was around 77% when electrocoagulation was performed with an initial wastewater pH of 6, ultrasonic irradiation time of 10 minutes, flow rates of 40 ml/minute, initial nitrate concentration of 150 mg/l, and applied current densities of 7.5 mA/cm^2. While the EC process is effective at removing nitrate from water, it can be expensive to operate due to the cost of the electricity needed to run the process (Yehya et al., 2015). This can make it difficult for some organizations, such as municipal water treatment plants, to justify the use of the EC process due to the high operating costs. However, the cost may be justified in situations where the removal of nitrate is necessary to meet strict water quality regulations or to protect public health.

4. Conclusions

The study aims to recover nitrogen and phosphorus nutrients from microalgae culture wastewater through a process called electrocoagulation. The results of the study show that this process is effective at reducing the concentration of these nutrients in the wastewater. The maximum percentage reduction in phosphate concentration was 90.20% in the 15th minute, while the maximum percentage reduction in nitrate concentration was 36.19% in the 30th minute. These reductions are likely due to the formation of struvite and the conversion of nitrate to nitrogen gas, respectively. Further research is needed to test the concentration of phosphate and nitrogen in the resulting precipitate from the nutrient recovery process using electrocoagulation.

Acknowledgement

The authors received funding from Universitas Diponegoro through High Reputation Of International Publication (RPIBT) UNDIP under Grant Number 225-50/UN7.6.1/PP/2022 for this research.

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