An Applied Research of the Recycled Economic Model for Spirulina Algae’s Cultivation from Ion-Life Alkaline Water and CO₂ Gas’s Boiler

Trinh Van Dung¹, Nguyen Truc Mai², Vo Dang Linh³, Pham Van Hung³

¹Ho Chi Minh City University of Technology, VNU- HCMC, Vietnam
²Hoang Minh Water Joint Stock Company, Vietnam
³Industrial University of HCM City, Vietnam

* Corresponding author. Email: trinhyandung@hcmut.edu.vn, trinhdung@hcmut.edu.vn

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ABSTRACT

This paper presents an investigation of Spirulina algae (S. platensis) cultivation from the research and application of the circular economy model for green production by combining Ion-Life alkaline water and the CO₂ gas emitted from the combustion of rice husk. This circular economy model for green production is applied in using the optimal pH values and the HCO₃⁻ in which S. platensis is much easier for using. The cost of prepared medium for S. platensis cultivation from the Ion-Life alkaline water is minimized thanks to the simplex algorithm. From this algorithm, the cost prepared medium for S. platensis cultivation from the Ion-Life alkaline water can be reduced approximately 71.86 VND/liter when comparing to the Zarrouk medium (nearly equal to 3.71 % of the cost for cultivation from the Zarrouk medium). Comparing the improved medium from Ion-Life alkaline water with the Zarrouk medium for cultivating S.platensis algae are at the same conditions as the temperature from 26 ± 40°C and pH value from 8.6 ± 10.6. During the first eight days of cultivation in improved medium from Ion-Life alkaline water, the concentration of biomass increases from 0.044 to 0.93 g/L. During the next eight days, the pH values are controlled to be from 8.5 to 9.5, which is suitable for Spirulina algae since feeding the CO₂ gas from the combustion of rice husk with amount of 7.6 % CO₂ with the 30 minutes a day. Finding a technology that blows CO₂ from smoke of boiler to make the effect of stirring the environment for achieving objectives. First, it helps to add carbon-nutrient source in the form of HCO₃⁻. Second, it helps to maintain the pH of environment in the optimal range of 8.5-9.7. As a result, the biomass concentration increases to 1.4 g/L, while this value is 1.23 g/L in the case non-using CO₂ from smoke of boiler. On the basis of the obtained results, it is basic to calculate equipment and to build a technology process for the green production of cultivation of Spirulina algae from by using the CO₂ molecules emitted from the combustion of biomass combining alkaline water ion-life can be applied practically.

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1. Introduction

Potential health benefits and nutritional value of Spirulina are mainly due to its chemical composition, which includes 50-70% of easily absorbed protein, many essential amino acids in which close to human needs. Furthermore, Spirulina's chemical composition also includes many antioxidants, aging ingredients, vitamins and microelements that are superior to many other foods. Therefore, Spirulina is called the food of the 21st century [1]. Besides, the technology of Spirulina cultivation also brings great significance to the environmental protection and the ecosystems that contribute to building a circular economy by converting the greenhouse gas CO₂ into valuable biomass based on photochemical reaction

\[ n\text{CO}_2 + n\text{H}_2\text{O} + \text{mineral} + \text{hv} \rightarrow (\text{CH}_2\text{O})_n + \text{O}_2 \]  

(1)
However, different from other green plants, the Spirulina platensis algae does not absorb CO$_2$ as a source of carbon nutrients. It only assimilates CO$_2$ as a form of bicarbonate HCO$_3^-$ [2, 3, 4] as the following reaction:

\[
n\cdot HCO_3^- + n\cdot H_2O \xrightarrow{hv} (CH_2O)_n + n\cdot OH^- + n\cdot O_2
\]  

(2)

Based on the references [4, 5] show that the concentration of carbon-containing components (CO$_2$, HCO$_3^-$ and CO$_3^{2-}$) changes with the environment’s pH value and the nutrient in the form HCO$_3^-$ is absorbed easily by Spirulina platensis algae in the condition of the pH values were kept in an optimal range of 8.5 to 9.5. Therefore, we need to maintain this optimal pH value [2, 3, 4].

Alkaline water has many different names such as alkaline drinking water, hydrogen-rich alkaline ionized water, hydrogen water, hydro water etc, is a type of drinking water in which researched and developed in Japan in recent years. In Viet Nam, alkaline ionized water is produced by Hoang Minh Water Joint Stock Company that have trademark is Ion-Life and have the pH value from 8.5-9.5 and also have chemical composition in Table 1

| Chemical formulas | C, mg/L |
|-------------------|---------|
| HCO$_3^-$         | 65.90   |
| Na$^+$            | 64.90   |
| K$^+$             | 18.75   |
| SO$_4^{2-}$       | 22.60   |
| Cl$^-$            | 66.70   |
| Ca$^{2+}$         | 1.11    |
| Mg$^{2+}$         | 2.41    |

In the food industry, boilers are always used as a source of heating and it emits greenhouse gas with CO$_2$ mainly. Therefore, from the aim of sustainable product development, this greenhouse gas emission should be utilized for producing valuable green products according to the circular economy model. The paper uses green catalyst with the technology of zero greenhouse gas’s emission to cultivate the green product as S. platensis with two contents:

1) Research technology of cultivation’s Spirulina algae by Ion-Life alkaline water with economic efficiency
2) Determining the technology mode of cultivation’s Spirulina by alkaline water Ion-Life and greenhouse gas CO$_2$ from biomass boiler;

The obtained results are the foundation of the application of the circular economy model in green production which has a high value from the CO$_2$ greenhouse gas.

**1.1. Minimizing the cost of S. platensis culture medium using Ion-Life alkaline water**

The nutrient medium is Zarrouk medium (Table 2), Spirulina was developed very well as the following indexes [5]:

- pH: 8.5 $\div$ 9.5
- Temperature: 30 $\div$ 38 °C
- Luminous intensity: 2.5 $\div$ 3.5 klux
Table 2. Composition of Zarrouk medium

| Chemical formulas     | Zarrouk, g/L |
|----------------------|-------------|
| NaHCO₃               | 16.8        |
| NaNO₃               | 2.5         |
| NaCl                 | 1.0         |
| K₂SO₄               | 1.0         |
| K₂HPO₄              | 0.5         |
| MgSO₄×7H₂O          | 0.2         |
| CaCl₂×2H₂O          | 0.04        |
| FeSO₄×7H₂O          | 0.01        |
| EDTA                 | 0.08        |
| Micronutrient solution 1 | 1.0 mL/L   |
| Micronutrient solution 2 | 1.0 mL/L   |

| Chemical formulas     | Micro. solution 1, mg/L |
|----------------------|-------------------------|
| H₃BO₃            | 2.86                    |
| MnCl₂×4H₂O       | 1.81                    |
| ZnSO₄×7H₂O       | 0.22                    |
| CuSO₄×5H₂O       | 0.08                    |
| MoO₃             | 0.01                    |
| Chemical formulas     | Micro. solution 2, mg/L |
| NH₄VO₃           | 0.023                   |
| NiSO₄×7H₂O       | 0.048                   |
| Na₂WO₄           | 0.018                   |
| Ti₂(SO₄)₃        | 0.040                   |
| Co(NO₃)₃×6H₂O    | 0.044                   |

The problem of minimizing the cost of the culture medium using Ion-Life alkaline water is set out as follows: the mineral content of the culture medium prepared is equivalent to Zarrouk medium but at a lower cost and also has the pH value of the culture medium from 8.5 to 9.5.

The mathematical model of minimizing the cost of *S. platensis* algae’s culture medium is described as [6]:

\[
\min f(X) = \sum_{i=1}^{8} c_i x_i \rightarrow \min
\]

Where \( x_i \) (\( i = 1 \div 8 \)) corresponds to the weight of 8 substances (Hₖ) to be added into Ion-Life alkaline water (g/L): NaHCO₃, NaNO₃, NaCl, CaCl₂.6H₂O, K₂HPO₄.3H₂O, K₂SO₄, MgSO₄.7H₂O, FeSO₄.7H₂O.

\( c_i \) (\( i = 1 \div 8 \)) are the prices of these substances Hₖ (VND/g) (in Table 5).

The amount of each mineral in medium prepared cannot be smaller than the amount available in Zarrouk medium:
\[
\begin{aligned}
\sum_{i=1}^{8} a_{ji} x_i &\geq b_j \\
x_i &\geq 0 \quad i = 1, 8
\end{aligned}
\] (4)

Where \( a_{ji} = \frac{M_j}{M_i} \) is the ratio of mineral composition \( j \) from compound \( i \); \( M_j \): the molecular weight of compound \( H_j \) (Zarrouk medium in Table 2) and \( M_i \): the molecular weight of compound \( H_i \) in which added the Ion-Life alkaline water in order to the weight \( x_i \);

\( b_j \) is amount to added to Ion-life water and is described as Eq(5). Therefore, culture medium has an amount of mineral \( j \) that not less than that Zarrouk medium (4):

\[ b_j = m_{j\text{Zar}} - m_{j\text{Ion-Life}} \] (5)

Ratio of mineral composition from 10 compounds \( (a_{ji}) \) in Zarrouk medium: \( \text{HCO}_3^-, \text{NO}_3^-, \text{Cl}^-, \text{HPO}_4^{2-}, \text{SO}_4^{2-}, \text{Na}^+, \text{Ca}^{2+}, \text{K}^+, \text{Mg}^{2+}, \text{Fe}^{2+} \).

\[ m_{j\text{Zar}} = \sum_{i=1}^{8} a_{ji} x_i \] : total quantity of mineral \( j \) from 10 compounds in Zarrouk medium;

\[ m_{j\text{Ion-Life}} = \sum_{i=1}^{8} a_{ji} x_i \] : total quantity of mineral \( j \) from 8 compounds must be added to Ion-Life alkaline water;

Some calculation results based on Eq(4) and Eq(5) are shown in table 3.

1.2. The \( \text{CO}_2 \) greenhouse gas’s technology for cultivation of \( \text{S.platensis} \) algae

The reaction (2) shows that the photosynthetic process of \( \text{Spirulina} \) not only consumes the greenhouse gases in the form of \( \text{HCO}_3^- \), but also produces \( \text{OH}^- \) that increases the pH value exceeding the appropriate pH ranges of \( \text{Spirulina} \) (from 8.5 to 9.5). Therefore, it is necessary to provide an extra amount of \( \text{HCO}_3^- \) and reduce pH values to maintain the growth of \( \text{Spirulina platensis} \) algae by using \( \text{CO}_2 \) from the boiler according to the reaction [2, 4]:

\[ \text{CO}_2 \text{ (k)} \rightarrow \text{CO}_2 \text{ (l)} \] (6)

\[ \text{CO}_2 \text{ (l)} + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{CO}_3 \] (7)

\[ \text{H}_2\text{CO}_3 \rightleftharpoons \text{H}^+ + \text{HCO}_3^- \] (8)

\[ \text{HCO}_3^- \rightleftharpoons \text{H}^+ + \text{CO}_2^{2-} \] (9)

This is the basis of technology that uses \( \text{CO}_2 \) from furnace gas to maintain the pH values in an optimal range and provide \( \text{HCO}_3^- \) for the growth of \( \text{S. platensis} \). For gas emissions having a high level of \( \text{CO}_2 \) (40-50\%) such as biogas and gas from alcohol fermentation tanks, the liquid or solid \( \text{CO}_2 \) can be separated and collected by using the compression and cooling process and then throttling [2]. For gas emissions from having a low level of \( \text{CO}_2 \) (6-14\%), \( \text{CO}_2 \) from the boiler, kilns can be collected by directly absorbing into the selected solvents based on the temperature [2,4]. With the same conditions (temperature and pressure) as dissolving in the water, the solubility of \( \text{CO}_2 \) is higher than that value of \( \text{O}_2 \), \( \text{N}_2 \) and \( \text{CO} \) is (25 ÷ 35) times, (50 ÷ 70) times and 40 times, respectively. Therefore, as transferring the \( \text{CO}_2 \) gas from the boiler into the cultivation medium to maintain the pH value in the optimal ranges and provide enough the amount of \( \text{HCO}_3^- \) for \( \text{Spirulina} \) based on reaction (2).

2. Materials, Apparatus and Methods

2.1. Materials

Ion-Life alkaline water is provided by Hoang Minh water Co.Ltd (64 Pho Quang, Ward 2, Tan Binh District, Ho Chi Minh City), its chemical composition is provided in Table 1;

Chemicals used for the experiment are bought from SOUTHCHIMEX JSC 130 Tran Hung Dao,
Pham Ngu Lao Ward, District 1, Ho Chi Minh City.

Spirulina platensis algae is bought from Research Institute for Aquaculture No 2, 116 Nguyen Dinh Chieu st, District 1, Ho Chi Minh City.

CO₂ source: collected from exhaust fume of rice husk burning by Rice Huck’s Viet Saigon Co., Ltd, Vietnam (259 Duong Dinh Hoi, Tang Nhon Phu B Ward, Thu Duc City, Ho Chi Minh City). The gas data include: 97 to 100 °C, 7,76% (v/v) CO₂, 12 ppm SO₂, 22 ppm NOₓ, 55,7 mg dry matter/m³ and it is cooled to 35 – 40 °C before used for the experiment.

2.2. Apparatus

The device for cultivating *Spirulina* has a volume of 1.25 liters and dimensions (ϕxHxδ is 80x220x0.1 mm); pump-stirred aerator.

Cylindrical porous stone nozzle has dimensions (dxh=20x20 mm).

Compressor capacity: 5W/220V/50Hz.

Glassware: 250 mL and 500 mL of glass jars; 100 mL and 500 mL of volumetric flasks; pipettes 2 and 10 mL; cylinder of 10 and 100 mL.

Other measuring tools: alcohol thermometer (scale: 0–100°C) from France; Model HI98172 for pH from Hanna; The American Beckman Coulter DU 750’s spectrophotometer (measured at 750 nm) with conversion factor k = 0.73 g/L.

\[
C (g/L) = k \cdot OD_{750} \tag{10}
\]

2.3. Methods

Solving the problem of minimizing the cost according to the mathematical model (3) with conditions (4) by Solver–Excel, the results are displayed in Table 3 and Table 4.

| Chemical formulas of Micronutrient solution | NaHCO₃ | NaNO₃ | NaCl | CaCl₂.6H₂O | K₂HPO₄.3H₂O | K₂SO₄ | MgSO₄.7H₂O | FeSO₄.7H₂O |
|--------------------------------------------|--------|-------|------|------------|------------|--------|------------|------------|
| Coefficients a_{ij} | Na⁺ | Na⁺ | Na⁺ | Ca²⁺ | K⁺ | K⁺ | Mg²⁺ | Fe²⁺ |
| NaHCO₃ | 0.2738 | 0.2706 | 0.3932 | 0.1826 | 0.3421 | 0.4483 | 0.0976 | 0.0397 |
| NaNO₃ | 0.2729 | 0.606 | 0.3242 | 0.4211 | 0.551 | 0.3902 | 0.0007 |
| NaCl | 0.560 | 0.17 | 0.21 | 0.22 | 0.23 | 0.24 | 0.25 | 0.26 |

| Anions | HCO₃⁻ | NO₃⁻ | Cl⁻ | HPO₄²⁻ | SO₄²⁻ | SO₄²⁻ | SO₄²⁻ |
|--------|--------|-------|------|--------|-------|-------|-------|
| HCO₃⁻ | 0.7262 | 0.729 | 0.606 | 0.3242 | 0.4211 | 0.551 | 0.3902 |
| NO₃⁻ | 4.000 | 4.000 | 4.000 | 4.000 | 4.000 | 4.000 | 4.000 |
| Cl⁻ | 8.000 | 8.000 | 8.000 | 8.000 | 8.000 | 8.000 | 8.000 |
| HPO₄²⁻ | 12134.1 | 1823.53 | 559.46 | 210.53 | 610.63 |
| SO₄²⁻ | 604.73 | 600.58 | 17.10 | 2.01 | 9.77 |
To prove the optimized medium from the mathematical model (3) by conducting two parallel experiments where \textit{S. platensis} is cultivated in 2 different PBR: I is Zarrouk medium and II is the optimized medium (Ion-life alkaline water) in the same weather condition.

For determining the technological mode for circulating CO$_2$ from the exhaust fume, we conduct two parallel experiments where \textit{S. platensis} is cultivated in Ion-Life medium with 2 different PBR: II is not aerated with fume and II is aerated with fume containing 7.76 \% (v/v) CO$_2$ within 30 minutes/day in the same condition of weather (sunny – rainy – shady)

Designing comparative experiment for the improved medium Ion-Life alkaline Water and Zarrouk medium.

Table 4. Designing comparative experiment for the improved medium Ion – Life và Zarrouk medium

| PBR            | 1000 (mL) | Spirulina platensis algae’s seed g/L (mL) | $Q_K$ (Liter/minute) | $Q_{smoke}$ (Liter/minute) |
|----------------|-----------|------------------------------------------|----------------------|----------------------------|
| I              | Zarrouk   | 100                                      | 1                    | 0                          |
| II             | Ion-Life + $x_i$ | 100                          | 1                    | 0                          |
| III            | Ion-Life + $x_i$ | 100                          | 0                    | 0.5                        |

The experiment is conducted from 15$^{th}$ April 2021 to 15$^{th}$ May 2021 at Thu Duc city, the temperature fluctuated from 26 to 40 $^\circ$C from 7 AM to 5 PM on sunny – rainy – shady days. At 7 am every-day, pH and OD$_{750}$ of the medium are measured, the result was displayed in Figure 3 for pH and Figure 4 for biomass concentration C, g/L in 16 days.

Table 5. Plan for determining the technology of CO$_2$ recirculation for algae production

| PBR            | Measuring data at 7 am everyday |
|----------------|--------------------------------|
| I              | Blow the air                  |
| II             | aerated with fume containing 7.76 \% (v/v) CO$_2$ within 30 minutes/day |

3. Results and Discussion

3.1. Minimizing the cost of preparing the algae cultivation from Ion-Life alkaline water.

Cost minimization was achieved through a simplex algorithm, calculated in Microsoft Excel [6], shown in Table 6. The prices of the components were provided by South Chemical Import Export Joint Stock Company (SOUTHCHIMEX JSC, Vietnam). The results in Table 6 show that preparing the medium with Ion – Life alkaline water will achieve a cost reduction of 71.86 VND/lit (3.71 \%) compared with Zarrouk medium.

The result from Table 6 shows that the total cost for cultivating the medium required for \textit{S. platensis} by Ion – Life alkaline water is 1863.44 VND/L, it is lower in comparison to the Zarrouk medium 1935.30 – 1863.44 = 71.86 VND/L or $\frac{71.86}{1935.30} \times 100\% = 3.71\%$.

The cost is minimised in comparison to the Zarrouk medium is not significant, lower than medium cultivated from Ion-Life alkaline water [2], due to the mineral content included in Ion-Life alkaline
water is not high (Table 1). But when using Ion-Life alkaline water with pH = 8.5 – 9.5 which is optimal for the growth of S. platensis even with low concentration of minerals.

### Table 6. Calculation results of cost model (3)

| Chem. formulas   | Prices $c_i$, VND/g | $x_i$ (Model (3)), g/L | Cost, VND/L |
|------------------|---------------------|------------------------|-------------|
| NaHCO$_3$        | 76.00               | 13.432                 | 1020.85     |
| NaNO$_3$         | 150.00              | 2.500                  | 374.98      |
| NaCl             | 62.00               | 1.044                  | 64.71       |
| CaCl$_2$·6H$_2$O | 70.00               | 0.081                  | 5.68        |
| K$_2$HPO$_4$·3H$_2$O | 104.00          | 0.500                  | 51.95       |
| K$_2$SO$_4$      | 148.00              | 0.929                  | 137.46      |
| MgSO$_4$·7H$_2$O | 90.00               | 0.297                  | 26.73       |
| FeSO$_4$·7H$_2$O | 70.00               | 0.005                  | 0.35        |

#### 3.2. Comparison of the modified medium and Zarrouk medium

Comparing the concentration of S. platensis algae cultivated in PBR I with the modified medium’s Ion-Life, $C_{\text{Ion-Life}}$ with $C_{\text{Zar}}$ in PBR II under the same condition of weather in the first 8 days shown on Figure 1.

![Figure 1. Comparison of algae’s growth rate in the Ion-life’s modified medium and Zarrouk medium](image)

Figure 1 shows that at the same condition of weather, the biomass growth rate of S. Platensis in PBR I and PBR II has the mean squared deviation:

$$
\varepsilon = \frac{1}{8} \sum_{i=1}^{8} \left( C_{i}^{\text{Ion-Life}} - C_{i}^{\text{Zar}} \right)^2 = 2.49 \times 10^{-5}
$$

The significance between the Ion – Life ‘s modified medium and Zarrouk medium is low because the amount of mineral in Ion–Life alkaline water is lower thus the concentration of nutrition is the same to the Zarrouk medium [2]

Because of there are not significant differences in comparison to Zarrouk medium, so it can be considered that growing S.platensis in the modified medium of Ion-Life that is the same to Zarrouk medium.
3.3. Variation of pH value of the cultivation medium of *S. platensis* during 16 days

Figure 2 shows the pH values of the cultivation medium of *S. platensis* as Zarrouk or the Ion-life’s modified medium in the first eight days and also the pH values of the Ion-life’s modified medium in the next eight days from two cases in which have the furnace gas that contains 7.76 % CO$_2$ or without furnace gas introduction.

Figure 2 shows the change of pH values in the first seven days from the Ion-life Alkaline water, as well as the Zarrouk medium that was increased from 8.6 to 10.2 and was not much in PBR I, II và III. The reaction (2) shows that the photosynthetic process of *Spirulina* produces OH$^-$ that increases the pH value. Meanwhile, the operating condition of PRB I and PRB II are the same, so the growth rate of biomass is similar. Thus, the pH values change alike. After the pH value increased to 10.6 that exceeded the appropriate pH ranges of *S. platensis*.

3.4. The rate of biomass growth

Figure 3 shows the changes of biomass concentration’s medium without the CO$_2$ gas from the furnace in PBR III and PBR II.

Figure 3 shows that using PBR II in the first seven days for the algae of growth and development to make an increase of the pH value, and at the same time consuming the nutrient in the form of HCO$_3^-$ in order to make an increase of biomass’s concentration to the maximum value is 1.2 g/Liter on the 12$^{th}$ day.

Figure 3 shows using PBR II that biomass’s concentration has decreased and the pH value has increased from 10.2 to 10.6 from the 13$^{th}$ day to the following days.
Figure 3. Comparison of biomass growth rate in the improved medium of Ion-Life alkaline water with aeration without the furnace gas.

Meanwhile, the biomass’s concentration was 1.59 g/Liter since using PBR III in the 16 days and the pH value was maintained in an optimal range is from 8.4 to 9.6.

4. Conclusions

From the research results of mathematical model and experiment can be drawn some following conclusions

- Using a simplex algorithm to make the formula for preparing an S. platensis algae’s culture medium with the cost which is lower than the traditional medium about 3.71%;
- Ion-Life alkaline water is suitable for cultivation of S. platensis as adding minerals with the suitable quantity based on simplex algorithm;
- Transferring the gas from the boiler containing the concentration of greenhouse gas about 14% which was cooled to 35 – 40 °C into the algae’s cultivation medium for adjusting the pH value and providing enough the amount of HCO₃⁻ for Spirulina.
- Greenhouse gas emissions are produced from a variety of industrial activities which are utilized to cultivate S. platensis, therefore it is the basis for building the recycle technology of these gases.

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Trinh Van Dung, Assoc. Prof. Chemical Engineering, Head of Department of Process and Equipment, Faculty of Chemical Engineering, Bach Khoa University, VNU-HCM

Ph. D. Degree in Technical Sciences, The Moscow State Academy of Fine Chemical Technology (MITXT) named after M. V. Lomonosov of Russia (1999).

Engineer Degree in Process Engineering, The Hanoi University of Technology (1985).

His research interest in the recent time includes utilizing the CO$_2$ gas from industrial emission for Spirulina algae’s cultivation to reducing greenhouse gas emissions and combating climate change; technology in slow release fertilizer and epoxy production from natural rubber and development of process and equipment for Chemical Engineering.

Email for contact: trinhdung@hcmut.edu.vn, trinhvandung@hcmut.edu.vn

Nguyen Truc Mai, received the B.S. degree in Chemical Engineering from Bach Khoa University, VNU-HCM, Vietnam. Her research interest includes the development of processing for Spirulina algae’s cultivation and calculation of Process and Equipment for Chemical Engineering.

Email: mai.nguyen1304@hcmut.edu.vn

Vo Dang Linh, Chairman of the board, Hoang Minh Water Joint Stock Company. His research interest includes the development of processing for Spirulina algae’s cultivation for reducing greenhouse gas emissions and processing of aquarium filter system.

Email: linhvdl@ionlife.com.vn

Pham Van Hung, Lecturer, Department of Process and Equipment, Faculty of Chemical Engineering, Industrial University of HCM city, Vietnam

He graduated from HCMUT, VNU, Vietnam with Bachelor of Chemical Engineering in 2004 and Master of Chemical Engineering in 2009.

His research interest in the recent time includes utilizing the CO$_2$ gas from industrial emission for Spirulina algae’s cultivation, green technology, freeze drying, chemistry computation and development of Process and Equipment for Chemical Engineering.

Email: pvhung@ruh.edu.vn