COBEM 2023
27TH INTERNATIONAL CONGRESS OF MECHANICAL ENGINEERING

ABCM
Brazilian Society of Mechanical Sciences and Engineering
27th ABCM International Congress of Mechanical Engineering
December 04-08, 2023, Florianópolis-SC, Brazil

COB-2023-0850

MATHEMATICAL MODELING OF MICROALGAE OIL EXTRACTION THROUGH FIXED BED REACTOR WITH SOLVENT PERFUSION

Heloísa Roberto Pinheiro da Silva
Wellington Balmant
Anne Caroline Defranceschi
Flávio Júnior Santiago Silva
Iago Gomes Costa
Diego de Lima Sousa
André Bellin Mariano
José Viriato Coelho Vargas
Federal University of Paraná (UFPR) 81531-980
helo.rps@gmail.com , wbalmant@gmail.com, annewcaroline@hotmail.com, flaviojrsantiago@gmail.com, iago_gomes_costa@hotmail.com, diegofine@hotmail.com, andrebmariano@ufpr.br, , vargasjvcv@gmail.com

Abstract. *Microalgae have gained growing attention globally due to their potential use in various industries, including the production of biofuels. One of the most valuable products derived from microalgae is oil, which can be converted into biodiesel. However, the extraction of oil from microalgae can be a challenging and costly process, mainly due to the energy demand required to operate the extraction processes. The suggested mathematical model relies on balancing mass transfer equations. By precisely anticipating the physical phenomena that occur during the extraction process, the model can ascertain the most favorable operational parameters like the rate of solvent flow and the duration of the extraction, among others. Knowledge of the mathematical model for this decisive stage of microalgae oil extraction enables obtaining valuable information regarding system behavior. Determining the key parameters makes it possible to identify critical variables in the process that affect extraction efficiency, an alternative for reducing the production costs of microalgae biodiesel. A subsequent study will be able to improve the yield of oil extraction since opportunities for optimizing the process can be identified through the determined kinetics.*

Keywords: *microalgae, lipid extraction, mathematical modeling.*

1. INTRODUCTION

Fossil fuels, such as oil, coal and natural gas, have been essential in meeting the global energy demand for decades. However, the exploration and use of these natural resources have caused significant negative impacts on the environment, especially with regards to climate change and greenhouse gas emissions. The burning of fossil fuels is a significant source of air pollution, causing respiratory and cardiovascular diseases. The pursuit for alternative renewable energy sources has become essential to ensure sustainability and preservation of the planet, leading to a steady increase in research for cleaner and renewable options, one of which includes biofuels (LETCHER, 2022).

This option sparked the search for different raw materials, and among them are microalgae, microscopic organisms with enormous potential to be used as a source of biofuels, as well as presenting various advantages compared to other biofuel sources such as soybean and corn. First, the production of biofuels from microalgae proves more sustainable, considering the entire process can be utilized - from biomass for biofuel production to residual gas for electricity production. Another advantage of microalgae is that they can be cultivated in various environments, such as rivers, lakes, and even the sea. Thus, microalgae present enormous potential as a renewable and clean energy source (SATHYA, 2023).

The process of obtaining biodiesel from microalgae involves various stages, starting from cultivation to the extraction of oil from the organisms. Microalgae oil extraction is a highly effective procedure for acquiring biomass that has high lipid content, suitable for producing biofuels, chemicals, and food items. Different techniques are employed for extracting oil from microalgae, but mechanical, solvent, and hybrid extraction methods are the most commonly used. The solvent extraction technique is frequently utilized in the industry for its high efficiency and the ability to extract substantial quantities of oil.

Solvent extraction is one of the most common techniques for separating raw materials. This can be done through repeated washings or percolations with an organic solvent (PÈREZ, 2007). In the percolation operation, the oil is extracted from the solid by the solvent in contact with it in the packed bed (MAJUMDAR and SENGUPTA, 1995).

Despite the potential of microalgae as a biodiesel source, there are still challenges to be overcome. Large-scale cultivation of microalgae is necessary to make production economically viable, but current production scale is limited.

Additionally, there is a need to improve oil extraction efficiency and refine transesterification processes (HOANG et al., 2022). To face these challenges, it is important to better understand the process of microalgal biodiesel production, particularly the extraction stage.

One of the main challenges in fixed bed extraction process is to optimize the mass transfer efficiency and minimize solvent loss. Techniques such as proper choice of solvent, temperature and pressure control, and selection of size and shape of porous material particles are used for this purpose (KUMAR and PRASAD, 2017). Mathematical models can be used to simulate the fixed bed extraction process, allowing the analysis of the influence of different parameters on the process variables and enabling future optimization of the extraction process. Thus, the development of mathematical models is crucial for the extraction of oil from microalgae, as it allows for a better understanding and optimization of the process.

The main objective is to develop a mathematical model for the extraction of oil from microalgae in a fixed bed, and through it, it is possible to determine the predicted quantity of oil extracted under different flow conditions. The development of mathematical models in this context is crucial as they allow for a more precise and efficient extraction process. By accurately predicting the amount of oil extracted, it becomes possible to optimize the process and ensure the maximum yield of oil from microalgae. Moreover, these models provide insights into the influence of different factors on the extraction process, enabling further research and improvements in the technology.

2. METHODOLOGY

2.1 Mathematical model

For the development of the mathematical model, the volume elements method was employed. The theory of volume element modeling (VEM) is a numerical modeling technique that involves dividing simulation domains into smaller elements. These elements are then treated collectively as a complete model, allowing for the analysis of mass flows in different parts of the system. VEM facilitates the creation of precise and efficient numerical models to analyze systems of varying complexities (DILAY, et al., 2015).

In this way, the extraction column was divided into volume elements, and within each volume element, mass transfer processes between the considered solvents and microalgal cells were evaluated. For this purpose, the control volume 1 (CV1) was defined as the interior of the microalgal cell and the control volume 2 (CV2) was stipulated as the region where the solvent is located. The schematic representation under consideration is shown in Figure 1. In (a), we have the fixed bed in its integral form, which has been divided into volume elements. This division can be observed in (b). In each volume element, we can define control volumes where mass transfers occur, both externally and internally within the cell, as depicted in the image in (c).

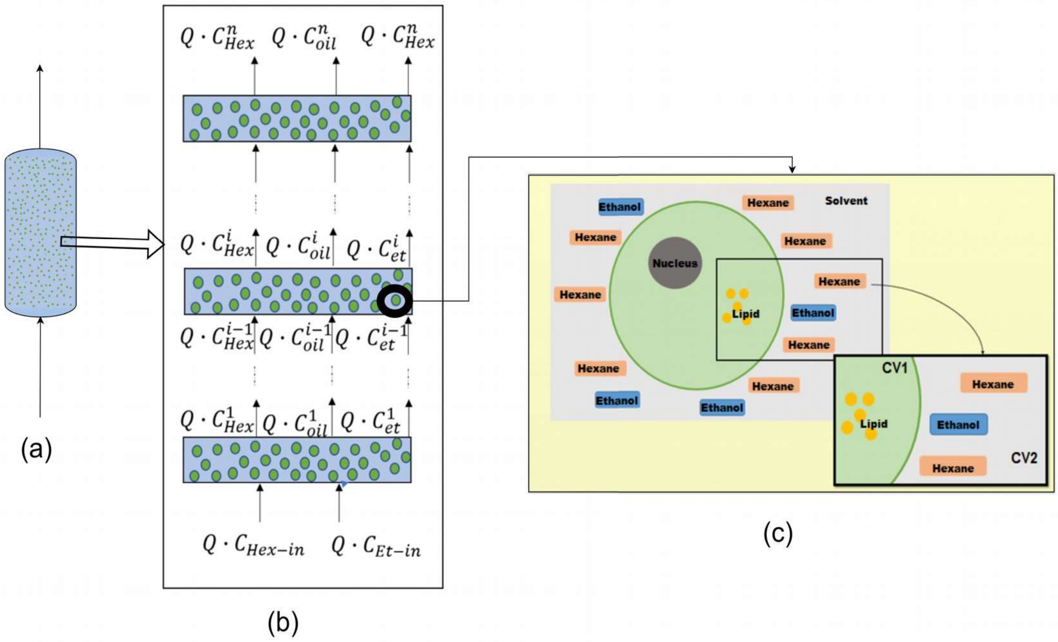

Figure 1. Schematic representation of (a) fixed-bed extraction; (b) Volume elements of the fixed bed; (c) Control volumes depicting the external region with the solvent and the interior of the microalgae.

2.2 Mathematical model

During the development of the mathematical model, several simplifying assumptions were made. These include assuming that convective mass transfer takes place between the control volumes and that the equilibrium concentrations can be determined using the Langmuir isotherm equation. It is also assumed that lipids within the cells combine with ethanol and/or hexane molecules to create a lipid-solvent complex, which is then able to exit the cell. Lastly, it is assumed that all cells have a uniform volume and composition.

The multicomponent Langmuir isotherm is based in a dynamic concept of the adsorption equilibrium, establishing equalities in adsorptions and desorption rates (LANGMUIR, 1918), it was considered here as a mathematical part of the proposed model to determine the equilibrium concentrations of the components, as shown below:

$$C_j^{*i} = \frac{a_j \cdot C_{j\_solv}^i}{1 + \sum_{j=1}^{n} b_j C_{j\_solv}^i} \tag{1}$$

where $C_j^{¿}$ (g mL^{-1}) is the equilibrium concentrations of *j*-th component, $C_{j_{solv}}^i$ (g mL^{-1}) is the concentration of *j*-th component in the solvent no element de volume *i*-th considered; a_j (-) is maximum adsorption capacity parameter of *j*-th component; b_j (mL g^{-1}) is the affinity constant of Langmuir model of *j*-th component.

Initially, we have the mass flux of the solvent (CV2) into the interior of the microalgae (CV2). In CV2, the complex formation process occurs because the lipids inside the cell combine with ethanol and/or hexane molecules, forming this lipid-solvent interaction. Only this complex has mobility and can exit the cell.

The variations for the first element (VEM$_1$) of volume for hexane, ethanol and oil (complex formed) are obtained through equations 2, 3 and 4. Figure 2 demonstrates the schematic representation for this volume element.

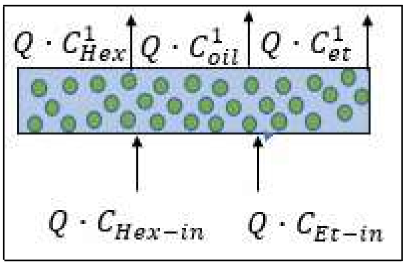

Figure 2. Volume element 1 (VEM$_1$).

$$\frac{dC_{hex\_solv}^1}{dt} = \frac{Q \cdot (C_{hex\_in} - C_{hex\_solv}^1)}{V_{solv}} - \mathrm{Ka}_{hex} \cdot (C_{hex}^{*1} - C_{hex\_cel}^1) \frac{V_{cel}}{V_{solv}} \tag{2}$$

$$\frac{dC_{et\_solv}^1}{dt} = \frac{Q \cdot (C_{et\_in} - C_{et\_solv}^1)}{V_{solv}} - \mathrm{Ka}_{et} \cdot (C_{et}^{*1} - C_{et\_cel}^1) \frac{V_{cel}}{V_{solv}} \tag{3}$$

$$\frac{dC_{oil\_solv}^1}{dt} = - \frac{Q \cdot (C_{oil\_solv}^1)}{V_{solv}} + \mathrm{Ka}_{oil} \cdot (C_{hex}^{*i} - C_{oil\_cel}^1) \frac{V_{cel}}{V_{solv}} \tag{4}$$

Where, Q is the flow rate of solvent used in the extraction (mL·min^{-1}); V_{cel} is the microalgae volume (mL); V_{solv} is the volume of solvent (mL); C_{hex_in} is the concentration of hexane at the inlet of the fixed bed (g mL^{-1}); $C_{hex\_solv}^1$ is the concentration of hexane leaving VEM$_1$ (g mL^{-1}); C_{et_in} is the concentration of ethanol at the inlet of the fixed bed (g mL^{-1}); $C_{et\_solv}^1$ is the concentration of ethanol leaving VEM$_1$ (g mL^{-1}); $C_{oil\_solv}^1$ is the concentration of oil leaving VEM$_1$ (g mL^{-1}); Ka_{hex} is the mass transfer coefficient of hexane (min^{-1}); Ka_{et} is the mass transfer coefficient of ethanol (min^{-1}); Ka_{oil} is the mass transfer coefficient of lipid-solvent complex (oil). The concentrations within the cell, for hexane ($C^1_{hex\_cel}$), ethanol ($C^1_{et\_cel}$) and for the oil ($C^1_{oil\_cel}$), will continue to vary until reaching equilibrium, and the resulting concentrations will then flow into the following volume element.

For the others volume elements, the schematic is considered (Figure 3):

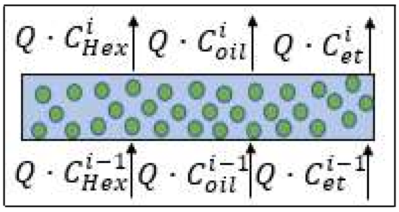

Figure 3. Control volumes along the fixed bed column.

$$\frac{dC^i_{hex\_solv}}{dt} = \frac{Q \cdot (C^{i-1}_{hex\_solv} - C^i_{hex\_solv})}{V_{solv}} - \mathrm{Ka}_{hex} . (C^{*i}_{hex} - C^i_{hex\_solv}) \frac{V_{cel}}{V_{solv}} \tag{5}$$

$$\frac{dC^i_{et\_solv}}{dt} = \frac{Q \cdot (C^{i-1}_{et\_solv} - C^i_{et\_solv})}{V_{solv}} - \mathrm{Ka}_{et} . (C^*_{et} - C_{et\_cel}) \frac{V_{cel}}{V_{solv}} \tag{6}$$

$$\frac{dC^i_{hex\_solv}}{dt} = \frac{Q \cdot (C^{i-1}_{oil} - C^i_{oil})}{V_{solv}} + \mathrm{Ka}_{oil} . (C^*_{hex} - C^i_{oil\_cel}) \frac{V_{cel}}{V_{solv}} \tag{7}$$

For the concentrations (g mL^{-1}) of lipids (C_{lip_cel}), lipid-solvent complex (C_{oil_cel}), hexane (C_{hex_cel}), and ethanol (C_{et_cel}) in the cell, equations 8, 9,10 and 11 are considered, respectively

$$\frac{dC_{lip\_cel}}{dt} = - \frac{Kb_{hex} \cdot C_{lip\_cel} \cdot C_{hex\_cel}}{M_{hex}} - \frac{Kb_{et} . C_{lip\_cel} \cdot C_{et\_cel}}{M_{et}} \tag{8}$$

$$\frac{dC_{oil\_cel}}{dt} = \frac{Kb_{hex} \cdot C_{lip\_cel} \cdot C_{hex\_cel}}{M_{hex}} + \frac{Kb_{et} . C_{lip\_cel} \cdot C_{et\_cel}}{M_{et}} - Ka_{oil} \cdot (C^i{}_{oil\_cel} - C^*_{oil}) \tag{9}$$

$$\frac{dC_{et\_cel}}{dt} = Ka_{et} \cdot (C^*_{et} - C_{et\_cel}) - \frac{Kb_{et} . C_{lip\_cel} \cdot C_{et\_cel}}{M_{lip}} \tag{10}$$

$$\frac{dC_{hex\_cel}}{dt} = Ka_{hex} \cdot (C^*_{hex} - C_{hex\_cel}) - \frac{Kb_{et} . C_{lip\_cel} \cdot C_{hex\_cel}}{M_{lip}} \tag{11}$$

where Kb_{hex} (mL/min·g) is the hexane-lipid interaction coefficient; Kb_{et} (mL/min·g) is the ethanol-lipid interaction coefficient Ka_{et} (min^{-1}) is the mass transfer coefficient of ethanol; Ka_{oil} (min^{-1}) is the mass transfer coefficient of lipid-solvent complex; Ka_{hex} (min^{-1}) is the mass transfer coefficient of hexane; and the molecular weights of (M_{et}), hexane (M_{hex}) and lipids (M_{lip})are also considered.

The mathematical model previously described consists of a total of 11 parameters, and in order to obtain their initial values, a simulation was conducted using the experimental data collected, which were presented at COBEM 2021. These data include the oil extraction from microalgae using pure hexane and a mixture of hexane and ethanol (da Silva et al., 2021). The description of each parameter is provided in Table 1.

Table 1. Parameters used in the mathematical model.

Parameter	Description	Unit of measurement
Ka_{hex}	Mass transfer coefficient of hexane	min^{-1}
Ka_{oil}	Mass transfer coefficient of lipid-solvent complex (oil)	min^{-1}
Ka_{et}	Mass transfer coefficient of ethanol	min^{-1}
Kb_{hex}	Lipid-hexane interaction coefficient	mL/min·g
Kb_{et}	Lipid-ethanol interaction coefficient	mL/min·g
a_{hex}	Langmuir adsorption capacity constant for hexane	(-)
b_{hex}	Langmuir constant for hexane	mL/g
a_{et}	Langmuir adsorption capacity constant for ethanol	(-)
a_{et}	Langmuir constant for ethanol	mL/g
a_{oil}	Langmuir adsorption capacity constant for lipid-solvent complex (oil)	(-)
b_{oil}	Langmuir constant for lipid-solvent complex (oil)	mL/g

3. RESULTS AND DISCUSSIONS

The mathematical model developed was implemented in Matlab. The Table 2 presents the values found with the adjustment of the parameters.

Table 2. Values of the parameters found with the adjustment of the model.

Parameter	Unit of measurement
Ka_{hex}	90. 2 min^{-1}
Ka_{oil}	19.3 min^{-1}
Ka_{et}	22.4 min^{-1}
Kb_{hex}	4.7 mL/min·g
Kb_{et}	29.5 mL/min·g
a_{hex}	35.0 (-)
b_{hex}	1.0 10^{-5}mL/g
a_{et}	$1.1 \cdot 10^{-3}$(-)
b_{et}	24.2 mL/g
a_{oil}	104.6 (-)
b_{oil}	144.0 mL/g

After parameter adjustment, in order to determine the volume element quantity, the mesh stabilization was evaluated. From 3 volume elements to 10, a significant variation was observed between two different flow loops, established to vary from 1 to 1 (ml/min) up to a maximum of 50 ml/min. With 5 volume elements, there was a variation of 0.4% between the last flows, whereas with 10 volume elements, a variation of 0.1% occurred. Therefore, there is no need to further increase the elements, as it would not be worth the computational time, considering that it is already very close to system stability. Figure 5 shows the mentioned variations.

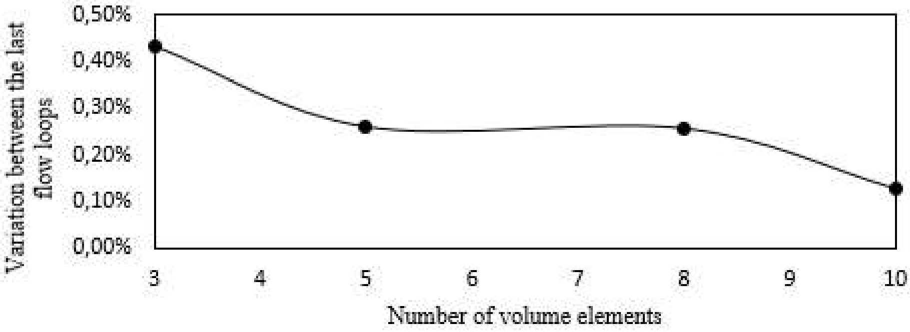

Figure 4. Amount of oil extracted as a function of extraction solvent variation

To evaluate the mathematical model that provides the amount extracted in a fixed bed process, the extraction solvent flow rate was modified from 0 to 50 mL/min. The amount of extracted oil as the extraction solvent flow rate increases is presents in FIGURE 5.

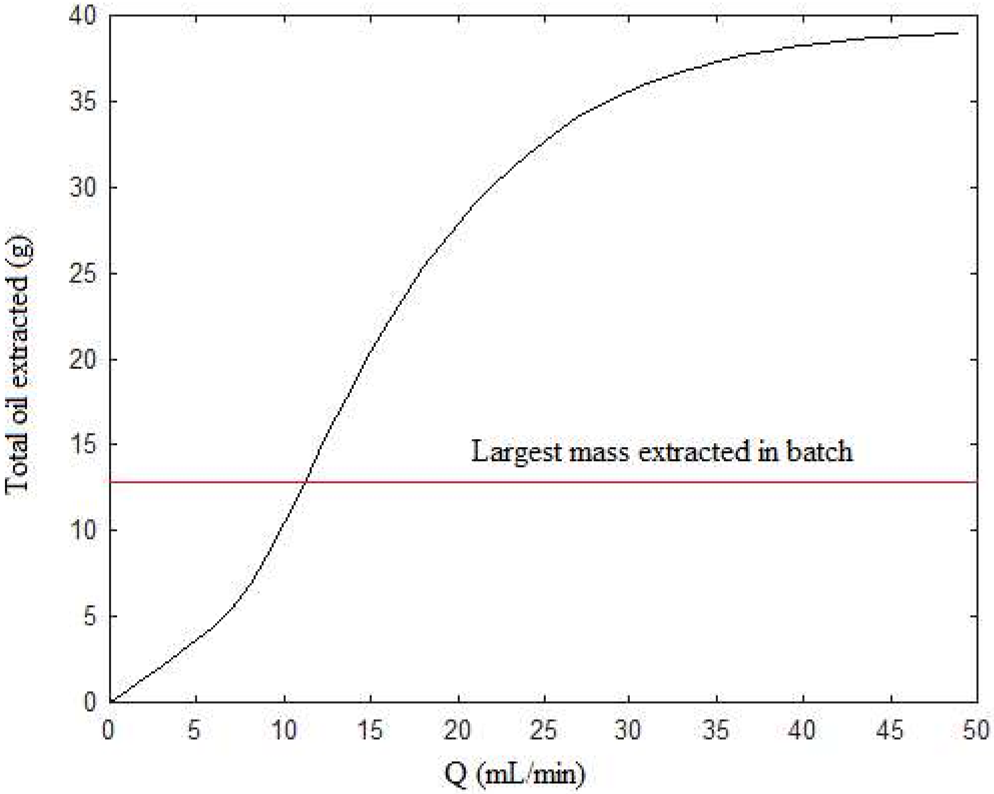

Figure 5. Amount of oil extracted as a function of extraction solvent variation

As shown in the chart of Figure 18, it can be observed that the amount of oil extracted increases more significantly from 0 to approximately 30 ml/min. From 35 mL/min onwards, we notice that this variation becomes progressively smaller, indicating that an increase in flow rate is not necessary beyond a certain value. These simulation results can serve as a basis for the next stage of the work, where experimental values can be adjusted more suitably, such as the solvent flow rate itself. It is also possible to compare the extraction efficiency between fixed bed extraction and batch extraction using the same solvents. Through this comparison, it was observed that the maximum yield obtained in batch extraction process was 12.5 grams (DA SILVA, 2020), while in fixed bed extraction, the values approached 39 grams. This difference in extraction yield can be attributed to the continuous renewal of pure solvent in the fixed bed extraction system, which enhances the extraction efficiency. It is important to note that a more accurate analysis will only be possible after the adjustment of parameters, which will be carried out in the next stages of the work.

As seen in the graph in Figure 5, it can be observed that from 0 to approximately 30 ml/min, the amount of extracted oil increases more significantly. From 35 mL/min onwards, we notice that this variation becomes progressively smaller, indicating system stabilization. It is also possible to compared the extraction efficiency between fixed bed and batch extraction using the same solvents. Through this comparison, it was observed that the maximum yield obtained in the batch extraction process was 12.5 g, while in the fixed bed extraction, the values approached 39 g. This significant difference in extraction yield can be attributed to the continuous renewal of pure solvent in the fixed bed extraction system, which enhances the extraction efficiency.

4. CONCLUSIONS

In conclusion, the mathematical model for fixed-bed extraction proves to be a crucial tool for analyzing the parameters governing the process and a predictive tool for experimental use. This model enables a comprehensive assessment of the extraction process and facilitates a deeper understanding of its dynamics. By comparing the fixed-bed extraction model with the agitation-based solvent extraction model, it was observed that the former yielded higher yields. This can be attributed to the continuous usage of pure solvent in the fixed-bed extraction model, which is not the case in batch extraction. These findings are supported by scientific evidence and reinforce the significance of the fixed-bed extraction model in optimizing extraction processes.

5. ACKNOWLEDGEMENTS

To the Brazilian National Council of Scientific and Technological Development, CNPq (projects 407198/2013-0, 403560/2013-6, 407204/2013-0, 430986/2016-5, 443823/2018-9, 313646/2020-1, 310708/2017-6, 308460/2020-0 and 446787/2020-5), CAPES, Ministry of Education, Brazil (projects 062/14 and CAPES-PRINT-UFPR88881.311981/2018-01), and Araucaria Foundation of Parana, Brazil (project 115/2018, no. 50.579 – PRONEX)..

6. REFERENCES

da Silva, Heloísa, et al. *Comparison of lipid extraction using pure hexane and a mixture of hexane and ethanol as extraction solvents for microalgae*. ABCM, 2021.

Dilay, E., et al. “A Volume Element Model (VEM) for Energy Systems Engineering: A Volume Element Model (VEM) for Energy Systems Engineering”. *International Journal of Energy Research*, vol. 39, nº 1, 2015, p. 46–74.

Hoang, Anh Tuan, et al. “Biofuel Production from Microalgae: Challenges and Chances”. *Phytochemistry Reviews: Proceedings of the Phytochemical Society of Europe*, 2022.

Kumar, S. P. Jeevan, et al. “Green Solvents and Technologies for Oil Extraction from Oilseeds”. *Chemistry Central Journal*, vol. 11, nº 1, 2017, p. 9.

Langmuir, Irving. “The Adsorption of Gases on Plane Surfaces of Glass, Mica and Platinum”. *Journal of the American Chemical Society*, vol. 40, nº 9, 1918, p. 1361–1403.

Letcher, Trevor M. “Global warming, greenhouse gases, renewable energy, and storing energy”. *Storing Energy*, Elsevier, 2022, p. 3–12.

Majumdar, G. C., et al. “Modeling solvent extraction of vegetable oil in a packed bed”. *Journal of the American Oil Chemists’ Society*, vol. 72, nº 9, 1995, p. 971–979.

Morales, C., et al. “Modeling and Simulation of a Liquid Extraction Column with Structured Packing”. *Computers & Chemical Engineering*, vol. 31, nº 12, 2007, p. 1694–1701.

Sathya, Arunachalam Bose, et al. “Microalgal Biofuel Production: Potential Challenges and Prospective Research”. *Fuel (London, England)*, vol. 332, nº 126199, 2023, p. 126199.

7. RESPONSIBILITY NOTICE

The authors are the only responsible for the printed material included in this paper.