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MODELING A GENSET EMISSIONS FIXATION COLUMN AND MICROALGAE GROWTH ENHANCEMENT IN LARGE SCALE PHOTOBIOREACTOR

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Abstract. *Flue gas from several industrial activities is damaging the environment, causing greenhouse effect, global warming, respiratory problems and changing life style in big urban centers. The microalgae cultures appear as solution for mitigation of such gases since their metabolism needs several chemical compounds that are present in these gases, such as nitrogen, phosphorus, carbon and sulfur. Furthermore, microalgae biomass has commercial value due to its high lipid and protein content, having potential commercialization utilization in the industry of biofuels, aliments, pharmaceutical and cosmetic. In order to optimize the process of mitigation of flue gases in microalgae culture to obtain as much biomass as possible, this work develops a mathematical model for genset emissions fixation column, and for predicting the influence of those emissions on microalgae biomass growth in a compact photobioreactor. This mathematical model employs a volume element model (VEM) for subdivide column purification where* CO_2, NO_2, SO_2 *are diluted, and subdivide compact tubular photobioreactor of microalgae culture. A microalgae culture with 3000* $L.h^{-1}$ *of volumes is capable to minimize 99 % of flue gases until a 40000* $L.h^{-1}$ *gas flow, and with a 35000* $L.h^{-1}$ *gas flow obtain the best microalgae grown (0.87* $g.L^{-1}$*). Within this model is possible to analyze a wide range of parameters, such as gas flow rate, concentration rate and exposition time of flue gas to obtain the maximum microalgae biomass growth in culture specific volumes.*

Keywords: *Mathematical model, flue gases, column purification, microalgae culture, photobioreactor.*

1. INTRODUCTION

The continuous flue gas emissions are increasing each year by the burning fossil fuels for electric energy generation and several industrial activities (Markandya and Wilkinson, 2007). Flue gas from combustion processes contains several compounds: those not restricted by legislation: N_2, O_2 and H_2O; and those restricted by legislation and: CO_2, NO_x, SO_x, CO, C_xH_y (Bharathiraja *et al.,* 2015).The gas emission contribute to intensify the greenhouse effect, global warming, acid rain and it exposure can affect human health with chronic effects as respiratory problems and cancer risk (Markandya and Wilkinson, 2007).

Because of the major contribution of burning fossil fuels utilized in electricity generation, there has been interest in the potential of these gas capture and storage to mitigate climate change (Van Den Hende *et al*., 2012). These gases are a resource yet to be fully utilized in microalgal biotechnology, not only to moderate the anthropogenic effects on our climate, but also to steer microalgal resource management towards innovative applications of microalgal biomass compounds (Becker, 1994). The metabolism of microalgae can be autotrophic, heterotrophic or mixotrophic (Hamed, 2016). Since the autotrophic microalgae are aquatic photosynthetic organisms that use CO_2 or HCO_3 as carbon source and nutrients like nitrogen, phosphorus, potassium and sulfur as well as other macronutrients (Na, K, Ca, Mg, Cl) and micronutrients (Fe, Zn, Mn, Br, Si, B, Mo, V, Sr, Al, Rb, Li, Cu, Co, I, Se, Ni) (Kroumov. *et al*., 2016). The interaction of flue gas compounds solubilized in aqueous medium and microalgae can be a way of mitigate the flue gas emission to the atmosphere and grow biomass (Aslam, A. *et al*., 2017). Furthermore, the microalgae biomass has commercial value due to its high lipid and protein content, having potential commercialization utilization in the industry of biofuels, aliments, pharmaceutical and cosmetic (Pires, *et al*., 2017). The microalgae cultures in commercial scale can be cultivated in open system, closed system or hybrid system. The open system is divided into natural ponds, artificial pond and raceway ponds. In closed system are used photobioreactor in deferent forms: tubular, vertical column, flat-plate and other (Hamed, 2016).

The aim of this work is to develop a mathematical model for genset emissions fixation column, and for predicting the influence of those emissions on microalgae biomass growth in a compact photobioreactor.

2. COMPUTATIONAL PROCEDURE

The mathematical model for computational simulation of this system is developed with volume element model (VEM) (Vargas, JVC. *et al*., 2001); the system is divided into two control volumes shown in

Figure 1. The first control volume (CV1) is the circular column purification with metal wall; this one has two flows in countercurrent: the flue gas and microalgae culture. The second control volume (CV2) is a compact tubular photobioreactor with transparent wall tubes. Each control volume is subdivided into volume elements, analyzing each one the mass transfer between flue gas and microalgal culture, and the influence in microalgae grow kinetic.

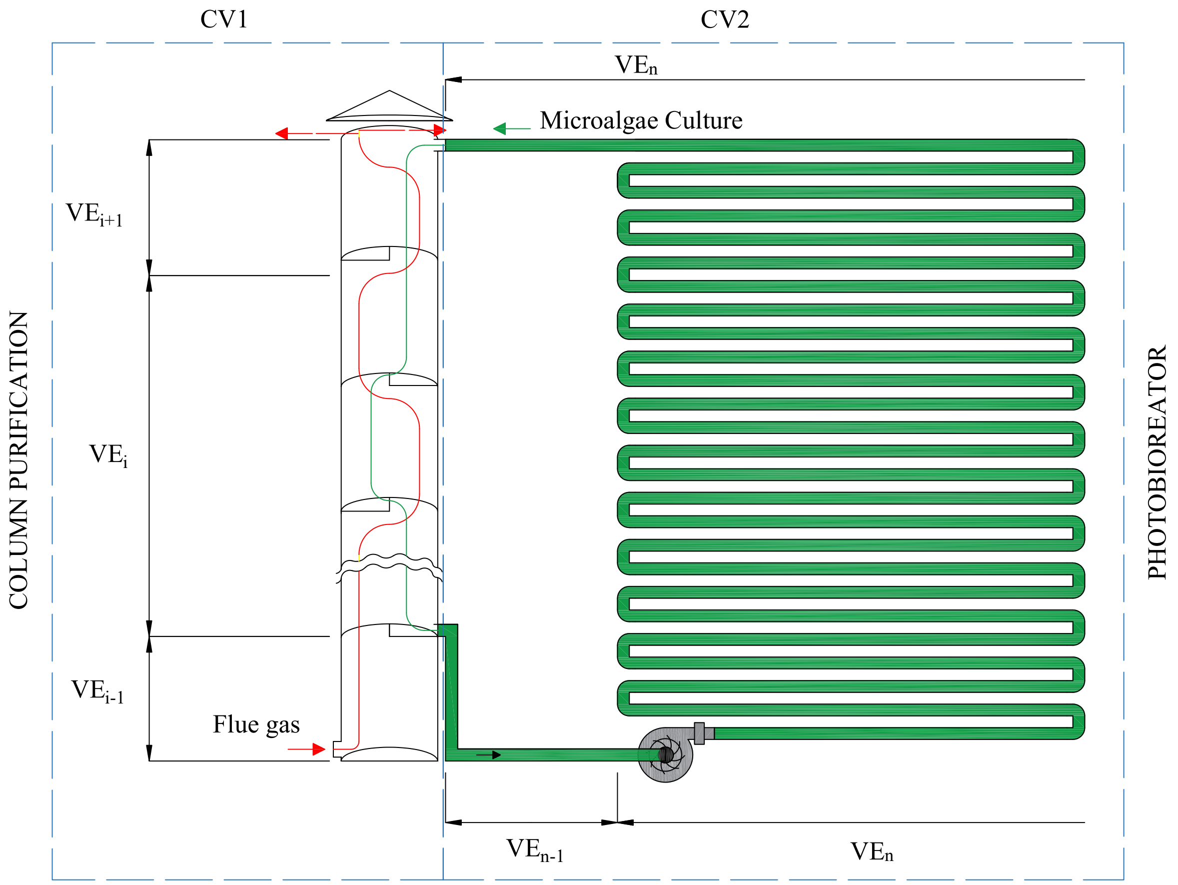

Figure 1. Diagram of modeling system

Assumptions

- Relevant gases for microalgae mitigation: carbon dioxide (CO_2), nitrogen dioxide (NO_2), sulfur dioxide (SO_2).
- Henry's law gives the mass transference.
- Microalgae with autotrophic metabolism.
- The equation for flue gases conversion by microalgae mechanism is proposed by Pruvost. *et al.* (2009).
- The microalgae specific grow velocity is dependent of temperature, light intensity, nutrients (CO_2, NO_2, SO_2), in accord with Balmant. *et al*. (2011).
- The microalgae grow is only in the compact photobioreactor for photosynthesis process due light capture in transparent tube wall.
- Each 8 hours represent one day of exposition to flue gases in microalgae culture medium.

Chemical reaction of aqueous phase of culture whit CO_2, NO_2, and SO_2 gas phase (Balmant, *et al*., 2016) are showed in the following equations:

$$CO_2 + H_2O \xleftrightarrow{K_{CO_2}} HCO_3^- + H^+ \tag{1}$$

$$NO_2 + H_2O \xleftrightarrow{K_{NO_2}} NO_3^- + H^+ \tag{2}$$

$$SO_2 + H_2O \xleftrightarrow{K_{SO_2}} SO_3^- + 2H^+ \tag{3}$$

Bioprocess of microalgae convert nutrients and light in biomass and oxygen:

$$CO_2 + N_{tot} + S_{tot} + H_2O \xleftrightarrow{light} CHONS + O_2 \tag{4}$$

The specific grow velocity is dependent of temperature, light intensity, nutrients:

$$\mu = \mu_{max} \cdot \mu(T) . \mu(I_0) . \mu(CO_2) . \mu(N_{tot}) . \mu(S_{tot}) \tag{5}$$

$$\mu(T) = a.T^2 + b.T^2 + c \tag{6}$$

$$\mu(I_0) = \frac{I_0}{\left(Ks_{I_0} + I_0 + \frac{I_0^{\,2}}{Ki_{I_0}} \right)} \tag{7}$$

$$\mu(CO_2) = \frac{[CO_2]}{\left(Ks_{CO_2} + [CO_2] + \frac{[CO_2]^2}{Ki_{CO_2}} \right)} \tag{8}$$

$$\mu(N_{tot}) = \frac{[N_{tot}]}{\left(Ks_{N_{tot}} + [N_{tot}] \right)} \tag{9}$$

$$\mu(S_{tot}) = \frac{[S_{tot}]}{\left(Ks_{S_{tot}} + [S_{tot}] \right)} \tag{10}$$

Variables of mass balance:

$$ACO_2 = \lfloor CO_2 \rfloor_{in} - \lfloor CO_2 \rfloor_{out} \tag{11}$$

$$ANO_2 = \lfloor NO_2 \rfloor_{in} - \lfloor NO_2 \rfloor_{out} \tag{12}$$

$$ASO_2 = \lfloor SO_2 \rfloor_{in} - \lfloor SO_2 \rfloor_{out} \tag{13}$$

$$BCO_2 = \lfloor CO_2 \rfloor_{out} \cdot R \cdot Temp \cdot H_{CO_2} - \lfloor CO_2 \rfloor_{out} \tag{14}$$

$$BNO_2 = \lfloor NO_2 \rfloor_{out} \cdot R \cdot Temp \cdot H_{NO_2} - \lfloor NO_2 \rfloor_{out} \tag{15}$$

$$BSO_2 = \lfloor SO_2 \rfloor_{out} \cdot R \cdot Temp \cdot H_{SO_2} - \lfloor SO_2 \rfloor_{out} \tag{16}$$

$$DHCO_3^- = \left[HCO_3^-\right]_{in} - \left[HCO_3^-\right]_{out} \tag{17}$$

$$DNO_3^- = \left[NO_3^-\right]_{in} - \left[NO_3^-\right]_{out} \tag{18}$$

$$DSO_3^- = \left[SO_3^-\right]_{in} - \left[SO_3^-\right]_{out} \tag{19}$$

$$DH^+ = \left[H^+\right]_{in} - \left[H^+\right]_{out} \tag{20}$$

2.1 The mass balance for reaction components in column purification CV1

Equations below show the mass transfer for gas phase, the mass transfer in liquid phase and the mass balance for microalgae biomass culture in CV1: with negligible biomass production, since microalgae photosynthesis does not occurs in the dark column.

$$\frac{d\lfloor CO_2 \rfloor_{gas}}{dt} = \left(ACO_2\right)_{gas} \cdot \frac{Q_{gas}}{V_{liq}} + Kla_{CO_2} \cdot \left(BCO_2\right)_{gas} \tag{21}$$

$$\frac{d\lfloor NO_2 \rfloor_{gas}}{dt} = \left(ANO_2\right)_{gas} \cdot \frac{Q_{gas}}{V_{liq}} + Kla_{NO_2} \cdot \left(BNO_2\right)_{gas} \tag{22}$$

$$\frac{d\lfloor SO_2 \rfloor_{gas}}{dt} = \left(ASO_2\right)_{gas} \cdot \frac{Q_{gas}}{V_{liq}} + Kla_{SO_2} \cdot \left(BSO_2\right)_{gas} \tag{23}$$

$$\frac{d\lfloor CO_2 \rfloor_{aq}}{dt} = \left(ACO_2\right)_{aq} \cdot \frac{Q_{liq}}{V_{liq}} + Kla_{CO_2} \cdot \left(BCO_2\right)aq - K_{CO_2}\left[CO_2\right]_{aq,out} \tag{24}$$

$$\frac{d\left[HCO_3^-\right]_{aq}}{dt} = \left(DHCO_3^-\right) \cdot \frac{Q_{liq}}{V_{liq}} + K_{CO_2}\left[CO_2\right]_{aq,out} \tag{25}$$

$$\frac{d[NO_2]_{aq}}{dt} = (ANO_2)_{aq} \cdot \frac{Q_{liq}}{V_{liq}} + Kla_{NO_2} \cdot (BNO_2)aq - K_{NO_2} [NO_2]_{aq,out} \tag{26}$$

$$\frac{d\left[NO_3^-\right]_{aq}}{dt} = \left(DNO_3^-\right) \cdot \frac{Q_{liq}}{V_{liq}} + K_{NO_2} [NO_2]_{aq,out} \tag{27}$$

$$\frac{d[SO_2]_{aq}}{dt} = (ASO_2)_{aq} \cdot \frac{Q_{liq}}{V_{liq}} + Kla_{SO_2} \cdot (BSO_2)aq - K_{SO_2} [SO_2]_{aq,out} \tag{28}$$

$$\frac{d\left[SO_3^-\right]_{aq}}{dt} = \left(DSO_3^-\right) \cdot \frac{Q_{liq}}{V_{liq}} + K_{SO_2} [SO_2]_{aq,out} \tag{29}$$

$$\frac{d\left[H^+\right]}{dt} = \left(DH^+\right) \cdot \frac{Q_{liq}}{V_{liq}} + K_{CO_2} [CO_2]_{aq,out} + K_{SO_2} [SO_2]_{aq,out} + K_{NO_2} [NO_2]_{aq,out} \tag{30}$$

The mass balance for microalgae biomass growth:

$$\frac{d[X]}{dt} = \frac{Q_{liq}}{V_{liq}} \left(X_{in} - X_{out}\right) \tag{31}$$

2.2 Mathematical model of photobioreactor CV2.

The mass balance for all components reaction and the kinetic microalgae growth due to photosynthesis process and nutrient consumption are presented in these equations related:

$$\frac{d[CO_2]_{aq}}{dt} = (ACO_2)_{aq} \cdot \frac{Q_{liq}}{V_{liq}} - K_{CO_2} [CO_2]_{aq,out} \tag{32}$$

$$\frac{d\left[HCO_3^-\right]_{aq}}{dt} = \left(DHCO_3^-\right) \cdot \frac{Q_{liq}}{V_{liq}} + K_{CO_2} [CO_2]_{aq,out} - Y_{\frac{CO_2}{X}} \cdot \mu . X_{out} \tag{33}$$

$$\frac{d[NO_2]_{aq}}{dt} = (ANO_2)_{aq} \cdot \frac{Q_{liq}}{V_{liq}} - K_{NO_2} [NO_2]_{aq,out} \tag{34}$$

$$\frac{d\left[NO_3^-\right]_{aq}}{dt} = \left(DNO_3^-\right) \cdot \frac{Q_{liq}}{V_{liq}} + K_{NO_2} [NO_2]_{aq,out} - Y_{\frac{NO_2}{X}} \cdot \mu . X_{out} \tag{35}$$

$$\frac{d[SO_2]_{aq}}{dt} = (ASO_2)_{aq} \cdot \frac{Q_{liq}}{V_{liq}} - K_{SO_2} [SO_2]_{aq,out} \tag{36}$$

$$\frac{d\left[SO_3^-\right]_{aq}}{dt}=\left(DSO_3^-\right).\frac{Q_{liq}}{V_{liq}}+K_{SO_2}\left[SO_2\right]_{aq,out}-Y_{\frac{SO_2}{X}}.\mu.X_{out} \quad (37)$$

$$\frac{d\left[H^+\right]}{dt}=\left(DH^+\right).\frac{Q_{liq}}{V_{liq}}+K_{CO_2}\left[CO_2\right]_{aq,out}+K_{SO_2}\left[SO_2\right]_{aq,out}+K_{NO_2}\left[NO_2\right]_{aq,out}-Y_{H^+/X}.\mu.X_{out} \quad (38)$$

The mass balance for grow microalgae biomass

$$\frac{d[X]}{dt}=\frac{Q_{liq}}{V_{liq}}\left(X_{in}-X_{out}\right)+\mu.X_{in} \quad (39)$$

Runge-Kutta (Vargas & Araki, 2017) method was programed in a FORTRAN® language program for the differential equation solutions. The initial model conditions, parameters and values for simulation are detailed in Tab. 1.

Table 1. Parameters and values used in this modeling

Symbol	Description	Value
$[CO_2]_{gas,in}$	Molar concentration of CO_2 inlet	$5x10^{-3}$[mol.L^{-1}]
$[NO_2]_{gas,in}$	Molar concentration of NO_2 inlet	$8x10^{-6}$[mol.L^{-1}]
$[SO_2]_{gas,in}$	Molar concentration of SO_2 inlet	$4x10^{-6}$[mol.L^{-1}]
Kla_{CO2}	CO_2 mass transfer coefficient	10-10000[h^{-1}]
Kla_{NO2}	NO_2 mass transfer coefficient	10-10000[h^{-1}]
Kla_{SO2}	SO_2 mass transfer coefficient	10-10000[h^{-1}]
H_{CO2}	Henry´s law constant of CO_2	$3.4x10^{-2}$[mol.L^{-1}atm^{-1}]
H_{NO2}	Henry´s law constant of NO_2	$1x10^{-2}$[mol.L^{-1}atm^{-1}]
H_{SO2}	Henry´s law constant of SO_2	1.24[mol.L^{-1}atm^{-1}]
K_{CO2}	CO_2 forward reaction constant	60×10^2[h^{-1}]
K_{NO2}	NO_2 forward reaction constant	10-10000[h^{-1}]
K_{SO2}	SO_2 forward reaction constant	10-10000[h^{-1}]
R	Gas constant	0.082057[atm.L.mol^{-1}.K^{-1}]
Q_{liq}	Volumetric flow of culture liquid	3000[L.h^{-1}]
V_{gas}	Gas volume	1000[L]
V_{liq}	Liquid volume	10000[L]
Temp	Temperature of control volume	300[K]
μ_{max}	Maximum specific growth rate	0.56[L.h^{-1}]
$Y_{CO2/X}$	CO_2 yield coefficient	1.88[g.g^{-1}]
$Y_{NO2/X}$	NO_2 yield coefficient	0.384[g.g^{-1}]
$Y_{SO2/X}$	SO_2 yield coefficient	0.043[g.g^{-1}]
$Y_{H^+/X}$	H^+ yield coefficient	0.0884[g.g^{-1}]
I_0	Light intensity	400[W.m^{-1}]
X_0	Initial biomass concentration	0.30[g.L^{-1}]
M_{CO2}	molar mass of CO_2	44.01[g.mol^{-1}]
M_{NO2}	molar mass of NO_2	44.012[g.mol^{-1}]
M_{SO2}	molar mass of SO_2	64.065[g.mol^{-1}]

3. RESULT AND DISCUTION

The simulation results for a parametric analyze of inlet gas flow (Q_{gas}) affecting the dilution of CO_2, NO_2 and SO_2 in the culture medium, as well as the microalgae biomass growth, this are shown in Tab. 2. The analysis is performed for 32 hours experiments, which represents 4 days of flue gases in microalgae culture. Under inlet gas flow rate lower than 40000 L.h^{-1} at the purification column, the flue gas dilution into the culture medium is 99 % greater than any other gas flow rate. Under 35000 L.h^{-1} of gas flow rate, the microalgae biomass growth (X) into the culture medium is higher than any other flow rate as well.

Table 2. Parametric analyses of flue gas flow in the column purification.

Q_{gas}(L.h^{-1})		4000	30000	35000	36250	37500	40000	400000	40000000
CO_2 gas (mol.L^{-1})	input	5.00E-03	5.00E-03	5.00E-03	5.00E-03	5.00E-03	5.00E-03	5.00E-03	5.00E-03
	output	1.02E-11	4.23E-09	6.69E-09	7.43E-09	8.22E-09	9.95E-09	7.21E-06	3.98E-03
Gas dilution		100.00 %	100.00 %	100.00 %	100.00 %	100.00 %	100.00 %	99.86 %	30.00 %
NO_2 gas (mol.L^{-1})	input	8.00E-06	8.00E-06	8.00E-06	8.00E-06	8.00E-06	8.00E-06	8.00E-06	8.00E-06
	output	4.29E-11	1.31E-08	1.96E-08	2.15E-08	2.39E-08	2.77E-08	2.10E-06	7.86E-06
Gas dilution		100.00 %	99.81 %	99.79 %	99.79 %	99.77 %	99.73 %	73.75 %	2.50 %
SO_2 gas (mol.L^{-1})	input	4.00E-06	4.00E-06	4.00E-06	4.00E-06	4.00E-06	4.00E-06	4.00E-06	4.00E-06
	output	1.13E-11	3.68E-09	5.58E-09	6.12E-09	6.70E-09	7.94E-09	8.21E-07	3.91E-06
Gas dilution		100.00 %	99.89 %	99.88 %	99.88 %	99.87 %	99.84 %	79.48 %	2.50 %
X(g.L^{-1})		0.37	0.86	**0.87**	0.86	0.73	0.63	0.33	0.30

For 35000 L.h^{-1} of flue gas flow, the composition (C) of CO_2, NO_2 and SO_2 at outputs of the column purification, presented in Fig. 2, are in permanent regime at 0.276, 3.102 and 3.006 minutes, respectively.

The microalgae growth (X) is presented in Fig. 3. Under 35000 L.h^{-1} of inlet gas flow rate at the column purification the culture exponential phase occurs on 3th day (24 h) followed by the stationary phase. Figure. 4 represent the simulation results for the flue gases consumption into the culture medium during 4 days (32 h), in which CO_2 concentration is constant for 20 h due to the microalgae consumption. The increase of carbon dioxide concentration in the culture from 20 h onward happened because culture medium becomes saturated with such gas and microalgae no longer can absorb it. During the 32 hours, the NO_2 is well sequestrated by microalgae. The SO_2 concentration is constant in the culture medium due to the low consumption on the microalgae and the low concentration on the inlet flue gas.

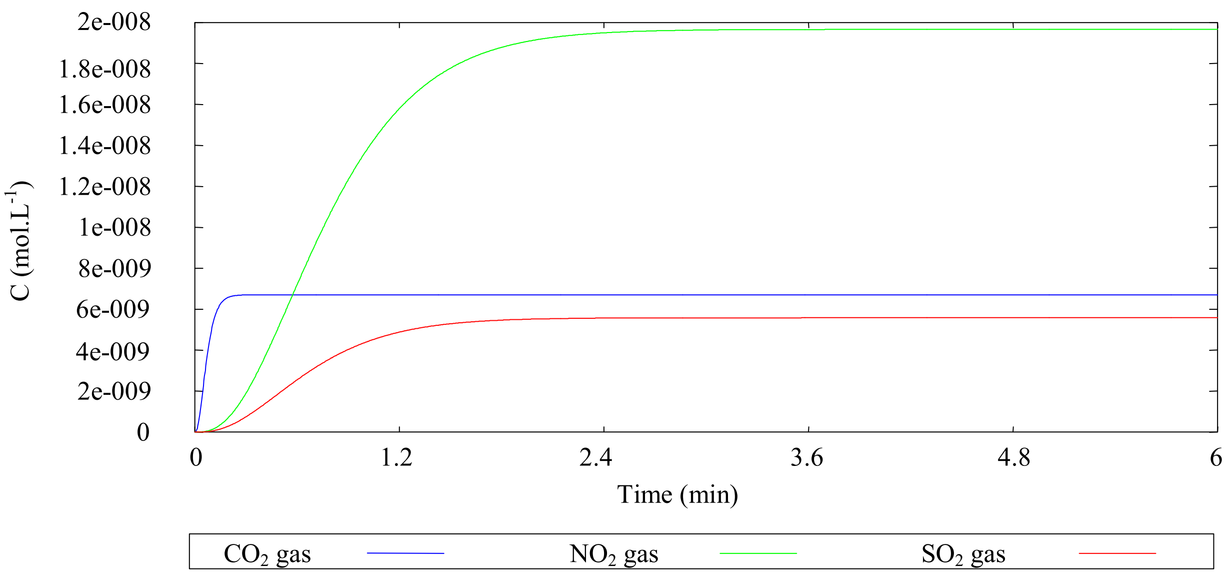

Figure 2. Exhaust gases at the column purification

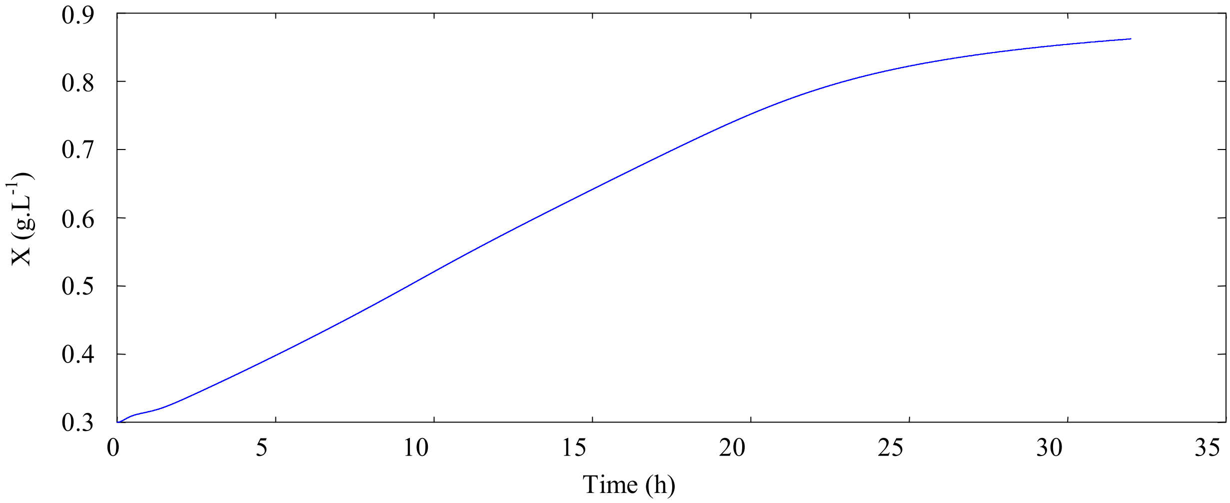

Figure 3. Microalgae biomass growth in a culture medium

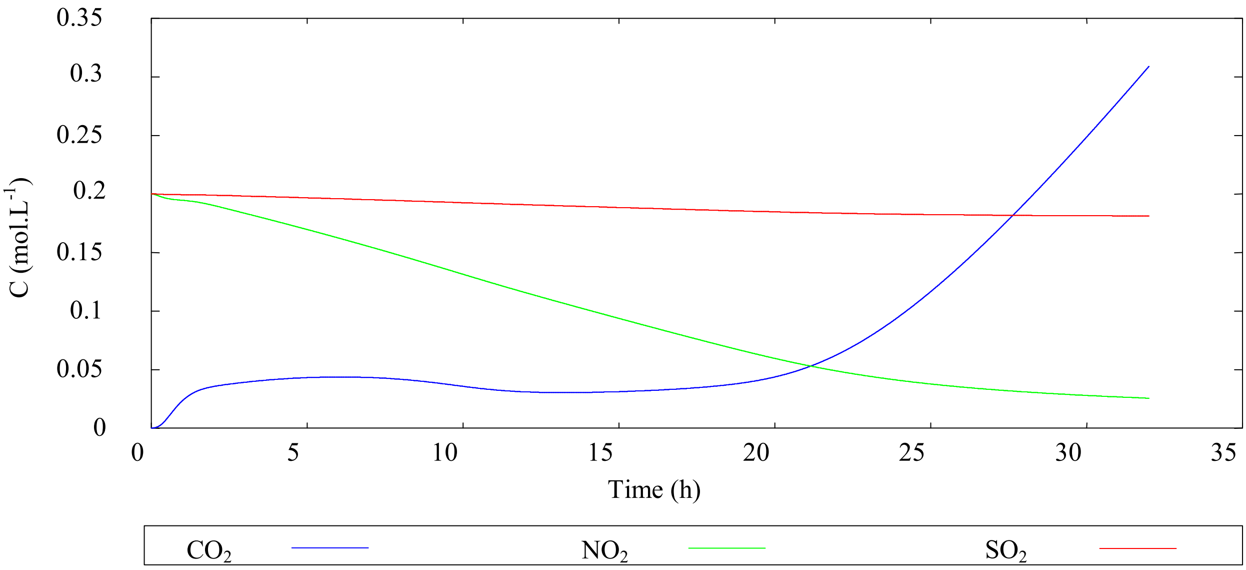

Figure 4. Consumption of gases in the culture medium

4. CONCLUSION

The mathematical model developed in this works has the capacity of predicting microalgae sequestration of flue gases and biomass grown under flue gas influence. Within this model was possible to analyze a wide range of parameters, such as gas flow rate, concentration rate and exposition time of flue gas to obtain the maximum microalgae biomass concentration in culture specific volumes. The evaluation for the microalgae culture with 3000 $L.h^{-1}$ of volume was able to capture 99 % of flue gas emission with a lower gas flow until 40000 $L.h^{-1}$. The best microalgae biomass growth in this simulation was found for 35000 $L.h^{-1}$ inlet gas flow. Furthermore, as we reduce the inlet gas flow the culture medium lacks elementary nutrients for microalgae metabolism and ends up being inhibited. Gas flow higher than 35000 $L.h^{-1}$ inhibits biomass growth.

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