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ABSORPTION RATE OF CO2 IN A BUBBLE COLUMN: A NUMERICAL MODELING USING OPENFOAM

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Abstract. *Salt fouling of carbonate origin is a major cause of problems related to the flow guarantee in petroleum industry and, in extreme cases, may lead to complete interruption of oil production. Dissolved* CO_2 *(carbon dioxide) in extracted species is the main triggering parameter identified as responsible for carbonate precipitation. With this in mind, this article aims to validate a model to evaluate the* $CO_{2(g)}$ *(gaseous state) absorption mechanism in a water column through CFD (Computational Fluid Dynamics) simulations in OpenFOAM environment using the multiphaseEulerFoam application, obtaining the numerical results of solubility, concentration and the residence time curve under specified pressure and temperature (p-T) conditions. Both phases are treated as multi-components and as the simulation progresses, the liquid phase becomes more saturated with gas due to mass transfer owing to Fick's Law and Henry's Law. The results related to* CO_2 *solubility in water validates the Henry's Law application (under 5 - 50 bar), reaching an error less than 0.5% regarding theoretical results with constant mass flow rate. The residence-time curve behavior is completely predicted by the mass-transfer model: decrease in solubilization time is expected for higher phases velocity as it reduces contact time and low pressures increase the absorption rate due to small number of molecules collision. The adopted theoretical model explained the numerical results with deviations smaller than 12%.*

Keywords: *cfd, gas absorption, multiphase flow, residence time, solubility.*

1. INTRODUCTION

Oil demand rise steadily and it remains the leading source of consumption in global energy matrix (IEA, 2020) , thus it is necessary to understand the mechanisms involving its production and extraction processes to optimize the world supply demand since it is a limited element. Salt fouling of carbonate origin is the accumulation of materials on surfaces and it is a major cause of problems related to the flow guarantee, may cause safety valves and pipes blockages or, in extreme cases, may lead to the economic unfeasibility of oil production or even its complete interruption (Cosmo, 2013) .

It is important to note that costs to remove fouling are extremely high,about US$ 1.4 billion/year in global oil industry (Frenier and Ziauddin, 2008) , therefore, understanding the oil production processes becomes highly important to the improvement of prevention techniques and fouling removal.

$CO_{2(g)}$ solubility is the main triggering parameter identified as responsible for carbonate precipitation, substantially contributing to salt crystallization, among 60% to 90% of the total precipitated content, due to its ability to acidify the medium (Cosmo, 2013) . High pressures in well conditions solubilize the gas in water, acidifying the medium and keeping the salts dissolved. Disturbances due to the very dynamism of production, as phases flow and the mixing of fluids in conjunction with the pressure drop caused by the completion elements and friction alter the equilibrium state of the dissolved species in the reservoir environment. $CO_{2(aq)}$ (aqueous phase) is transformed to the $CO_{2(g)}$ by flashing mechanism (or desorption) which disfavors the solubilization of salts and implies their precipitation (Cosmo, 2013) .

During absorption process CO_2 rich gas is contacted directly with absorbent, in this case, plain water. During this process, CO_2 is transferred from gas bulk into liquid body (Treybal, 1981) . This condition continues until liquid reaches a saturated point where absorption can no longer take place since absorbent has already lost its absorption capability. It is noteworthy that in multiphase flows, the species absorption rate is controlled not only by system pressure and temperature, but also by mass transfer resistance, concentration gradients, reaction kinetics, activation energy, etc (Whitman, 1923) .

The species transport between gaseous phase (solute) to the liquid phase (solvent) may occurs by diffusion mechanism (physical absorption) and / or reactions (chemical absorption). Current data explicitly indicate for majority cases that investigated rate of absorption from a gas phase to a liquid phase is limited by the diffusion process. Any other reaction that may occur is much faster with respect to the speed of diffusion so that it has no necessary effect on the diffusion

(Whitman, 1923) .

Some models were developed to evaluate the flux of solute transferred between the gas phase and the liquid phase: two-film Model (Whitman, 1923) ; penetration Model (Higbie, 1935) ; surface renewal Model (Danckwerts, 1951) .

All three models aim to express the mass transfer coefficient, $k_{s,i}$.

2. MATHEMATICAL MODELING

The CO_2 solubility data in water are obtained through the basic model of the following equilibrium reaction (Diamond and Ankinfiev, 2003) :

$$CO_{2(g)} \leftrightarrow CO_{2(aq)} \tag{1}$$

The influence of CO_2 hydrolysis products, that is, bicarbonate ion (HCO_3^-) and carbonate ion (CO_3^{2-}), in the $CO_{2(aq.)}$ solubility is insignificant in the p-T region of interest. The CO_2 hydrolysis reaction is extremely slow, so slow in fact that it barely affects the CO_2 absorption rate at all (Seagraves and Weiland, 2009) . The solubility implied by equilibrium reaction (1) can be expressed in terms of the Henry's law constant as follows:

$$x_{CO2_{(aq)}} = \frac{f^0_{CO2(p,T)} y \gamma_y}{K^{pc}_{(p,T)} \gamma_{CO2_{(aq)}}} \tag{2}$$

where $x_{CO2_{(aq)}}$ and y are the mole fractions of CO_2 in the aqueous and non-aqueous phases, respectively, $K^{pc}_{p,T}$ (in MPa) is the Henry constant of CO_2 in pure water ($H_{2(l)}O$) on a mole fraction basis at specified p-T conditions, $f^0_{CO2(p,T)}$ is the fugacity (in MPa) of pure CO_2 at specified p-T conditions, $\gamma_{CO2_{(aq)}}$ is the unsymmetric (Henry's law) activity coefficient of aqueous CO_2 and γ_y is the symmetric (Raoult's law) activity coefficient of CO_2 in the non-aqueous phase. Both activity coefficient are assumed equal to unity. All variables can be obtained through the CO2SOL software that implements the equation of state for CO_2 solubility in pure water.

The multiphaseEulerFoam is the single solver that allows evaluating the mass transfer in multiphase flows, may enabling phases composed of more than one species. Choosing the two-phase system type as interfaceCompositionPhaseChangeTwoPhaseSystem adds the mass transfer effect to the OpenFOAM basic multiphase model (OpenFOAM, 2020) . The mass transfer between phases is calculated according to the interface composition model, where the driving force is the concentration gradient. The species transport equation is needed to describe the concentration of a s-species within a i-phase to further define the mass transfer rate (OpenFOAM, 2020) . In OpenFOAM's enviroment is defined as follows:

$$\frac{\partial(\alpha_i \rho_i Y_s)}{\partial t} + \nabla.(\alpha_i U_i \rho_i Y_s) - \nabla.(\alpha_i D_{s,i} \nabla(Y_s)) = \dot{R}_i + \frac{dm_s}{dt} \tag{3}$$

here the subscript i refers to phase i and s refers to species s. U is velocity (m/s), α is volume fraction, ρ is density (kg/m³), Y is the concentration (kg/kg) and $D_{s,i}$ is the mass difusivity (m^2/s) of species s in phase i.

In a two-phase case where each phase has two components, each phase will have two species transport equations, therefore having four species transport equations. In this study, reactions are disregarded, thus $\dot{R}_i$ which represents the species rate of variation due reaction is equal to zero.

The mass transfer rate of species s dm_s/dt is described by Eq. (4) below:

$$\frac{dm_s}{dt} = k_{s,i} a (Y_{s,sat} - Y_s) \tag{4}$$

where a is the interfacial area (m^2) and the subscript sat refers to saturation condition determined by Henry´s Law in Eq. (2).

The velocity field U are obtained through the continuity and momentum conservation equations, since they are coupled by the volume fraction. The Y field affects the volume fraction (due gas absorption) and, at some level, α affects the U field since it is found in the convective term from Eq. (3). Equation (5) and Eq. (6) express the continuity and momentum conservation equations, respectively. In this study, the process is considered isothermal, and the energy conservation equation is dispensed with.

$$\frac{\partial(\alpha_i)}{\partial t} + \nabla.(\alpha_i U_i) = 0 \tag{5}$$

$$\frac{\partial(\alpha_i U_i)}{\partial t} + \nabla.(\alpha_i U_i U_i) + \nabla.(\alpha_i R_i^{eff}) = -\frac{\alpha_i}{\rho_i}\nabla p + \alpha_i g + \frac{M_i}{\rho_i} \tag{6}$$

where R_i^{eff} is the combined viscous and Reynolds tensor, p is pressure (N/m²), g is the gravitational constant ($g = 9.81 m/s^2$) and M_i is the average moment transfer term between phases (e.g. drag, lift, virtual mass, turbulent dispersion, surface tension, etc.) and it is necessary to ensure momentum conservation.

M.Tokumura, M. Baba, H.T. Znad and Y. Kawase (Tokumura *et al.*, 2006) develop a theoretical model of dynamics of CO_2 absorption in a completely mixed bubble column filled with water and supporting experimental data. Effects of CO_2 injection rate, salinity and temperature was considered as variables. The model may be written in a similar structure to Eq. (4):

$$\frac{dC_s}{dt} = k_{s,i}a(C_{s,sat} - C_s) + EHP \tag{7}$$

where EHP are the equations for the material balances of hydrolysis products and C is the solute concentration (kg/m³). Here, the subscript s refers to CO_2 species and i to liquid (or water) phase.

The analytical solution of the mass transfer equation (Eq. (6)) is shown bellow in Eq. (7) omitting the EHP terms for its insignificance in the regions of interest:

$$\frac{C_s(t)}{C_{s,sat}} = 1 - e^{-k_{s,i}at} \tag{8}$$

The liquid-side volumetric mass transfer coefficients, $k_{s,i}a$, were measured for oxygen transfer from air to seawater and tap water. The value of $k_{s,i}a$ for oxygen increased as U_g (gas phase velocity) increased. From the experimental data presented, the authors (Tokumura *et al.*, 2006) obtained the following correlation for CO_2 mass transfer, in which the volumetric mass transfer coefficient was corrected for diffusivities, according to Higbie's penetration theory (Higbie, 1935) :

$$(k_{s,i}a)_{CO_2} = \left(\frac{D_{CO_2,H_2O}}{D_{O_2,H_2O}}\right)^{0.5} (k_{s,i}a)_{O_2} = \left(\frac{D_{CO_2,H_2O}}{D_{O_2,H_2O}}\right)^{0.5} (0.19{U_g}^{0.44}) \tag{9}$$

The diffusivity values for CO2 and O2 (D_{CO_2} and D_{O_2}, respectively) were taken from the literature. It was assumed that their ratio (D_{CO_2}/D_{O_2}) in seawater is same as that in tap water, as well as in the study: "Kinetics of removal of carbon dioxide by aqueous 2-amino-2-methyl1,3-propanediol" (Yoon *et al.*, 2003) . The theoretical model estimated the amount of DIC (total dissolved inorganic carbon), but in this work just the CO_2 was considered.

3. CASE SETUP

The problem is defined in a bi-dimensional vertical column with a portion of stationary liquid composed of pure water. The column has the following dimensions: 0.5 m high and 0.2 m long and the thickness of 0.02 m is only defined to determine the mass of water in the column (and thus evaluate the total mass of dissolved gas). Liquid phase occupies 40% of the total column volume. A constant gas injection rate $\dot{m}_g$ = 60 kg/h of CO_2 is made at the bottom of the column through an orifice (area A_o = 0,8 cm^2), in a vertically ascending direction.

The domain has 1550 cells and is discretized with 25 cells in the direction of the length and 62 cells in the direction of the height. Figure 1 presents the basic schematic of the problem under analysis and its domain is described above.

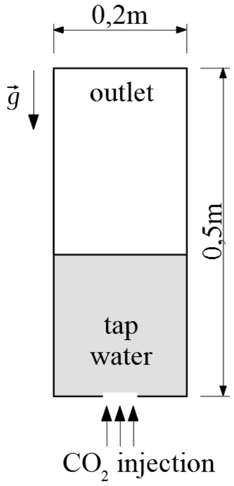

Figure 1. Schematic diagram of the water column.

Both phases are treated as multi-components and it is expected that, during the simulation progress, the water will become more saturated with the gas.

Accurate thermophysical properties of liquid and gas phases (density, viscosity, thermal conductivity, specific heat, etc) was obtained in The NIST (National Institute of Standards ans Technology) Chemistry WebBook NIST (1997) that provides convenient access to a variety of physical and chemical property data on well defined chemical species and reactions. All properties are evaluated in isothermal conditions of T = 298.15K.

Table 1 below describes all the initial variables used to run the simulation and their significations. Note: p and U_g (Eq.10) are defined for each case, where

$$U_g = \frac{\dot{m}_g}{\rho_g A_o} \tag{10}$$

by continuity equation.

Table 1. Boundary conditions variables defined in t = 0 s directory and its values.

Variable	Signification	Initial Value
CO2.gas	CO2 mass fraction in gas phase	fixed value = 1
CO2.liquid	CO2 mass fraction in liquid phase	fixed value = 0
alpha.gas	gas phase volume fraction	fixed value = 0.6
alpha.liquid	liquid phase volume fraction	fixed value = 0.4
p	pressure	calculated
p_rgh	pressure minus hidrostatic pressure	fixed value = p
U.gas	gas phase velocity	fixed value = U_g
U.liquid	liquid phase velocity	fixed value = 0
H2O.gas	water mass fraction in gas phase	fixed value = 0
H2O.liquid	water mass fraction in liquid phase	fixed value = 1

4. RESULTS AND DISCUSSION

Initially, the numerical results for solubility is obtained. All solubility values were compared with the values of the CO2SOL software, fruit of the article: The solubility of CO2 in water from -1.5 to 100ºC and 0.1 to 100 MPa: an evaluation of literature data and thermodynamic modeling (Diamond and Ankinfiev, 2003) . The first simulation´s objective is to validate the Henry's Law application by comparing numerical predictions and theoretical data. In this way, the same configuration was run by varying the system pressure from 5 to 50 bar in an isothermal analysis (T = 298.15 K).

Figure 2 expresses the solubility values (in gCo2/kgH2O) obtained by numerical simulation and the values extracted from CO2SOL software.

Figure 2 shows the proportionally linear relationship of absorbed content as a function of system pressure up to approximately 15 bar, in accordance with Henry's Law theory for single-component isothermal absorption. Above this value, this linear behavior ceases to exist due to the high pressures that compress the molecules close to each other, making the volume of the molecules themselves a significant fraction of the volume of the container, invalidating the first postulate of the Kinetic Theory of Gases and, consequently, nullifying the Ideal Gas Law (Kotz *et al.*, 2015) . Furthermore, the fall in CO_2 fugacity changes both the solubility value and the Henry's volatility constant in Eq. (2) .

Table 2 below highlights the values used to build the Figure 2 and the difference achieved between the two results.

Table 2. Comparison of theoretical solubility and simulation results.$^{(1)}$

Pressure (bar)	Solubility - CO2SOL (gCO2/kgH2O)	Solubility - OpenFOAM (gCO2/kgH2O)	Error (%)
05	7,34	7,32	0,20
10	14,32	14,26	0,41
25	32,49	32,50	0,01
50	54,19	54,41	0,39

$^{(1)}$ Measured at 298.15 K.

The results protruded above validate the application of Henry's Law modeling by OpenFOAM, as it achieves an error between the numerical and theoretical results less than 0.5% for the solubility values of CO_2 in tap water in all analyzed situations.

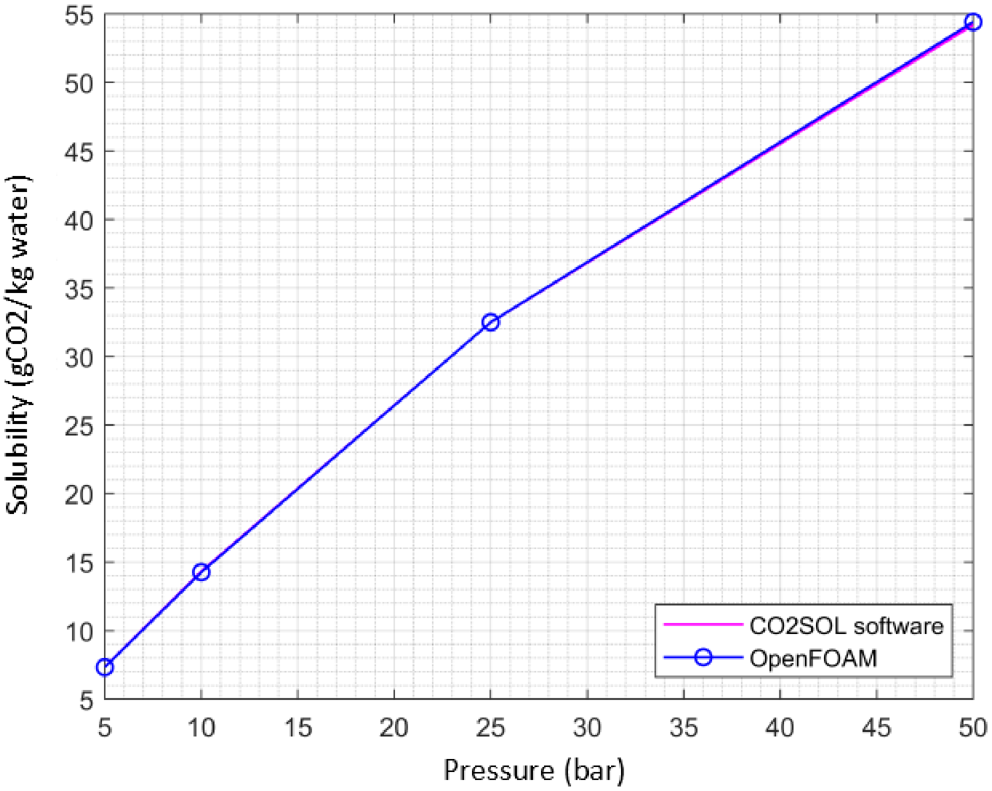

Figure 2. Effect of pressure on the amount of gas dissolved in water.

The second object of analysis in this case was to evaluate the total dissolution time of the gaseous component in the liquid phase, taking into account the mass flow by diffusion. This time is also known as residence time. In the definition, residence time (sometimes treated as removal time) is the average amount of time a particle resides or spends in a particular system. This measure varies directly with the amount of substance present in the system (Nauman, 2008) . In this case, the residence time is understood as the time elapsed until the liquid phase reaches the saturation condition.

Figure 3 shows the behavior of the solubilization curve in isothermal condition as a function of pressure and velocity. The mass flow is kept constant at $\dot{m}_g$ = 60 kg/h.

Following the Ideal Gas Law, the decrease in pressure leads to a decrease in the density of the gas and, consequently, preserving the area of the injection orifice, the velocity increases. Therefore, velocity is inversely proportional to pressure. Here, there are two factors which affect the residence time: gas phase velocity and pressure. The increase in speed consequently increases the degree of agitation (or mixing) of the phases in the bubble column, reducing the contact time according Higbie's Penetration Model (Higbie, 1935) . As for the pressure, it acts in low pressures it allows the increase in absorption rate due to small number of molecules collision based on kinetic theory of gases.

Table 3 below explicit the residence time results with the appropriate system pressure and gas phase velocity values. The residence time is the elapsed time to achieve 99.9% of saturation concentration. Therefore, high pressures or low gas phase velocity of injection promote a slow CO_2 absorption rate.

Table 3. Effect of pressure and gas velocity in residence time.(2)

Pressure (bar)	**Density (kg/m³)**	**Gas Velocity (m/s)**	**Residence time (s)**
05	9,10	3,05	18
10	18,71	1,48	20
25	51,4	0,54	26
50	131,03	0,21	36

(2) Measured at 298.15 K.

The last analysis is to verify if the theoretical model proposed fits the numerical results obtained via CFD in order to validate the gas absorption results.

This way, the data obtained numerically are compared with the solution of the mass transfer equation (Eq. (6)) using the correlation obtained for the volumetric mass transfer coefficient in Eq. (7) as shown in Fig 4.

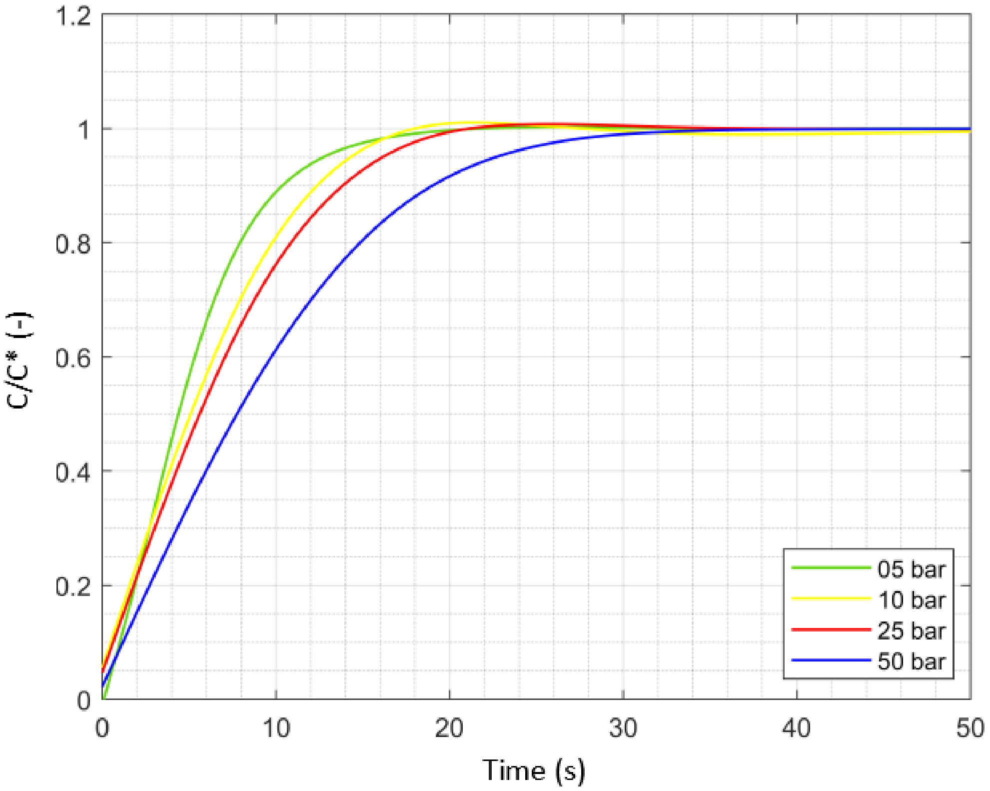

Figure 3. Effect of pressure on CO2 absorption rate in pure water.

To assess the goodness of fit of the theoretical model with the curve obtained numerically, a statistical model is used that describes how well it fits a set of observations. R-squared or R² is a statistical measure of how close the data are to the fitted regression line. It is also known as the coefficient of determination, or the coefficient of multiple determination for multiple regression (Devore, 2011) .

The definition of R-squared is fairly straight-forward; it is the percentage of the response variable variation that is explained by a linear model. R-squared is always between 0 and 100%: 0% indicates that the model explains none of the variability of the response data around its mean and 100% indicates that the model explains all the variability of the response data around its mean. In general, the higher the R-squared, the better the model fits your data (Devore, 2011) .

As shown in Tab 4 is possible to perceive a high value in the coefficient of determination. These values express how the numerical model is explained by the theoretical model. It is observed in the residuals analysis that they always have the the maximum residual error (MRE) less than 12%. It is possible to see that the curves have a similar behavior, even with some deviations in their values. These variations can occur for some reasons: the typical uncertainties in material-property data, the difference in temperature in numerical and theoretical analyzes, gas flow rate in numerical study that exceeds the theoretical condition range and the consideration of the DIC in theoretical model (numerical model does not consider it).

Table 4. Effect of pressure and gas velocity in residence time.

Pressure (bar)	**R² (%)**	**MSE (%)**
05	92,98	11,70
10	99,81	4,99
25	99,63	6,93
50	99,49	9,13

5. CONCLUSION

In this study, a case was developed in CFD OpenFOAM software with the application of the multiphaseEulerFoam solver to simulate the dynamic process of gaseous absorption of CO_2 in a bubble column filled with water. The model's capability to predict the saturation concentration of the system, which is an aspect related to solubility, was evaluated.

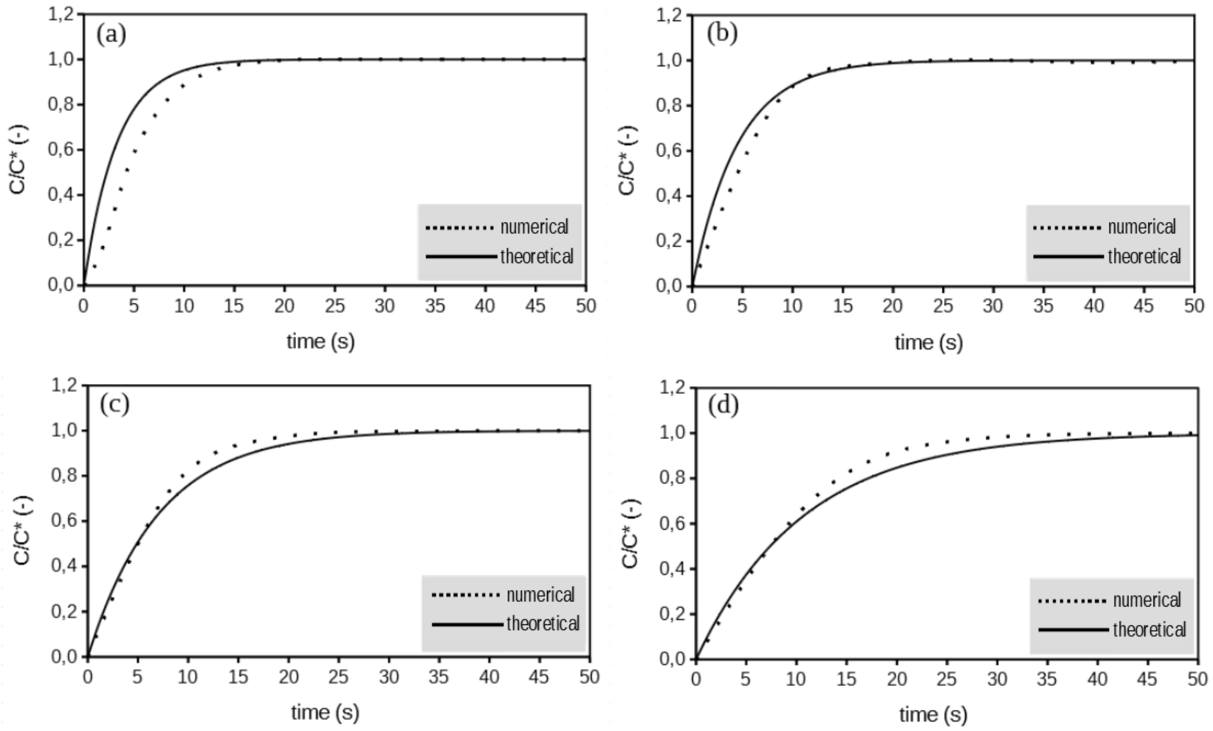

Figure 4. Comparison between numerical results and theoretical model: (a) 05bar; (b) 10bar; (c) 25bar e (d) 50bar.

The computational model showed good ability to predict the concentration values of CO_2 in water presenting a maximum error of 0.41% in relation to theoretical values governed by the Henry's Law.

Furthermore, the gas absorption rate in a bubble column was validated with the model proposed by M.Tokumura, M. Baba, H.T. Znad and Y. Kawase (Tokumura *et al.*, 2006) , with a high coefficient of determination and all maximum residual errors less than 12%. Thus, residence time and absorbed mass can be predicted by the numerical model developed in OpenFOAM environment if used with some parsimony.

Therefore, it is easy to make preliminary design calculations, as presented now for application in CO_2 absorption in liquid phases.

6. ACKNOWLEDGEMENTS

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