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Modelling of Enzymatic Reactive CO_2 Absorption

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Post-combustion CO_2 capture strategy asks for novel effective processes avoiding the use of polluting solvents and oriented towards CO_2 utilization. Recent research efforts are focused on the development of CO_2 absorption processes promoted by the activity of the enzyme carbonic anhydrase (EC - 4.2.1.1) (Leimbrik *et al.*, 2017; Russo *et al.*, 2013). This ubiquitous enzyme is able to catalyse the CO_2 hydration reaction and can be used to enhance CO_2 absorption rate into aqueous alkaline solvents such as carbonate solutions. The adoption of the biomimetic strategy for post-combustion CO_2 capture is based on the use of environmental friendly solvents. Recent studies on the development of carbonic anhydrase biocatalysts for CO_2 capture through enzymatic reactive absorption focused on different enzyme immobilization techniques. Moreover, theoretical studies showed the potential use of immobilized enzymes in typical gas-liquid contactors. The present contribution concerns the rational design of absorption columns through the use of kinetic parameters assessed for carbonic anhydrase immobilized on fine particles. The kinetics of CA immobilized on magnetic nanoparticles have been previously characterized under conditions relevant for the industrial application (K_2CO_3 solutions at 25-40°C and at different carbonate conversion degrees) (Peirce *et al.*, 2017; Peirce, 2017). The model simulations provided information on the performances of the technical grade CA and of the biocatalyst made with nanoparticles (NPs) coated with covalently immobilized CA. The results showed that effective intensification of the capture process can be achieved using the fine slurry biocatalyst.

1. Introduction

Aqueous solutions of alkanolamines have been proposed for CO_2 capture processes based on reactive absorption. The development of amine-based absorption processes advanced thanks to a good compromise between the rate of CO_2 capture and the cost of solvent regeneration (Rochelle, 2009). The current research is focused on the selection of green alternatives to reduce pollutant emissions related to the use of amines (*e.g.* ammonia and heat stable salts). The use of the enzyme carbonic anhydrase (CA) as catalysts for the CO_2 hydration in aqueous solvents (Lacroix and Larachi, 2008; Russo *et al.*, 2013) seems to be an environmental friendly alternative. The use of CA improves CO_2 absorption rate with minimal impact on the environment since enzymatic reactive absorption processes do not require organic solvents and do not release toxic compounds. Low temperature and low pressure process based on K_2CO_3 solutions (Chen *et al.*, 2007) has been proved to be consistent with the use of enzymes as biocatalysts to enhance CO_2 absorption rate. The process includes vacuum desorption at temperature lower than 100°C (Chen *et al.*, 2007). Still open issues related to the development of industrial scale units for enzymatic reactive absorption of CO_2 from flue gas concern the reactor design. Numbers of reactor configurations have been proposed in the literature (Lacroix and Larachi, 2008; Russo *et al.*, 2013). Thermostable CA dissolved in the liquid may be used in conventional random packing columns (Reardon *et al*., 2015). The immobilization of the enzyme on solids in the absorption unit allows to increase the enzyme stability and the biocatalyst loading. Moreover, it is known that above few hundred grams per cubic meter of liquid solvents the precipitation of the enzyme occurs. This phenomenon can lead to biocatalyst deactivation whenever it occurs under not controlled conditions (Peirce *et al.*, 2017).

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The proposed reactor configuration may differ a lot depending on the biocatalyst morphology (dispersed solids, monolith washcoat, etc.) (Lacroix and Larachi, 2008; Russo *et al.*, 2013; Leimbrink *et al.*, 2017).
The absorption of gas in the presence of slurries of fine particles have been proposed as effective strategy for biomimetic CO_2 capture process. Slurry biocatalyst is able to effectively enhance CO_2 absorption rate through heterogeneous catalysis of the CO_2 hydration reaction (Alper *et al.*, 1980; Russo *et al.*, 2013; Penders-van Elk *et al.* 2013). Modelling of gas absorption into heterogeneous systems includes a large number of cases: liquid droplet emulsions, inert solids, solid reactive species, sorbent particles, or catalyst particles (Beenackers and Van Swaaij, 1993; Ramachandran, 2007). In the presence of catalyst particles and reversible reactions, the resolution of diffusion-reaction equations is quite complex and asks for numerical computation. An attempt to model CO_2 chemical absorption assisted by immobilized CA has been made in a previous work (Russo *et al.*, 2016). The results showed promising performances of slurry biocatalyst made of CA immobilized on micro-metric particles and operated in a slurry-bubble column.
The present study aims at the simulation of the same Slurry-Bubble-Column (SBC) unit for the enzymatic reactive absorption of CO_2 on the basis of real biocatalyst properties and kinetics assessed in recent work (Peirce, 2017). In particular, technical grade CA was characterized in terms of first order kinetics of CO_2 hydration in K_2CO_3 solutions at 25°C. The resulting kinetic parameters referred to both free and immobilized CA has been included in the present theoretical model in order to simulate the CO_2 absorption process in the SBC.

2. Theoretical model

The proposed model describes a SBC unit operated with K_2CO_3 solutions as liquid solvent. Further consideration on the selection of the SBC as reference configuration are reported in Russo *et al.* (2016). The SBC was operated as counter-current gas-liquid contact system in the presence of fine dispersed solids (CA immobilized on NPs). The mass transfer and gas hold-up in bubble column operated with fine dispersed solids were fully characterized by Zahradnik (2001). Thus, this configuration was used as a relevant case study that enables the use of slurry biocatalyst. Moreover, gas and liquid flow rates were fixed according to Zahradnik (2001) because these conditions allowed the onset of homogeneous bubbling regime and negligible liquid backmixing. Similarly, the model can be used to simulate the performances of any other counter-current gas-liquid contact provided that mass transfer and gas hold-up are known in the presence of the fine solids and provided that the configuration allows the effective operation of the slurry biocatalyst.

2.1 Model assumptions

Figure 1 shows a scheme of the modelling approach according to Russo *et al.* (2016).

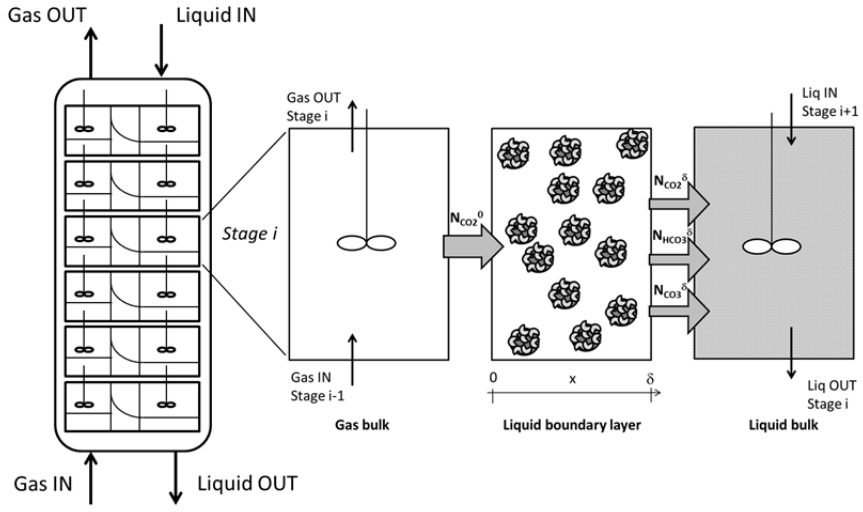

Figure 1: scheme of the model for counter-current gas liquid reactive absorption unit with immobilized enzyme as slurry catalyst.

The absorption unit has been modeled according to the 'tank in series' approach. Counter-current operation of the gas and liquid phases was considered in each stage. Liquid phase in each stage was modelled according to the film theory including: i) mass balances at the steady state on reactive species CO_2, HCO_3^- and CO_3^{2-} extended to both the liquid bulk and the liquid boundary layer at gas-liquid interface; ii) the overall carbon balance; iii) the electroneutrality condition. The chemical reactions considered were:

$$CO_2 + H_2O \leftrightarrow HCO_3^- + H^+ \quad (1)$$

$$CO_2 + OH^- \leftrightarrow HCO_3^- \quad (2)$$

$$HCO_3^- \leftrightarrow CO_3^{2-} + H^+ \quad (3)$$

$$H_2O \leftrightarrow OH^- + H^+ \quad (4)$$

Equilibrium for reaction 4 was considered in the liquid phase.
Carbon dioxide was selected as reference species in the calculation of the average depth of the liquid boundary layer because CO_2 has the highest diffusivity among the considered chemical species (Russo *et al.,* 2016).
The rate of reactions (1), (2) and (3) were described according to Russo *et al.* (2016). The reaction rate of CO_2 hydration (1), catalysed by free or immobilized CA, was assumed first order with respect to CO_2 according to eq. 5. According to the previous theoretical model (Russo *et al.*, 2016), in the case of CA immobilized on fine particle the biocatalyst was assumed as pseudo-homogeneous having an effectiveness factor expressed as a function of the Thiele modulus. Because the kinetic parameters available from recent experimental work (Peirce, 2017) referred to non-porous particles (Fe_3O_4 NPs having nominal average size of 10^{-7} m), the modelling of the biocatalyst effectiveness factor was excluded in the adaptation of the model to the present study.

$$r_e = k_e[CA](c - c_{eq}) \quad (5)$$

The performance of the immobilized CA was assessed fixing 2% solid biocatalyst hold-up and considering a depletion (50 and 95%) of such value due to the possible particle aggregation. Indeed, the contribution of the biocatalyst is related to the availability of the particles as close as possible to the gas-liquid interface, that is to those particles having size smaller than the average depth of the liquid boundary layer (about 3 10^{-6} m according to Table 1). Any further detail on the model assumptions as well as the entire set of the model equations are reported in Russo *et al.* (2016).

2.2 Operating conditions and parameters

The operating condition were selected among those adopted for the characterization of the biocatalyst and so that a comparison between free and immobilized CA was possible. In particular 10% wt K_2CO_3 solution was considered at 25°C, because this condition was adopted for the kinetic characterization of the biocatalyst. The properties of the biocatalyst were: enzyme loading 28 g CA/kg solid support; particle radius between 10^{-7} and 10^{-6} m; solid density 5170 kg/m^3 Fe_3O_4 (Peirce, 2017).
Kinetic parameters for reaction 2-3; equilibrium constants for reaction 1, 3, and 4; CO_2 solubility and diffusion coefficients were fixed according to and to Peirce (2017). The values of the kinetic constant k_e assessed in 10%wt K_2CO_3 with partial carbonation (20% carbonate to bicarbonate conversion degree) were 6.5 10^4 and 2.1 10^4 m^3/(mol s) for the free and immobilized CA, respectively.

2.3 Computational method

The system of differential and algebraic equations was solved using the commercial software package Comsol Multiphysics®.

3. Results

Table 1 summarizes the conditions adopted for the simulations. Effects of gaseous pollutant on the biocatalyst are out of the aim of the work for this reason gas phase was assumed as N_2/CO_2 mixture. It is worth to note that there is evidence in the literature of satisfactory and promising performances of different CA forms in terms of resistance to pollution from flue gases (*e.g.* SO_2 and NO_x) (Russo *et al.*, 2013).

*Table 1: conditions adopted for the simulation. CTBC – carbonate to bicarbonate conversion. *See Russo* et al., *2016.*

	free CA	Immobilized CA
Solvent composition	10% wt K_2CO_3 20%CTBC	
Temperature	25°C	
Pressure	1 atm	
CO_2 inlet gas	10%vol	
Total SBC volume	0.13 m^3	
Liquid flow rate	3 10^{-4} m^3/s	
Gas flow rate	1.7 10^{-3} m^3/s	
*k_l	5.1 10^{-4} m/s	4.6 10^{-4} m/s
*a_l	194 m^{-1}	108 m^{-1}
*Liquid hold-up	0.72	0.84
Solid hold-up	-	0.2
CA concentration	0-100 g/m^3	28 g/kg solid

Figure 2 and 3 show the results of the base case simulations referred to CO_2 capture in the SBC with carbonate solution as solvent and with the carbonate solution supplemented with free CA at 100 g/m^3. The CA concentration was fixed at 100 g/m^3 because, in the carbonate solution having large ionic strength, higher enzyme concentration causes protein precipitation. In the presence of precipitated enzyme aggregates the actual dissolved enzyme concentration (homogeneous biocatalyst) can not be safely fixed.

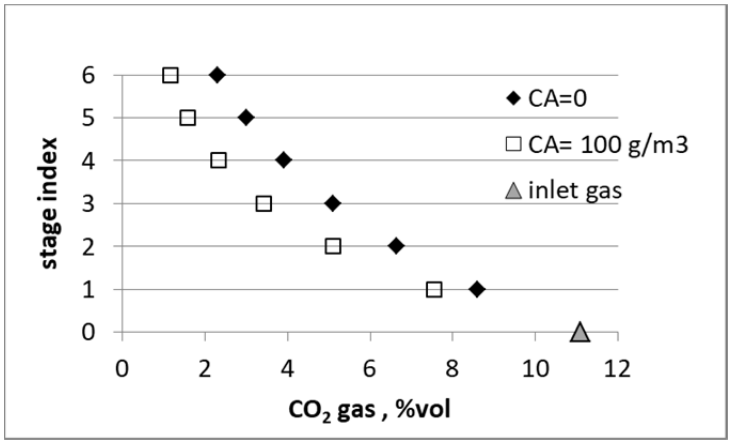

Figure 2: Percentage of CO_2 in the gas phase along the SBC stages.

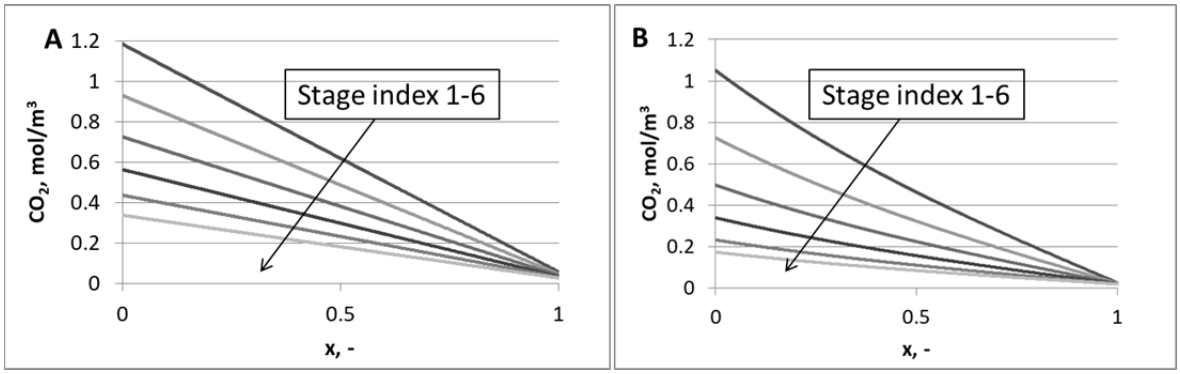

Figure 3: Dissolved CO_2 concentration in the boundary layer of the liquid phase at each SBC stage. A) alkaline solvent; B) alkaline solvent supplemented with 100 g/m^3 free CA.

Simulations of the base cases, referring to the use of free enzyme as CO_2 capture rate promoter, highlighted how the presence of the free enzyme allows to increase the percentage of captured CO_2 from 79 to 89% (Figure 2). Moreover, the model provided the concentration profiles of each species (data not shown) in the boundary liquid layer including dissolved CO_2 (Figures 3 A-B). It is evident how the effect of catalysed reaction (1) between CO_2-CA-H_2O provided not linear CO_2 concentration profiles.
Figure 4 reports results of simulations referred to the use of CA immobilized on NPs by a covalent attachment technique (Peirce, 2017).

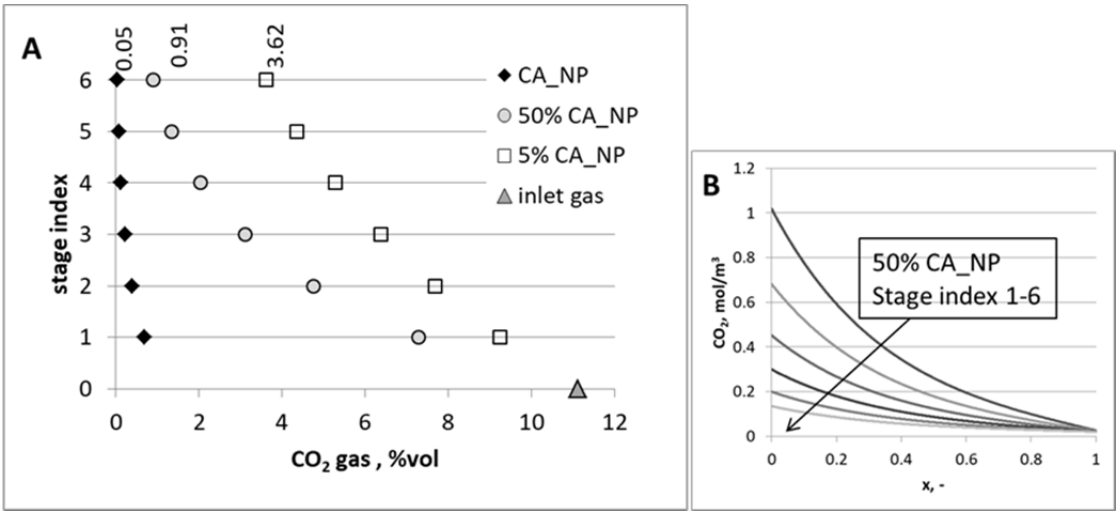

Figure 4: A) Percentage of CO_2 in the gas phase along the SBC stages in the presence of CA immobilized on NP, 50 and 5% of the entire solid hold-up shows the effect of biocatalyst particle aggregation; B) dissolved CO_2 concentration in the boundary layer of the liquid phase at each SBC stage in the case of 50% effective biocatalyst particle contribution.

Results in Figure 4A show how the performances of the immobilized CA were better that those of the free CA (Figure 2). This result is due to the effect of process intensification related with the use of immobilized enzyme. As expected, the values of k_e suggested that the enzyme is less active after immobilization on NPs, notwithstanding this partial deactivation, the large enzyme loading per unit volume of solids provides biocatalyst concentration in the solvent much higher than those typically adopted in the case of free enzyme (limited by protein precipitation). The overall resulting effect was a strong enhancement of CO_2 capture rate and, as a consequence, of the percentage of captured CO_2 at the outlet gas stream. A more realistic case was simulated taking into account partial reduction of the actually active biocatalyst (50 and 5% of the entire solid hold-up) due to the aggregation of NPs up to micro-metric clusters that might not to be available at the gas-liquid interface. The contribution of 50% biocatalyst hold-up was again satisfactory and provided outlet gas having 0.91%vol CO_2. It is worth to note that the performances of the case referring to 5% biocatalyst hold-up are slightly worse than that of the base case referring to the only alkaline solvent (3.62 vs 2.31 %vol CO_2) reported in Figure 2 because the values of k_L and a_L are lower in the presence of dispersed fine particles than in the case of liquid homogeneous solvent (see table 1). Figure 4B shows how the activity of immobilized biocatalyst (50% of the total solid hold-up available) provided nonlinear profiles of CO_2 concentration in the liquid boundary layer, the increased slope of the profiles at x=0 (gas-liquid interface) caused the enhancement of CO_2 absorption rate per unit area.

Conclusions

The results from simulations of the SBC unit operated with partially carbonated K_2CO_3 solution as solvent showed satisfactory performances for the biocatalyst made by CA immobilized on NPs. These results suggested the use of enzyme immobilization on NPs as an effective strategy to make feasible and effective the enhancement of CO_2 capture rate in carbonate solutions. Further use of the developed theoretical tool will be focused on the assessment of the performances of slurry biocatalyst at different temperatures and in structured packed columns that allow the use of slurry solvents. More complex modelling approach (see Iliuta *et al.*, 2008) might be adopted in future work to properly describe effect of convective mass transfer in the liquid phase that might affect the performances of the slurry biocatalyst.

Acknowledgments

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