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Membrane Contactors for Water Carbonation

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Abstract: A theoretical and experimental study made in order to determine the performance of membrane contactors in water carbonation is presented. In particular, on the basis of experimental results previously obtained, it has been derived an expression in which the effect of some parameters as temperature, water and CO_2 flow rate, CO_2 pressure, trans-membrane pressure on the performance of the process is taken into account. The study refers to hollow fiber membrane contactors used for the experimental tests. The main scope has been to verify if, by membrane contactors, it is possible to reach the same degree of water carbonation as by traditional methods (1-5 g/l) and to derive, for the module used, a correlation able to describe the performance of the process at several operating conditions. The high CO_2 removal observed confirms the interesting potentialities of membrane contactors also in gas streams purification.

1. Introduction

Membrane contactors are becoming very interesting systems for carrying out several processes of mass transfer between phases. Semiconductor industry, food and beverages, waste water treatment, are all examples of fields in which they find application. In these systems the two phases are in contact at the pores of microporous hydrophobic membranes which act as inert support. Being the membranes hydrophobic, the aqueous solutions don't go through pores and the mass transfer occurs at the pores entrance. Fig. 1 shows this mechanism. Todate, several have been the studies carried out with these systems like liquids degassing (e.g. water deoxygenation for ultrapure water production), adding gases into liquids (e.g. water ozonation), liquid-liquid extractions, VOCs removal from aqueous solutions etc [1-7] that evidenced their potentialities in terms of higher surface areas with respect to conventional systems. The main characteristics of membrane contactors (main advantages and disadvantages) are reported in Table 1. In the present work the membrane contactor concept has been applied to the water carbonation process. At first, experimentals have been carried out in a hollow fiber device in order to determine the effect of several parameters (water and CO_2 flow rates, temperature, CO_2 pressure, transmembrane pressure) on the degree of water carbonation achievable. Thus, on the basis of the experimental results, a mathematical expression which describes the mass transport of CO_2 between the two phases for the membrane device used has been derived. At the right operating conditions it has been possible to achieve the

desired degree of water carbonation.

2. Experimental System

The membrane module used in this work has been purchased from the Hoechst Celanese Corporation. It contains thousand microporous hydrophobic hollow fibers in polypropylene and offers a surface area of 1.4 m^2. The maximum transmembrane differential pressure allowed is 4 bar and the maximum operating temperature range is between 1 and 40℃.

Being the mass transport coefficient at the shell side higher than that at the lumen side, it is preferable to feed at the shell side the stream which presents the higher mass transport resistance. For this reason, the water stream is supplied at the shell side. In particular, the water is fed countercurrently and in cross-flow mode by a gear pump through the shell of the module and the flow rate is varied by a flow meter with integral valve. The CO_2 stream is fed to the lumen of the membrane fiber from a bottle and its flow rate is varied by means of a mass flow controller. The water pressure is controlled by varying the speed drive of the pump, whereas the CO_2 pressure is regulated by acting on a valve lodged at the exit of the gas stream. The inlet and outlet streams pressures are read on pressure gauges. The temperature is varied by feeding water to the module at different temperatures. The temperature of the module is calculated as an average of the inlet and outlet temperatures of the water. The concentration of CO_2 in water is determined at steady-state both by a mass balance on the gas stream and by titration of the water produced. The results obtained by the two methods of analysis are in agreement each others.

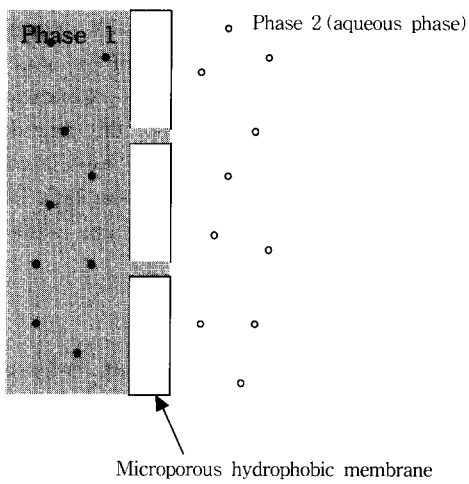

Fig. 1. Section of the membrane.

3. Results and Discussion

Fig. 2 shows the CO_2 concentration in water as function of the water and CO_2 flow rates. Higher CO_2 concentrations are obtained at lower water and higher CO_2 flow rates, respectively. This result can be explained by considering that at higher CO_2 flow rates more pores are gas filled at steady-state and a higher quantity of gas comes in contact with liquid and it is easier, thus, to reach higher CO_2 concentrations.

Table 1. Main Advantages and Disadvantages of Membrane Contactors with Respect to Conventional Systems

Advantages	Disadvantages
Higher interfacial area per volume	Operative pressures dependent on breakthrough ones
No dispersion between phases	Additional resistance to mass transfer due to the membrane
No loading or flooding limitations	
Non foaming	
Low pressure drop	
Constant interfacial area between phases	
Flexibility and campactness	
Easy scale-up due to a modular design	

In Fig. 3 the effect of the water pressure is analyzed. By increasing this pressure there is an increase of the CO_2 concentration due to the more stable interface between phases. The higher water pressure pushes the water through the fiber; because of the hydrophobicity of the membrane, the liquid stream doesn't pass through pores, and thus the higher pressure results in a more defined interfacial surface and in a consequently better mass transfer between phases. From initial test the pressure of the water has been increased up to 2.9 atm and no water flow through pores has been releated. The breakthrough pressure of the membrane is, thus, higher than 2.9 atm.

The influence of temperature is shown in Fig. 4. The CO_2 concentration increases by reducing temperature because of the higher solubility. Table 2 reports the effect of the CO_2 pressure on the CO_2 concentration for three different temperatures. The observed trend is in agreement with the solubility one.

The degree of CO_2 removal achieved in some of

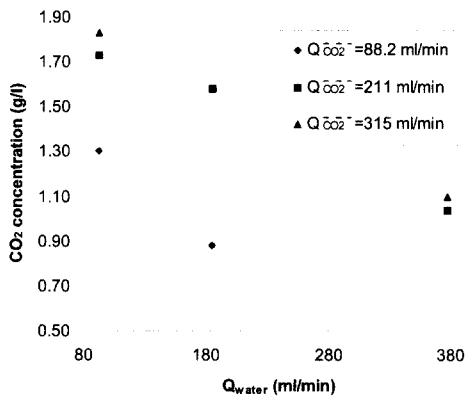

Fig. 2. Dependence of the CO_2 concentration on the water and CO_2 flow rates. P_{CO_2}=1atm; Pwater=1.1 atm; T=17℃ *(Solubility value, 1.99 g/l).*

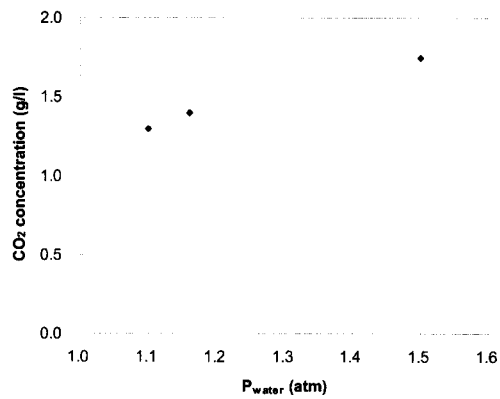

Fig. 3. The effect of the water pressure on the CO_2 concentration. Q_{water}=92 ml/min; Q_{CO_2}= 88.2 ml/min; P_{CO_2}=1atm; T=17℃. *(Solubility value, 1.99 g/l).*

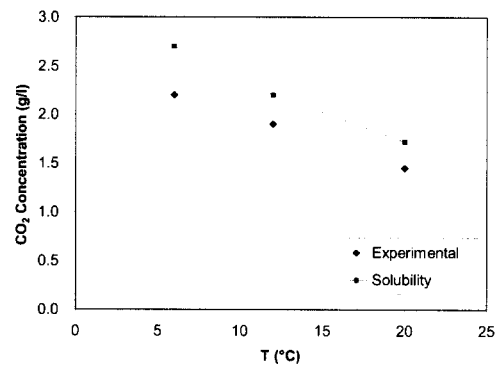

Fig. 4. The influence of the temperature on the CO_2 concentration. Q_{CO_2}=315 ml/min; Q_{water}= 92 ml/min; P_{CO_2}=1atm; P_{water}=1.1 atm.

Table 2. The Effect of the CO_2 Pressure on the CO_2 Concentration. Q_{CO_2}=315 ml/min; Q_{water}=92 ml/min; P_{water}-P_{CO_2}=0.5 atm.

P_{CO_2} (atm)	C_{CO_2} (g/l)-6℃	Solubility-6℃	C_{CO_2} (g/l)-12℃	Solubility-12℃	C_{CO_2} (g/l)-20℃	Solubility-20℃
1	2.4	2.7	1.93	2.2	1.6	1.72
1.5	3.18	4.24	2.7	3.4	2.3	2.4
2	4.18	5.5	3.5	4.3	2.5	3.3
2.5	5	6.34	4.1	5.4	3.7	4.1

Table 3. %CO_2 Removal ($CO_2|_{water}$ (g/s)/$CO_2|_{gas}$ (g/s)) as Function of Flow Rates. T=17 ℃; P_{water}=1.1 atm; P_{gas}=1 atm

Q_{H_2O} (ml/min)	Q_{CO_2} (ml/min)	R_{CO_2} (%)
92	88.2	74
	211	40
	315	29
180	88.2	98
	211	72
378	211	99
	315	71

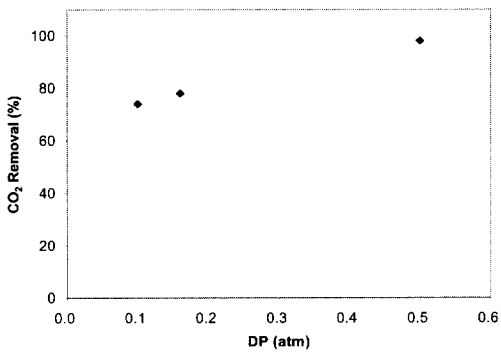

Fig. 5. CO_2 Removal (%) versus DP. T=17℃; Q_{water}=92 ml/min; Q=88.2 ml/min; P_{CO_2}=1 atm.

the cases analysed is reported in Table 3 and Fig. 5. Whereas transmembrane pressure, temperature and CO_2 pressure influence the removal in the same way they affect the CO_2 concentration into water, higher degree of removal are obtained at lower CO_2 flow rates and higher water flow rates. Depending on the type of application, the operating conditions have to be, thus, rightly chosen.

In some experiments a CO_2 dispersion in the liquid phase has been detected higher than the solubility values; these results are still under investigation and to be confirmed.

4. Modelling Study

The transfer of CO_2 from gas phase to the liquid phase depends on the overall mass transfer coefficient and the mass transfer driving force. For gas-liquid applications, being the membrane pores gas-filled, the overall mass transfer coefficient coincides with the liquid phase mass transfer one. The membrane, thus, acts just as a mean of contacting between the two phases and its morphology doesn't influence the mass transport. However, the pore size and the pore size distribution of the membrane affect the breakthrough pressure and the bubble gas size. Generally, lower pore sizes are preferred because lead to higher breakthrough pressures and to lower bubble gas size. Lower bubble gas sizes allow to achieve a better efficiency of process by enhancing the mass exchange. Also the pore size distribution is important to guarantee the production of stable small gas bubbles. When a "mimimum" distance among pores is obtained, the coalescence is avoided and the small bubbles rest permanently into the liquid phase.

In the water carbonation the CO_2 doesn't react with water (low value of the equilibrium constant) and the CO_2 absorption is limited by the liquid phase resistance. In the experimental work, all data have been collected by feeding the water at the shell side. In the hollow fiber module used, the liquid flows radially outward or inward at the shell side and the local shell-side mass transfer coefficient is position-dependent. An overall mass transfer coefficient can be however considered.

The mass transfer coefficient can be predicted using correlation of the type:

$$Sh = \alpha \, Re^{\beta} \, Sc^{\gamma} \tag{1}$$

where, Sh: Sherwood number;
Re: Reynolds number;
Sc: Schmidt number;
α, β, γ: derived as function of the operating conditions and of geometry.

A differential mass balance on the liquid phase has the following form:

$$kl \, dA \, (x_g - x_w) = Ql \, dx_w \tag{2}$$

Table 4. Comparison between experimental and theoretical results. Effect of the flow rates on the CO_2 concentration into water. T=17℃, Pwater=1.1 atm; Pgas=1 atm.

Q_{H2O} (ml/min)	Q_{CO2} (ml/min)	C_{CO2} (g/l) exp.	C_{CO2} (g/l) theoretical
92	88.2	1.3	1.2
	211	1.7	1.5
	315	1.8	1.7
180	88.2	0.89	1.0
	211	1.6	1.3
378	211	1.03	1.18
	315	1.1	1.3

Table 5. Comparison between experimental and theoretical results. Effect of the CO_2 pressure on the CO_2 concentration into water. T=20℃; $P_{water}-P_{gas}$=0.5 atm; Q_l=92 ml/min; Q_{gas}=315 ml/min

P_{gas} (atm)	C_{CO2} (g/l) exp.	C_{CO2} (g/l) theor.
1	1.6	1.8
1.5	2.3	2.4
2	2.5	2.9
2.4	3.7	3.4

where, k_l : local mass transfer coefficient at the liquid phase;
x_g : CO_2 molar fraction at the gas phase;
x_w: CO_2 molar fraction at the liquid phase;
Q_l : liquid flow rate;
A : exchange area between phases.

At low gas flow rates not all pores are CO_2-filled and just a part of the membrane area is used for the phases contacting. To take into account this, the following expression has been used to calculate the effective interfacial area:

$$A = A_t \cdot (Q_g/Q_{grif})^{0.30} \quad (3)$$

where, A_t: overall membrane area;
Q_g : gas flow rate;
Q_{grif}: reference gas flow rate.

The reference gas flow rate has been taken equals to the highest gas flow rate used during the experimental tests, 315 ml/min. Once the overall K_l is achieved from (1), the equation (2) can be integrated along the module and the theoretical degree of water carbonation can be calculated. For the membrane module used in this work the following dependence of the mass transfer coefficient on the operating conditions has been found:

$$Sh = 0.00034\ (P_{CO2}/P_0)^{0.7}\ [(\Delta P_{min}*8.3)+((\Delta P-\Delta P_{min})/10)^{(Qg/Qgrif)}] \cdot Re^{((2-Qlrif/Ql))^{0.07}} \cdot Sc^{1.15} \quad (4)$$

where, P_{CO2}: CO_2 pressure;
P_0: reference pressure, 1 atm;
ΔP_{min}: minimum trans-membrane pressure, 0.1 atm;
ΔP: trans-membrane pressure;
Q_{lrif}: reference liquid flow rate, 92 ml/min;

In Tables 4-5 the comparison between experimental and theoretical data is reported.

5. Conclusions

The present work shows that it is possible, choosing the right operating conditions, to obtain by membrane contactors interesting water carbonation. The values achieved approached the solubility ones at low temperatures, water flow rates, high pressures, and CO_2 flow rates. The mathematical expression derived for the experimental system used adequately describes the performance of the process. Membrane contactors seem, thus, to be useful for the process studied. By acting on the membrane morphology several advantages could be achieved with respect to conventional systems as well defined bubble gas size and, then, better efficiency of the mass exchange. Furthermore, at parity of water carbonation degree, the possibility of introducing in a controlled way the gas into the

liquid phase leads to a reduced consumption of gas with a consequent saving with respect to conventional apparatus.

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