


ABSORPTION AND DESORPTION OF CARBON DIOXIDE IN SEVERAL WATER TYPES

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This study investigated the effect of water type on the rate of CO₂ transfer from/to an aqueous phase with varying degree of water salinity. The absorption and desorption experiments were conducted on reverse osmosis product, brackish well, and brackish water reverse osmosis reject waters as well as seawater in a mechanically agitated tank. Results show that the direction of mass transfer has a major impact on the value of the volumetric mass transfer coefficient, $k_L a$, with the absorption experiments always rendering higher values. Furthermore, $k_L a$ values always decreased with salinity in both absorption and desorption experiments until a certain critical salinity value was reached, beyond which mass transfer increased again. However, $k_L a$ values were found to decrease continuously with an increase in the water alkalinity in absorption experiments, while no clear conclusion could be drawn for the alkalinity effect in the case of desorption experiments. These observations suggest that the effect of alkalinity should be further investigated to elucidate its impact along with the salinity on the volumetric mass transfer rate.

Keywords: CO₂ capture, mass transfer, absorption, desorption, water systems

INTRODUCTION

The absorption/desorption of CO₂ in pure water without chemical reactions is of great importance for advancements in the process of remineralization of soft waters, design of photo-bioreactors, improving water quality in recirculating aquaculture systems, conditioning of product water and pretreatment of seawater in desalination plants, and protection of ion exchange systems in ultrapure water applications, among others.^[1] In a recent study, Elhadj et al.^[1] provided a thorough review of the various investigations related to the absorption and desorption of CO₂ in the myriad of available contactors. They showed inconsistent trends and an abundance of system- and geometry-specific correlations/models to predict the mass transfer performance of carbon dioxide absorption/desorption operations, which may explain the inefficient design of most industrially available contactors. Furthermore, the authors found no agreement in the literature on the effect of temperature and pressure of the system, as well as the presence of additives, especially electrolytes, in the water on the solubility of CO₂. Further, Elhadj et al.^[1] also highlighted that even for similar system configurations, the extent and nature of the dependence on a particular operating parameter is often contradictory. However, agreement exists on the role of the energy input, gas flow rate, liquid flow rate, and temperature (only for the case of desorption) on their positive effect on the value of $k_L a$. Nonetheless, the situation remains ambiguous when considering the presence of salts in the system. Contradictory results are found in the literature and a consensus on a positive or negative impact has yet to be reached. This is aggravated by the fact that only a few investigators studied their effect on the absorption of CO₂ in water, rendering the need for further investigations of paramount importance.^[1]

Consequently, the aim of this study is to investigate the efficiency of CO₂ transfer to and out of various aqueous solutions in a mechanically agitated tank (MAT). The absorption and desorption of carbon dioxide in reverse osmosis (RO) product

water, brackish well water, brackish water reverse osmosis (BWRO) reject, as well as seawater will be studied.

To accomplish these objectives, time-dependent pH data were measured and analyzed to estimate the total carbon content and the dissolved CO₂ concentration. The effects of agitation speed and water salinity on the mass transfer coefficient ($k_L a$) were studied. In addition to the aforementioned objectives that aim at investigating the reported discrepancies in the literature regarding the effect of salinity on $k_L a$, an additional goal of this study is to evaluate the differences and similarities between both the absorption and desorption operations in terms of mass transfer rates.

EXPERIMENTAL

It is well known that the type of the gas-liquid contactor plays an important role in determining the efficiency of gaseous transfer into and out of water. This is often reported in terms of the volumetric mass transfer coefficient, $k_L a$. As previously stated, CO₂ absorption/desorption has been studied using a myriad of reactor types, including but not limited to mechanically agitated tanks,^[2–8] bubble columns,^[9,10] packed-bed absorption columns,^[11,12] and hollow fibre membranes.^[13,14] The mass transfer performance of most of these reactors/contactors is summarized in a previous work,^[1] which in turn highlighted major obstacles when comparing these studies against each other. For example, in the case of carbon dioxide absorption, various investigators

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Can. J. Chem. Eng. 96:274–284, 2018

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DOI 10.1002/cjce.22901

Published online 11 July 2017 in Wiley Online Library (wileyonlinelibrary.com).

reported an increase in the value of $k_L a$ with an increase in water salinity, while many others reported an opposite trend.^[7,8]

Upon dissolution in water, carbon dioxide undergoes three chemical reactions involving four chemical species (namely, carbon dioxide, CO_2 ; carbonic acid, H_2CO_3 ; bicarbonate ion, HCO_3^- ; and carbonate ion, CO_3^{2-}). The slightest alteration of the water chemistry would therefore greatly affect the kinetics of dissolution of CO_2 and the thermodynamic equilibrium. Consequently, the extent of mass transfer between the gas and liquid phase would also be affected. All this renders the comparison between the various studies a tedious, if not an impossible, task.

To mitigate such problems, this investigation focuses on measuring the mass transfer performance of a mechanically agitated tank, operating under various design configurations, for cases of absorption and desorption of CO_2 using waters of varying salinity while maintaining the consistency of its source.

Experimental Setup:

Standard methods for the measurement of carbon dioxide concentration in aqueous solutions are described in previous research.^[15,16] Several of these methods have been utilized by researchers investigating the absorption and desorption of carbon dioxide. They include measurements in the liquid phase, measurements in the gas/vapour phase, and methods based on calculation (mass balance). For a complete list of these methods and the investigations in which they were utilized, the reader is referred to the work of Elhajj et al.^[1]

In the current work, in-situ measurements in the liquid phase will be conducted using a pH probe, the outcome of which will be utilized to determine the CO_2 content of the water. Furthermore, the absorption and desorption of carbon dioxide will be studied in a MAT. CO_2 and/or air flowed through calibrated mass flowmeters (Precision Medical and Timeter Instrument Corporation). After the two streams were mixed, the gas mixture enters the bottom of the gas-liquid contactor under investigation as shown in Figure 1.

Mechanically agitated tank design

The mechanically agitated tank is 34 cm high, with a diameter of 20 cm, and equipped with a 6-blade Rushton-type impeller (diameter of 7 cm). A 5 mm orifice, placed 30 mm from the bottom of the tank, was used for gas sparging. The blades of the Rushton-type impeller are 15 mm high, 15 mm wide, and 2 mm thick. Two diametrically opposing baffles (30 mm wide and 3 mm thick) were used as the need for a larger number, to eliminate the swirling at the liquid surface under the investigated operating conditions, was not necessary. An IKARW20 digital rotator

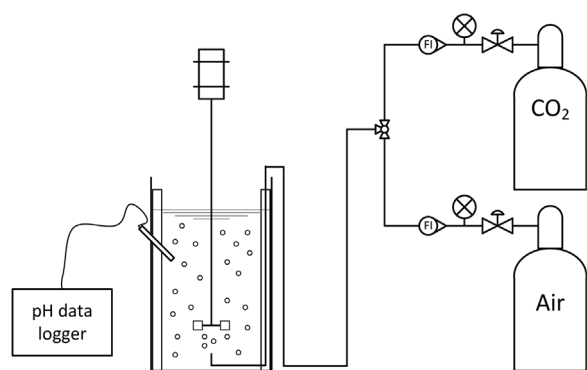


Figure 1. Schematic representation of the experimental setup showing the mechanically agitated tank.

operating at either 200 or 465 rpm was used to rotate the impeller which was placed at 120 mm from the bottom of the tank. The pH meter (Lovibond Senso Direct pH10) was installed 20 cm from the bottom of the tank which was filled up to a level of 24 cm with water to obtain a working volume of 7.54 L.

Operating conditions

The absorption and desorption of CO_2 experiments were performed on reverse osmosis (RO) water, brackish water, brackish water reject, and seawater from the Mediterranean sea off the coast of Beirut, Lebanon.

Variables affecting the overall mass transfer coefficient ($k_L a$) were investigated, including impeller speed (200 and 465 rpm), total gas flow rates ($5\text{--}40 \text{ L} \cdot \text{min}^{-1}$), and water salinity. All experiments were conducted at atmospheric temperature and pressure. It should be noted that absorption experiments were conducted using pure CO_2 streams, whereas desorption studies utilized compressed air. Figure 1 represents a schematic of the gas/liquid contactors.

System Investigated

In this investigation, four different types of water were studied, the physical properties of which are summarized in Table 1. Densities and alkalinities were determined gravimetrically. The salinities were equated by measuring the total dissolved solids (TDS) by means of a TDS meter (EUTECH instruments, CON 11) for the low salinity range, and gravimetrically for seawater, then multiplying these values by the corresponding density. The maximum relative measurement error was 2 % stemming from the air and CO_2 flowmeters, pH, and TDS measurements.

The initial alkalinity of the water (where it is brackish, RO, or seawater) was measured at the start of each experiment using the APHA standard method # 2320, and was then used unchanged throughout the course of the calculations. This was further confirmed by calculating the variation of the alkalinity during the experiments, which was found to vary by less than 0.35 % of its initial value in the most extreme cases of absorption, a factor that was deemed negligible and was therefore not included in the calculations.

METHODOLOGY

In order to calculate the volumetric mass transfer coefficient of CO_2 absorption or desorption in water, the solubility of CO_2 needs to be measured. Hill^[8] used a pH meter to track the dissolution of CO_2 in water in a stirred tank reactor. He developed a $k_L a$ correlation based on temperature, aeration rate, and stirring speed. On the other hand, and based on Hill's^[8] experimental setup, Kordač and Linek^[7] developed a different model to calculate $k_L a$, where they noticed higher $k_L a$ values

Table 1. Physical properties of the investigated waters

Type of water	Density (kg/m^3)	Salinity as TDS (mg/L)	Alkalinity (mg/L) as CaCO_3
RO product	999.8	40	12
Brackish	1002.0	2345.7	330
BWRO reject	1003.1	5025.5	510
Seawater	1026.8	39 200	280

compared to Hill's especially in saline solutions. Lisitsin et al.^[17] conducted studies on CO₂ desorption from water. Their overall volumetric mass transfer coefficient was calculated based on the difference between the bulk CO₂ concentration and that at equilibrium following the work of Rixon^[18] and others.^[19,20] The concentrations of the various carbonate species were calculated as a function of the pH of the solution and alkalinity values. The method used by Rixon^[18] and others^[19,20] to convert pH measurements to CO₂ concentrations will be followed in this work and is briefly described in the following paragraphs along with the various equations that describe the chemistry and behaviour of the various waters.

Carbon dioxide dissolves in water as follows:



where the concentration of all dissolved CO₂ is denoted by [H₂CO₃], even though the concentration of CO₂(aq) far exceeds that of dissolved H₂CO₃. The equilibrium condition is quantified by Henry's law:

$$H_{CO_2} = \frac{[H_2CO_3]}{P_{CO_2}} \quad (2)$$

where P_{CO_2} is the partial pressure of CO₂ in atm, H_{CO_2} is Henry's law constant in mol · atm⁻¹ · L⁻¹, and [H₂CO₃] is the concentration of dissolved CO₂ in mol · L⁻¹.

H₂CO₃ dissociates in water according to the following:



and



where the dissociation constants K_1 and K_2 are in mol · L⁻¹ and are quantified as follows:

$$K_1 = \frac{[H^+][HCO_3^-]}{[H_2CO_3]} \quad (5)$$

$$K_2 = \frac{[H^+][CO_3^{2-}]}{[HCO_3^-]} \quad (6)$$

The dissociation constant of water, K_w , is represented as follows:

$$K_w = 10^{-14} = [H^+][OH^-] \quad (7)$$

By measuring the pH of the solution, the concentrations of the different dissolved carbon species can be calculated with the help of the total alkalinity, where in the absence of other weak acids:^[17]

$$T_{Alk} = [HCO_3^-] + 2[CO_3^{2-}] + [OH^-] - [H^+] \quad (8)$$

From Equations (5–8), the concentrations of [CO₂], [HCO₃⁻], [CO₃²⁻], and total carbon content, [C_T], are calculated according to Equations (9–12). It should be noted that [CO₂] is the same as [H₂CO₃].

$$[CO_3^{2-}] = \left(T_{Alk} + [H^+] - \frac{K_w}{[H^+]} \right) \frac{K_2}{2K_2 + [H^+]} \quad (9)$$

$$[HCO_3^-] = \left(T_{Alk} + [H^+] - \frac{K_w}{[H^+]} \right) \frac{[H^+]}{2K_2 + [H^+]} \quad (10)$$

$$[H_2CO_3] = [CO_2] = \left(T_{Alk} + [H^+] - \frac{K_w}{[H^+]} \right) \frac{[H^+]^2}{2K_1K_2 + [H^+]K_1} \quad (11)$$

$$[C_T] = [HCO_3^-] + [CO_3^{2-}] + [CO_2] \\ = \left(\frac{T_{Alk} + [H^+] - \frac{K_w}{[H^+]}}{1 + 2\frac{K_2}{[H^+]}} \right) \left(1 + \frac{K_2}{[H^+]} + \frac{[H^+]}{K_1} \right) \quad (12)$$

For brackish water reject and seawater, K_1 and K_2 are taken from Lee and Millero:^[21]

$$\ln K_1 = 3.17537 - \frac{2329.1378}{T} - 1.597015 \ln(T) \\ + \left(-0.210502 - \frac{5.79495}{T} \right) S^{0.5} + 0.0872208S - 0.00684651S^{1.5} \quad (13)$$

$$\ln K_2 = -8.19754 - \frac{3403.8782}{T} - 0.352253 \ln(T) \\ + \left(-0.08885 - \frac{25.95316}{T} \right) S^{0.5} + 0.1106658S - 0.00840155S^{1.5} \quad (14)$$

For RO water and brackish water, K_1 and K_2 equations are taken from Millero:^[22]

$$\ln K_1 = 290.9097 - \frac{14554.21}{T} - 45.0575 \ln T \\ + \left(-228.39774 + \frac{9714.36839}{T} + 34.485796 \ln T \right) S^{0.5} \\ + \left(54.20871 - \frac{2310.48919}{T} - 8.19515 \ln T \right) S \\ + \left(-3.969101 + \frac{170.22169}{T} + 0.603627 \ln T \right) S^{1.5} \\ - 0.00258768S^2 \quad (15)$$

$$\ln K_2 = 207.6548 - \frac{11843.79}{T} - 33.6485 \ln T + \\ \left(-167.69908 + \frac{6551.35253}{T} + 25.928788 \ln T \right) S^{0.5} + \\ \left(39.75854 - \frac{1566.13883}{T} - 6.171951 \ln T \right) S + \\ \left(-2.892532 + \frac{116.270079}{T} + 0.45788501 \ln T \right) S^{1.5} \\ - 0.00613142S^2 \quad (16)$$

K_w is used for all types of water, T up to 35 °C, S up to 44g/kg, and is taken from Dickson and Riley:^[23]

$$\ln K_w = -\left(\frac{3441}{T} + 2.241 - 0.09415S^{0.5}\right) \quad (17)$$

Henry's constant equation is used for all four types of water, is applicable for $0^\circ\text{C} < T < 40^\circ\text{C}$ and $0 < S < 40 \text{ g/kg}$, and is taken from Weiss:^[24]

$$\ln H_{\text{CO}_2} = -60.24 + 93.45\left(\frac{100}{T}\right) + 23.36\ln\left(\frac{T}{100}\right) + S\left[0.0235 - 0.0236\left(\frac{T}{100}\right) + 0.0047\left(\frac{T}{100}\right)^2\right] \quad (18)$$

The value of $k_L a$ is then obtained by following the variation of C_T with time and applying an overall mass transfer equation based on the liquid phase driving force^[17–20] as shown in Equation (19), which is written for the desorption case.

$$-\frac{dC_T}{dt} = k_L a ([\text{CO}_2] - [\text{CO}_2]^*) \quad (19)$$

where $[\text{CO}_2]^*$ is the equilibrium concentration of CO_2 at equilibrium with the gaseous phase. Therefore, plotting $-dC_T/dt$ as a function of $[\text{CO}_2]$ should render a straight line, the slope of which is equivalent to $k_L a$ and the intercept is equal to $k_L a \times [\text{CO}_2]^*$.

RESULTS

As previously mentioned, the experimental runs consisted of monitoring the variation of the water pH under absorption and desorption conditions at pre-set time intervals. In all experiments, it was observed that the case of absorption reached a steady state pH value much faster than the case of desorption, with the magnitude of the change being a function of the operating conditions. Steady state, which was defined as a change less than 1 % in 100 s, was reached within 300 s for the absorption cases. A larger time interval of approximately 2000 to 3000 s was generally needed for the desorption experiments. This behaviour is clearly shown in Figure 2 where the variation of pH is plotted against time for the absorption and desorption cases in a MAT. The plot shows a sudden decrease in pH due to the introduction of CO_2 to the system. After reaching steady state the CO_2 flow is switched to air and the pH starts to increase again.

The raw data presented in Figure 2 is then reconverted to CO_2 concentration profiles which clearly shows the effect of absorption and desorption. These trends are shown in Figure 3 for the same conditions presented in Figure 2.

Effect of Gas Flow Rate

Absorption

The variation of the volumetric mass transfer coefficient, $k_L a$, with CO_2 gas flow rate during absorption for all four water types is shown in Figure 4 for the MAT at two different impeller speeds. From Figure 4 it can be seen that an increase in the gas flow rate leads to an increase in the value of $k_L a$. Changing the CO_2 flow rate from 5 to 40 L/min induced a growth in the $k_L a$ value of 2–3 fold for the MAT at an impeller speed of 200 rpm, 2.5–4 fold for the MAT at an impeller speed of 465 rpm. These results agree with the observations of several investigators^[8,25]

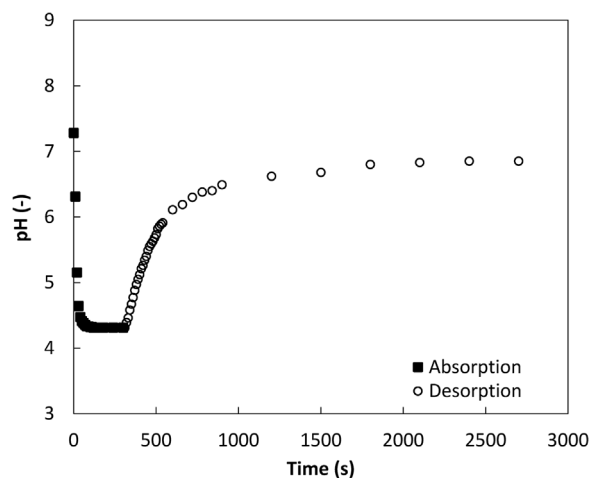


Figure 2. Variation of the pH with time for the absorption and desorption studies for MAT at $N = 465 \text{ rpm}$ and $Q_g = 40 \text{ L/min}$.

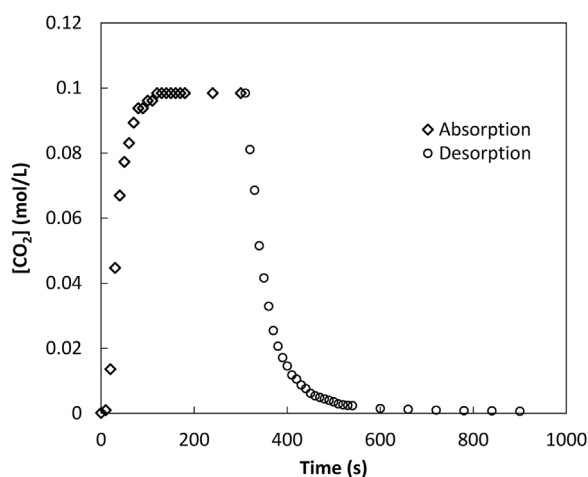


Figure 3. Profile of CO_2 versus time for the absorption and desorption studies for MAT at $N = 465 \text{ rpm}$ and $Q_g = 40 \text{ L/min}$.

who have shown that an increase in the gas flow rate will induce an increase in the value of $k_L a$ which is attributed to an increase in the value of the interfacial area of contact, a .

Desorption

The variation of the volumetric mass transfer coefficient, $k_L a$, with air gas flowrate for all four water types is shown in Figure 5 for the MAT at two different impeller speeds. From this figure, it can be seen that an increase in the gas flow rate also leads to an increase in the value of $k_L a$. The magnitude of this increase is such that the increase in $k_L a$ with the increase in CO_2 gas flow rate (from 5 to 40 L/min) was 2–4.5 fold for the MAT at a rotator speed of 200 rpm and 2 fold for the MAT at a rotator speed of 465 rpm. These results also agree with the observations of several investigators^[17,26,27] who reported that an increase in the gas flow rate, independently of the contactor/reactor type, will induce an increase in the value of $k_L a$.

Effect of Salinity and Alkalinity

Absorption

The variation of $k_L a$ with salinity is shown in Figure 6 for the MAT at two different impeller speeds. From Figure 6, it can be seen that

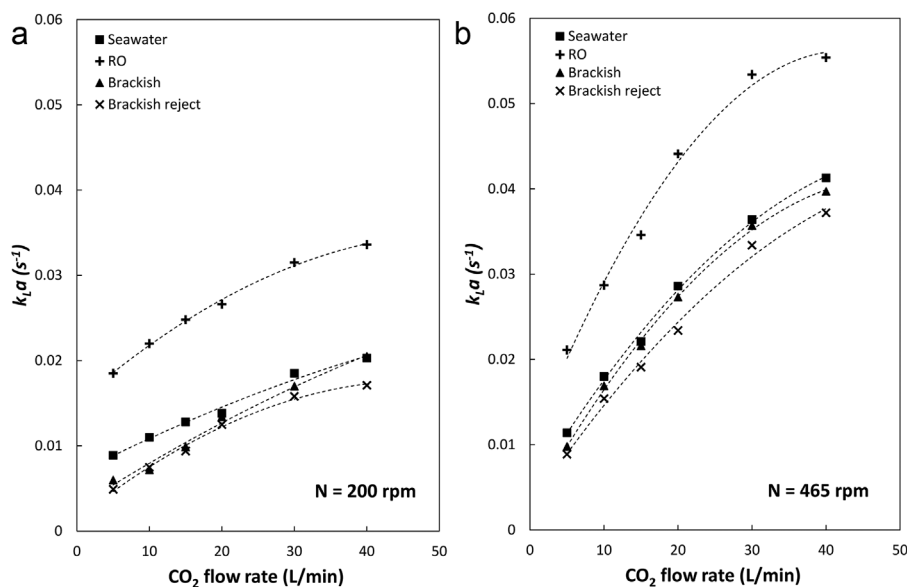


Figure 4. Effect of impeller speed on $k_L a$ of CO₂ absorption in various waters.

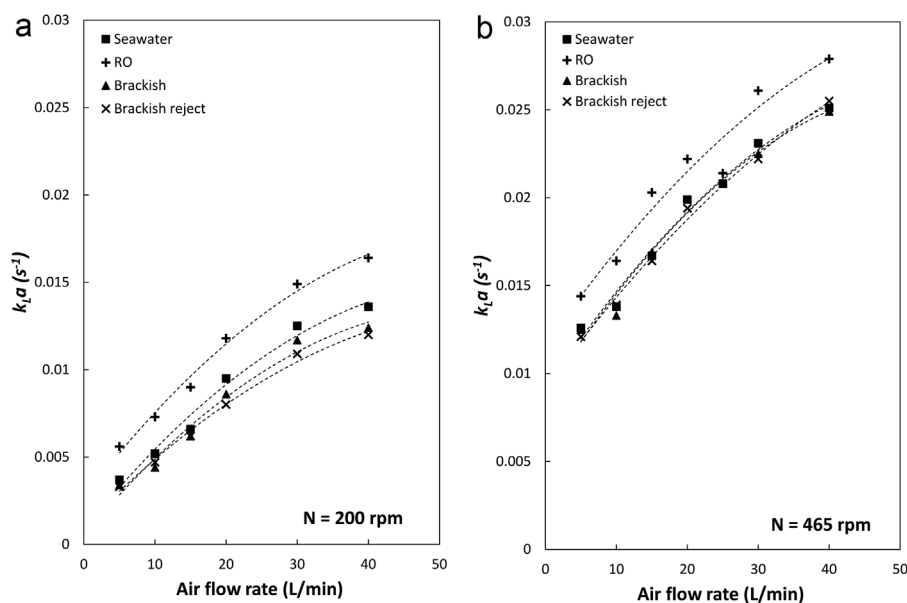


Figure 5. Effect of impeller speed on $k_L a$ of CO₂ desorption in various waters.

the volumetric mass transfer coefficient, $k_L a$, for the two contactor types, irrespective of the impeller speed of the MAT, decreases with increasing salinity until it reaches a minimum value for the brackish water reject, at a TDS of 5025 mg/L, and then the $k_L a$ is observed to increase for seawater (at a TDS of 39 200 mg/L). This phenomenon applies for the entire gas flow rate range. At the highest CO₂ gas flow rate of 40 L/min, the volumetric mass transfer coefficient of CO₂ into seawater is 40 % lower than that recorded for absorption into RO water for the MAT at a rotator speed of 200 rpm, 25 % lower for the MAT at a rotator speed of 465 rpm. Note that at lower CO₂ gas flow rates the difference between the two $k_L a$ values becomes much higher: 52 % for the MAT at a rotator speed of 200 rpm and 46 % for the MAT at a rotator speed of 465 rpm. For the range of CO₂ gas flow rates investigated, the volumetric mass transfer coefficients of CO₂ into

brackish water RO reject (lowest $k_L a$ values) are 49–74 % lower than those recorded for absorption into RO water (highest $k_L a$ values) for the MAT at a rotator speed of 200 rpm and 33–58 % lower for the MAT at a rotator speed of 465 rpm, with the difference being highest at the lower gas flow rates.

The variation of $k_L a$ with alkalinity is shown in Figure 7 for the MAT at two different impeller speeds where it can be seen that for the two contactor types, irrespective of the impeller speed of the MAT, $k_L a$ decreases with increasing alkalinity. For the same operating conditions, the volumetric mass transfer coefficients of CO₂ absorption into brackish water reject (lowest $k_L a$ and highest alkalinity) are 49–66 % lower than those recorded for absorption into RO water (highest $k_L a$ values and lowest alkalinity) for the MAT at 200 rpm and 33–58 % lower for the MAT at 465 rpm with the difference being highest at the lower gas flow rates.

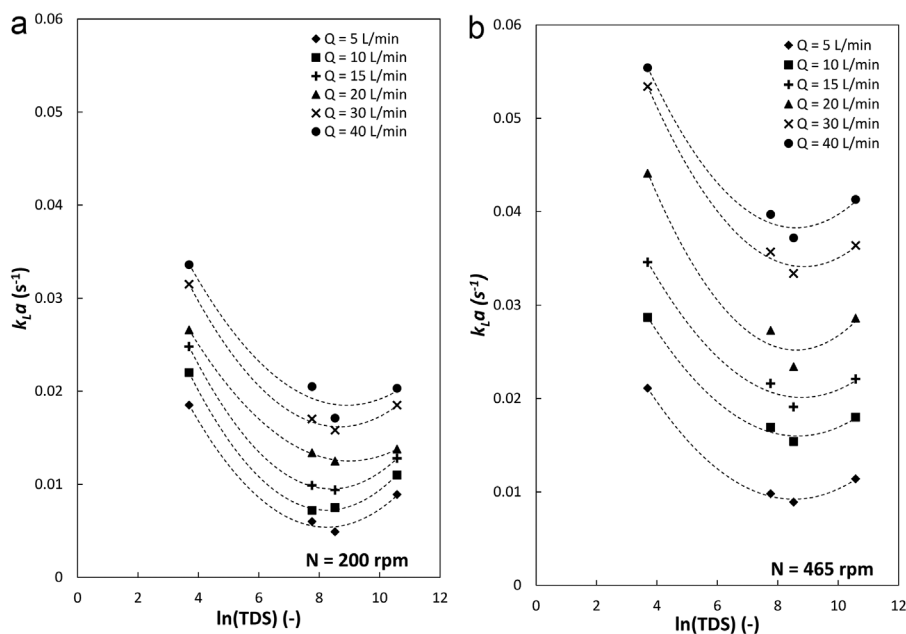


Figure 6. Effect of salinity on k_La for CO_2 absorption at two different impeller speeds.

There are a limited number of studies that have directly measured the values of k_La for carbon dioxide absorption into water streams at different salinities; there are none that have considered the effect of alkalinity on k_La in absorption studies. Therefore a direct comparison of the results reported in this work with others will be difficult. Nevertheless, and as elucidated in Elhajj et al.,^[1] contradictory results are found in the literature and a consensus on a positive or negative impact of salinity on k_La is yet to be reached. Hill^[8] reported that the addition of salt (2.85 % NaCl solution) to distilled water in a well-mixed mechanically agitated contactor results in a slight decrease in k_La , which is in contradiction with the findings of other workers.^[7,28] The reduction in k_La is caused by ionic charge effects at the bubble

surface reducing the ability of CO_2 molecules to diffuse away from the surface. Tokumura et al.^[29] reported the increase in salinity inhibited the absorption of CO_2 into aqueous streams. Kordač and Linek^[7] criticized the analysis of Hill^[8] for the estimation of CO_2 solubility and determination of k_La and stated that for systems with a $\text{pH} < 5$, the addition of electrolytes to distilled water will in fact lead to an increase in the k_La values.

Contradictory results are also found for the effect of electrolytes on the volumetric mass transfer coefficient, k_La , in absorption studies for oxygen-water systems. In these studies, several workers have reported that the presence of electrolytes in water results in increasing value of k_La ^[30–33] while others have reported an opposite trend where the presence of electrolytes has resulted in

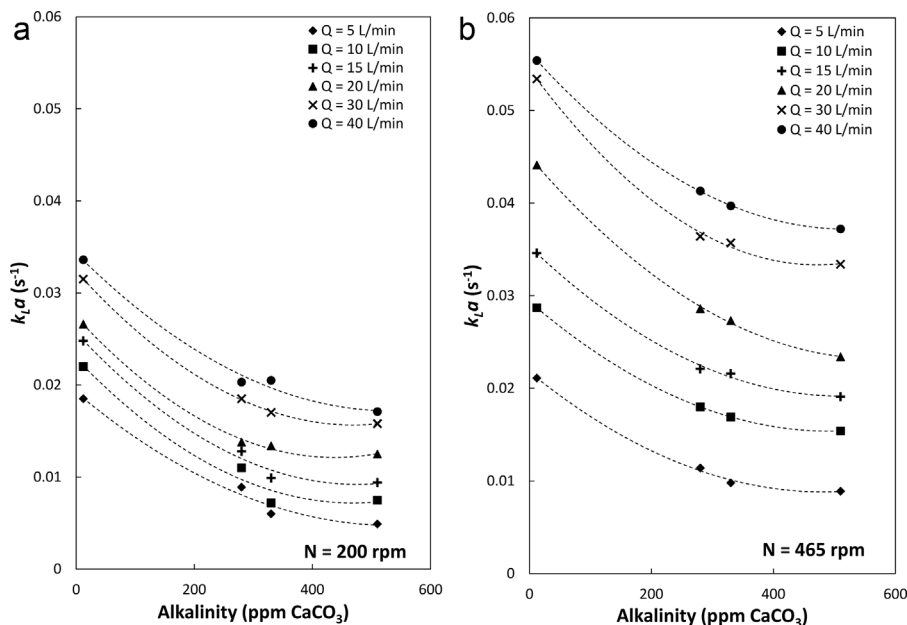


Figure 7. Effect of alkalinity on k_La for CO_2 absorption at two different impeller speeds.

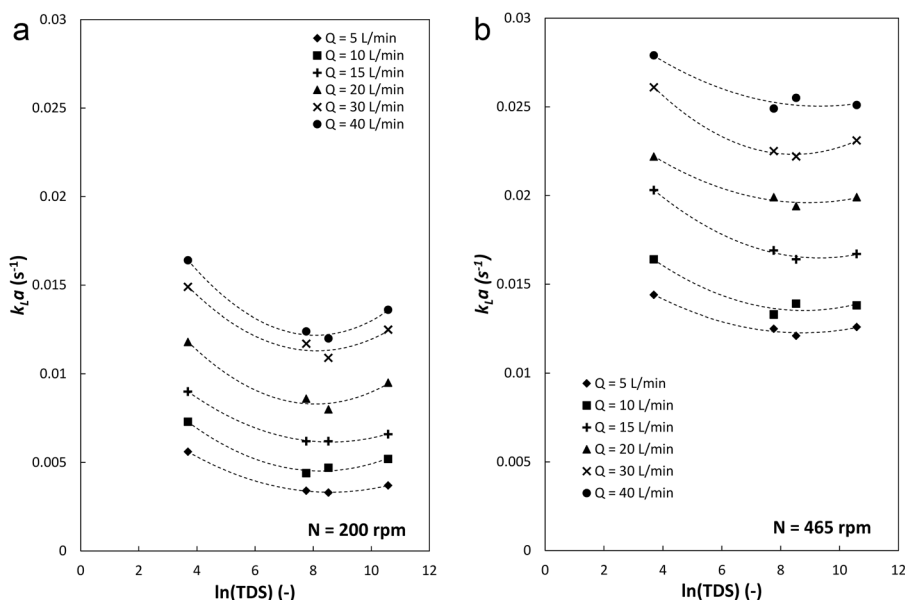


Figure 8. Effect of salinity on $k_L a$ for CO₂ desorption at two different impeller speeds.

a decrease in the volumetric mass transfer coefficient.^[34,35] Investigators who have observed an increase in $k_L a$ with salinity have often reported this increase to be related to the ionic strength of the solution ($k_L a$ increases with ionic strength). They explained this increase in terms of the increase in the interfacial area of contact, a , caused by the occurrence of smaller gas bubbles arising from the ability of electrolytes to retard bubble coalescence with the mass transfer coefficient, k_L , remaining almost constant and not being affected by the presence of electrolytes.^[30–33] On the other hand the decrease of $k_L a$ with salinity has been attributed to the reduction of the mass transfer coefficient (k_L) with salinity overriding the increase in the interfacial area,^[34] the formation of relatively large bubbles and/or reduced solubility of gases^[33] and the increased viscosity and reduced diffusion in the boundary layer in salt water.^[35]

Desorption

The variation of $k_L a$ with salinity is shown in Figure 8 for the MAT at two different rotator speeds. It can be seen that $k_L a$ for the MAT decreases with increasing salinity until it reaches a minimum value for the brackish water reject, at a TDS of 5025 mg/L, and then the $k_L a$ is observed to increase for seawater (at a TDS of 39 200 mg/L). Although these observations are similar to those recorded for absorption, the difference between the two values is much lower for desorption. At the highest air flow rate of 40 L/min, the volumetric mass transfer coefficient of CO₂ desorption from seawater is 17 % lower than that recorded for CO₂ desorption from RO water for the MAT at a rotator speed of 200 rpm and 9 % lower for the MAT at a rotator speed of 465 rpm. The range of variation is also much less pronounced when compared to the absorption results. For the range of air flow rates investigated, the volumetric mass transfer coefficients of CO₂ desorption from brackish water RO reject (lowest $k_L a$ values) are 27–41 % lower than those recorded for absorption into RO water (highest $k_L a$ values) for the MAT at a rotator speed of 200 rpm and 9–16 % lower for the MAT at a rotator speed of 465 rpm.

The variation of $k_L a$ with alkalinity is shown in Figure 9 for the MAT at two different rotator speeds where it can be seen that

the volumetric mass transfer coefficient for the MATs decreases with increasing alkalinity. For the same operating conditions, the volumetric mass transfer coefficients of CO₂ desorption from brackish water reject (lowest $k_L a$ and highest alkalinity) are 27–41 % lower than those recorded for desorption into RO water (highest $k_L a$ values and lowest alkalinity) for the MAT at 200 rpm and 9–19 % lower for the MAT at 465 rpm with the difference being highest at the lower air flow rates. It is worthwhile noting however that Aitchison et al.^[36] reported reduced $k_L a$ values at higher water alkalinities (in the range of 12–39 %) for surface and submerged aerator systems.

The effect of salinity on the rate of CO₂ desorption from water has been investigated by a number of workers and, as with absorption studies, the results are somewhat contradictory. Barrut et al.'s^[27] experimental results showed that $k_L a$ was not affected by the salinity of the water. A similar observation was made by Moran^[37] who noted that water salinity does not appear to have an effect on mass transfer. On the other hand, Tokumura et al.^[38] reported the $k_L a$ values for desorption of CO₂ from seawater to be ~1.5 times larger than those in tap water and postulated that this higher rate is due to the salting out effect. MW Kellogg^[39] found the seawater $k_L a$ to be slightly higher than that for tap water. Hikita and Konishi^[40] observed a 1.4-fold increase in the $k_L a$ for electrolytic solutions, while in a different study^[41] they found the presence of electrolytes led to enhanced $k_L a$ values, when compared to distilled water, and the factor by which the $k_L a$ increased was a function of the ionic strength of the solution. On the other hand, several investigators have reported lower CO₂ desorption rates from seawater compared to desorption rates from fresh or slightly saline water.^[37,42,43] Moran^[37] explained that desorption of carbon dioxide is not a purely physical process but involves both mass transfer and chemical reactions. According to him, the relatively slow dehydroxylation of HCO₃⁻ to CO₂ (Equations (1) and (2)) combined with the ionization fractions of the inorganic carbon species prevent the system from achieving equilibrium and thus hinder the replenishment of the desorbed CO₂, leading to a slowing of the desorption process. Howe and Lawler^[44] on the other hand

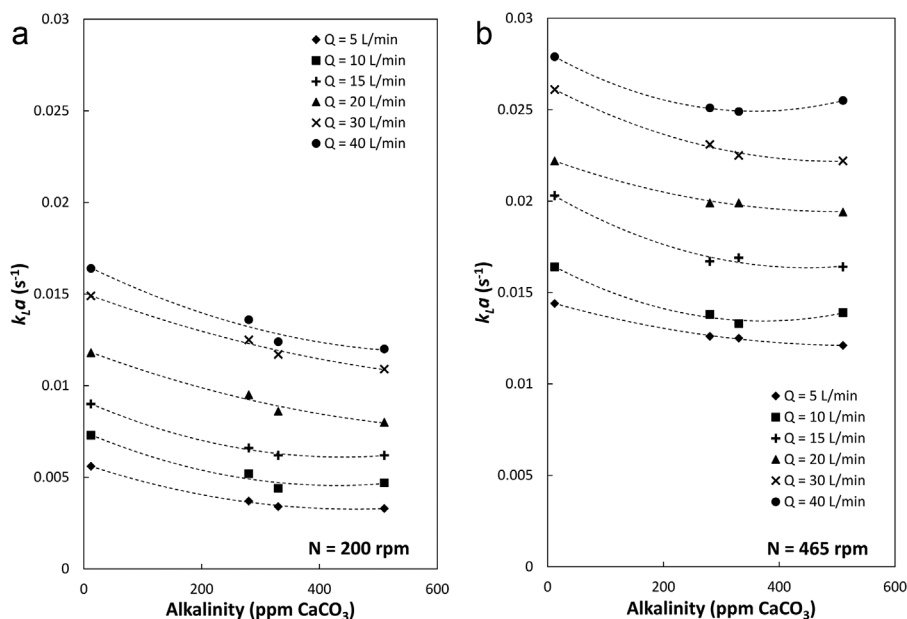


Figure 9. Effect of alkalinity on k_La for CO_2 desorption at two different impeller speeds.

noted that the acid-base reactions are much faster than diffusion across the mass-transfer zone and, therefore, kinetics will not have any bearing on the rate of desorption.

Absorption versus Desorption

The volumetric mass transfer coefficients for absorption and desorption of CO_2 at various gas flow rates are compared for MAT at 200 rpm and 465 rpm for RO water and for seawater in Figure 10 and Figure 11, respectively. From Figure 10 it can be seen that for the gas flow rate range investigated in this work the absorption k_La of CO_2 into RO water is always larger than the desorption k_La of CO_2 from RO water (in the range of 12–70 %). With the exception of one value (at the flowrate of 5 L/min) where the difference is less than 15 % (and could be due to an experimental error), the same pattern is observed for the absorption and desorption of CO_2 from seawater (cf. Figure 11).

The k_La values for the absorption of CO_2 into seawater are up to 50 % larger than those for desorption.

Several authors^[29,38,45–47] have stated that the volumetric mass transfer coefficients for the absorption and desorption processes of CO_2 to and from water are equivalent^[48] since both processes are considered as purely physical as opposed to chemical processes, such as desorption/absorption of CO_2 to and from diethylamine (DEA) where absorption/desorption is accompanied by chemical reaction. On the other hand, several other authors have reported differences between desorption and absorption rates and their respective volumetric mass transfer coefficients. A few authors^[9,18,49] reported higher k_La values for desorption than for absorption in packed towers, bubble columns, and mechanically stirred columns respectively. Rixon^[18] stated that the rate of hydration of CO_2 in the absorption process may account for the difference between absorption and desorption, while Panja and

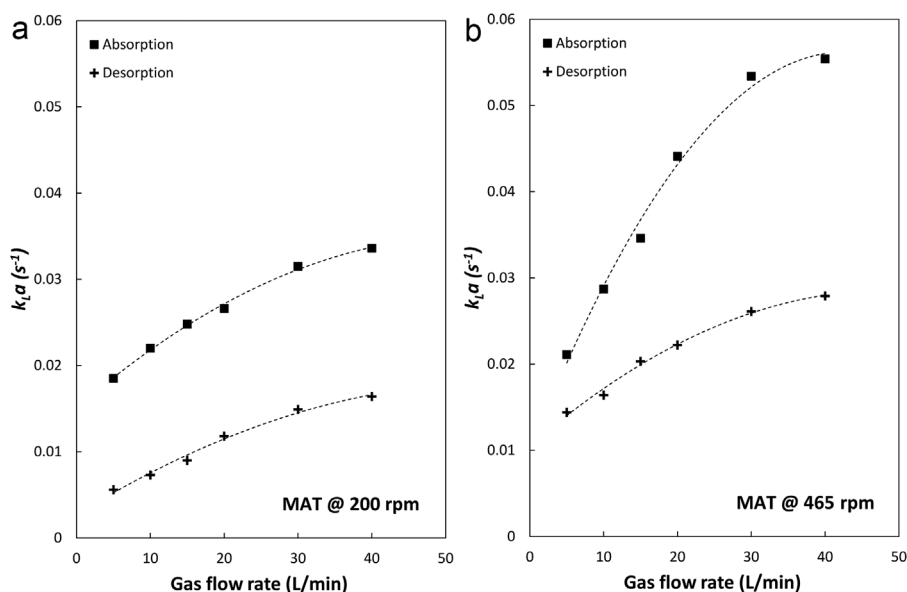


Figure 10. Comparison between the absorption and desorption k_La for RO water at two different impeller speeds.

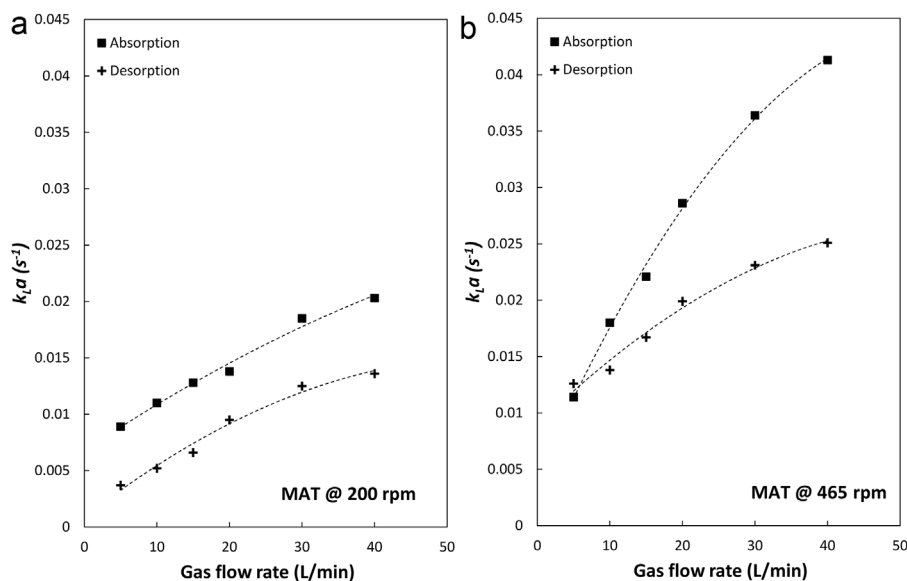


Figure 11. Comparison between the absorption and desorption k_La for seawater at two different impeller speeds.

Phaneswararo^[49] concluded that the higher values for desorption may be the result of the additional surface area caused by bubble nucleation arising from the super-saturation conditions. On the other hand, Thuy and Weiland^[50] noted that for agitated pressurized vessels the mass transfer coefficients were higher for absorption than for non-bubbling desorption due to lower (interfacial) resistance during absorption. Thomas et al.^[51] also reported that the desorption rate in a liquid film flow over inclined plates to be approximately 75 % of the transfer rate of absorption over a wide operating range. Al-Mashhadani et al.^[52] found the stripping time in an airlift loop sparged tank to be substantially longer than the absorption time, which is in line with the observations in this work.

In an attempt to reach a conclusion on this matter, experimental runs for both absorption and desorption using pure de-ionized water (initial conductivity of $\sim 40 \mu\text{S}/\text{cm}$) were conducted at the lowest stirring speed and flow rates of 5 and 10 L/min. The k_La values were 0.0101 s^{-1} and 0.014 s^{-1} for the absorption case, and 0.00915 s^{-1} and 0.0123 s^{-1} for the desorption case, respectively.

These findings show that regardless of the direction of transfer, the values of k_La fell within $\pm 10 \%$ of each other, which is considered within experimental errors. Therefore, it can be concluded that the presence of electrolytes and/or other contaminants in the water does contribute to the discrepancies in the measured values of the volumetric mass transfer coefficient with respect to mass transfer direction.

Effect of equilibrium conditions

Kordač and Linek^[7] warned from the wrong assumptions of ideal mixing and negligible mass transfer resistance in the gas phase where $[\text{CO}_2]^*$ would be in equilibrium with the CO_2 leaving the vessel. According to them, these conditions hold for the absorption of sparingly soluble gases, such as oxygen and carbon dioxide while the former assumption remains questionable. However, they stated that all the aforementioned assumptions hold for low k_La values ($< \sim 0.055 \text{ s}^{-1}$). Kordač and Linek^[7] further criticized the analysis of Hill^[8] who based his analysis on the ideal mixing assumption and presented two mathematical models that can be used to account for the depletion of CO_2 from the gas phase and calculate the value of k_La .

In the current work, the assumption of ideal mixing holds true in the absorption studies since pure CO_2 gas was used to conduct the experiments, leaving a uniform composition of the gas phase. However, these assumptions had to be checked for the case of desorption where air was used to strip the CO_2 out of the aqueous phase. Under these conditions, the concentration of carbon dioxide in the gas phase is expected to build-up over time thereby affecting the value of $[\text{CO}_2]^*$.

The two models of Kordač and Linek^[7] were presented for the cases where the first dissociation reaction, Equation (3), is instantaneous or moderately reversible while the second dissociation reaction, Equation (4), is always at equilibrium. This latter assumption was also observed in the current work, where the effect of K_2 was found very minimal compared to that of K_1 ($K_2 \ll K_1$) and does not have a significant contribution. Furthermore, the models of Kordač and Linek^[7] were solved for the case of desorption and were found to render very close results (amongst each other) and had an average deviation within $\pm 15 \%$ from the reported values in the current study. This is in line with the statement of Kordač and Linek^[7] that the assumptions of ideal mixing and negligible mass transfer resistance in the gas phase can hold true for low k_La values ($< \sim 0.055 \text{ s}^{-1}$), which is the case for the current work where the maximum recorded k_La value in the desorption studies was 0.0255 s^{-1} .

Correlating the Results

The volumetric mass transfer coefficient, k_La , data presented in this work were correlated with the operating conditions, namely, gas flow rate (in L/min), TDS (in mg/L), alkalinity (in mg/L as CaCO_3), and impeller rotational speed, N (in rpm). The correlations for absorption and desorption followed Equation (20), and the results are summarized in Table 2. Furthermore, another

Table 2. Correlation parameters for the volumetric mass transfer coefficient according to Equation (20)

Experiment	A_N	α	β	γ	δ	R^2
Absorption	1.988×10^{-4}	0.695	0.033	-0.243	0.557	0.954
Desorption	1.248×10^{-5}	1.022	0.011	-0.089	0.498	0.952

Table 3. Correlation parameters for the volumetric mass transfer coefficient according to Equation (21)

Experiment	A_{pV}	b	c	d	e	R^2
Absorption	1.99×10^{-3}	0.231	0.033	-0.243	0.557	0.954
Desorption	3.68×10^{-4}	0.34	0.011	-0.089	0.498	0.952

Table 4. Range of $k_L a$ values obtained in the current work for various water types

Experiment	$k_L a \times 10^3 \text{ (s}^{-1}\text{)}$
Absorption	4.9–55.4
Desorption	3.3–27.9

attempt to correlate the data with an industrially important parameter, Po/V (in W/m^3), power per unit volume, was also undertaken. This dependency is shown in Equation (21) and the results are summarized in Table 3.

$$k_L a = A_N \cdot N^\alpha \cdot TDS^\beta \cdot Alk^\gamma \cdot Q_g^\delta \quad (20)$$

$$k_L a = A_{pV} \cdot (Po/V)^b \cdot TDS^c \cdot Alk^d \cdot Q_g^e \quad (21)$$

While it is very hard to compare most of these results with published data due to their unavailability, the dependency on the flow rate of CO_2 into the contactor was found to be comparable with some published data. Panja and Rao^[53] found that $k_L a$ varies with $u_g^{0.75}$ which is comparable to the current value of 0.557 found in this work. The situation is not any easier for the case of desorption because of the lack of available data in the open literature. However, Hikita and Konishi^[41] reported a dependency of the desorption $k_L a$ in electrolyte solutions on the impeller rotational speed proportional to $N^{0.93}$ in the high bubbling regime, which compares favourably with the current value of $N^{1.022}$.

One should note that the constant power factor β for TDS in Equation (20) might not reflect the observed minimum in the reported trends. To explain this, one should consider the combined effect of the exponents of salinity and alkalinity (i.e. β and γ) in the correlation (positive exponent for salinity and a negative one for alkalinity) to predict the presence of a minimum for TDS. The minimum $k_L a$ with respect to salinity corresponds to the brackish reject water, which has the highest alkalinity of all investigated waters and therefore the combined effect of both alkalinity and salinity would reflect a low $k_L a$ value.

When comparing the results obtained in this work with the various $k_L a$ values for CO_2 absorption and desorption in water, we find that the range of these values as shown in Table 4 is very similar to the range of reported results in various published studies as compiled by Elhajj et al.^[1]

CONCLUSIONS

This study investigated the rate of CO_2 transfer from/to aqueous phases of varying degrees of alkalinity and salinity to study the effect of the presence of electrolytes in a mechanically agitated tank. In all these studies, $k_L a$ values were calculated for absorption and desorption experiments and the results showed many interesting trends.

In accordance with most published data, the volumetric mass transfer coefficient, $k_L a$, values always increased with an increase in the gas flow rate for both absorption and desorption experiments. In desorption experiments, the highest $k_L a$ values were always recorded for the MAT running at the highest impeller speed (i.e. 465 rpm). This fact clearly highlights the importance of energy input to the system on the value of $k_L a$. Furthermore, absorption experiments always showed a higher $k_L a$ value when compared to desorption studies, with a difference up to 70 % in certain cases.

A notable finding was that in both absorption and desorption studies, $k_L a$ decreased steadily with the salinity of water until a certain critical value was reached, beyond which the effect was reversed and mass transfer increased again. However, interpreting the data by means of water alkalinity showed a different trend, where $k_L a$ continuously decreased with an increase in the water alkalinity for the absorption experiments. But, the effect of alkalinity was not as clear in the case of desorption with the trends being a function of the mixing intensity.

Finally, it can be concluded that the effects of both alkalinity and salinity need to be taken into account while investigating the effect of electrolytes on the mass transfer coefficient and/or bubble size evolution. When accounted for, the effect of alkalinity might help interpret the reported contradictory results obtained for the effect of salinity on $k_L a$. However, systematic studies where alkalinity is changed independently of the salinity (and vice versa) are still required to discern the impact of each parameter on the value of $k_L a$. Furthermore, an in-depth look at the effect of density, viscosity, turbulence, dynamic surface tension, and the decoupling of the measurements of k_L and the interfacial area, a , is still required to obtain concrete conclusions on this matter.

ACKNOWLEDGEMENTS

The financial support of the Lebanese National Council for Scientific Research (LNCSR) and the University Research Board (URB) of the American University of Beirut is greatly acknowledged. The authors would also like to thank Dina Ibrahim Abouelamaiem, Jessy Elhajj, Said Rahal, Ramez Zayat, and Michael Serhan for their assistance in this work.

NOMENCLATURE

A	correlation parameter
a	interfacial area of contact (m^2/m^3)
Alk	water alkalinity ($mg \cdot L^{-1}$ as $CaCO_3$)
b, c, d, e	correlation parameters
C_T	total carbon content ($mol \cdot m^{-3}$)
H_{CO_2}	Henry's constant of CO_2 in water ($mol \cdot atm^{-1} \cdot L^{-1}$)
K_1, K_2	dissociation constants ($mol \cdot m^{-3}$)
k_L	overall mass transfer coefficient ($m \cdot s^{-1}$)
$k_L a$	volumetric mass transfer coefficient (s^{-1})
K_w	equilibrium constant of water ($mol \cdot m^{-3}$)
N	impeller rotational speed (rpm)
P	total pressure (Pa)
P_{CO_2}	partial pressure of CO_2 (Pa)
Po	power input to the tank (W)
Q_g	gas flow rate ($L \cdot min^{-1}$)
S	% salinity ($g \cdot kg^{-1}$)
T	temperature (K)
T_{alk}	total alkalinity ($mol \cdot m^{-3}$)
TDS	total dissolved solids (mg/L)
V	tank volume m^3

Greek Letters

α , β , γ , δ correlation parameters

REFERENCES

- [1] J. Elhajj, M. Al-Hindi, F. Azizi, *Ind. Eng. Chem. Res.* **2014**, *53*, 2.
- [2] A. E. Al-Rawajfeh, H. Glade, J. Ulrich, *Desalination* **2005**, *182*, 209.
- [3] H. Glade, A. E. Al-Rawajfeh, *Desalination* **2008**, *222*, 605.
- [4] J. M. Smith, S. W. Davison, G. F. Payne, *Biotechnol. Bioeng.* **1990**, *35*, 1088.
- [5] P. N. C. Royce, N. F. Thornhill, *AIChE J.* **1991**, *37*, 1680.
- [6] R. W. Babcock, J. Malda, J. C. Radway, *J. Appl. Phycol.* **2002**, *7*, 169.
- [7] M. Kordač, V. Linek, *Ind. Eng. Chem. Res.* **2008**, *47*, 1310.
- [8] G. A. Hill, *Ind. Eng. Chem. Res.* **2006**, *45*, 5796.
- [9] K. Thaker, D. P. Rao, *Chem. Eng. Res. Des.* **2007**, *85*, 1362.
- [10] J. C. M. Pires, M. C. M. Alvim-Ferraz, F. G. Martins, M. Simões, *Renew. Sust. Energ. Rev.* **2012**, *16*, 3043.
- [11] R. Chavez, J. D. J. Guadarrama, *Chem. Eng. Trans.* **2010**, *21*, 577.
- [12] D. Gómez-Díaz, J. M. Navaza, *Chem. Eng. J.* **2005**, *114*, 131.
- [13] R. Maceiras, X. R. Nóvoa, E. Álvarez, M. A. Cancela, *Chem. Eng. Process. Proc. Intens.* **2007**, *46*, 1006.
- [14] H. Chaumat, A. M. Billet-Duquennois, F. Augier, C. Mathieu, H. Delmas, *Chem. Eng. Sci.* **2005**, *60*, 5930.
- [15] American Public Health Association, American Water Works Association, Water Environment Federation, *Standard Methods for the Examination of Water and Wastewater*. 21st edition, A. D. Eaton, M. A. H. Franson, Eds., American Public Health Association, American Water Works Association, Water Environment Federation, Washington DC **2005**.
- [16] American Society for Testing and Materials (ASTM), "ASTM Standard D513-11E1," in *2006 ASTM Annual Book and Standards*, ASTM, West Conshohocken **2006**.
- [17] D. Lisitsin, D. Hasson, R. Semiat, *Desalination* **2008**, *222*, 50.
- [18] F. F. Rixon, *Trans. Inst. Chem. Eng.* **1948**, *26*, 119.
- [19] G. Vázquez, M. A. Cancela, R. Varela, E. Alvarez, J. M. Navaza, G. Vazquez, M. A. Cancela, R. Varela, E. Alvarez, J. M. Navaza, *Chem. Eng. J.* **1997**, *67*, 131.
- [20] R. E. Loewenthal, G. V. R. Marais, *Carbonate chemistry of aquatic systems; Theory & application*, Ann Arbor Science, Ann Arbor **1976**.
- [21] K. Lee, F. J. Millero, *Deep-Sea Res. Part I* **1995**, *42*, 2035.
- [22] F. J. Millero, *Geochim. Cosmochim. Ac.* **1995**, *59*, 661.
- [23] A. G. Dickson, J. P. Riley, *Mar. Chem.* **1979**, *7*, 89.
- [24] R. F. Weiss, *Mar. Chem.* **1974**, *2*, 203.
- [25] N. C. Panja, D. P. Rao, *Chem. Eng. J.* **1993**, *52*, 121.
- [26] N. Matsunaga, K. Kano, Y. Maki, T. Dobashi, *J. Biosci. Bioeng.* **2009**, *107*, 419.
- [27] B. Barrut, J.-P. Blancheton, J.-Y. Champagne, A. Grasmick, *Aquacult. Eng.* **2012**, *46*, 18.
- [28] K. Van't Riet, *Ind. Eng. Chem. Process D. D.* **1979**, *18*, 357.
- [29] M. Tokumura, M. Baba, Y. Kawase, *Chem. Eng. Sci.* **2007**, *62*, 7305.
- [30] S. A. Zieminski, R. C. Whittemore, *Chem. Eng. Sci.* **1971**, *26*, 509.
- [31] C. W. Robinson, C. R. Wilke, *AIChE J.* **1974**, *20*, 285.
- [32] H. Hikita, S. Asai, K. Tanigawa, K. Segawa, M. Kitao, *Chem. Eng. J.* **1981**, *22*, 61.
- [33] A. M. Al Taweel, A. O. Idhbeaa, A. Ghanem, *Chem. Eng. Sci.* **2013**, *100*, 474.
- [34] D. Ruen-ngam, P. Wongsuchoto, A. Limpanuphap, T. Charinpanitkul, P. Pavasant, *Chem. Eng. J.* **2008**, *141*, 222.
- [35] G. A. Hill, *Ind. Eng. Chem. Res.* **2009**, *48*, 3696.
- [36] T. F. Aitchison, M. B. Timmons, J. J. Bisogni, R. H. Piedrahita, B. J. Vinci, *International Journal of Recirculating Aquaculture* **2007**, *8*, 21.
- [37] D. Moran, *Aquacult. Eng.* **2010**, *43*, 29.
- [38] M. Tokumura, M. Baba, H. T. Znad, Y. Kawase, C. Yongsiri, K. Takeda, *Ind. Eng. Chem. Res.* **2006**, *45*, 6339.
- [39] M. W. Kellogg Co., *Desorption of Carbon Dioxide and Oxygen from Sea Water*, Office of Saline Water, Res. Develop. Progr. Rept. No. 1958, Dept. of Interior, Washington DC **1965**.
- [40] H. Hikita, Y. Konishi, *AIChE J.* **1984**, *30*, 945.
- [41] H. Hikita, Y. Konishi, *AIChE J.* **1985**, *31*, 697.
- [42] J. Colt, B. Watten, T. Pfeiffer, *Aquacult. Eng.* **2012**, *47*, 38.
- [43] J. Colt, B. Watten, T. Pfeiffer, *Aquacult. Eng.* **2012**, *47*, 47.
- [44] K. J. Howe, D. F. Lawler, *J. Am. Water Works Ass.* **1989**, *61*.
- [45] H. L. Shulman, M. C. Molstad, *Ind. Eng. Chem.* **1950**, *42*, 1058.
- [46] H. Kataoka, H. Takeuchi, K. Nakao, H. Yagi, T. Tadaki, T. Otake, T. Miyauchi, K. Washimi, K. Watanabe, F. Yoshida, *J. Chem. Eng. Jpn.* **1979**, *12*, 105.
- [47] Y. T. Shah, M. M. Sharma, *Trans. Inst. Chem. Eng.* **1976**, *54*, 1.
- [48] E. S. Hamborg, S. R. A. Kersten, G. F. Versteeg, *Chem. Eng. J.* **2010**, *161*, 191.
- [49] N. C. Panja, D. Phaneswararao, *Chem. Eng. Res. Des.* **1994**, *72*, 633.
- [50] L. T. Thuy, R. H. Weiland, *Ind. Eng. Chem. Fund.* **1976**, *15*, 286.
- [51] W. J. Thomas, M. A. El-Sawy, E. W. Palmer, *Chem. Eng. Commun.* **1982**, *16*, 53.
- [52] M. K. H. Al-Mashhadani, H. C. H. Bandulasena, W. B. Zimmerman, *Ind. Eng. Chem. Res.* **2011**, *51*, 1864.
- [53] N. C. Panja, D. P. Rao, *Chem. Eng. Res. Des.* **1991**, *69*, 302.

Manuscript received January 31, 2017; revised manuscript received April 10, 2017; accepted for publication April 10, 2017.