

Article

Removal of HFC-134a from Brackish Water Using a Semi Batch Jet Loop Reactor

Devi Marietta Siregar, Yiseul Park, Yong Sun Won and Jun Heok Lim *

Department of Chemical Engineering, Pukyong National University, Busan 48547, Korea; devimarietta@gmail.com (D.M.S.); dewpark@pknu.ac.kr (Y.P.); yswon@pknu.ac.kr (Y.S.W.)

* Correspondence: jhlim@pknu.ac.kr; Tel.: +82-51-629-6437

Received: 2 December 2018; Accepted: 16 January 2019; Published: 19 January 2019



Abstract: Mineral salt components (Na^+ , Ca^{2+} , K^+ , Mg^{2+} , etc.) are naturally excluded during the gas hydrate in which water molecules form cavities by hydrogen bonding and guest gas molecules are encapsulated into the cavities to stabilize the overall gas hydrate structure. However, when using refrigerant hydrofluorocarbon-134a (HFC-134a) for guest gas, it resided in resulting brackish water after the desalination process because of its high solubility in water. Jet loop reactors (JLRs) are frequently employed in many commercial applications because of their high mass transfer capabilities. In this study, a semi-batch type JLR was introduced to improve the degassing of HFC-134a from brackish water. The effect of parameters, such as the initial HFC-134a concentration (200–772 mg/L), liquid circulation (40–80 L/min) rate, and air flow rate (10–30 L/min), were studied in this JLR. The removal efficiency and overall volumetric transfer were calculated and it was determined that increasing the air flow rate has a high effect on $K_L a$.

Keywords: gas hydrate; desalination; brackish water; HFC-134a; jet-loop reactor

1. Introduction

Desalination is a method to remove salts and minerals from seawater. Several techniques of desalination were investigated by gas hydrate formation [1,2]. With a proper guest gas, a salt removal efficiency of more than 90% is achievable. Park et al. used CO_2 for the hydrate formation, and produced brackish water by melting hydrates and releasing CO_2 gas at atmospheric conditions with rejection efficiencies of 92–97% for Ca^{2+} , Mg^{2+} , Na^+ , K^+ , and B^{3+} . Recently, refrigerants, such as hydrofluorocarbons (HFCs), have drawn much attention as a guest gas due to their mild operating temperature (10 °C at the atmospheric pressure). However, during the process where brackish water is produced by thermal dissociation of gas hydrates, most refrigerants are separated, but some reside in the product water because of their solubility in water [3]. Thus, there is a need for an additional method to remove refrigerants in product water and discard any potential harm to produce potable water.

In recent years, gas liquid-contactors with a high mass transfer rate have been used for the gas-liquid operation. Jet loop reactors (JLRs) are classified as innovative and efficient reactors and are distinguished by their high mass transfer capabilities. Bohner et al. developed a JLR that can form micro bubbles, thus achieving a higher absorption rate and improving the turbulence intensity of the gas-liquid absorption system [4]. The JLR generates micro bubbles due to the shear field induced by the liquid jet at the nozzle outlet when gases and liquids are sprayed from the two-fluid nozzle installed in the draft tube. It produces a wide contact area between the gas and liquid, and a high turbulence intensity. Moreover, due to its small size, the bubble residence time increases as the liquid flows down the draft tube and flows up through the annular space, and parts of the gas and liquid recirculate in the up-flow stream into the draft tube [5]. Degermenci et al. investigated ammonia removal with air stripping in a semi batch JLR [6]. They concluded that the JLR provided higher mass

transfer capabilities than other types of reactors. Volatile substances can thus be transferred from the water to gas phase rapidly with these characteristics of the JLR.

In this study, a method to remove HFC-134a (1,1,1,2-tetrafluoroethane, R-134a) from the brackish water using a JLR was proposed. The ultimate goal of this study is the complete removal of HFC-134a gas out of the product water from the desalination using gas hydrate formation. The volumetric mass transfer was calculated to evaluate the efficiency of the proposed reactor design.

2. Materials and Methods

2.1. Materials and Apparatus

A laboratory scale JLR system (Figure 1) consisted of storage tank, JLR, circulation pump, air compressor, and HFC-134a bomb. The JLR used in this work had a downstream circular cylinder shape, reaction tube, draft tube, gas-liquid separation tank, and two-fluid nozzle. The JLR system (except for the two-fluid nozzle) was shaped like cylinders and made from transparent acrylic. The total height and effective volume of the JLR were 1 m and 20 L, respectively. The height and the inner diameter of the reaction tube were 0.75 m and 0.10 m, while those of the draft tube were 0.60 m and 0.049 m, and those of the gas-liquid separation tank were 0.35 m and 0.30 m, respectively. The liquid induction tube of the two-fluid nozzle was used with a PVC tube with an inside diameter of 16 mm. The inside of the bottom part of the nozzle was conical-shaped, and the inside diameter of the nozzle was 40 mm and gradually decreased down to 5 mm at the liquid nozzle end. The contraction started at the point of 40 mm above the liquid nozzle tip. Air was supplied by the air compressor (KAC-20S, Keyang Electric Machinery Co., Seoul, Korea), connected to the air bubbling stone and supplied to the reactor.

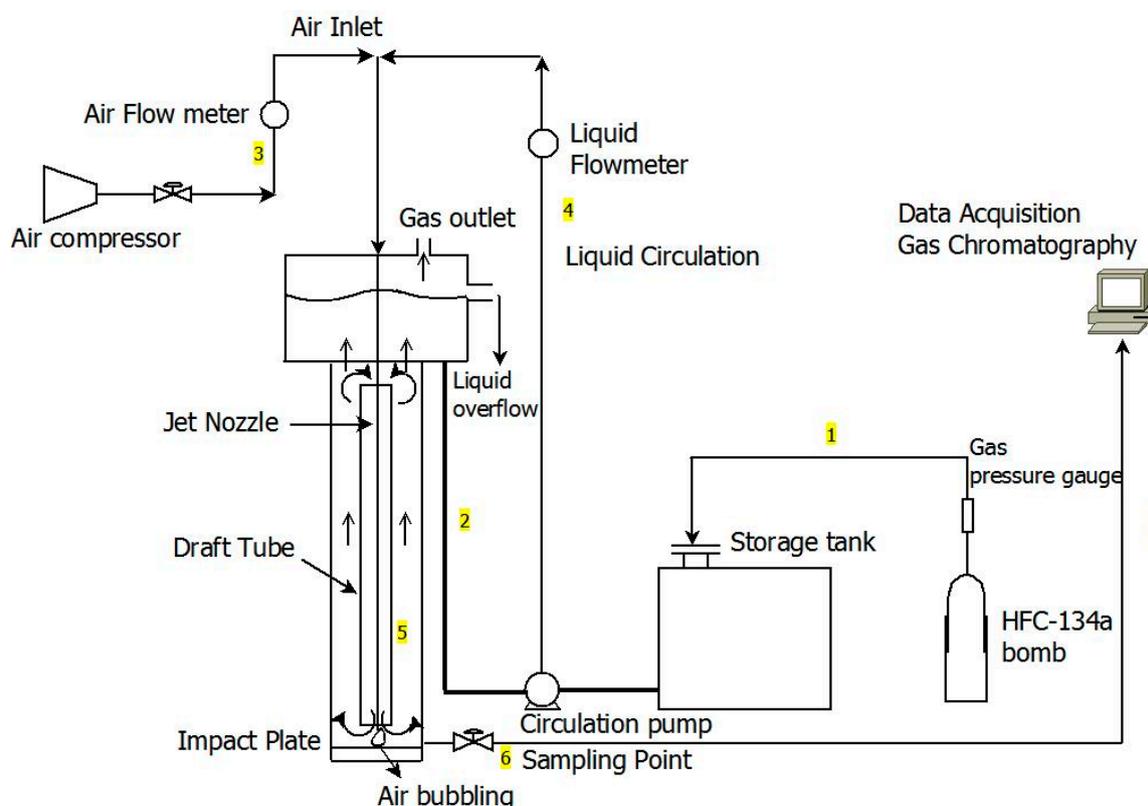


Figure 1. The flow diagram of the experimental setup (1. Air bubbling (HFC 134a to brackish water), 2. Feed from storage tank to JLR, 3. Air flow parameter, 4. Liquid circulation parameter, 5. Separation gas in JLR, 6. Sampling product, 7. Analyzing data with Gas Chromatography-Mass Spectrometry).

HFC-134a with a purity of 99.5% (Dongsun Finetech Co., Ltd., Busan, Korea) was purchased as an object gas. Artificial brackish water was prepared using oceanic sea salt mix (Oceanic Systems, Inc., Franklin, WI, USA) with a salt concentration of 3.5 ppt. Salinity was measured using a Pro30 conductivity meter (YSI Environmental, Yellow Springs, OH, USA). The concentration of HFC-134a in the gas phase was analyzed by a gas chromatography (HP 6890, Hewlett Packard, Palo Alto, CA, USA) using a flame ionization detector. HP-5 column and nitrogen gas were used for the column and carrier gas. All HFC-134a samples were collected by a fixed-needle type gas tight syringe of 100 μ L (SGE Analytical Science, Pflugerville, Texas, USA). The temperature and pressure was maintained at 25 °C and 1 atm.

2.2. Procedure

In all experiments, artificial brackish water of 20 L with a salt concentration of 3.5 ppt was used. The feed was prepared by bubbling with HFC-134a gas for 1 h before being supplied into the JLR. The air was provided to the reactor through small tubes and was connected to the air bubbling stone in the inside bottom of JLR via a gas flow meter. The two-phase (liquid-gas) jet then passed down to the reactor tube and rose up to the outer annulus of the reactor (Figure 1). The feed was withdrawn from the top of the reactor and pumped back to the reactor by the circulation pump. The gas-liquid jet stream flow through the inner tube to the head of the reactor, and then reversed to enter the annular space between the inner and outer tubes. The HFC-134a gas was separated and discharged through the gas discharge valve in the upper part and the liquid in the separation tank was recirculated through the circulation pump outside the reactor and discharged again through the nozzle. Samples of 2 mL were taken and analyzed. The experimental parameters and their levels are shown in Table 1.

Table 1. Parameters and their levels.

Parameters	Levels		
Initial concentration (mg/L)	200	500	772
Liquid circulation rate (L/min)	40	60	80
Air flow rate (L/min)	10	20	30

3. Results and Discussion

3.1. Determination of the Removal Efficiency and Mass Transfer Coefficient of HFC-134a

The overall HFC-134a balance over a JLR is derived by Matter-Muller et al. and shown as follows [7]:

$$Q_G C_{Gin} - Q_G C_{Gout} = V_L \frac{dC_L}{dt} + \varepsilon_G V_L \frac{dC_G}{dt} \quad (1)$$

Q_G is the air volumetric flow rate (L/min), C_{Gin} and C_{Gout} are the HFC-134a concentration in the air inlet and outlet of JLR (mg/L), V_L is the liquid volume (L), C_L is the HFC-134a concentration in the gas phase (mg/L), and ε_G is the gas holdup or the volume fraction of the gas bubbles entrained in the liquid. For a dilute system, a differential material balance for the HFC-134a over a differential height dz of the JLR gives Equation (2):

$$Q_G C_G - Q_G (C_G + dC_G) + K_L a S (C_L - C_L^*) dz = \varepsilon_G S dz \frac{dC_G}{dt} \quad (2)$$

$K_L a$ is the overall volumetric mass transfer coefficient based on the liquid phase (h^{-1}), S is the JLR cross-sectional area (m^2), dz is the differential height (m), a is the specific interfacial area of bubbles per unit volume of gas-liquid mixture (m^2/m^3), and C_L^* is the HFC-134a concentration in the gas phase in equilibrium with the gas bubbles (mg/L). Equation (2) can be solved with Henry's law to obtain (3)–(5):

$$-\ln \frac{C_{Lt}}{C_{L0}} = \frac{K_H Q_G}{V_L} \left[1 - e^{-(K_L a S L e / Q_G K_H)} \right] t \quad (3)$$

If the dimensionless group, $K_L a S L e / Q_G K_H \leq 1$, Equation (3) becomes:

$$-\ln \frac{C_{Lt}}{C_{L0}} = K_L a t \quad (4)$$

$$\text{Efficiency } (\eta) = \frac{C_{L0} - C_{Lt}}{C_{L0}} \quad (5)$$

C_{Lt} is the HFC-134a concentration in the gas phase at any time (mg/L) and C_{L0} is the initial HFC-134a concentration in the gas phase (mg/L). Equation (5) is then used to presume the rate of HFC-134a removal by air bubbling from the solution containing brackish water in a semi-batch JLR.

3.2. Effect of the Initial HFC-134a Concentration

The effect of the initial HFC-134a concentration on the air bubbling efficiency of HFC-134a is shown in Figure 2. The initial concentration was set in the range of 200–772 mg/L and the circulation of the flow rate and the air flow rate were kept constant at 80 L/min and 10 L/min, respectively. The HFC-134a removal efficiency increased slightly upon raising the initial HFC-134a concentration. It is because the driving force required for the mass transfer increases with the raising of the initial HFC-134a concentration. The influence of the initial HFC-134a on the overall volumetric mass transfer ($K_L a$) is shown in Figure 3. The $K_L a$ values for each level of the parameters were obtained from (3). By plotting $-\ln(C_{Lt}/C_{L0})$ vs. retention time, t (min), the $K_L a$ values for each level of the parameters were calculated. Figure 2 also shows the air bubbling efficiency of HFC-134a is almost independent of the HFC-134a concentration. It is further explained by the analysis of the mass transfer process. From Equation (2), the following equation is easily obtained within the same period of bubbling time because of the almost constant mass transfer coefficients, $K_L a$:

$$\ln(1 - \eta) = -K_L a t \quad (6)$$

It was observed that $K_L a$ values are not significantly affected by the initial concentration. It suggests that the HFC-134a removal operation is mainly controlled by the diffusion through the gas film [8]. A higher concentration resulted in a higher air bubbling rate. Raising the HFC-134a concentration can increase the driving force for the mass transfer, resulting in a higher rate of HFC-134a removal.

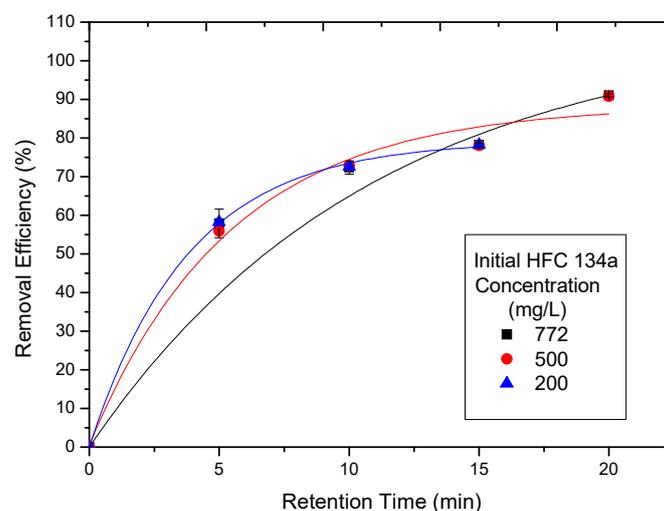


Figure 2. Effect of the initial HFC-134a concentration on the efficiency of HFC-134a removal. (Liquid circulation rate: 80 L/min, air flow rate: 10 L/min).

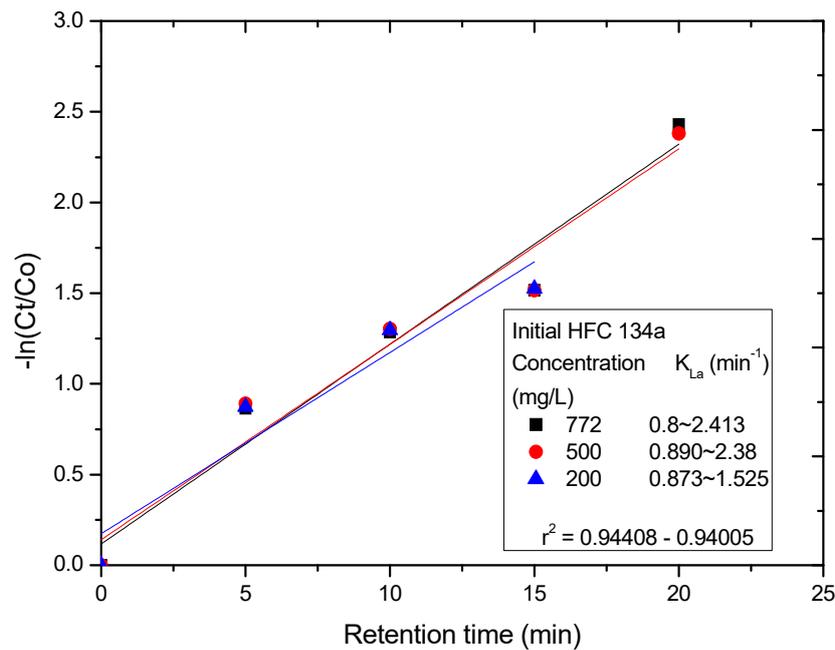


Figure 3. Effect of the initial HFC-134a concentration on the K_{La} . (Liquid circulation rate: 80 L/min, air flow rate: 10 L/min).

3.3. Effect of the Liquid Circulation Rate

The liquid circulation rate was set at 40, 60, and 80 L/min to determine the effect of the liquid circulation rate (or liquid jet rate) on the efficiency of HFC-134a removal, while keeping the initial concentration and air flow rate. The results are shown in Figures 4 and 5. It can be seen that the efficiency of the HFC-134a removal and K_{La} increase slightly when the liquid circulation rate is raised at around 40 L/min, but decreases upon raising the liquid circulation rate at around 80 to 60 L/min. It might be because the flow regime is irregular in our semi-batch JLR. When the liquid circulation rate is varied, there is a transition from the uniform bubbly flow regime to the turbulent flow regime. During the transition region, the eddy development reduces the recirculation of the gas bubbles and increases their rising rate and coalescence, so that the gas-liquid interfacial area for the mass transfer is reduced. The mass transfer rate is reduced because the driving force is also lower in the transition region than in the bubbly flow region. However, at a higher liquid injection rate, energy is more available, resulting in higher circulation velocities. The bubbly flow regime, predominant at lower gas velocities, undergoes transition to the churn turbulent regime at higher gas loadings, resulting in non-uniform velocity profiles [9].

A HFC-134a removal efficiency of higher than 92% was achieved with 20 min of retention time. However, using the same volume of feed, it took more than 12 h to achieve this removal efficiency in JLR. Liquid circulation characteristics in a JLR are significant for evaluating the liquid residence time, recirculation ratio, degree of mixing, effective heat transfer rates, etc.

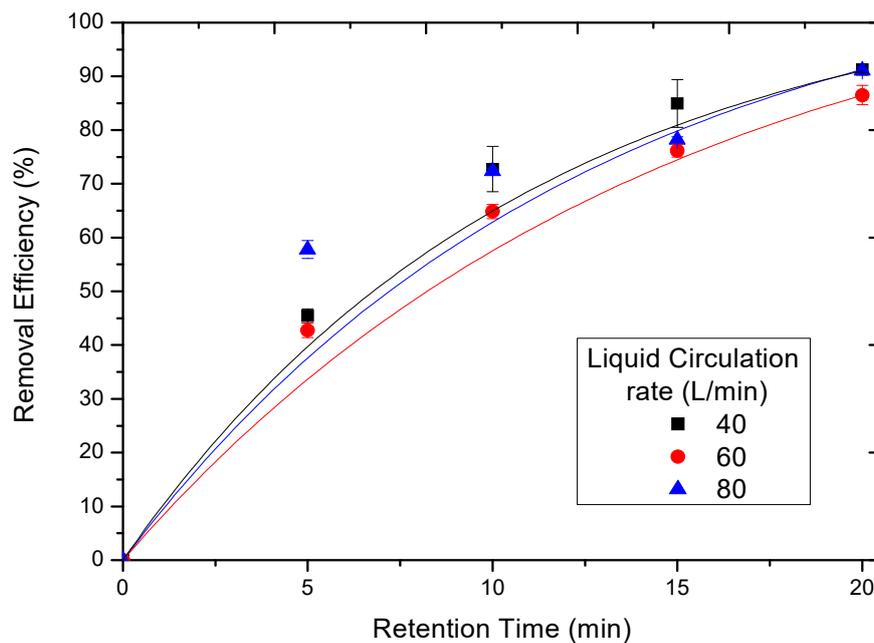


Figure 4. Effect of the liquid circulation rate on the efficiency of HFC-134a removal. (Initial HFC-134a conc.: 772 mg/L, air flow rate: 10 L/min).

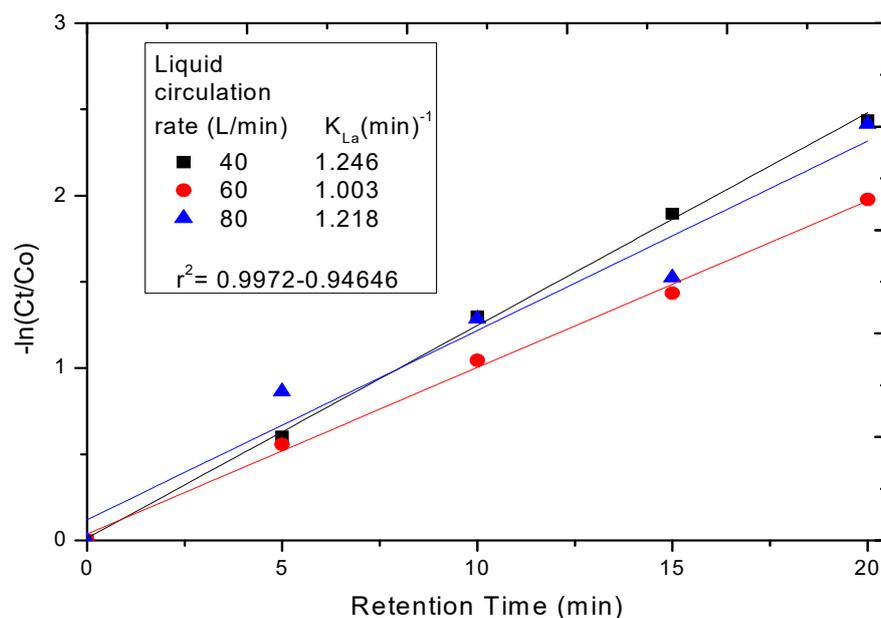


Figure 5. Effect of the liquid circulation rate on the K_{La} . (Initial HFC-134a conc.: 772 mg/L, air flow rate: 10 L/min).

3.4. Effect of the Air Flow Rate

It was exposed that the HFC-134a removal efficiency increases upon raising the air flow rate as shown in Figure 6. It is probably because raising the air flow rate decreases the size of gas bubbles dispersed in the liquid of JLR and increases gas hold-up. This also leads to the increase of gas entrainment and gas-liquid interfacial area, thus increasing the efficiency of HFC-134a removal as well as the K_{La} . When the air flow rate was below 20 L/min, it had a negligible effect on the efficiency and the mass transfer, but when the air flow rate was 30 L/min, it resulted in a significant increase in the efficiency and K_{La} (Figure 7). It was also associated with the effect of the air flow on the interface of the gas-liquid phases. The removal efficiency with the highest air flow rate reaches above 92% only in

rapid time. A higher air flow rate produces larger shear stress and by exerting on the surface of the water droplets and along the porous tube surface, it causes the breakage of water drops into fine drops, leading to an obvious increase in the mass transfer.

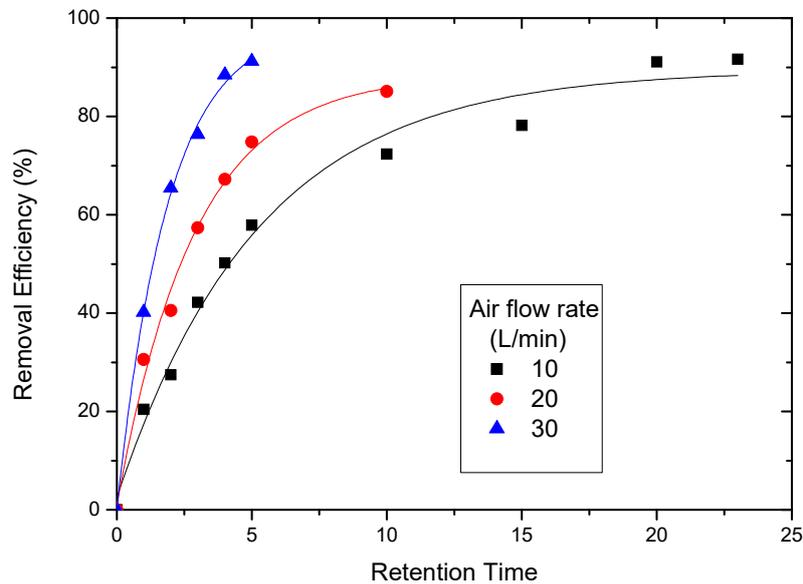


Figure 6. Effect of the air flow rate on the efficiency of HFC-134a removal. (Initial HFC-134a conc.: 772 mg/L, liquid circulation rate: 80 L/min).

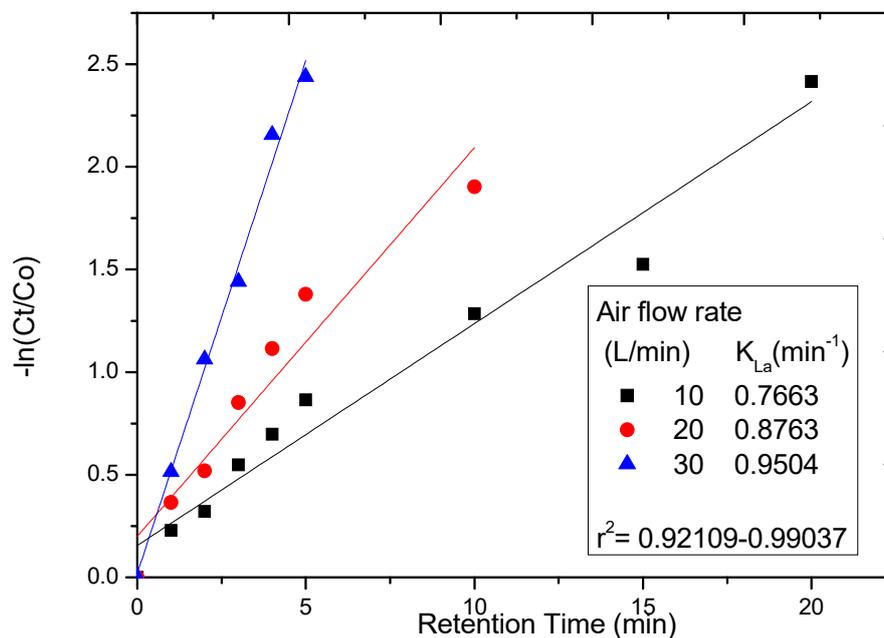


Figure 7. Effect of air flow rate on the K_{La} . (Initial HFC-134a conc.: 772 mg/L, liquid circulation rate: 80 L/min).

4. Conclusions

It was shown that the most effective parameter on the efficiency of HFC-134a removal is the air flow rate. The liquid circulation rate and initial concentration had a limited effect. The overall volumetric mass transfer coefficient (K_{La}) in our semi-batch JLR was also estimated and it also demonstrated that increasing the air flow rate has a very important effect on K_{La} . The HFC-134a removal efficiency with the highest air flow rate of 30 L/min was above 92% only in a rapid

time. In summary, JLRs are expected to be effective for gas removal from brackish water by the desorption process.

Author Contributions: Conceptualization, J.H.L.; methodology, J.H.L. and D.M.S.; Data analysis, D.M.S. and Y.S.W.; validation, J.H.L.; investigation, D.M.S. and J.H.L.; writing—original draft preparation, D.M.S.; writing—review and editing, J.H.L., Y.S.W. and Y.P.; project administration and funding acquisition, J.H.L.

Funding: This research was funded by the Research Grant of Pukyong National University.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Park, K.N.; Hong, S.Y.; Lee, J.W.; Kang, K.C.; Lee, Y.C.; Ha, M.G.; Lee, J.D. A New Apparatus for Seawater Desalination by Gas Hydrate Process and Removal Characteristics of Dissolved Minerals (Na^+ , Mg^{2+} , Ca^{2+} , K^+ , B^{3+}). *Desalination* **2011**, *274*, 91–96. [[CrossRef](#)]
2. Williams, P.M.; Ahmad, M.; Connolly, B.S. Freeze Desalination: An Assessment of an Ice Maker Machine for Desalting Brines. *Desalination* **2013**, *308*, 219–224. [[CrossRef](#)]
3. Aliev, A.M.; Yusifov, R.Y.; Kuliev, A.R.; Yusifov, Y.G. Method of Gas Hydrate Formation for Evaluation of Water Desalination. *Russ. J. Appl. Chem.* **2008**, *81*, 588–591. [[CrossRef](#)]
4. Bohner, K.; Blenke, H. Gsgehalt und flüssigkeits umwälzung im Schlaufen-reaktor. *Verfahrenstechnik* **1972**, *6*, 50–57. [[CrossRef](#)]
5. Pohorecki, R.; Moniuk, W. Kinetics of Reaction between CO_2 and Hydroxyl Ions in Aqueous Electrolyte Solutions. *Chem. Eng. Sci.* **1998**, *43*, 1677–1684. [[CrossRef](#)]
6. Degermenci, N.; Ata, O.N.; Yildiz, E. Ammonia Removal by Air Stripping in a Semi-batch Jet Loop Reactor. *J. Indus. Eng. Chem.* **2012**, *18*, 299–404. [[CrossRef](#)]
7. Matter-Müller, C.; Gujer, W.; Giger, W. Transfer of volatile substances from water to the atmosphere. *Water Res.* **1981**, *15*, 1271–1279. [[CrossRef](#)]
8. Sertkaya, S.; Farizoglu, B.; Uzuner, S. Ammonium Removal from Balikesir Providence Solid Waste Landfill Leachate via Jet Loop Reactor. *J. Selcuk Univ. Nat. Appl. Sci.* **2014**, 188–197.
9. Jain, D.K.; Patwari, A.N.; Rao, M.B.; Khan, A.A. Liquid circulation characteristics in jet loop reactors. *Can. J. Chem. Eng.* **1990**, *68*, 1047–1051. [[CrossRef](#)]



© 2019 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<http://creativecommons.org/licenses/by/4.0/>).