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# Water Purifying by Gas Hydrate: Potential Applications to Desalination and Wastewater Treatments

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Freshwater scarcity has been troubling the high-quality development of many countries and regions, and water purification process is a vital source of freshwater. The traditional water purification processes such as distillation (multi-stage flash) and membrane processes (reverse osmosis) have been evaluated to be reliable and established processes. The desalination or water treatment technologies are mature enough to be a reliable source for fresh water but there is still a need to develop innovative technologies that can reduce energy costs. The water purifying by gas hydrate (hydrate-based) process is based on a liquid to solid phase change coupled with a physical process to separate the solids from the remaining liquid. In this study, we investigated the water purification by hydrate process for seawater and wastewater samples. In a single stage of hydrate process without any pre-treatment, dissociated water from the extracted hydrate pellets show that the removal efficiency of each ionic compound in seawater was 89 % (average). In the case of wastewater test from leachate sample, 77-95 % of dissolved contaminants and nutrients were excluded. Therefore, the experimental proposal and results of this study are of great significance to the development of water purification technology.

## 1. Introduction

The demand of freshwater has been growing with the rapid increase in population and urbanization (Chong et al., 2019). The limit of freshwater resources forces human to develop the water purification process. Therefore, novel, robust, efficient, and environmentally compatible technologies for desalination and wastewater treatments are urgently required. Traditional treatments of produced water often include prior single phase (membrane processes) and phase change (thermal processes) (Shatat and Riffat, 2012). In the single-phase routes, membranes are widely employed for the desalination of saline water or wastewater treatments of polluted water. Their prime examples are commercially important desalination processes like Reverse Osmosis (RO) processes (Khawaja et al., 2008). RO is a process where a semi-permeable is need to separate solvent from solution by the help of concentration gradient (Yahya et al., 2017). Phase change routes require a thermal energy source perhaps used for vaporization of saline water or polluted water (evaporation), which subsequently condensed to acquire fresh water.

Overall, these technologies have been proven to be reasonably efficient but each of the desalination technology has its own intrinsic limitation *(*Seo et al., 2019*)*. RO requires substantial pre- and post-treatments and membranes are liable to be fouled by large particles (Shatat and Riffat, 2012). Whereas, multistage flash (MSF) processes are energy intensive, which require both thermal and mechanical energy (Javanmardi and Moshfeghian, 2003). In order to overcome the problems, alternative desalination technology must be explored for the efficient and economically feasible solutions. Among those, the application of gas hydrate seems to be a good option as future water treatment technology.

Gas hydrates (or clathrate hydrates) are non-stoichiometric compounds formed by a lattice of water molecules that are strongly hydrogen bonded and that encage low molecular weight gases or volatile liquids in different cavities under appropriate thermodynamic conditions (Englezos, 1993). The hydrate-based water treatment is

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solid-liquid separation process, in which water molecules form cages around a guest gas/liquid component, thereby effectively separating themselves from brine solution even at temperatures higher than the normal freezing temperature of water. These hydrate crystals when melted are essentially fresh water and the guest component can be reused (Babu et al., 2018). As seen Figure 1, the hydrate-based water treatment process includes the following steps: (i) formation of gas hydrates, (ii) separation of hydrates (iii) post-treatment to improve quality of water (e.g., washing, centrifuging), and (iv) hydrate dissociation to produce treated water and reuse of gas (Seo et al., 2019).

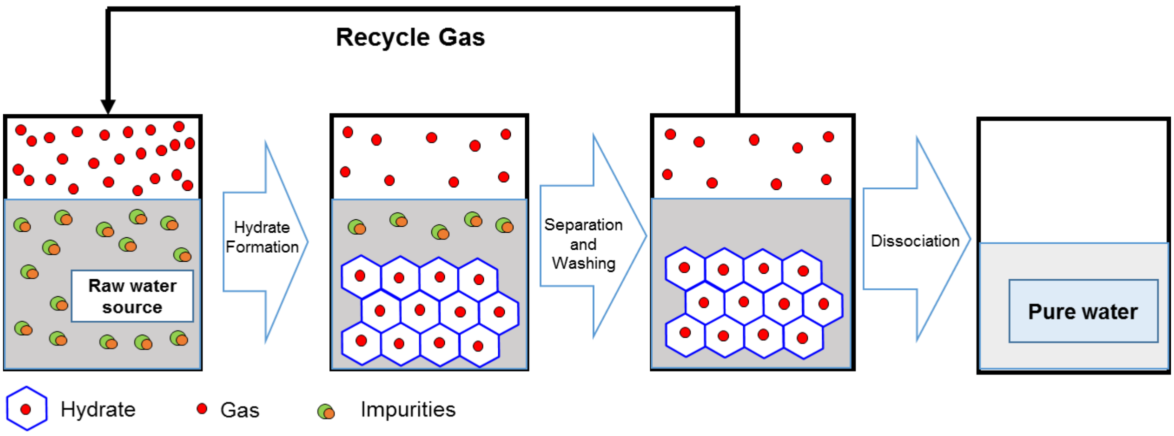


*Figure 1: A concept for water treatments via gas hydrate process*

Several researchers have devoted their efforts to understanding the hydrate-based water treatment. The various guest molecules used were cyclopentane (CP) (Han et al., 2014), cyclohexane (CH) (Cha and Seol, 2013), $CO_2$ (Park et al., 2011).  CP and CH are toxic and highly volatile, and they need to be removed separately after decomposition of hydrate, whereas the cost of the pressurization of $CO_2$ and the cost of refrigeration are high. However, this technology is not yet being used at industrial or commercial scale because it has slower kinetics of hydrate formation and higher energy consumption than those of conventional technologies (Seo et al., 2019). Therefore, the finding of hydrate formers to improve the kinetics of hydrate formation and reduce the energy required is a key issue. Barduhn's group was suggested the criteria for choosing a gas hydrate former for seawater desalination. A suitable gas hydrate former for seawater desalination should be non-toxic, non-flammable, stability, a class II hydrate former, low cost, compatible operating conditions (low pressure and high temperature) (Barduhn et al., 1962). Based on the above criteria, HFC-134a was selected as gas hydrate formers for this work because it was easily formed hydrates under relatively low pressures and high temperatures compared to other gases (Lee et al., 2016).
A novel apparatus was developed to conduct seawater desalination and wastewater treatment. The purpose of this work is to identify and evaluate the efficiency of the water purification process using the gas hydrate principle and related apparatus. The removal efficiencies of anions and cations in seawater sample were tested by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) and Ion Chromatography (IC). In addition, the most important physicochemical characterisation of the leachate sample such as nitrogen, phosphorus, ionic compounds and chemical oxygen demand (COD) were also analysed. In order to improve water quality, further experiments on hydrate dissociation were carried out. This work shows that the apparatus can be applied for more effective seawater desalination and wastewater treatment.

## 2. Experimental

### 2.1 Materials

Two categories of samples were used for this experiments: (i) seawater samples were obtained from southeast coast of Korea (35º5'1"N, 128º47'11"E) and (ii) leachate samples from landfill sites (35°07' 56"N, 128°52'42"E) in Korea. Leachate is the liquid that drains from a landfill. It usually contains with organic contaminant and higher ammoniac ($NH_3$-N) than commonly found in any other organic effluent. For additional experiments, Sodium Chloride (99.0 %, Duksan Co, Korea) and distilled de-ionized water were used to prepare 4.0 wt% of NaCl solution. HFC-134a (99.99 %) gas supplied from PS CHEM (Korea) was used as a guest substance for hydrate formation.

**2.2 Apparatus and procedure**

In this study, the gas hydrates are continuously produced and pelletized in the reactor by the squeezing operation of a double cylinder unit. A detailed description of the hydrate-based water purifying apparatus was available in previous papers (Kang et al., 2014). The main part of the apparatus was the hydrate reactor, which was made of stainless steel and has an internal volume of 20 L. A high pressure liquid metering pump (model 2HM, Eldex, USA) was used to mix the reactor contents. The temperature was controlled by an external refrigerator (Model RW3-2035, JEJO TECH, Korea). Two pressure transmitters (PT) (model A10, WIKA Co. Germany), a pressure gauge (PG) and four copper-constantan thermocouples (TC) (Omega, T-type, USA) were employed for the pressure and temperature measurements of the hydrate reactor, gas tank and hydrate pellet production system.
Several modifications have been made to the experiments performed in the previous paper (Kang et al., 2014). In this experiment, the slurry compression process was adopted by two servo motors (HG-SR702, Mitsubishi, Japan). Compared to the previous hydraulic pressure method, a rapid and accurate pelletizing process was performed, and the pressure per unit area of the hydrate pellets was further increased.
As shown in Figure 2, the hydrate reactor was flushed with the guest gas for removing any residual air at least three times, and then 10 L of seawater or wastewater sample was charged to the reactor.

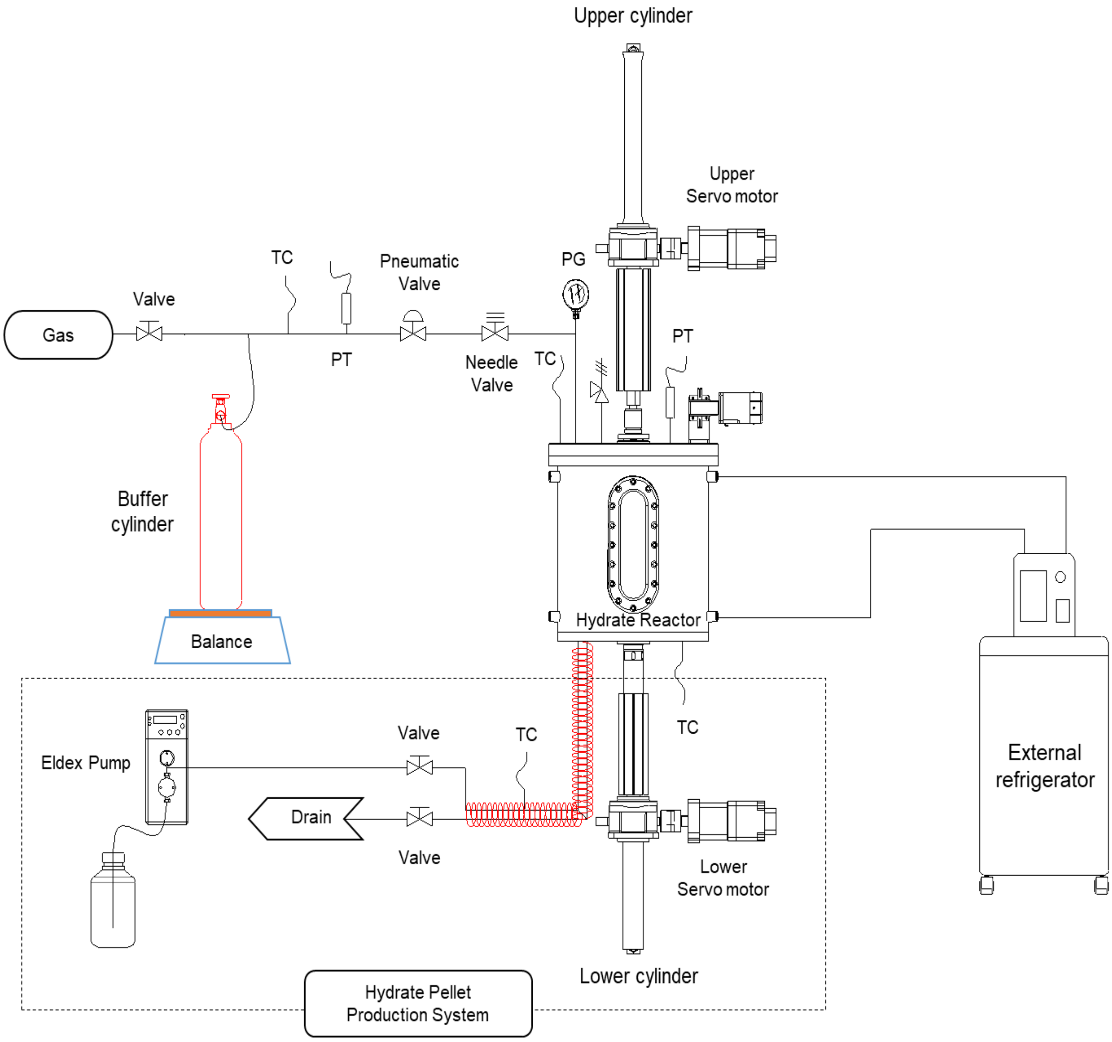


*Figure 2: Schematic of the experimental apparatus for water purifying process by gas hydrate method*

The system was cooled down to the experimental temperature. After the temperature of liquid phase in the reactor was stabilized at 277.15 K, HFC-134a is introduced into the system from the gas cylinder to the reactor until the system pressure reached a desired experimental pressure 0.28 MPa at 277.15 K. As guest gas in the reactor was consumed for hydrate formation, additional gas was automatically supplied from gas cylinder and the pressure in the reactor was maintained constant with the help of a proportional integral derivative (PID) controller. During an experiment, the data acquisition system scans the pressure, temperature and weight of consuming gas every 10 s. The weight of consuming gas was measured by balance (model CBX32KH, CAS Co., Korea). HFC-134a hydrates were formed for 2 h and then hydrate pellet was released out from the reactor for further analysis.

Before and after the desalination process, anions (Cl-, SO42-) and cations (Na+, K+, Mg2+, Ca2+ and B3+) were analysed by IC and ICP-AES. Dissolved contaminants and nutrients such as chlorides (Cl-), chemical oxygen demand (COD), total phosphorus (T-P), ammoniac-nitrogen ($NH_3$-N), nitrate ($NO_3^-$-N), nitrite ($NO_2^-$-N), total inorganic nitrogen (TIN) and total nitrogen (T-N) were also measured before and after wastewater treatments, according to the methods described in standard methods for examination of water and wastewater (Rice et al., 2017)

## 3. Results and discussion

After the completion of hydrate formation process, the separation of hydrate crystals from residual solution was performed by hydrate pellet production process. Subsequently, the removal efficiency of any contaminants from the dissociated hydrate pellets was measured. The removal efficiency was calculated from the following Eq(1)

$$Removal\ efficiency = \frac{C_{A0} - C_A}{C_{Ao}} \times 100\% \tag{1}$$

where CA0 and CA are the concentration in the feed sample and dissociated hydrate pellet.

In a single stage of hydrate-based desalination process without any pre-treatment, 89 % (average) of each cations and anions were removed. It is also noted from Figure 3 that the removal efficiencies of all ions were higher than previous results (Kang et al., 2014). The previous data of desalination efficiency was around 68.86-75.49 % (Kang et al., 2014). There are two factors to consider. The first one is type of guest molecular and another factor is pelletizing pressure. In the previous study, $CH_4$ or $CO_2$ was used as a guest molecular (structures I) and the pelletizing pressure was 82-100 kgf/cm$^2$. Whereas, in this study, HFC-134a was chosen as hydrate former (structure II) and the pelletizing pressure was 140 kgf/cm$^2$.

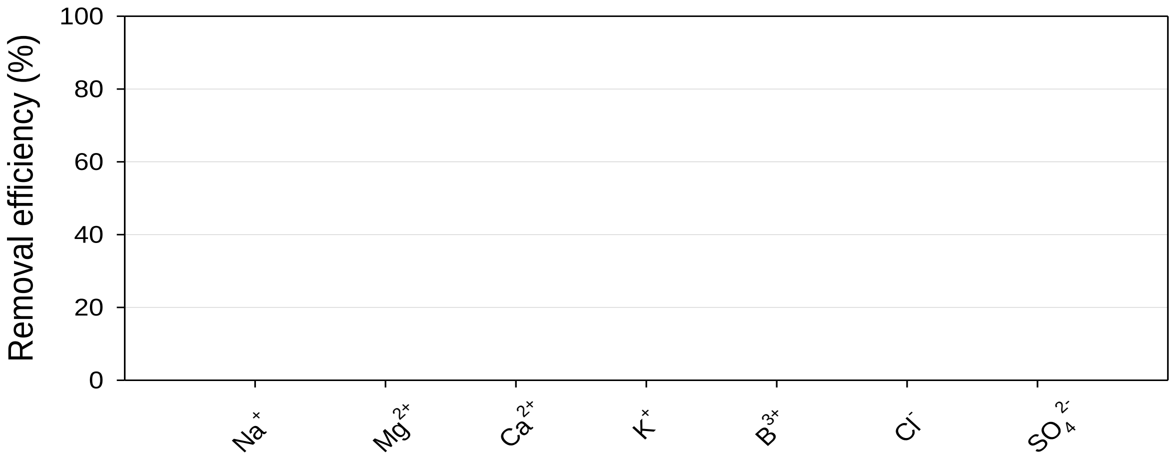


*Figure 3: Removal efficiency of each dissolved mineral in seawater sample by 1 stage of hydrate process.*

Further application was investigated by testing leachate sample from landfill sites in South Korea. As seen Figure 4, in a single stage of hydrate process, 77-95 % of each contaminant such as nitrogen, phosphorus, chloride and COD were removed. Some research shows that high salinity can obviously inhibit the nitrogen removal ability by physicochemical and biological treatment. Li et al. (2014) reported that when the salt was present in wastewater sample, the removal efficiency of nitrogen was sharply reduced. However, the current results show that any dissolved contaminants and nutrients in leachate were effectively removed by hydrate-based process even in the presence of salt. It is worth noting that the hydrated-based wastewater treatment was superior to the conventional method such as physicochemical and biological method.

The hydrate-based process, which is a principle of the crystallization method, theoretically can make pure hydrate crystals and clean waters can be obtained from the crystals. However, some contaminants are probably adsorbed on the surface of crystals or enclosed between the crystals, making it difficult to obtain pure water by hydrate dissociation. Therefore, further experiments on hydrate dissociation have been carried out to improve water quality.

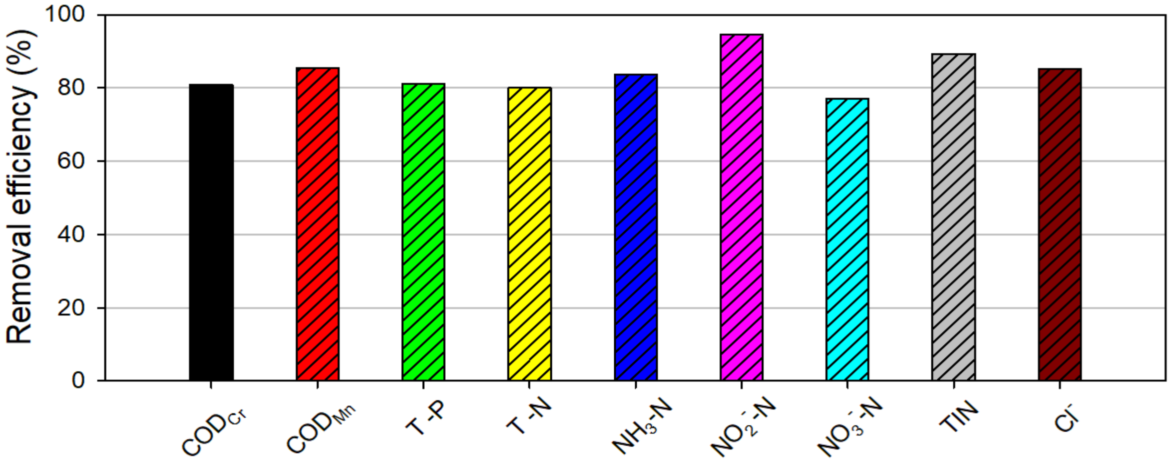


*Figure 4: Removal efficiency of each dissolved contaminants and nutrients in leachate sample by 1 stage of hydrate process. (Initial $Cl^-$ concentration was 1,600 mg/L in leachate sample).*

In this experiment, 4.0 wt% NaCl solution was used for hydrate formation and subsequent pellet production, and then the pellet was dissociated in atmosphere pressure and room temperature (23 °C). During hydrate dissociation, the salt concentration and melted volume were also measured every 10 min.  As shown in Figure 5, the salt is not distributed uniformly in the whole hydrate crystals but more in the crystal surface. In other words, the surface cleaning (or washing) process can be a good concept for further water purification because there are more pure crystals inside the pellet.

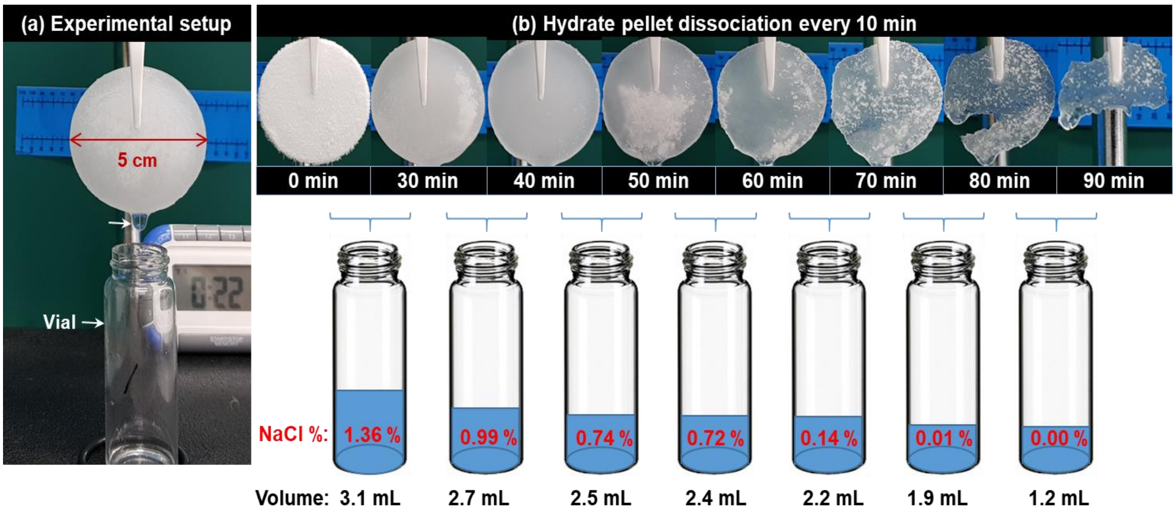


*Figure 5: (a) Experimental setup of HFC-134a hydrate dissociation (b) Morphology of hydrate pellet dissociation, (every 10 min, salt concentration and melted volume were recorded).*

## 4. Conclusion

This study evaluated potential application of water purification technology using HFC-134a hydrate former. The results indicated that the all ions of seawater were reduced by approximately 89 % and 77-95 % of each dissolved contaminants and nutrients in leachate were effectively removed by the single-stage of hydrate process without any pre- and post-treatment. This study also showed that residual interstitial brines between hydrate crystals can be effectively removed by an additional washing process. It is believed that the self-dissociated cleaning (or washing) process can play an important role in the effective achievement of the water purification process. Despite the advantages of water purifying by gas hydrate method, many challenges remain. Future works focus on studies of enhance the purity of hydrates and the seawater and wastewater by better separation to achieve higher water quality.

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