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Hydrate-based desalination process enhanced via graphite

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Abstract. Desalination via hydrate processes is a novel and attractive method for desalting seawater. However, it is a great challenge to form hydrates with large amount in a short time, especially in the presence of high concentrations of salts. In this study, we used cheap and easily separated graphite particles to promote hydrate-based desalination. It was confirmed that graphite has no impact on the structures and compositions of cyclopentane hydrates. The dosage of used graphite can dramatically increase the conversion rate of water to hydrate, without degradation of the desalination efficiency. Due to the presence of graphite, the ratio of NaCl solution to cyclopentane has little impact on the conversion rate. A multi-stage desalination via hydrate formation was demonstrated, which can produce high quality freshwater with a purity of 99.76% meeting the drinking water standard. The findings in this study will help to rationally select and design the desalination process based on hydrates.

1. Introduction

Human is facing the crisis of water shortage. Most of the global population is under the pressing threat of water security in the near future.[1] Seawater as the most abundant water resource on Earth cannot be directly used for people's daily life due to the high content of salts.[2]. Therefore, desalination processes are required for removing salts and producing freshwater from seawater.[3] Thermal- and membrane-based technologies are the most common desalination technologies, with various other novel methods been invented.[3] It is highly desired to produce high quality freshwater at low cost. Recently, the hydrate-based desalination has attracted growing attention worldwide due to its merits of high efficiency and low cost.[4]

Hydrates, also named as clathrate hydrates, are composed of water and small molecules. Water molecules as the hosts form three-dimensional cages via hydrogen bonds, where the small molecules are accommodated as the guests. The molar content of water is about 85% for hydrates, and salts are rejected out of the hydrates during the hydrate formation. So hydrate formation has been proposed as a novel freezing desalination technology.[5] Because the energy requirement is much lower for the phase change in water freezing (6.02 kJ/mol), compared with that of liquid water to vapor during distillation (40.7 kJ/mol). [2] So desalination by freezing has attracted growing attention worldwide.[6] The heat of cyclopentane (CP) hydrate formation can be reduced as low as 4.84 kJ/mol,[14] thus there is potential for further reducing the energy consumption using hydrate-based desalination.[2] Another merit of desalination via freezing or hydrate formation is that the process can be conducted at relatively low temperature near room temperature, so the challenge of corrosion would be less serious



compared with the processes producing water vapor. So desalination based on freezing processes, especially the ones using hydrate formation, is superior in terms of cost and safety.

CP is an ideal guest molecule for the hydrate-based desalination, [2, 7, 8] because CP hydrate can form above ice point at atmospheric pressure [9], which only uses inexpensive equipment and cost less energy. Additionally, CP is hydrophobic and not miscible with water, so it is easily to separate CP from water after decomposition of CP hydrates. However, due to the low solubility of CP, the formation is sluggish and the conversion rate of water to CP hydrate is quite low, these problems are also shared by other hydrates.[10] The presence of salts also hinders the hydrate formation in thermodynamics.

Nanoparticles, particularly carbon nanomaterials, such as carbon nanotubes and graphene, have been confirmed to be promising promoters to improve hydrate formation. [11-14] Nevertheless, few reports on hydrate formation in salty solutions with the presence of nanoparticles. It is well known that salts can hinder the formation of hydrate and ice, due to the thermodynamic limitation.[15, 16] It always requires higher pressure and larger degree of super-cooling to drive the formation of desired hydrates. In addition, the expensive nanoparticles and the difficulty of separation of them from produced freshwater will inescapably increase the cost. The uncertain composition and contained impurity in nanomaterials also make it challenge to pin down what contributes to the improved performance. Therefore, cheap graphite with high purity is proposed to promote the desalination of hydrates.

In the study, we used commercial graphite particles with high purity, low cost and easy separation from produced freshwater as promoters to enhance the formation of CP hydrates. The impact of graphite on the hydrate structures were analyzed. The effects graphite dosage, the ratio of NaCl solution to CP were systematically studied. Multi-stage desalination via hydration formation were also demonstrated. The findings in this study would help to rationally choose and design the desalination process based on the hydrate method.

2. Experimental section

2.1. Materials

CP was purchased from Aladdin Industrial Corporation. Graphite powders, with average sizes of 6.5 μ m (2000 mesh) and purity of 99.95%, were bought from Shanghai Macklin Biochemical Co., Ltd. NaCl was got from Sinopharm Chemical. All the chemical agents used in this study were analytical pure and used without any further treatment. The deionized water with a specific resistance of 18 M Ω was produced in our lab via reverse osmosis.

2.2. Experimental procedure

In this study, the NaCl aqueous solution with a concentration of 3.5 wt% was used as the artificial seawater. The reactions of CP hydration formation were conducted in the sealed glass bottles. In a typical run, CP hydrate formation was conducted at 2 °C and atmospheric pressure under constantly stirring at 600 rpm. Each reaction ran for 5 h, after that the hydrate crystals were separated by vacuum filtration for 30 s. In order to remove the salt solution remaining among the hydrate crystals, the separated hydrate crystals were centrifuged at -5 °C, 6000 rpm for 3 minutes using a centrifuge. After that, the hydrate crystals were naturally decomposed at room temperature. Since CP and water are immiscible systems, it is easy to separate the decomposed fresh water from the CP, and the graphite remains in the CP system. The conductivity of the produced water was measured by conductivity meter (ET915, eDAQ TECH, Australia). The concentration of produced water and original solution were calculated using a calibration curve based on the conductivity curve.

To study the impact of graphite dosage, graphite powders were added into the CP/NaCl aqueous solution mixture at ratios of 10, 20, 50, 100, 200 mg for every 80 mL mixture of NaCl aqueous solution (volume ratio at 3:1). For analysis the effect of the ratio of NaCl solution to CP on conversion rate, the volume of NaCl solution and the amount of graphite were kept constant at a ratio of 50 mg/60

mL NaCl solution. The volume ratios of NaCl solution to CP at 2:1, 3:1, 4:1, 5:1, 6:1 were studied. As for the multi-stage desalination, the reactions were conducted using 50 mg graphite per 80 mL mixture (the volume ratio of NaCl to CP is 3:1). The produced water from decomposed hydrate was used as the feeding solution in the next stage.

The desalting efficiency in this study was calculated using the equation (1)

$$\text{Desalting efficiency} = \frac{C_0 - C_f}{C_0} \times 100\% \quad (1)$$

where C_0 is the initial concentration of the feeding NaCl solution, C_f is the concentration of produced freshwater from the dissociated CP hydrates.

The conversion rate was calculated using the equation (2)

$$\text{Conversion rate} = \frac{V_f}{V_0} \times 100\% \quad (2)$$

where V_0 is the volume of the feeding NaCl solution, V_f is the volume of the produced freshwater from the dissociated CP hydrate.

The Raman analysis was conducted using 532 nm laser (Thermal Scientific, DXR).

3. Results and discussions

3.1. Raman spectra of the CP hydrates

The crystal structure and composition of the formed CP hydrates with and without added graphite were analyzed by the Raman spectra of the samples, as shown in Figure 1. The Raman peaks near 895.6 cm^{-1} are assigned to the ring breathing of CP.[7] The peaks locating at around 2875 and 2983 cm^{-1} can be assigned to C-H stretching modes of symmetric vibration and C-H stretching modes of asymmetric vibration of CP, respectively. These results are consistent with the CP hydrate reported in the literature.[17] The peak positions of the Raman spectra show no difference for the formed CP hydrates with and without graphite, which indicates the addition of graphite having no impact on the structure of the produced CP hydrates.

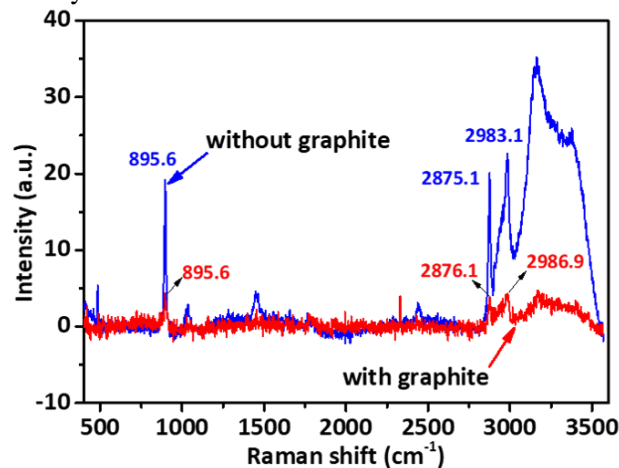


Figure 1. The Raman spectra of the formed CP with and without graphite powders.

3.2. The effect of graphite dosage on desalination efficiency and conversion rate

Our previous study confirms that graphite can promote the formation of hydrates.[19] Here, we studied the effect of graphite dosage on the CP hydrate formation, with the aim to figure out the impacts of added graphite on the desalination efficiency and the conversion rate of water to hydrate. As shown in Figure 2a, the desalination efficiency remains at a level of about 80%, showing no detectable change with the increasing of used graphite. However, as shown in Figure 2b, the conversion rate of water to hydrate was dramatically improved from 28% to 45% with the increase of

graphite dosage. This indicates the critical role of the amount of graphite playing in enhancing the formation of hydrate.

The conversion rate is important for hydrate-based desalination, since it determines the amount of produced freshwater. According to the literature, without the help of surfactants, the solid hydrate films formed around the water droplets hinder the transport of CP to the water trapped in the formed hydrate shell.[18] So the conversion rate is usually limited and very low in previous reports.[19, 20] However, in this paper, a high conversion rate of 45% can be obtained in a very short hydrate formation time. It is reasonable to believe that the more graphite powders, the more hydrate nucleation sites that can be provided, and the faster the heat transfer, allowing more CP hydrates to form during the reaction. It is worth to mention that the hydrate conversion rate is enhanced without causing the degradation of desalination efficiency (see Figure 2a). This is the critical merit for our hydrate-based desalination.

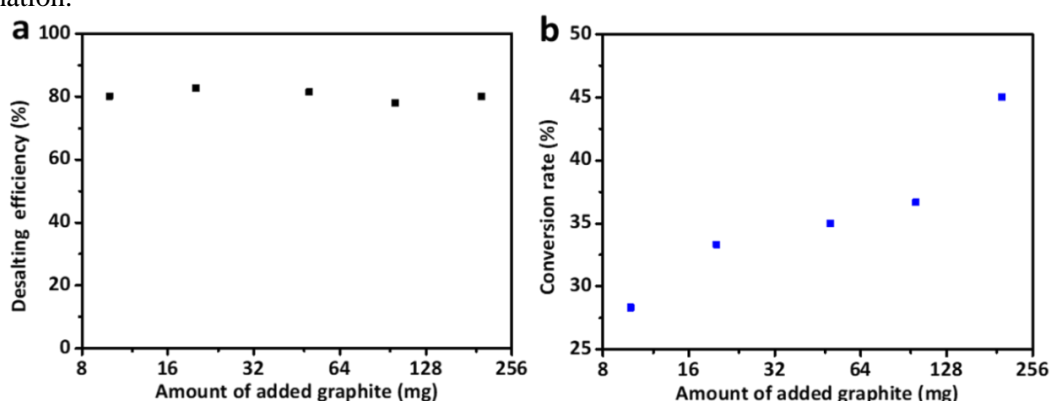


Figure 2. The impact of graphite dosage on (a) desalination efficiency and (b) conversion rate of water to CP hydrate.

3.3. The effect of the ratio of NaCl solution to CP on conversion rate

According to theoretical calculations, the ratio of water molecule to CP molecule in the CP hydrate structure is 17:1.[21] Intuitively, more CP would extract more water from salty water. Some literature reports that the amount of hydrates increases with the percentage of used CP.[21] So we studied the effect of the ratio of NaCl solution to CP on the conversion rate in the presence of graphite. As shown in Figure 3, the ratio of NaCl solution to CP has little impact on the conversion rate of water to CP hydrates. The conversion rate remains at about 33%. We believe that the used graphite is responsible for the result. The identical amount of used graphite provides the same nucleation sites, which gives the same conversion capacity for hydrates under the similar experimental conditions.

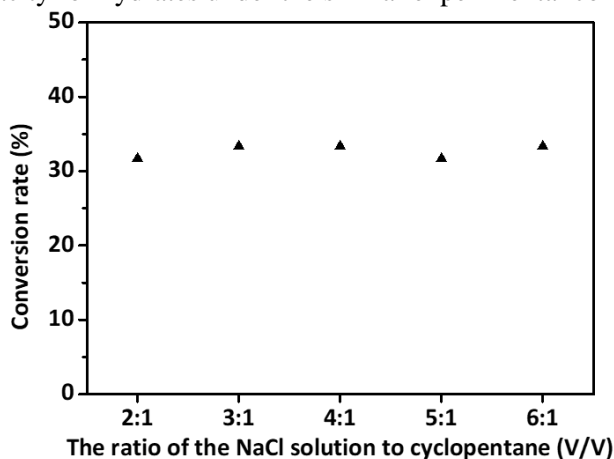


Figure 3. The impact of the ratio of solution to CP on the conversion rate of water to CP hydrates.

3.4. Multi-stage hydrate desalination

Due to the high salt concentration of real and artificial seawater, the one-stage desalination process is insufficient to produce freshwater meeting the standard of domestic water. So we studied the multi-stage hydrate desalination process in order to get fresh water that can meet the domestic water. We conducted hydrate-based desalination via multi-stage. The desalination efficiency of each stage is shown in Figure 4. We carried out the four-stage desalination and obtained a desalting efficiency of up to 99.76%. The salt concentration after each stage of the multi-stage desalination process can be seen from Table 1. After the four-stage desalination, the salt concentration was reduced to 83 mg/L. It meets the standard of drinking water (less than 250 mg/mL). Therefore, it is feasible to use the hydrate method to produce fresh water for daily use from salty water. The result indicates the great promising for the hydrate-based desalination to produce freshwater with high quality.

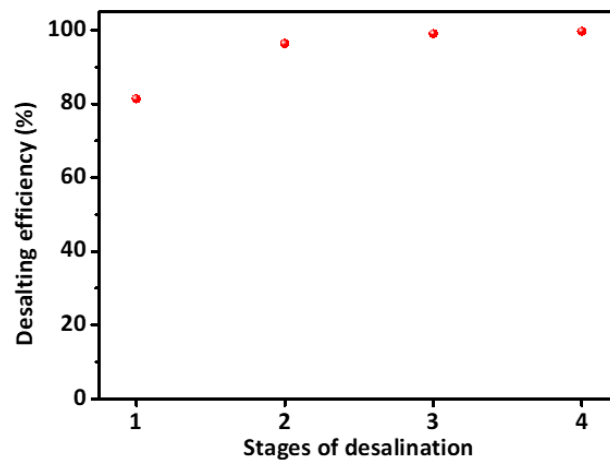


Figure 4. The performance of hydrate-based desalination via multi-stage

Table 1. The NaCl concentration at each stage of the multi-stage desalination via CP hydrate.

Stage	Concentration (mg/L)
Original	3.50×10^4
1	6.50×10^3
2	1.26×10^3
3	320
4	83

4. Conclusion

This study shows the desalination via the CP hydrate process with the help of graphite. The results demonstrate that the added graphite particles had no impact on the structure of the produced CP hydrate. The amount of used graphite can greatly improve the conversion of water to hydrate without degradation of the desalination efficiency. Therefore, more water can be obtained via increased the graphite dosage. The ratio of NaCl solution to CP shows no detectable impact on the conversion rate of water to hydrate due to the same amount of used graphite. Hydrate-based desalination via multi-stage was demonstrated, high quality freshwater with a purity of 99.76% can be obtained by a four-stage treatment. This study shows that the hydrate process with assistance of graphite particles is a promising desalination method, with the advantages of rapid nucleation, large conversion ratio and reasonable desalting efficiency. The method proposed in this work can be a good alternative or complement method for the existing desalination processes.

Acknowledgments

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