Gas Hydrate Technology

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Innovating methods for treating industrial wastewater containing heavy metals frequently incorporate toxicityreduction technologies to keep up with regulatory requirements. This research reviews the latest advances, benefits, opportunities and drawbacks of several heavy metal removal treatment systems for industrial wastewater in detail. The conventional physicochemical techniques used in heavy metal removal processes with their advantages and limitations are evaluated. A particular focus is given to innovative gas hydrate-based separation of heavy metals from industrial effluent with their comparison, advantages and limitations in the direction of commercialization as well as prospective remedies. Clathrate hydrate-based removal is a potential technology for the treatment of metal-contaminated wastewater. In this research, a complete assessment of the literature is addressed based on removal efficiency, enrichment factor and water recovery, utilizing the gas hydrate approach. It is shown that gas hydrate-based treatment technology may be the way of the future for water management purposes, as the industrial treated water may be utilized for process industries, watering, irrigation and be safe to drink.

heavy metals

wastewater

hydrate-based desalination

efficiency toxicity

1. Introduction

An ecosystem is the combination of biotic components, such as microbes, plants and animals, to develop a selfcontained entity with their abiotic, physicochemical environment. The connection between stability and ecosystem has been extensively studied; in a way there should be more species, increased diversity gives greater resistance to change, or stress has been thoroughly invalidated, as proven by ecosystem modelling and investigations ^[1]. Indeed, complex ecosystems are thought to be more fragile than relatively simple dynamically stable systems, making them more vulnerable to human intervention. Because each ecosystem type reacts differently, it is impossible to accurately evaluate the impact of contaminants and heavy metals on ecosystems.

Conventional treatment methods like adsorption, membrane, chemical precipitation and electrochemical techniques are used to eliminate heavy metals from inorganic effluent ^{[2][3][4]}. These techniques are robust but faced with major disadvantages like less selectivity, limited removal of metal, excess energy requirements and large amount of sludge generation. Many methods have been researched lately in order to advance/yield more economical and effective results in decreasing the quantity of wastewater generated and also enhancing the treated water quality. Alternative ways to water recovery are still needed, with a focus on further reducing energy demand while improving water recovery and yield.

To overcome the aforesaid limitations, novel technologies must be studied in order to provide efficient and costeffective alternatives. In this context, clathrate hydrate-based technology has recently emerged as a viable option for treating wastewater containing dissolved minerals and heavy metals [5]6. Gas hydrates are a nonstoichiometric crystalline structure in which the guests are encased within a crystal structure framework of host water molecules ^[6]. There has been a huge interest in the application of gas hydrates in desalination sector. Hydrates have three different crystal structures depending on the type of guest molecule: Structure I (methane, ethane carbon dioxide), structure II (propane, nitrogen, isobutane) and structure H. Each construction is made up of cages of various sizes and forms that are held together by van der Walls forces. Depending on their structure and formation conditions, different hydrate formers retain different numbers of water molecules. This hydration property qualifies them for water treatment applications ^[6]. Thus, the elimination of heavy metal ions via formation of the gas hydrate mechanism attracts substantial interest from researchers because of its ease of operation, low toxicity and good selectivity. It has the advantage of purifying the water using the application of the gas hydrate technique. The hydrate formation requires two basic raw materials, namely water and hydrate, the former which is readily available and accessible. After dissociation of hydrate, 1 m³ of hydrate generates about 164 m³ of gas and 0.87 m³ of freshwater, which signifies a huge potential to produce treated water using gas hydrate applciation in the desalination process ^[6]. During this hydrate formation it eliminates all the metal ions, producing pure water. Hence this method seems to be a promising technique compared to conventional methods. This would help to address environmental problems and scarcity of water issues simultaneously.

2. Overview of Gas Hydrate Technology

The lattice of the host molecule is created by hydrogen-bound water molecules, inside which the guest molecule is incorporated, is called gas hydrate and is nonstoichiometric in nature ^[Z]. The basic requirements for gas hydrate formation are water and gas (guest molecule). The favorable conditions for formation of hydrate are low temperature and high pressure. The guest molecule spins within the water cage during hydrate formation, causing a physical change. The initial nucleation of gas hydrate crystals, followed by growth, and then dissociation of the gas hydrate, are various stages of gas hydrate process. Pressure, temperature, gas composition and the system's thermodynamic behavior conditions play a major role in determining the hydrate formation, stability and structure formation ^{[3][8][9]}.

Clathrate hydrates have been identified as a potential energy resource as well as a source of problems, primarily in the area of flow assurance. On the plus side, the research discovered that gas hydrate can provide energy from a different source, with an individual hydrate unit containing significant energy can make hydrate as as sustainable energy resource. The relevance of gas hydrate as a sustainable energy resource, as well as the prospect of employing gas hydrate for storage, transportation and capture can be applied to hydrate-based applications with increased energy and environmental capabilities ^[10]. Hydrate-based desalination and the development of gas separation or capturing are two more prominent technical applications of hydrates. When the hydrate is formed, the dissolved impurities/salts are dispersed from the hydrate. When the hydrate is heated the gas inside is then released. This produces pure water ^[11]. On the other hand, the flue gas from large power plants might be used to

extract carbon dioxide, thereby reducing global warming and emissions using this mechanism. This concept has advantages over present transportation techniques like liquefied natural gas (LNG) and compressed natural gas (CNG) because they do not need cryogenic temperatures or high pressure requirements ^{[12][13][14]}. Hydrates can be employed as a secondary refrigerant in refrigeration systems ^[15].

2.1. Gas Hydrate-Based Desalination

Desalination is the process of desalinating salty water to produce drinkable water or water beneficial for agricultural purposes ^[16]. Many conventional desalination processes are energy intensive, together with multi-stage flash distillation (MSF), reverse osmosis (RO) and multi-effect desalination (MED) ^[17]. The recovery of pure water from a saline water stream is an important factor in making any desalination process profitable or marketable.

In this hydrate-based desalination process, seawater acts as an electrolyte solution, with a gas hydrate former (suitable guest molecule) at promising conditions of temperature and pressure. A detailed review of the gas hydrate-based desalination developments has been discussed elsewhere ^{[18][19][20][21]}. A detailed process of hydrate formation, dissociation and separation of pure water and residual water is shown in **Figure 1**. As salt has no effect on the shape of the hydrate crystal, it acts as a thermodynamic hydrate inhibitor (THI) by shifting the phase equilibrium curve to a higher pressure at a given temperature condition, thereby lowering the driving force essential to form hydrates. The formed hydrate is then separated from the residual brine and further dissociated to yield pure drinking water and the guest gas (hydrate former) could be further recycled ^{[18][19]}.



Figure 1. Hydrate formation, dissociation and water recovery process in hydrate-based desalination process.

The water recovery relates to the quantity of freshwater retrieved from the feed, and is estimated based on kinetics of formation of hydrate. The fraction of the volume of water converted to hydrates, and the quantity of recoverable hydrate crystals during the separation process, is estimated by hydrate formation kinetics ^[21]. The maximum amount of water that can be recovered is limited by the initial eutectic solution composition. Other statistics that relate to assessing the efficiency of removing salt is salt rejection. This is defined as the change in concentration of salt after hydrate formation to its initial value ^[18]. Scientists started researching gas hydrates and their application in the field of seawater desalination about four decades ago. Since then, numerous studies have been conducted around the world to develop appropriate hydrate formers that are environmentally friendly, stable, non-toxic, easily available and economically feasible ^[22]. Some of the hydrate former studies available in the literature up to today are based on propane (C3H8) ^{[23][24]}, cyclopentane (C5H10), ^{[18][19][25][26][27][28][29]}, carbon dioxide (CO2), ^{[30][31]}, refrigerants (HFC, HCFC, and CFC) ^{[32][33][34][35]} and sulphur hexafluoride (SF6) ^[36]. Several studies have been performed in determining the phase equilibrium through a pilot scale set up ^{[37][38][39][40][41][42]} and the kinetics of

hydrate formation have been boosted (by using secondary hydrate forming gases) ^{[43][44][45][46]}. Early commercialization of hydrate-based desalination was delayed based on the difficulty in separating the hydrate phase from the residual brine; however, the efficiency of salt exclusion has been examined, and ways to improve hydrate formation via subsequent treatment operations have been devised ^{[46][47][48][49]}.

Following that, several improvements for hydrate separation from salt water, eliminating salt from the slurry and reducing induction time are discussed below. Despite being atmospheric guest molecules (hydrate formers) like CFC, SF6, HCFC and HFC, and also because of the influence of ozone depletion, these hydrate formers are considered inapt and the flammability of cyclo-alkanes and alkanes generates threat for large-scale applications. A thermodynamically integrated technique, on the other hand, suggests that propane and ethane are good guest molecules ^[22]. Several hydrate formers, namely liquid, gaseous and other additives, have been analyzed to check the feasibility of the hydrate-based desalination process ^[35]. Moreover, after a thorough examination, cyclopentane (CP) was discovered to be an atmospheric hydrate-forming agent and it forms a suspension which requires further post-treatment ^[41]. The economic viability must be examined as the cost of the operation is reliant on basic variables like temperature of brine, favorable thermodynamic conditions of temperature and pressure, concentration of salt, salt mobility and yield ^{[49][50][51]}. Hydrate-based desalination methods are still desirable since they are environmentally useful and energy efficient in terms of use in large-scale applications.

A hybrid system with an RO-hydrate system for seawater desalination has recently been proposed, along with an optimum design strategy. Additionally, a novel desalination process based on hydrates has been developed and simulated using LNG waste cold energy as a heat sink, and the economic viability of the method has been assessed ^{[52][53][54]}. The outcome of substituting the external refrigeration cycle with an LNG plant is very encouraging; as a result, desalination of high strength brine solution may be performed with little energy usage, making the gas hydrate-based desalination technique commercially viable. An apparatus for multi-use desalination by gas hydrate was developed, with several unit operations and its application as a continuous process with multiple injection, separation and purging phases has been examined ^[55]. The desalination efficiency was determined to be greater than 80%, with a water recovery rate greater than 30%.

Utilizing CO2 as a hydrate former in hydrate formation has a dual role: It provides drinkable water from salt water and also separates the gas. As a result, clathrate hydrates could be considered a viable working medium for CO2 storage and desalination purposes ^{[53][54][55][56]}. Despite the fact that only limited studies have been carried out so far ^{[57][58]}, additional research based on the reactor design configuration, separation of hydrate from effluent and enhancement of the kinetics of hydrate formation would undoubtedly open the door to more research in this area, particularly concerning, e.g., appropriate thermodynamics and kinetics conditions combined with minimization of cost. Recent scientific and economic breakthroughs have hastened the development of commercially viable clathrate-hydrate desalination devices. More experimental research is desirable to lower the amount of salt stuck in hydrate crystals throughout each cycle and to adjust important operational parameters based on hydrate former to improve desalination efficiency.

2.2. Gas Hydrate Desalination Reactor Design Innovations

The clathrate hydrate formation technique has been used to desalinate seawater worldwide. The slow kinetics and the difficulty in separating the crystal from the brine and removing salt from hydrate that has occluded the surface of the crystal have all been addressed by researchers. To separate the crystals, a conveyor belt was employed. Hydrate formation and then later dissociation was performed in different compartments using a non-stirred reactor. After dissociation of hydrate, some of the recovered water was utilized to wash the salts in the washing stage that had stuck to the surface of hydrate [59]. Ben produced hydrates at a certain depth in seawater and the hydrates rose high due to the buoyancy effect and wash water was introduced to wash the hydrate above the hydrate production zone [60].

Another breakthrough was the use of liquid propane as hydrate former to produce hydrates at the bottom of the reactor. The formed hydrate rose higher through the brine due to the buoyancy effect. It was created to flow through risers in partition plates, thereby efficiently separating hydrate crystals from saline solution. The wash process was utilized by using the produced fresh water after dissociating the hydrate ^[61]. To utilize the heat of hydration for decomposition of hydrate and as a solvent for formation of hydrate, a heat exchange (HE) liquid that was immiscible in water was used. To solve the problem of washing of the formed hydrate a HE liquid having a specific gravity lower than aqueous saline solution was introduced to overcome washing of hydrate. The HE liquid helped with the passage of formed hydrates from the hydrate formation zone to the dissociation section. The gas and liquid utilized in HE were recycled back to the hydrate formation zone ^[62]. A gas bubble was delivered by a nozzle into precooled water in another invention, resulting in the production of hydrates. Because of pressure variations between the pipeline and the mobile tank, hydrates were passed through the pipeline into the mobile tanks and then depressurized in the tank ^[63].

Using concentric and coaxial pipes, a high-pressure, low-temperature hydrate former was injected to an appropriate ocean depth, leading to a large investment in injecting gas to further depths. The annular zone generated hydrate slurry, which was retrieved from the surface [64]. Another invention involves injecting methane at a depth into columns and allowing hydrates to develop. Because of the buoyancy, the hydrate rose, and the heat from the hydration was dissipated into the surrounding water [65]. Atomized water is used inside the reactor to improve the interaction and surface area of gas and liquid water. Hydrate crystals are deposited as they form on a conveyor belt. Because of the porous moving surface, it was feasible to extract hydrate from feed. A roller and grinder in the production area were used to carry the washed hydrates to the dissociation zone [66]. Seawater was introduced from the top of the reactor, while gas was pumped in from below. Hydrate particles served as fluidized bed particles, thereby giving more surface area for gas-liquid contact. Fluidized hydrate particles obstruct the gas and water flow, enhancing the residence time and helping in the formation of additional hydrates [67]. The hydrate formation and dissociation took place in a single reactor, resulting in crystal formation due to buoyancy. The hydrate formed in the reactor's bottom rose upward towards the decomposition zone due to positive buoyancy [68]. It was decided to use a desalination system with a porous constraint. A thick impermeable hydrate mat was produced under this porous restriction. A thick layer of hydrate was blocking the entry of saltwater water. The hydrate close to the restraint is separated by lowering the pressure on the collection side of the constraint [69][70]. It was discovered that employing a blend of hydrochlorofluorocarbons (HFCs), hydrofluorocarbons and chlorofluorocarbon molecules might reduce the dendritic growth of the hydrate.

In another invention, ice formation over hydration was implemented to minimize the need for washing. Salts that have occluded on to the surface of crystal are washed by the melting of ice [71]. A vertical tubular reactor with upper and lower parts was employed for hydrate formation and decomposition, respectively. Stirring produced hydrate production in the reactor's lower half, and the buoyancy effect promoted easier crystal separation. The top of the reactor produced pure water for recovery [72]. It has been suggested that CO2 could be sequestered by dissolving in seawater. Desalination using hydrates has been proposed as a method of concentrating brine solutions with dissolved CO2 ^[73]. Desalination, thermal energy storage and natural gas storage have all been produced using gas hydrate modular systems [74]. A dual cylinder with a piston was employed in another design to compress the slurry, and saline water was passed through the perforations. To boost the efficiency during salt separation, concentrated saltwater from the reactor's bottom was returned to the hydrate formation region; however, maintaining hydraulic pressure requires a high energy throughput ^[75]. In another invention a hydrate-forming gas was pumped into a saline-water reactor utilizing a microbubble generating device for hydrate formation ^[76]. In order to promote hydrate nucleation in gas bubbles with diameters between 10^{-3} and 10^{-2} mm, an ultrasonic transducer was utilized to supply sonic energy. Solid material particles, such as silica gel, were introduced to the stream to increase the surface area of gas-liquid contact. A wash column was used to remove the saline solution from the interstitial pores of the crystal [77]. In a recent reactor invention [78] where hydrate formation, separation, washing and dissociation took place in a single reactor, the formation of CO2 hydrate in the presence of 2 wt.% brine solution at different pressures was observed and there was a removal efficiency of 60.08% at 3.0 MPa.

The hydrate-based desalination method advances have mostly focused on resolving the fundamental problem of efficient hydrate crystal separation from the residual brine. Because hydrate nucleation is a stochastic process, researchers have tried to shorten induction time by using microbubbles, ultrasonic energy and localized supercooling by depressurizing liquid propane. While various attempts to commercialize the HyDesal process have been made, these efforts have failed due to additional technological obstacles like the difficulty in separating small crystals from effluent and the fact that a few guest molecules are toxic and they pose environmental risks. Hence, there is a need to address the challenges of energy efficiency and cost and crystal/brine separation and of course to carry out the process in a manner that fully addresses potential environmental concerns.

2.3. Heavy Metal Separation Mechanism Based on Gas Hydrates

New strategies for removing heavy metals from wastewater, such as separation of heavy metal by hydrate method, appear to be in high demand. The scientific relevance of this research into purification and separation using a gas hydrate approach has pricked the interest of many scholars. Parker proposed a method for producing drinkable water from highly saline sources using gas hydrate formation as early as 1942, and it has received a lot of interest over the last decade ^[79]. Hesse and Harrison observed a noteworthy reduction in interstitial water chlorinity when they used hydrate in deep-water sedimentary layers, and they discovered that hydrate rejects salt ions from the crystal structure, which affords the theoretical foundation for separating mixtures using hydrate-based methods ^[80]. Knox et al. presented a method for separating inorganic mixtures using seawater desalination, and a pilot plant was built to test this process, which produced drinking water ^[23]. Furthermore, Bulot et al. devised a method for purifying a solute from an aqueous solution of water and solute ^[81].

Using experimental and thermodynamic models, Ngema et al. assessed the accurate phase equilibrium data of hydrate formation in saline aqueous solutions. They measured the hydrate phase equilibrium of R134a, R410a and R507 in MgCl2, NaCl and CaCl2 to give the parameters for hydrate-based desalination. Despite the fact that the hydrate phase equilibrium of many guest molecules has been extensively researched, most studies only look at a single solute at low concentrations. As a result, experimental studies of phase equilibrium with mixed solutes of higher concentration are required. Gas hydrate technology could be used to develop wastewater treatment and desalination systems based on this information ^[34]. Huang et al. used methyl bromide, trichlorofluoromethane and 1,1-difluoroethane for separation of organic mixtures to study the concentrations of apple, orange and potato juices by gas hydrate method and found that this method removed 80% of water content ^[82]. When comparing hydrate desalination to reverse osmosis, Bradshaw et al. discovered that the water throughput rate and recovery are faster with hydrate-based desalination ^[32]. All this research suggests that hydrate-based separation methods can be applied for desalination purposes to treat wastewater.

The hydrate-based water treatment technology facilitates the solid–liquid separation more efficiently at high temperatures than conventional water freezing temperature by enriching the guest molecule with the water molecules. The guest molecule can be recycled in the system after melting the gas hydrate crystals, which is mostly freshwater, as addressed in detail in reviews elsewhere ^{[18][19]}. The following steps are followed in the hydrate-based water treatment process, as indicated in **Figure 2**: (i) Creation of gas hydrates, (ii) hydrate separation from effluent, (iii) post-treatment (e.g., washing, centrifuging) to improve water quality and (iv) dissociation of hydrate crystals to produce treated water and reuse gas ^[83].

Song et al. proposed a system for isolating heavy metals from aqueous solution built on gas hydrates, based on the aforesaid principles and mechanism. Raman spectroscopy was used to examine the separation efficiency of this approach with various R141b–effluent volume ratios, as well as the influence of a washing operation on heavy metal removal. The heavy metal ion concentration decreased from roughly 140 mg/L to less than 0.4 mg/L after hydrate-based desalination, demonstrating that the heavy metal ions had been excluded from the hydrate structure. The process employed is an intriguing method for separating heavy metal salts of different concentrations from industrial effluents using an extrapolation of hydrate-based desalination. Cr^{3+} , Cu^{2+} , Ni^{2+} and Zn^{2+} were removed from an aqueous solution utilizing R141b as the hydrate forming in this research ^[84].



Figure 2. Heavy metal ion removal by gas hydrate technique.

Yang et al. investigated hydrate-based treatment looked at using hydrates to treat Ni²⁺-contaminated wastewater. At a volume ratio of 3:1, cyclopentane (CP) was added to a NiCl2 aqueous solution, and hydrates were produced at 2 °C with agitation at 600 rpm. Overall, the separation efficiency of the hydrate-based approach varied from 62% to 88% ^{[85][86][87][88]}. This research involved the separation of specific ions rather than series of metal ions. The separation efficiency of the method is found to be dependent on the metal ion trapped on the solid hydrate. If proper post-treatment is used, separation efficiency can be increased to up to 95% ^{[47][89]}. It is worth noting that, when the Ni²⁺ concentration rises, the separation efficiency also improves.

Dong et al. devised a new hydrate-based approach for removing heavy metal ions by implementing stages of posttreatment techniques. The formation of hydrate, separation of solid from liquid, dissociation of hydrate and analysis of the effluent/residual are the four main steps in this system. They looked into a number of variables, including ion exclusion and the process for removing the hydrate from the mother liquor. Following that, a unique approach was developed to obtain high separation efficiency from high concentrations of heavy metal ions in wastewater. R141b was used as the former and copper sulphate solutions were used ^[90]. R141b reacts with water at temperatures less than 8.4 °C and pressures greater than 42 kPa to form sII hydrate ^{[90][91]}. Solid–liquid separation unit operations were carried out once the hydrate formation was completed. The hydrate was then melted down by adjusting the system's temperature, and separation occurred due to R141b's immiscibility with water. Cu²⁺ concentrations were measured using an inductively coupled plasma optical spectrometer (ICP), and electrical conductivity variations were recorded using an electrical conductivity meter (ECM). **Figure 3** shows a conceptual picture of the hydrate process for removing heavy metals from aqueous solution.



Hydrate dissociation

Figure 3. Schematic diagram for hydrate-based desalination process.

2.4. Water Recovery

Water recovery denotes the volumetric efficiency of the process. It is defined as the volume of water in the initial feed that is converted into hydrate. However, in most situations, less than 100% of the hydrate crystals are recovered. As a result, after the hydrate crystal separation process, the volume of hydrate recovered from the brine is utilized to compute the amount of water recovered. The percentage of water recovered from the feed can be stated as follows:

Water recovery $\% = \frac{\text{Volume of water converted to hydrate}}{\text{Initial volume of feed solution}} \times 100$

Volume of water converted to hydratelnitial volume of feed s

Water recovery relies on the kinetics of hydrate formation and efficiency of separation. Higher water recovery necessitates the production of more hydrates and efficient separation of crystals from salt water. Addition of propane as co-guest molecule to guest molecules argon, nitrogen and carbon dioxide for hydrate-based desalination using a fixed bed reactor was studied by Nambiar et al. ^[92]. There was less than 2% water recovery achieved using propane with argon and nitrogen, whereas with carbon dioxide it resulted in water recovery of 41.38% due to the formation of sII structure constituting 136 water molecules. However, the amount of water that can be recovered is dependent on the wastewater concentration, hydrate former, stirring mechanism and effectiveness in separation of crystal from hydrate ^[18]. Babu et al. ^[93] used a unique cylindrical annular bed reactor design that incorporated a scraper for scraping the generated hydrate crystals on the mesh. They looked into the salt rejection rate and water recovery rate of a carbon dioxide/propane mixed gas used as a hydrate forming in porous media, and discovered that the salt rejection rate and water recovery rate could both reach 87.5% and 34.85%, respectively. The hydrate crystals that detached from the salt solution, however, remained connected to salt particles, which was unexpected.

According to Dong et al. ^[94], the removal effectiveness of R141b–effluent volume ratios on water recovery increased from 1:4 to 1:6. Total water content would theoretically be converted to hydrate at a ratio of 1:3.21 for R141b–effluent. As a result, there are less heavy metal ions trapped between hydrate crystal or adsorbed onto their surfaces. At ambient temperature and pressure, the dissociation of hydrate occurs, leaving lesser metal ions in the dissociated water. Therefore, an increased R141b–effluent volume ratio led to an increase in dissociated water production. Y. Yang et al. studied an innovative hydrate-based method to separate Ni²⁺ from wastewater with cyclopentane at a ratio of 3:1 (v/v). This technique has a water recovery rate of about 43% (the average), according to the findings of this research, when using a low-concentration feeding solution. In terms of water recovery, this hydrate-based technique is on par with or even better than those used in traditional wastewater treatment. The fact that the water recovery has been relatively stable shows that this approach can treat wastewater with a wide concentration range ^[84].

An experimental study by Gaikwad et al. identified As⁵⁺, Pb²⁺, Cd²⁺ and Cr³⁺ in industrial effluents and prepared a 1000 ppm solution of each salt to imitate an industrial wastewater effluent. As the hydrate-forming gas, natural gas was chosen, cyclopentane as a liquid co-former and as the promoter, lecithin (surfactant) was selected. A maximum 30 percent water recovery has been recorded when the concentration of lecithin is increased up to 300 ppm. However, the individual metal ion removal efficiency is not discussed in this case ^[90]. Another study, by Nallakukkala et al. ^[95], found a water recovery of 66% when operating at 2.5 MPa using CO2 as hydrate former by treating 2 wt% brine solution. This recovery is higher than that obtained by ^[92], in which the recovery was 41.38% using 10% propane and 90% CO2. Ling et al. ^[96] evaluated the induction time, water recovery and desalination effectiveness of the LiCl, LiBr and Lil salts on the production of cyclopentane hydrates. The results showed that increasing the amount of lithium haloids improved desalination efficiency; nevertheless, these salts hinder induction time and water recovery. The inhibitory impact of halide ions on the formation of hydrates and desalination was discovered to be in the order I⁻ > Br⁻ > Cl⁻.

2.5. Removal Efficiency

The removal efficiency of the hydrate-based separation process is used to assess its effectiveness.

$\label{eq:Removal Efficiency} \ensuremath{\mathbb{R}} \operatorname{emoval Efficiency} \ensuremath{\%} = \frac{\operatorname{Initial conc. in feed} - \ensuremath{\operatorname{Conc. in dissociated water}}{\operatorname{initial conc. in feed}} \times 100$

Song et al. investigated volume ratio of 1:6 using R141b–effluent. The removal effectiveness of hydrate crystals without washing ranged from 67.82 to 71.87%. The highly concentrated residual effluent was retained on the hydrate surface due to the porous structure of the hydrate crystal. As a result, the dissociated water still includes a significant amount of heavy metal ion, resulting in poor removal efficiency. A washing technique was employed to remove any leftover heavy metal ions, and resulted in a 19% increase in removal efficiency and a separation efficiency range of 88.01 to 90.82% ^[83].

To perform multi-stage desalination, Yang et al. utilized an aqueous solution with a Ni²⁺ concentration of 1000 mg/L. In a single stage an efficiency of 84% was produced, whereas two stages produced an efficiency of 96%. The third-stage treatment produced efficiency of 99.2%, demonstrating that this hydrate-based technique can deliver high-quality water ^[84]. For separation of heavy metals during the formation and dissociation phase, Dong et al. reported that some pores inside the hydrate were interconnected and formed channels, and the hydrate former R141b was trapped in the channels inside the bulk of the aqueous solution. The hydrate decomposition shattered the small solution pockets, allowing them to pass through aqueous solutions in the hydrate slurry, thereby reducing the removal efficiency. As a result, separating the trapped solution from hydrates slurries was crucial to improving removal efficiency [93]. This experimental research used five different hydrate washing unit processes, which were referred to as: (1) No operation, (2) vacuum filtration (VF), (3) washing with a guest species followed by VF (WHVF), (4) washing with fresh water followed by VF (WFVF) and (5) VF followed by centrifugation (VCF). The highest removal efficiency was reached by utilizing VCF, which was 90.46%. When using fresh water for washing and using the vacuum filtering method, better results were obtained. Fresh water can be conserved, costs can be reduced and removal efficiency can be improved at all times with this method. This research led the researcher to the conclusion that the solid-liquid separation process has a direct impact on hydrate-based ion elimination efficacy, and that VF and centrifugation is the most successful solid-liquid separation method amongst those investigated [89].

Heavy metals with concentrations of 500 ppm, containing Zn, Cu, Ni and Cr, were utilized in a system created by Al-Hemeri et al. ^[97], together with CP as an additive. The removal efficiency for copper ions was as high as 92% in a CP/water solution volume ratio of (1/6) v/v. Due to the low strength of heavy metal ions in the discharge, the outcome in lower metal ion adherence to the hydrate crystal surface, hence the percentage removal efficiency, improved when the volume ratio was changed from 1/2 to 1/6. Heavy metal ions pollute the fresh water during hydrate dissociation by lowering the ion exclusion efficiency significantly. Increasing the water volume ratio from 0.115 to 0.192 to estimate the optimum volume, the removal efficiency was found to increase from 30.08% to 60.08% ^[95] when operated at 3.5 MPa. Effective desalination and kinetics of hydrate growth were observed by ^[89] using 6 mole % CP and there was a water recovery of 25.72% As⁵⁺ aqueous solution of 1000 ppm; similar results were obtained using lecithin as a promoter along with 6 mole % CP. No further studies were mentioned related to removal efficiency aspect.

2.6. Enrichment Factor (Ef)

Industrial waste has a significant environmental impact, as wastewater treatment regulations are very stringent. Wastewater reduction and zero liquid discharge (ZLD) are important goals to remove waste from a system ^[98]. The enrichment factor is a crucial parameter in ZLD because it determines how much wastewater is reduced and how difficult it is to produce value-added products from the residual adueous solution. concentration of heavy ion in the residualeffluent.initial heavy metal ion cocncnetration in water solutio

Enrichment Factor = $\frac{\text{concentration of heavy ion in the residual effluent.}}{\text{initial heavy metal ion concnetration in water solution}} \times 100$

The influence of volume ratios on the enrichment factor was investigated by Al-Hameri et al. ^[99]. According to the findings of the experiments, the (Ef) dropped when the volume ratio increased from 1/2 to 1/6 because heavy metal ion concentrations in the residual effluent are a major determinant of the Ef. As a result of the lower cyclopentane/water solution volume ratio, there was a higher (Ef) and the concentrated effluent accumulates a significant percentage of heavy metal ions. The research removed heavy metals from industrial wastewater, utilizing a cyclopentane as hydrate former in the production method, in which cyclopentane was used to form hydrate due to its immiscibility, thermodynamic stability and non-toxicity. During the experiments it was noted that the (Ef) was approximately equal for all four (Ni, Cr, Zn and Cu) heavy metal ions, despite the fact that each ions' radii and charges are different. Yang et al. performed the investigation and extracted the water from the Ni²⁺ contaminated wastewater using clathrate hydrate separation. The enrichment factor was found to be between 1.15 and 1.60. Like water recovery, the enrichment factor for Ni²⁺ falls as the concentration of feeding solution increases. Due to the fact that water activity decreases as Ni²⁺ concentration increases, it was difficult to remove water from concentrate and the feeding solution [84].

Dong et al. found that, when Cu²⁺ concentration enhanced, the enrichment factor dropped, and it peaked at 2.80. This was due to the fact that less hydrate formed when the aqueous solution concentration was greater. Conversely, there was less leftover water due to increased hydrate formation. The adoption of gas hydrate technology can therefore help to minimize wastewater by reducing liquid discharges ^[89]. Song et al. found the enrichment factor for each heavy metal ion, an indicator of how difficult it will be to treat any remaining wastewater. They observed that the enrichment factor decreased when the R141b–effluent volume ratio was changed from 1:4 to 1:6. Even with varied ionic radii and charges, the enrichment factor was roughly the same for all four heavy metal ions (Cu, Cr, Ni, Zn) ^[83].

2.7. Gas Hydrate and Hybrid Technologies

Another hybrid desalination process should be used as a post-treatment for the gas hydrate (GH) process to produce fresh water to improve water quality. Reverse Osmosis (RO) uses GH to make freshwater that meets design specifications, concentration and drinking water regulations ^[100]. From the standpoint of the RO process, the GH process is one of the pretreatment options for reducing the salinity of saltwater. Lee et al. ^[101] used a hybrid GH-RO simulation to find the best RO recovery approach that used the least amount of energy. The GH and RO units were connected in series in their system, and the seawater was fed into the GH system. The RO unit received the desalinated product water from GH as feed, but the concentrate was rejected. The RO unit's permeate was collected as product water, and the retentate was recycled into the GH process' feed stream. Due to their intrinsic reliance on thermal energy primarily obtained from fossil fuels, the conventional processes have significant capital and operating costs and are regarded to be highly energy intensive. The optimum RO recovery values for GH processes with salt rejections of 78, 84 and 90 percent were calculated to be 0.6, 0.8 and 0.8, respectively. According to the simulation results, the maximum permissible energy consumption of the GH process is 1.4 kWh/m³ (with GH salt rejection of 78 percent) to overcome the saltwater RO process with an energy recovery

device, and it can be increased to 1.9 kWh/m³ when GH salt rejection is increased to 90 percent. The data revealed that by merging these procedures, energy consumption might be reduced. In another hybrid process of GH+.

Capacitive deionization (CDI) method ^[102] electrodes are made up of activated carbon to avoid the dissolution of binder, polyvinyl alcohol (PVA) is a binder and glutaric acid acts like a crosslinking agent. The hydrate is allowed to form and later is compacted into pellets with only a small amount of brine retained inside the pores. To boost the salt removal efficiency, the CDI approach is utilized as a post-treatment step. The hybrid desalination process could remove 82% of Na⁺ and 100% of K⁺, Ca²⁺ and Mg²⁺ ions. The researcher studied the effects of NaCl, KCl, MgCl2 and CaCl2 on CO2 hydrate production and salt removal efficiency. These salts lowered the amount of water converted to hydrate and desalination efficiency. As each of the traditional desalination processes has its own set of advantages and demerits, researchers ^{[98][103][104]} have proposed hybrid approaches to increase desalination efficiency while cutting costs. In hyper-saline water treatment, where the RO system becomes energy intensive and expensive, such hybrid systems may be more useful.

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