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Review

Gas Hydrate-Based Heavy Metal Ion Removal from Industrial Wastewater: A Review

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Abstract: Innovating methods for treating industrial wastewater containing heavy metals frequently incorporate toxicity-reduction technologies to keep up with regulatory requirements. This article 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 work, 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.

Keywords: 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 self-contained 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.

The most harmful chemical industries are those that use heavy metals such as Cd, Cu, Ni, Cr, As, Zn and Pb and dump large amounts of metal-contaminated effluent, as shown in Table 1. Due to the high solubility of heavy metals in water these metals can be absorbed by living organisms. Heavy metals can build up in significant amounts in the human body once they reach the food chain. When metals are overconsumed beyond the allowed concentration limit, they can cause serious health issues [2]. Hence, as a result, heavy metal-contaminated wastewater must be treated before being released into the environment.

Conventional treatment methods like adsorption, membrane, chemical precipitation and electrochemical techniques are used to eliminate heavy metals from inorganic effluent [3–5]. 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 cost-effective alternatives. In this context, clathrate hydrate-based technology has recently emerged as a viable option for treating wastewater containing dissolved minerals and heavy metals [6,7]. Gas hydrates are a non-stoichiometric crystalline structure in which the guests are encased within a crystal structure framework of host water molecules [7]. 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 [7]. 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 m^3 of hydrate generates about 164 m^3 of gas and 0.87 m^3 of freshwater, which signifies a huge potential to produce treated water using gas hydrate applciation in the desalination process [7]. 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.

The goal of this review paper is to summarize the conventional and novel technologies used in heavy metal treatment from industrial wastewater and evaluate their advantages and limitations based on their application. Based on this approach the conevntional treatment methods are discussed as shown in Figure 1 along with their advanatges and limitations. This paper also gives the overview of research and progress on novel technique gas hydrate-based desalination, recent innovations based on reactor design, mechanism and heavy metal ion separation, water recovery and the opportunities and challenges with the application of the gas hydrate process. The latest developments in the process of commercialization and various hydrate formers that are used to remove heavy metals and that can produce higher water recovery have been reviewed and discussed in depth.

1.1. Wastewater

The discharge of wastewater which is polluted with metal ions has increased significantly in a few decades as a result of urbanization, industry and agricultural activities [8,9]. In general, wastewater is divided into two types, namely industrial wastewater and domestic wastewater. Wastewater from domestic sources is comprised of solid and liquid wastes generated by non-manufacturing processes and may contain sewage, bacteria, viruses, hazardous materials, sanitary outputs, detergents, non-toxic organisms and trash [10]. However, the primary source of water contamination is untreated wastewater discharged by industries. Dyes, aromatics, pesticides, heavy metals, oil [11–16], etc., are some of the pollutants found in industrial wastewater that end up in the environment and these toxic contaminants constitute a serious risk to human health and the ecosystem [17].
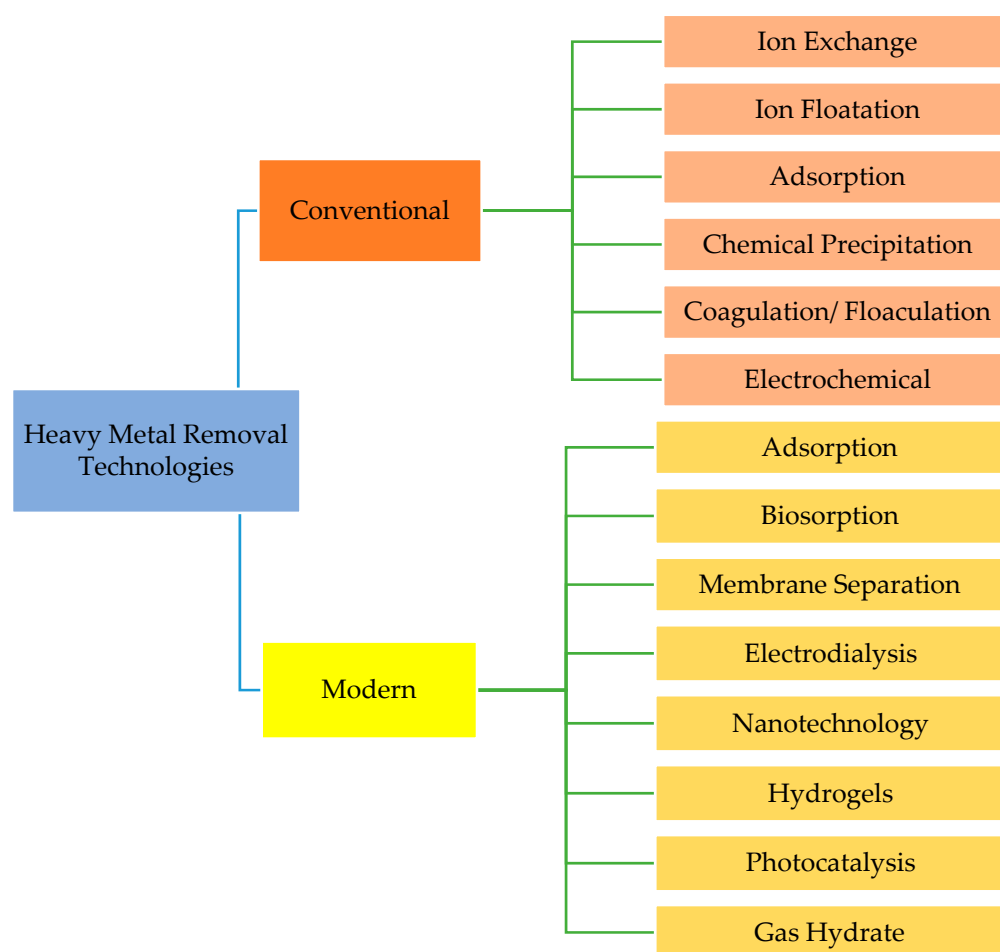
Figure 1. Technologies available for removal of heavy metals from industrial wastewater.

1.2. Heavy Metals

A heavy metal element is defined as having a specific gravity greater than 5.0 and atomic weight between 63.5 and 200.6 g/mole [18]. The term "heavy metal" denotes a high-density element that is unsafe even in trace quantities. Heavy metals in wastewater have recently become a major environmental problem, posing considerable harm to ecosystems and human health even at very low strengths. Pollution by heavy metals is a noteworthy burden on the environment due to their non-biodegradability, accumulation, adaptability and persistence [16,17,19,20]. Heavy metals removed from dyes like amido black dye are targeted by doping cobalt where, due to the negative free energy values obtained, the elimination process has been discovered to be spontaneous. Because of the increased surface area and enhanced contact between the catalyst and the pollutant, cobalt doping resulted in up to 90% degradation [3]. Biosorption employing waste biomass materials, on the other hand, is chosen due to its low cost, simplicity, biodegradability and environmental friendliness [4]. Khan et al. [5] substantiated the need to integrate and optimise treatment approaches in order to effectively tackle the cleaning challenge.

Table 1. Heavy metals in wastewater from common industrial sources [16].

Metals	Al	As	Cd	Cr	Co	Cu	Fe	Hg	Mn	Ni	Pb	Zn	References
Industries													
Aviation	X		X	X		X	X	X		X		X	[17]
Allies, Chlorine		X	X	X				X			X	X	
Urea/Fertilizers	X	X	X	X		X		X		X	X	X	
Glass	X	X		X			X			X	X		
Cement	X	X							X	X	X	X	
Organic chemistry	X	X	X	X				X			X	X	
Paper manufacturing			X	X		X		X		X	X	X	
Petroleum refiner	X	X	X	X		X				X	X	X	
Power plants				X									
Steel works		X	X	X	X	X		X		X	X	X	
Tanning				X									
Textile mills				X									
Pharmaceutical		X	X	X		X				X	X	X	[21]
Dyes			X	X		X	X			X	X	X	[22]
Engineering			X	X		X	X			X	X	X	
Fine chemicals			X	X		X	X			X	X	X	
Batteries								X					[23]
Brass manufacture										X			
Electroplating			X	X		X						X	
Ferromanganese alloy production								X	X				
Fungicides		X											
Metal smelters		X											
Mining										X			
Nuclear fission			X										
Pesticides		X	X			X		X			X		
Welding			X						X				

1.3. Various Heavy Metals and Their Effects

When heavy metals (such as Ag^+, Hg^{2+}, Cd^{2+}, As^{3+} and Pb^{2+}) in their ionic forms mix with bioparticles in the human body, hazardous chemicals are produced; these types of interactions are also important to identify. When heavy metal concentrations exceed the tolerance limits, they become toxic and alter the cell metabolism [24]. Due to the multiple negative effects on human health and the ensuing impairment to marine life, several regulatory bodies have set acceptable limits and stringent regulations for heavy metal disposal. Furthermore, due to the severe consequences of wastewater, researchers have focused on developing improved treatment technologies [25]. The health effects of several heavy metals are summarized in Table 2 [26–28]. These heavy metals represent major dangers to the human population as well as the animals and plants that live in the water bodies. These can be absorbed into the human body, resulting in health problems such as organ damage, cancer, nervous system impairment and, in the worst-case scenario, death.

The heavy metals mentioned above can build up at any time and do so faster than they can be expelled, making them extremely dangerous to humans and the environment. Heavy metals have severe effects on aquatic environments even at low concentrations, and natural degradation of these metals does not occur. It suppresses the activity of microbes that were previously existing in waste waterways. Consequently, researchers are focusing their efforts on removing heavy metals from waste waterways at the moment.

Table 2. Toxicological effects of metal ion on human health.

Metal	Route of Entry	Toxicity Effect	Disposal Limit Recommended by WHO * (mg/L)
Copper	Ingestion and inhalation	intestinal irritation, liver illness, anemia, and cancer in respiratory tract	0.02
Cadmium	Inhalation and ingestion	lung damage and limits the respiratory system	0.06
Chromium	Inhalation, ingestion, and absorption through skin	damage the lungs and limits the respiratory system	0.05
Mercury	Inhalation, ingestion, and absorption through skin	imitation of respiratory system, liver and kidney damage and loss of hearing	0.01 (vapor)
Lead	Inhalation and ingestion	lungs and kidney damage	0.15
Nickel	Inhalation	lung, liver kidney damage	0.1
Zinc	Inhalation and ingestion	It causes a number of health problems, including fever, nausea, vomiting, skin irritation and anemia, despite the fact that it is required by humans at a trace amount.	0.05

* World Health Organization.

2. Conventional Technologies for Heavy Metal Removal in Wastewater

Pollutants in wastewater are discharged in accordance to strict regulations. Due to the pollutants' inhibitory properties, a high removal strategy is required to meet the discharge protocols. Thus, the industrial sector faces several challenges in order to reduce discharge of pollutant, water usage and consumption of energy [29]. As a result, a number of treatment options to assure environmental safety were created, resulting in a noteworthy study. Each technology has its own set of benefits and drawbacks. As a result, a number of treatment options to assure environmental safety were created and every technology has its own set of benefits and drawbacks.

The conventional techniques used for wastewater treatment are precipitation, filtration, electrodialysis [30], ion exchange, supercritical fluid extraction, adsorption [31], the microbial system [32], electrochemical process, bioreactors and an advanced oxidation process [29]. These methods are robust and exciting techniques existing to remove the heavy metals. Physical, chemical and biological approaches are the three major categories that can be used to classify the methods discussed so far; each technique has a set of advantages and disadvantages, which are detailed in Table 3. A combination of procedures can be used to efficiently remove heavy metals.

Table 3. Merits and demerits of different metal ion removal techniques.

S. No	Techniques	Merits	Demerits	Reference
1.	Coagulation	cheap, dewatering mechanism	Production of sludge, Chemicals are utilized extensively.	[32]
2.	Filtration through membrane	Heavy metals exclusion at a rapid rate demands less room.	Extremely costly, membrane fouling, and complicated procedure.	[32]
3.	Adsorption	Simple operation, minimal sludge formation, and the utilization of low-cost adsorbents	Desorption cost for regenerable adsorbent is high.	[33]
4.	Electrochemical treatment	Effective in eliminating metal ions with slight chemical use	The initial expenditure is significant, and a large quantity of electrical power is essential	[32]
5.	Electrodialysis	Metals are separated to a higher degree.	Clogging and loss of energy	[34]
6.	Ion exchange	High transformation of components	removes a little amount of metal ions, and the operational cost is significant.	[35]
7.	Oxidation	No requirement for electricity	oxidation process causes rusting in the system.	[36]

2.1. Coagulation/Flocculation

Precipitation of heavy metals into insoluble compounds such as sulphides, hydroxides and carbonates can now be treated with coagulation [37]. Coagulation is the destabilsation of a suspension, resulting in the formation of aggregates. On the other hand, flocculation refers to the process of causing destabilized particles to come together in order to create larger aggregates [38]. To eliminate these colloidal particles, coagulation treatment procedures are utilized to enhance the density. The efficacy of coagulation is dependent on the coagulant used, pH, dosage of the coagulant, mixing, temperature and alkalinity. Flocculants, which agglomerate the destabilized particles into larger particles, are added with the help of the agitation mechanism.

Unit operations like filtration, straining and flotation are used to separate the larger particles. By combining chitosan and mercaptoacetic acid, Chang et al. produced a novel type of macromolecule flocculant, termed mercaptoacetyl [39], that was demonstrated to eliminate turbidity and heavy metals with 98% efficiency. In a study by Sakhi et al. [40] heavy metals with their removal rates like Cd^{2+} (40%), Pb^{2+} (78%), Ni^{2+} (62%), Cr^{2+} (22%), As^{2+} (81%) and Se^{2+} (44%) are removed using ferric chloride as a coagulant and anionic polymer as flocculant and their respective dosage quantities and pH influenced the rate of removal. Removal percentage was found to vary with the initial concentration and dosage in the case of Sb^{5+} (96%) and Sb^{3+} (98%) [41] in the presence of polymeric ferric sulphate and this might be attributed to the presence of phosphate and humic acid. Colloidal particles are neutralized by coagulants, which destabilize them and allow the sludge to settle down. When colloidal particles become entrapped on a metal surface, precipitation occurs. The generation of huge amount of sludge as a result of usage of chemicals in the separation process is one of the key drawbacks of this method [42].

The sludge generated contains heavy metal elements such as nickel, cadmium, lead, chromium and zinc [43]. Recovery, recycling and reuse are all the possible options for the management of sludge [44]. Though coagulation/flocculation are robust methods in eliminating heavy metals from wastewater, they also generate by-products such as flocs, categorized as secondary pollutant, along with reusable solvents that are harmful to humans and ecosystems.

2.2. Ion Exchange

Ion exchange is a separation technique that effectively removes heavy metals from wastewater by substituting one type of ion for another. The ion exchange technique produces substantially less sludge compared to coagulation [45]. Ion exchange resin is used to recover or eliminate metal ions. According to Hubicki et al. [46], the chemical features of resins cause the isolation of a certain set of metal ions. There are two kinds of resins, namely synthetic and natural resins. Metal ions are substituted for the cations using both types of resins. Synthetic ion exchange resins are commonly employed in water treatment to remove a variety of unwanted dissolved particles/solids, most commonly concerning the hardness from water [45]. The resins are built on a cross-linked polymer skeleton called a matrix. Arsenic metal ion was eliminated from drinking water by means of synthetic resins [47]. The main disadvantages of synthetic resins is fouling, which happens when a metal solution with high concentration is passed through the matrix [48].

The most common ion exchanger is the cationic exchange resin, which is made up of extremely acidic and weak basic resin. Natural zeolites have been found to have the best cation exchange capability for eliminating heavy metal ions from wastewater in several investigations [49]. In the indirect elimination of chromium (Cr) metal ion, zeolites are noteworthy because they are unable to perform direct ion exchange of Cr(VI) compounds, as charge repulsions from the negatively charged framework, which limits its permeability to anion [50]. Jamil et al. [51] used two zeolites manufactured from Egyptian Kaolin to remove nickel (Ni) metal ions from industrial effluent, as well as heavy metals like Cu, Cd, Pb and Zn. They demonstrated that zeolite can eliminate metal ions up to 98%.

The anion exchange resins are best suited for treating wastewater with minimal level of pollution because of the type of functional group, composition and matrix structure. For the removal of hazardous metals like chromium (VI) and manganese, Kononova et al. [52] employed cation and anion exchangers. Ion exchange resin has the disadvantage of requiring chemical reagents for regeneration, which further leads to secondary pollution [45]. Furthermore, it adds to the operational costs and cannot be used for wastewater treatment on a large scale.

2.3. Flotation

Flotation is a liquid–solid separation technique in which small gas bubbles are introduced into the sample of wastewater and the heavy metals attach themselves to the bubbles, allowing them to leave the water. This is achieved by adding surfactants or collectors to aqueous solutions to remove surface-inactive ions, usually with an ion with the opposite charge to the metal ion to be removed. Once the bubbles rise to the surface, the hydrophobic particles that are concentrated are collected. Flotation contributes significantly to wastewater treatment due to its low quantity of sludge generation and high efficiency of separation. This process is most appropriate for the metals with different chemical and physical properties [53]. A few parameters, like the bubble velocity, size of the bubble and frequency of the formation of bubble, are the most vital aspects for managing the flotation method. Due to the continuous operation of flotation equipment, its drawback is that it is costly to maintain and operate [54]. Ion flotation, dissolved air flotation (DAF) and precipitate flotation are the other forms of flotation processes.

Ion flotation looks inefficient when the metal ion concentration in wastewater is low [55]. Low energy consumption, restricted volume demands, reduced sludge quantities and selective treatment were demonstrated by the ion flotation process. Microbubbles are used in the precipitation flotation process, which is essentially a chemical procedure and its precipitation takes only a few minutes [56]. The flotation methods provide a number of advantages, including quick operation, a compact process and cost effectiveness.

Synthetic chemical surfactants have been developed to have a higher capacity, to have superior selectivity and to be easy of manufacture. They are, however, constrained by cost and toxicity concerns. Biosurfactants, on the other hand, appear to be more environmentally friendly, but they have low removal rates and huge dosage amounts and are a time-consuming process. Nanoparticles have been proposed as new collectors in this area, demonstrating both synthetic and biosurfactant benefits [57].

2.4. Membrane Filtration

Membrane filtration is a pressure-driven technique for separating heavy metal ions [58]. Membrane filtration separates metal ions according to the concentration of solution, size, pH and pressure applied over the membrane. The filtration process can be accelerated by treating the membrane with chemical agents [50]. The membrane is made up of a porous material that has been developed to help in removing metals ions from contaminated wastewater [54]. Polymer and ceramic types are two kinds of membrane materials used for wastewater treatment. Ceramic membranes are often favored over polymer membranes for use in industrial wastewater treatment due to their chemical resilience and water-repellent nature. Despite these advantages they are faced with a major significant drawback—being fragile and expensive to manufacture [59]. Inorganic salts and organics may be extracted up to 95–99% using the RO technique [60]. The reverse osmosis process has a higher rejection rate but is faced with issues like membrane fouling and degradation.

Despite its advantages it is faced with some challenges, like membrane fouling and the fact that there is a need for membrane replacement on a frequent basis [61]. Membrane fouling is caused by dissolved organic debris (DOM) and organic matter (OM). Pretreatment is essential to lessen the impact of DOM and OM on membrane filtration, which in turn boosts the separation process' efficiency [62]. However, depending on the size of the metal ion the conventional pressure driven processes like nanofiltration, ultrafiltration,

reverse osmosis and microfiltration are employed to isolate heavy metal from wastewater. Because of its low removal capabilities, the use of micro filtration in heavy metal removal has received little consideration. It has, however, been employed by changing the feed solution's membrane or chemical pre-treatment. These techniques can handle and treat enormous volumes of wastewater but, faced with the limitations of huge amounts of sludge generation, they exhibit disposal issues and post-treatment requirements. Fouling and scaling inhibition could increase membrane separation even more. Pretreatment and periodic cleaning of membranes, on the other hand, require additional costs.

2.5. Chemical Precipitation

Chemical precipitation is a low-cost, high-efficiency method for removing heavy metals that is used in a variety of industrial sectors. Chemicals that affect the pH of a solution cause a metal precipitate to form, in which the precipitate is prevented from dissolving in the solution [63]. Separation of phases by sedimentation results in precipitates [61]. Chemical precipitation is the most effective way to remove hazardous metals including Cu (II), Zn (II), Mn (II) and Cd (II) [45]. Tanong et al. [64] discovered that the addition of sodium carbonate (Na_2CO_3) aids in the exclusion of Mn and Ni metal ions by totally precipitating and raising the pH to 9.

This approach is rarely relevant for treating wastewater with less metal ion concentration, but it is relevant for large metal ion concentrations. As the insoluble metals precipitate, it results in huge amounts of sludge generation with higher content of water; this is difficult to treat and discard of, and hence is regarded as harmful waste [65]. After precipitation, the purified water could be reused or disposed of into reservoirs. To precipitate the metal ions, however, a large number of chemicals are necessary. This removal process is widely employed in various industrial applications due to its simplicity and low cost.

The sulphide precipitation and hydroxide precipitations are other methods of chemical precipitation. Hydroxide precipitation is often used because of its low cost, simplicity and changeable pH [66]. It is carried out by adding hydroxide to the agitated wastewater, resulting in the formation of insoluble metal hydroxide precipitates. However, as this approach necessitates a substantial dosage of precipitates, a high pH value is considered as a drawback. The majority of metal ions eliminated by this approach are Zn^{2+}, Cu^{2+}, Ni^{2+}, Pb^{2+} and Cr^{3+}. Ain et al. could remove Ni^{2+} and Cu^{2+} from industrial effluent with removal efficiency of 76.66% and 100% using NaOH as precipitant [67]. In another research study by Vu et al., the authors found that the carbonation method increased Pb^{2+} removal and decreased pH with a removal efficiency of 49.3% and sulphate removal of 97% [68]. There are certain downsides, such as relatively huge sludge generation, leading to dewatering, disposal difficulties and the formation of precipitation of metal hydroxide in the presence of complex agents, in addition to the need for a high dosage to achieve appropriate pH.

The sulphide participation approach outperforms the hydroxide method in terms of higher removal efficiency and low dissolved solids. This approach was found to be effective in the treatment of hazardous heavy metal ions [69]. A Cu^{2+} removal of 96% was achieved in treating arsenic wastewater [70]. Lower sulphide means more concentration of zinc in the effluent, while higher sulphide means a bad odor resulting from residual sulphide. It may also produce hydrogen sulphide gas, which is noxious and odorous.

2.6. Electrochemical Treatment

Electrochemical (EC) treatment is a different approach that involves applying an electric current to the aqueous medium to destabilize the dissolved contaminants. These contaminants are maintained in the solution by electrical charge. These ions and other charged particles become destabilized and precipitate in a stable form when they are neutralized with ions of opposite electrical charges provided by the electrocoagulation system. Electrochemical methods are simple, quick, cheap, easy to use and environmentally friendly. By charge neutralization, these coagulants can remove contaminants or heavy metal ions from solution [71]. Electrochemical treatment is a good alternative for wastewater treatment

because of its flexibility. The efficiency of electrochemical reactors is determined by the electrode materials used and the operating parameters, like mass transfer rate, current density and effluent water content [72].

Liu et al. [73] reported a removal efficiency for the metal ions Cu^{2+} (97.7%), Cd^{2+} (97.3%) and Pb^{2+} (98.5%) using graphene oxide and carbon as an electrode. Yang et al. [74] figured that Cr^{6+} reduction was faster with the existence of K_2SO_4 with a removal percentage of 93.7%. The usage of electrochemical treatment becomes increasingly more difficult as a result of more stringent environmental restrictions or regulations. This method works effectively for a variety of contaminants, including those that cannot be separated from their by-products. It requires a large facility as well as a steady supply of power to function. Additionally, as electrodes only last for a short period, there is an inadequate rate of mass transfer along with an increasing temperature limit with the application of this approach [75]. Electrocoagulation, electrolytic flotation, electrodeposition, electro deionization and electrodialysis are some of the electrochemical methods. The critical difficulties of using this technology are large-volume sludge production and post-treatment requirements, which are not cost effective.

2.7. Adsorption

Sorption is the transfer of ions from solution-to-solid phase transition. Adsorption and precipitation reactions are both included in the term "sorption" process. Adsorption has recently emerged as another treatment method for wastewater containing heavy metals. Adsorption comprises transfer of mass from liquid to solid surface, resulting in the chemical or physical process mechanism [76]. New biodegradable adsorbents [77] reliant on variety of low-cost resources, such as by products from industries, agricultural waste, natural materials or modified biopolymers have recently been produced and used to remove heavy metals from polluted wastewater. In general, sorption on solid sorbents includes three main phases: (i) Transport of the impurity from the bulk to the sorbent surface; (ii) adsorption on to the surface of a particle; and (iii) passage inside the particle sorbent [78]. As both the adsorption and desorption processes are reversible, whenever an adsorbent has been desorbed, it can be renewed and utilized for a variety of purposes. Though there are a few factors that can affect the adsorbent selection, cost effectiveness and suitability are two of the most important primary requirements [79]. The effectiveness of the adsorption process is controlled by the polarity of the adsorbent, as well as its large surface area and pore size distribution [80]. The primary limitations of this technology are the adsorbent regeneration medium and regulating the pH. Some of the key challenges of the adsorption mechanism are its capacity to remove multiple ions at once, a long retention time and adsorbent cycling stability. The heavy metal removal by conventional methods are shown in Table 4.

Table 4. Heavy metal ion removal from different conventional technique.

Technique	Material Used	Metals	Removal %	Remarks	Reference
Adsorption	Modified graphene (GN) with cetyltrimethylammonium bromide	Cr	98.2	Low selectivity, production of waste. It is difficult to synthesize. The cost of adsorbent is too high.	[81]
	Activated Carbon from Prawn shell and green alga Ulva lactuca	Cr, Cd	98, 95	Higher quantities on larger scales are difficult to manage	[82,83]
Membrane Filtration	RO	Cr, Cu, Cd	98, 99, 90	High operational cost due to membrane fouling	[84]
	Ultrafiltration	Cu	90		
Electrodialysis principles	perfluorosulfonic Nafion 117	Co, Ni	90, 69	Clogging and energy loss	[85]
	HNO_3	Cd	70		[86]

Table 4. *Cont.*

Technique	Material Used	Metals	Removal %	Remarks	Reference
Chemical Precipitation	Magnesia and lime-water	Fe(III), Cr(III), Cu(II), Pb(II), Ni(II) & Cd(II)	97	The cost of producing high-water-content sludge and disposing of it has increased. Precipitation with lime and bisulphide, lacks specificity. When it comes to removing metal ions of low concentration, this method can be useless.	[87]
Ion Exchange	Magnetic ion exchange	Cr, Cu, Cd, Hg	99.9	Not effective when employing concentrated metal solutions since the exchange matrix is easily fouled by organic/other wastes and is the major limitation.	[88]
Floatation	potassium ethyl xanthate (KEtX)	Ni, Cd, Co	98.3, 97.5 and 94.7	High concentration of floatation agents are employed which affects the economy of the process.	[53]

2.8. Gas Hydrate-Based Mechanism in Eliminating Heavy Metal Ions

The above-mentioned conventional technologies are robust methods in treating wastewater but are faced with limitations like fouling, poor selectivity, less efficiency in metal removal, high processing costs and generation of huge amounts of sludge. New concepts have lately been examined for producing less expensive and more efficient solutions to reduce wastewater production while also enhancing the quality of treated effluent. As a result, scientists are interested in gas hydrate-based removal since it is less dangerous, easier to operate, has higher selectivity and may be used for multiple purposes other than heavy metal removal methods. This not only cleans the water by generating gas hydrate, but it also makes it easier to remove harmful metals from industrial wastes.

This technology produces hydrates by using two basic requirements, namely water and gas, where the gas molecules are enclosed inside the water cage formed by the hydrogen bond. To better understand the mechanism of the formation of hydrate in the existence of salts, it is essential to consider the hydrogen bonding of water in the bulk phase as well as at the gas–liquid interface. The gas molecules do not bind chemically to the hydrate cages, but instead interact with water cages weakly via van der Waals interactions. When 1 m^3 of hydrate is dissociated, it can produce up to 164 m^3 of gas and 0.8 m^3 of pure water at standard temperature and pressure. Moreover, the hydrate constitutes about 85% water and 15 mole % gas, which signifies a huge potential to produce treated water which can further be utilized for industrial or domestic usage.

Unlike ice crystals, hydrates form close to ambient conditions when a sufficient hydrate former (guest gas) and water are present. As the hydrogen-bonded water cages are so small, only small gaseous molecules and lower hydrocarbons can fit inside the cage, so it entirely depends on the type of guest component being utilized. Furthermore, the guest molecule does not interact chemically with the hydrate cages; instead, it interacts through Van der Waals forces. Hydrate-based desalination is a technique in which pure water crystallizes as a solid hydrate phase from brine solution with the help of a gaseous molecule. The ions or salt dissolved in water are surrounded by water molecules. The water molecules surround the cations and stabilize. As a result, ions in aqueous solutions are constantly hydrated, which means that they are strongly attached to water molecules via ion–dipole interactions. The amount of water molecules in the main hydration shell, which completely surrounds the ion, varies depending on the ion's radius and charge. During the formation of hydrate, all the metal ions are rejected into the effluent. Only water and gas are left in the solid hydrate, leaving significant metal ions in the effluent. This mechanism allows

the elimination of salts from the wastewater, thereby producing no sludge. The freshwater produced from the hydrate provides us an opportunity to effectively eliminate metal ions from the effluent. When the solid hydrate is depressurized, it dissociates easily into liquid water and gas. Several unit operations, such as centrifugation and extrusion, can be used to separate the hydrated crystals from the brine or as a post-treatment technique [89]. Thermal stimulation or depressurization can easily disintegrate the crystals, releasing salt-free water and allowing the gas to be recovered and reused. The advantages of using the gas hydrate method over conventional technologies is high water recovery, less energy consumption, no pretreatment required, less maintenance and above all the formation of hydrate excludes all metal ions A gas hydrate-based desalination method has been suggested as being simple to install, cost effective and environmentally beneficial [90]. The formed hydrate when dissociated results in freshwater.

3. 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 [91]. 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 [4,92,93].

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 study 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 [94]. 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 [95]. 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 [96–98]. Hydrates can be employed as a secondary refrigerant in refrigeration systems [99].

3.1. Gas Hydrate-Based Desalination

Desalination is the process of desalinating salty water to produce drinkable water or water beneficial for agricultural purposes [100]. Many conventional desalination processes are energy intensive, together with multi-stage flash distillation (MSF), reverse osmosis (RO) and multi-effect desalination (MED) [101]. The recovery of pure water from a saline water stream is an important factor in making any desalination process profitable or marketable. As shown in Table 5, hydrate-based desalination is a promising technology (HBD) based on water recovery and energy consumption when compared with the traditional technologies. It would be useful to practice utilizing the HBD method because it runs at a temperature greater than the freezing point of water, as shown in the comparison Table 5. Desalination systems based on indirect and direct freezing have also been developed, although they are not widely used commercially due to their high costs, though ice crystals are constituted of nearly pure water [102]. Only by developing cutting-edge desalination technologies

that can deliver safe and appropriate adequate quantities of clean water while minimizing the consumption and the associated costs, as well as being environmentally benign, can this have a meaningful impact both on the environment and society [103]. The freezing or crystallization process, called hydrate-based desalination, was developed as a technique for desalinating saline water more than seven decades ago [89,90].

Table 5. Comparison of conventional technologies with hydrate-based technology.

Method	Principle	T (°C)	P (MPa)	Water Recovery	Total Average Specific Energy Consumption (kWh/m^3 of Water)	Maintainance	Advanatge/Constraints
Distillation	Flash process	90–120	Less than 0.1	20% [3]	23.4 [104]	Corrosion/ scaling	Used for high TDS (total dissolved solid) concentration/High energy, less water recovery
Reverse Osmosis	Solute diffusion	20–35	5.5–7.0	55%	5 [104]	Sludge generation/membrane replacement	Requires pretreatment, less water recovery, resistant to impurities
Hydrate desalination	Phase change	Near to 0	0.45–0.65	58.6% [105]	0.6 [106]	No maintainance	suitable for greater TDS concentrations/higher water recovery

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 [89,90,107,108]. A detailed process of hydrate formation, dissociation and separation of pure water and residual water is shown in Figure 2. 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 [89,90].
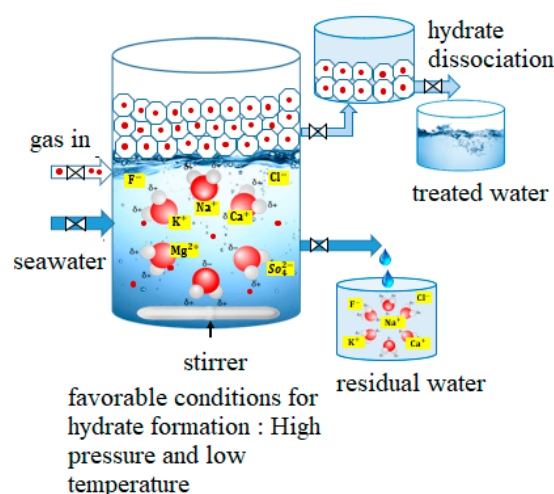

Figure 2. Hydrate formation, dissociation and water recovery process in hydrate-based desalination process.

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 [108]. 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 [89]. 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 [109]. Some of the hydrate former studies available in the literature up to today are based on propane (C_3H_8) [110,111], cyclopentane (C_5H_{10}), [89,90,112–116], carbon dioxide (CO_2), [117,118], refrigerants (HFC, HCFC, and CFC) [119–122] and sulphur hexafluoride (SF_6) [123]. Several studies have been performed in determining the phase equilibrium through a pilot scale set up [124–129] and the kinetics of hydrate formation have been boosted (by using secondary hydrate forming gases) [130–133]. 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 [133–136].

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, SF_6, 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 [109]. Several hydrate formers, namely liquid, gaseous and other additives, have been analyzed to check the feasibility of the hydrate-based desalination process [122]. 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 [128]. 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 [136–138]. 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 [139–141]. 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 [142]. The desalination efficiency was determined to be greater than 80%, with a water recovery rate greater than 30%.

Utilizing CO_2 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 CO_2 storage and desalination purposes [140–143]. Despite the fact that only limited studies have been carried out so far [144,145], 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.

3.2. 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 [146]. 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 [147].

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 [148]. 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 [149]. 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 [150].

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 [151]. 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 [152]. 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 [153]. 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 [154]. 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 [155]. 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 [156,157]. 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 [158]. 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 [159]. It has been suggested that CO_2 could be sequestered by dissolving in seawater. Desalination using hydrates has been proposed as a method of concentrating brine solutions with dissolved CO_2 [160]. Desalination, thermal energy storage and natural gas storage have all been produced using gas hydrate modular systems [161]. 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 [162]. In another invention a hydrate-forming gas was pumped into a saline-water reactor utilizing a microbubble generating device for hydrate formation [163]. 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 [164]. In a recent reactor invention [165] where hydrate formation, separation, washing and dissociation took place in a single reactor, the formation of CO_2 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.

3.3. 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 study 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 [166]. 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 [167]. 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 [110]. Furthermore, Bulot et al. devised a method for purifying a solute from an aqueous solution of water and solute [168]. An overview of the metal ions removed along with their removal efficiency using gas hydrate method is listed in Table 6.

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 $MgCl_2$, NaCl and $CaCl_2$ 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 [121]. 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 [169]. When comparing hydrate desalination to reverse osmosis, Bradshaw et al. discovered that the water throughput rate and recovery are faster with hydrate-based desalination [119]. All this study 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 [89,90]. The following steps are followed in the hydrate-based water treatment process, as indicated in Figure 3: (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 [170].

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 study [171].
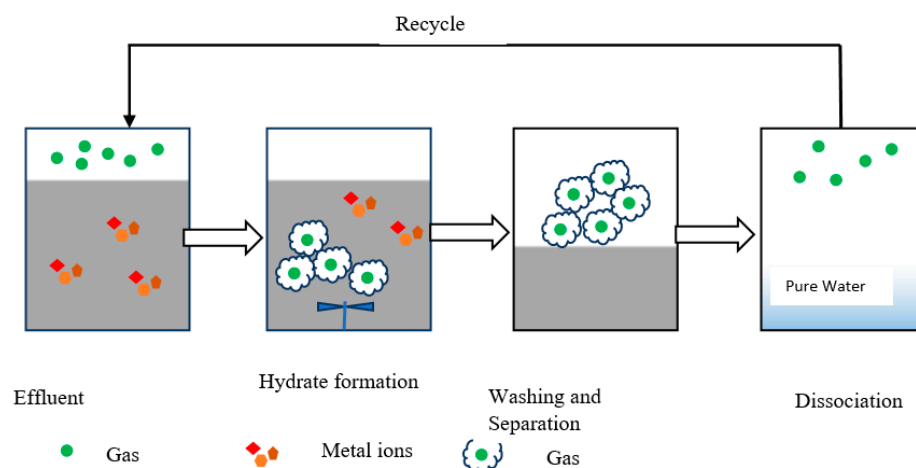

Figure 3. Heavy metal ion removal by gas hydrate technique.

Yang et al. investigated hydrate-based treatment looked at using hydrates to treat Ni^{2+}-contaminated wastewater. At a volume ratio of 3:1, cyclopentane (CP) was added to a $NiCl_2$ 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% [172–175]. This study 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% [134,176]. It is worth noting that, when the Ni^{2+} 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 post-treatment 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 [177]. R141b reacts with water at temperatures less than 8.4 °C and pressures greater than 42 kPa to form sII hydrate [177,178]. 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. Cu^{2+} concentrations were measured using an inductively coupled plasma optical spectrometer (ICP), and electrical conductivity variations were recorded using an electrical conductivity meter (ECM). Figure 4 shows a conceptual picture of the hydrate process for removing heavy metals from aqueous solution.
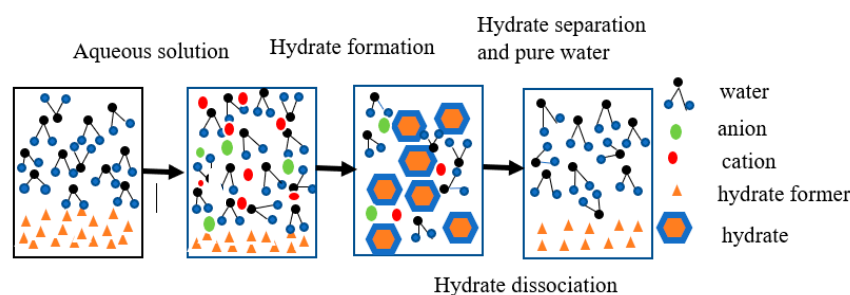

Figure 4. Schematic diagram for hydrate-based desalination process.

Table 6. Removal of heavy metals using different hydrate formers by hydrate-based desalination.

System and Concentration	Hydrate Former	Metals Removed	Removal Efficiency	Remarks	Reference
NaCl 3.2 wt%	CO_2	K^+, Na^+, Mg^{2+}, B^{3+}, Ca^{2+}	K^+ (80.4%), Na^+ (78.7%), Mg^{2+} (76.6%), B^{3+} (73.3%), Ca^{2+} (72%)	Hydraulic pressure is applied to make the hydrate into the form of pellets uisng piston which is energy intensive. 1 stage operation	[162]
Saline solution of 3.0 wt%	CO_2	-	20.26%	Semi batch reactor system carried out at 3.0–3.5 MPa and 6 °C. The efficiency based on individual metal ion is not discussed	[142]
Nacl 3.5 wt%	CP	-	(49–72%).	Post hydrate formation series of unit operations were carried to enhance efficiency. Centrifuging provided a high removal efficiency of 96%. Post-treatment is expensive as CP leaves a suspension and is also not environemnt friendly.	[178]
Synthetic produced water 8.9 wt%	CO_2 CO_2+CP CO_2+CH	Na^+, Mg^{2+}, K^+, Ca^{2+}	74 91 95	Addition of CP and CH to CO_2 enhance the hydrate formation temperature. Post-treatment is required as they form a suspension at interface	[179]
Synthetic seawater 3.5 wt%	CO_2 CH_4	Na^+, K^+, Mg^{2+}, Ca^{2+}, B^{3+}, Cl^-, SO_4^{2-}	Cations 71–94% Anions 73–83% 68.86%	CO_2 based hydrate based desalaintion is better compared to CH_4 and might be as CO_2 is more soluble in water comapred to CH_4	[118]

Table 6. *Cont.*

System and Concentration	Hydrate Former	Metals Removed	Removal Efficiency	Remarks	Reference
NaCl 4 wt% at 4 °C	R 141 b	NaCl	61.46%	Better at removing alkaline metals than it is at removing alkaline earth metals. Not environment friendly have higher global warming potential.	[121]
Seawater 3.5 wt%	Not available	K^+ $Na^+, Mg^{2+}, B^{3+},$ Ca^{2+}	80.4% 78.7% 76.6% 73.3% 72%	The reverese osmosis recovery is inversely related to the gas hydrate energy consumption. With the increase in energy consumption it was founf that the efficienccy of metal ion removal increased. Optimumratio of waterto R141b is found to be 1:5	[180]
$CuSO_4·5H_2O$ Coppersulphate pentahydrate	R141b	Cu^{2+}	90.82%	Involves post-treatment techniques due to usgae of R141b and is not environment friendly	[181]
NaCl	R141 b	$Cr^{3+}, Cu^{2+},$ Ni^{2+}, Zn^{2+}	70.02%, 71.87%, 71.79%, 67.82%	Lower effluent volume ratio yielded higher removal efficiency. R141B is likewise extremely flammable and when discharged into the atmosphere, this causes ozone depletion.	[170]
NaCl 3–5 wt%	CP	-	Removal efficiency increased from 50 to 79% by washing the hydrate.	Higher frequency, lower temperature (274.1 K), lower salinity could all help to form more hydrates, albeit at the expense of removal efficiency. Post-treatment of seperating the suspension is expensive	[107]
Produced Water 8.6 wt%	Compressed natural gas	$Mg^{2+}, Na^+.$ $Ca^{2+}. K^+,$ $HCO_3^-, Cl^-,$ SO_4^{2-}	79.5–84.3% 3 stage process	The number of water molecules in the hydrate structure decreased, resulting in powerful electrostatic interactions that cause the hydration of salt ions and ion clustering also decreased the solubility of gas	[182]
Brine 3.5 wt%	CP	-	81% 3 step process, gravity seperation, flitration and washing	Because of the fine cyclopentane droplet sizes formed by the spray injection approach, more water can be turned into hydrates.	[183]
Seawater 3.4 wt%	CP	-	63%	Washing the hydrate enhanced removal efficiency by 42%. Emulsion formed could be difficult to separate from treated water.	[184]
PW 8.6 wt%	CO_2	-	82–89.2% In 3 stage process	Application of hydrate-based desalination of produced water. Removal efficiency of each metal ion is not listed.	[185]
Seawater 3.42 wt%	CO_2+CP	$Na+, K^+,$ $Mg^{2+}, Ca^{2+},$ Cl^-, SO_4^{2-}	85.52%, 83.93%, 80.73%, 78.21%, 55.72%, 62.09%	A piston is used to separate the solid from liquid stream hence higher energy requirement.	[130]
Aqueous $NiCl_2$ solution 200–10,000 ppm	CP	Ni^{2+}	62–88%	Water recovery of 43% is attained. The water recovery and enrichment factory decreases with increase in concentration whereas removal efficiency increased with increased in aqueous concentration.	[171]
Saline solution 3.3 wt% + dodecane	CH_4+C_2H_6	-	80%	The decreased viscosity of the dodecane system allows the hydrate crystals to move through the oil layer quicker, resulting in better desalination efficiencies.	[186]
$CuSO_4$ aqueous solution	R141b	Cu^{2+}	44.79–90.82%	efficient approach was discovered to be vacuum filtration and centrifugation	[176]

Table 6. *Cont.*

System and Concentration	Hydrate Former	Metals Removed	Removal Efficiency	Remarks	Reference
PW 8.6 wt%	CO_2/ Natural gas	-	73% 74%	CO_2/NG hydrate formers can be utilized to desalinate produced waters. Post-treatment/separation is not listed	[135]
NaCl 3.5 wt%	Graphite +CP		99.76% in 4th stage	The hydrate process with graphite particles is a viable desalination technology, according to the research, with advantages such as quick nucleation, a high conversion ratio, and a fair desalting efficiency.	[187]
$CuSO_4$ 3 wt%	R141b	Cu^{2+}	84%	Post-treatment by vacuum filtration combined with washing produced maximum removal efficiency Water yield and enrichment factor decreased with increase in concertation	[188]
NaCl 3 wt%	$CO_2+C_3H_8$ (90:10)	Na^+ Cl^-	87.5% 84%	Novel reactor design of flat bed reactor was used for hydrate-based desalination. The influence of salts on water recovery and salt rejection rate was not discussed	[177]
Coca cola NaCl 15 wt%	HFC134a	Na^+, Mg^{2+}, Ca^{2+}, K^+, B^{3+}, Cl^-, SO_4^{2-}	75.72% 80%	With HFC134a in coca cola formed sII hydrate and ions did not effect the structure of hydrate	[189]
LiCl, LiBr, LiI	CP+graphite	$I^- > Br^- > Cl^-$	70%	The efficiency of desalination was enhanced by increasing lithium halides, but salts restrict induction time and water recovery.	[190]

3.4. 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:

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

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. [191]. 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 [89]. Babu et al. [192] 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. [181], 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 Ni^{2+} 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 study, 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 [171].

An experimental study by Gaikwad et al. identified As^{5+}, Pb^{2+}, Cd^{2+} and Cr^{3+} 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 [177]. Another study, by Nallakukkala et al. [105], found a water recovery of 66% when operating at 2.5 MPa using CO_2 as hydrate former by treating 2 wt% brine solution. This recovery is higher than that obtained by [191], in which the recovery was 41.38% using 10% propane and 90% CO_2. Ling et al. [190] evaluated the induction time, water recovery and desalination effectiveness of the LiCl, LiBr and LiI 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 $I^- > Br^- > Cl^-$. Water recovery by using various hydrate formers is shown in Table 7.

Table 7. Water recovery with removal of metal ion via gas hydrate technique.

Metal Ion	Hydrate Former	Conc. of Former	Water Recovery		Reference
			With Additive	Without Additive	
As			28.75	25.72	
Cd	CP	1:6	24.51	19.76	[177]
Cr			23.33	14.97	
Pb			27.92	15.51	
Cr				80	
Cu	R141b	1:4		80	[170]
Ni				80	
Zn				80	
Ni	CP	1:3		43	[176]
Cu	R141b	1:5		80.83	
Cu				76	[170]
Ni		1:6		75	
Zn	CP	1:2		70	[171]
Cr				74	

3.5. Removal Efficiency

The removal efficiency of the hydrate-based separation process is used to assess its effectiveness. A brief overview of the removal efficiencies of metal ions with washing and without washing is represented in Table 8.

$$\text{Removal Efficiency}\% = \frac{\text{Initial conc. in feed} - \text{Conc. in dissociated water}}{\text{initial conc. in feed}} \times 100$$

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% [170].

To perform multi-stage desalination, Yang et al. utilized an aqueous solution with a Ni^{2+} 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 [171]. 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 [192]. 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 [176].

Heavy metals with concentrations of 500 ppm, containing Zn, Cu, Ni and Cr, were utilized in a system created by Al-Hemeri et al. [193], 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% [105] when operated at 3.5 MPa. Effective desalination and kinetics of hydrate growth were observed by [176] using 6 mole % CP and there was a water recovery of 25.72% As^{5+} 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.

Table 8. Heavy metal ion removal efficiencies reported.

| Metal Ion | Hydrate Former | Effluent to Former Ratio | Removal Efficiency (%) | | Reference |
			With Washing	Without Washing	
Zn	CP	1:6		85	[193]
Cu				92	
Cr				50	
Ni				80	
Cr	R141b	1:6	89.72	70.02	[170]
Cu			90.82	71.87	
Ni			89.93	71.79	
Zn			88.01	67.82	
Cu	R141b			44.7	[176]

Table 8. *Cont.*

			Removal Efficiency (%)		
Metal Ion	**Hydrate Former**	**Effluent to Former Ratio**	**With Washing**	**Without Washing**	**Reference**
			90.82 VF	71.87	
			87.69 WHVF		
			90.82 WFVF		
			90.46 VCF		
Cu	R141b	1:5			[192]
			51.8 VF		
Cu	R141b	1:4	83.80 VFC		[192]
			87.42 VFWW		
			84 (1-stage)		
Ni	Cyclopentane	1:3	96 (2-stage)		[171]
			99.2 (3-stage)		

3.6. 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 [194]. 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 aqueous solution. An overview of the enrichment factor obtained in removing the metal ions is shown in Table 9.

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

The influence of volume ratios on the enrichment factor was investigated by Al-Hameri et al. [195]. 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 Ni^{2+}-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 Ni^{2+} falls as the concentration of feeding solution increases. Due to the fact that water activity decreases as Ni^{2+} concentration increases, it was difficult to remove water from concentrate and the feeding solution [171].

Dong et al. found that, when Cu^{2+} 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 [176]. 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) [170].

Table 9. Enrichment factors of metal ions.

Metal Ion	Hydrate Former	Initial Conc. (ppm)	Enrichment Factor	Reference
Cr	R141b	96.7	1.8501	
Cu		104.4	1.8247	
Ni		97.12	1.805	[170]
Zn		93.36	1.8691	
Ni	CP	20	1.6	[171]
Cu	R141b	16.75	2.8	[176]
Zn		10	1.4	
Ni	CP	10	1.32	
Zn		10	1.31	[178]
Cr		10	1.29	

3.7. 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 [188]. 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. [180] 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/m^3 (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/m^3 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 [196] 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^+, Ca^{2+} and Mg^{2+} ions. The researcher studied the effects of NaCl, KCl, $MgCl_2$ and $CaCl_2$ on CO_2 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 [194,197,198] 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.

3.8. Limitations in Adopting Gas Hydrate Technique

Maintaining low temperature and high-pressure conditions needs additional energy requirements and is the fundamental challenge in commercializing the gas hydrate-based desalination process. The kinetics of hydrate formation and dissociation is another important parameter for the commercialization potential of clathrate-based separation. Slow kinetics restrictions for hydrate-based desalination can be overcome with careful selection of a favorable guest gas/liquid and improved reactor architecture design. CO_2, methane,

propane, cyclopentane (CP) and refrigerants like CFC were mostly used in the literature. Faster kinetics with appropriate promoters could allow the hydrate-based desalination process to be combined with a gas separation process at an industrial scale, increasing its commercial feasibility and overall efficiency.

Since the mid-nineteenth century, researchers have been looking for ideal hydrate formers that meet the criteria of non-toxicity, eco-friendliness, stability, availability and that are economically feasible [109]. Furthermore, CP is an atmospheric hydrate-forming agent and has been demonstrated by a thorough and systematic investigation, although due to its suspension formation, it requires additional post-treatment technique in desalination. Despite the fact that the hydrate-based separation method has encountered a number of technological, energy-efficiency and environmental challenges, no commercially viable systems have emerged. Because the cost of the operation is based on various factors, including the temperature of the brine, appropriate thermodynamic conditions, mobility of salt, salt concentration and yield [137,138,196], financial viability must be considered. As a result, environmentally acceptable and energy-efficient hydrate-based heavy metal exclusion procedures are still required.

A recent study [139–141] was based on utilizing LNG cold energy as a heat sink that was modelled and simulated as an energy source for a gas hydrate plant, and its economic feasibility was assessed. The results were surprising, demonstrating that the LNG heat sink can effectively replace the need for an external refrigeration arrangement, allowing for the separation of high-strength ions with minimal energy consumption, demonstrating that this type of integration can lead to the commercialization of the hydrate process. The salt separation efficiency of the process, as well as the quantity of cooling energy required for freezing and subsequent crystal formation, are used to evaluate the process efficiency of freeze desalination. As a result, the hydrate-based desalination technique, which is part of freeze desalination, is of great interest since the crystallization process runs at a significantly higher temperature than the freeze desalination process (typically above the freezing point of water), resulting in a significant reduction in energy usage for crystallization [89,90,139,140]. A hydrate-based desalination continuous module was developed, with a series of operations and separation techniques, with numerous injections, separation and purging times tested [142] with a water recovery rate of more than 30%, and with an ultimate removal efficiency of greater than 80%. As a result, the best operating parameters for the HBD process should be calculated by taking into account the greatest water yield based on the goal of beginning salinity, as well as the trade-off between salt enrichment efficiency and solid–liquid separation efficiency.

Highly saline water or produced water, for example, can have a salinity of up to 35%. Under those circumstances, the traditional desalination technologies are inefficient in dealing with such high salinity. As a result, there is a lot of potential for using the HyDesal method to treat produced water. The development of commercially effective clathrate-hydrate-based separation has been expedited by recent technological and economic developments. More research is needed, however, to improve the separation efficiency by reducing the amount of salts trapped within hydrate crystals in each cycle and optimizing the key operating factors such as the suitable hydrate formers, the use of various additives or promoters and the best operating conditions of pressure and temperature [143]. In this case the water separation is simple but the cost of pressurization is high.

3.9. Opportunities

However, as listed above, the limitations of hydrate-based desalination, the technology difficulties of slow hydrate formation kinetics, the difficulty of crystal separation from brine and the recovery of hydrate former, making it a continuous system and high energy consumption [198], have yet to be fully handled. From an energistics standpoint, water treatment techniques using hydrate formers with lower equilibrium formation pressure are preferable. The use of appropriate hydrate formers to increase nucleation and growth is recommended to address slow kinetics. At the plant scale, improving the hydrate

formation kinetics will encourage a continuous mode of operation. Further research into benign promoters may be able to ameliorate various liquids' harmful impact on product water quality and also post-treatment.

The hydrate-based technology has proven to be competitive and cost-effective when compared to traditional methods. The years of process improvement provide a compelling rationale for promoting the use of hydrate technology in water treatment applications. However, more evaluations on the economic viability of the suggested reactor and post-treatment unit operational designs in the direction of commercialization are required. It would be interesting to investigate the appropriate integration possibilities for hydrate technology. For example, to lower the total energy consumption connected with clathrate hydrate technology, the potential refrigeration load available at LNG regasification facilities can be used for hydrate-based water reclamation. Hybrid procedures like hydrate process + RO may also be appealing for enhanced water quality and energy efficiency. As a result, future research should focus on developing sustainable solutions that combine the use of LNG cold energy, selecting appropriate gas/liquid as a guest and reforming reactor designs, as well as focusing on the combinations of various hydrate formers that are biodegradable. In addition, energy analysis and cost estimation are important variables in hydrate desalination's industrialization. It is critical to continue developing novel energy-saving technologies.

4. Conclusions

During the past two decades, environmental regulations have become more stringent, requiring to discharge a higher grade of treated effluent. A range of traditional technologies have been developed for the removal of heavy metals from polluted wastewater. This review summarized the numerous interactions of hydrate formers used in gas hydrate-based desalination and their natural occurrence, using gas hydrates in eliminating heavy metal ions The constant research into developing/designing new reactors, or the hydrate formers that can enhance the capability of forming more hydrates or numerous effective ways for using gas hydrates in sustainable development have been established by evaluating the feasibility of processes and enhancing their rates of formation and dissociation. In spite of the advantages of the hydrate-based mechanism for heavy metal separation methods, slow kinetics, suitable thermodynamics and separation of hydrates are still substantial barriers to overcome. More research is needed on the selection of a proper hydrate former/promoter, the cost efficient post-treatment separation techniques for higher water recovery and improvement of the efficiency of the process.

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