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Transforming Industrial Wastewater Treatment with CO_2 Gas Hydrates: The Impact of Machine Learning on Desalination: A Review

Akshat Sabnis[1], Tanvi Patil[2], Vishal Wakarekar[3]

[1,2,3]Tatyasaheb Kore Institute of Engineering and Technology (TKIET), Warananagar, Kolhapur - 416113, Maharashtra, India

Abstract:
Industrial wastewater treatment is a critical challenge due to increasing water scarcity and stringent environmental regulations. Conventional treatment methods, including membrane-based, thermal, biological, and advanced oxidation processes, have limitations such as high energy requirements, scalability issues, and inefficiency in handling non-biodegradable contaminants. To overcome these challenges, CO_2 gas hydrate-based treatment is a promising technique for desalination and pollutant removal. Gas hydrates, formed under specific thermodynamic conditions, enable the separation of pure water from saline and contaminated sources. This process offers energy-efficient and environmentally sustainable wastewater treatment. The integration of machine learning (ML) enhances the efficiency of CO_2 hydrate-based desalination by optimizing process parameters such as pressure, temperature, and hydrate formation kinetics. ML models, including Adaptive Neuro-Fuzzy Inference Systems (ANFIS) and Support Vector Machines (SVM), improve prediction accuracy and real-time monitoring, leading to cost reduction and operational efficiency. Despite its potential, challenges remain, including limited understanding of hydrate formation mechanisms, the need for suitable hydrate promoters, and the development of scalable reactor designs. This study explores the feasibility of CO_2 gas hydrate-based wastewater treatment, emphasizing its advantages over conventional techniques.

1. Introduction

The treatment of Industrial wastewater management is very crucial nowadays. Industrial wastewater treatment is a serious challenge in modern environmental management, which is driven by the twin pressures of increasing water demand and strict environmental regulations.

So many techniques are available for wastewater treatment. The conventional methods used for industrial wastewater treatment are Membrane based technology like Reverse osmosis, Nanofiltration, Electrodialysis, etc., Thermal treatments like Multi stage flash distillation, Multi effect distillation, etc., Advanced Oxidation processes (AOP's) like Ozone based, Fenton/Photo Fenton, UV/H_2O_2, Photocatalysis, Electrochemical oxidation, Ultrasound cavitation, etc., Biological treatments like Aerobic treatment, Anaerobic treatment, Microbial fuel cell, etc. these techniques have some limitations and challenges, like for biological treatment high salinity interrupts metabolic function of bacteria and some biological treatments may struggle with non-biodegradable contaminants, while chemical methods can leave harmful residues, Microbial fuel cell has less efficiency, Thermal treatment requires more energy, Membrane based technology requires high pressure and economically unfeasible for large-scale

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applications, Advanced oxidation processes have scalability and cost issues. Methods such as chemical coagulation produce sludge that requires further treatment or disposal, creating additional environmental challenges, and requiring efficient and inexpensive catalyst preparation for photocatalytic treatment. Innovative methods that are both effective and sustainable are needed to address these issues [1], [2], [3], [4].

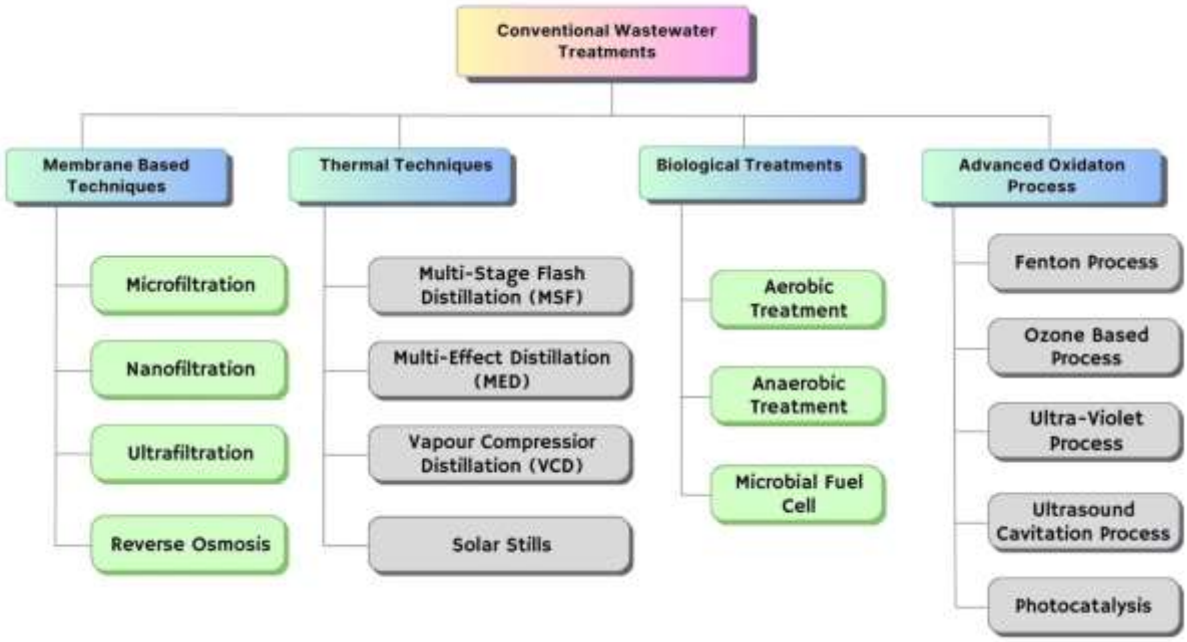

Fig.No.1 Comparison of CO_2 hydrate-based desalination with conventional methods.

The high population density, coupled with industrial and agricultural activities, presents significant challenges related to water scarcity, which is a matter of concern. Nearly 2.5 billion individuals suffer from various diseases stemming from the use of contaminated water [5]. Compounds formed by water molecules bonded via hydrogen bonds with low molecular weight gases, with a variable ratio, are classified as 'gas hydrates.' These compounds are also referred to as Clathrate hydrates and require specific thermodynamic conditions for formation [6], [7]. One example of free crystallization is hydrate-based water purification, wherein water and gas molecules crystallize at temperatures above the typical freezing point, allowing for the separation of crystals from brine solutions for purification purposes. This method is also considered energy-efficient [6], [7]. Gas hydrates form in three distinct structural types depending on the nature of the gas molecules involved: Structure I (comprising methane, ethane, carbon dioxide), Structure II (including propane, nitrogen, isobutane), and Structure H (sH), which contain 46, 136, and 34 water molecules, respectively [8]. [9].

In order to minimize environmental impact, one of the methods, known as the Gas hydrate-based method, can be used, which ensures that gaseous molecules do not introduce pollutants into the produced fresh water [10]. There are three steps in the desalination process with the help of gas hydrates: the first step is the formation of hydrate crystals in saltwater solution, the next step is the separation of crystals from the residual concentrated saline water, and the final step is the decomposition of hydrate crystals [8].

Sr. No.	Type of Industrial Wastewater	Composition	Percentage Produced	References
1	Textile Industry Wastewater	Dye conc.- 700 (mg/l) Chloride - 15867(mg/l) Sulfate -1400(mg/l) NH_4 1-7(mg/l) Na - 2900 (mg/l) COD -1781(mg/l)	More than 50%	[92]
2	Pulp and Paper Industry Wastewater	High organic content, which include lignin and cellulose. Chlorinated compounds and other organic pollutants.	10 % of total industrial wastewater.	[93]
3	Food Industry Wastewater	Consists of organic matter, fats, oils, and grease. High levels of BOD and COD	Less Toxic Wastewater.	[93]
4	Petrochemical And Refinery Wastewater	It contains mainly hydrocarbons, sulfides, phenols, and heavy metals. Levels of chlorides, sulfates, and nitrates are commonly high with concentration often exceeding environmental standards.	15% of total industrial waste water.	[94]
5	Chemical Industry Wastewater	Consist of organic and inorganic materials which includes toxic pollutants from pharmaceuticals and fertilizers.	5-10% of total industrial waste water.	[95]

6	Pharmaceutical Wastewater	High levels of suspended solids and dissolved salts. High chemical oxygen demand (COD).	Around 5% of total industrial wastewater	[96]

7	Mining Wastewater	High levels of heavy metals, acid mine drainage, and inorganic pollutants.	Around 5% of total industrial wastewater	[97]
8	Electroplating Wastewater	High heavy metal ions and organic matters.	Around 2% of total industrial wastewater	[98]
9	Dyes Industry Wastewater	Reactive dyes, unfixed dyes, carcinogenic and mutagenic compounds, oxidants and catalysts.	1-20 % of total dye production	[99]
10	Paints Industry Wastewater	High concentration of ions, organic debris and heavy metals. Pigments, binders, solvents and additives.	70 % of wastewater from paint production is discharged untreated.	[100]
11	Sugar Industry Wastewater	High Biological Oxygen Demand (BOD) and Total suspended solids (TSS). COD: 5000 to 8000 mg/L Total nitrogen: 22.73 to 22.97 mg/L	Generates 1000 litres of wastewater per ton of cane crushed.	[101]

12	Distillery	COD: 1,10,000 to 2,05,000 ppm. 1-2% sugar, 30-36% carboxylic acids, 5-6% alcohol, 50-57% melanoidins and caramels.	Average generation of 10 15 liters of wastewater per liter of alcohol production.	[102]
13	Dairy Industry Wastewater	Organic components, phosphates and chlorides. High levels of BOD and COD.	Generates between 0.2 and 10 liters of wastewater per liter of milk produced.	[103]

Table No.1 Types of Industrial Wastewater and Percentage Produced with Composition.

Artificial Intelligence (AI) and Machine learning (ML) plays a very important role for wastewater treatment and desalination using CO_2 gas hydrate. ML models play a crucial role in prediction of gas hydrate formation conditions. ML models can significantly improve the operational parameters of this technique (Tanko et al., 2024). This type of technology uses large datasets to model behaviour of hydrate formation. This algorithm involves adjusting to continuously changing variables like pressure, temperature and concentration in order to achieve maximum formation of hydrate [11]. AI powered systems improve scalability and sustainability by reducing the operational cost and allowing real me monitoring. There are different types of techniques among which are the Adaptive neuro-fuzzy inference system (ANFIS) and support vector machine (SVM) which predict desalination efficiency [12]. It will handle the nonlinearity and uncertainty in gas hydrate formation. It is found to be a powerful tool for wastewater treatment and desalination processes [13]. This method consists of collecting and preparing data, designing the structure of the model and finally training it using algorithms [14]. The trained model then undergoes a validation process. MATLAB or Python libraries are used to implement the model [15]. There are significant research gaps hampering the improvement of industrial wastewater treatment using CO_2 gas hydrates and the effective application of machine learning for desalination. A key problem is the limited understanding of how CO_2 hydrates form [16], [17]. Comprehensive research on their shape and how their molecules move is also needed to optimize hydrate-based separation. While existing optimization and modelling efforts provide a starting point, they are limited by the lack of available data and the complex nature of real wastewater. The application of machine learning is hampered by unreliable predictions, which are directly related to the limited amount and quality of training data. This highlights the crucial need to generate more comprehensive and standardized datasets to improve the accuracy and reliability of machine learning models for predicting hydrate behaviour and optimizing desalination processes integrated with wastewater treatment [18], [19].
The goal is to change how we treat industrial wastewater using CO_2 gas hydrates and using machine learning to improve desalination, creating a sustainable and efficient treatment method. A main focus is to

understand and improve how CO_2 hydrates form [17]. The research aims to create sustainable desalination methods that work with CO_2 hydrate-based treatment to solve the problems of treating salty water. To make predictions more accurate and efficient, machine learning will be used to predict how hydrates form and to analyze how well the whole treatment process works [17], [19]. This includes carefully analyzing the salt particles in the water and using machine learning to make the salty water treatment better. By using experiments, advanced computer models, and machine learning together, this research aims to create a new, energy-saving, and eco-friendly way to treat industrial wastewater and desalinate water, helping to meet the growing need for sustainable water use [20].

2. Advanced Wastewater Treatment Using CO_2 Gas Hydrates: Mechanisms, Applications, and Challenges

2.1 CO_2 Gas Hydrates for Wastewater Treatment

a. Formation and stability of CO_2 gas hydrates:

The conditions required for hydrate formation and factors affecting their stability:

I. Thermodynamic conditions

The formation of gas hydrate is a complicated process that requires specific conditions. Low temperature and high pressure favor the gas hydrate formation. The hydrate formation process is entirely physical, with no chemical bonds forming between the water and guest molecules. The formation of hydrate is a crystalline process, which involves nucleation, crystal growth, followed by a substantial accumulation process [21]. The chemical potential of each component must be the same in all the coexisting phases (liquid, hydrate, and vapor) at equilibrium conditions. This is the fundamental principle of hydrate formation in thermodynamics [6]. The temperature range varies between 264K to 300K, and the pressure is between 50 bar. This results in as temperature increases, the equilibrium pressure for hydrate formation also increases and vice versa [22].

The T-cycle method is a standard approach used for measuring thermodynamic hydrate liquid-vapor equilibrium (HLVE). This is used for understanding how temperature and pressure conditions affect the hydrate formation. The dissociation temperature of CO_2 hydrates gets affected by the presence of thermodynamic hydrate inhibitors (THIs). The T-cycle can also be used for estimating the performance of these thermodynamic hydrate inhibitors by calculating the depression in hydrate formation temperature [23].

In the aqueous phase, the presence of salts significantly affects the gas hydrate stability. The activity of water gets lower by the presence of salts, which shifts the equilibrium conditions to lower temperatures, which impacts the hydrate stability [6].

Understanding these thermodynamic conditions is critical for the industries that work with natural gas and oil recovery. Operators can implement strategies to avoid hydrate blockage in pipelines by determining the equilibrium conditions [22].

II. Kinetic factors

The creation of hydrates happens at low temperatures and high pressure, alongside the formation of hydrate gases. Aqueous saturated phases make a stable environment for them. The created hydrates will be stable under these conditions because the water and gas molecules will be able to interact as needed. Several aspects take part in ensuring that the hydrates will be stable, such as pressure and temperature, or impurities within the water phase, which may enhance or impede the nucleation and build-up of hydrates [24]. The level of supercooling observed has a substantial effect on the rate of formation of the CO_2

hydrates. Reducing the temperature increases the formation rate; however, it can have an effect on the stability of the hydrate structure [25]. The above factors, together with the introduction of any surfactants and promoters, can change the kinetics of hydrate formation by modifying the interfacial energy and mass transfer rates [19]. The hydrate formation rate is dependent on the size of the ice powder particles used in the formation process. Smaller-sized particles have higher gas interaction surface area, which increases the formation rate, but as the reaction proceeds, gas diffusion is impeded [26]. A Kinetic model is important in estimating the conditions under which hydrate would form and in the expansion of the existing hydrate, both of which are still being studied [17]. In addition, hydrate inhibitors such as salts and antifreeze compounds play an important role in preventing unwanted hydrate formation in industrial processes [20].

Sr. No.	**Category**	**Kinetic parameters**	**Examples**	**Advantages**
1	Kinetic	Hydrate Growth Rate	Rate at which hydrate crystals grow after nucleation. Affected by mass transfer (CO_2 dissolution) heat transfer (latent heat release) interfacial area. Faster leads to quicker contaminant removal and desalination.	More efficient contaminant removal and water separation.
2		Induction Time	Time elapsed before the onset of rapid hydrate formation. Affected by temperature, pressure, salinity, impurities, additives (e.g., salts, polymers, surfactants). Shorter is desirable.	Faster treatment process, smaller reactor size.
3		Hydrate formation Rate Constant	Rate at which hydrate crystals grow after nucleation. Affected by mass transfer (CO2 dissolution) heat transfer (latent heat release) interfacial area. Faster leads to quicker contaminant removal and desalination.	More efficient contaminant removal and water separation.
4		Water to hydrate conversion	Percentage of water converted into hydrate. Higher conversion is crucial for effective desalination. Affected by temperature, pressure, and the presence of promoters.	Higher water recovery rates, improved desalination efficiency.

5	Factors Affecting Kinetics	Thermodynamic Conditions (T, P)	Lower temperatures and higher pressures generally favor hydrate formation. However, high pressures are economically less viable. Optimization for lower pressure operation is crucial for wastewater treatment.	Reduced energy consumption, lower operating costs.
6		Wastewater Composition (Salinity, Impurities)	Salinity, organic matter, heavy metals, and other pollutants significantly impact hydrate formation. Specific additives may be needed to overcome inhibition effects or enhance contaminant removal.	Effective treatment of diverse industrial wastewater streams.

Table No. 2 Kinetic parameters, Category, examples and Advantages

III. Hydrate Structure

The Hydrate formation requires the prior existence of a water lattice, thereby stabilized by hydrogen bonding. The water molecules form a hydrogen-bonded network and create cavities that are able to trap gas molecules [3]. For the hydrate formation, guest molecules must fit into the cavities of the water lattice. Typically, these molecules are small and non-polar, with molecular sizes between 4 and 10 Å. Common gases forming hydrates include methane (CH_4), ethane (C_2H_6), propane (C_3H_8), carbon dioxide (CO_2), and hydrogen sulfide (H_2S) [25].

There are three principal hydrate crystal structures: Structure I (sI), Structure II (sII), and Structure H (sH). Each type presents arrangements of cavities that are stabilized under certain gas molecules. Type I hydrate is formed by small gas molecules such as methane and carbon dioxide. Two types of cavities are present: small (5^{12}) and large ($5^{12}6^2$). sI unit cell has 46 water molecules. Type II hydrate is formed by gas molecules of modest size, such as propane and isobutane form type II hydrate. It is characterized by two types of cavities: small (5^{12}) and large ($5^{12}6^4$). One sII unit cell contains 136 water molecules. The gas hydrate type H consists of larger hydrocarbons such as neo-hexane in hydrates and hydrogen mixtures. It characteristically has three kinds of cavities: small (5^{12}), medium ($4^35^66^3$), and large ($5^{12}6^8$) [27], [28], [29].

Hydrate Structure	sI	sII	sH
Unit Cell Dimensions (a, Å)	12.03	17.09	12.0 (hexagonal)
Cavity Type	Large / Small	Large / Small	Large
Cavity Radius (r, Å)	4.33 / 3.95	4.73 / 4.00	5.00
Cavity Volume (V, Å^3)	100.2 / 80.5	120.5 / 85.0	140.0
Water Molecules	46	136	34
Stability (T/P)	273 K / 30 MPa	277 K / 40 MPa	283 K / 50 MPa

Table No. 3 Geometry for hydrate crystal unit cells & Cavities.

2.2 Applications of CO_2 gas hydrates in wastewater treatment: The potential of CO_2 gas hydrates for desalination, pollutant removal, and resource recovery.

I. Desalination

There are various desalination processes, which include physicochemical processes, biological processes, and hybrid treatment techniques. Physicochemical processes involve filtration, ion-exchange, adsorption, etc. [3].

As shown in Figure 2, this method includes three steps as formation of gas hydrate in polluted water under controlled temperature and pressure. Second is the Separation of pollutant or saline and gas hydrate, and third is the decomposition of hydrate to release pure water, which can then be used for industrial or potable purposes or easily discharged [104].

Hydrate-based desalination process is an innovative technique that is able to desalinate both high and low salinity streams, which include seawater, brackish water, and effluents [6]. Clathrates are formed when seawater contact with the gas hydrate former at a suitable temperature and pressure, excluding dissolved ions from the resulting crystals. With the help of depressurization or thermal stimulation, hydrates are dissociated to produce pure water [6]. The energy cost of the gas hydrate-based desalination process depends on the formation conditions of hydrates [10]. Theoretically, the minimum energy required for seawater desalination is approximately 0.77 kWh/m3 [6].

The hydrate-based desalination process is conducted under specific conditions of approximately 3.5 Mpa pressure and a temperature of 274.2 K. Under these conditions, hydrates are formed from different produced water samples [30]. The selection of hydrate formers affects the thermodynamics of hydrate formation. It is important to focus on different reactor designs and the use of various hydrate formers to increase the efficiency of the desalination process [31]. A novel apparatus design was suggested for the application of gas hydrate-based desalination techniques. By using the squeezing operation of a dual cylinder unit, this equipment continuously produces and pelletizes CO_2 gas hydrate. The reactor contains hydrate slurries. This equipment is able to extract hydrated pellets from the reactor [32]. The CO_2 nano bubbles (NBs) are used as a sustainable kinetic promoter of gas hydrate formation in hydrate-based desalination (HBD). The separation step is not required from the recovered water [23]. The study concludes that the CO_2 hydrate-based desalination is a viable method for the treatment of radioactive wastewater containing Cesium (Cs^+) and strontium (Sr^{2+}) ions to produce fresh wastewater [33]. To apply hydrate-based desalination processes to large-scale applications, it is important to select suitable porous materials that promote hydrate formation, which enhances the efficiency of the hydrate-based desalination process (HBD) [34]. It is also necessary to consider the salinity of the produced water, as the salt content in the water increases, it becomes difficult to remove the salt [35]. A novel filtration-based reactor design for hydrate desalination achieved 62 to 80% desalination efficiency depending on the types of metal ions and anions present in the wastewater [36].

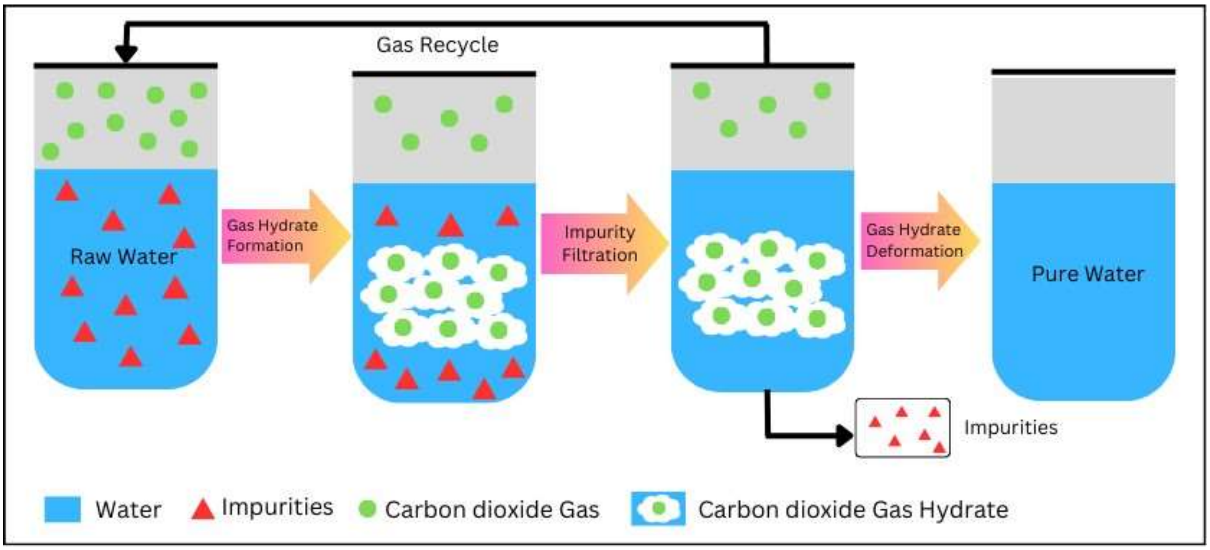

Fig. No. 2 Schematic representation of a CO_2 hydrate-based desalination process.

II. Pollutants Removal

Ion removal efficiency in hydrate-based desalination depends on ion size and charge. Due to stronger hydration bonds of higher charge density ions, they have lower removal efficiency
[6].

Hydrate-based desalination (HBD) is used to remove the harmful gases such as H_2S and CO_2 from the natural gas mixtures under various conditions, and also it removes a range of contaminants, including salts, nutrients, heavy metals, and organic compounds [6], [27].

H_2S forms hydrates at lower pressure and higher temperature compared to methane (CH4). For example, if a mixture of 70% CH4 and 30 % H_2S, after the first stage operation, researchers found a gas stream with 90% H_2S and then refined it to 99% CH4 in the second stage. For CO_2 + N2 mixtures, two stages are sufficient to achieve the efficiency of 99% of CO_2 removal from the feed stream at low pressure [37].

Hydrate-based desalination for the treatment of Ni2+ contaminated wastewater by using hydrates was investigated by Yang et al. In this, cyclopentane was added to a NiCl2 aqueous solution, and hydrates were produced at 2°C and at an agitation speed of 600 rpm. The efficiency achieved is 62% to 88% [9].

There are different types of pollutants, such as organic, inorganic pollutants, nutrients, and suspended solids. Organic pollutants include pharmaceuticals, personal care products, and other chemicals that are harmful to human health and the environment. Nutrients such as nitrogen and phosphorus released into the main streams without treatment will cause algal blooms. The gas hydrate method of sewage treatment is designed to remove these pollutants from the wastewater effectively [38].

The researchers proposed an operating procedure for the process of heavy metal ion removal. This process includes specific conditions for the formation of hydrate and solid-liquid separation. The study achieved an efficiency of 96.63% for the removal of copper ions (Cu^{2+}) from the wastewater [39].

Synthetic wastewater containing two types of colored compounds, potassium permanganate and povidone-iodine, the R134a, a refrigerant gas, was used for the formation of hydrate with synthetic wastewater. This gives a removal rate that ranged between 90-95% for potassium permanganate and 86-92 % for the povidone-iodine [40]. Ammonium sulfate can be effectively removed from wastewater by using CO2 gas hydrate formation. Researchers conducted a test in which the concentration of ammonium sulfate in an aqueous solution was 9.5 wt%. After hydrate dissociation, the concentration of ammonium sulfate decreased from 1.5 wt% to between 0.38 and 0.449 wt%. The energy requirement of this process is low [41].

The HyPurif process is a sustainable method for recycling and reducing the effluent from the wastewater treatment plant (WWTP) and spent caustic treatment plants (SCTP). The results indicate a decrease in the value of biological oxygen demand (BOD) from 2097 mg/L to 220 mg/L, achieving a purification efficiency of 90.5%. Similarly, the chemical oxygen demand (COD) reduced from 3100 mg/L to 503 mg/L, giving a purification efficiency of 84%. In addition to COD and BOD, the process also reduces total dissolved solids (TDS) and total suspended solids (TSS) [42].

III. Resource Recovery

Appropriate selection of hydrate formers and porous media and understanding of these processes, how different hydrate formers affect the thermodynamics and dynamics of hydrate formation, which impacts the overall efficiency of water recovery [34]. Various factors such as temperature and pressure conditions, ionic types, guest molecules, and concentration influence the freshwater separation efficiency [42].

The researchers measured the amount of fresh water from the seawater samples, resulting in 72-80% removal of dissolved minerals from the seawater. If two-stage hydrate processes were implemented, then the removal efficiency can increase about 92-97% [32]. The HyPurif process can achieve a water recovery rate of at least 40% for wastewater processing through every unit [42].

If a mixture of carbon dioxide (CO2) and propane is used as a hydrate former, then the water recovery rate achieved is 41.38%. Nallakukkala et al. found a recovery rate of 66% by using CO2 hydrate formerly operating at 2.5MPa by treating 2 wt% brine solution [T19]. Two-level gas hydrate process enhances the efficiency of water recovery [32]. A three-stage gas hydrate process removes 82-89% dissolved minerals from the produced water [30].

2.3 Challenges and limitations:

The technical and economic challenges associated with CO_2 gas hydrate-based wastewater treatment. Energy consumption is a challenge in CO_2 gas hydrate-based wastewater treatment, as high energy input is required to produce the hydrate. This increases operational costs and reduces the overall efficiency of the treatment process. Also, the process requires significant investment in equipment, energy, and maintenance. The cost of treatment must be balanced between CO2 capture and wastewater treatment. It is required to run the process at a specific pressure and temperature range, which will reduce the cost. The Artificial Intelligence and Machine learning module helps to predict pressure and temperature range, which helps to reduce cost. [43], [44], [45]. The kinetics of gas hydrate formation is a critical technical challenge in this technology. As kinetics plays an important role in the efficiency and stability of processes. To optimize the process, we must understand the kinetics of gas hydrate. [45], [46],[47] . To get efficient CO_2 gas hydrate-based wastewater treatment, optimization of operating conditions such as temperature, pressure, concentration, pH, etc. required; also, the quality of wastewater plays an important role in the efficiency and effectiveness of CO2 gas hydrate-based wastewater treatment. The impurities and high concentration of contaminants in wastewater decrease the efficiency and effectiveness of treatment.[48], [49] Real-time controlling and monitoring are required for this.

3. Machine Learning in CO_2 Hydrate Formation and Desalination

It is quite difficult to accurately predict the formation and behaviour due to continuously changing factors such as temperature(T), pressure (P), gas composition, water content, and presence of inhibitors or promoters. There are some traditional methods to predict hydrate behaviour, which depend on a thermodynamic equilibrium model that uses the Van der Waals equation of state:

$$(P + a/V^2)(V - b) = nRT$$

where P is pressure, V is molar volume, T is temperature, R is the ideal gas constant, a and b are van der Waals constants specific to the gas. This equation helps describe the behaviour of CO_2 gas.

The Clausius-Clapeyron equation:

$$d\ln(P)/dT = \Delta Hvap/RT^2$$

relates the change in vapor pressure (P) of water to temperature (T) and the enthalpy of vaporization (ΔHvap), which provides insights into hydrate stability.

Kinetic models employ the Arrhenius equation:

$$k = A * \exp(-Ea/RT)$$

where k is the rate constant, A is the pre-exponential factor, Ea is the activation energy, R is the ideal gas constant, and T is the temperature.

These models are found to be complex and do not accurately capture the effect of impurities' non-ideal behavior.[50], [51], [52] Artificial intelligence and Machine learning techniques give an effective alternative to that. They study large datasets and identify parameters and relationships between input variables like temperature, pressure, composition, etc., and output parameters like the condition of gas hydrate formation, stability, and kinetics. The rate of hydrate formation plays an important role in optimizing reactor design and operation [53].

ML is found to help optimize process parameters to increase the amount of freshwater recovered from wastewater. It can predict the quality of treated water along with salt content, dissolved impurities, and the potential required for microbial contamination [54].

For the reduction of energy consumption, optimal operating conditions are required, which will make the process cost-efficient along environmentally sustainable. ML will also guide the design and operational phase of hydrate-based wastewater treatment plants, which leads to improvement in process stability, reduction in downtime, and an increase in productivity. ML model can also accelerate the development in the process and new technology related to hydrate-based wastewater treatment [55], [56].

It helps develop the predictive model, which results in more accurate predictions about CO_2 hydrate behaviour. There are different techniques that consist of Artificial Neural Network (ANNs), Support Vector Machine (SVMs), Random Forest (RFs), and Gaussian Process Regression (GPRs), used to handle the data. They accurately predict the pressure and temperature at which hydrate formation takes place. Traditional methods for identifying the chemicals are dependent on trial-and-error experiments. They are found to be costly as well as time-consuming, and limited results are available. ML helps to identify chemicals that can promote hydrate formation in less time [57], [58]. The performance of these ML models highly depends on the high-quality experimental and simulation data [54].

There are several techniques of ML used for hydrate-based desalination optimization. The Reinforcement learning algorithm (RL) can learn policies for the desalination process, which adjust the parameters dynamically to increase water recovery, energy efficiency, and reduce cost [59]. The Bayesian optimization technique explores the parameters to find the condition by iteratively selecting and evaluating based on a probabilistic model. Genetic algorithms look like natural selection of conditions, which will further go through an iteration and evaluation process [60].

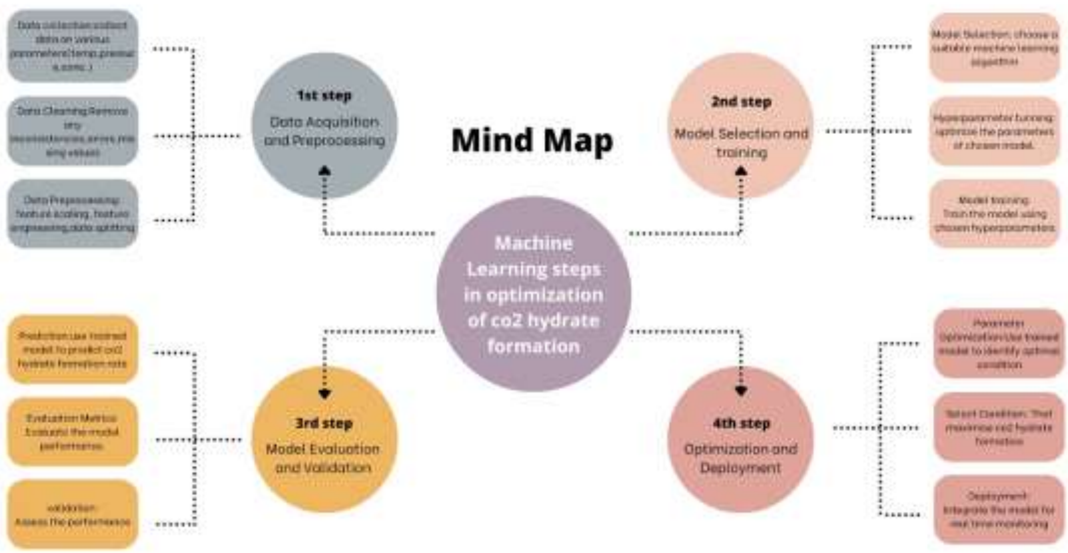

Fig. No. 3 ML workflow for optimizing CO_2 hydrate formation.

Adaptive Neuro-Fuzzy Inference System (ANFIS)

It is a model that combines neural networks and fuzzy logic. ANFIS is used for nonlinear systems. ANFIS works in two phases, the Forward phase and the backward phase. The forward phase involves defining a fuzzy membership function and a fuzzy rule that describe the relationship between input and output variables. The backward phase involves the optimization of fuzzy rules and membership functions using a learning algorithm. Then the data is preprocessed to remove any noise and ensure that it is a suitable format for training the ANFIS model. The input data is fuzzified using a fuzzy membership function. These functions convert the crisp function value into fuzzy sets. For example, low, medium, and high sets. That decides the degree to which input belongs to a specific category. The rules are generated according to previous studies. During the training phase, the model adjusts rules and applies algorithms to optimize the parameters. This step ensures the generation of models. Although there are challenges related to the quality of data, computational cost, and adaptability of the model, the ANFIS makes it a better choice for hydrate modelling techniques [61], [62], [63].

ML helps in real-time monitoring and controlling of CO_2 hydrate-based wastewater treatment.

Real time required to carry out safe and efficient operation of the CO_2 gas hydrate-based system. This system involves complex interactions between temperature, pressure, and composition of gas and other factors, which are responsible for the impact on hydrate formation and their stability. ML gives a powerful way/method to establish real-time monitoring and control by providing different adaptive control strategies and predictive capabilities. ML is used for predictive maintenance and fault detection [64]. ML algorithms analyse the sensor data like temperature, pressure, flow rate, etc., in order to identify anomalies or deviations from expected behaviour. For example, an anomaly detection algorithm might identify a sudden decrease in the pressure within a system, which could indicate inhibition to hydrate formation. It is a type of early warning that allows the operator to start corrective measures, including adjusting flow rate, injection of promoters, etc. Early warning systems were found to be useful to study the historical data, real-time sensor readings to predict the potential risk due to hydrate or failure in equipment [65]. The second part is adaptive control, which has two stages: dynamic process optimization and model predictive control (MPC). In dynamic process optimization, ML algorithms can dynamically adjust operating parameters, which are used in the optimization process of performance, based on the conditions that are continuously changing. The ML model analyzes the real-time data on the consumption of energy and the rate of hydrate formation, or adjusts the flow rate of CO_2 gas. It will also maintain optimal hydrate production during the desalination process. For example, in a plant where hydrate-based treatment takes place, ML models can analyze energy consumption and water recovery rate. If the model finds that a little increase in temperature will significantly improve water recovery. In model predictive control, ML models predict the future behaviour of a system and, based on this prediction, make changes in action. It allows for adjustment and strictly prevents outcomes that are undesirable [66]. Minimization of downtime and optimization of operating parameters are necessary. The factors, such as proactive maintenance, lead to reducing the operational cost. The real-time monitoring and control enhance the security of the system, increase its reliability by making early predictions, to improve the overall efficiency and productivity of CO_2 hydrate-based systems [67].

4. Future Perspectives

4.1 Successful applications of CO_2 gas hydrates in industrial wastewater treatment:

Desalination of High-Salinity Wastewater, such as wastewaters with a standard, typical amount of salt from industries like chemical manufacture, oil and gas, and textiles, presents a serious challenge to treatment because reverse osmosis (RO) and thermal distillation fail to yield high salt concentrations. This is now the treatment solution offered with CO_2 hydrates [68]. CO_2 hydrates were employed to desalinate hypersaline wastewater. This process rejected more than 90% of the salt, and the hydrates formed a solid phase, thus excluding ions from the phase [69]. The recovered water after dissociation was considered safe for irrigation, demonstrating its use in industries where reverse osmosis has failed. Thus, a pilot-scale trial in Saudi Arabia was conducted in 2022, producing 85% water recovery from brine generated by a desalination plant, reducing energy consumption by some 30% as compared to conventional treatment methodologies [70].

The CO_2 hydrates, as envisaged, have managed to obtain their place in ZLD schemes in order to improve performance. CO_2-hydrate ZLD system to treat textile dyeing wastewater that recovered 80% of water in cycles involving hydrate formation and dissociation phases, with the remaining dyes and salt being used as disposal sludge. Due to its modular concept, the system could be scaled up, which resolves key ZLD implementation issues [71].

Mining effluent often contains toxic heavy metals, such as lead, cadmium, arsenic, etc., which conventionally are cumbersome to remove via precipitation or ion exchange. CO_2 hydrates selectively perform very well [72].

Pharmaceutical wastewater is a totally different and substantial environmental hazard, mainly due to organic pollutants like antibiotics and hormones that are resistant to biological degradation [73] [74]. These pollutants could compromise water bodies, and they pose serious risks to aquatic life and human health [75]. Conventional treatment methods have found it difficult to remove these pollutants from waste streams; hence, new solutions will be developed. One of the candidate options in the degradation of organic pollutants that arose is CO_2 hydrates, making a pathway forward for sustainable wastewater management [76]. The application of these CO_2 hydrates may help increase the removal efficiency of antibiotics and hormones, which may assist in risk mitigation associated with antibiotic resistance and hormone contamination of the environment. A new method could potentially help alleviate problems with the drug treatment of pharmaceutical wastewater [77].

4.2 Future research directions:

b. Promising areas for future research, such as the development of new CO_2 hydrate-forming materials, improved process control strategies, and economic feasibility analysis.

The study emphasizes the need for more research on various additives that can enhance the formation and stability of hydrates. Understanding how different promoters affect the formation of hydrate can lead to efficient systems [78].

In recent years, the studies have focused on improving the kinetics of hydrate formation and the use of porous media, which helps in increasing the surface area available for the hydrate formation. Another potential topic is the use of nanofluids for the hydrate formation process. Researchers should investigate how nanoparticles can influence the kinetics and thermodynamics of hydrate formation [79].

The efficiency of CO2 gas hydrate systems can be enhanced by deeper research into optimizing operational procedures. Future studies could explore how additional reactor designs and configurations affect hydrate stability and thermodynamics. Further future research could investigate the stability of CO2 hydrate for the long term under the environmental conditions and also focus on testing CO2 hydrate technologies on a pilot scale to assess their stability and effectiveness [80].

The paper notes that reactors with fewer moving parts, such as spray columns, may be more effective in dealing with the difficulties posed by hydrate development [81].

To predict the behaviour of hydrates under various conditions, enhanced modeling and simulation techniques are needed. Increased investment in R&D is essential to lower the costs associated with hydrate technology, which includes developing more efficient materials that can reduce operational costs and improve efficiency [82].

The study highlights the positive impact of I-tryptophan as a kinetic promoter that enhances hydrate formation. The process of hydrate formation can be made environment-friendly by the use of environment-friendly promoters, which optimize this process [83].

The necessary advancements in the process control strategies are needed to optimize the conditions for the formation of CO2 hydrate. These advancements involve fine-tuning of temperature, pressure, and gas composition to maximize the hydrate formation efficiency and stability [81], [84].

To compare the cost-effectiveness of CO2 hydrate technologies with other carbon capture and storage methods, there is a need to study and analyze overall expenses. It means that looking at the cost of material used, how much it takes to run the process, and whether there is any possible risk involved [82].

Gaining detailed information about the economic effects of CO2 hydrate technologies will help in policy creation and investment choices [82].

There is a lack of detailed economic analysis of gas hydrate separation processes in the literature. More detailed research is required to evaluate the sustainability and economic feasibility of this technology. The economic feasibility will depend on future advancements and studies to optimize the process involved [85].

Development and refinement of the thermodynamics models for predicting hydrate formation conditions in complex systems with inhibitors [86].

4.3 Environmental and economic impacts:

There are several benefits of CO_2 gas hydrate technology in wastewater treatment related to the environment and economics. The applications of gas hydrate technology are vital for preserving ecosystems by managing water quality, effective wastewater treatment, which reduces harmful pollutants that damage aquatic life and habitats. Also, this technique can mitigate heavy metal concentration in wastewater [87].

Carbon dioxide can be captured and sequestered by using CO_2 gas hydrate technology in wastewater treatment, which results in reducing greenhouse gas emissions. This contributes to cleaning the air and a healthier environment, and it aligns with the global efforts to slow down climate change and reduce the reliance on fossil fuels, and decrease carbon emissions [88] [88].

The integration of gas hydrate technology with solar energy provides the necessary heat for the formation of gas hydrates, leading to a reduction in energy requirements for the gas hydrate process. This reduces the operating cost associated with wastewater treatment and makes CO_2 gas hydrate-based wastewater treatment more economically viable. This is especially important for the regions where fresh water resources are scarce and the water treatment cost is high [89], [90].

The process not only treats the wastewater, but it also has the potential to recover valuable resources and nutrients from the wastewater streams that can be utilised for agricultural purposes. Due to these dual benefits, it adds an economic incentive to the wastewater treatment process [91].

5. Conclusion

Industrial water treatment is a crucial aspect of environmental management, particularly with the growing concerns over pollution of water and discharge regulatory standards. Conventional wastewater treatment methods, including membrane filtration, biological treatment, thermal treatment, and chemical coagulation, have proven effective, but some drawbacks, like high energy consumption, less water recovery, high cost for treatment, and production of secondary waste. These challenges may be overcome by CO_2 Gas Hydrate-based wastewater treatment.

CO_2 Gas Hydrate-based wastewater treatment is cost-effective and sustainable. Gas hydrate, also known as clathrate hydrate, is a crystalline water structure that can encapsulate gas molecules under specific conditions. This phenomenon allows for to separation out of salts and pollutants from water and making viable method for water purification and desalination. This method includes three steps as formation of gas hydrate in polluted water under controlled temperature and pressure. Second is the Separation of pollutants or saline and gas hydrate, and third is the decomposition of hydrate to release pure water, which can then be used for industrial or potable purposes or easily discharged.

The application of CO_2 gas hydrates for industrial wastewater treatment and desalination is an energy-efficient and environmentally sustainable solution. However, optimizing hydrate formation, improving desalination efficiency, and reducing operational costs are challenges in this technique. Machine learning (ML) plays a major role in addressing these limitations by enhancing process modeling, optimizing parameters, and enabling real-time control and predictive maintenance.

ML techniques, including Artificial Neural Networks (ANNs), Support Vector Machines (SVMs), Random Forest (RF), and Adaptive Neuro-Fuzzy Inference Systems (ANFIS), have been instrumental in predicting hydrate formation conditions. These models analyze large datasets to establish relationships between variables such as temperature, pressure, gas composition, and impurity levels, thereby optimizing the hydrate formation process.

Moreover, real-time monitoring and adaptive control using ML enhance process stability and reliability. ML algorithms analyze sensor data (e.g., temperature, pressure, flow rate) to detect inconsistencies, predict potential failures, and optimize system performance. Predictive maintenance models help prevent system downtimes, while model predictive control ensures continuous optimization of hydrate-based desalination. By integrating ML-driven automation, industries can significantly reduce energy consumption, minimize costs, and improve the overall efficiency of wastewater treatment.

In summary, CO_2 gas hydrate-based wastewater treatment is an innovative and sustainable approach to water purification and desalination. While challenges remain, ongoing advancements in machine learning, reactor design, and material science bring this technology closer to large-scale implementation. With continued research and investment, it has the potential to play a major role in global water sustainability efforts, ensuring clean and accessible water for the future.

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