Removal of heavy metals from industrial wastewater by use of Cyclopentane - Clathrate Hydrate formation technology

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Abstract In this research, the experimental system was built up for treatment of wastewater containing substantial metal particles by the hydrate-based technique. The whole experimental system comprises of five fundamental methodologies: hydrate formation, hydrate separation, hydrate dissociation, centrifugal separation, and characterization. Many technologies were being utilized to remove substantial metal particles; however these frameworks had special prerequisites for raw wastewater, such as pH, temperature, contamination type and amount. Consequently, there is a evolving requirement for elective techniques for treating wastewater containing heavy metals, for which hydrate-based separation seems promising. The removal of the heavy metal ion Cu$^{2+}$, Ni$^{2+}$, Zn$^{2+}$ and Cr$^{3+}$by the hydrate-based method gives an enhancement to the ordinary wastewater treatment innovation. Aqueous solutions of the wastewater were synthesized by adding a certain amount of each salt such as copper sulfate anhydrous (CuSO$$_4$$•5$$H_2$$O), nickel sulfate (NiSO$$_4$$), Zinc chloride (ZnCl$$_2$$) and tri-chloro chromium (CrCl$$_3$$) to the distilled water. Cyclopentane was employed to form hydrate in this research on account of its immiscibility with water, non-toxicity, and thermodynamic stability. Clathrate for ternary systems (cyclopentane, water and ionic salt) were formed at different types and concentrations of salts in the liquid state at temperature below 7 °C and normal atmospheric pressure. An effect of the cyclopentane-heavy metal solution volume ratio and concentration of the heavy metal on removal efficiency of heavy metal ions, the enrichment factor and a yield of the dissociated water are discussed. The results show that the technology has higher removal efficiency upon changing the volume ratio from 1/2 to 1/6, and achieve wastewater minimization, but lower enrichment factor and yield of dissociated water. This work gives thoughts into low-energy, serious treatment of wastewater.

Keywords
Cyclopentane, Enrichment factor, Heavy metals, Hydrates, yield

1. Introduction
Clathrate hydrate formation process is of major interest in both environmental and industrial fields. Hydrates are naturally crystalline compounds that are formed of water (host) and small molecules (guest) at low temperature and high pressure, hydrate need for expanding the knowledge on hydrate phenomena [1]. A guest (gas or liquid) molecule gets entrapped within a hydrogen bonded water cavities center as shown in figure 1.

The guest molecules are able to rotate inside the cages, but they cannot diffuse between the cages. The occupancy is directly related to the guest size and to the pressure, temperature and composition of the system as shown in figure 2. Clathrate formation is highly undesirable especially in the systems of oil production and in natural gas process. In these systems the hydrates can shape quickly into large plugs and agglomerate in the lines for transportation and cause blockage in the systems, particularly in the deep ocean and permafrost locales [2].
The most recent decades, clathrates have been seen both as a potential resource and as well as an issue in different ways. On the positive side, the studies decided that the hydrates have an alternative source of energy where each hydrate unit has contained amount of energy significantly more than enough to support its own combustion [3]. The other technological application is the use of hydrates to desalinate seawater; the process starts with brine being mixed with a hydrate former gas. Once clathrate is formed, isolating water from the dissolved solids and salts, it precipitates. After that, the hydrate is heated to release the gas. Thus, the final product is freshwater [4,5,6]. Another application for clathrate technology is using the hydrates to extract carbon dioxide from flue gas emitted by large power plants in an attempt to reduce carbon emissions and global warming [7].

The hydrate system is also being used for storage and transportation of natural gas. The rising demand for natural gas required finding and developing alternatives to store and supply the natural gas to different regions. This method presents advantages since it does not involve cryogenic temperatures or the high pressures of cylinders when compared to the conventional transporting technologies, such as liquefied natural gas and compressed natural gas [8, 9].

Hydrates can also be used as a secondary refrigerant in cooling systems such as air condition [9, 10]. In this sense, we used a formation process of the cyclopentane hydrate. Cyclopentane(C5H10) is used as hydrate former, a salicylic hydrocarbon with a stoichiometric ratio of 1:17 of cyclopentane to water molecules [11]. Cyclopentane is immiscible in water and forms the cubic hydrate structure II

![Figure 1. Hydrate former (guest) in cavity of host (water molecules) lattices [1]](image-url)
2. Experimental

2.1. Preparation of Samples

The experiments of forming the hydrate from liquid-guest were carried for various samples; every sample was constituted from distilled water, cyclopentane and single heavy metal or salt of the heavy metal. A volume ratio of the water-to-cyclopentane at (2,4and 6)v/v with five initial concentrations at surrounding pressures and at temperatures, meaning that the experiments do not require increasing pressure but only arise in temperature to about $T_f \leq 6^\circ C$. Experiments at atmospheric pressure are usually more accomplished, less expensive and more secure than the ones involving a pressurization process. The temperature of partition or dissociation is 7.7°C for cyclopentane hydrates shaped at environmental pressure.

Temperature of three-phase equilibrium at which a cyclopentane-rich liquid, a water-rich liquid, and a hydrate are in common balance is 280.9 K at atmospheric pressure [12]. The analyzed structure could not decide any significant contrast in the water structure before formation of hydrate and after decomposition [13]. Overall, gases such as methane and carbon dioxide that have lower molecular weight require higher pressures and lower temperatures to form stable hydrates, for example (methane forms a stable hydrate at 4°C when the pressure reaches 3.9MPa), whereas hydrocarbons such as propane require less hard conditions. On the other hand, liquid components such as tetrahydrofuran (THF) and cyclopentane (CP) form hydrates at atmospheric pressure [14]. A removal of heavy metal ion from aqueous solution by hydrate technology is a potential application based on many key physical properties of clathrate that exclude salt ions from hydrate structure [6]. The pollution of water resources by heavy metals such as Cu$^{2+}$, Ni$^{2+}$, Zn$^{2+}$ and Cr$^{3+}$ further worsens the issue, and causes various adverse health effects [15]. Wastewaters discharged into the environment containing heavy metals has increasingly faced more rigorous standards therefore these toxic heavy metals should be removed from the wastewater to protect the people and the environment. To remove heavy metal ions, there are several practices being used - for instance, treatment by electrochemical techniques, adsorption, precipitation, ion-exchange, membrane filtration, etc.[16]. But these methods have specific needs with respect to raw wastewater, such as a pH, kind of pollutant, temperature, and pollutant quantity; therefore, a limitation of the applicability confines their broad application. Moreover, the separation of heavy metals in treating wastewater which is based on hydrate system is a promising alternative method [14]. There are a few reports on removal of heavy metals from wastewater via hydrate formation, especially using liquid former (liquid guest) in hydrate formation for a removal of the heavy metal from industrial wastewater. In this study, we focused our attention on a hydrate system that excludes salt ions from hydrate structure and the involved substance other than a gas former, i.e., cyclopentane. The effect of cyclopentane on heavy metal solution volume ratio and initial concentration of the heavy metal on clathrate hydrate phenomena and removal characteristics were discussed.

2. Experimental Work

2.1. Preparation of Samples

The experiments of forming the hydrate from liquid-guest were carried for various samples; every sample was constituted from distilled water, cyclopentane and single heavy metal or salt of the heavy metal. A volume ratio of the water-to-cyclopentane at (2,4and 6)v/v with five initial concentrations
[10, 50, 100, 300 and 500] ppm of different type heavy metals ($\text{Cu}^{2+}$, $\text{Ni}^{2+}$, $\text{Zn}^{2+}$ and $\text{Cr}^{3+}$) is shown in Table (1). The purity, the supplier and the formula of the materials used are presented in Table 2.

### Table 1. Specification of Test Samples

| Cyclopentane/water solution (v/v) | 1/2 | 1/4 | 1/6 |
|-----------------------------------|-----|-----|-----|
| **Heavy Metal** | **Initial concentration (ppm)** |
| Cu$^{2+}$ | 10 | 10 | 10 |
|       | 50 | 50 | 50 |
|       | 100 | 100 | 100 |
|       | 300 | 300 | 300 |
|       | 500 | 500 | 500 |
| Ni$^{2+}$ | 10 | 10 | 10 |
|       | 50 | 50 | 50 |
|       | 100 | 100 | 100 |
|       | 300 | 300 | 300 |
|       | 500 | 500 | 500 |
| Zn$^{2+}$ | 10 | 10 | 10 |
|       | 50 | 50 | 50 |
|       | 100 | 100 | 100 |
|       | 300 | 300 | 300 |
|       | 500 | 500 | 500 |
| Cr$^{3+}$ | 10 | 10 | 10 |
|       | 50 | 50 | 50 |
|       | 100 | 100 | 100 |
|       | 300 | 300 | 300 |
|       | 500 | 500 | 500 |
### Table 2. Properties of materials used in this study

| Material                     | Chemical formula | Purity  | Supplier         |
|------------------------------|------------------|---------|------------------|
| Distilled water              | H₂O              | -       | Own              |
| Cyclopentane                 | C₅H₁₀            | 98.0%   | J.T.Baker India  |
| Antifreeze Ethylene glycol   | (CH₂OH)₂        | 99.0%   | J.T.Baker India  |
| Copper sulfate unhydrous     | CuSO₄.5H₂O       | 99.0%   | HiMedia India    |
| Nickel sulfate               | NiSO₄            | 98.5%   | HiMedia India    |
| Zinc chloride                | ZnCl₂            | 99.5%   | HiMedia India    |
| Tri chloro chromium         | CrCl₃            | 99.0%   | HiMedia India    |

#### 2.2. Rigs and Methodology

Figure 3 illustrates a process flow diagram of the experimental work. There was a reactor consisting of a flask with three necks and a round bottom and it was placed on a metal stand inside a cooling bath. The flask was immersed except for the neck in the cooling liquid which was prepared by mixing ethylene glycol and distilled water in a volume ratio (1/3).

The reactor was connected to a stirrer. Two temperature sensor thermocouples type K were placed into the necks 1 and 3, in order to measure the temperature inside the flask during the formation of clathrate. The cooling bath was set at 2 °C to regulate temperature in the reactor at stable sub-cooling. The experimental procedures involved five major steps that are formation of hydrate, clathrate layer separation, dissociation of hydrate, centrifugal separation and detection.

At first the wastewater was intended by putting a specific weight of heavy metal salt to distilled water, then mixed with liquid cyclopentane at 900 RPM and cooled down while continuous stirring to the specified temperature which must be within the region of stable hydrate that correspond to phase diagram, i.e. below 7 °C. We collected the experimental data by using acquisition instrument (DAI) that was connected to computer. During the period of hydrate formation a rapid increase in temperature was observed, meaning the hydrate formation had occurred and this step completed when no change was detected in temperature within the flask. Then the hydrate produced was separated from residual water in separation funnel which carried out for preliminary separation.

Next, dissociated process of the hydrate occurred at ambient temperature and atmospheric pressure, and cyclopentane was separated from the produced mixture of cyclopentane and dissociated water by centrifugal separator was an additional way to separate water from cyclopentane which is immiscible in water.
Figure 3. Schematic diagram of the experimental setup

An efficiency of heavy metal removal (Re) was calculated from equation below [17,18]:

Removal efficiency (Re) = \( \frac{C_o - C_1}{C_o} \times 100\% \) \hspace{1cm} (1)

Where \( C_o \): initial concentration of heavy metal ion in water solution,

\( C_1 \): concentration of heavy metal ion in the water of hydrate dissociated.

To distinguish the remainder drainage, the enrichment factor (Ef) is calculated as follows [18,19]:

Enrichment factor (Ef) = \( \frac{C_2}{C_o} \times 100\% \) \hspace{1cm} (2)

where \( C_2 \): concentration of heavy ion in the residual effluent.
And, the yield of dissociated water was calculated as follows [19]:

\[
\text{Yield of dissociated water (} Y_w \text{)} = \frac{V_1}{V_0} * 100\% \tag{3}
\]

where \( V_0 \): initial volume of heavy metal solution,
\( V_1 \): volume of water obtained from hydrate dissociation.

### 3. Results and Discussion

#### 3.1. Liquid-Clathrate Formation Behavior

The overall time based on behavior of the liquid clathrate formation may be demonstrated by the change of temperature inside the reactor during each experiment due to the exothermic behavior for the clathrate formation. For instance, a sample of chromium ion of initial concentration 500 ppm and cyclopentane to water solution is (1/2)v/v, the temperature rise about the bath temperature 2°C should relate to a high rate of hydrate arrangement, as shown in figure 4.

![Figure 4. The relation between temperature and time during hydrate formation](image)

In the overall tests, the temperatures increased during ten minutes from the start of experiment due to the heat release since the hydrate formation are approximately the same. These results show that the duration of hydrate formation neither depend on the sort of heavy metal ion nor its initial concentration in the wastewater in the given range.

#### 3.2 Effect of cyclopentane: wastewater volume ratios

3.2.1 Effect of volume ratios on the percentage removal efficiency: The variation in calculating the percentage efficiency of heavy metal ions removal verses different cyclopentane: wastewater volume ratios are illustrated from the experimental results in figure 5.
The percentage efficiency attained to maximum value of (92) % of copper ion in the cyclopentane/water solution ratio for (1/6) v/v. As presented in figure (5), the percentage efficiency increased when the volume ratio changed between 1/2 and 1/6, because heavy metal ions at low concentration in discharge layer (C₂) causes less adherence of metal ions on the surface of the clathrate crystallites. Then at the hydrate dissociation stage, heavy metal ion goes easily in the water that produced from hydrate and therefore the removal efficiency was reduced. Whenever a large quantity of clathrate only (cyclopentane −water) layer was produced at the volume ratio of cyclopentane −wastewater was 1/6. The results show the same trend as obtained by Yongchen et al. [19].

3.2.2 Effect of volume ratios on the enrichment factor: From the experimental results are plotted in Figure (6) the (Ef) decreased when increasing the volume ratio between 1/2 and 1/6 because the (Ef) is an essentially dependent on the concentrations of heavy metal ions in the residual effluent (C₂). The littler cyclopentane/water-solution volume proportion led to a higher (Ef) and large amount of heavy metal ions are rejected into the concentrated effluent. Noting that the (Ef) was around the equivalent for one of every four heavy metal particles, in spite of difference in radius of ions and their charges; that as studied by Hajar et al. [20].
3.2.3 Effect of volume ratios on the water yield: The water yield decreased as the volume ratio of (heavy metal solution/cyclopentane) changed from 2 to 6. This ratio specified the percentage conversion of water into clathrate as shown in figure (7). Therefore, at a higher cyclopentane volume (i.e) lower heavy metal solution volume, more hydrate crystallites were produced. Also a higher water yield occurred at more volume of cyclopentane. Some researchers such as Ho-Van et al. [21] studied a yield of the water from hydrate produced dissociation.

3.3 Impact of $C_o$ of metal ion in water solution
3.3.1 Effect of initial concentration on the percentage purification efficiency. The results presenting the removal efficiency in the tests are explained in a line graph as figure 8, with particular amounts of
initial concentration of heavy metal ions. As shown in Figure 8, at a cyclopentane–discharge ratio by volume of 1: 6, the increase in initial heavy metal ion concentration led to the high-concentration residual effluent during the hydrate formation process because the heavy metals ion are rejected from the clathrate cages. However, the ingering profluent becomes concentrated in heavy metals as initial concentration of heavy metal increased. This leads to the removal efficiency showing sharp increase from 13% to 91% with increasing initial concentration until 300 ppm, and then become constant subsequently, specifically, with Cu\(^{2+}\) ion. Since successive growth of the hydrate phase hinder due to excess cyclopentane to water contact which have been caused appearance of hydrate phase in the form of a thin film which interfere between the cyclopentane and the liquid-water phases [22]. This eventually produced small amount of effluent solution was covered into the clathrate crystals. Moreover, the electrolytes heavy metal salts in wastewater depress the activity coefficient of water and prevent water particles in connected hydrogen bonds [23, 24].

![Figure 8](image)

**Figure 8** The percentage removal efficiency at cyclopentane: wastewater volume ratio (1/6) v/v versus different initial concentration of four heavy metal ions

3.3.2 Impact of \((C_0)\) on the enrichment factor: From figure (9) it is evident that as the initial concentration of heavy metal increased the enrichment factor decreased, because an amount of water was not involved in the formation of the hydrate and remained in lower layer. These phenomena led to lower the metal ions concentration in the discharge and then decrease the enrichment factor. So it was increased by increasing volume of hydrate former, i.e. the cyclopentane to heavy metal solution to increase the production quantity of hydrate crystallites, as studied by Zucheng et al.[18] and Yongchen et al.[19].
3.3.3 Impact of \((C_o)\) on the water yield: The results of liquid clathrate was obtained from this work of four types of heavy metal ions demonstrate that the water yield decreased remarkably with a growth in initial concentrations of \(\text{Cu}^{2+}\), \(\text{Ni}^{2+}\), \(\text{Zn}^{2+}\) and \(\text{Cr}^{3+}\), and the results of the experimental research are organized in figure 10. Where the water yield was measured of the percentage conversion of water into clathrate, and further layer of clathrate were produced with a greater cyclopentane volume, so a higher water yield must come at the expense of substantially more cyclopentane. When lowering the cyclopentane–wastewater volume ratio \((1/6)\, v/v\) with \((C_o)\) increased from 10 mg/L to 500 mg/L, hydrate phase form a thin film contained low volume of liquid-water phases which would lead to a large volume of residual solution into the \((C_2)\) layer.
4. Conclusions

1. This study is based on an essential working technique for handling of discharge containing heavy metal ions using the liquid clathrate process.
2. The experimental outcomes depict the hydrate system method could minimize liquid effluent and lower heavy metal ions.
3. The results indicate when the volume ratio of cyclopentane–wastewater at maximum value within the limited range such as (1/6) v/v contributed to lower the (Ef) and water percentage that obtained from clathrate dissociation, however higher in the percentage removal efficiency.
4. Noting that the removal efficiency, (Ef) measurement of heavy ion concentration in wastewater and percentage conversion of water to clathrate layer, were roughly the equivalent of whole four ions of heavy metals which were studied in this work.
5. In summary, higher of initial concentrations heavy metal ions led to decrease (Ef) and (Yw), however, causes increase in removal efficiency.

References

[1] Djurdjica Corak, Tanja Barth, Sylvil Høiland, Tore Skodvin, Roar Larsen and Tore Skjetne 2011 Effect of subcooling and amount of hydrate former on formation of cyclopentane hydrates in brine Desalination 278, 268–274
[2] Bashir Mohamed and Hissen Abdulkader June 2013 Cyclopentane Hydrate for Hydrate Wetting Studies”, M.Sc. thesis, University of Bergen
[3] Rio de Janeiro; Paulo Roberto and Gerald Fuller 2016 Kinetics of cyclopentane hydrate formation - an interfacial rheology study M.Sc. thesis, Pontifical University Catolica, July 2016
[4] Jitendra S Sangwai, Rachit S Patel, Prathyusha Mekala, Deepjyoti Mech and Marc Busch 2013 Desalination of seawater using gas hydrate technology – current status and future direction Proceedings of Hydro International, IIT Madras, Chennai, India 4-6 Dec 2013
[5] Shurooq T AL-Hemeri, Riyadh S AL-Mukhtar and Lina W Mahmood 2019 Thermodynamic and kinetic investigation of desalination by refrigerant clathrate hydrate formation Engineering and Technology Journal, Vol. 37, Part C, No. 1
[6] Carolyen Koh and Dendy Sloan 2011 Fundamentals and applications of gas hydrates Heinz Heinemann Academic, 3rd edition
[7] Seong-PIL Kang and Huen Lee 2000 Recovery of CO₂ from flue gas using gas hydrate: Thermodynamic verification through phase equilibrium measurements Environ. Sci. Technol. 34 pp 4397-4400
[8] Michael T Kezirian and S Leigh Phoenix 2017 Natural gas hydrate as a storage mechanism for safe, sustainable and economical production from offshore petroleum reserves”, Energies 10 p 828
[9] Hongxia Zhou 2017 Hydrate slurry as cold energy storage and distribution medium M.Sc. thesis, Chinese Academy of Science, China
[10] 10) Azeez G Aregbe 2017 Gas hydrate—properties, formation and benefits Open Journal of Yangtze Gas and Oil 2 pp 27-44 January 2017
[11] Genti Zylyftari and Jeffrey F Morris 2014 Hydrate forming emulsion: A Rheological, Thermodynamic and Morphological Study PhD thesis, The City University of New York
[12] Amir H Mohammadi and Dominique Richon 2009 Phase equilibria of clathrate hydrates of methyl cyclopentane, methyl, cyclopentane or cyclohexane+ carbon dioxide Chemical Engineering Science, 64 pp 5319–5322
[13] Shol Kim, SeongHyuk Lee and Yong Tae Kang 2016 Characteristics of CO₂ hydrate formation/dissociation in H₂O+THF aqueous solution and estimation of CO₂ emission reduction by district cooling application Energy pp 1-12
[14] Hongfei Xu, Carolyn A Koh and Amadeu K Sum 2013 Hydrate desalination using cyclopentane hydrates M.Sc. thesis, Colorado School of Mines
[15] Mukesh Parmar and Lokendra Singh Thakur Heavy metal Cu, Ni and Zn: Toxicity, health hazards and their removal techniques by low cost adsorbents: A short overview International Journal of Plant, Animal and Environmental Sciences, vol 3, 2013
[16] Renu Bisht, Madhu Agarwal and Kailash Singh 2017 Methodologies for removal of heavy metal ions from wastewater: an overview Interdisciplinary Environmental Review Vol. 18, No. 2
[17] Yongkoo Seol and Jong-Ho Cha 2013 Increasing gas hydrate formation temperature for desalination of high salinity produced water with secondary guests. American Chemical Society Sustainable Chemistry & Engineering 1, 10, pp 1218-1224
[18] Zucheng Wu, Xuefen Chen and Xiao Feng 2007 Removal of metal ions from electroplating effluent by EDI process and recycle of purified water Separation and Purification Technology, 57 pp 257–263
[19] Yongchen Song, Hongsheng Dong, Lei Yang, Mingjun Yang, Yanghui Li, Zheng Ling & Jiafei Zhao 2016 Hydrate-based heavy metal separation from aqueous solution. Scientific reports, 18, February, 2016
[20] Hajer Fakharian, Hamid Ganji and Abbas Naderifar 2017 Desalination of high salinity produced water using natural gas hydrate Journal of the Taiwan Institute of Chemical Engineers 72 pp 157–162
[21] Ho-Van S, Douzet J. Bouillot B and Herri J 2017 Experimental study and modelling of Cyclopentane Hydrates in the presence of NaCl, KCl and a mixture of NaCl – KCl 9th International Conference on Gas Hydrates - ICGH9, Center for Hydrate Research; Colorado School of Mines, Jun, Denver, United States. pp 02P058_1665
[22] Ryosuke Fujioka, Li Pang Wang, Gjergj Dodbiba and Toyohisa Fujita 2013 Application of progressive freeze-concentration for desalination Desalination 319 pp 33–37
[23] Shurooq T AL-Hemer, Riyadh S AL-Mukhtar and Mustafa Saadi Mohammed 2018 Study the effect of tween 80 on Clathrate Hydrate Formation Behavior for R-134a Journal of Al-Qadisiyah for Engineering Science Vol 11 No 3
[24] Riyadh Sadiq AL-Mukhtar, Shurooq Talib AL-Hemer and Mustafa Saadi Mohammed 2018 Study the effect of Silica Gel Powder on Clathrate Hydrate Formation Behavior for HFC-134a Gas Journal of University of Babylon for Engineering Sciences Vol 26 No 10