Engineering and Technology Journal

Clathrate-Based Recovery of Sulfuric Acid from Spent Acid

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HIGHLIGHTS

- One method for recovering sulfuric acid (H_2SO_4) from spent acid is based on Clathrate.
- Conducting hydrate formation experiments on a guest liquid to extract H_2SO_4.
- Different volume ratios of Cyclopentane to spent acid at initial concentrations to produce H_2SO_4.
- The hydrate method was effective in recovering H_2SO_4 from spent acids.
- Hydrate formation is examined by increasing the time it takes to create hydrates.

ARTICLE INFO

ABSTRACT

Recently, the applications of hydrate phenomena in industrial processes have been increasing. A clathrate or hydrate is a solid, ice-like compound that forms when water/guest is mixed under certain conditions. Hydrogen water molecules bond with the guest molecules to form a crystal lattice. Different guests can form the Clathrate (e.g., gases or liquids). Dilute Sulfuric acid is usually generated at different industrial plants, and these dilute acids are considered waste because they cannot be reused again. Many treatment processes handle this environmental problem, like electrochemistry, precipitation, adsorption, membrane filtration, and ion exchange. Although such processes have significant operational advantages, their disadvantage is that many of the high costs of the treatment process and the generated products of treatment are considered toxic pollutants. This work utilized clathrate phenomena experiments to re-concentrate dilute sulfuric acid. The selected clathrate guest was Cyclopentane. Each experiment s consists of a mixture of Cyclopentane and dilute sulfuric acids. The volume ratios of dilute sulfuric acid to Cyclopentane were (6:1, 4: 1, 3:1, and 2:1) with different initial concentrations (12.5%, 10%, 7.5%, 5%, 2.5%) of acid. It was found that the clathrate method was effective in re-concentrate dilute sulfuric acids with a maximum efficiency of 94% at the ratio of acid /cyclopentane (6:1) at 12.5% concentration. It can be concluded that the increase in dilute sulfuric acid /cyclopentane volume ratio leads increasing in removal efficiency while reducing the yield percentage and enriched Factor.

1. Introduction

Clathrate includes molecules that join together, usually by hydrogen bonding, to form a cage, so it holds another molecule inside[1]. Clathrate is a water-based crystalline solid that affects ice, including small non-polar molecules, polar molecules, and, in most cases, gases. Extensive hydrophobic moieties are entrapped inside other large hydrophobic moieties. Firstly, Clathrate was discovered when crystals clogged. The investigated results of transporting natural gas pipelines in cold climates explain that the crystal was natural gas and water at a low temperature. Clathrate phenomena were also recognized in deep-sea, where large clear crystals fall on the deck.

Clathrate or hydrates phenomena can occur with several gases and liquids. The difference between these guests is the molecular dimensions. For example, nitrogen, carbon dioxide, and hydrogen sulfide form saturate hydrates. They're supposed to have originated when a molecule guest is mixed with cold, highly pressured water, and the water molecules begin to form hydrogen bonds and build a cage around it. Although some of these cages are found empty, they may be formed first, and then the guest molecule will move in. The conditions for them to form cages require water molecules to have fewer hydrogen bonds, which is a higher energy situation. Then, to have water organized around the other molecule is more ordered, known as a loss of entropy; it only occurs under high-pressure and cold temperatures [2].

The majority of Clathrate is known to form one of three structures, namely: structure I (sI), structure II (sII), or structure H (sH), where each structure is comprised of small and large cavities formed by the water molecules. The SI hydrates consist of 46 water molecules per eight cavities, two small spherical cavities with 12 pentagonal faces (5^{12}) and six large oblate cavities with two hexagonal faces and 12 pentagonal faces ($5^{12}6^2$). The SII hydrates consist of 136 water molecules per 32 cavities, 16

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small cavities with 12 pentagonal faces (5^{12}) and eight large cavities with 12 pentagonal and four hexagonal faces ($5^{12}6^4$), all in a spherical shape. Figure 1. shows these cavities [3].

There has been an interest in hydrate applications in recent years. Mainly those encapsulating guest molecules of natural gas because hydrates could be used as an alternative energy source. The equilibrium data on the hydrate phase and the surroundings of dissociation and hydrate formation were examined in various gaseous mixes of compounds [4,5,6,7 and 8]. It's important to remember that physical procedures can be used to separate intense metals from aqueous solutions, particularly electroplating effluent treatment, a physical partitioning method for removing contaminants [9]. This study uses the Cyclopentane-Clathrate Hydrate production technique to remove heavy metals from industrial effluent. Cyclopentane was used to form hydrate/clathrate due to its immiscibility with water, thermodynamic stability, and non-toxicity [10]. The work discussed the desalination via refrigerant clathrate/hydrate formation, a thermodynamic and kinetic study dealing with hydrate formation for the ternary system (water, refrigerant gas, salt) at different initial pressures. The salts were NaCl, KBr, and NaF. The isochoric pressure search method measured the pressure and temperature for hydrate formation and conduction of the three phases of hydrate-liquid-vapor [11].

Different technologies have been utilized in recovering waste dilute spent acids [12,13,14,15,16 and 17]. Because the amount of sulfuric acid is high here, the study [15] conducted experiments for H_2SO_4 recovery from spent dilute acid using bentonite as an adsorbent (82%). The acid is generated during petroleum handling industries in the alkylation processes stage. Sulfuric acid (H_2SO_4) is used as a catalyst to fabricate iso-octane material. First, the paper described a molybdenum-diluted acid recovery system that uses various wastes to neutralize ammonia gas. Then filtration and crystallization followed [18]. The precipitation method involves adding particular chemical compounds to chemical coagulation and separating the effluent from the precipitation [19].

Although these studies introduced high-removal efficiency while recovering spent acids, the process of chemical coagulations may create the resulting pollution caused by the addition of chemical materials and the creation of unsafe sludge [20,21]. The electrochemical technique needs an electrode material at all times. Still, its limitation is that it consists of sludge formation of electrodes' passivation layer and energy consumption associated with high operational cost [22]. There are rivals in recovering diluted acid recycling and adsorbent complexes in the adsorption method. Although the advantages of the ion-exchange method are more significant than those of the adsorption technique, adequate ion-exchange resins are unavailable.

Moreover, operational and capital costs remain high [23]. The selection of a suitable membrane to recover diluted acid by filtration involves aspects such as quality, the characteristics of the effluents, pH, and temperature variations[24]. Also, this technique was associated with high maintenance and operating costs [25]. The expansion of hydrate-crystal plates into the bulk of the water phase was a surprising discovery, as Sugaya and Mori [26] had not observed such a mechanism in identical studies.

In this approach, we tried to avoid the above drawbacks of the comparative studies by presenting an effective procedure for re-concentrate dilute sulfuric acid using hydrate formation, as Cyclopentane a guest. Moreover, the experiments were conducted for the first time at different acid concentrations.

2. Materials and Methods

2.1 Materials and Equipment

A dilute acid solution was used in the experiments by diluting concentrate sulfuric acid with distilled water at different concentrations (2.5 %-5 %-7.5 %-10 %-12.5 %). The used chemicals: distilled water (H_2O) was supplied by Own, Cyclopentane (C_5H_{10}, 98%) and Antifreeze Ethylene glycol (($CH_2OH)_2$, 99%) were purchased from J.T.Baker India, Sulfuric acid (H_2SO_4, 98%) and Sodium hydroxide (NaOH, 99%) were purchased from HiMedia India and Belgium, respectively.

2.2 Research Procedure

The dilute sulfuric acid is tested throughout the experiment at various starting concentrations and volume ratios of Cyclopentane diluted acid. A flask with three necks served as a clathrate reactor. A metal pedestal was placed near a cooling bath, and the flask was immersed in a cooling liquid filled with distilled water and ethylene glycol in a volume ratio of (1/3). The reactor is equipped with an adjustable stirrer. To detect mixture temperature in the reactor, two thermocouples sensors (type K) are immersed at two-level, one near the mixture surface and the other one down the reactor near the bottom; these thermocouples are placed to measure hydrate formation temperature and hydrate induction time. The following five processes are to make experimental measurements: hydrate formation, clathrate layer separation, hydrate dissociation, centrifugal separation, and detection. Hydrate is first constructed by mixing Cyclopentane and diluted sulfuric acid at a predetermined concentration.

The jacket gradually cooled the mixture inside the reactor. When the temperature decreases to about 2.7°C, the hydrate layer is visually observed and the mix temperature is recorded on a database. The hydrate formation was completed when there was no significant change in the hydrate amount. A funnel has been used to separate the hydrate layer (as the hydrate layer is semisolid) from the remaining acid solution. The separated hydrate layer dissociated at room temperature into two layers of Cyclopentane at the top and water at the bottom. For separation between these layers, a centrifugal separator was used. The volume ratios of diluted acid to Cyclopentane to were (6:1, 4: 1, 3:1, and 2:1) with five initial concentrations (12.5%, 10%, 7.5%, 5%, 2.5%) of diluted acid (H_2SO_4). Figure 1 (a and b) shows the procedure used in the experiment.
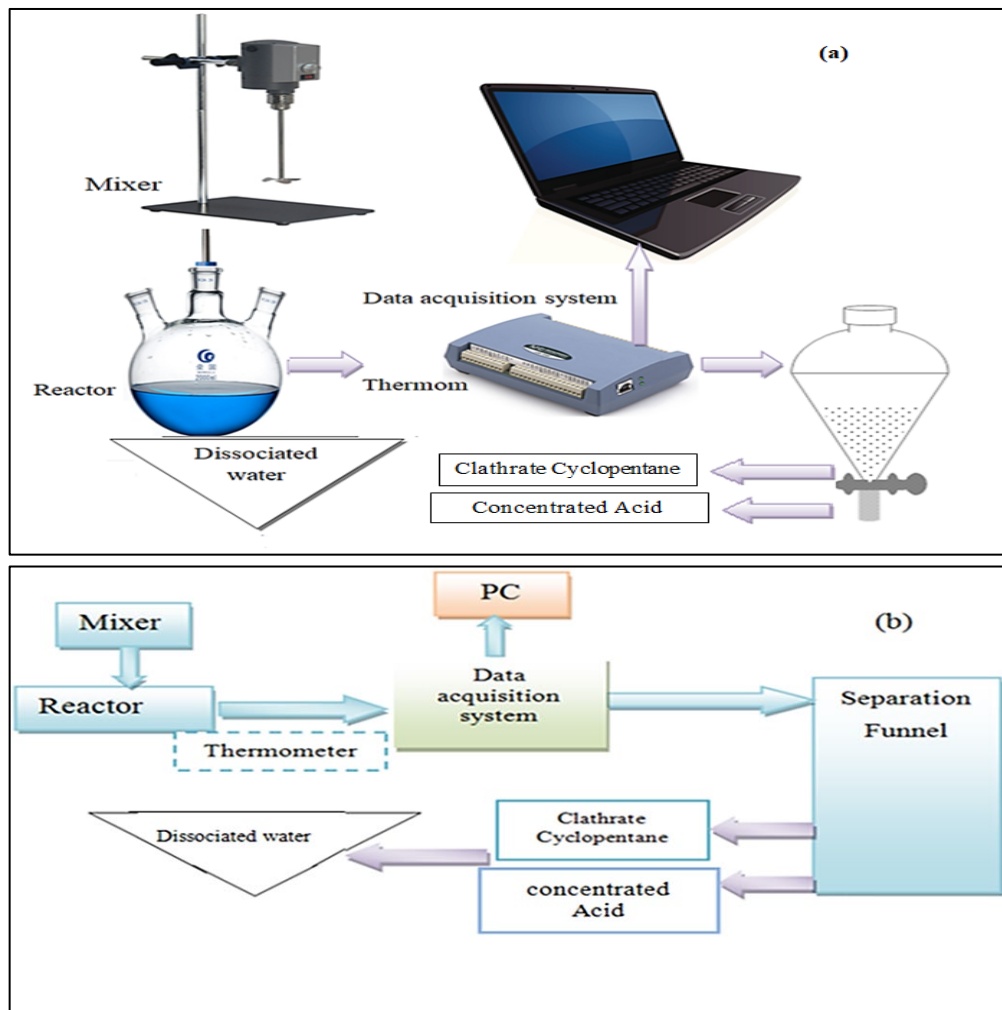
Figure 1: The experiment of the adopted procedure: (a) Devices, (b) Block diagram

The Removal efficiency (Re) is computed according to [27,28]:

$$\text{Removal efficiency } (Re) = \frac{c_O - c_1}{c_O} \times 100\% \tag{1}$$

Co and C_1 represent the initial and steady-state concentrations of diluted acid in hydrate-dissociated water.
The Enrichment Factor (Ef) is calculated according to distinguish the residual mixture [27,10]:

$$\text{Enrichment factor } (Ef) = \frac{c_2}{c_O} \times 100\% \tag{2}$$

C_2 denotes the diluted acid in the residual effluent. The yield of dissociated water is computed using the equation:

$$\text{The Dissociated Water Yield } (Yw) = \frac{V_1}{V_O} \times 100\% \tag{3}$$

V_0 represents the diluted acid solution volume, while V_1 denotes the volume of water obtained from hydrate dissociation. The concentration of the acid produced by the experiment obtained by the acid-base titration method is calculated using the following normality equation:

$$N_1 V_1 = N_2 V_2 \tag{4}$$

Where NaOH is the base, while the acid is H_2SO_4. N_1 denotes the normality of NaOH, V_1 denotes the volume of NaOH, N_2 refers to the normality of H_2SO_4, and V_2 refers to the volume of H_2SO_4. The concentration of H_2SO_4 (C) can be given as a function of its equivalent weight (Eq) by:

$$C = N_2 * Eq \tag{5}$$

For accuracy, each experiment was repeated at least three times

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3. Results and Discussion

The obtained experimental results showing the effects of Cyclopentane to volume ratio can be divided into three parts:

3.1 The Estimated Effect of Volume Ratios for Removal Efficiency as A Percentage

The calculated percentage efficiency was obtained from experimental measurements for the diluted acid removal versus different Cyclopentane to diluted acid volume ratios, which is displayed in Figure 2.

The maximum percentage efficiency obtained is (94%) at Cyclopentane to diluted acid ratios of (1:4 and 1:6) v/v. Increasing the percentage efficiency is caused by an increase in the volume ratio from 1:2 to 1:6. This increase is caused by the low concentration of spent acid in the discharge layer (C_2), which causes fewer ions at the clathrate crystallites' surfaces. During the dissociation stage of hydrate, the easily dissolved diluted acid in the water produced by the hydrate decreases the removal effectiveness.
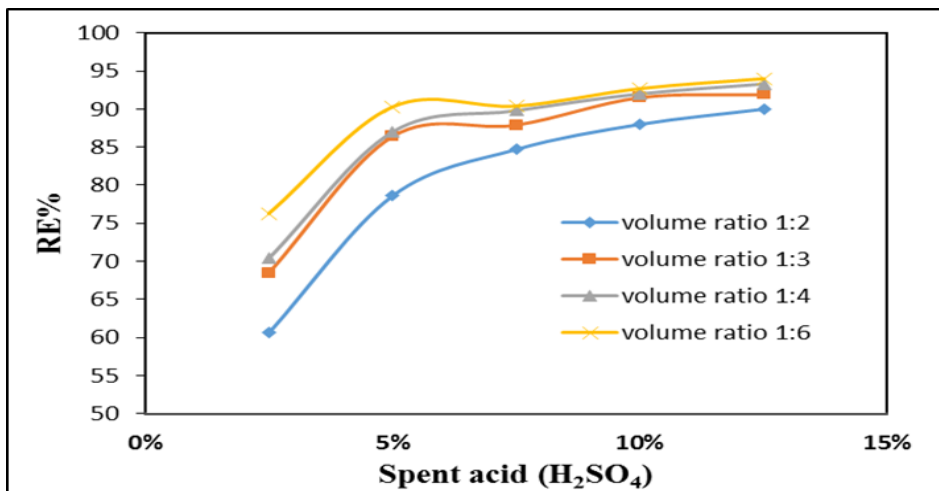

Figure 2: Percentage removal effectiveness for four diluted acids at various volume ratios to Cyclopentane at varied concentrations: diluted acid

3.2 Volume Ratio Effects on The Enrichment Factor

According to the data acquired experimentally of the enrichment factor, it has been established that as the volume ratio expands from 1:2 to 1:6, the Ef decreases accordingly, as shown in Figure 3. The data mentioned clearly indicates that the diluted acid concentration highly influences Ef (C_2). The cyclopentane proportion in the water solution is inversely proportional to the Ef. Reduced amounts of Cyclopentane lead to an increased Ef, and as a result, a significant quantity of spent acid might end up in the concentrated effluent. The highest Ef achieved in the Cyclopentane to diluted acid ratio is (16.205) (2.5%).
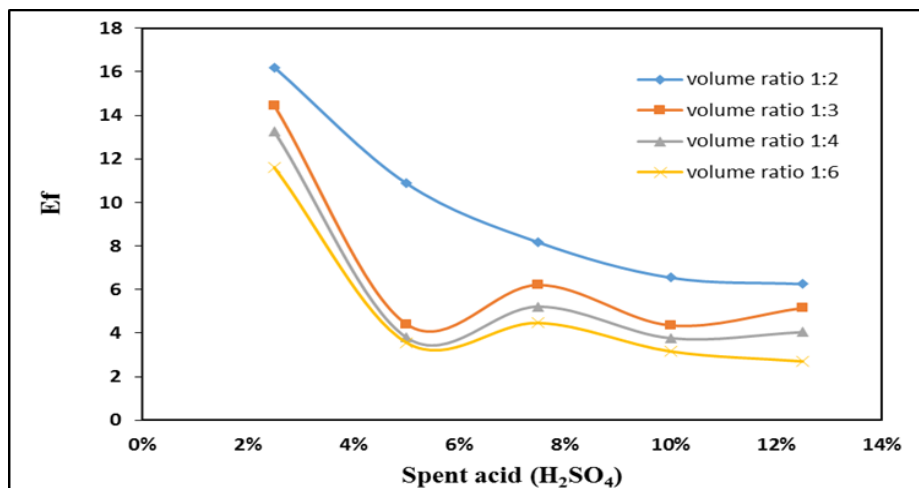

Figure 3: The enrichment factor for four spent acids at various (Cyclopentane: diluted acid) volume ratios

3.3 The Effect of Volume Ratios on The Percentage of Water Yield

According to Figure 4, an expansion in the volume ratio of (Cyclopentane to diluted acid ratio) from 1:2 to 1:6 is followed by a decline in the water yield percentage. The results indicate that hydrate crystallites are generated in higher amounts when a

higher cyclopentane is applied. Consequently, a higher percentage of water yield is also achieved at a greater cyclopentane volume. The acquired results confirm what has been obtained[29], which is that the most significant water yield percentage achieved in the experiment was (80%) at a (2.5%) cyclopentane to diluted acid ratio.
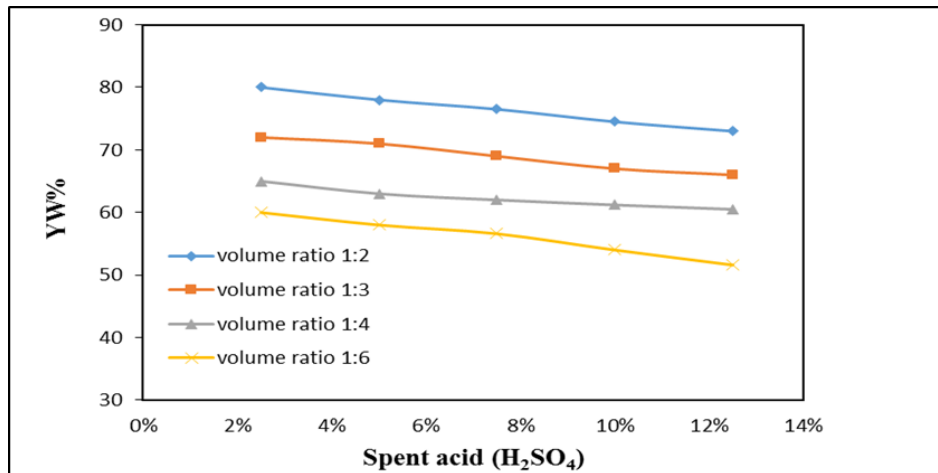

Figure 4: The percent water yield for four spent acids at various (Cyclopentane: diluted acid)

3.4 Cyclopentane-Pure Water Hydrate Formation

Figure 5 represents the hydrates generation in Cyclopentane – Pure water system at different volume ratios stretching from 1:2 to 1:6 at a temperature starting from 6°C. The horizontal axis represents the time recorded during the experiment. Hydrate was generated when the system temperature was reduced and minimized. It has been well–established during the experiment that as the volume ratio of Cyclopentane is reduced, the formation temperature, as a result, is also reduced. The final measurements indicate that the hydrate formation temperature obtained during the experiment was (2.8, 2.1, 2.8, 1.7, and 1) C° against volume ratios of (1:2, 1:2, 1:3, 1:4, and 1:6), respectively.

The results also demonstrate that higher induction time leads to a reduced cyclopentane-pure water volume ratio due to the two extended periods required to reduce the system temperature and initiate the nucleation phase. The nucleation phase is deemed the initial stage of hydrate generation because hydrate formation is an exothermic process.
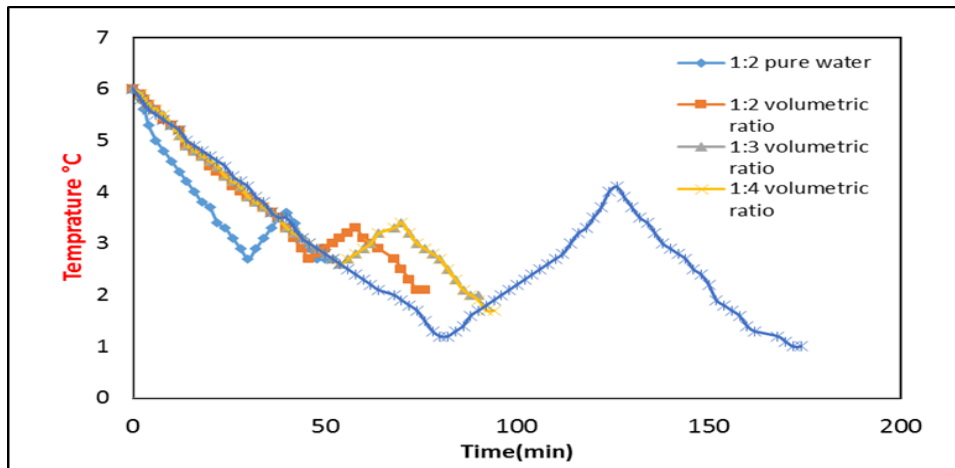

Figure 5: Temperature vs. time for forming CP clathrate at 2.5% H_2SO_4 at different volumetric ratios (1:2-1:6)

Figure 6 shows a noticeable temperature decline due to the chill, which drives the temperature down. Hydrate formation is accelerated subsequently during the administration of ice which is clear evidence of the exothermic crystallization nature. A slight temperature rise ensued. Over time, an unprecedented level of hydration was identified. The temperature stability during this process gives information on the hydrate development kinetics and thermodynamics [30].

The study aims to investigate the time-temperature behavior of cyclopentane formation and dissociation, and this field of research was selected because common behaviors were identified in other concentrations. According to the results, the initial concentration of CP clathrate (5, 7, 10, and 12.5) % significantly impacted the duration required for hydrate formation. Different Volume ratios ranging from 1:2 to 1:6 result in a different hydrate formation time and temperature, which is displayed in Figures (6,7,8, and 9).

The results were 60 minutes at 2.6°C, 84 minutes at 2.3°C, and 120 minutes at 1.6°C, respectively, for all initial temperatures.
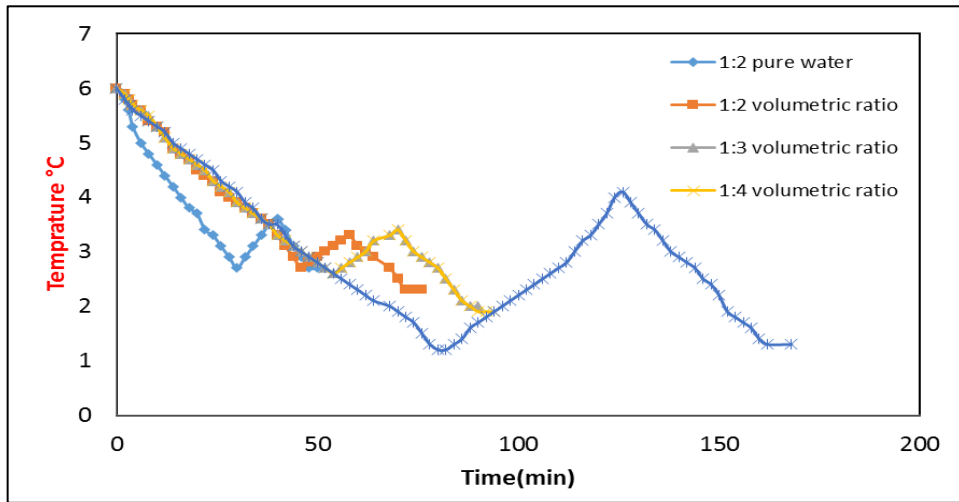
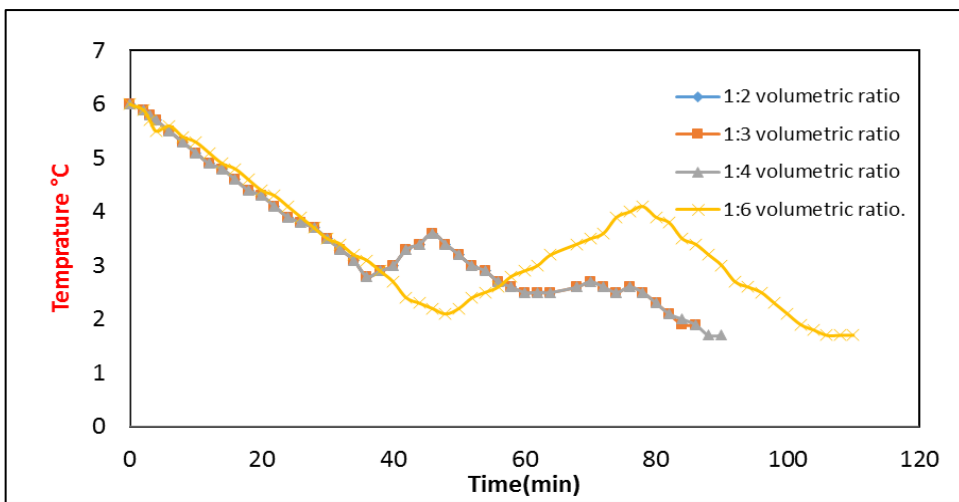**Figure 6:** CP clathrate temperature vs. formation time at 5% H_2SO_4 at various volumetric ratios (1:2-1:6)

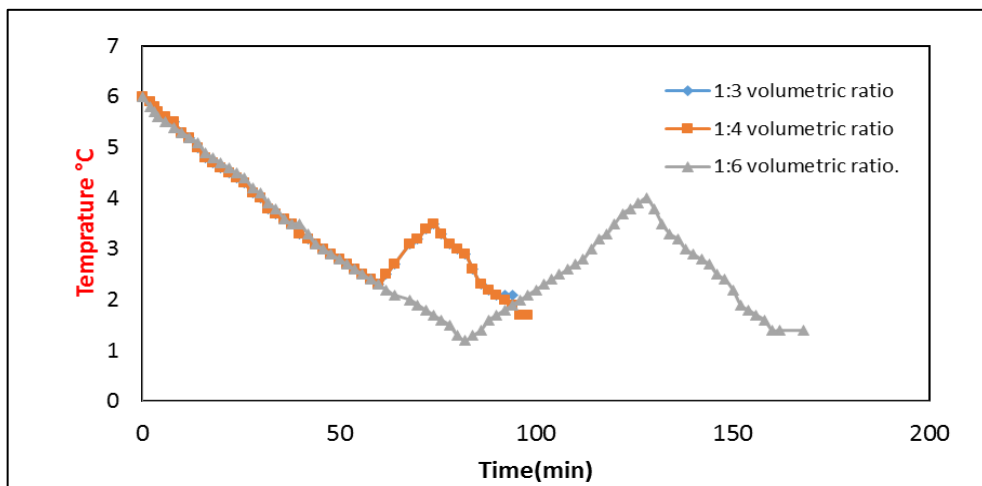**Figure 7:** Temperature vs. time of formation of CP clathrate in 7.5 % H_2SO_4 (1:2-1:6) at various volumetric ratios

Figure 8: Temperature vs. formation time of CP clathrate at 10% H_2SO_4 at various volumetric ratios (1:2-1:6)
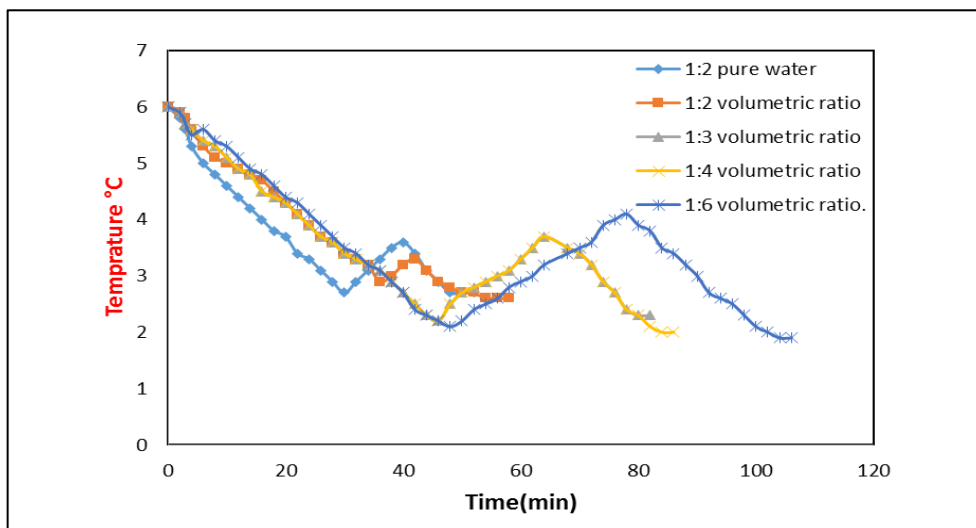
Figure 9: Temperature vs. time to generate CP clathrate at 12.5% H_2SO_4 at various volumetric ratios (1:2-1:6)

The specifications of the test samples are listed in Table 1.

Table 1 shows that the highest and the lowest value of final Concentrations were (57.5%) and (16.6%) respectively. The highest value was recorded at a 1:2 cyclopentane/water solution and a (12.5%) diluted acid concentration. In comparison, the lowest was recorded at 1:6 Cyclopentane.

Table 1: Test sample specifications

Cyclopentane/water solution(v/v)	1:2	1:3	1:4	1:6
Spent sulfuric acid	*Final concentration (wt%)*			
2.5%	33%	30%	28%	25%
5%	42.5%	20%	17.5%	16.6%
7.5%	47%	38%	33%	29%
10%	50%	36.6%	32.5%	28%
12.5%	57.5%	50%	41.6%	30%

4. Conclusion

In this work, the formation of hydrate in guest liquid for different samples to extract diluted sulfuric acid was developed. The analysis of experimental data shows the feasibility and effectiveness of recovering diluted acids from sulfuric acid. The results indicate that the maximum ratio of Cyclopentane to diluted acid ratio is (1:6) v/v. As a result, the Ef and water yield % obtained by clathrate dissociation were reduced. At a cyclopentane/ diluted acid ratio of 1:6 and 12.5% H_2SO_4 concentration, the percentage efficiency reached 96 %. Sulfuric acid attained a minimum percentage efficiency of 60.6 % at a cyclopentane/diluted acid ratio of 1:2 and a concentration of 2.5 %. With a decrease in the water volume ratio of Cyclopentane by (1:6, 1:4, 1:3, and 1:2), the hydrate formation time was increased by (60, 84, and 120) minutes, respectively. Raising the volume ratio increases removal efficiency while decreasing yield percentage and enrichment factor, as deduced.

The advantages of hydrate formation in guest liquid methods are to recover diluted acids, and various challenges continue. Additional efforts are necessary for choosing a suitable promoter, solid-liquid, and hydrate former separators to improve efficiency. This newly developed hydrate-forming procedure for spent acid separation promises helpful in acid treatment. The kinetics and thermodynamics of hydrate growth are shown by the rise, decline, and stabilization of temperature during hydrate formation because the formation of hydrates is an exothermic process.

Author contributions

Methodology, Najlaa Jabbar Lazim, and Riyadh Sadiq AL-Mukhtar; Software Najlaa Jabbar Lazim; Formal Analysis Najlaa Jabbar Lazim.; Writing-Original Draft Preparation, Najlaa Jabbar Lazim; Writing-Review & Editing, Riyadh Sadiq AL-Mukhtar. All authors have read and agreed to the published version of the manuscript.

Funding

Data availability statement

The data that support the findings of this study are available on request from the corresponding author.

Conflicts of interest

The authors declare no conflict of interest.

References

[1] A. A. Atamas, H. M. Cuppen, M. V. Koudriachova, S. W. De Leeuw, Monte Carlo calculations of the free energy of binary sII hydrogen clathrate hydrates for identifying efficient promoter molecules. J. Phys. Chem. B,117 (2013) 1155-1165. https://doi.org/10.1021/jp306585t

[2] A. M. O. Mohamed, E. K. Paleologos, F. Howari, Pollution Assessment for Sustainable Practices in App. Sci. and Eng. (2020). https://doi.org/10.1016/B978-0-12-809582-9.00019-0

[3] M. F. Kheshty, F. Varaminian, & N. Farhadian, Exploring the effect of important parameters on decomposition of gas hydrate structure I: A molecular dynamics simulation study, J. of Nat. Gas Sci. Eng., 52 (2018) 1-12. https://doi.org/10.1016/j.jngse.2018.01.025

[4] I. B. A. Sfaxi, V. Belandria, A. H. Mohammadi, R. Lugo, D. Richon, Phase equilibria of CO^{2+} N_2 and CO^{2+} CH_4 clathrate hydrates: Experimental measurements and thermodynamic modelling, Chem. Eng. Sci. 84 (2012) 602-611. https://doi.org/10.1016/j.ces.2012.08.041

[5] H. Najibi, K. Momeni, M. T. Sadeghi, A. H. Mohammadi, Experimental measurement and thermodynamic modelling of phase equilibria of semi-clathrate hydrates of (CO^{2+} tetra-n-butyl-ammonium bromide) aqueous solution, The J. of Chem. Therm., 87 (2015) 122-128. https://doi.org/10.1016/j.jct.2015.03.024

[6] M. Seif, A. Kamran-Pirzaman, A. H. Mohammadi, Phase equilibria of clathrate hydrates in CO_2/CH^{4+}(1-propanol/2-propanol)+ water systems: Experimental measurements and thermodynamic modeling, J. Chem. Therm., 118 (2018) 58-66. https://doi.org/10.1016/j.jct.2017.09.034

[7] K. Momeni, A. Jomekian, & B. Bazooyar, Semi-clathrate hydrate phase equilibria of carbon dioxide in presence of tetra-n-butyl-ammonium chloride (TBAC): Experimental measurements and thermodynamic modeling, Fluid Phase Equilib.,508 (2020) 112445. https://doi.org/10.1016/j.fluid.2019.112445

[8] H. Hassan, H. Pahlavanzadeh, Thermodynamic modeling and experimental measurement of semi-clathrate hydrate phase equilibria for CH_4 in the presence of cyclohexane (CH) and tetra-n-butyl ammonium bromide (TBAB) mixture, J. Nat. Gas. Sci. Eng., 75 (2020) 103128. https://doi.org/10.1016/j.jngse.2019.103128

[9] A. Sonune, & R. Ghate, Developments in wastewater treatment methods, Desalination, 167 (2004) 55-63. https://doi.org/10.1016/j.desal.2004.06.113

[10] S. T. AL-Hemeri, R. S. AL-Mukhtar, M. N. Hussine, Removal of heavy metals from industrial wastewater by use of Cyclopentane-Clathrate Hydrate formation technology, In IOP Conference Series: Mater. Sci. Eng., 737 (2020) 012178. https://doi.org/10.1088/1757-899X/737/1/012178

[11] S. T. AL-Hemeri, R. S. AL-Mukhtar, L. W. Mahmood, Thermodynamic and kinetic investigation of desalination by refrigerant clathrate hydrate formation, Eng. Technol. J.,37 (2019) 29-44. https://doi.org/10.30684/etj.37.1C.6

[12] E. Romanovskaia, V. Romanovski, W. Kwapinski, & I. Kurilo, Selective recovery of vanadium pentoxide from spent catalysts of sulfuric acid production: Sustainable approach, Hydr., 200 (2021) 105568. https://doi.org/10.1016/j.hydromet.2021.105568

[13] X. Chen, Y. Chen, T. Zhou, D. Liu, H. Hu, S. Fan, Hydrometallurgical recovery of metal values from sulfuric acid leaching liquor of spent lithium-ion batteries, Was. Man., 38 (2015) 349-356. https://doi.org/10.1016/j.wasman.2014.12.023

[14] K. Várnai, L. Petri, & L. Nagy, Prospective Evaluation of Spent Sulfuric Acid Recovery by Process Simulation, Per. Poly. Che. Eng., 65 (2021) 243-250. https://doi.org/10.3311/PPch.15679

[15] M. Asof, S. Arita, W. Andalia, C. Rahmayati, Recovery of H2SO4 from spent acid waste using bentonite adsorbent, In MATEC Web of Conf., 101,2017,02007 . https://doi.org/10.1051/matecconf/201710102007

[16] J. Castilla-Archilla, S. Papirio, P. N. Lens, Two step process for volatile fatty acid production from brewery spent grain: hydrolysis and direct acidogenic fermentation using anaerobic granular sludge, Proc. Bio., 100 (2021) 272-283. https://doi.org/10.1016/j.procbio.2020.10.011

[17] L. Ulloa Guntiñas, M. Martínez Minchero, E. Bringas Elizalde, A. Cobo García, & M. F. San Román San Emeterio, Split regeneration of chelating resins for the selective recovery of nickel and copper, Sep. Purif. Technol.   , 253 (2020) 117516. https://doi.org/10.1016/j.seppur.2020.117516

[18] G. Chauhan, K. K. Pant, K. D. Nigam, Metal recovery from hydroprocessing spent catalyst: a green chemical engineering approach. Indus. Eng. Chem. Res., 52 (2013) 16724-16736. https://doi.org/10.1021/ie4024484

[19] J. Charles, B. Sancey, N. Morin-Crini, P. M. Badot, F. Degiorgi, G. Trunfio, & G. Crini, Evaluation of the phytotoxicity of polycontaminated industrial effluents using the lettuce plant (Lactuca sativa) as a bioindicator, Ecoto. and envir. safety, 74 (2011) 2057-2064. https://doi.org/10.1016/j.ecoenv.2011.07.025

[20] A. Dąbrowski, Z. Hubicki, P. Podkościelny, & E. Robens, Selective removal of the heavy metal ions from waters and industrial wastewaters by ion-exchange method, Chem., 56 (2004) 91-106. https://doi.org/10.1016/j.chemosphere.2004.03.006

[21] L. Marder, A. M. Bernardes, J. Z. Ferreira, Cadmium electroplating wastewater treatment using a laboratory-scale electrodialysis system, Sepa. Puri. Tech., 37 (2004) 247-255. https://doi.org/10.1016/j.seppur.2003.10.011

[22] N. Adhoum, L. Monser, N. Bellakhal, J. E. Belgaied, Treatment of electroplating wastewater containing Cu^{2+}, Zn^{2+} and Cr (VI) by electrocoagulation, J. hazar.mater., 112 (2004) 207-213. https://doi.org/10.1016/j.jhazmat.2004.04.018

[23] S. Ahmed, S. Chughtai, M. A. Keane, The removal of cadmium and lead from aqueous solution by ion exchange with Na Y zeolite, Separa. and pur. tech., 13 (1998) 57-64. https://doi.org/10.1016/S1383-5866(97)00063-4

[24] H. Alvares-Vazquez, B. Jefferson, S. J. Judd, Membrane bioreactors vs. conventional biological, Chem. Tech., Bio., 79 (2004) 1043-1049. https://doi.org/10.1002/jctb.1072

[25] R. S. Juang, H. C. Kao, F. Y. Liu, Ion exchange recovery of Ni (II) from simulated electroplating waste solutions containing anionic ligands. J. of hazar.mater128 (2006) 53-59. https://doi.org/10.1016/j.jhazmat.2005.07.027

[26] M. Sugaya, Y. H. Mori, Behavior of clathrate hydrate formation at the boundary of liquid water and a fluorocarbon in liquid or vapor state, Chem. Eng. Sci., 51 (1996) 3505-3517. https://doi.org/10.1016/0009-2509(95)00404-1

[27] Y. Song, H. Dong, L. Yang, M. Yang, Y. Li, Z. Ling, J. Zhao, Hydrate-based heavy metal separation from aqueous solution, Sci. Rep., 6 (2016) 1-8. https://doi.org/10.1038/srep21389

[28] N. Gaikwad, R. Nakka, V. Khavala, A. Bhadani, H. Mamane, & R. Kumar, Gas hydrate-based process for desalination of heavy metal ions from an aqueous solution: Kinetics and rate of recovery, ACS EST Water, 1 (2020) 134-144. https://doi.org/10.1021/acsestwater.0c00025

[29] E. Atangana, Production, disposal, and efficient technique used in the separation of heavy metals from red meat abattoir wastewater,Env. Sci.and Poll. Res., 27 (2020) 9424-9434. https://doi.org/10.1007/s11356-019-06850-z

[30] D. Corak, T. Barth, S. Høiland, T. Skodvin, R. Larsen, T. Skjetne, Effect of subcooling and amount of hydrate former on formation of cyclopentane hydrates in brine, Desa., 278 (2011) 268-274. https://doi.org/10.1016/j.desal.2011.05.035