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Study of The Influence of Different Variables on Clathrate Practical Applications in Phenol Removal

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KEYWORDS

Clathrate system, Cyclopentane, Enrich factor, liquid guest, Phenol.

ABSTRACT

In this work, effluent wastewater treated by using cyclopentane-water Clathrate system to treat water contaminates with phenols at concentrations (300, 250, 200, 150, 100 and 50) ppm in order to investigate the capability of process performance. Clathrate or hydrate are strong crystal structures including water (host particles) and little particles (guest particles). The experiments were conducted at different cyclopentane-water volume ratios (1: 2 and 1: 4). The work was done in a 250 ml glass cell with an electric mixer at a constant speed of 280 cycles per minute. Phenol was highest removal percent at 300ppm at 1: 4volume ratio was (92.3%), while the lowest concentration at 50 ppm and 1: 2volume ratio was (55%). Yield and Enrich factor had the highest values at the lowest concentration 50ppm and 1:2 volume ratio were (85% and 2.42) respectively. The technique of the Clathrate proved that it has a high capacity in the separation and achieve high removal percentage compared to other methods at standard conditions when the pressure of 1 atmosphere and temperature higher than the degree of freezing water and less economic costs compared to other methods..

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1. Introduction

Compounds which involve of phenol are pollutants high poisonous even when at low composition. Effluent water from industrial processes especially that from oil refinery and factories of coking contain quantities of phenols [1]. Water contaminated with phenol less than 0.02 mg /l is considered unpolluted water. The concentration level of phenols in drinking water is considered by WHO's guidelines for drinking water quality as 0.001 mg /l and the phenol concentration in industrial effluents above 50mg/l. [2]. Discharge of phenolic compounds that are available in the effluents of different enterprises such as pharmaceuticals, petrochemicals, oil refining, pulp paper, resin manufacturing, plastics, paint, coking activities and wood items without treatment may prompt genuine dangers to people, animals and aquatic revival [3-6]. The National Pollutant Release Inventory (NPRI) and Environmental Protection Agency (EPA) in Canada identified the phenol as a dominion pollutant. The toxicity levels usually are in the range 9–25 mg/l for both humans and aquatic life [7]. Human exposure to phenol results in the irritation of the skin, eyes and mucous membranes. Constant introduction to phenols prompts aggravation in the gastrointestinal and focal sensory systems and liver, kidney, and cardiovascular tissues in creatures [3]. The phenol effects on animals had shown fetal body weight reduction, development hindrance and irregular advancement in the posterity. Therefore, there is a need to treat wastewater influenced with phenolic mixes before release. Treatment of wastewater effluent from industry is any procedure that isolates and evacuate contaminants out of process waters, or profluent. These contaminants incorporate oils, suspended solids, disintegrated heavy metals and organic mixes, for example, phenol. Many points are set to decide the reasonableness for release of pollutant [8]. A pollutant is considered a dangerous if it is reactive, ignitable, toxic or corrosive. Ninety-five chemicals have been defined as toxic including phenol based on production volume, exposure, and biological effects [9]. Phenolic substances are used in many industrial processes as shown in Table 1. Various methods have been used for removing phenol from aqueous solutions and each of them has several advantages and disadvantages. Conventional methods have been applied to remove phenol out of waste water for example, extraction method , distillation , adsorption , oxidation for wet air, wet air oxidation using catalyst, and biodegradation [6]. A scientific survey recommended that the suggested methods for high phenol concentration are liquid–liquid extraction, evaporation, membrane-based solvent extraction, adsorption, and distillation, whereas the useful methods in low phenol concentrations are biodegradation, chemical, electrochemical, and photo catalytic oxidation, solid phase extraction, ozonation , reverse osmosis/nano filtration, and wet air oxidation [7].

Table 1: Levels of phenol reported in industrial wastewater [10].

Industrial source for phenol	Concentration of Phenol (ppm)
Refineries of oil	40 – 185
Petrochemical	200 -1220
Textile	100 – 150
Leather	4.4 - 5.5
Coke ovens (without dephenolization)	600–3900
Coal conversion	1700-7000
Ferrous industry	5.6 - 9.1
Rubber industry	3 – 10
Pulp and paper industry	22
Wood preserving industry	50 – 953
Phenolic resin production	1600
Phenolic resin	1270 – 1345
Fiberglass manufacturing	40 –2564
Paint manufacturing	1.1

Wastewater discharged contain phenol to the environment increasingly has faced more rigorous standards, therefore factories should remove phenol out of wastewater to protect environment and people. Since, there is an increasing need for new method to remove phenol, Clathrate -based separation appears promising correlational research into purification and separation of pollutants.

Hydrate or Clathrate hydrate is a type of non-stoichiometry solid crystalline structures involved from host molecule and guest molecule [11]. Host molecules are water molecules that form the lattices in a cage structure by hydrogen-bonded. Guest molecules gas or liquid are enclosed within water cavities consisting of hydrogen bonded water molecules such as (CH_4, CO_2, C_2H_6, C_5H_{10}, tetrahydrofuran (THF), cyclopentane (CP), refrigerant’s gases, etc.) [12]. For forming stables hydrates, lower-molecular-weight gases such as carbon dioxide need lower temperatures and higher pressures. Whereas part compounds for example tetrahydrofuran (THF) and cyclopentane (CP) form Clathrates at atmospheric pressure and avoiding the use of high-pressure equipment and flammable gases [13,14].

The two components (guest and host) are not chemically connected, it physical interaction molecules under appropriate thermodynamic conditions. The mechanism of Clathrate formation is principle completely dissimilar from ice as shown in Figure 1. Ice formation could be a bulk normal action of water from fluid to hard. In comparison, Clathrate crystallization includes additional molecule guest in addition to H_2O [15,16].

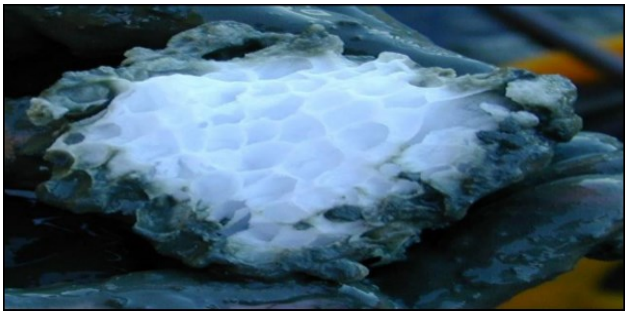

Figure 1: Crystal forming of Clathrate-hydrate [17]

As early as Clathrate formation was proposed as a technique to produce potable water from saltwater, which has recently expected considerable attention, and noted that Clathrate excludes the salt ions from the crystal structure which provides the theoretical foundation for separating mixtures in a Clathrate -based method [18]. Moreover Ngema et al. [19] proposed a process for forming purified solute from an aqueous combination of solute and water. For separation of organic mixtures, Frois et al. [20]studied the concentrations of orange , apple, and potato juices using methyl bromide, trichlorofluoromethane, and 1,1- difluoroethane, and reported that their method reduced 80% of the water content. Therefore, based on the theory and previous achievements, a Clathrate-based method is proposed for separation of phenol from mixture solution. Dirdall et al. [21] presented that the equilibrium temperature for cyclopentane hydrate formation is approximately 7.7 °C and since, these hydrates are structure II and formed at atmospheric pressure. Sefidroodi et al. [22] investigated the impact on formation of cyclopentane hydrate for different degrees of superheating and timespans. It was discovered that gave the superheating (7.7 °C)above the temperature of equilibrium for cyclopentane hydrates was close to 2–3 °C, could reliably acquire hydrates a lot quicker during cooling to 0.0 °C than if hydrates were shaped from the liquids just at the first time. Abdulkader B. [23] studied the cyclopentane hydrate systems have been investigated to determine the effects of three additives used for enhancing the kinetic rate using two types of surfactants tween20 and tetra-hydro-furan (THF) in two proportions of water for formation the hydrate so as to accomplish a set of experimental data to assessment. Zylyftari et al. [24] experimentally reported the impacts of cyclopentane hydrate nucleation on the properties of hydrate shaped and investigated the rheological properties of density-matched 40% (v/v) aqueous fraction hydrate-forming emulsions. Hashemi et al. [3] indicated that the toxicity of phenol even at low concentration methods will be suggested for each concentration range at the influent and, of course, is allowable in the final effluent. Delroisse et al. [25] investigated cyclopentane hydrate formation to measure phase change properties where, the technical system made it possible to form pure CP-hydrate with complete conversion of water to hydrate. Mustafa [26] conclude that Clathrate system was powerful in expelling colors or diminishing their fixations in water, where colors utilized in this examination was iodopovidone with focus 100 mg/l and permanganate of potassium with grouping of 60 mg/l. The expulsion proficiency increments with including the promoters this expands the water sum that delivered by the hydrates. Shurooq et al. [27]investigated a removal of the heavy metal ion Cu^{2+}, Ni^{2+}, Zn^{2+} and Cr^{3+} from Industrial wastewater by using of cyclopentane - Clathrate hydrate formation technology where, Clathrate for ternary systems (cyclopentane, water and ionic salt) examine hydrate formation at different sorts and concentrations of salts in the liquid state at temperature below 7 ºC and 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 were discussed.

In this work cyclopentane was used as liquid former for Clathrate, cyclopentane Clathrate -forming mixtures in the presence of phenol and forms the cubic hydrate structure II at temperature near 280 K and under atmospheric pressure. Cyclopentane had a high temperature at equilibrium to get as same level of sub cooling as possible and was cheap enough for using in bulk quantities on a regular basis. The major aims of the present work to investigate the effect of water contaminated with phenol on the Clathrate formation (water +cyclopentane) system in addition to calculate the percentage removal ratio, water yield and enrichment factor at different phenol solutions experiments.

2. Experimental Work

I. Experimental Chemicals

The main chemicals used are cyclopentane, distilled water and phenol. The formula and the supplier are shown in Table 2.

Table 2: Properties of Materials, Formula, Purity and Supplier.

Materials	Chemical formula	Purity	Supplier
Distilled Water	H_2O	-	Laboratory double distillation
Cyclopentane	C_5H_{10}	98.0%	Sigma Germany
Antifreeze Ethylene glycol	$(CH_2OH)_2$	99.0%	J.T.Baker India
Phenol	C_2H_5	99.0%	Fluka Germany

II. Experimental Setup

The experimental set up shown in Figure 2 includes:

- Hydrate formation
- Hydrate separation
- Hydrate dissociation
- Analysis

The Clathrate formation cell was a round bottom three neck flask immersed in coolant inside a water bath excepting the bottlenecks. The stirrer fitted inside the cell at constant rotation speed 280rpm, two thermocouples type K placed into the first neck and the third, reading temperature inside the cell throughout Clathrate formation, the thermocouples were associated with the interphase type (MAX6675 Temp Module Arduino). The information was transmitted to the laptop by consequent program as appeared in Figure 3. The reading of a thermocouple was standardized by using mercury thermometer at various temperature as be seen in Figure 4. The cooling bath was set at 1 ^{o}C, so as to reach steady sub-cooling temperature in the reactor to keep reactor temperature at certain temperature, the cooling liquid was used water and ethylene glycol ratio (1:3) v/v, supplied by chiller type Julabo F10-Ve model, and the chiller was supplied with PID control to keep the temperature with in ± 0.1 ^{o}C.

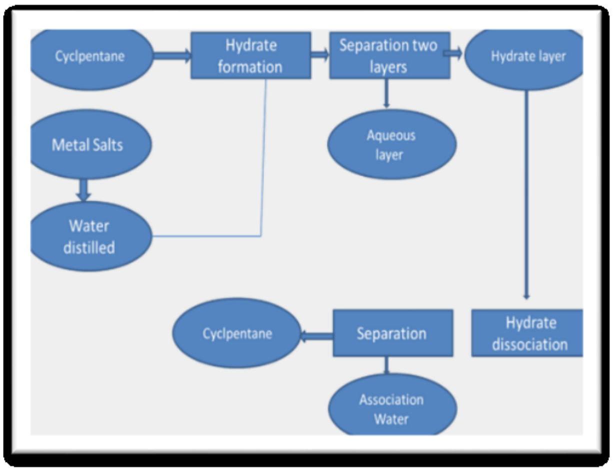

Figure 2: Flow chart for experiments that separate pollutants from wastewater

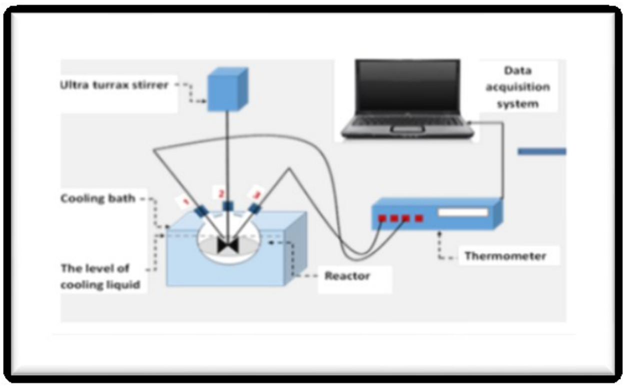

Figure 3: Hydrate formation cell for removal phenol

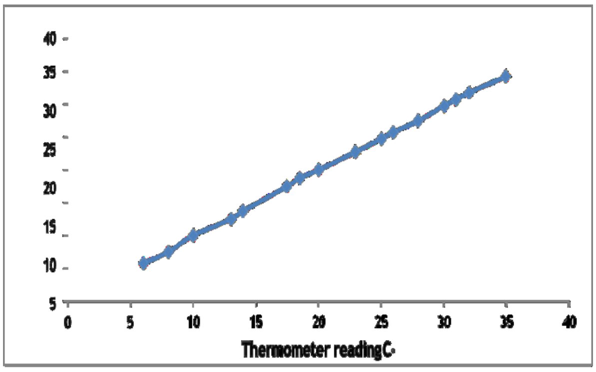

Figure 4: Calibration of the temperature sensor, the actual temperature

III. Experimental Procedure

This work describes the preparation of liquid-based hydrate forming samples each composed of cyclopentane and distilled water contaminated with phenol. The specification of test samples is presented in Table 3.

Table 3: Experimental ranges for Phenol

Cyclopentane-Wastewater Volume ratio (V/V)	Initial concentration C∘ (mg/L)					
1:2	50	100	150	200	250	300
1:4	50	100	150	200	250	300

The first step was to prepare water contaminated with phenol. The contaminated water prepared by taken 250 ml of distilled water then added certain volume of phenol, mixed by stirrer, then dilute contaminated water to the required concentration for each experiment. Then, cyclopentane poured to the flask with the stirrer kept running, the mixture cooled down by chiller till it reach the temperature about (2.7-1.6) ^{o}C depends on cyclopentane- water volume ratio. The hydrate began to appear. The temperature recorded till it was kept constant. Separating funnel was used to separate hydrate layer out of aqueous layer, the hydrate layer dissipated after raising the temperature to (5-7) ^{o}C and broke up into two layers: cyclopentane and water because cycolpentane is immiscible with water. It can be used after hydrate dissociation one more time to next experiment, the separated cyclopentane was pure without phenol. The next step was to separate cyclopentane and dissociated water by using centrifuge (origin: Almena), and time of centrifuge was 15 min with 280 rpm. The concentration of phenol in obtained water conducted by U.V-1100 spectrophotometer (Chrom Tech / Chine) at maximum wavelengths of the phenol (λ max= 274 nm). A calibration curve of absorbance versus concentration of phenol was constructed using standard hydrate solutions phenol as shown in Figure 5. The obtained measurements were plotted resulting the relation in 1st order of polynomial.

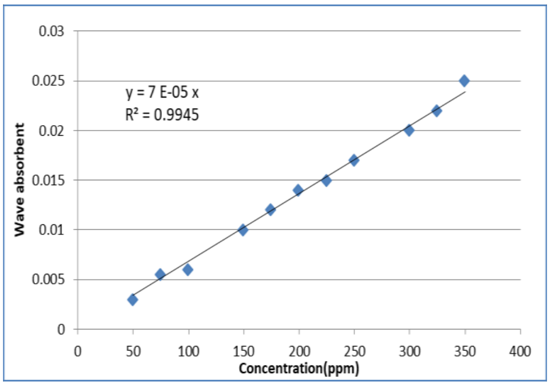

Figure 5: Phenol standardization at various concentrations by Ultraviolet–visible Spectrophotometry

Percentage removal efficiency (Re) % was calculated as follows [28]:

$Re = (C_o - C_1) / C_o \times 100\%$ (1)

Where

C_o : Initial concentration of phenol in water solution (ppm)

C_1: Concentration of phenol in the water of hydrate dissociated (ppm)

To distinguish the remainder drainage, the enrichment factor (Ef) was calculated as follows [29]:

$(Ef) = C_2 / C_0$ (2)

Where,

C_2: Concentration of phenol in the residual effluent (ppm)

And, the yield of dissociated water was calculated as follows [18]:

$(Yw) = V_1/V_0 \times 100\%$ (3)

Where

V_0: Initial volume of phenol solution (L)

V_1: Volume of water obtained from hydrate dissociation (L).

3. Results and Discussion

I. Visual Observation

The visual observation of cyclopentane –pure water system, and for cyclopentane- wastewater system in the reactor, during the hydrate formation, was done in this work. As shown in Figure 6, a main amount of a little homogeneous solid substance of a Clathrate stuck was made which could be seen into the aqueous during the main Clathrate formation. As the formation rate of the hydrate increased, the hydrate could be observed very distinctly. When the aqueous is cooled and the temperature is steadied, the crystals spray covered the whole surface of the aqueous. Which mean whole the liquid cyclopentane in the aqueous mixture is spent, and the Clathrate formation, the ice solid-like crystals at the beginning was floating in the extra water, then the solution was transformed as emulsion due to the increase hydrate formation, as defined Ohmura et al. [30].

Figure 6: Pictures had been taken for cyclopentane – waste water contaminated with phenol

II. Cyclopentane - Water Pure Hydrate Formation

Figure 7 explains the hydrate formation of cyclopentane - pure water system for different volume ratios from 1:2 to 1:6, the initial temperature was 6 °C. The system cooled down to allow for hydrate formation, it was noticed that when the volume ratio increased, the formation temperature decreased too. From the figure, the hydrate temperature started at 2.7 °C when the volume ratio of 1:2 while it was 2.2 °C and 1.8 °C for volume ratio of 1:4 and 1:6 respectively.

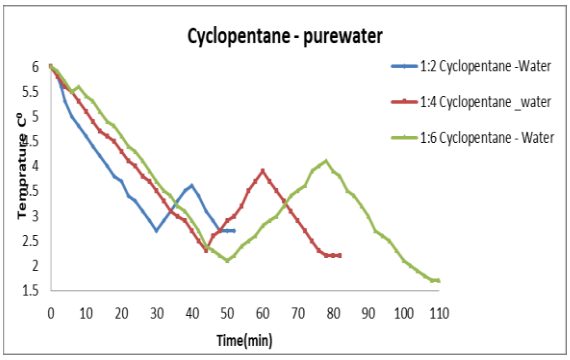

Figure 7: The formation Cyclopentane - pure water system at volume ratio 1:2, 1:4, and 1:6

III. The time of Clathrate formation in presence of phenol

Figures 8-13 show the results obtained for the conducted experiments of cyclopentane – water waste with phenol hydrate at different volume ratios (1:2, 1:4), the experiments was also conducted for different phenol concentrations from (300 to 50) ppm. The results indicate that phenol concentration did not effect on induction time, but the only essential effective parameter on the induction time was the volumetric ratio between cyclopentane and water. It is very clearly obvious in the following figures that decreasing in volume ratio leads to increase induction time. The induction time plays an important role to describe the nucleation pending a formation of the hydrate, where beginning the growth inside a critical size for stable nuclei which known as processes of nucleation [17].

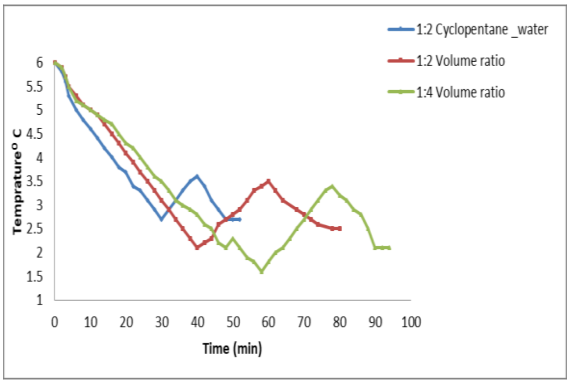

Figure 8: Formation rate CP Clathrate with phenol at 300 ppm and volume ratio 1:2 and 1:4

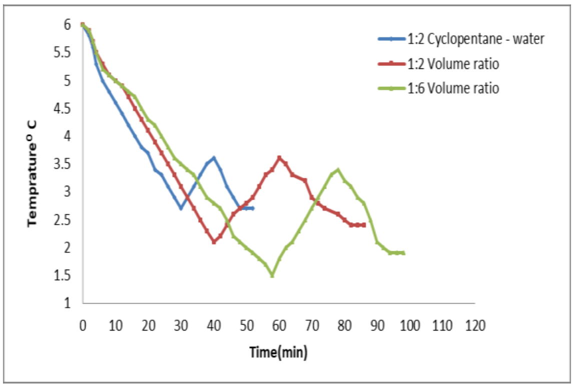

Figure 9: The formation rate CP Clathrate with phenol at 250 ppm and volume ratio 1:2 and 1:4

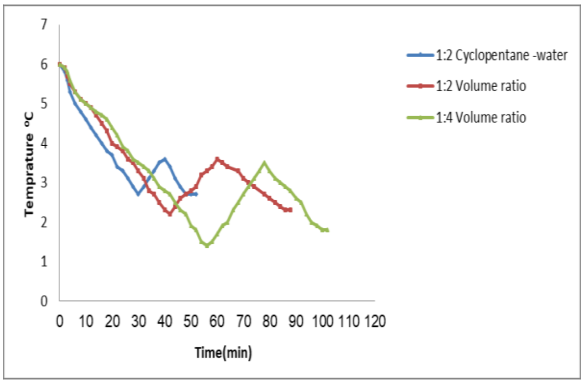

Figure 10: The formation rate CP Clathrate with phenol at 200 ppm and volume ratio 1:2 and 1:4

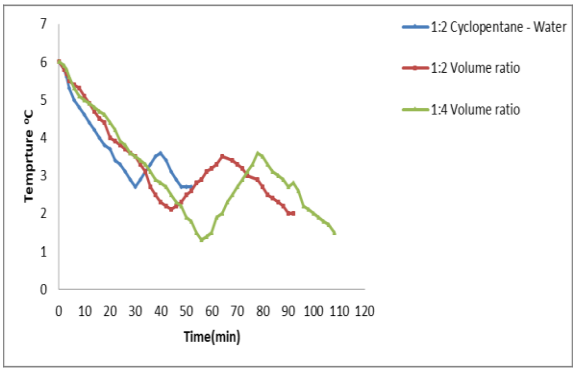

Figure 11: The formation rate CP Clathrate with phenol at 150ppm and volume ratio 1:2 and 1:4

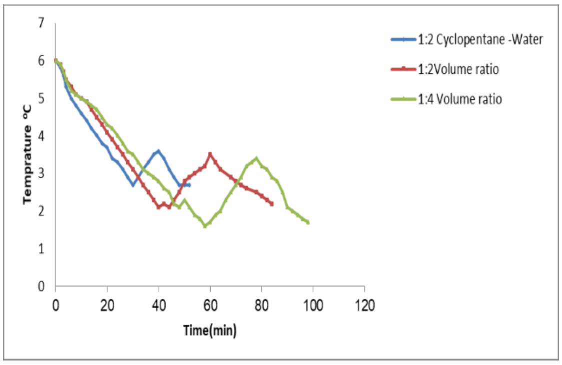

Figure 12: The formation rate CP Clathrate with phenol at 100ppm and volume ratio 1:2 and 1:4

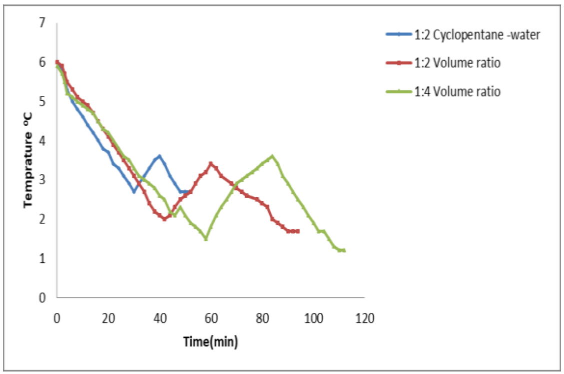

Figure 13: The formation rate CP Clathrate with phenol at 50 ppm and volume ratio 1:2 and 1:4

IV. Effect of initial concentrations on the removal ratios

As shown in Figure 14, it is clear that the removal phenol percentage increased with phenol concentration increasing and with the change in the volume ratio from 1:2 to 1:4. At the concentration of 300 ppm, the removal ratio was 92.3% with volume ratio 1:4, but when the volume ratio 1:2, the removal dropped to 73.5%. The experiment results at 50 ppm phenol concentration, the removal ratio was 65% with the volume ratio 1:4 and at the volume ratio 1:2, the removal percent was 55%.The percentage of efficiency increased when the volume ratio changed between 1:2 and 1:4, because the phenol at low concentration in discharge layer (C_2) causes the adhesion of less phenol on the surface of the Clathrate crystallites. Then, at the hydrate dissociation stage, phenol 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 1:4 of cyclopentane –wastewater. The results showed the same trend as obtained by Song et al. [18].

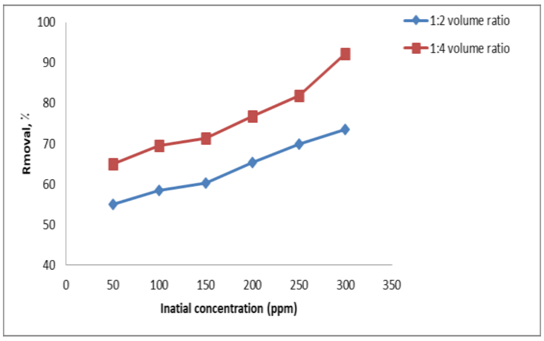

Figure 14:The relationship between initial phenol concentration and removal percent at (1:2, 1:4) volume ratio

V. Effect of initial concentrations on the water yield

The results showed that water yield decreases at higher phenol concentrations, it was also decrease with decreasing volume ratio as shows in Figure 15. The water dissociated at volume ratio 1:4 was lower than 1:2. The highest yield gained was 85% at volume ratio 1:2, while the lowest value 71% at volume ratio 1:4 phenol concentration was 50 ppm at phenol concentration 300 ppm the yield was 74% at volume ratio 1:2, but yield was 60% at volume ratio 1:4. Higher cyclopentane-effluent volume ratio meaning 1:2 contributed to the higher yield of the dissociated water with lower removal efficiency. Lower cyclopentane–water volume ratio results in higher removal efficiency but lower yield of dissociated water, as described [18]. This could be enhanced by subjecting a residual effluent to a second turn of the hydrate formation. When the advance speed of the hydrate front is high, there is not enough time to diffuse the liquid phase to the uniform concentration, leaving the concentration of the hydrate front high, and impurities easily transferred into hydrate, as described Fujioka et al. [31].

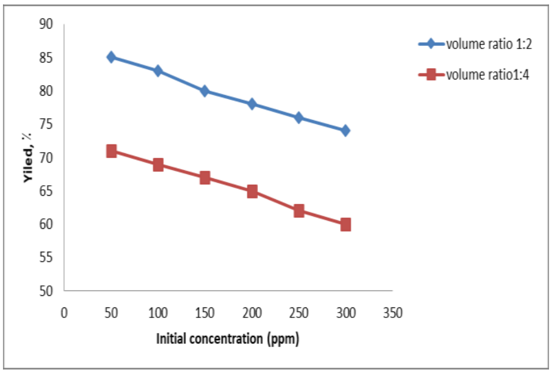

Figure 15: The relationship between initial concentration and yield percent at volume ratio (1:2 and1:4)

VI. Effect of initial concentrations on Enrich Factor

The results showed that the enrich factor (Ef) decreases with phenol concentrations increasing. At 50 ppm concentration and 1:2 volume ratio, the enrich factor was 2.42, while at 1:4 volume ratio, it decreased to 2.13. At concentration 300 ppm, it was 1.89, 1.69 at volume ratio 1:2, and 1:4 respectively. From Figure 16, it was noticed that as the initial concentration of phenol increased, the enrichment factor decreases, 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 phenol concentration in the discharge and then decrease the enrich factor. So, it was increasing the enrichment factor by increased volume of hydrate former, i.e. the cyclopentane to phenol solution to increase the production quantity of hydrate crystallites, as studied by [18, 29].

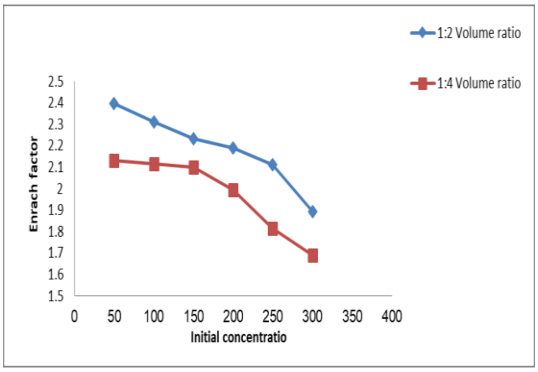

Figure 16: The relationship between initial concentration and enrich factor for phenol at (1:2, 1:4) volume ratio

4. Conclusion

Hydrate formation of pure water – cyclopentane system was studied, the hydrate formed at 2.7 ^{o}C. Water contaminated with phenol hydrate temperature was 2.4 ^{o}C. The formation temperature reduced to about 0.3 ^{o}C less, the experiments conducted at 1 atmospheric pressure.

Hydrate formation of waste water – cyclopentane (contaminated with phenol) behavior at different concentration, where increased initial phenol concentration led to decrease (Ef) and (Yw), however they caused an increase in the removal efficiency. The increased in the waste water – cyclopentane volume ratio effects on the increased in phenol removal efficiency but decreased in Enriched factor and the water Yield percentage.

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