

EVALUATION OF VERSATILE ULTRASONIC EFFECTS ON DEGRADATION OF ORGANOMETALLICS FROM PETROLEUM

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(received November 2002, accepted January 2003)

Abstract : Ultrasonication process with the help of chemical additives was evaluated as means of removing metal organic compounds in different operating conditions of power intensity, pulse cycle, surfactant, oxidant, solvent, temperature, pH value, and reaction time. This paper attempts to find an economical process by promoting the effect of ultrasound. Particularly, control of the energy output of ultrasound can be manipulated through the alteration of power intensity, pulse cycle, and many other parameters.

It was found that an ultrasound with a higher intensity increased the sonochemical effects. The decomposition and demetallation efficiency of NiTPP (nickel tetraphenylporphyrin) and VOTPP (vanadyl tetraphenylporphyrin) increased linearly with an increase of power intensity. Higher pulse cycle mode generally showed a higher decomposition efficiency of NiTPP. 80% of pulse cycle was similar to 100% of pulse cycle, continuous operation with respect to the removal efficiency. During the sonication time, concentration of model compounds decreased gradually. Within the 60-min scale, 92.9% of NiTPP and 88.8% of VOTPP were removed. Also, chlorinated solvents increased the ultrasonic effects. Selecting the appropriate solvent, surfactant, oxidant, operation temperature, and reaction time will make a big difference in saving the cost of the system when ultrasonication process is feasibly implemented.

Key Words : decomposition, demetallation, metalloporphyrin, oxidant, power intensity, pulse cycle, solvent, surfactant, ultrasonication

INTRODUCTION

Potentially toxic metals/metalloids have globally and omnipresently contaminated the earth's ecosystem. It has been worse with increasing populations and their requirements for natural resources and metal products. The health impacts of pollution from the ingestion of heavy metals/metalloids via respiration, food, and drinking water are often persistent and manifest themselves in many ways in human body, creating such ailments as critical organ dysfunction,

concomitant suffering, incapacitation, and many other acute and chronic illnesses. This is initiated by many mechanisms such as mobilization, interaction, deposition, and accumulation of metals in source systems and earth ecosystems.

Nearly all heavy oils contain a relatively high portion of contaminants like sulfur, nitrogen, oxygen, metals, and many derivatives of these compounds. These metals are sometimes in excess of 1,000 ppm.^{1,2)} Among the metals, nickel and vanadium are the most abundant in natural petroleum.¹⁾ A porphyrin is a symmetrical macrocyclic tetrapyrrole structure consisting of two dipyrrolic units. The most common compound is metalloporphyrin, formed when a

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metal atom displaces two central hydrogen ions from the porphyrin ligand. In other words, metals are strongly chelated or complexed in porphyrinic ligands that are completely stable and compatible in the form of petroleum. Due to the structural properties of metal-porphyrinic compounds, decomposition or demetallation of these compounds is difficult to achieve.

Metalloporphyrins (nickel and vanadium) are concentrated in the high molecular weight fraction of the asphaltenes. Nickel and vanadium increase with the asphaltic content of the crude oil. Normally, lighter oils contain fewer metals. Metalloporphyrins in natural petroleum are known as poisonous inhibitors to catalysts in the catalytic cracking processes of the heavy oil refinery industry, and are apt to pollute the air in a petroleum-based power plant.

NiTPP and VOTPP were taken as examples to identify the most optimum removal conditions under the UACP (Ultrasound-Assisted Chemical Process), which has widely and effectively utilized in desulfurization, denitrogenation, demetallization, and toxic compounds removal in one way or another. This process will help alleviate metal pollution problems in the earth's vast array of living environments.

In this study, the ultrasonic effects were evaluated through comparison with previous works by many other researchers. First of all, a variety of research studies have been conducted in the past for monitoring the intensity of ultrasonic energy in different chemical reactions. Jellinek³⁾ examined the kinetic studies for the ultrasonic degradation of polystyrene, indicating the rate constant of degradation of polystyrene increased linearly with an increase of ultrasonic intensity. Chen et al.⁴⁾ in their studies for ultrasonic oxidation of phenol with a high frequency of ultrasound, also concluded that the oxidation rate of phenol increased with increasing ultrasonic power intensity and there was no optimum intensity found.

Mason et al.⁵⁾ found out that 50% pulse cycle mode was similar to the continuously sonicated reaction (100% pulse cycle mode) in terms of

oxidation rate of tetrahydronaphthalene (THN). It was concluded that continuous sonication is not necessary to achieve the highest enhancement of reaction, particularly when the process is applied to large scale since the pulse cycle mode is strongly related to energy saving. Orzechowski et al.⁶⁾ also added that conductivity changes did not make a difference between 100% pulse mode operation and 80% pulse mode for the degradation of chlorinated hydrocarbons in water.

Lin et al.⁷⁾ investigated the performance of many different kinds of surfactants under ultrasonic reactions. Cationic, anionic, and nonionic surfactants were tested through surfactant screening and hydrogenation of asphaltene. Span 20 was shown to be the best performing surfactant for upgrading the asphaltenes into lighter fractions. According to Tu et al.⁸⁾, the removal efficiency increased with an increase of surfactant content (% v/v of water). The increasing degree of destruction rate was about 15% at 0.05% of surfactant content for both copper and nickel phthalocyanine. Good emulsification is favorable for promoting the reactions by supplying the large surface areas in the surfactant system. The increasing rates slowed down when the quantity of surfactant was in excess of 0.05%.

Tu et al.⁸⁾ studied the effect of hydrogen peroxide as an oxidant on the decomposition of metallophthalocyanine (Cu- and Ni-phthalocyanine). Addition of oxidant generally boosted the reaction with increasing removal efficiency. Maximum increment of destruction efficiency was 6% for both model compounds. Excessive amount (> 2.7%) of oxidant slightly retarded the removal reactions of metallophthalocyanine due to radical's scavenging effect.

Careful selection of solvent type can positively affect the ultrasonic irradiation. Tu⁸⁾, Kim⁹⁾, and Shiu¹⁰⁾ discussed the performance of different solvents and synergistic effect from the various ratios of solvent mixture. Mostly, chlorinated type solvents have showed better performance than any other organic solvents. Chloroform was the best as a single solvent and cosolvent.

The effect of operating temperature on the efficiency of ultrasonication should not be underestimated, since the factor of temperature is known to affect the cavitation threshold. The threshold limit has been found to increase with the lowering of temperature.¹¹⁾

EXPERIMENT

Materials

The model compounds used in this experiment are nickel tetraphenylporphyrin (NiTPP), vanadyl tetraphenyleporphyrin (VOTPP) purchased from Strem Chemical, Inc. (Newburyport, MA). Chloroform was employed as a solvent. The stock solution of 100 mg/L initial concentration of NiTPP was prepared in chloroform and used for all of the following experiments. Deionized/distilled (D/D) water with 2.7% (v/v of water) of hydrogen peroxide was used as an oxidant. Two surfactants, Span 20 and Tween 80 purchased from Aldrich Chemical Company and J.T. Baker Chemical Company, respectively, were utilized as surfactants. Ultrasound equipment unit (VCX-600) was used, manufactured by Sonics & Materials Inc.

Sample Preparations

Nickel tetraphenyl porphyrins (NiTPP) is a solid compound at room temperature and has poor solubility in some solvents; heating is needed to dissolve this compound in the solvent. However, this organometallic compound is easily oxidized when exposed to oxygen, given that the solid compound is dissolved into the required solvent. The oxygen dissolved in the required solvent is sufficient enough to convert a significant fraction of metalloporphyrinic forms to non-porphyrinic forms.^{12,13)} Therefore, the argon gas at 5 psig was introduced into the organic solvent with the required quantity of samples to help keep an inert environment where reactions occur. The mixture was stirred for two hours to completely dissolve samples. After two hours of stirring, the mixture solution was filtered through 5 μm filter papers to remove undissolved

metallo-compounds. It was found that the mass balance of model compound was well matched after filtration. The filtered solution was stored in black bottles and then filter papers were dried and weighed to obtain the solubility limit of this compound in the required solvent.

Sonication Process

For each individual run, 5 mL of sample solution was pipetted into the reaction vessel (150 mL beaker) containing 50 mL of deionized water with 0.05% Span 20 and 2.7% of hydrogen peroxide. The horn probe of ultrasound was directly immersed into the reaction vessel at a depth of about 1 cm for every running of experiment. The ultrasonic reaction was performed in the mixture of solution in open system. A 3 psig of pure argon gas was applied to the vessel to prevent oxygen from dissolving into mixture solution and thus achieving higher removal efficiency of model compound.¹⁴⁾ A 5 L cooling container was used to provide a constant temperature inside of the reaction container at approximately 20°C. Experiments were carried out under different conditions and parameters such as power intensity, pulse cycle mode, surfactant type, oxidants, solvent type, operation temperature, and sonication time.

Under continuous operation mode, several intensities from 36.74 to 58.77 watts/cm² were studied to observe the best power intensity of ultrasound. The power intensity can be adjusted by amplitude and tuner of ultrasound equipment. The sonication time was 30 min for each running.

To investigate the effect of pulse cycle mode, various pulse modes were applied. Ultrasonic vibrations were transmitted into the reaction vessel at a rate of one pulse per sec, and one cycle per 10 sec. The pulse duration was manually adjusted from 0% to 100% (i.e., 90% of pulse mode = 9 sec of ultrasound on, 1 sec off, every cycle is 10 sec). The total sonication time was 60 min with 10-min interval.

To determine the effect of surfactant, two surfactants (Span 20 and Tween 80) were tested

in terms of the enhancement of ultrasonic decomposition efficiency. Span 20 was also investigated to see the optimum amount of surfactant among various quantities of surfactant like 0–0.2% (v/v of water). Microscopic phenomena of emulsion solutions caused by surfactants were investigated and discussed according to the membrane mimetic chemistry.

For identifying the effect of oxidants on the efficiency of ultrasonication, hydrogen peroxide was chosen as an oxidant due to its powerful hydroxyl radicals. Different amounts of oxidant were applied to identify the best dosage of oxidant to promote the ultrasonic reactions.

Regarding the effect of solvent type, five solvents such as chloroform, dichloromethane, toluene, pyridine, and dioxane were studied under the same ultrasonic conditions. This test indicated the order of solvent effectiveness by showing which solvent was more effective in removing the model compounds.

Three operating temperatures were experimented with VOTPP in order to study the influence of temperature and efficiency of cavitation reactions.

Analytical Methods

After ultrasonic reactions, chloroform was used for solvent extraction. The solution was shaken several times in the separation funnel. Two layers appeared almost immediately. The chloroform with remaining model compounds was shown in the bottom layer. After 20 min, the bottom layer in the separation funnel was collected for analysis by a Hewlett-Packard 8452A Diode Array spectrophotometer. For example, NiTPP is red in color having intensive absorption peak in visible band at 526 nm of wavelength. Prior to UV-visible spectrometry analysis, sodium sulfate (Na_2SO_4) hydrate powder was used to absorb the water content, which presumably remains in chloroform phase so as to avoid water interference for UV-visible unit.

In addition, the mixture solution was neutralized to $\text{pH} = 7$ by adding the required amount

of 0.1 M NaOH and stirring for 10 min. Then, this solution was centrifuged at 1,000 rpm for 20 min. The upper layer (clear aqueous phase) was collected for the metal analysis by ICP/MS (a Hewlett-Packard L500 series). For the analysis of reaction products, GC-MS was used (Hewlett-Packard 5880A gas chromatograph equipped with a flame ionization detector, a DB-608 capillary column).

Selection of Solvents

Choosing an appropriate solvent type is of great importance for the cavitation process of ultrasonic reaction. The formation of cavitations in a liquid requires that negative pressure in the rarefaction region must overcome the natural cohesive forces happening within the liquid. Cavitation production is difficult in viscous liquids, or liquids with high surface tensions. Therefore, less viscous solvents are more preferable.

Chloroform is a hydrophobic volatile compound and can be thermally decomposed in the gas phase interior of the cavitation bubbles as well as in the interfacial regions between cavitation bubbles and the bulk solution under ultrasonic irradiation. The reaction between chloroform and hydroxyl radicals in the bulk solution generated from thermal decomposition (or pyrolysis) of hydrogen peroxide or water molecules, is also very important.¹⁵ Chloroform can eventually be completely degraded into chloride under ultrasonic conditions.^{8,15,16}

Due to its strong oxidation properties, chloroform has also shown the swelling effect to rubber and propellant composite molecules.^{9,10} Also, chloroform can be used with other solvents as a cosolvent to help the synergistic effects of two or more solvent mixture. The destruction efficiency of copper phthalocyanine in different ratios of solvents of chloroform and pyridine was studied so that the removal reactions were better facilitated by mixing with chloroform than pyridine only.⁸ The combination of two solvents increases the solubility of tire fragmentations because the

total processing time was shortened owing to more bond scissions.⁹⁾

Choosing chloroform as a solvent provides many advantages for ultrasonic reactions. First of all, chloroform can be converted into strong oxidant radicals that are contributable to the oxidative decomposition of target compounds. Accordingly, chloroform plays an essential role in the production of oxidant radicals such as $\text{Cl}\cdot$, $\text{H}\cdot$, $\text{CHCl}_2\cdot$, $\text{CCl}_3\cdot$, $\text{CCl}_3\text{O}_2\cdot$, HOCl through the chain reactions. When chloroform or dichloromethane is used as a solvent and mixed in D/D water, the hydroxyl radical ($\cdot\text{OH}$) and other radicals will be generated from water molecules and chloroform (or dichloromethane), respectively under thermal dissociation by ultrasonic cavitation.^{11,17)}

Second of all, chloroform can create an acidic environment, which means that hydrochloric acid (HCl) is produced as a byproduct. The solution becomes acidic (pH 2~4) after 10 minutes of sonication. The porphyrin type compound is a macrocyclic-chelating agent having similar characteristics with other metal-chelating compounds. The chelating force between metal and chelating agent becomes weaker under acidic conditions. Metalloporphyrins are more unstable at lower pH because of the reduction-oxidation potential.¹⁸⁾ Thus, the acidic condition of solution caused by chloroform can promote the oxidative reaction, creating strong oxidants to efficiently oxidize metalloporphyrins in a low pH environment. Additionally, some heavy metals are mobilized by acid environments, which results in the high metal recovery in this study.

In addition, sonochemical reactions depend on the energy of cavitation collapse, which is related to the vapor pressure of the solvent. Typically, a more violent collapse of cavitation is achieved at lower vapor pressure.¹¹⁾ Comparing chloroform (b.p. = 62°C) and dichloromethane (b.p. = 39.75°C), it seems that a solvent with higher vapor pressure will reduce temperature and pressure associated with the rapid bombardment of cavitation bubbles. Chloroform, with lower vapor pressure, has

10% higher removal efficiency than dichloromethane. However, removal efficiency is more attributable to free radical mechanism than low vapor pressure, since other solvents tested with much higher boiling points showed lower removal efficiency.

Free Radical Generation by Ultrasound

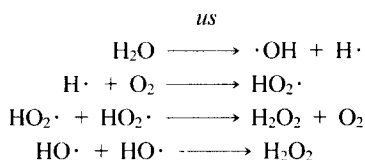
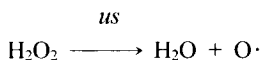
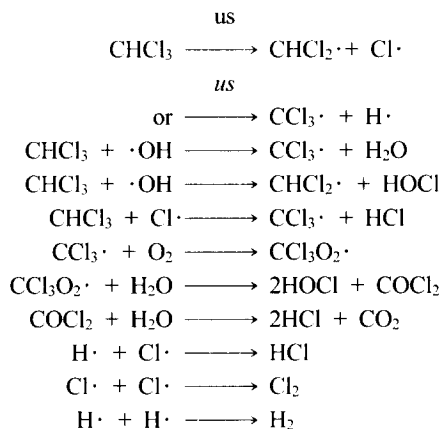
The cavitation processes of ultrasound generate high energy to cleave the bonds of reacting molecules. This means that through the formation, growth, and collapse of cavitation bubbles, the low energy density of a sound wave is converted to the high energy characteristic of the interior and surrounding of a collapsing gas bubble.¹⁹⁾ During these mechanisms, free radicals are produced and react with other radicals and/or solutes in the aqueous solutions. Radical generations and reactions can occur in three different regions by way of ultrasonic cavitation.²⁰⁾

The first region involves the interior of the collapsing cavitation bubbles where extremely high temperature and pressure exist transiently, which gives rise to typical gas phase pyrolysis reactions.²¹⁾ In this region, some free radicals are generated from water molecules and/or volatile solutes by thermal dissociation of aqueous solution.

The second region is the interfacial region between the collapsing cavitation bubbles and bulk solution where pressure and temperature are relatively lower than those of the first region. However, they are still high enough to thermally destroy non-volatile solutes accumulating in the interfacial region to generate free radicals whereas thermal dissociation and radical-induced reaction take place simultaneously.

The third region is the bulk solution at ambient temperature and pressure where free radicals escape from the first and/or second regions that undergo scavenging reactions with solutes.

Typically, the generation, propagation, and termination of free radicals are caused by ultrasonic irradiation (us). Ultrasonic radical-induced reactions can be summarized as follows:

(Eq. 1) Ultrasonic decomposition of H_2O ¹¹⁾(Eq. 2) Ultrasonic decomposition of H_2O_2 as an oxidant(Eq. 3) Ultrasonic decomposition of volatile solvents (e.g., CHCl_3)(modified after Alippi et al.,²²⁾ Mason and Lorimer¹¹⁾)

RESULTS AND DISCUSSION

The results were examined by studying the effects promoting ultrasonic reactions and the decomposition and demetallation of model compounds, and considering economic factors.

Effect of Ultrasonic Power Intensity

The power of intensity from ultrasonic irradiation is one of the most important factors directly affecting ultrasonic reactions. An ultrasound with higher intensity is likely to increase the sonochemical effects. However, the power intensity of ultrasound should exceed the threshold level of intensity due to the lack of cavitation occurring below the limiting thresh-

hold.¹⁹⁾ Based on the following equation (4), the high acoustic pressure of sound waves provided by high ultrasonic intensity results in an increase of cavitation effects.

$$I = \frac{P_A^2}{2\rho C} \quad (\text{Eq. 4})$$

Where, I is the intensity of ultrasound, P_A is the applied acoustic pressure, ρ is the density of the medium, and C is the velocity of sound in medium.¹⁴⁾ The effect of ultrasonic power intensity at 20 KHz and 20°C operation temperature is illustrated in Figure 1. Decomposition efficiency of NiTPP increases with an increase of ultrasonic power intensities that are 36.74, 44.35, 51.23, 58.77 watts/cm². The initial conditions of this set of experiments were 100 mg/L concentration and 30 min-sonication time. In this experiment, it is concluded that the decomposition efficiency of NiTPP increases almost linearly with increasing power intensity between 36.74 and 58.77 watts/cm².

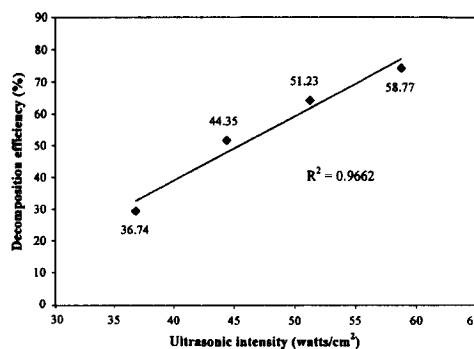


Figure 1. The effect of ultrasonic intensity on the decomposition efficiency of NiTPP (100 mg/L), 20 KHz, 30 min-sonication, and 20°C.

Effect of Ultrasonic Pulse Cycle Mode

Energy control can be obtained through pulse mode operation. For most of commercial ultrasonic probe systems (not bath types), the instruments often allow ultrasonic irradiation to be applied in different pulse modes which can enable the sound waves to be delivered intermit-

tently, allowing for periods of cooling. Different pulse modes were manipulated in this experiment. For instance, pulse mode was adjusted from 0%, where no energy is supplied, to 100%, where energy is supplied continuously, at a rate of one pulse per one second and one cycle per 10 seconds. From the results in Figure 2, 80% pulse mode was similar to 100% pulse mode for 30 min of sonication with respect to removal efficiency of NiTPP. Continuous operation (100% pulse mode) and 80% pulse mode showed 74.8% and 72.6% of decomposition efficiency, respectively, during 30 min sonication. A slight decrease was found in 60% pulse mode, and 40% and 20% modes showed relatively low efficiency for 30 min sonication, which can indicate that removal efficiency is likely to drop off during pulse-off period and the acoustic energy may not last long enough to create the effective cavitation bubbles and pressure. However, removal efficiency was mostly over 75% so long as pulse mode was more than 60% after 30 min of sonication.

Table 1 lists the decomposition efficiency of NiTPP in three different ultrasonic pulse modes during 60 min of reaction time and energy output time. The difference between the reaction time and energy output time is the pause-period of ultrasound. Decomposition efficiencies in 100% pulse mode are higher than those in other

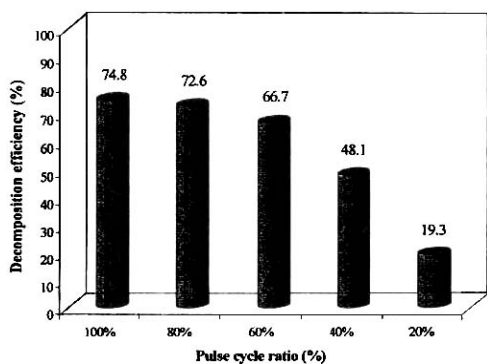


Figure 2. The decomposition efficiency of NiTPP at different ultrasonic pulse cycle modes under 30 min of sonication time at 58.77 W/cm² of power intensity and 100 mg/L of initial concentration.

Table 1. The decomposition efficiency and energy output of NiTPP at different ultrasonic pulse cycle modes

Sonication pulse mode						
Reaction time (min)	Efficiency (%)	Energy output time (min)	Efficiency (%)	Energy output time (min)	Efficiency (%)	Energy output time (min)
10	42.1	10	37.5	8	29.1	6
20	61.9	20	58.3	16	51.2	12
30	74.8	30	72.6	24	66.7	18
40	83.3	40	81.9	32	76.9	24
50	88.4	50	86.7	40	84.0	30
60	92.8	60	91.6	48	88.1	36

^aOptimum conditions: 100 mg/L initial concentration, 0.05% of Span 20, 2.7% of H₂O₂, 58.77 W/cm² of power intensity, and 20°C reaction temperature.

pulse modes that gradually decrease with increasing pause-period of ultrasound.

The data of energy output time shown in Table 1, however, indicate that intermittent pulse mode can save more energy than continuous pulse mode. For example, the energy output of 36 min in 60% pulse mode can reach the similar decomposition efficiency of continuous pulse mode in 50 min. However, the energy saved is about 28% from 60% pulse mode when compared to a continuous mode. Figure 3 shows that 60% pulse mode is higher than 80% and 100% pulse modes in terms of energy efficiency. Energy can be saved up to around 30%

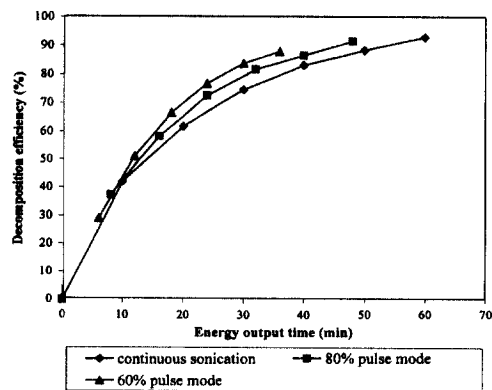


Figure 3. The comparison of different pulse ratios on the decomposition efficiency of NiTPP under ultrasonication at 58.77 W/cm² of power intensity, 100 mg/L of initial concentration.

from 60% pulse mode operation. These results confirm that 100% pulse mode is not necessary to reach the optimum reaction conditions, which were approved by Mason⁵⁾ and Orzechowsk,⁶⁾ respectively.

Effect of Surfactant Type

Surfactant can be employed to provide a stable emulsion system and promote the reaction of ultrasonic decomposition of target compound. Surfactant is able to reduce the interfacial tension between two immiscible phases to allow spontaneous or nearly spontaneous emulsification in very small droplet sizes, since surfactants are amphipathic molecules having both distinct hydrophobic and hydrophilic regions. According to the principle of membrane-mimetic chemistry, various membrane-mimetic agents such as micelle, microemulsion, vesicle, etc., can be formed when a surfactant is added into the dispersion of two mutually insoluble liquids and its concentration is beyond the critical micelle concentration.

In this experiment, two types of surfactants, Span 20 and Tween 80, were used to investigate the effect of surfactant on the removal efficiency under ultrasound. Both of them belong to nonionic surfactants and the HLB (Hydrophile-Lipophile Balance) values are 8.6 and 15.0, respectively. These surfactants are suitably used in oil-in-water emulsion system while Tween 80 is much easily dispersed in aqueous solution.²³⁾ Self-propagation vesicles containing onion-like multicompartiment structures will be formed when these surfactants are added into two immiscible solutions. Those multicompartiment vesicles can be sonicated and contribute to the formation of fairly uniform single-walled vesicles.

Under the transmitted light of microscope, the vesicle formation of surfactant during ultrasonic agitation was observed for the analysis of structural behavior. Microphotographs of chloroform-in-water emulsion with Span 20 and Tween 80 are shown in Figure 4. Based on these observations, fairly uniform single-walled and/or

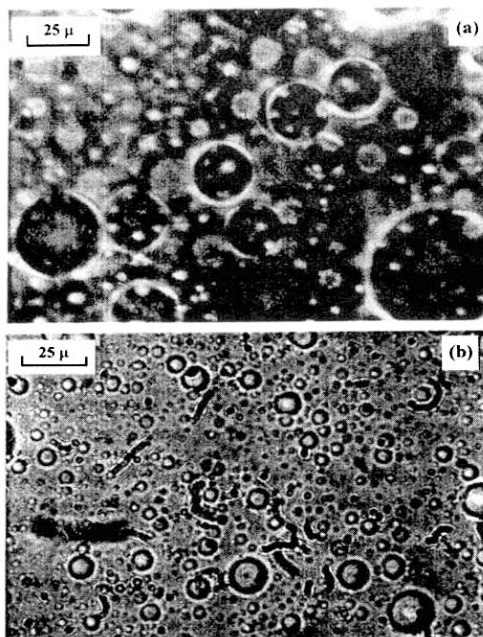


Figure 4. The microphotographs of chloroform-in-water emulsified solution with different surfactants. (a) with Span 20, (b) with Tween 80.

multicompartiment spherical vesicles of Span 20 are larger than those of Tween 80. The average diameter of the vesicles can be estimated 30 μm for Span 20 and 10 μm for Tween 80.

In Figure 5, the comparison of two surfactants is shown. Ultrasound was applied under the same conditions. Tween 80 was more effective than Span 20 with small differences. Both reactions of surfactants also fit for the first-order reaction. For the best fitting, rate constants of reactions are 2.67 hr^{-1} for Span 20 and 3.35 hr^{-1} for Tween 80. Although these kinetics are complicated because they may be affected by numerous reaction conditions, it can be concluded that Tween 80 could promote the ultrasonic reaction by providing relatively larger surface areas for the reaction, thus increasing decomposition efficiency of metalloporphyrin.

Furthermore, Span 20 was studied to see the optimum dosage of surfactant with higher efficiency. For comparison, VOTPP (vanadyl tetraphenylporphyrin) was also used as a model compound with NiTPP. Surfactant, Span 20,

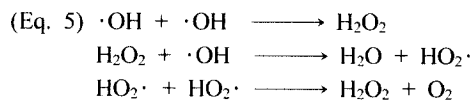
helps reduce the interfacial tension and enhance the transportation between two phases of chloroform and water by rearranging the vesicles and making the micelles disperse. Accordingly, free radicals will easily transfer from water phase to organic solvent phase and stay in micelle.²⁴⁾ Figure 6 shows the variations of efficiency of NiTPP and VOTPP with application of different quantities of surfactants. Decomposition efficiency generally increased for both models. 15-20% of increase was obtained at 0.05% of surfactant content, but the increasing rate gradually slowed down afterwards. Surfactant is essential to achieve the maximum efficiency with the stable emulsion.

Effect of Oxidants

Hydroxyl radicals are known as very powerful and effective chemical oxidants, and have much greater one-electron oxidation potential (about 2.7 V) in a low pH environment.²⁵⁾ As a result, hydroxyl radicals are extremely reactive and have a tendency to gain an additional electron by reacting with other molecules to form a chemical bond while releasing energy. In Figure 7, the decomposition efficiency of model compounds is enhanced by the consistent supply of hydrogen peroxide. Hydroxyl radicals are also generated from water (Eq. 1). Hydroxyl radicals have high potential to break carbon-chlorine and carbon-carbon double bonds.²⁶⁾ Based on these results, more efficient decomposition levels can be achieved when more hydroxyl radicals are produced in the solution by adding hydrogen peroxide.

NiTPP and VOTPP have the similar trend of decomposition efficiency with different quantities of hydrogen peroxide. The maximum decomposition rate was shown at 2.7% (v/v of water) of oxidant supply and then was lowered due to the scavenging effect of radicals. Hydroxyl radicals are very unstable, therefore they are rapidly terminated by forming back to H₂O₂ and/or H₂O molecules in higher concentration of hydroxyl radicals (Eq. 5), which results in the reduction or retardation of efficiency of reaction. Accord-

ing to Chen,¹⁵⁾ in a study of the radical-induced destruction of chloroform in the presence of hydrogen peroxide, this kind of retardation was due to the self-decomposition of hydrogen peroxide when it exists in high concentrations.



The resultant hydroperoxyl radicals, HO₂·, are much less reactive than the hydroxyl radicals. It is concluded that the addition of oxidants results in the contribution to the progress of the ultrasonic reaction.

Effect of Solvent Type

Different organic solvents such as dioxane, pyridine, toluene, dichloromethane, and chloroform were evaluated under the same conditions with respect to decomposition rate of metalloporphyrins. The effectiveness of solvents are as follows; CHCl₃ > CH₂Cl₂ > toluene > pyridine > dioxane (Figure 8). This sequence of effectiveness was true for both NiTPP and VOTPP and can result from the characteristic of chlorinated solvents. Chlorinated solvents like CHCl₃ and CH₂Cl₂ demonstrated the best destruction results as the first and the second in order of effectiveness. These chlorinated solvents are apt to provide more destructive conditions, such as more powerful free radicals by way of chain reactions and more acidic environments that are favorable for the chain reaction of hydroxyl radical and other strong radical formations, and the mobilization of metals. In addition, these chlorinated solvents experience sonolytic decomposition and eventually turn into the non-toxic materials.

Effect of Operating Temperature

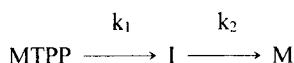
Three different temperatures were utilized to determine the influence of operating temperature on the cavitation reactions. The reaction temperature in solution gradually increases when it starts to operate, due entirely to the thermal

energy from ultrasound irradiation. The increasing temperature in the reaction is believed to prevent the ultrasonication process, and therefore, a cooling water bath was needed to keep the operating temperature stable. Actual temperatures measured inside of the reaction container were 20°C, 27°C, and 40°C with controlling temperatures of cooling water (respectively 8°C, 15°C, and 27°C). Temperature error was manipulated within 2°C.

In an Arrhenius plot for reaction constants of VOTPP shown in Figure 9, the efficiency rates appear to decrease with the increase of temperature. Generally speaking, the chemical reaction rate usually increases as temperature rises, which does not comply with the cavitation reaction due to these reasons; 1) An increasing temperature is liable to reduce the amount of gas molecules dissolved in the aqueous solution, and, hence, decreases the number of cavitations. The fewer the cavitations, the lower the efficiency of ultrasonic irradiation.⁴¹ 2) An increasing temperature is subject to increase the vapor pressure of the solvent. High vapor pressure tends to reduce the efficiency of reaction.

Decomposition and Demetallation of VOTPP and NiTPP

All steps in this reaction were assumed to be the first order and irreversible reaction.



Where, MTPP is the original metallotetra-phenyl porphyrin, I is the reaction intermediate, M is the metal recovery in aqueous solution, k_1 is the disappearance rate constant of MTPP, and k_2 is the rate constant for the decomposition of intermediate or for the final metal removal. From the Figure 10, this kinetic model is suitable for the experimental data. The reaction rate of the first step ($k_1 = 0.0445$) is lower than that of the second step ($k_2 = 0.159$). Overall reaction is controlled mainly by the first step,

which has then become rate limiting.

An intensive absorption peak in visible range at a wavelength of 548 nm was displayed in the UV-visible spectra of pure VOTPP in chloroform in Figure 11. The peak of the intermediate compounds was also found around 650 nm. For NiTPP, the characteristic absorption and intermediate peak were found at 526 nm and 622 nm, respectively.²⁷⁾ Figure 12 shows the absorbance-time profiles of VOTPP whose concentration is decreased in accordance with absorbance under different sonication times, while intermediate compounds appear at the same time. The concentration of intermediates during ultrasonic irradiation is changeable in accordance with the removal concentration of model compound. The concentration of intermediates reached its maximum at 30–40 min and slightly decreased for the rest of sonication time. The final major products from the decomposed model compounds can be categorized to paraffinics, naphthenics, and aromatics observed by GC/MS, as well as metals.

The porphyrin macrocycle is highly conjugated, and a number of resonance forms can be found. The porphyrins and their metal derivatives are intensely colored; their main absorption bands have very high molar extinction coefficients. Thomas and Martell²⁸⁾ found that all kinds of free-metal porphyrins not only have one strong absorption band (Soret band) around 400 nm, but also have four absorption bands (I, II, III, and IV peak) ranging between 500 and 700 nm. When the metal replaces two hydrogen atoms in the center of the porphyrin's ring and forms a metal complex (metalloporphyrins), only single absorption band around 500–600 nm, K band is found within the visible spectrum regime. Nonetheless, Soret band still exists and its wavelength is always higher than that of free-metal porphyrin. Table 2 shows the absorption wavelength NiTPP, VOTPP, and free-metal TPP in chloroform in the UV-visible range.

Metalloporphyrin -cation and -anion radicals usually display characteristic UV-visible and near-IR absorption bands that are quite different

Table 2. The absorption band in UV-visible range of porphyrin compounds (nm)

Compounds	Soret band	I	II	III	IV	K band
Free-metal TPP	408	646	590	550	514	--
NiTPP	414	--	--	--	--	526
VOTPP	422	--	--	--	--	548

from those for an electrooxidized or electro-reduced metalloporphyrin where the oxidation or reduction has occurred at the central metal ion or axial ligand.²⁹⁾ The interaction of metalloporphyrins with some oxidants such as chlorine or hydrogen peroxide may involve the formation of a π -cation (charge-transfer complex) with the function of metalloporphyrin as an electron donor to the electron-deficient oxidants. Loss of an electron from the metalloporphyrin would lead to a cation-radical. Cation-radicals have been shown to be intermediates in the reaction of metalloporphyrin with hydrogen peroxide.³⁰⁾ The intermediates from the oxidation of nickel (II)-tetraphenylporphyrin is π -cation radical, Ni^{II}(TPP)⁺, and the oxidation of NiTPP changes the color of the solution from orange to green.³¹⁻³³⁾ In the experiment, these intermediates, -cation radicals, in the oxidation process of metal porphyrin turned to green from red in solution and will shift the UV-visible spectra. Through the consecutive formation of intermediate complexes, metalloporphyrin is oxidized into cation-radical intermediates and disintegrated into colorless products. At the same time, metal is released from the center of tetrapyrrol after the disappearance of intermediates.

Based on the assumption that one mole of metalloporphyrin gives one mole of metal after the destruction of macrocyclic ring, the metal concentration can be used to describe the difference between the equivalent amount of decomposed metalloporphyrin and produced intermediates. In other words, the decomposition efficiency of metalloporphyrin is reasonable with the efficiency of metal recovery. Table 3 indicates that 86.3% (VOTPP) and 89.7%

Table 3. The mass balance of metal recovered and decomposition rate for VOTPP and NiTPP under ultrasonication

Samples	Metal content before sonication* (mg)	Metal content in water phase after sonication**	Metal recovery	Decomposition efficiency (%)
VDTTPP	0.0408	0.0352	86.3	88.8
NiTPP	0.0516	0.0463	89.7	92.9

*100 mg/L of sample in chloroform was analyzed by ICP/MS.

**Sonication time is 60 min for NiTPP and 80 min for VOTPP, analyzed by ICP/MS.

(NiTPP) of metal recovery were similar to 88.8% (VOTPP) and 92.9% (NiTPP) of decomposition efficiency, respectively. Also, the results in Figure 13 show that the efficiency of metal recovery (w/o EDTA) was much different from the decomposition efficiency under ultrasonic irradiation. The difference of data between metal recovery and removal efficiency can be explained by the fact that partial quantities of metal ions released from organometallic compounds become inorganic metal compounds by reacting with anionic atoms. These insoluble inorganic metals are not detected by ICP/MS in aqueous phase after neutralization and centrifugation processes. A strong metal-chelating agent, EDTA (ethylenediaminetetraacetic acid) was introduced to the mixture solution after sonication in order to reduce this deficiency. EDTA chelates the metals from either metal ion forms remaining in water phase or inorganic metal forms that are dissolved in water. Therefore, metal recovery efficiency with EDTA was close to removal efficiency of NiTPP.

CONCLUSION

UACP (ultrasound-assisted chemical process) was performed to investigate the effects of different power intensities, pulse modes, surfactant types, oxidants, solvent types, and operating temperatures of ultrasonication and also to evaluate the optimal decomposition effectiveness of metalloporphyrins from an economical view-

point. The manipulation of these parameters will make a difference in reducing the cost of the process. The decomposition of metalloporphyrin under sonication process appears to be a pseudo-first-order reaction and inhibited by initial feed concentration.

The metalloporphyrins experienced the decomposition mechanisms (ultrasonic radical-induced process), such as sonolytic decomposition of chloroform and consecutive oxidative decomposition spurred by powerful oxidants. Under the optimal conditions, the maximum decomposition rates of metalloporphyrins can reach 92.9% and 88.8% for NiTPP and VOTPP, respectively. For metal recovery, the demetallation rates can reach 89.7% and 86.3% for NiTPP and VOTPP. Based on the results, UACP can be a feasible and effective option to treat the metal-porphyrinic contaminants or wastes.

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