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Extracting metallurgy contaminants and hydrocarbons removing from water and industrial wastewater using enhanced emulsion liquid membrane with nanoparticles and ionic liquid

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EXTRACTING METALLURGY CONTAMINANTS AND HYDROCARBONS REMOVING FROM WATER AND INDUSTRIAL WASTEWATER USING ENHANCED EMULSION LIQUID MEMBRANE WITH NANOPARTICLES AND IONIC LIQUID

by

QUSAY JAAFAR RASHEED AL-OBAIDI

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ABSTRACT

It is an uphill battle to extract pollutants such as heavy metals, hydrocarbons, and radioactive metals from water and industrial wastewater. Emulsion liquid membrane (ELM) is an emerging technology that combines extraction/recover and stripping in one stage to extract/recover heavy metals and/or hydrocarbons from water and wastewater. ELM devised a way to clean up heavy metals and/or hydrocarbons from the water and wastewater where its primary chemicals can be recycled and reused.

In this work, the Emulsion Liquid Membrane (ELM) has been enhanced by adding nanoparticles and ionic liquid to significantly improve the recovery of the water-based contaminants of heavy metal and hydrocarbon compounds to near completion in a shorter duration of time and sustain the emulsion stability for longer time.

Recovery of heavy metals of vanadium and lead have been studies separately and in combination where the nanoparticles have been added to the internal aqueous phase and the ionic liquid has been added to the organic phase. A recovery of 97 % in 3min and with emulsion stability exceeding for more than 78 hours have been obtained using 0.01% (W/W) nanoparticles and 5% (V/V) ionic liquid concentration. For hydrocarbon, 4-Nitrophenol compounds were removed effectively by achieving 99% in 1 minute removal with emulsion stability exceeding 6 hours using 0.05% (W/W) nanoparticles and 0.05% (V/V) ionic liquid concentration.

The method is more efficient, cost effective and has a potential for a wide commercial application that could also potentially save entire regional ecosystems from harmful chemicals.

ACKNOWLEDGMENTS

I would like to express my sincere gratitude to my supervisor, Dr. Muthanna Al Dahhan.

Many thanks to the University of Technology, Department of Chemical Engineering, Ministry of Higher Education and Scientific Research in Iraq (MOSHER), and Iraqi Cultural Office in the USA for their financial support. I wish to extend special appreciation to Missouri University of Science and Technology, Department of Chemical and Biochemical Engineering, and my committee members, Dr. Douglas Ludlow, Dr. Parthasakha Neogi, Dr. Xinhua Liang, Dr. Joontaek Park, and Dr. Fatih Dogan.

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I dedicate this work to the soul of my father, Jaafar Al-Obaidi, who, thanks to his prayers and encouragement to me, I am successful. You remain in my heart and mind, Father; may Allah have mercy upon you.

Finally, I would like to express my sincere gratitude to my mom, wife (Saba), daughters (Abrar, Noora, and Hasnaa), and brothers and sisters for their unconditional support, patience, understanding and encouragement.

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1. INTRODUCTION

Many manufactures and industrial processes are producing different types of wastewaters that introduce toxic pollutants (hydrocarbons and heavy metals) into groundwater and water which are the sources of serious environmental concerns, since they are known to be hazardous (Lawrence et al., 2006). Hydrocarbons, including phenolic compounds such as 4-Nitrophenol, and other derivatives, are often found in tap water and in many industrial processes such as dyes, and pesticides production, petroleum refinery, petrochemical, pharmaceuticals, mineral, and mining. The United States Environmental Protection Agency (EPA) has classified hydrocarbons as dangerous aqueous chemicals and may cause severe health hazards, due to their ability to destroy important tissues such as kidneys, central nervous system, liver, and blood cells in human and animal bodies. Therefore, the removal of hydrocarbons from industrial effluents is a serious, and practical issue. Similarly, heavy metal compounds, such as Pb(II) and V(V), and others are contaminants produced by the mining, mineral, petroleum, and other processing industries. When these heavy metals are released into the environment, they accumulate in the food chain and persist in nature. For instance, lead is extremely toxic to humans and can damage the nervous system, kidneys, organs, and reproductive system when the concentration of lead exceeds the limit of 0.01 ppm that has been set by the World Health Organization (WHO) and EPA. In addition, vanadium is a hazardous metal belonging to the same class as lead, arsenic, and mercury.

In the United States, the maximum recommended exposure level of vanadium is 35 mg/m^3 according to the National Institute for Occupational Safety and Health.

Furthermore, industrial water consumption is responsible for 22% of global water use. Therefore, treatment of wastewater for reuse is reguierd.

Accordingly, during the twentieth century a variety of new treatment technologies were introduced at various times in response to more complex treatment goals. But the challenges of water and wastewater treatment have become more complex as the twenty-first century begins (John C. Crittenden et al., 2012). A large part of industrial pollution control has been carried out and a wide range of unit processes have been developed to service the needs of the industry (Lawrence K. Wang. et al., 2010). A part of the U.S. National Pollutant Discharge Elimination System (NPDES) program is pollution presentation practice working with the best management practices to reduce pollutants releases. Thus, reducing costs as well as pollution risks through source reduction and recycling/reuse techniques have been sought (U.S. EPA, 1993). Many methods have been reported to extract/recover heavy metals and hydrocarbons from water and industrial wastewater. These methods include coagulation-flocculation, chemical precipitation, ion exchange, electro-oxidation, flotation, adsorption, and advanced oxidation (Ho, W. S. and Kamalesh, K. S. (1992) (Othman, N. et al., 2014). Membrane processes have also been presented as an emerging technology for such need. Porous and nonporous membranes, made of a variety of materials such as polymers and ceramics, and optionally functionalized to enhance treatment, have been reported. Further, beyond solid membranes, liquid membranes have also recently been used. Liquid membranes can be present in a variety of forms, including bulk liquid membrane (BLM), supported liquid membrane (SLM), and emulsion liquid membrane (ELM).

An emulsion liquid membrane (ELM) is double emulsion systems which have a Water-Oil-Water (W-O-W) or Oil-Water-Oil (O-W-O) structure. ELM (W1-O-W2) that contains tiny drops (0.1-10 µm) of the stripping aqueous phase (W1), also known as the internal phase, dispersed in the water or wastewater to be trated (W2), also known as the external phase, that are enclosed inside the organic phase (O) drops (0.1-2 mm) called globules which are dispered in the water or wastewater to be treated (W2), also known as the exernal phase. In ELM, the pollutants transfer through the organic phase (O) from phase (W2) to phase (W1) to react with the stripping agent in phase (W1) as shown in Figure 1.1. A similar mechanism occurs in an O1-W-O2 emulsion system. ELMs represnt a single process of extraction/recovery and stripping with high capacity of separation and high selectivity at low cost. Such systems can concentrate the contaminant up to 10-100 times more than other methods. However, although ELMs are effective in extracting/removal and stripping, they can swell and break in emulsion systems. Furthermore, lack of emulsion stability decreases extraction/removal efficiency.

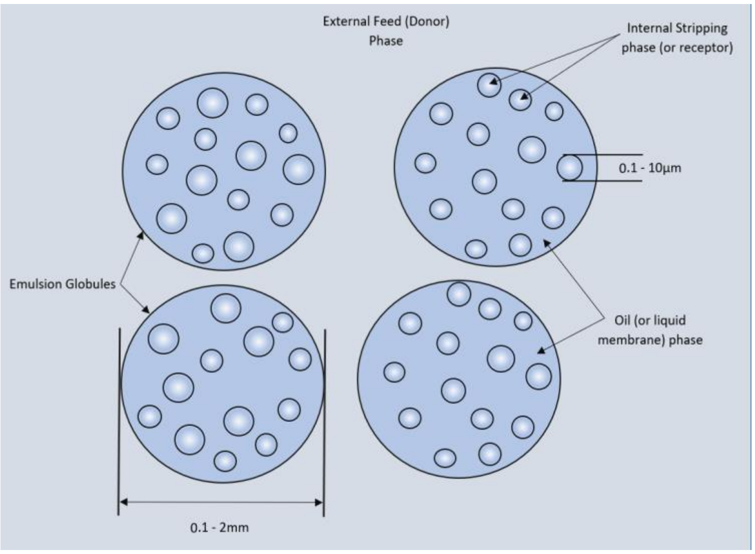

Figure 1.1. Proposed mechanism for ELM process (Le 1968).

Despite the promising results of (ELM) as reported in the literature, it has not been advanced widely toward industrial applications because ELM is still suffering from critical technical issues that are related to: 1) swelling and breakage that decrease the emulsion stability which affects negatively the removal efficiency, 2) not a high percentage of removal, 3) longer duration of time, and 4) inefficient way of demulsification to separate, the waste and to recycle the organic phase (Mokhtari and Pourabdollah, 2012; Bhavyank and Jaimin, 2016). Hence, emulsion stability extraction efficiency and duration of ELM have been studied to understand the relationship between the properties of the emulsion membrane and these operating factors (H. Weingrtner (2008).

Recently, to further improve on stabilization of ELM, ionic liquid as a stabilizer has been demonstrated. Goyal et al. (2011) showed that the stability of W1-O emulsion was improved by incorporating an ionic liquid in the organic phase (O) as a stabilizer. Methods of using ELMs comprised an ionic liquid combined with a surfactant have been used to increase the improvements in stability and pollutant removal efficiency. In a different approach, the addition of nanoparticles in the organic phase (O) rather than ionic liquid was also found to enhance the stabilization of the ELM (Lin et al., 2015, and Kim et al., 2013). Furthermore, stabilization of ELMs with nanoparticles enhances the strength between emulsion droplets and prevents collision or coalescence of the droplets. In addition, collecting the magnetic nanoparticles after extracting and stripping by magnet enhances the step of demulsifying. This stabilization is needed for scaleup to industrial practices.

Emulsion liquid membrane (ELM) methods is a cost-effective and environmentally friendly. Around 52 years ago it was observed the removal and separation hydrocarbon from wastewater and was given a noticeable attention. Hence many studies using ELM have been reported in literatures. ELM started when Li (1968) first proposed a single process of removal and striping with high capacity of separation and high selectivity at low cost called liquid surfactant or emulsion liquid membrane (ELM). This process has been applied on wastewater treatment because it's capability to separate and extract/recover solutes from organics to metal ions. ELM can be prepared by using simple materials and equipment (Kumbasar and Sahin, 2008, Chakraborty et al., 2002, and Ferraz et al., 2007). It was introduced as an alternative method to the liquid-liquid extraction and to solid polymeric membranes. The driving force of the solute transport through the membrane is the concentration gradient (Simon Judd and Bruce Jefferson, 2003). The main steps of ELM process are emulsification, dispersion, extraction, settling, and demulsification (Norela Jusoh, et al., 2016). This method combines two steps of the conventional treatment which are extraction and stripping steps into one step. However, ELM method was limited by its instability (Wan and Zhang, 2002). Low stability causes partial rapture of the membranes which reduces the efficiency (Tjoon Tow Teng, et al., 2013). Also, ELM method suffers from serious problem such swelling and breakage in W1/O/W2 emulsions (Mohammed, et al., 2017). Many techniques have been proposed to improve emulsion stability (Goyal, et al., 2011).

One of the methods that used to stabilize ELM process is the using of nanoparticles which also enhance the separation. Nanoparticles have been successfully used to stabilize both simple emulsions (i.e., W/O and O/W) types and multiple emulsions O/W/O and W/O/W) types (R. Aveyard, et al., 2003).

The effects of the magnetic Fe_3O_4 nanoparticles in the organic phase (O) on the emulsion stability were studied by Lin et al., (2016) for the removal of the 4-methoxyphenol from wastewater. Stabilization of ELMs with nanoparticles enhances the strength between emulsion droplets and prevents collision or coalescence of the droplets. The results showed that the 0.5wt% Fe_3O_4 magnetic nanoparticles have a strong effect on the percentage reduction of the emulsion leakage (emulsion stability) giving 86% removal for 4-methoxyphenol in 2 min in a batch operation. Mohammed et al (2017) in their research used magnetic Fe_2O_3 nanoparticles to extract benzoic acid from aqueous solutions in combination with Span 80 as the emulsifier stabilizes water in oil. The stabilization of emulsions depends on the ability of nanoparticles to move to the interfacial region, to remain there, and to form an interfacial film that retards coalescence of the droplets. Results of Mohammed et al. (2017) show that 0.1% (W/W) of magnetic Fe_2O_3 nanoparticles concentration has a strong effect on the percentage removal and extraction of benzoic acid which was 99.7%.

Another method of improving stabilization is the use of ionic liquid as stabilizer. Goyal et al. (2011) showed that the stability of W1-O emulsion was improved by incorporating an ionic liquid, 1-butyl-3-methylimidazolium bis (trifluo¬romethylsulfonyl) imide, $[BMIM]^+[NTf2]^-$, in the organic phase (O) as a stabilizer. Mohammed et al. (2016) studied the ELM method with ionic liquid $[BMIM]^+[NTf2]^-$ in combination with the surfactant of Span 80 to remove benzoic acid from wastewater. The results indicated that the increase in the concentration of ionic liquid $[BMIM]^+[NTf2]^-$ up to 0.2% (V/V) in the organic phase (O) yields an improvement in stability which also leads to enhanced removal efficiency of benzoic acid of 99.7% after 5 min in a batch operation. Mohammed et al. (2018) also studied the removal of phenol compounds (phenol, 2-chlorophenol, and 4-nitrophenol) from wastewater. The results indicated that the increase in the concentration of ionic liquid $[BMIM]^+[NTf2]^-$ up to 0.3% (V/V) in the organic phase (O) yields an improvement in stability which also leads to enhanced removal efficiency of phenol of 78% after 30 min, and 2-chlorophenol and 4-nitrophenol of 95 % and 98.5 % after 30 min in a batch operation, respectively.

Accordingly, there is a need to further advance ELM technology to address the shortcomings in percentage of recovery or removal to be improves, in stability to be enhanced and in the batch operation time to be reduced and to further enhance the demulsification step which represent the focuse of this work as per the objectives below.

The overall objective is to enhance the emulsion liquid membrane (ELM) using nanoparticles and ionic liquid to improve percentage recovery to near completion, sustain emulsion stability for longor time and to reduce the batch operation time to be suitable to transform to industrial continuous operation.

Accordingly, the detailed objective are:

- ✓ Enhancing the ELM for hydrocarbons removal from industrial wastewater.
- ✓ Enhance the ELM for extraction and recovery of heavy metals from industrial wastewater.
- ✓ Investigating the effects of nanoparticles and ionic liquid added to ELM (W1/O/W2) on stability, % removal, time and demusification of removing

selected hydrocarbon and heavy metal compounds of interest to (e.g.,4-Nitrophenol , Vanadium, and Lead):

- ✓ From synthetic wastewater of one metal compound at a time and on combining metal compounds of interest
- ✓ Evaluating the capability of ELM (W1/O/W2) in removing pollutants hydrocarbon / heavy metals from aqueous phases enhanced by nanoparticles and ionic liquids
- ✓ Evaluating various methods to create effective emulsion with less energy consumption and with high quality of the emulsion

PAPER

1. ADVANCED REMOVAL OF 4-NITROPHENOL BY EMERGING AND INTENSIFYING TECHNOLOGY OF EMULSION LIQUID MEMBRANE WITH MAGNETIC NANOPARTICLES

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ABSTRACT

4-nitrophenol is one of the phenolic compounds found in industrial wastes that needs to be removed from treated wastewater. Emulsion liquid membrane (ELM) has been introduced as a developing technology for advanced wastewater and water treatment. This emerging technology of treatment can be intensified by strategically adding nanoparticles to organic membrane phase (O). To facilitate the industrial implementation of ELM with nanoparticles, we used magnetic iron nanoparticles added to the organic phase (O) to recover them by a magnet for reuse. This also assists in de-emulsification step. The results show that with the use of 0.1% (W/W) of magnetic nanoparticles of 30-60 nm, the removal efficiency increased from 54.48% without nanoparticles to 97.4% with nanoparticles in reaction time of 1.5 minutes, and both the stability and extraction activity of ELM are enhanced. The outcomes of this work can be

extended to other hydrocarbons and polar pollutants removal from industrial wastewater and water.

1. INTRODUCTION

Different industrial processes and manufacturing introduce toxic pollutants into the surface water and groundwater. Most contaminants are not biodegradable; therefore, they are not removed from the environment, but instead they increase in concentration. This is a serious environmental concern, especially because pollutants are known to be carcinogenic. Phenol compounds such as 4-Nitrophenol and other derivatives are often found in tap water and in many industrial processes of dyes, pesticides, and petrochemical industries. This substance has been of such a concern that the United States Environmental Protection Agency (USEPA) recorded it as a dangerous aqueous chemical, due to its ability to destroy the important tissues in human and animal body like kidney, central nervous system, liver, and blood cells [16]. Therefore, the removal of 4-Nitrophenol from industrial effluents is a serious practical issue.

The challenges of wastewater and water treatment has become more multifaceted, and a multiplicity of advance treatment methods are introduced at different times in response to more complex treatment goals [9]. Most of the treatment methods (i.e., coagulation-flocculation, chemical precipitation ion exchange, electro–oxidation, flotation, and adsorption) have their own limitations for hydrocarbon removal and extraction [1]. Therefore, in general a huge of industrial pollutants control has been conducted and many unit processes have been developed [12]. The removal and separation of 4-Nitrophenol and phenol compounds from wastewater were given noticeable attention and hence many studies and recommended technology have been reported in literatures. Noman Li, (1974) proposed a single process of extraction and stripping with emulsion liquid membrane (ELM) with high capacity of separation and high selectivity at low cost since then many studied have been conducted to remove pollutants including heavy metal [20,23]. This system can concentrate the contaminant up to 10-100 times than other methods [22]. ELMs are double emulsion systems which have the Water-Oil-Water (W-O-W) or Oil-Water-Oil (O-W-O) structure [26].

Although the ELM is effective methods for removal, but it suffers from serious problem such as swelling and breakage in emulsion system and the privation of emulsion stability which decrease the extraction efficiency [17]. The ELM must be able to withstand the mixing, but it must also be broken enough to remove the internal phase. For this, suitable parameters must be chosen by investigating the different factors that affect the membrane stability [2]. The stability and extraction efficiency of ELM can be determined by studying the relationship between the properties of emulsion membrane and operating factors. Surfactant is usually used in organic phase to achieve emulsion stability. Stability can be improved by using some materials such as nanoparticles, and inorganic anions which form a salt with a low melting point and high hydrophobicity.

Also, the stabilization of ELM by nanoparticles can enhance the strength between the droplets of emulsion and prevent the droplets to collision or coalescence [14]. The Emulsion liquid membrane stabilized by magnetic Fe_2O_3 nanoparticles is an example on this system where the magnetic Fe_2O_3 nanoparticles can demulsify by attraction of particles from droplets interface in presence of external magnetic field [11]. Effects of the nanoparticles on the emulsion stability using Fe_2O_3 nanoparticles were studied by Mohammed et al (2017) on the extraction of hydrocarbon (benzoic acid) from industrial wastewater and the results show that the magnetic Fe_2O_3 nanoparticles has a strong effect on the percentage of emulsion leakage (emulsion stability) giving removal percent for hydrocarbon as 99.7% [27].

Hence, the main objective of this study is to investigate the use of magnetic Fe_2O_3 nanoparticles in ELM for extraction and improvement of stability in removing 4-Nitrophenol from Industrial wastewater. In this case the 4-Nitrophenol is transported from W2 phase through the O phase to the W1 phase which is reacted with the stripping agent (NaOH) forming of sodium phenolate.

2. MATERIALS AND METHODS

2.1. CHEMICALS

The materials that used in this study were Kerosene (Boiling Point 175 – 325 oC) as the organic phase, Span-80 (sorbitan monoolate) as the surfactant, sodium hydroxide (NaOH) as the stripping agent, hydrochloric acid (HCl), and 4-Nitrophenol which obtained from Sigma Aldrich (St. Louis, MO 63103, USA). The magnetic Fe_2O_3 nanoparticles with a size range (30 – 60 nm) taken from Alfa Aesar (Ward Hill, MA 01835, USA).

2.2. EXPERIMENTAL PROCEDURE

ELM (W/O/W) extraction method with reaction is preparing by Forman emulsion of two immiscible liquid phases (aqueous and organic W/O). The emulsion consists of aqueous droplets distributed into the organic phase (Figure 1). The NaOH solution (0.5 N) used as the aqueous internal receiving phase (W1) contains the stripping agent (NaOH) which mixed with the organic membrane phase (O) (surfactant Span-80 and oil phase kerosene) to create emulsion of tiny drops of W1 in O.

Many factors affect the removal process such as organic phase (O) to internal receiving phase (W1) ratio, surfactant concentration, emulsification speed, treatment ratio (volume ratio of W1/O to W2), treatment agitation speed, additive concentration magnetic nanoparticles, and pH of external feed phase.

Volume ratios of the NaOH solution to organic phase (W1/O) is this work used were 1/1, 1/3 and 1/5 (V/ V), Span 80 surfactant concentrations used were 2%, 3% and 4% (W/V). Emulsion was achieved using ultra-high-speed (Turrax IKA-T25) homogenizer at emulsification speeds of 5000, 7000, and 8000 (rpm) for 10 minutes to produce a milky white color liquid membrane.

Then this emulsion was dispersed with mixer as globules in the external feed wastewater phase (W2) (4-Nitrophenol, 300 ppm) using ratios of 1/1, 1/2, 1/3, 1/5, and 1/8 (V/V) with agitation of low speed of 250, 300 and 400 rpm for 15 min. IKA overhead stirrer (Model: RW20 digital). The tested pH values of the external feed (W2) were of 1.5, 2.5, 3.5, 4.5, and 6.5 measured by pH meter (Okton Acron). When the 4-Nitrophenol is transported from W2 to W1 through O, it reacts with the stripping agent (NaOH) forming of sodium phenolate. Samples from the agitated solution were taken at different periods of time using micropipette, and then was separating from the emulsion phase via nylon syringe filter 0.2 µm (Simsii Inc. USA). The 4-Nitrophenol is analyzed using 96 well UV–microplate at a wavelength bands range 200 to 500 nm. It was measured in terms of wavelengths and intensities of the 400 band maxima, respectively [25]. The concentration of 4-Nitrophenol and sodium phenolate was found from the absorbance–calibration curves.

Fe_2O_3 nanoparticles was applied to ELM at different concentrations to increase the stability where the concentrations used were 0.05%, 0.1, and 0.15% (W/W).

The mixture placed in a separating funnel to separate the upper emulsion phase (W1/O) and lower aqueous feed (W2) phase. Then the upper phase breaks using magnetic force (1T magnet). The accumulated Fe_2O_3 washed with acetone and distilled water and dried under vacuum at 50 ºC for 10 hours to be reused again.

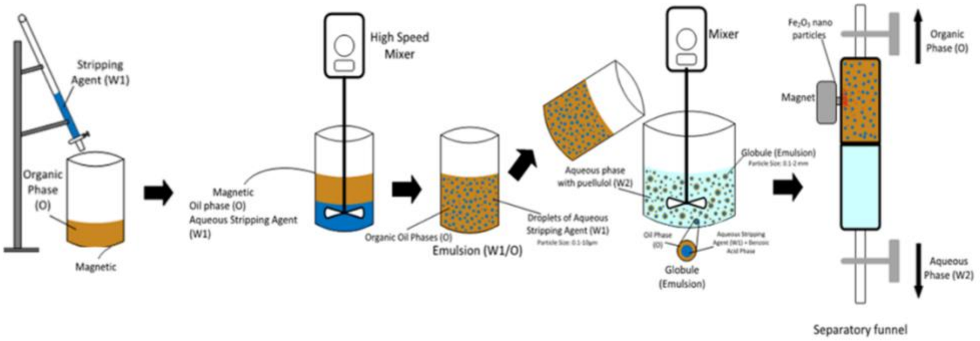

Figure 1. Schematic of ELM process.

2.3. CALCULATION OF ELM STABILITY

To measure the ELM stability dye was used as a breakage indicator which has no interaction with both organic and aqueous molecules. The leakage% calculated by the following Equation:

$$\%Leackage = \left(\frac{Concentration\,(ext)}{Concentration(in, \max t)} X\,100 \right) \tag{1}$$

where: (ext) is the concentration of dye leaked from the internal receiving phase (W1) to the external feed phase (W2), and the concentration (in, max t) is the max concentration of dye in the external feed phase, when all red dye leaked from the internal receiving phase (W1) phase to external feed phase (W2).

2.4. ANALYTICAL METHODS

The extraction remaining was calculated by the following equation

$$\%Extraction\ remaining = 100 - \left(\frac{initial\ concentration - final\ concentration}{initial\ concentration}\ X\ 100 \right) \tag{2}$$

3. RESULTS AND DISCUSSION

3.1. THE EFFECT OF THE VOLUME RATIO OF THE INTERNAL RECEIVING PHASE (W1) TO ORGANIC PHASE (O)

The volume ratio of the internal receiving phase (NaOH) (W1) to the organic phase (Kerosene and Span-80) (O) plays a significant role in emulsion stability. A higher concentration of NaOH may seem desirable as it is useful in trapping and converting the 4-Nitrophenol. However, too much increase will lead to emulsion instability [7]. Therefore, three selected ratios were taken (1/1, 1/3, and 1/5) (V/V) to investigate the effect of the internal receiving phase (W1) to organic phase (O) as proposed by Ng. Y.S. et al (2010) and shown in Figure 2.

The ratio 1/1 (V/V) has low extraction efficiency, due to the forming of large emulsion globule with thin wall which increase the possibility of the leakage as indicated by Jilska and Geoff (2008) [8]. The volume ratio 1/3 (V/V) shows higher extraction efficiency of 4-Nitrophenol because the increase of the volume ratio led to increase in thickness of the membrane phase (increase the membrane phase to encapsulate internal receiving phase), which resulting in forming high stable emulsion droplets with low leakage and enhancing in mass transfer [7].

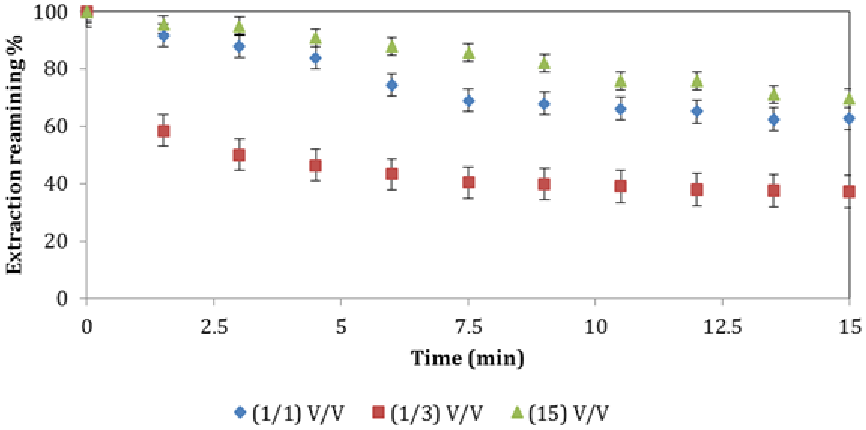

Figure 2. Effect of volume ratio of W1/O in ELM process.

Then the extraction efficiency decreased at volume ratio of 1/5 (V/V) due to the increase in the thickness of membrane wall and built-up resistance around the W1 droplets which offered resistance of the membrane and show decline in 4-Nitrophenol removal rate and emulsion stability. Hence, the best condition was at 1/3 (V/V) internal receiving phase to organic phase ratio (W1/O) and this is in agreement with the results obtained by Norela and Norasikin (2016) [21].

3.2. THE EFFECT OF THE SURFACTANT PERCENT (%) IN ELM

The concentration of the emulsifier is playing a very important role in performance of the emulsion because it works as a protective barrier between the feed phase (W2) and the internal receiving phase (W1) which reduces the emulsion leakage

[6]. Due to different properties of the surfactant, increasing concentration can be both desirable and, inversely, harmful to removal efficiency. Three different percent concentrations of span-80 were studied (2%, 3%, and 4%) as shown in Figure 3. The best concentration was found to be 2%. A concentration percent 3% does not create the increased in contact area as compared to 2% and increasing the concentration to 4% will lower surface tension of emulsion with formation of small globules.

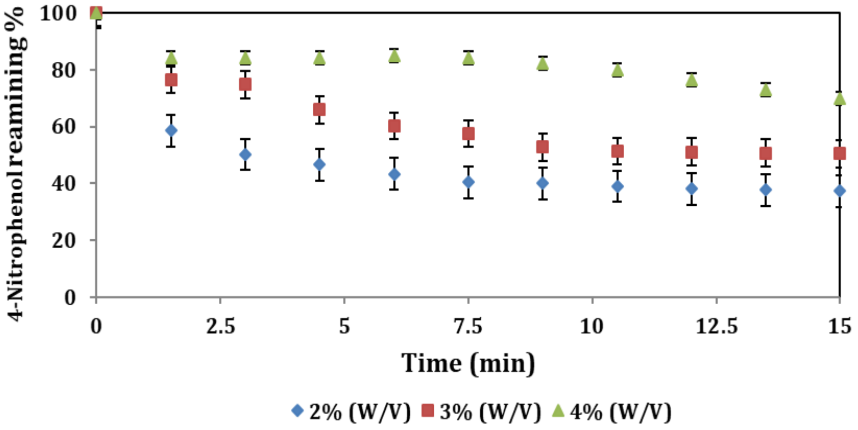

Figure 3. Effect of span 80 concentration in ELM process.

More adding of emulsifier may lead to increase the swelling, emulsion instability, decrease in removal efficiency and higher emulsion leakage due to thicker emulsion globules. Thus, these yield higher mass transfer resistance and decrease the extraction efficiency [18].

3.3. THE EFFECT OF THE EMULSIFICATION AGITATION SPEED ON THE EXTRACTION EFFICIENCY

The efficiency of extraction increases with an increase in the emulsification agitation [19]. The agitation is increased by using proper stirring speeds. To find the suitable emulsification, three speeds were examined (5000, 7000, and 8000) rpm. Emulsification speed of 8000 rpm gives best condition as showed in Figure 4. Emulsion stability was increased as the homogenizer speed is increased from 5000 to 8000 rpm. This result is confirmed with Djenouhat et al (2008) study which stated that increasing the homogenizer speed leads to the generation of more droplets (increase the droplet formation) and a more stable emulsion because of better mixing and a reduction of interfacial tension between the aqueous and organic phase [5]. The droplets merge with each other due to rapid mixing.

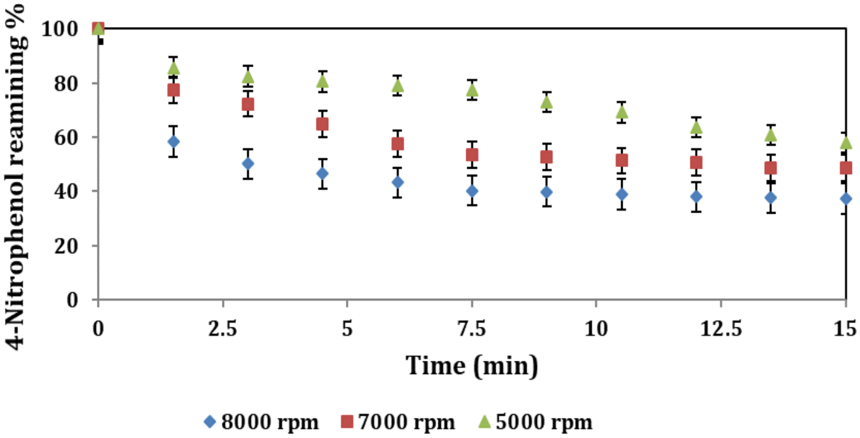

Figure 4. Effect of emulsification speed in ELM process.

Thus, the increased homogenizer speed causes a “mayonnaise-like” emulsion to form. This can be explained by a forming mechanism where air-bubbles are incorporated into the emulsion phase and leads to a more rigid system. Bjorkegren (2012) stated that the higher speed results in highly viscous emulsion that producing a stable emulsion due to a reduction in emulsion leakage which is also in agreement with the results of this study [3].

3.4. THE EFFECT OF THE TREATMENT VOLUME RATIO (W1/O) TO (W2)

The treatment volume ratio (W1/O) phase to external (W2) feed phase has an important effect on the ELM efficiency. The rate of mass transfer is straight related to the specific mass transfer area. Regarding the treatment ratios of 1/1, 1/2, 1/3, 1/5, and 1/8 (V/V) were used, the treatment ratio of 1/2 was found to be the best ratio for the removal as shown in Figure 5, and which will provide an increase in overall surface area for mass transfer and extraction capacity.

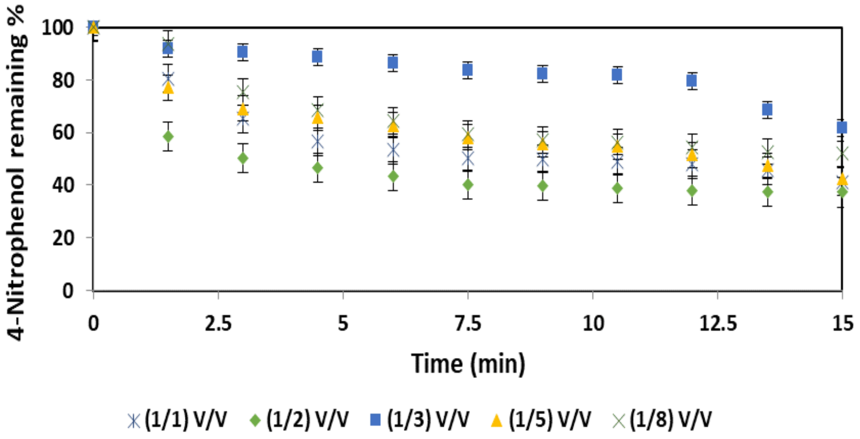

Figure 5. Effect of volume treatment ratio (W1/O/W2) on ELM process.

The other treatment ratios decrease the removal efficiency and that can be attributed to the increase in membrane layer around the droplets. Therefore, the stability of emulsion increases when reducing the volume fraction of internal phase as stated by M. Djenouhat et al. (2008). In addition, Ng. Y.S et al. (2010) reported that mechanical resistance of the membrane also increased at higher organic fraction, thus preventing coalescence of the dispersed droplet and indicating the size is within the range of the standard droplets size [5,19]. In general, larger droplets increase the emulsion instability because the droplet easily coalesces.

3.5. THE EFFECT OF THE MIXING INTENSITY OF THE WASTEWATER (W2) AND EMULSION (W1/O)

To examine the effect of the mixing intensity of the W2 with (W1/O) on the removal efficiency of the 4-Nitrophenol, variable speeds were tested such as 250, 300, and 400 rpm.

The mixing speed was first running at (250) rpm, and then increased to (300) rpm and eventually to (400) rpm in the third experiment. The results (Figure 6) show that (300) rpm is the most suitable, and hence it is used for the remainder experiments as it displays the lowest amount of emulsion leakage. The decrease in the stirring speed leads to a decrease in the mass transfer rate of 4-Nitrophenol due to an increase in the emulsion globules size. The higher mixing speeds create a greater shear force on the droplets and greatly reduce the diameter of the emulsion globules.

Increasing the mixing speed increases the contact area for mass transfer because of decrease in the globules size. The increase in the speed may also lead to the emulsion breaking because of high intensity (Hamid and Mortaheb, 2008). However, the higher mixing speed makes globules rupture more likely causing leakage of the W1 phase into the wastewater, W2 phase [27]. The results are significantly agreed with the fact that at best stirring speed produces smaller globules and consequently, higher surface areas exposure resulting in a higher extraction rate as noted by Lelin Zeng (2015) [14].

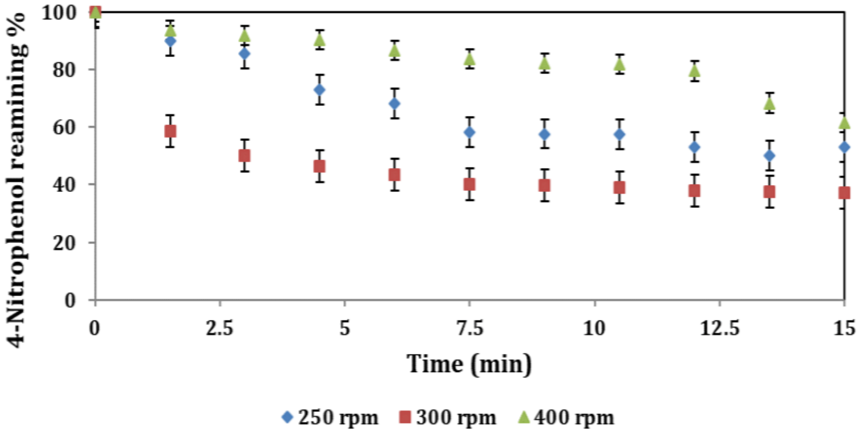

Figure 6. Effect of mixing speed on ELM process.

3.6. THE EFFECT OF THE PH OF THE EXTERNAL FEED PHASE (W2) ON THE REMOVAL EFFICIENCY OF 4-NITROPHENOL

The initial pH of the wastewater (W2) plays a significant role in the surface charges, states of functional groups on the surface of adsorbent, and the pollutant species in solution [10]. A series of experiments were conducted with a pH value range of (1.5–6.5), and the corresponding results are presented in Figure 7. From the results the practical 4-Nitrophenol removal from wastewater was at pH 1.5 because 4-Nitrophenol tends to precipitate in alkaline solutions as indicated by Zhaoyun (2016) [28]. Considerably at low wastewater pH (as 1.5 in this study), the surface was surrounded by H^+ resulting in the increase in the adsorption efficiency that might be accounted for the lower competition of H^+ with 4-Nitrophenol for the active sites and the adsorption process was due to the interaction of the positively charged 4-Nitrophenol with the negatively charged surface [10].

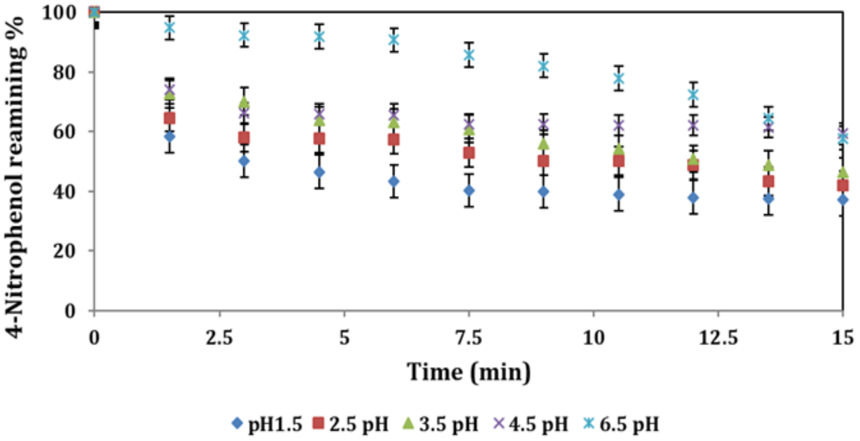

Figure 7. Effect of pH on ELM process.

3.7. THE EFFECT OF MAGNETIC NANOPARTICLES ON THE ELM PROCESS PERFORMANCE

The 4-Nitrophenol that transported from the feed phase (W2) to NaOH phase (W1) reacts with the NaOH as given in Eq.3, forming precipitate of sodium phenolate. The 4-Nitrophenol diffuses across the organic membrane from the wastewater phase (W2) to encapsulate-receiving phase NaOH (W1).

The formed Sodium 4-Nitrophenolate insoluble in the membrane phase (O) and then it was trapped in W1. The zero concentration of 4-Nitrophenol in internal receiving phase results in highly concentration gradient, and high driving force through membrane phase and hence the removal process carries on until it is completed [4].

$$C_6\,H_4NO_2OH + NaOH \longrightarrow C_6\,H_4NO_2O\,Na + H_2O \qquad (3)$$

The magnetic Fe_2O_3 nanoparticles enhance the stability of the ELM method and the mass transfer of 4-Nitrophenol from the W2 to W1 through O phase due to the ability of forming film by the particles at (O/W) [22]. The results from this study indicated that the ratio 0.1% (W/W) of magnetic Fe_2O_3 nanoparticles to internal receiving phase elevates the 4-Nitrophenol extraction to higher level as compared to the ratios (0.05 and

0.15) % (W/W) concentration as presented in Figure 8. This result agrees with the results obtained by Mohammed et al. (2017) which indicate that the increased in Fe_2O_3 magnetic nanoparticles concentration extraordinary will dispersed in the external phase and some particles may aggregate on the (W1/O) interface [22], affecting the emulsion stability and slow transfer process because the emulsion droplets tend to be non-spherical or non-uniform shape as shows in Figure 8. [23].

Extraction time is considered as the target to determine the ELM effectiveness which represents the period till the concentration of 4-Nitrophenol becomes zero. The ratio 0.1% (W/W) of Fe_2O_3, gives higher removal efficiency percent for 4-Nitrophenol of 97.375 % in 15 min as in Figure 9. at above optimum operating conditions which were 2% surfactant Span 80 and 0.05 N NaOH at 1/3 organic phase to receiving phase, 8000 rpm agitation seed, 1/2 (V/V) treatment ratio at 300 rpm, and wastewater pH 1.5.

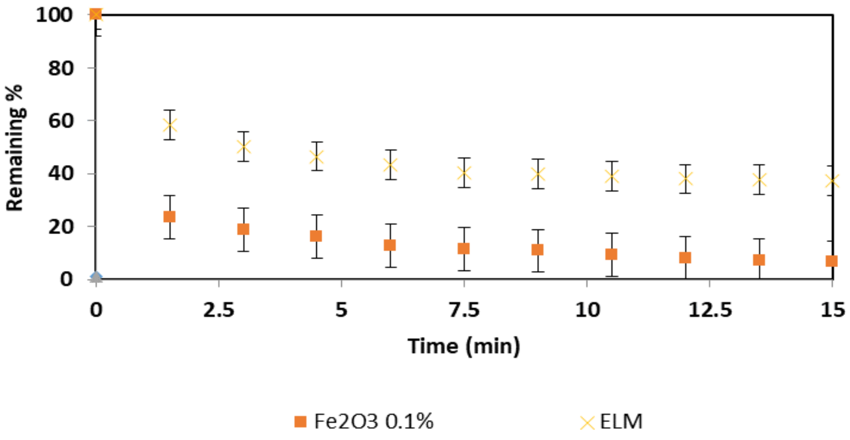

Figure 8. Effect of Fe_2O_3 nanoparticles concentrations on ELM process

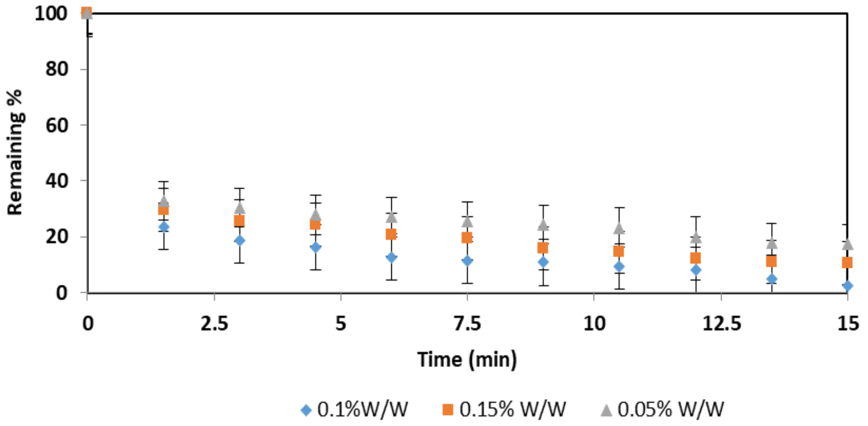

Figure 9. Removal efficiency of 4-Nitrophenol.

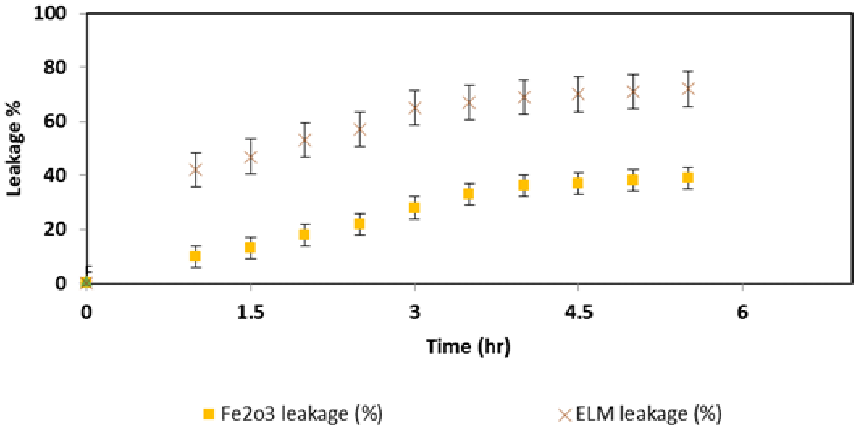

Figure 10. ELM stability in terms of percentage leakage.

4. REMARKS

In this work the following have been demonstrated and noticed.

-Best operation conditions obtained for the removal of 4-Nitrophenol were, volume ratio of internal receiving phase to organic phase (W1/O) was 1/3 (V/V), Span-80 percentage was 2% of the weight of the ELM the homogenizer speed was 8000 rpm, treatment ratio was 1/2 (V/V), mixing speed was 300 rpm, and pH of W2 was 1.5.

- The magnetic Fe_2O_3 nanoparticles enhance the stability of the ELM and extraction activity due to the ability of forming protective film by the particles at (O/W) and increased the binding sites on the surface of the solute. The results indicated that the ratio of 0.1% (W/W) of magnetic Fe_2O_3 nanoparticles to internal receiving phase elevates the 4-Nitrophenol extraction to higher level spicily of 97% in 1.5 min.

- The best ratio of combination obtained was 0.1% (W/W) Fe_2O_3, which give higher removal efficiency for 4-Nitrophenol of 97.375 % in 1.5 min. This clarifies the ability to increase the emulsion stability and extraction. With further increasing the concentration after emulsion droplets covering totally, nanoparticles will disperse in W2 phase and some of the particles probably cause aggregation in W1/O mediator, which reflect on the stability of emulsion and leads to reducing the removal/ separation process.

REFERENCES

1. Agarwal A, Manoj MK, Kumari S, Bagchi D, Kumra V, et al. (2008). *Extractive separation of copper and nickel from copper bleed stream by solvent extraction route*. Miner Eng. 21: 1126-1130.

2. Bhavyank Panchal, Jaimin Pandya. (2016). *Extraction of phenol from aqueous streaminto emulsion liquid membrane*. International Journal of Current Trends in Engineering & Research (IJCTER). e-ISSN 2455–1392 Volume 2 Issue 4, pp. 145 – 153.

3. Bjorkegren, R.F. Karimi, (2012). *A Study of the Heavy Metal Extraction Process using Emulsion Liquid Membranes.* Chalmers University of Technology, Sweden.

4. Chaouchi, Sarah, and Oualid Hamdaoui. (2016). *Removal of 4-Nitrophenol from Water by Emulsion Liquid Membrane.* Journal Desalination and Water Treatment. 57-5253–5257.

5. Djenouhat M., Hamdaoui O., Chiha M. and Samar M.H. (2008). *Ultrasonication assisted preparation of water-in-oil emulsions and application to the removal of cationic dyes from water by emulsion liquid membrane. Part 1: membrane stability*. J. Sep. Purif. Technol. 62-636–641.

6. Gasser M.S., El-Hefny N.E., Daoud J.A. (2008). *Extraction of Co (II) from aqueous solution using emulsion liquid membrane*. J. Hazard. Mater. 151-610-615.

7. Hamid R. Mortaheb, M. H. (2008). *Study on a new surfactant for removal of phenol from wasterwater by emulsion liquid membrane*. Journal of Hazardous Materials, 582 - 588.

8. Jilska M.P., Geoff W.S. (2008). *Use of Emulsion Liquid Membrane Systems in Chemical and Biotechnological Separations*. CRC Press.

9. John C. Crittenden, R. Rhodes Trussell, David W. Hand, Kerry J. Howe, George Tchobanoglous (2012). *MWH's Water Treatment Principles and Design*. 3rd Edition. John Wiley & Sons, Inc.

10. Kargar. A., Kaghazchi. T., Sohrabi. M. and Soleimani. M. (2006). *Application of experimental design to emulsion liquid membrane pertraction of gold (III) ions from aqueous solution*. Iranian journal of chemical engineering. Vol.3, No.1 (winter). IAChE.

11. Kim Y.J., Liu Y.D., Seo Y., Choi H.J. (2013). *Pickering- emulsionpolymerized polystyrene/*Fe_2O_3 *composite particles and their magnetoresponsive characteristics*. Langmuir, 29 -4959–4965.

12. Lawrence K. Wang, Yung-Tse Hung, Howard H. Lo, Constantine Yapijakis. (2006), *Handbook of Industrial and Hazardous Wastes Treatment*.2nd Edition. MARCEL DEKKER, INC.

13. Lelin Zeng, L. Y. (2015). *Influences of axial mixing of continuous phase and polydispersity of emulsion drops on mass transfer performance in a modified rotating disc contractor for an ELM system*. Ind. Eng. Chem. Res., 54, 9832 - 9843.

14. Lin Z., Yu D. Li Y. (2015). *Study on the magnetic ODSA-in-water Pickering emulsion stabilized by Fe3O4 nanoparticle*. Colloid Polym. Sci. 293-125–134.

15. M. Djenouhat, O. Hamdaoui, M. Chiha, M.H. Samar. (2008). *Ultrasonication-assisted preparation of water-in-oil emulsions and application to the removal of cationic dyes from water by emulsion liquid membrane. Part 1. Membrane stability*. Sep. Purif. Technol., 62 636–641.

16. Meda, V., Lope, T., Tyler, R., Baik, O. D., and Soltan, J. (2014). *Treatment of Phenol in Water Using Microwave-Assisted Advanced.* Nasralla R. A., Nasr-El-Din H. A., 2014. Impact of cation type and concentration in injected brine on oil recovery in sandstone reservoirs. J Petrol Sci Eng. 122: 384–95

17. Mokhtari, B., Pourabdollah, K. (2012). *Inclusion Separation of Alkali Metals in Emulsion Liquid Membranes by Nano-baskets of Callx [4] Crown-3*. Brazilian Journal of Chemical Engineering, Vol. 29, No. 04, pp. 783 – 793.

18. Mortaheb H.R., Amini M.H., Sadeghian F., Mokhtarani B. and Daneshyar H. (2008). *Study on a new surfactant for removal of phenol from wastewater by emulsion liquid membrane*. J. Hazard. Mater. 160-582–588.

19. Ng. Y.S., Jayakumar N. S. and Hashim. M.A. (2010). *Performance Evaluation of Organic Emulsion Liquid Membrane on Phenol Removal*. J. Hazard Mater. 184(1-3) 255-260. DOI: doi: 10.1016/j.jhazmat.2010.08.030.

20. Noman Li, N. (1974), *Separating Hydrocarbons with Liquid Membranes*. U.S. Patent RE27, 888.

21. Norela Jusoh, Norasikin Othman. (2016). *Stability of water-in-oil emulsion in liquid membrane prospect*. Malaysian Journal of Fundamental and Applied Sciences Vol. 12, No. 3-114-116.

22. Ooi, Z.-Y., Harruddin, N. Othman, N. (2015), *Recovery of kraft lignin from pulping wastewater via emulsion liquid membrane process*. Biotechnology Progress. 31(5): 1305 - 1314.

23. Park H.J., Chung T.S. (2003). *Removal of phenol from aqueous solution by liquid emulsion membrane*. Korean J. Chem. Eng. 20-731-735.

24. Park, Y., Skelland, A. H. P., Forney, L. J., Kim, J. H. (2006). *Removal of phenol and substituted phenols by newly developed emulsion liquid membrane process*. Water Res., 40, 1763-1772

25. Raita Murnieks, C. E. Gonter. (1962). *Ultraviolet spectrophotometric determination of benzoic acid in refined Phthalic Anhydride*. Analytical Chemistry. Vol. 34, NO. 2.

26. Sawsan A.M. Mohammeda, Nasser Zoulib, Muthanna Al-Dahhan. (2017). *Removal of benzoic acid from wastewater by pickering emulsion liquid membrane stabilized by magnetic* Fe_2O_3 *nanoparticles*. Desalination and Water Treatment. 68-114–121.

27. Tjoon Tow Teng, Muthuraman, Mubeena, Sathya (2013). *Emulsion Liquid Membrane: Removal and Recovery of Organic and Inorganic Ions*. J Membra Sci Technol, 3:2.

28. Zhaoyun Lin, Zhe Zhang, Youming Li, Yulin Deng. (2016). *Magnetic nano-Fe3O4 stabilized Pickering emulsion liquid membrane for selective extraction and separation.* Chemical Engineering Journal 288-305–311.

II. REMOVAL OF HYDROCARBONS OF 4-NITROPHENOL BY EMULSION LIQUID MEMBRANE (ELM) USING MAGNETIC FE2O3 NANOPARTICLES AND IONIC LIQUID

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ABSTRACT

Emulsion liquid membrane (ELM) is an emerging technology to remove the hydrocarbons from industrial wastewater and water. For the first time, the effects of the combination of magnetic nanoparticles and ionic liquid in ELM (water/organic/water) on the removal efficiency of 4-Nitrophenol as an example of hydrocarbons from synthetic wastewater was investigated. The 4-Nitrophenol removal efficiency of 99% in 1 min was achieved and the emulsion stability was improved significantly to 81% for 6 hours with the use of combination of surface-modified 0.05% (W/W) magnetic Fe_2O_3 nanoparticles and 0.05% (V/V) ionic liquid $[BMIM]^+[NTf2]^-$ in ELM. Demulsifying emulsifier particles from the interfaces of the droplets can be enhanced by using a magnetic force without causing a change in the oil phase chemistry. The outcomes of this study can be extended to the removal of other hydrocarbons and polar pollutants from industrial wastewater and water

1. INTRODUCTION

Various industrial and manufacturing processes produce multiple types of wastewaters that introduce toxic contaminants into water and groundwater. Most of these contaminants are sources of pollution to the environment. This causes serious environmental concern, primarily because these industrial waste contaminants are known to be hazardous. Hydrocarbons such as phenolic compounds of 4-Nitrophenol and other derivatives are often found in wastewater of many industrial processes such as dyes, pesticides, petroleum refinery, and petrochemical, pharmaceuticals, and mineral and mining processes [1]. The United States Environmental Protection Agency (USEPA) has labeled the 4-Nitrophenol among others as toxic aqueous chemicals due to their ability to extinguish the important issues, such as kidneys, central nervous system, liver, and blood cells, in the human and animal body [2]. Therefore, the wastewater generated from these industries needs efficient treatment before it is discharged to the environment.

Many studies and technologies have been reported in the literature for hydrocarbons removal from water and industrial wastewater [1; and 3]. Among these treatment methods are coagulation-flocculation, chemical precipitation, ion exchange, electro-oxidation, flotation, adsorption, and advanced oxidation (Kurniwan et al., 2006 and [4]). Membrane method has also been introduced to treat the wastewater, which exploits either porous or nonporous polymeric and ceramic membranes to provide a selective barrier between the wastewater and the internal receiving phase [5]. Instead of using a solid barrier as the membrane material, liquid also has been used as a membrane barrier between phases [6]. This liquid membrane method has been further advanced to introduce a new technology of emulsion liquid membrane (ELM) to further enhance the removal of the pollutants from the wastewater or waste organic phases (Li. N., 1968), which is the focus of this work.

The emulsion liquid membrane (ELM) consists of either Water-Oil emulsion mixed (W1/O) in the treated aqueous water (W2) phase (W1-O-W2) or Oil-Water emulsion mixed (O1/W) in the treated organic oil (O) phase (O1-W-O2) [7]. ELM started when Li. N.(1968) proposed a single process of extraction, or stripping, known as a liquid surfactant or emulsion liquid membrane (ELM) of W1-O-W2 featured with high removal rate, high selectivity at a low cost, and the removal is enhanced by a reaction to form precipitate [8.9.10].

An emulsion liquid membrane (ELM) for the W1-O-W2 system is first formed by mixing two immiscible phases and dispersing the resulting emulsion (W1-O) in another batch reactor containing aqueous feed (wastewater) phase (W2). The emulsion consists of tiny aqueous droplets (W1) distributed in the organic membrane phase (O), forming globules of (W1-O) when it is mixed with the aqueous feed (synthetic wastewater) phase (W2) containing hydrocarbons of 4-Nitrophenol. The 4-Nitrophenol that is in the aqueous feed (synthetic wastewater) phase (W2) soluble in the oil membrane phase (O), it can diffuse through the membrane phase of the globules and reacts with a stripping agent (reactant), NaOH in the internal receiving phase (W1). The 4-Nitrophenol transported is converted into solute precipitate which is not soluble in the membrane phase; consequently, it was trapped in the stripping agent (reactant) in internal receiving phase (W1) and be removed easily through filtration or sedimentation. This means that the driving force of the concentration gradient of the pollutants transport from W2 phase to

W1 phase through O membrane phase remains at its maximum, and hence the transport of the pollutants continues until about the completion of the removal [11] during a particular duration of time. Figure 1 shows the schematic of the transport in ELM.

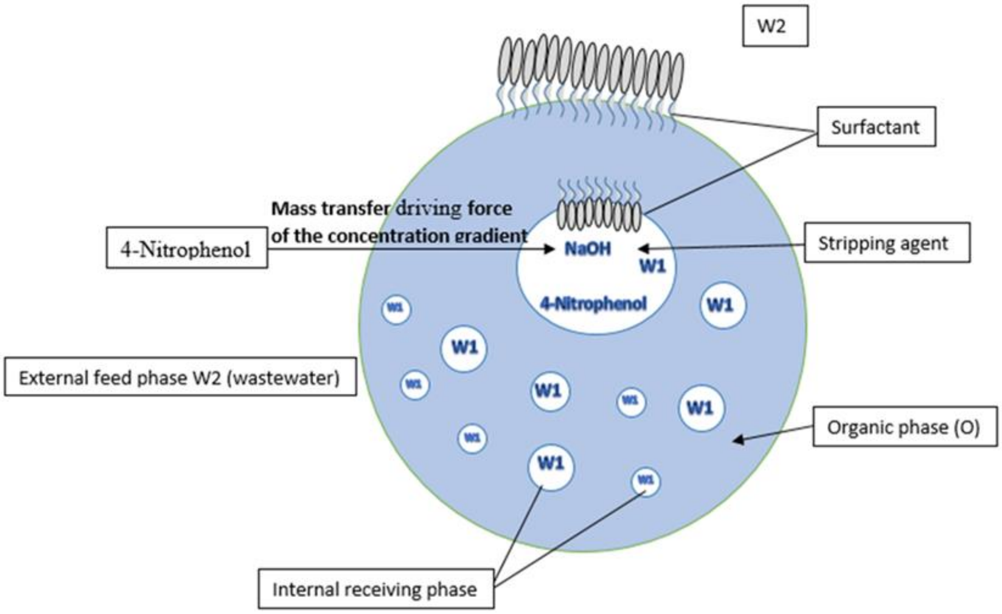


Figure 1. Schematic of Emulsion liquid membrane.

Despite the promising results of (ELM) as reported in the literature, it has not been advanced toward industrial applications because ELM is still suffering from critical technical issues that are related to: 1) swelling and breakage that decrease the emulsion stability which affects negatively the removal efficiency, 2) not a high percentage of removal in a longer duration of time, and 3) inefficient way of demulsification to separate, the solute waste and to recycle the organic phase [12, 13]. Hence, emulsion stability extraction efficiency and duration of ELM have been studied to understand the relationship between the properties of the emulsion membrane and the operating factors

(H. Weingrtner [14]). In the literature, the surfactant has been used in the organic phase to improve emulsion stability.

Recently, to further improve on stabilization of ELM, ionic liquid as a stabilizer has been demonstrated. Goyal et al. [15] showed that the stability of W1-O emulsion was improved by incorporating an ionic liquid, 1-butyl-3-methylimidazolium bis (trifluo¬romethylsulfonyl) imide, $[BMIM]^{+}[NTf2]^{-}$, in the organic phase (O) as a stabilizer. Sawsan et al. (2016) studied the ELM method with ionic liquid $[BMIM]^{+}[NTf2]^{-}$ in combination with the surfactant of Span 80 to remove benzoic acid from wastewater. The results indicated that the increase in the concentration of ionic liquid $[BMIM]^{+}[NTf2]^{-}$ up to 0.2 % (V/V) in the organic phase (O) yields an improvement in stability which also leads to enhanced removal efficiency of benzoic acid of 99.7% after 5 min in a batch operation. Sawsan et al. [16] also studied the removal of phenol compounds (phenol, 2-chlorophenol, and 4-nitrophenol) from wastewater. The results indicated that the increase in the concentration of ionic liquid $[BMIM]^{+}[NTf2]^{-}$ up to 0.3% (V/V) in the organic phase (O) yields an improvement in stability which also leads to enhanced removal efficiency of phenol of 78% after 30 min, and 2-chlorophenol and 4-nitrophenol of 95 % and 98.5 %, respectively after 30 min in a batch operation.

In a different approach, the addition of nanoparticles in the organic phase (O) rather than ionic liquid was also found to enhance the stabilization of the ELM [17, 18]. The effects of the magnetic Fe_3O_4 nanoparticles in the organic phase (O) on the emulsion stability were studied by Lin et al. [19] for the removal of the 4-methoxyphenol from wastewater. The results showed that the 0.5 wt% Fe_3O_4 magnetic nanoparticles have a strong effect on the percentage reduction of the emulsion leakage (emulsion stability) giving 86 % removal for 4-methoxyphenol in 2 min in a batch operation. The effects of the magnetic Fe_2O_3 nanoparticles in the organic phase (O) on the emulsion stability were also studied by Al-Obaidi and Al-Dahhan [20] for the removal of the 4-Nirtophenol from synthetic wastewater. The results also showed that the 0.1 % (W/W) of magnetic Fe_2O_3 nanoparticles have a strong effect on the percentage reduction of the emulsion leakage (emulsion stability) giving 93.4 % removal for the 4-Nirtophenol after 15 min in a batch operation.

Currently, no studies have been reported in the literature about the effects of the combination of ionic liquid and nanoparticles in the organic phase (O) for the emulsion stabilization, removal efficiency, and the time duration for the removal of pollutants using ELM. Therefore, the present study focuses on investigating the emulsion stability, the enhancement removal, and the duration of the batch operation of the removal of 4-Nitrophenol from the synthesis wastewater using combined magnetic Fe_2O_3 nanoparticles and $[BMIM]^+[NTf2]^-$ ionic liquid in the organic phase (O) in the emulsion liquid membrane (ELM).

2. MATERIALS AND METHOD

2.1. CHEMICALS

The materials that are used in this study were Kerosene (Boiling Point 175 – 325 ^oC) as the organic phase (O), Span-80 (sorbitan monooleate) as the surfactant, sodium hydroxide (NaOH) as the stripping agent to react with the hydrocarbon pollutants to form a solute precipitate, hydrochloric acid (HCl) to adjust for the pH of W2, 4-Nitrophenol, and ionic liquid of 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, [BMIM]+ [NTf2]-, which obtained from Sigma Aldrich (St. Louis, MO 63103, USA). The magnetic Fe_2O_3 nanoparticles with a size range of 30 – 60 nm were acquired from Alfa Aesar (Ward Hill, MA 01835, USA). This size of nanoparticles has a noticeable lower cost than the smaller size, where the cost is an important factor for large-scale applications. The magnetic characteristic of the nanoparticles has been selected to be easily removed and recycled by a magnetic field. In addition, this will facilitate the step of the demulsification and separation of the formed solutes, and aqueous and organic phases where the organic phase can be recycled.

2.2. EXPERIMENT WORK

In this work, the ELM of W1/O/W2 phases has been implemented since the pollutants (300 ppm of 4-Nitrophenol) are in the aqueous feed phase (W2). The organic phase (O) represents the membrane that is part of the emulsion formed by mixing the organic phase (O) with the aqueous phase (W1) (internal phase) that contains the stripping agent as the reactant of 0.5 N NaOH solution at a high agitation speed of rotation per minutes (rpm) of the mixer to form an emulsion of small aqueous droplets in the organic phase. The organic phase (O) consists of surfactant Span-80 and kerosene. The emulsion (W1/O) is then dispersed in the aqueous feed (synthetic wastewater) phase (W2).

The 4-Nitrophenol transfers from W2 phase through O phase to W1 phase where it reacts with the stripping agent (NaOH) to form a solute precipitate which makes a reaction product incapable of diffusing back through the membrane phase were presence in Figure 1. Consequently, the 4-Nitrophenol concentration in the internal stripping phase is also maintained at zero by the reaction. The equations exhibiting removal and stripping agent process of 4-Nirophenol occurring in liquid emulsion membrane technology was given below.

$$C_6\,H_4NO_2OH + NaOH \longrightarrow C_6\,H_4NO_2O\,Na + H_2O \qquad (1)$$

Several factors affect the removal of the pollutant using ELM such as the volume ratio of aqueous phase (W1) to organic phase (O) (W1/O ratio, V/V), a surfactant concentration of (%W/V), agitation intensity to form an emulsion (rpm) (emulsion agitation), volume treatment ratio of (W1/O) to the aqueous feed phase (W2) (ELM/W2 ratio V/V), agitation intensity of the treatment and globules formation (rpm) (treatment agitation), concentrations of magnetic nanoparticles and ionic liquid, and pH of the aqueous feed phase (W2), for each range of a variable studied, the other variables were fixed as based on the best value of that variable for the removal of a hydrocarbon reported in litterers [10]. Figure 2 illustrates the steps of the experimental work of the ELM employed in this work.

Therefore, the first step is to identity the best combination values of these variables to remove 4-Nitrophenol before study the effects of nanoparticles and ionic liquid on the ELM stability, removal efficiency, and duration of the removal. If needed, the following evaluation of the variation of the values has been performed as the Table 1 below:

Samples from the agitated solution were taken at different time periods using a micropipette and then separated from the emulsion phase using a nylon syringe filter of 0.2 µm (Simsii Inc. USA). The 4-Nitrophenol was analyzed using a 96 well

UV – microplate at a wavelength band of 400 nm.non pulvinar neque laoreet suspendisse interdum.

The second step of experimental work, the effects addition of the Magnetic Fe_2O_3 nanoparticle alone in the organic phase (O) of 0.05 %, 0.1 %, and 0.15 % (W/W) and the separately of ionic liquid $[BMIM]^+[NTf2]^-$ alone in the organic phase (O) of 0.05 %, 0.1 %, 0.1 5% and 0.2 % (V/V) will be investigated on the stability of the ELM, percentage removal of the 4-Nitrophenol and the time duration of the batch removal. Then the identified best values of nanoparticles and ionic liquid will be used when both are combined to examine the effect of such combination on the mentioned parameters of the ELM performance as the Table 2 below.

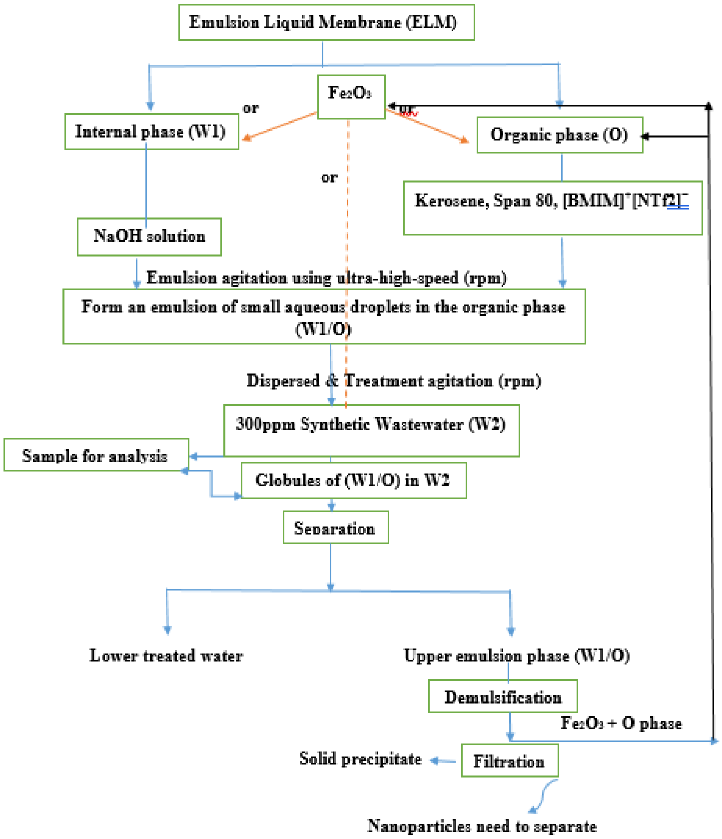


Figure 2. Block diagram.

Table 1. Factors affect the removal of the pollutant

No	Factors	Variable studied
1	Ratios of the NaOH solution to the organic phase (W1/O)	1/1 (V/V) 1/3 (V/V) 1/5 (V/V)
2	Span 80 surfactant concentrations	2% (W/V) 3% (W/V) 4% (W/V)
3	Emulsion agitation using ultra-high-speed (Turrax IKA-T25) for 10 minutes (a milky white color liquid membrane is produced)	5000 rpm 7000 rpm 8000 rpm
4	Ratios of the ELM (W1/O) to W2	1/1 (V/V) 1/2 (V/V) 1/3 (V/V) 1/5 (V/V) 1/8 (V/V)
5	Treatment agitation of W2 with (W1/O) of for 15 min using IKA overhead stirrer (Model: RW20 digital)	250 rpm 300 rpm 400 rpm
6	The pH of W2 of measured by a pH meter (Oakton Acron)	1.5, 2.5 ,3.5, 4.5, and 6.5

Since the key goal is to identify the lowest possible amount of nanoparticles and ionic liquid with the best performance of the ELM as illustrated in Table 1. For all the conditions studied, each experiment was repeated three times where the error bars were estimated.

Table 2. Combination of the concentration ionic liquid and nanoparticles

No	$[BMIM]^+[NTf2]^-$ (V/V)	Fe_2O_3 (W/W)
1	0.05%	0.05%
	0.1%	
	0.15%	
	0.2%	
	0.25%	
2	0.1%	0.1%
	0.15%	
	0.2%	
	0.25%	
3	0.1%	0.15%
	0.15%	
	0.2%	
	0.25%	

At the end of the removal of 4-Nitrophenol, the mixture is placed in a funnel to separate the upper emulsion phase (W1/O) and the lower aqueous feed phase (W2). Then a magnetic field (1T magnet) is applied on the upper phase which pulled the nanoparticles from the emulsion phase (W1/O) by the magnetic field and with this demulsification occurs where both nanoparticles and organic phase will be reuse after the solute precipitate is filtered and separated. The accumulated Fe_2O_3 was washed with acetone and distilled water then dried under a vacuum at 50 ºC for 10 h to be reused again. The recycled nanoparticles and organic phase will be used for preparing a new experiment of ELM, as shown in Figure 3.

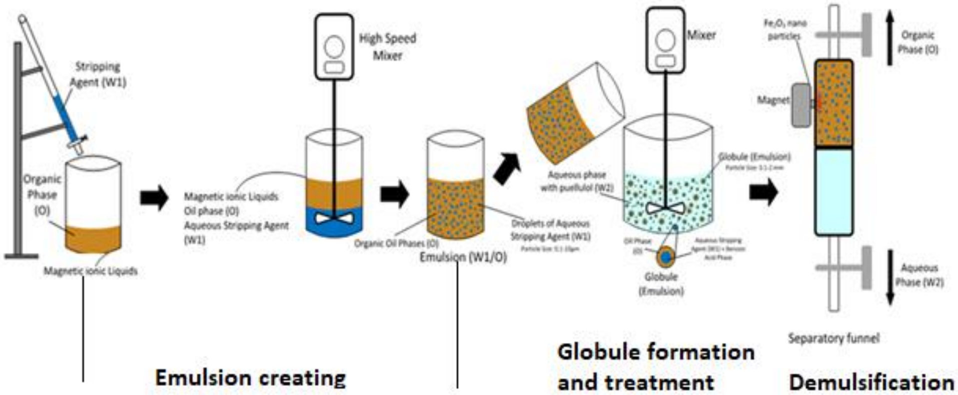


Figure 3. Emulsion liquid membrane.

2.3. CALCULATION OF THE ELM STABILITY

To measure the ELM stability, volume ratio 0.5/1 (V/V) of red dye to the internal phase (W1) as a leakage indicator which has no interaction with both organic and aqueous molecules [21]. The percentage (%) of leakage is determined using the following Equation:

$$\%\,Leakage = \left(\frac{dye\,concentration\,(W2)}{dye\,concentration`in W2`(with\,\max.time'\,allowed)}\,X\,100 \right) \tag{2}$$

where, the red dye concentration in W2 is the concentration of the dye in the external phase (W2) received from W1, and the concentration with maximum time in W2 is the maximum concentration of the dye that is reached in the external aqueous phase (W2) when all the red dye leaked from the internal aqueous phase (W1) to the external aqueous phase (W2).

The percentage of the pollutant remaining in W2 phase is defined by the following equation:

$$Extraction, E\% = \left(\frac{initial\, concentration - final\, concentration}{initial\, concentration} X\, 100 \right) \tag{3}$$

Percentage Extraction remaining = 100 – E (4)

3. RESULTS AND DISCUSSIONS

3.1. DEFINING THE BEST VALUE OF THE VARIABLE FOR 4-NITROPHENOL REMOVAL USING ELM WITHOUT NANOPARTICLES AND IONIC LIQUID

The following experiments have been performed to define the best values possible of the variables to be used to examine the effects of magnetic nanoparticles (Fe_2O_3) and ionic liquid on the removal of 4-Nitrophenol and its duration and the stability of the emulsion. For all these experiments the emulsion stability was examined as outlined earlier using dye technique and the emulsion stability of 27 % for 6 h.

1. The volume ratio of W1/O phase

The W1/O volume ratio has a significant role in emulsion stability and the removal because of its usefulness in trapping the droplets of W1 in the organic phase (O) in reacting the 4-Nitrophenol to the stripping agent (NaOH) in W1. The increase in the volume ratio will lead to emulsion instability [22]. W1/O Volume ratios of 1/1, 1/3, and 1/5 (V/V) as proposed by Ng et al. [23] were used to assess its effects on emulsion stability and the removal of the 4-Nitrophenol. Figure 4.a shows the results of the removal of 4-Nitrophenol. The volume ratio of 1/1 (V/V) forms large emulsion globules with a thin thickness of organic phase (O) between W1 droplets of the globules, which causes an increase in the leakage and lowers the removal efficiency [24]. While the volume ratio of 1/3 (V/V) forms tiny droplets with an increase in thickness (organic membrane) that causes a reduction in the leakage with high removal efficiency. Increasing the volume ratio to more than 1/3 (V/V) leads to a reduction in the stability of the emulsion with poor removal efficiency because of the promotion of the resistance for diffusion through the membrane large thickness of organic between droplets. Hence, the value of 1/3 (V/V) volume ratio of W1 phase to O phase has been selected [25].

2. The surfactant concentration of span 80 in the organic phase

Span 80 has been used as the surfactant added to the organic phase (O). Surfactant has a significant effect on the emulsion stability and the reduction of the emulsion leakage because it works as a protective barrier between the external feed phase (W2) and the stripping agent (W1) [26] as shown in Figure 2. The surfactant concentrations (Span 80) of 2 % (W/V), 3 % (W/V), and 4 % (W/V) were used. It was distinguished that a surfactant concentration of 2% (w/v) caused the highest percentage removal of 4-Nitrophenol and the lowest emulsion leakage, as shown in Figure 4.b. Increasing the concentration of Span 80 can negatively affect the removal of pollutants due to lowering the surface tension of the emulsion causing the formation of a small globules containing small number of droplets of W1. In addition, adding more of Span 80 would lead to an increase in the leakage, a reduction in the emulsion stability, and a decrease in the removal efficiency due to the formation of small emulsion globules [25].

3. The agitation intensity (rpm) to create emulsification (emulsion agitation)

The agitation (rpm) to create proper emulsion is essential as the formation of designable emulsion that can increase the removal efficiency [23], and [27]. The agitation of 5000, 7000, and 8000rpm were used to form the emulsion and to study the removal of the 4-Nitrophenol. Emulsion stability increases by increasing the agitation. The emulsion agitation of 8000rpm was found suitable by forming a “mayonnaise-like” emulsion due to the generation of more droplets. Increasing the droplet formation results in a highly viscous emulsion, and droplets merge with each there due to rapid mixing. Emulsification agitation of 8000rpm gives the better removal of the pollutants [28], as shown in Figure 4.c.

4. The volume ratio of (W1/O) globules to W2 phase

ELM (W1/O) globules to the W2 volume ratio plays a significant role in the performance of the ELM. The volume ratios of 1/1, 1/2, 1/3, 1/5, and 1/8 (V/V) were selected to examine the removal efficiency of 4-Nitrophenol. The volume ratio of 1/2 was found to be desirable, as shown in Figure 4.d. This ratio provides an increase in the overall surface area for mass transfer and removal capacity. The stability of emulsion increases by reducing the volume fraction of the internal phase, as stated by M. Djenouhat et al. [29].

The other volume ratios decrease the removal efficiency, which can be attributed to the increase in the membrane (O) thickness around the droplets. In addition, the mechanical resistance of the membrane increases at a higher organic fraction, thus preventing coalescence of the dispersed droplets and maintaining the size of the droplets to be within the range of the size of the standard droplets of $0.1 - 2$ mm. In general, larger droplet sizes increase the emulsion instability because the droplets easily coalesce (Ng et al. [23]).

5. The agitation intensity (rpm) of the mixing of (W1/O) globules and W2 phase (treatment agitation)

The effect of the agitation intensity (rpm) of 250, 300, and 400rpm was studied on the removal of the pollutants, as shown in Figure 4.e. The 300rpm was found to be the desire for increasing the emulsion stability as it displays the lowest amount of emulsion leakage. Producing a greater shear force on the droplets significantly reduces the emulsion globules size and increases the contact area for mass transfer [30]. At a low mixing intensity, the emulsion globules size increases, which causes a decrease in the mass transfer rate of 4-Nitrophenol. Increasing the agitation intensity of rpm can lead to reducing the emulsion stability because high intensity produces globules rupture, causing leakage of the W1 into the W2 phases ([22]; [31]).

6. The pH of the W2 phase

The pH values used 1.5 - 6.5 and are presented in Figure 4.f, is observed that when the value of the pH of the external feed (synthetic wastewater) phase was 1.5 improved the removal efficiency and the emulsion stability [32]. Removal of the 4-Nitrophenol from synthetic wastewater (W2) precipitate in alkaline solutions (Zhaoyun. 2016). The removal efficiency enhances at a lower pH due to an increase in the hydrogen ion (H^+) concentration of the external feed (synthetic wastewater) phase (W2), which reacts with NaOH (W1) to form a precipitate of complex acid-base. The increase of the pH decreases the hydrogen ion (H^+), which reduces the removal efficiency [32].

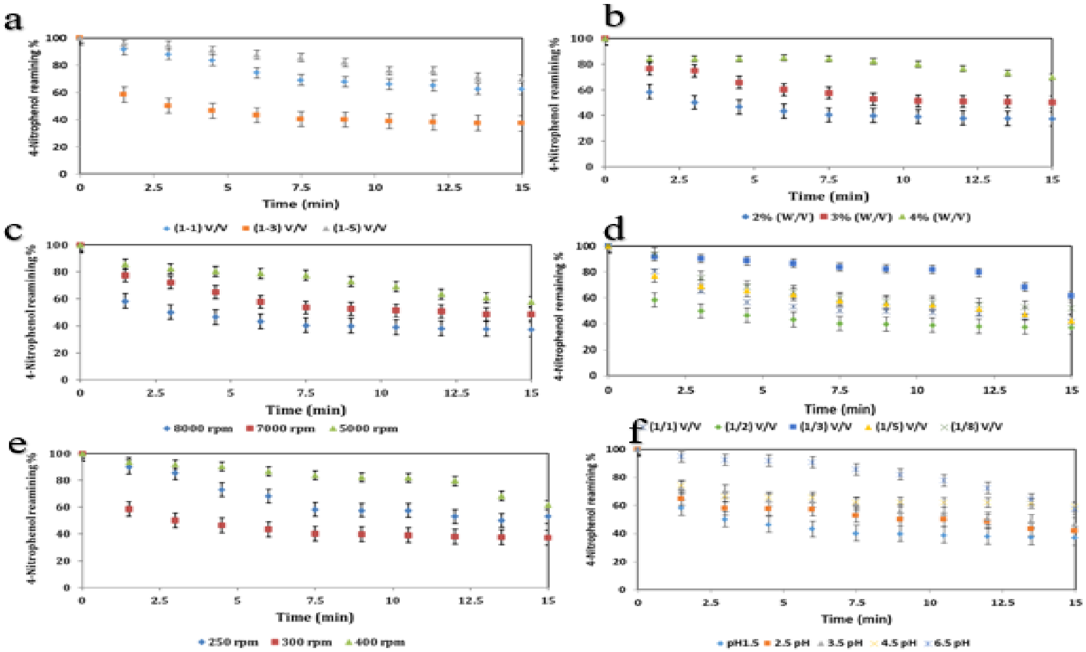


Figure 4. The effect of the ELM removal for 4-Nitrophenol using the following values of variable: W1/O volume ratio of 1/3 (V/V), Span 80 concentration of 2% (W/V), emulsification agitation speed to create emulsion of 8000 rpm, ELM (W1/O)/W2 volume ratio of 1/2 (V/V), treatment agitation mixing speed of W2 of 300 rpm, and pH of W2 of 1.5.

3.2. THE EFFECT OF NANOPARTICLES AND IONIC LIQUID ON THE REMOVAL OF 4-NITROPHENOL

The effects of the magnetic nanoparticles (Fe_2O_3) and ionic liquid in the organic phase (O) on the removal of 4-Nitrophenol, at the selected best values of the variable studied above have been investigated using the values of the W1/O volume ratio of 1/3 (V/V), Span 80 concentration of 2% (W/V), emulsion agitation of 8000 rpm, ELM (W1/O)/W2 volume ratio of W2 of 1/2 (V/V), treatment agitation of W2 of 300 rpm and pH of 1.5. For all the experiments performed here the emulsion stability was examined, as outlined earlier.

3.2.1. The Effect of the Fe_2O_3 Nanoparticles on the Removal of 4-Nitrophenol.

Figure 5 shows the results of the removal of 4-Nitrophenol using 0.05% (W/W), 0.1% (W/W), 0.15% (W/W) of magnetic nanoparticles of Fe_2O_3 in the O phase. The results illustrate that the ratio of 0.1% (W/W) of magnetic Fe_2O_3 nanoparticles alone in the O phase elevates the 4-Nitrophenol removal to higher level of 93.4% during 15 min and 54% of the emulsion stability during 6 h, as compared to the ratios of 0.05% (W/W) and 0.15% (W/W). The presence of the magnetic Fe_2O_3 nanoparticles in the organic phase (O) enhances the stability of the ELM and the mass transfer of 4-Nitrophenol from W2 to W1 through the O phase [33]. This improves the solute removal due to forming film of the particles at (W1/O) interface and increasing the binding sites on the surface of the solute (Sawsan et al., 2017).

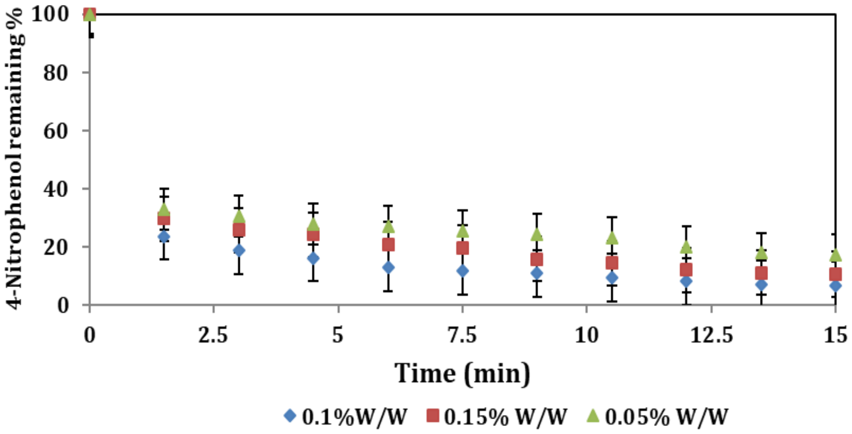


Figure 5. The effect of magnetic Fe_2O_3 nanoparticles in organic phase (O) on the ELM removal for 4-Nitrophenol removal: W1/O volume ratio of 1/3 (V/V), surfactant concentration of 2% (W/V), emulsification speed of 8000 rpm, ELM (W1/O)/W2 volume ratio of 1/2 (V/V), treatment agitation mixing speed of W2 of 300 rpm, and pH of w2 of 1.5.

The findings are in agreement with the results obtained by Sawsan et al. [31] which indicate that the increase in magnetic nanoparticles Fe_2O_3 concentration beyond full coverage of the W1 droplets in O phase, as extra magnetic Fe_2O_3 nanoparticles concentrations will be dispersed in the W2 phase, and some of the magnetic nanoparticles might form aggregates on W1-O interface, which affect the stability of the emulsion and slow the transfer process [34]; hence the removal efficiency decreases (Qusay Al-Obaidi, Muthanna Al-Dahhan. 2020).

3.2.2. The Effect of Ionic Liquid in the Organic Phase (O) on the Removal of 4-Nitrophenol. Regarding the use of ionic liquid in the organic phase (O) as another method to improve the stability of the ELM, the ionic liquid $[BMIM]^+[NTf2]^-$ was chosen to be used in this study because it has been shown to be extracted and striped more efficiently as shown in a schematic Figure 6 of the packed ionic liquid molecules between the span 80 molecules [35]. The relation between the concentration (0.05 % (V/V) to 0.25 % (V/V)) of ionic liquid $[BMIM]^+[NTf2]^-$ and emulsion stability time is shown in Figure 7. Increasing the concentration of ionic liquid $[BMIM]^+[NTf2]^-$ up to 0.2 % (V/V) of $[BMIM]^+[NTf2]^-$ will increase the stability time. Hence, at 0.2 % (V/V) ionic liquid concentration, a removal of 83.9% of 15 min of 4-Nitrophenol was achieved and 49% of emulsion stability during 6 h. At a higher ionic liquid concentration, the stability time decreased due to increased emulsion sedimentation by considering the high density of the ionic liquid $[BMIM]^+[NTf2]^-$. The emulsion liquid membrane (ELM) stability was increased due to the ionic liquid $[BMIM]^+[NTf2]^-$ which could be caused by Coulombic interactions of the charges on the NaOH and ions of the ionic liquids $[BMIM]^+[NTf2]^-$. This strong interaction enhances the emulsion stability by lowering the coalescence of the internal droplets [27]. There is probability of hydrogen bonding between [OH] group of NaOH and ionic liquid $[BMIM]^+[NTf2]^-$.

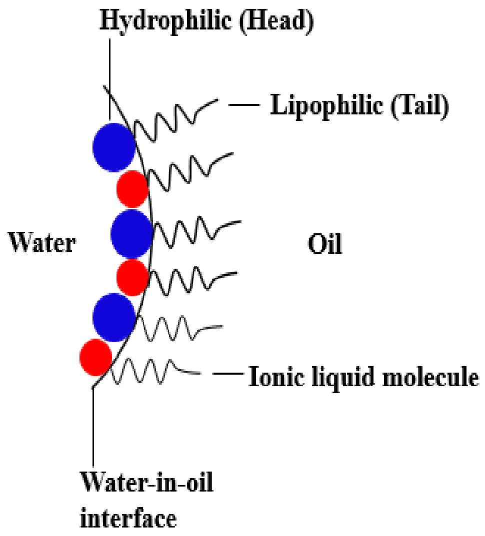


Figure 6. Schematic of the hydrophilic head and lipophilic tail of the Span 80 and ionic liquid $[BMIM]^+[NTf2]^-$ molecules packed between the surfactants.

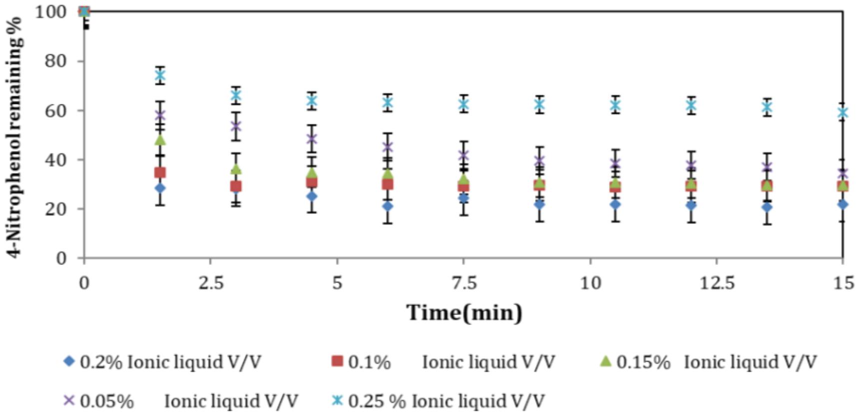


Figure 7. The effect of ionic liquid $[BMIM]^+[NTf2]^-$ in organic phase on the ELM removal for 4-Nitrohenol removal: W1/O volume ratio of 1/3 (V/V), surfactant concentration of 2% (W/V), emulsification speed of 8000 rpm, ELM (W1/O)/W2 volume ratio of 1/2 (V/V), treatment agitation mixing speed of W2 of 300 rpm, and pH of W2 of 1.5.

The hydrogen bonding may cause a strong protection surrounding the internal droplets to avoid coalescence. The increase of ionic liquid $[BMIM]^+[NTf2]^-$ can further reduce the interfacial tension, also through adsorbing in the W1- O interface and thereby minimizing the repulsion of the hydrophilic head-groups of the Span 80, which contributes to a more efficient packing of the Span 80 at the interface and reduces the droplet size of W1 [35].

3.2.3. The Effect of Combining Nanoparticles and Ionic Liquid on the Removal of 4-Nitrophenol. As per the previous results of 3.2.1 and 3.2.2 sections, above the 0.1% (W/W) of magnetic nanoparticles Fe_2O_3 alone and 0.2 % (V/V) of ionic liquid $[BMIM]^+[NTf2]^-$ alone provide better removal of 4-Nitrophenol. Here, we combine both concentrations to examine the effects of the combination of the magnetic nanoparticles Fe_2O_3 and ionic liquid $[BMIM]^+[NTf2]^-$ added in organic phase (O) on the removal of 4-Nitrophenol. Also to examine the effects of the variation of ionic liquid concentration (0.05 % V/V to 0.25 % V/V) while maintaining the concentration of nanoparticles at 0.05% (W/W), 0.1% (W/W), and 0.15% (W/W) have been investigated as per Figure 8, and Table.3. The results of the leakage test were used as indicator for assessing stability as shown in Figure 9. The stability of the prepared ELM was assessed before performing the 4-Nitrophenol removal experiments. The breakage of the emulsion globules when the ELM is instable causes decreasing in the removal efficiency. The ELM stability highly affects the removal rate in the receiving phase (W1). The stability of ELM process was detected as indicated before via trace of the loaded dye in the receiving phase (W1) in a period of the ELM preparation and detected it in the external feed phase (W2) [36].

The lowest leakage and higher stability time were obtained with the combination of the magnetic nanoparticles Fe_2O_3 and ionic liquid $[BMIM]^+[NTf2]^-$ after 1 h which sustain during the experiments. This confirms that the combination improves the stability of ELM as compared with ELM alone, ELM + nanoparticles, and ELM + ionic liquid.

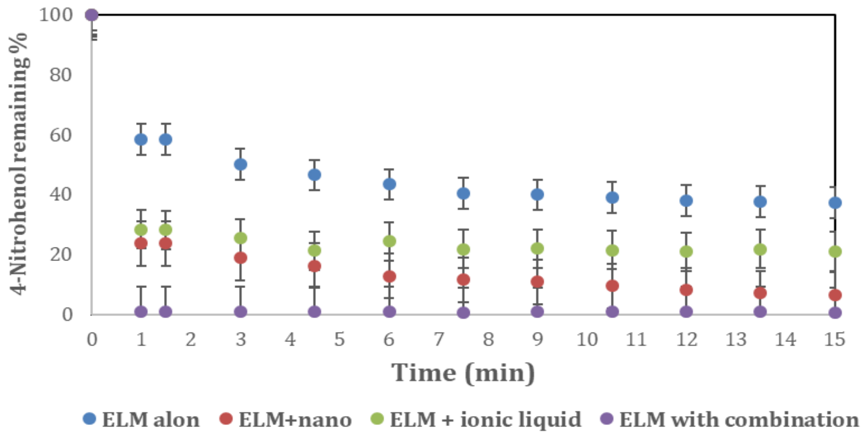
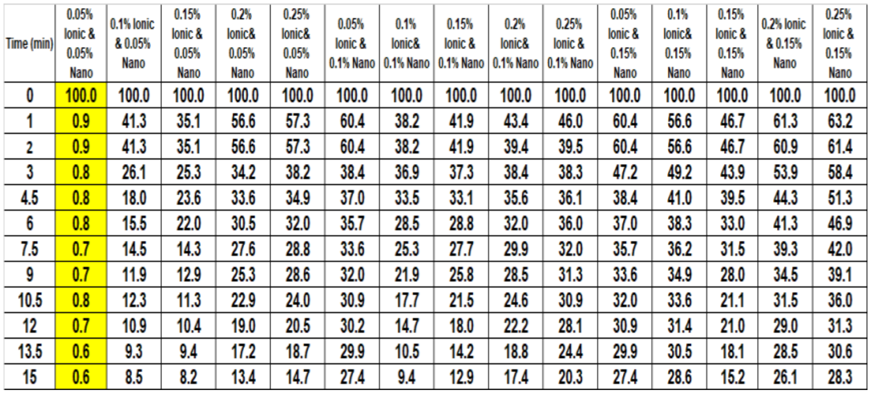


Figure 8. The effect of combination 0.05% (V/V) ionic liquid $[BMIM]^+[NTf2]^-$ and 0.05% (W/W) magnetic Fe_2O_3 nanoparticles in organic phase on the ELM removal for 4-Nitrophenol: W1:O volume ratio of 1/3 (V/V), surfactant concentration of 2% (W/V), emulsification speed of 8000 rpm, ELM (W1/O)/W2 volume ratio of 1/2 (V/V), treatment agitation mixing speed of W2 of 300 rpm, and pH of W2 of 1.5.

Hence, the combination enhances the stability and forms droplets that are particularly stable in the emulsion. Removal time is considered as the target to determine the ELM effectiveness which represents the period for the concentration of 4-Nitrophenol to real close to zero. The ratio of 0.05% (V/V) of ionic liquid $[BMIM]^+[NTf2]^-$ and 0.05% (W/W) of Fe_2O_3, gives higher removal efficiency for the 4-Nitrophenol 99% in 1 min and the emulsion stability was improved significantly to 81% for 6 h.

Table 3. The effect of combination (V/V) ionic liquid $[BMIM]^+[NTf2]^-$ and (W/W) magnetic Fe_2O_3 nanoparticles in organic phase on the ELM removal for 4-Nitrophenol: W1/O volume ratio of 1/3 (V/V), surfactant concentration of 2% (W/V), emulsification speed of 8000 rpm, ELM (W1/O)/W2 volume ratio of 1/2 (V/V), treatment agitation mixing speed of W2 of 300 rpm, and pH of W2 of 1.5.



Time (min)	0.05% Ionic & 0.05% Nano	0.1% Ionic & 0.05% Nano	0.15% Ionic & 0.05% Nano	0.2% Ionic& 0.05% Nano	0.25% Ionic& 0.05% Nano	0.05% Ionic & 0.1% Nano	0.1% Ionic& 0.1% Nano	0.15% Ionic & 0.1% Nano	0.2% Ionic& 0.1% Nano	0.25% Ionic & 0.1% Nano	0.05% Ionic & 0.15% Nano	0.1% Ionic& 0.15% Nano	0.15% Ionic & 0.15% Nano	0.2% Ionic & 0.15% Nano	0.25% Ionic & 0.15% Nano
0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
1	0.9	41.3	35.1	56.6	57.3	60.4	38.2	41.9	43.4	46.0	60.4	56.6	46.7	61.3	63.2
2	0.9	41.3	35.1	56.6	57.3	60.4	38.2	41.9	39.4	39.5	60.4	56.6	46.7	60.9	61.4
3	0.8	26.1	25.3	34.2	38.2	38.4	36.9	37.3	38.4	38.3	47.2	49.2	43.9	53.9	58.4
4.5	0.8	18.0	23.6	33.6	34.9	37.0	33.5	33.1	35.6	36.1	38.4	41.0	39.5	44.3	51.3
6	0.8	15.5	22.0	30.5	32.0	35.7	28.5	28.8	32.0	36.0	37.0	38.3	33.0	41.3	46.9
7.5	0.7	14.5	14.3	27.6	28.8	33.6	25.3	27.7	29.9	32.0	35.7	36.2	31.5	39.3	42.0
9	0.7	11.9	12.9	25.3	28.6	32.0	21.9	25.8	28.5	31.3	33.6	34.9	28.0	34.5	39.1
10.5	0.8	12.3	11.3	22.9	24.0	30.9	17.7	21.5	24.6	30.9	32.0	33.6	21.1	31.5	36.0
12	0.7	10.9	10.4	19.0	20.5	30.2	14.7	18.0	22.2	28.1	30.9	31.4	21.0	29.0	31.3
13.5	0.6	9.3	9.4	17.2	18.7	29.9	10.5	14.2	18.8	24.4	29.9	30.5	18.1	28.5	30.6
15	0.6	8.5	8.2	13.4	14.7	27.4	9.4	12.9	17.4	20.3	27.4	28.6	15.2	26.1	28.3

In addition, it gives least amount of nanoparticles and ionic liquid to be used. The results illustrate that the combination of magnetic nanoparticles Fe_2O_3 and ionic liquid $[BMIM]^+[NTf2]^-$ increase the emulsion stability and the removal efficiency with less duration of time.

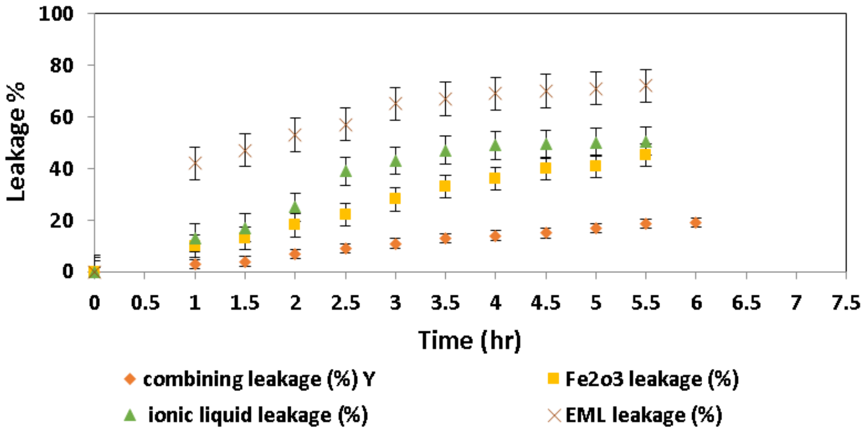


Figure 9. Effect of the combination ionic liquid $[BMIM]^+[NTf2]^-$ and magnetic Fe_2O_3 nanoparticles in organic phase on the ELM emulsion stability: W1:O volume ratio of 1/3 (V/V), surfactant concentration of 2% (W/V), emulsification speed of 8000 rpm, ELM (W1/O)/W2 volume ratio of 1/2 (V/V), treatment agitation mixing speed of W2 of 300 rpm, and pH of W2 of 1.5.

4. CONCLUSIONS

The experimental results viewed that the best operational conditions achieving for 4-Nitrophenol removal were: concentration of surfactant= 2 % (W/V), the volume ratio of internal phase to organic phase= 1/3 (V/V), agitation intensity 8000rpm, volume ratio ELM/W2= 1/2 (V/V), the agitation mixing speed=300 rpm, and pH of the W2 was 1.5. At the best conditions, the removal of 4-Nitrophenol was achieved with an efficiency of 63 % from aqueous solutions within 15 min.

The removal efficiency with the concentration of 0.1% (W/W) magnetic Fe_2O_3 nanoparticles was 93.4% at 15 min. While the removal efficiency with the concentration of 0.2% (V/V) of ionic liquid $[BMIM]^+[NTf2]^-$ was 83.9% at 15 min.

The long term of emulsion stability was greatly improved by the combination of the magnetic Fe_2O_3 nanoparticles and ionic liquid $[BMIM]^+[NTf2]^-$ in organic phase (O) by the formation of a three-dimensional network among the droplets and particles that give the higher removal efficiency at a shorter time of 1 min with the lowest leakage and higher stability of the ELM process time starting after 1hr and sustains during the experiments time. The best combination in organic phase (O) was of 0.05% (W/W) Fe_2O_3 nanoparticle and 0.05 % (V/V) ionic liquid $[BMIM]^+[NTf2]^-$, which gives higher removal efficiency for 4-Nitrophenol of 99% for 1 min of batch separation and the emulsion stability of 81% for 6 hours. This confirms the ability of such combination in increasing the emulsion stability and removal.

REFERENCES

1. Lawrence K.Wang, Hung Yung-Tse, Howard H.Lo.Lo, Yapijakis Constantine. (2006). *Handbook of Industrial and Hazardous Wastes Treatment, 2nd edition*.MARCEL DEKKER, INC.

2. Meda V., Lope T., Tyler R., Baik O.D., Soltan J. (2014). *Treatment of phenol in Water Using Microwave-Assisted Advanced*.

3. Crittenden John C., Rhodes Trussell R., Hand David W., Howe Kerry J. (2012). *Tchobanoglous George, MWH's Water Treatment Principles and Design*. 3rd edition, John Wiley & Sons, Inc.

4. Agarwal A, Manoj MK, Kumari S, Bagchi D, Kumra V. (2008). *Extractive separation of copper and nickel from copper bleed stream by solvent extraction route.* Miner Eng. 1126-1130.

5. Alsalhy Qusay Fadhel. (2007). *Effect of ethanol concentrations in internal coagulant on the morphology and separation performance of polyethersulfone (PES) hollow fiber UF membranes prepared by PES/Ethanol/NMP solution. Eng*. Technology. J. 25, 253-265 Issue suppl. of No.2, Pages.

6. Othman, N., Noah, N. F. M., Harruddin, N., Abdullah, N. A. and Bachok, S. K. (2014) *Selective extraction of palladium from simulated liquid waste solution by emulsion liquid membrane process using D2EHPA as a mobile carrier*. J. Teknol. 69(9) 1 - 4.

7. Teng Tjoon Tow, Muthuraman, Mubeena, Sathya. (2013). *Emulsion Liquid Membrane: Removal and Recovery of Organic and Inorganic Ion*s. J. Membra Sci Technol. 3 (2).

8. Park Y., Skelland A.H.P., Forney L.J., Kim J.H. (2006). *Removal of phenol and substituted phenols by newly developed emulsion liquid membrane process, Water Res*. 40,1763–1772.

9. Ooi Z.-Y., Harruddin N., Othman N. (2015). *Recovery of kraft lignin from pulping wastewater via emulsion liquid membrane process*. Biotechnology Progress.Biotechnol. Prog. 31 (5) 1305–1314.

10. Al-Obaidi Qusay, Monroe Jasmine, Smith Hannah, Haha Zaid, Al-Dahhan Muthanna. (2020). *assessing the removal of heavy metals using emerging and intensifying technology of emulsion liquid membrane with ionic liquid*. Elsevier JElsevier J. SSRN. 3601713.

11. Chaouchi Sarah, Oualid Hamdaoui. (2016). *Removal of 4-Nitrophenol from water by emulsion liquid membrane.* Water Treatment. J. Desalination Water Treatment. 57, 5253–5257.

12. Mokhtari B., Pourabdollah K. (2012). *Inclusion separation of alkali metals in emulsion liquid membranes by nano-baskets of callx [4] Crown-3*. Braz. J. Chem. Eng. 29 (04) 783–793.

13. Bhavyank Panchal, Jaimin Pandya. (2016). *Extraction of phenol from aqueous streaminto emulsion liquid membrane*. Int. J. Current Trends Eng. Res. (IJCTER) 2 (4) 145–153 e-ISSN 2455–1392.

14. Weingrtner H., (2008). *Understanding ionic liquids at the molecular level: facts, problems and controversie*s. Angew. Chem. Int. Ed. 47 (2008) 654–670.

15. Goyal K., Jayakumar N.S., Hashim M.A. (2011). *Chromium removal by emulsion liquidmembrane using [BMIM]+[NTf2]−as stabilizer and TOMAC as extract ant*. Desalination 278 (1) 50–56.

16. Sawsan A. Mohammed, Zouli Nasser, Al-Dahhan Muthanna. (2018). *Removal of phenolic compounds from synthesized produced water by emulsion liquid membrane stabilized by the combination of surfactant and ionic liquid*. Desalin. Water Treat. 110 168–179.

17. Lin Z., Yu D., Li Y. (2015). *Study on the magnetic ODSA-in-water Pickering emulsion stabilized by* Fe_3O_4 *nanoparticle.* Colloid Polym. Sci. 293, 125–134.

18. Kim Y.J., Liu Y.D., Seo Y., Choi H.J. (2013). *Pickering- emulsionpolymerized polystyrene/*Fe_2O_3 *composite particles and their magnetoresponsive characteristics*. Langmuir 29, 4959–4965.

19. Lin Zhaoyun, Zhang Zhe, Li Youming, Deng Yulin. (2016). *Magnetic nano-*Fe_3O_4 *stabilized Pickering emulsion liquid membrane for selective extraction and separation*. Chem. Eng. J. 288, 305–311.

20. Al-Obaidi Qusay, Al-Dahhan Muthanna. (2020). *Advanced removal of 4-Nitrophenol by emerging and intensifying technology of emulsion liquid membrane with magnetic nanoparticles*. Elsevier J. SSRN. 3601736.

21. Yossry Aly Abd El-Aziz Yossef. (2013). *Removal of Radioactive Pollutants by Liquid Emulsion Membrane from Liquid Waste.* International Atomic Energy Agency (IAEA), INIS-EG--472INIS-EG--472.

22. Hamid R., Mortaheb M.H. (2008). *Study on a new surfactant for removal of phenol from wasterwater by emulsion liquid membrane*. J. Hazard. Mater. 582–588.

23. Ng Y.S., Jayakumar N.S., Hashim M.A. (2010). *Performance evaluation of organic emulsion liquid membrane on phenol removal.* J. Hazard. Mater. 184 (1–3) 255–260, doi:10.1016/j.jhazmat.2010.08.030.

24. Jilska M.P., Geoff W.S. (2008). *Use of Emulsion Liquid Membrane Systems in Chemical and Biotechnological Separations*. CRC Press.

25. Mortaheb H.R., Amini M.H., Sadeghian F., Mokhtarani B., Daneshyar H. (2008). *Study on a new surfactant for removal of phenol from wastewater by emulsion liquid membrane*. J. Hazard. Mater. 160, 582–588.

26. Gasser M.S., El-Hefny N.E., Daoud J.A. (2008). *Extraction of Co (II) from aqueous solution using emulsion liquid membrane*. J. Hazard. Mater. 151-610–615.

27. Venkatesan S., Balasubramanian A. (2016). *Experimental analysis and mass transfer model for removal of Phenol from wastewater using emulsion ionic liquid Membrane*. CHEMCON, At IIT, Guwahati.

28. Bjorkegren R.F.Karimi. (2012). *A Study of the heavy metal extraction process using emulsion liquid membranes*. Chalmers University of Technology, Sweden.

29. Djenouhat M., Hamdaoui O., Chiha M., Samar M.H. (2008). *Ultrasonication assisted preparation of water-in-oil emulsions and application to the removal of cationic dyes from water by emulsion liquid membrane.* Part 1: membrane stability, J. Sep. Purif. Technol 62, 636–641.

30. Lelin Zeng L.Y., Influences of axial mixing of continuous phase and polydispersity of emulsion drops on mass transfer performance in a modified rotating disc contractor for an ELM system, Ind. Eng. Chem. Res. 54 (2015) 9832–9843.

31. Sawsan A. Mohammed, Zouli Nasser, Al-Dahhan Muthanna. (2017). *Removal of benzoic acid from wastewater by pickering emulsion liquid membrane stabilized by magnetic* Fe_2O_3 *nanoparticles.* Desalin. Water Treat. 68, 114–121.

32. Kargar A., Kaghazchi T., Sohrabi M., Soleimani M. (2006). *Application of experimental design to emulsion liquid membrane pertraction of gold (III) ions from aqueous solution*. Iranian J. chem. Eng. 3 (1) (winter). IAChE.

33. Rasheed Qusay J. (2015). *Synthesis and optimization of nisin-silver nanoparticles at different conditions.* Eng. Technol. J. 33 (2) 331–341 Part (A) Engineering, Pages.

34. Mahdy Saba A. (2016). *Synthesis of MgO nanoparticles and its enhanced broad Spectrum antimicrobial activity against selected Bacteria and fungus*. Eng. Technol. J. 34 (1) 65–72 Part (B) Scientific, Pages.

35. Sawsan A.M. (2016). *Investigating the performance of ELM systems in separating organic pollutants from industrial wastewater*. J. Water Process. Eng. 13, 79–87.

36. Park H.J., Chung T.S. (2003). *Removal of phenol from aqueous solution by liquid emulsion membrane*. Korean J. Chem. Eng. 20, 731–735.

III. EMULSION LIQUID MEMBRANE (ELM) ENHANCED BY NANOPARTICLES AND IONIC LIQUID FOR HYDROCARBONS REMOVAL FROM WASTEWATER

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ABSTRACT

For the ELM method, the effects of ferric oxide (Fe_2O_3) nanoparticle in the W1 phase, W2 phase, and in both phases (W1&W2), alone and with combining of 1-Ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ($[BMIM]^+[NTf2]^-$) ionic liquid in the O phase to enhance the stability of the ELM, separation/removal time, and the separation/removal efficacy for p-nitrophenol from synthesis wastewater. Use a ELM combination of 0.05% (W/W) Fe_2O_3 NPs in both phases (W1&W2) phases with 0.05% (V/V) of ($[BMIM]^+[NTf2]^-$) ionic liquid in the O phase; it raised the separation/removal efficiency of p-nitrophenol to 98.8 % at 2 minutes with the lowest leakage to 19% for 6 hours. While using 0.05% (W/W) Fe_2O_3 NPs alone in the W1 phase, the efficiency of p-nitrophenol removal was 99.5 % in 1 minute with leakage to 46% for 6 hours. The study's outcomes could apply to remove other types of pollutants and polar contaminants from the aqueous (W2) phase.

1. INTRODUCTION

Many manufactures and manufacturing developments are producing different wastewater types which introduces lethal pollutants into groundwater & water which are the sources of serious environmental concerns, since they are recognized to be deleterious [1]. The hydrocarbons are among these toxic pollutants such as p-nitrophenol, and other types which are found in many industrial wastewaters, for example the production of dyes, petrochemicals processes, and petroleum refinery [2]. The USEPA labeled the p-nitrophenol along the hazards of chemicals because of its capability to destroy important tissues like the liver, nervous system, kidney, and hematocytes. Therefore, wastewater from these manufacturers needs effective treatment before it is disposed [3].

Plethora of studies and methods that have been shown in literature on hydrocarbon removal from industrial wastewater & water [4]. In midst of these methods of treatment are ion exchange, coagulation-flocculation, flotation, adsorption, chemical precipitation, advanced oxidation, and electro–oxidation [5]. The membrane process has been announced as an emerging technology for wastewater treatment by providing a selective barrier between the internal receiving phase and wastewater using either polymeric or ceramic membranes [6]. Among these types of liquid membranes, the emulsion liquid membrane (ELM) has emerged as a new technology which additionally promotes the pollutant removal from wastewater or organic waste phases [7].

In the ELM, the removal of pollutants is improved by a reaction in W1 which allows maintaining maximum driving force for the species transport. Li (1968) proposed a single removal method, or stripping mechanism, identified as ELM (W1-O-W2) with highest separation & highest selectivity with low cost [8, 9&10]. The emulsion for the case of W1-O-W2 consists of aqueous tiny droplets (0.1 to10 µm in size droplets) (W1) produce in the O phase composing globules in W2 (0.1-2 mm in size like balls) when the emulsion (W1/O) is mixed with W2. The globules are spheres of emulsion accommodating large number of tiny droplets of W1 that contains the stripping agent to react with the pollutant to form precipitated (solute particles). In this work, p-nitrophenol has been taken as an example of toxic hydrocarbons in general to be removed from the wastewater and/or water (W2). In ELM, the 4-Nitrophenol is transported from W2 phase, via the membrane O phase of the globules which is also soluble in it, to the W1 phase of droplets in the globules to react with the NaOH as the stripping agent (reactant) in W1 forming sodium phenolate in a form of solute particulates which can be easily removed through sedimentation or filtration [7].

The ELM promising results as known in the literature [11], it has very limited manufacturing process because ELM still has encountered critical method barriers such as: 1) long duration of time (i.e., residence time) to achieve high percentage of removal , 2) swelling and breakage of the emulsion that reduces the stability of emulsion which effects on the efficiency removal negatively, and 3) an ineffective method of separating waste & phases to recycle the O phase and its constituents [12]. The surfactant was used in the O phase to enhance the stability of the emulsion [13]. To understand the relationship between emulsion membrane properties and operating variables the ELM removal efficiency has been further studied [14]. Recently, for enhancement stability of emulsion, ionic liquid has been proven as another stabilizer. Goyal et al. (2011) demonstrated the emulsion stability was enhanced by the ionic liquid of

1-butyl-3-methylimidazolium bis (trifluo¬romethylsulfonyl) imide in the O phase as additional stabilizer [15]. Mohammed et al. (2018) studied the impact of ionic liquid on the phenol removal from synthetic wastewater. The results showed that the concentration of ionic liquid increased to 0.3% (V/V) caused an enhancement in the emulsion stability and improved the efficiency separation of phenol of 78%, 2-Chlorophenol of 95%, 4-Nitrophenol of 98.5% after 30 minutes in a batch operation [16]. Al-Obaidi et al. (2021) studied the effect of ionic liquid of $[BMIM]^+[NTf2]^-$ on the emulsion stability using dye method and on removing the hydrocarbon of 4-Nitrophenol from synthesis external phase [17]. 0.2% (V/V) of $[BMIM]^+[NTf2]^-$ produced an improved in the stability of the emulsion and improved efficiency removal of 4-Nitrophenol of 83.9% at 15 minutes and reduced the percentage of emulsion leakage (improved emulsion stability). Nanoparticles in the O phase has been introduced and studied to enhance emulsion stability and pollutants removal [18 and 19]. Our previous study described some evidence that the ELM combines 0.05% (W/W) Fe_2O_3 NPs and 0.05% (V/V) ionic liquid in the O phase enhanced the separation of 4-Nitrophenol by 99% in 1 min [7 and 20].

This study investigates ELM with Fe_2O_3 NPs in the W1 phase, W2 phase, and both (W1&W2) phases alone. Furthermore, the ELM combining with Fe_2O_3 NPs in W1 phase, W2 phase, and both (W1 and W2) phases, with $[BMIM]^+[NTf2]^-$ ionic liquid in the O phase on the emulsion stability, reducing the time of the batch operation, and improved percentage p-nitrophenol removal from synthesis wastewater in terms of estimating and following up with the p-nitrophenol removal in W2 by ELM.

2. EXPERIMENTAL METHODS

2.1. CHEMICAL

In this study, the chemicals were used: mineral oil (organic solvents kerosene) at boiling point 175-325°C, surfactant span 80, internal aqueous phase (W1) was contained the stripping agent sodium hydroxide (NaOH). The hydrochloric acid used to celebrate pH of external feed phase (W2), an ionic liquid 1-butyl-3-methylimidazolium bis (trifluoromethylsulfonyl) imide, $[BMIM]^+[NTf2]^-$. All the chemicals above were obtained from Sigma Aldrich. The Fe_2O_3 NPs rang size 30-60 nm obtained from Alfa Aesar. This size of Fe_2O_3 NPs was chosen since it costs relatively less compared to the smaller sizes. Size is a significant factor for further applications. The magnetic property of the Fe_2O_3 NPs has been chosen for its easy removal and recycling by applying a magnetic field. Will improve the step and removal & demulsification of the solute formed, and the Fe_2O_3 NPs where they can be recycled, and the organic phase as long as the organic phase (O) chemistry will not be altered.

2.2. THE EXPERIMENTATION WORK

In In this work, the W1/O/W2 system was used in Emulsion Liquid Membrane because the contaminants are in the external feed phase (W2). The ELM is created via mixing W1 with the organic phase (O) at a high homogenization speed (rpm) of the mixer, formed a W1/O consisting of tiny aqueous droplets in the organic phase. The organic phase (O) content of kerosene & Span-80. Then W1/O were dispersed in the W2 phase, which contains the hydrocarbon of p-nitrophenol pollutant to form globules of the organic phase (O) containing small droplets of the aqueous internal phase (W1).

The p-nitrophenol was transferring from W2 into O, where it elapses from O to the W1 phase to react with NaOH (Equation 1). Figures 1 and 2 illustrate the steps of transport of the pollutant and the experimental work of the ELM process.

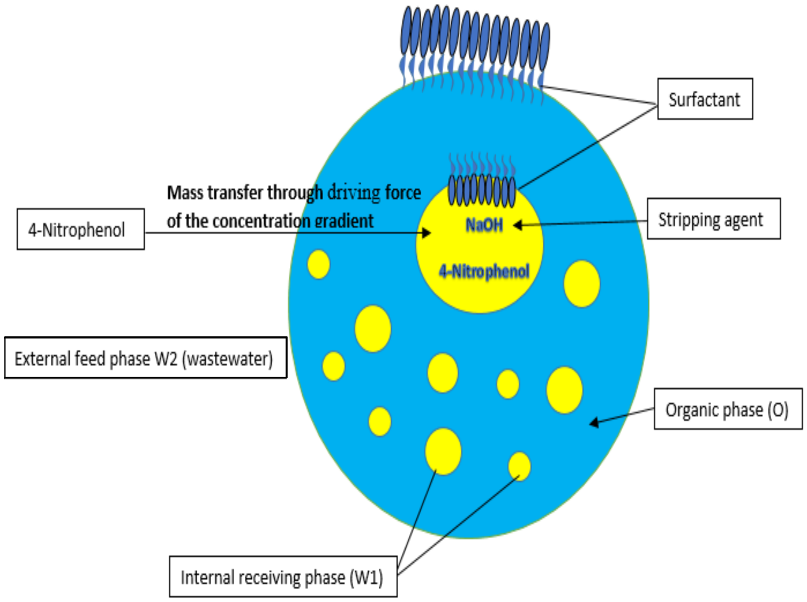

Figure 1. Schematic of Emulsion liquid membrane

Many variables influence separation contaminants by the ELM method: the ratio of W1 phase volume to the O phase volume, homogenization speed (rpm), surfactant concentration (%W/V), the ratio of W1/O volume to the W2 volume, treatment mixing speed(rpm), pH of the W2, and concentrations of Fe_2O_3 NPs & $[BMIM]^+[NTf2]^-$ ionic liquid. Hence, the first step determines the best compounds and the best values of these variables to separate p-nitrophenol from W2. The ELM performance was quantified in terms of stability, removal efficiency of the p-nitrophenol in W2, and extraction duration time [17].

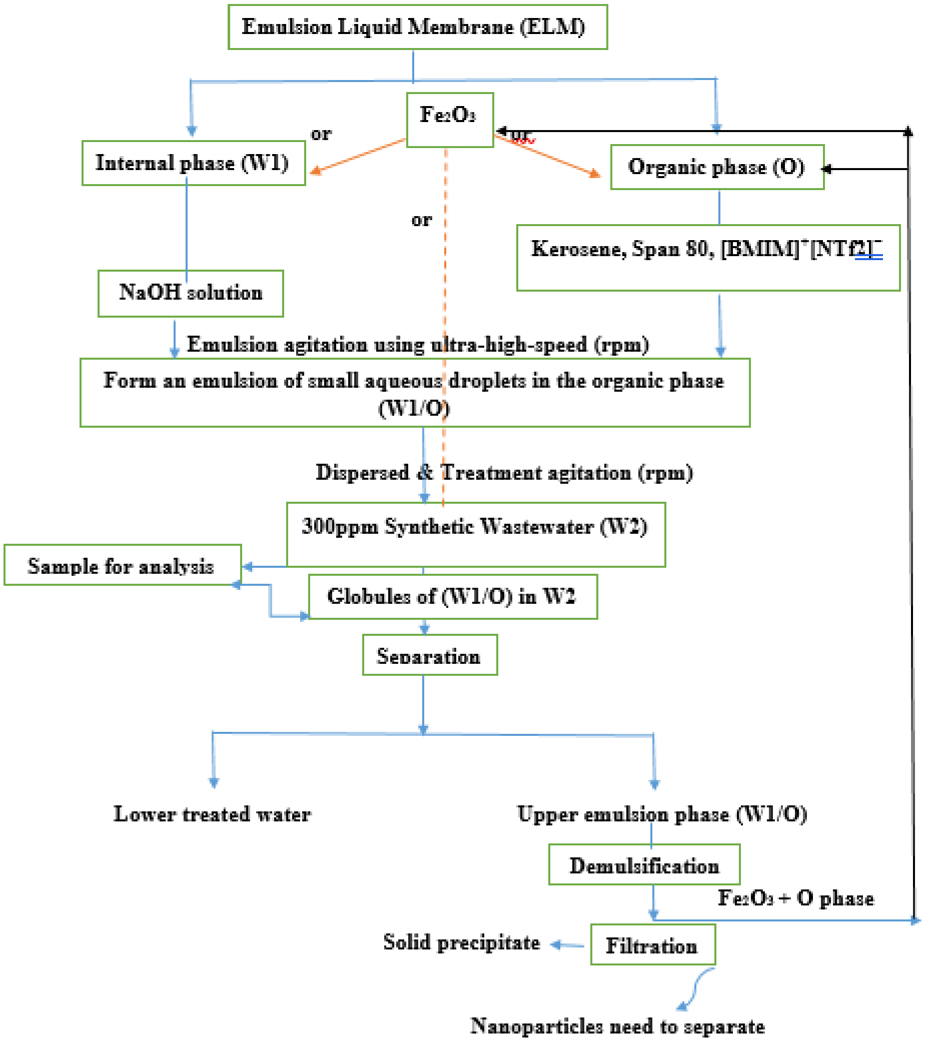

Figure 2. Block diagram that shows the steps of ELM treatment

The emulsion (W1/O) was dispersed and mixed by homogenization speed model, RW20 digital IKA overhead stirrer, with the W2 phase that contains p-nitrophenol, as shown in Figure 3. Samples from the agitated solution started with 300 ppm of p-nitrophenol. Samples from the homogenization solution began with 300 ppm of p-nitrophenol. Using a micropipette, the sample solution was separated from the emulsion phase by a nylon syringe filter of 0.2 µm (Simsii Inc. USA). The 96 well UV-microplate analyzed the p-nitrophenol at a wavelength band range of 200 to 900 nm. Concentrations of p-nitrophenol were found from the absorbance–calibration curves [17].

$$C_6H_4NO_2OH + NaOH \xrightarrow{\quad\quad} C_6H_4NO_2ONa + H_2O \tag{1}$$

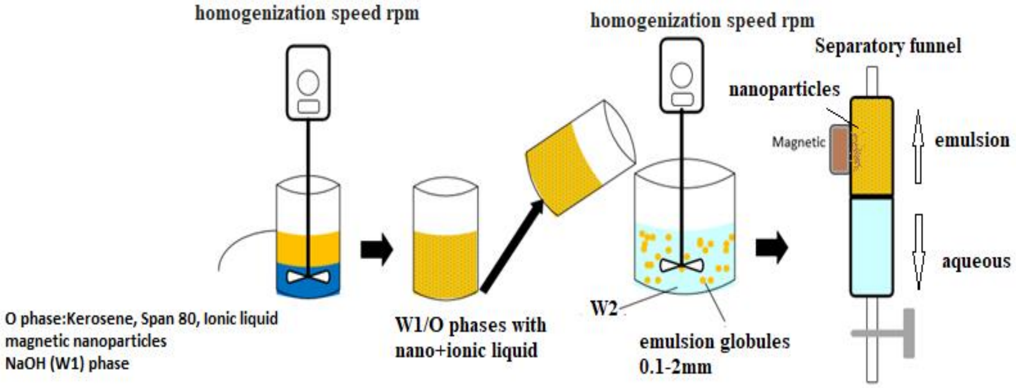

Figure 3. Emulsion liquid membrane process

Using the best values of the variables mentioned above, the effects of adding the 0.05% (W/W) Fe_2O_3 NPs in the W1 phase, W2 phase, and in both (W1&W2) phases with and without the 0.05% (V/V) $[BMIM]^+[NTf2]^-$ in the O phase on the ELM performance have been investigated. Examine the effect and detect of this combination on the performance parameters of the ELM mentioned above with the consideration to select the least amounts of nanoparticles and ionic liquid. All experiments were repeated three times for every condition examined, where the error bars were evaluated.

At the end of the p-nitrophenol removal, the mixtures are stored in a funnel that separates the lower W2 phase & the upper W1/O layer. Then, apply a 1T magnet field to it, which pulls the Fe_2O_3 NPs by the magnetic field, and in the meantime, demulsification occurs.

Table 1. Combination of the concentration of ionic liquid and nanoparticles

No	Ionic liquid $[BMIM]^+[NTf2]^-$ (V/V)	Fe_2O_3 nanoparticles (W/W)
1	0.05%	0.05%
	0.1%	
	0.15%	
	0.2%	

Since this will not change the chemistry of the organic phase (O), the kerosene will be reused. The aqueous phase will be separated from the organic phase by heating after the nanoparticles are collected. The accumulated Fe_2O_3 NPs will be cleansed with distilled water & acetone and later dried under a vacuum at 50 °C for ten hours for reuse, as presented in Figure 3 [17].

Our results are presented in terms of the removal percentage of the p-nitrophenol in the W2 phase (removal efficiency) as per the following equation:

$$\% \, 4 - Nitrophenol \text{ removal} = \left(\frac{initial\,concentration - final\,concentration}{initial\,concentration} \, X \, 100 \right) \qquad (2)$$

2.3. STABILITY OF THE EMULSION MEMBRANE

The stability of the ELM has been evaluated by using a red dye in the W1 phase as a leakage detector at room temperature, which does not react with compounds and aqueous & organic phases. Therefore, high leakage percentage indicates less emulsion stability and vice versa. The concentration of the dye that is leaked from (W1) to (W2) was measured using a UV spectrophotometer (96 well microplates UV). The percentage of the leakage was determined as follows:

$$\%\ Leakage = \left(\frac{dye\,concentration\,(W2)}{dye\,concentration\grave{}\,in\,W2\grave{}\,(with\,\max.time'\,allowed)}\ X\,100 \right) \qquad (3)$$

The concentration of the dye in W2 leaked from W1; moreover, the maximum time allowed, with a W2 concentration, the maximum concentration of the dye in W2 leaks to the W2 when all the red dye leaks from the W1 phase to the W2 phase.

3. RESULTS AND DISCUSSION

The effect of Fe_2O_3 NPs alone and combined with $[BMIM]^+[NTf2]^-$ ionic liquid on emulsion stability has been studied. For the p-nitrophenol removal & the duration time of the removal, the following steps were performed.

The The first is the effects of each of the best values reinvestigating by varying one variable while keeping the other variables unchanged to confirm these best values or adjust any one of them if needed. We confirmed that the best values of the variables are as mentioned before and listed again here as the ratio of W1 volume to O volume (1/3 V/V), concentration of Span 80 (2% W/V), 8000 rpm of emulsion agitation, (1/2 V/V) of volume ratio of W1/O to W2, 300 rpm of treatment agitation, and 1.5 pH of W2. It was found that these values of the variables provided the best results of the ELM performance

to remove p-nitrophenol. This is consistent with our previously work [7&17] as shown in Figure 1.

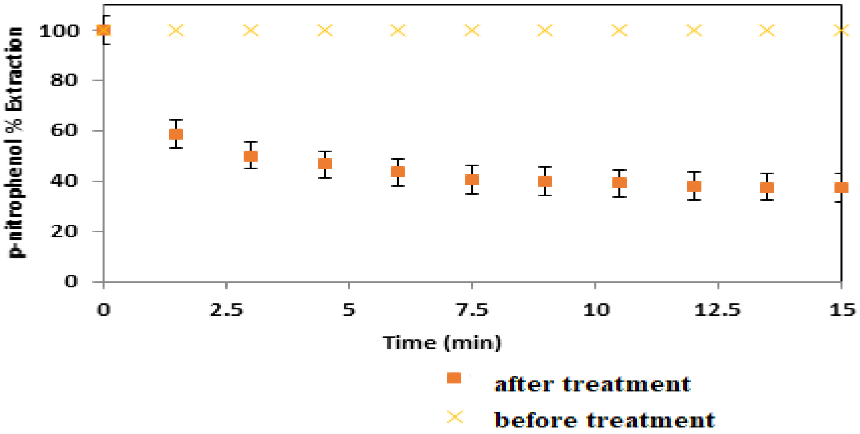

Figure 4. Best values of the variables on ELM as the ratio of W1 volume to O volume (1/3 V/V), concentration of Span 80 (2% W/V), 8000 rpm of emulsion agitation, (1/2 V/V) of volume ratio of W1/O to W2, 300 rpm of treatment agitation, and 1.5 pH of W2

3.1. THE EFFECT OF NANOPARTICLES ALONE IN W1, W2 AND IN BOTH PHASES (W1 AND W2), AND THE COMBINATION OF THE NANOPARTICLES IN W1, W2, AND IN BOTH PHASES (W1 AND W2) AND IONIC LIQUID IN ORGANIC PHASE (O) ON THE REMOVAL OF 4-NITROPHENOL

Here, we used the concentrations of the magnetic 0.05% (W/W) Fe_2O_3 NPs in W1, W2, and in both phases (W1&W2) and their combination with 0.05% (V/V) $[BMIM]^+[NTf2]^-$ in the O phase on the stability of the emulsion, removal of p-nitrophenol and duration time of removal. The results are illustrated in Tables 1 and 2.

The 0.05% (W/W) of Fe_2O_3 NPs alone in W1 provided the ELM performance to 99.5% removal in 1 minute while using 0.05% (W/W) of Fe_2O_3 NPs alone in both (W1&W2) phases was 98.3% in 2 minutes, and 0.05% (W/W) of Fe_2O_3 NPs alone in W2 was 89.2% in 3 minutes with leakage 46% for 6 hours.

Table 2. 0.05% (W/W) Fe_2O_3 nanoparticles alone with diameters in the range size 30 to 60 nm used to extract 4-Nitrophenol from synthesis wastewater.

Time (min)	(W1+NP) + O + W2	(W1+NP) + O + (W2+NP)	W1 + O + (W2+NP)
1	99.50	58.37	45.83
2	99.33	98.83	78.93
3	99.00	99.33	89.24

Table 3. 0.05% (W/W) Fe_2O_3 nanoparticles with diameters in the range size of 30-60 nm combined with a 0.05% (V/V) $[BMIM]^+[NTf2]^-$ ionic liquid used to extract 4-Nitrophenol from synthesis wastewater.

Time (min)	(W1+NP) + (O+ ionic liquid) + W2	W1 + (O+ ionic liquid) + (W2+NP)	(W1+NP) + (O+ ionic liquid) + (W2+NP)
1	50.00	40.00	61.67
2	94.53	92.73	98.83
3	98.33	98.33	99.33

The ELM combining with 0.05% (W/W) Fe_2O_3 NPs in W1 phase, W2 phase, and in both (W1&W2) phases with 0.05% (V/V) $[BMIM]^+[NTf2]^-$ ionic liquid in the O phase were providing ELM performance: 94.5%, 92.7%, and 98.8% removal in 2 minutes respectively, and the leakage 19% for 6 hours. That indicates the improvement of the emulsion stability, representing the least amount used for the nanoparticles, which are desirable from an economic point of view for large-scale applications.

The stability and removal efficiency increased by the combination of 0.05% (W/W) Fe_2O_3 NPs and 0.05% (W/W) $[BMIM]^+[NTf2]^-$ ionic liquid due to the coverage of more internal phase droplets interface and the globules as shown in Figure 5 and 5.

The removal time, which represents the period until the concentration of p-nitrophenol becomes zero, is considered one of the objectives to determine the best parameters on the performance of the ELM. This is because a shorter time would facilitate the transformation of the process from batch to continuous interest from an industrial application point of view.

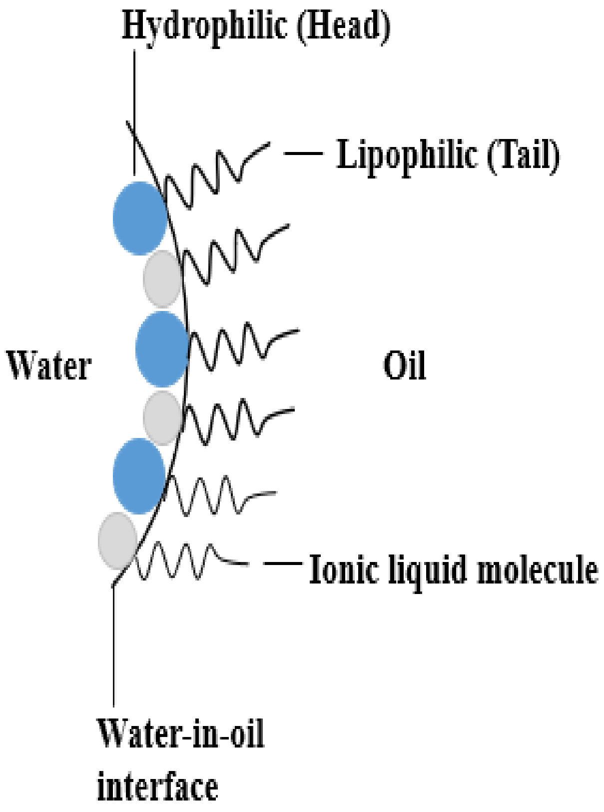

Figure 5. Schematic of the hydrophilic head and lipophilic tail of the Span 80 and ionic liquid $[BMIM]^+[NTf2]^-$ molecules packed between the surfactant.

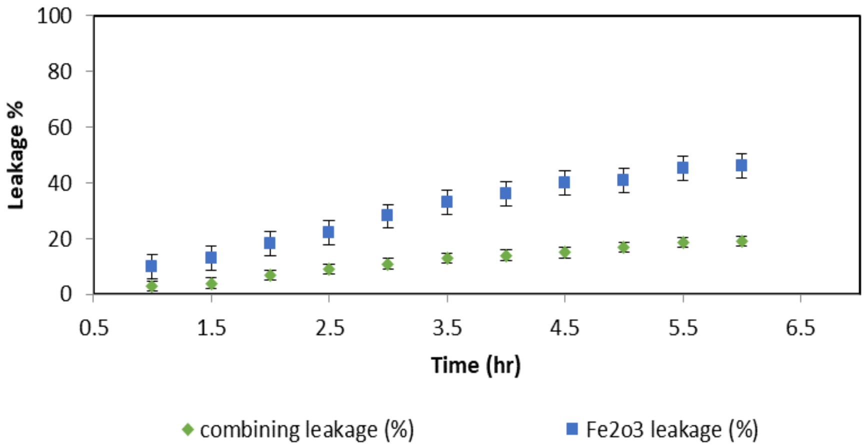

Figure 6. Effect ELM with 0.05%(W/W) Fe_2O_3 NPs alone and the ELM combination with 0.05% (W/W) Fe_2O_3 NPs and 0.05% (V/V) $[BMIM]^+[NTf2]^-$ ionic liquid on the emulsion stability: W1:O volume ratio of 1/3 (V/V), surfactant concentration of 2% (W/V), emulsification speed of 8000 rpm, ELM (W1/O)/W2 volume ratio of 1/2 (V/V), treatment agitation mixing speed of W2 of 300 rpm, and pH of W2 of 1.5.

4. CONCLUSION

The removal of p-nitrophenol efficiency in batch operation was enhanced to 99.5% in 1 minute with 46% breakage for 6 hours after adding 0.05% (W/W) of the Fe_2O_3 NPs alone in the W1 phase. However, ELM combination with 0.05% (W/W) Fe_2O_3 NPs in both (W1 & W2) phases and 0.05% (V/V) $[BMIM]^+[NTf2]^-$ ionic liquid in the O phase, reaching p-nitrophenol removal to 98.8 in 2 minutes which continues till the end of the reaction after 15 minutes with leakage 19% for 6 hours.

That means the percentage removal does not drop after 3 minutes, confirms that the leakage of the emulsion would not occur, and promotes the transformation of the process from batch to continuous ELM that facilitates its industrial applications.

REFERENCES

1. Qusay J. Rasheed, Karuppan Muthukumar. (2012). *Studies On Treatment Of Petroleum Refinery Wastewater*. LAP LAMBERT Academic Publishing. ISBN-10 3659247138, ISBN-13 978-36592471.

2. Qusay Al-Obaidi, Muthanna Al-Dahhan (2019). *Advanced Removal/Extraction of the Hydrocarbons by Emulsion Liquid Membrane Enhanced by Nanoparticles.* AIChE Annual Meeting.

3. Lawrence K.Wang, Yung-Tse Hung, Howard H.Lo, Constantine Yapijakis. (2006), *Handbook of Industrial and Hazardous Wastes Treatment.* 2nd Edition. MARCEL DEKKER, INC.

4. Q.J., Rasheed, F., Ghanim and T.A., Abdullah. (2016). *Wastewater Treatment by Electro-Oxidationprocess With TiO2.* Journal of Advanced Manufacturing Technology. ISSN: 1985-3157, Vol. 10, No.1.

5. Qusay Jaffer, and K. Ghanapriya. (2014). *Effect of Ferric Oxide on Electricity Generation and Waste Water Treatment Using Microbial Fuel Cell Technology.* Journal of Engineering. Number 9 Volume 20 September.

6. Norela Jusoh, Norasikin Othman1, Nur Alina Nasruddin. (2016), *Emulsion Liquid Membrane Technology in Organic acid Purification.* Malaysian J. of Analytical Sciences, Vol 20 No 2 (2016): 436 – 443.

7. Qusay Al-Obaidi, Muthanna Al-Dahhan. (2020), *Advanced Removal of 4-Nitrophenol by Emerging and Intensifying Technology of Emulsion Liquid Membrane with Magnetic Nanoparticles*. Elsevier Journal. SSRN. 3601736.

8. Qusay Al-Obaidi, Jasmine Monroe, Hannah Smith, Zaid Haha, Muthanna Al-Dahhan. (2020), *Assessing the Removal of Heavy Metals using Emerging. and Intensifying Technology of Emulsion Liquid Membrane with Ionic Liquid.* Elsevier Journal. SSRN. 3601713.

9. Li. (1968), *Separation hydrocarbons with liquid membrane,* U.S. Patent 3,410,794.

10. Ferraz, H. C., Duarte, L. T., Di Luccio, M., Alves, T. L. M., Habert, A. C., Borges, C. P. (2007), *Recent achievements in facilitated transport membranes for separation processes*. Braz. J. Chem. Eng., 24, 101-118.

11. Tjoon Tow Teng, Muthuraman, Mubeena, and Sathya. (2013), *Emulsion Liquid Membrane: Removal and Recovery of Organic and Inorganic Ions.* J Membra Sci Technol, 3:2.

12. Mousumi Chakraborty, Chiranjib Bhattacharya, and Siddhartha Datta. (2010), *Liquid Membranes: Principles and Applications in Chemical Separations and Wastewater Treatment.* Elsevier B.V. DOI: 10.1016/B978-0-444-53218-3.00004-0.

13. Wan, Y., Zhang, X. (2002), *Swelling Determination of W/O/W Emulsion Liquid Membranes.* J. Membr. Sci., 196, 185-201.

14. Bharat A. Bhanvase, Rajendra P. Ugwekar, Raju B. Mankar. (2017). *Novel Water Treatment and Separation Methods: Simulation of Chemical Processes.* Book. CRC Press, Science - 336 pages.

15. Goyal R.K., Jayakumar N.S., Hashim M.A. (2011), *Emulsion Stabilization Using Ionic Liquid $[BMIM]^+[NTf2]^-$ and Performance Evaluation on the Extraction of Chromium.* J. Hazard. Mater. 195 (2011) 55–61.

16. Sawsan A. Mohammed, Zouli Nasser, Al-Dahhan Muthanna. (2018). *Removal of Phenolic Compounds From Synthesized Produced Water by Emulsion Liquid Membrane Stabilized by the Combination of Surfactant and Ionic liquid*. Desalin. Water Treat. 110 168–179.

17. Qusay Al-Obaidi, Malak Alabdulmuhsin, Alice Tolstik, Jacob G Trautman, Muthanna Al-Dahhan. (2021). *Removal of hydrocarbons of 4-Nitrophenol by emulsion liquid membrane (ELM) using magnetic Fe_2O_3 nanoparticles and ionic liquid.* Journal of Water Process Engineering. Volume 39. Pages 101729.

18. Z Lin., Zhang Z., Y. Li, Deng Y. (2016). *Magnetic nano-Fe_3O_4 Stabilized Pickering Emulsion Liquid Membrane for Selective Extraction and Separation.* Chem. Eng. J., 288 -305–311.

19. QJ Rasheed. (2011). *Effect of Additive Agents on Sono-degradation Petroleum Refinery Wastewater*. Hydrology: Current Research 2011 Vol.2 No.1 pp.109 ref.18.

20. Qusay J. Rasheed. (2015). *Synthesis and Optimization of Nisin-Silver Nanoparticles at Different Conditions.* Eng. & Tech. Journal, Vol.33, Part (A), No.2.

IV. ASSESSING THE REMOVAL OF HEAVY METALS USING EMERGING AND INTENSIFYING TECHNOLOGY OF EMULSION LIQUID MEMBRANE WITH IONIC LIQUID

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ABSTRACT

(Pb(II)) is one of the heavy metals compounds founds in the industrial wastes that needs to be removed from treated wastewater. Emulsion liquid membrane (ELM) has been introduced as an emerging technology for advanced wastewater and water treatment. This emerging technology of treatment can be intensified by strategically adding the hydrophobic ionic liquid of [OMIM][PF6] and ({[BMIM]$^+$[NTf2]$^-$) ionic liquid to organic membrane phase (O) to facilitate the industrial implementation of ELM with ionic liquid. The results show that with the use of 5% (V/V) [OMIM][PF6] ionic liquid has increased the removal efficiency to 70.37% in reaction time of 5 minutes and both the stability and extraction activity of ELM are enhanced (2–3 times greater than the ELM alone). The outcomes of this work can be extended to other heavy metal removal from industrial wastewater and water.

1. INTRODUCTION

The treatment process of industrial wastewater and water is acritical challenge of worldwide due to the presence highly contaminants which it’s highly toxic and no-biodegradable. Heavy metal compounds during particularly processing of mining and mineral processing industry [1] are the most important examples of these contaminants. Pb(II) When lead is released into the environment, it will be accumulated in the food chain and exist in nature. Lead can cause a severe health hazard. For instance, lead is extremely toxic to humans and can damage the nervous system, kidney, organ, and reproductive system when the concentration of lead exceeds the limit set by WHO and USEPA (0.01ppm).

The complexity and verity of new wastewater treatment with different goals are produce different methods to remove/extract the lead such as chemical precipitation, electrochemical techniques, ion exchange, and liquid membrane techniques [2]. Emulsion liquid membrane (ELM) has been introduced as an emerging and intensifying technology for advanced wastewater treatment, because of ELM’s low operating costs, high selectivity, high surface area, rapid extraction, single step operation, and nondispersive phase [3]. The II Types of the ELM has produced by emulsifying an internal aqueous phase, an organic membrane phase they are two immiscible phases involves the facilitated transport of a solute across the membrane phase by incorporating a carrier agent (extractant). The main steps of the ELM process are emulsification, dispersion, and extraction, and demulsification [4].

Izatt et al. (1983) performed a study with $Pb(NO_3)_2$ by using the surfactant Span 80 and lead was determined to be the first transported metal. The studies report binary partitioning data for lead and cadmium extraction from dilute waste streams using an extractant, di-2-ethylhexyl phosphoric acid (D2EHPA) that can be incorporated into an ELM formulation. Also, a study was conducted with D2EHPA-Span 80 that demonstrated lead extraction with high removal efficiencies from synthetic water [5].

However, the ELM method is limited by its instability. Low stability causes partial rupture of the membranes, which reduces the extraction efficiency, causes swelling, and breakage in W1/O/W2 emulsions. Higher emulsion stability prevents membrane leaching of solute during phase interaction [6].

Avinash at, el. 2014, Ionic liquids are proven to improve the ELM process's stability and mass transfer rate. Avinash used ionic liquid during the emulsion preparation and for the extraction of Pb ions. The ionic liquid improved emulsion stability by increasing Pb ion transport. The stripping, mass transfer rate, and one stage extraction properties of the ELM method make it favored by scientists [7].

The specific objective of studying has been the performance of ELM with and without two different types of ILs was compared based on stability, enrichment factor, and removal efficiency for Pb(II) extraction and recovery from waste streams and leached or deposits to evaluate the best of the ionic liquids with the emulsion as a stabilizer.

2. EXPERIMENTAL METHODS

2.1. CHEMICAL REAGENTS

The carrier di-2-ethylhexyl phosphoric acid (D2EHPA), surfactant (Span 80), and kerosene, whose boiling points range from (175-325) °C, were used as solvents (O). 1-Methyl-3-octylimidazolium hexafluorophosphate ([OMIM]PF6), 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, $[BMIM]^+[NTf2]^-$, lead (II) nitrate $Pb(NO_3)_2$, sodium hydroxide pellets (NaOH), and hydrochloric acid (HCl) were from Sigma Aldrich (USA). The other chemicals used in this study, 0.5N sulfuric acid (H_2SO_4) as internal aqueous phase are from Fisher Scientific.

2.2. ELM PREPARATION

ELM (W/O/W) extraction method with reaction was prepared by first forming an emulsion from two immiscible liquid phases (aqueous and organic W/O). The emulsion consists of aqueous droplets distributed into the organic phase (Figure 1). The H_2SO_4 solution (0.5N) is used as the internal aqueous phase (W1) contains the stripping agent (H_2SO_4) which mixed with the organic membrane phase (O) (carrier di-2-ethylhexyl phosphoric acid (D2EHPA), surfactant Span-80, and oil phase kerosene) to create emulsion of tiny drops of W1 in O.

Many factors affect the removal process such as organic phase (O) to internal receiving phase (W1) ratio, surfactant concentration, emulsification speed, treatment ratio (volume ratio of W1/O to W2), treatment agitation speed, additive concentration magnetic nanoparticles, and pH of external feed phase.

Volume ratios of the H2SO4 solution to organic phase (W1/O) is this work used were 1/1, 2/1 and 3/1, 4/1, 5/1, and 6/1 (V/ V), Span 80 surfactant concentrations used were 1%, 2%, 3% , 4% and 5% (W/V) , D2HAPA carrier concentrations used were 1%, 2%, 3%, 4% and 5% (V/V). Emulsion was achieved using ultra-high-speed (Turrax IKA-T25) homogenizer at rotational speeds of 4000, 5000, 6000, 7000, and 8000 (rpm) for 10 minutes to produce a milky white color liquid membrane.

Then this emulsion was dispersed with mixer as globules in the external feed wastewater phase (W2) (Pb(II), 300 ppm) using ratios of 1/1, 1/2, 1/8, and 1/15 (V/ V) with agitation of low speed of 250, 300 and 400 rpm for 30 min. IKA overhead stirrer (Model: RW20 digital). The tested pH values of the external feed (W2) were of 1, 2, 3, 4, 5, and 6 measured by pH meter (Okton Acron). When the Pb(II) is transported from W2 to W1 through O, it reacts with the stripping agent (H_2SO_4) forming solid precipitate of lead(II) sulfate. Samples from the agitated solution were taken at different periods of time using micropipette, and then separated from the emulsion phase using nylon syringe filter 0.2 µm (Simsii Inc. USA). The concentration of Pb(II) was found from the calibration curves. Ionic liquids {$[BMIM]^+[NTf2]^-$, and ([OMIM]PF6)} added to (O) phase were applied to ELM at different concentrations to increase the stability where the concentrations used were 5% (V/V).

The mixture placed in a separating funnel to separate the upper emulsion phase (W1/O) and lower aqueous feed (W2) phase. Then the upper phase breaks using heating 80oC for 1hr in a closed vessel for final recovery of the internal receiving phase with Pb(II), and oil from the broken emulsion was separately collected. Finally, the W1 and Pb were washed with alcohol to extract the Pb(II).

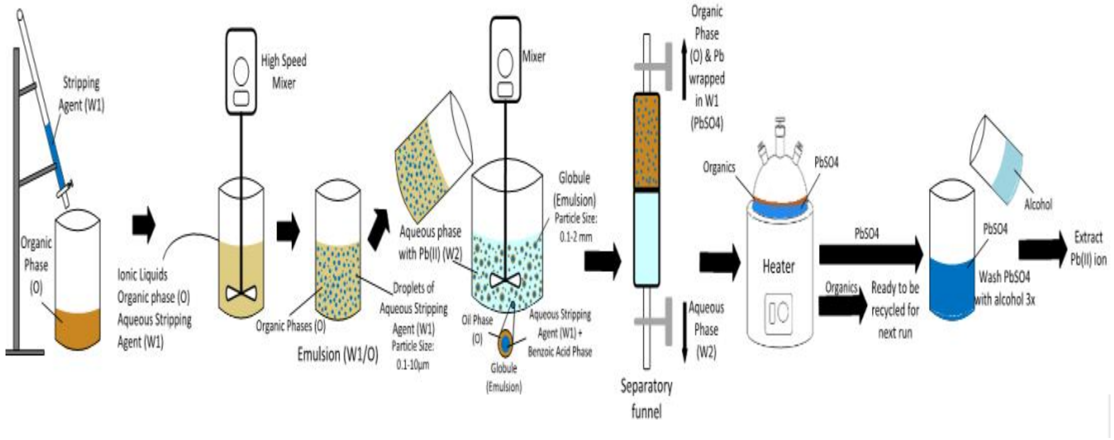

Figure 1. ELM process.

2.2.1. Calculation of Elm Stability. To measure the ELM stability by the percentage of leakage (%) determined by the following Equation:

$$\text{Breaking rate } \% = \frac{Vr}{Vint} \text{ X } 100 \tag{1}$$

$Vr = Vext *[(10^{\wedge pHo}) - (10^{\wedge pH})] / [(10^{\wedge pH}) - (H^{\wedge +})\ i]$

Where Vext = initial emulsion volume, pH0= pH initial of the emulsion,

pH= pH of the emulsion after certain time,

$[H^{\wedge +}]I$ = protons initial concentration in the internal phase.

Vint= left volume of the emulsion

2.2.2. Analytical Methods. The extraction remaining was calculated by the following equation.

$$\text{Extraction } \% = \frac{initial\ concentration - final\ concentration}{initial\ concentration} X100 \tag{2}$$

3. RESULTS AND DISCUSSION

3.1. THE EFFECT OF THE CARRIER (D2EHPA) PERCENT (%) IN ELM

The concentration of the carrier is playing a very important role in performance of the emulsion because it transports Pb(II) from the feed phase (W2) to the internal receiving phase (W1) Through organic phase (O). Due to different properties of the carrier, increasing concentration can be both desirable and, inversely, harmful to removal efficiency. Five different percent concentrations of mobile carrier D2HEPA were studied (1%, 2%, 3%, 4%, and 5%) as shown in Figure 2. The best concentration was found to be 2%. Concentration 3%–5% (V/V) led to a decrease in Pb(II) extraction, as the carrying capacity of the mobile carrier was saturated in this occasion [8]. The higher viscosity affects the extraction of solute and reduces membrane stability, resulting in a low mass transfer efficiency [9].

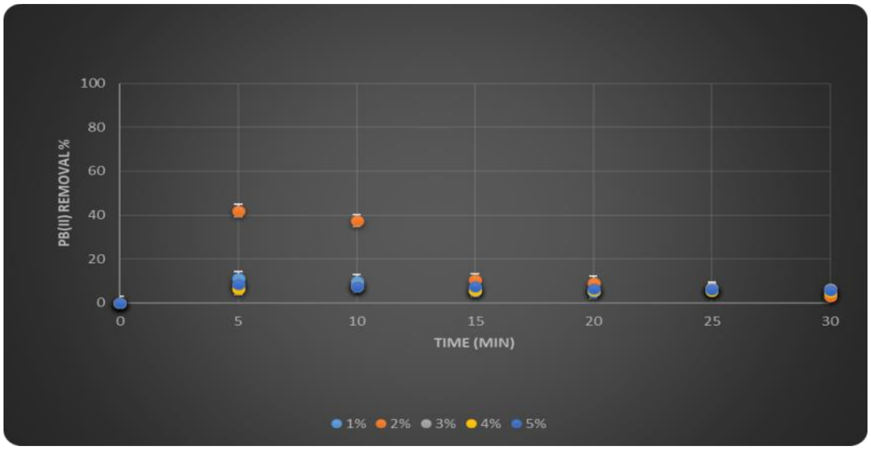

Figure 2. The effects of carrier concentration (V/V).

On the other hand, excessive amounts of the carrier may be due to the interfacial properties of the extractant, which favors oil-in-water emulsions and is opposed to the span 80 action as referred to by Bourenane et al. [10]. It was illustrated by Reis et al. [11] that increasing the concentration of extractant promotes the permeation swelling, which dilutes the aqueous receiving phase and decreases the efficiency of the process.

3.2. THE EFFECT OF SURFACTANT (SPAN 80 PERCENT (%) IN ELM)

The concentration of the emulsifier is playing a very important role in performance of the emulsion because it works as a protective barrier between the feed phase (W2) and the internal receiving phase (W1) which reduces the emulsion leakage [6]. Due to different properties of the surfactant, increasing concentration can be both desirable and, inversely, harmful to removal efficiency. Three different percent concentrations of span-80 were studied (1%, 2%, 3%, 4%, and 5%) as shown in Figure 3. The best concentration was found to be 3%. A concentration percent 4% does not create the increased in contact area as compared to 3% and increasing the concentration to 5% will lower surface tension of emulsion with formation of small globules.

Figure 3. The effects of Span 80 concentration (W/V)

More adding of emulsifier may lead to increase the swelling, emulsion instability, decrease in removal efficiency and higher emulsion leakage due to thicker emulsion globules. Thus, these yield higher mass transfer resistance and decrease the extraction efficiency [12], and [13].

3.3. THE EFFECT OF THE EMULSIFICATION SPEED ON THE EXTRACTION EFFICIENCY

The efficiency of extraction increases with an increase in the emulsification agitation [14], and [15]. The agitation is increased by using proper stirring speeds. To find the suitable emulsification, five speeds were examined (4000, 5000, 6000, 7000, and 8000) rpm. Emulsification speed of 6000 rpm gives best condition as showed in Figure 4. Emulsion stability was increased as the homogenizer speed is increased from 4000 to 6000 rpm, which stated that increasing the homogenizer speed leads to the generation of more droplets (increase the droplet formation) and a more stable emulsion because of better mixing and a reduction of interfacial tension between the aqueous and organic phase. The droplets merge with each other due to rapid mixing. Thus, the increased homogenizer speed causes a “mayonnaise-like” emulsion to form.

This can be explained by a forming mechanism where air-bubbles are incorporated into the emulsion phase and leads to a more rigid system. These results indicate that emulsification speed can be increased up to a certain limit (6000 rpm), but an increase beyond that limit obtains a Pb-D2EHPA complex with lower diffusion capability (diffusivity).

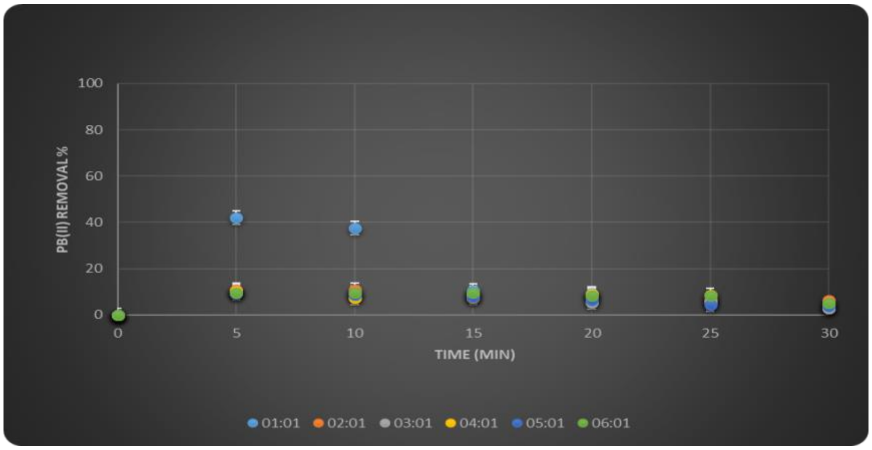

Figure 4. The effects of Volume ratio of W1: O (V/V).

3.4. THE EFFECT OF THE VOLUME RATIO OF THE INTERNAL RECEIVING PHASES (W1) TO THE ORGANIC PHASE (O), (W1/O)

The volume ratio of the internal receiving phase (H_2SO_4) (W1) to the organic phase (Kerosene, D2EHPA, and Span-80) (O) plays an important role in emulsion stability. Concentration of H2SO4 may seem desirable as it is useful in trapping and converting the Pb(II). However, too much increase will lead to emulsion instability [19]. Therefore, six selected ratios were taken (1/1, 2/1, 3/1, 4/1, and 5/1) (V/V) to investigate the effect of the internal receiving phase (W1) to organic phase (O) as proposed by [19] and shown in Figure 5. The ratio 1/1 (V/V) has higher extraction efficiency, due to the forming of small emulsion globule with thick wall (increase the membrane phase to encapsulate internal receiving phase) which reduce the possibility of the leakage [20]. Then the extraction efficiency decreased at volume ratio increase due to the increase in the thickness of membrane wall and built-up resistance around the W1 droplets which offered resistance of the membrane and show decline in Pb(II) removal rate and emulsion stability. Hence, the best condition was at 1/1 (V/V) internal receiving phase to organic phase ratio (W1/O) [21].

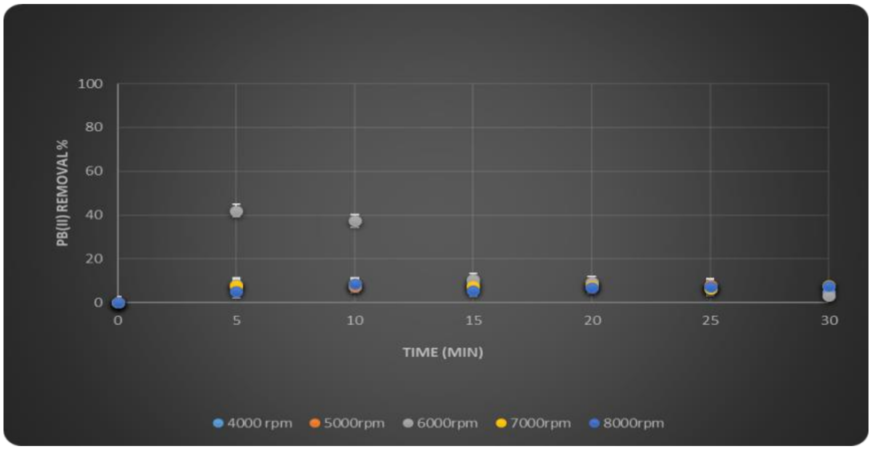

Figure 5. The effect of homogenous speed (rpm).

3.5. THE EFFECT OF THE MIXING INTENSITY OF THE WASTEWATER (W2) AND EMULSION (W1/O)

The mixing speed was first running at (250) rpm, and then increased to (300) rpm and eventually to (400) rpm in the third experiment. The results (Figure 6) show that (300) rpm is the most suitable, and hence it is used for the remainder experiments as it displays the lowest amount of emulsion leakage. The decrease in the stirring speed leads to a decrease in the mass transfer rate of Pb(II) due to an increase in the emulsion globules size. The higher mixing speeds create a greater shear force on the droplets and greatly reduce the diameter of the emulsion globules.

Increasing the mixing speed increases the contact area for mass transfer because of decrease in the globules size. The increase in the speed may also lead to the emulsion breaking because of high intensity [22]. However, the higher mixing speed makes globules rupture more likely causing leakage of the stripping agent into the feed phase (wastewater, W2 phase) [23]. The results are significantly agreed with the fact that at best stirring speed produces smaller globules and consequently, higher surface areas exposure resulting in a higher extraction rate [24].

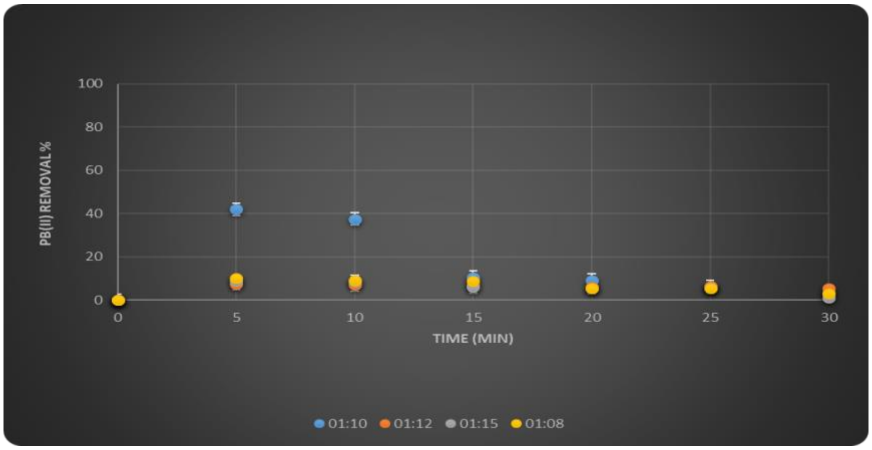

Figure 6. The effects of volume treatment ratio (V/V).

3.6. THE EFFECT OF THE TREATMENT VOLUME RATIO (W1/O) TO (W2)

The treatment volume ratio (W1/O) phase to external (W2) feed phase has a significant effect on the ELM efficiency. The rate of mass transfer is directly related to the specific mass transfer area. Regarding the treatment ratios of 1/8, 1/10, 1/12, and 1/15 (V/V) were used, the treatment ratio of 1/10 was found to be the best ratio for the removal as shown in Figure 7, and which will provide an increase in overall surface area for mass transfer and extraction capacity.

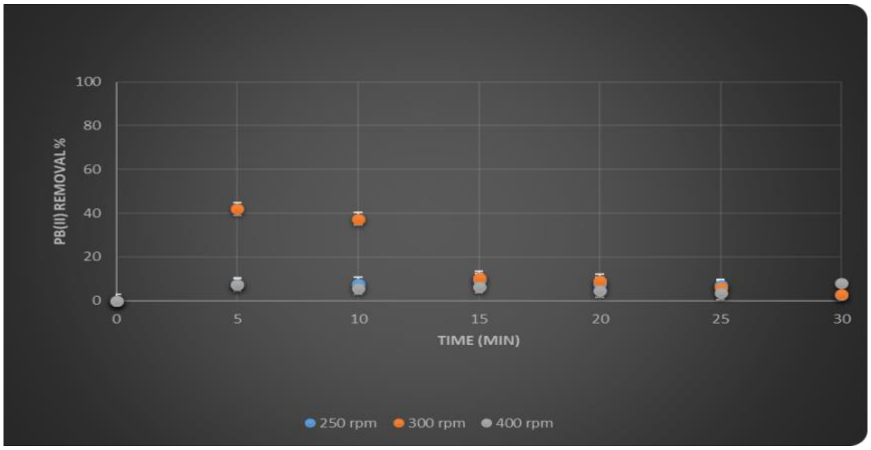

Figure 7. The effects of sped of treatment ratio (rpm).

The other treatment ratios decrease the removal efficiency and that can be attributed to the increase in membrane layer around the droplets. Therefore, the stability of emulsion increases when reducing the volume fraction of internal phase. In addition, that mechanical resistance of the membrane also increased at higher organic fraction, thus preventing coalescence of the dispersed droplet, and indicating the size is within the range of the standard droplets size. In general, larger droplets increase the emulsion instability because the droplet easily coalesces [7].

3.7. THE EFFECT OF THE PH OF THE EXTERNAL FEED PHASE (W2) ON THE REMOVAL EFFICIENCY OF PB(II)

The initial pH of the wastewater (W2) plays an important role in the surface charges, states of functional groups on the surface of adsorbent, and the pollutant species in solution. A series of experiments were conducted with a pH value range of (1–6), and the corresponding results are presented in Figure 8. From the results the practical Pb(II) removal from wastewater was at pH 5 because Pb(II) [25, 26, 27, and 28].

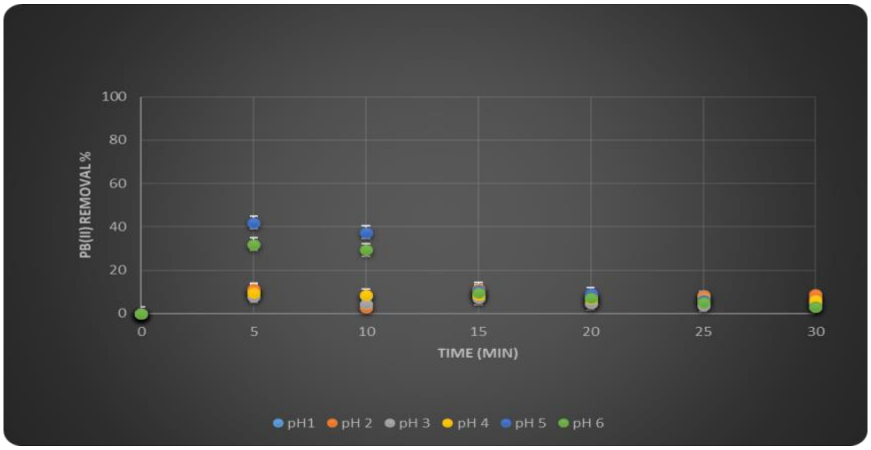

Figure 8. The effects of external phase pH

Considerably at high wastewater pH (as 5 in this study), the surface was surrounded by H+ resulting in the increase in the adsorption efficiency that might be accounted for the lower competition of H+ with Pb(II) for the active sites and the adsorption process was due to the interaction of the positively charged Pb(II) with the positively charged surface [29].

3.8. THE EFFECT OF IONIC LIQUID ON THE ELM PROCESS PERFORMANCE

The Pb(II) is not able to cross the membrane phase (O), so it a carrier agent is needed to transport the Pb(II) from the external feed phase (W2) to the internal stripping receiving phase (W1). This process involves several reactions, as seen below.

$2Pb(NO_3)_2 + H_2O \rightarrow Pb(OH)_2 + 2HNO_3$ (3)

$Pb(OH)_2$ (extrenal) + 2HR ⇆ Pb(OH)2R2 [interface (external\membrane)]+ $2H_2$ (external) (4)

When the feed and membrane phase meet, external interface reaction (4) occurs. The metal-ligand complex, PbR2, carries Pb(II) ions to the stripping phase. Note that here, HR represents D2EHPA in kerosene.

$Pb(OH)2R2 + 2H^+ \leftrightarrows Pb^{+2} + 2HR + H_2O$ (5)

Internal interface reaction (4) occurs at the meeting of the membrane and stripping phase, the metal complex and the hydronium ions combine at the beginning of the membrane-stripping phase. Then the extractant ligand, D2EHPA, returns to the interface of the feed and membrane phase. The D2EHPA dissolved in kerosene is applied successfully for the transportation of Pb(II) from the donor phase to the acceptor phase forming precipitate of lead(II) sulfate.

$Pb^{+2} + H_2SO_4 \rightarrow PbSO_4 + H_2$ (6)

The ionic liquid enhances the stability of the ELM method and the mass transfer of Pb(II) from the W2 to W1 through O phase due to the ability of forming film by the particles at (O/W) [32, and 33]. The results from this study indicated that the ratio 5% (V/V) of ionic liquids ([OMIM][PF6], and {[BMIM]$^+$[NTf2]-). The Pb(II) extraction to higher level as compared to the ELM alone as presented in Figure 9. This result is indicating that the increased in ionic liquid concentration extraordinary will sedimentation of the emulsion, enhancing the emulsion stability and higher transfer process because the emulsion droplets tend to be spherical or uniform shape as shows in Figure 10. [29].

Extraction time is considered as the target to determine the ELM effectiveness which represents the period till the concentration of Pb(II) becomes zero. The ratio 5% (V/V) of ([OMIM][PF6], gives higher removal efficiency percent for Pb(II) of 70.37% in 5 min as in Figure 9, and 10. at above optimum operating conditions which were 2% carrier D2EHPA, 3% surfactant Span 80 and 0.05 N H2SO4 at 1/1 (V/V) organic phase to receiving phase, 6000 rpm agitation seed, 1/10 (V/V) treatment ratio at 300 rpm, and wastewater pH 5.

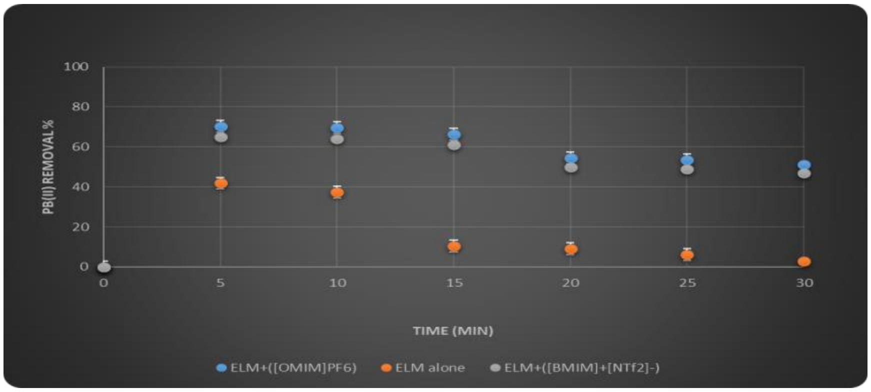

Figure 9. ELM alone vs. ELM with ionic liquids in Pb(II) removal.

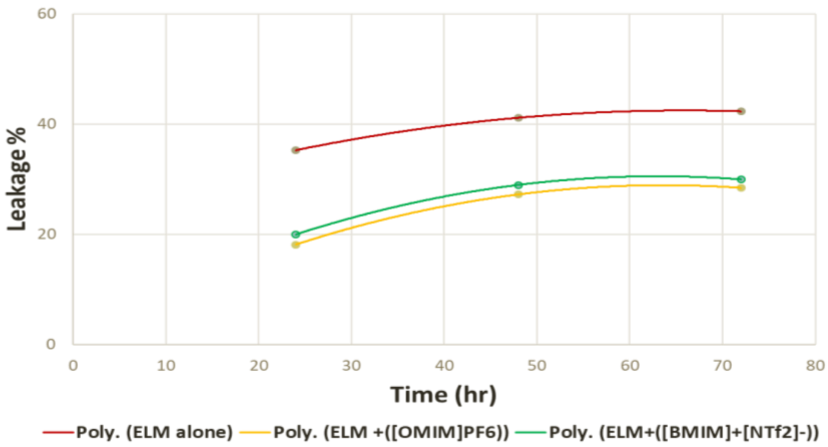

Figure 10. ELM Stability.

4. REMARKS

In this work the following have been demonstrated and noticed.

•Best operation conditions obtained for the removal of Pb(II) were, volume ratio of internal receiving phase to organic phase (W1/O) was 1/1 (V/V), carrier D2HEPA percentage was 2% (V/V), Span-80 percentage was 3% of the weight of the ELM the homogenizer speed was 6000 rpm, treatment ratio was 1/10 (V/V), mixing speed was 300 rpm, and pH of W2 was 5.

•The ionic liquid [OMIM][PF6] enhances the stability of the ELM and extraction activity due to the interfacial attraction of ionic liquid with the membrane phase components either by electrostatic attraction (van der Waals interaction) or by hydrogen bonding, which results into the prevention of coalescence of the emulsion globules. The results indicated that the ratio of 5% (V/V) of [OMIM][PF6] to internal receiving phase elevates the Pb(II) extraction to higher level spicily of 70% in 5 min.

•This clarifies the ability to increase the emulsion stability and extraction. With further increasing the concentration after emulsion droplets covering totally, ionic liquid will disperse in the aqueous feed phase and some of the particles probably cause aggregation in W1/O mediator, which reflect on the stability of emulsion and leads to reducing the removal/ separation process.

REFERENCES

1. Prasad V., Thitame and Sanjeev R. Shukla. (2017). *Removal of Lead (II) from Synthetic Solution and Industry Wastewater Using Almond Shell Activated Carbon*. American Institute of Chemical Engineers. DOI 10.1002/ep.12616.

2. Kang. K. C., Kim. S. S., Choi. J. W., and Kwon S. H. (2008). *Sorption of* Cu^{2+} *and* Cd^{2+} *onto acid- and base-pretreated granular activated carbon and activated carbon fiber samples*. Journal of Industrial and Engineering Chemistry, vol. 14, no. 1, pp. 131–135.

3. Li N.N. (1968). *Separation hydrocarbons with the liquid membrane*, U.S. Patent 3,410,794.

4. Levent Gürel, Levent Altas¸, and Hanife Büyükgüngör. (2005). *Removal of Lead from Wastewater Using Emulsion Liquid Membrane*. Technique. Environmental Engineering Scince. DOI: 10.1089/ees.22.41.

5. ALTAS, L. (2002). *Emulsiyon sıvı membran tekni˘ giyle sulardan kur, sun giderimi. Doktora Tezi, Ondokuz Mayıs Universitesi Fen Bilimleri Enstitusu, Samsun, Turkiye. (Removal of lead ions from waters using emulsion liquid membrane technique.* Doctoral Dissertation, Ondokuz Mayis University Institution of Science, Samsun, Turkey).

6. Sawsan A.M. Mohammed. (2016). *Investigating the performance of ELM systems in separating organic pollutants from industrial wastewater*. J. of Water Process Engineering. 13-79-87.

7. Avinash B. Lende, Manish K. Dinker, Vikas K. Bhosale, Sanjay P. Kamble, Pawan D. Meshramc and Prashant S. Kulkarni. (2014). *Emulsion ionic liquid membranes (EILMs) for removal of Pb(II) from aqueous solutions*. The Royal Society of Chemistry. 4, 52316–52323.

8. Amiri A., Shanbedi M., Chew B. T., Kazi S. N., Solangi K. H.(2016). Chem. Eng. J. 289, 583.

9. Wu D., Zhu H., Wang L., Liu L. (2009). Curr. Nanosci. 5, 103.

10. Buongiorno J., Venerus D. C., Prabhat N., McKrell T., Townsend J., Christianson R., Tolmachev Y. V., Keblinski P., Hu L. W., Alvarado J. L., Bang I. C., Bishnoi S. W., Bonetti M., Botz F., Cecere A., Y- Chang, Chen G., Chen H., Chung S. J., Chyu M. K., Das S. K., DiPaola R., Ding Y., Dubois F., Dzido G., Eapen J., Escher W., Funfschilling D., Galand Q., Gao J., Gharagozloo P. E., Goodson K. E., Gutierrez J. G., Hong H., Horton M., Hwang K. S., Iorio C. S., Jang S. P., Jarzebski A. B., Jiang Y., Jin L., Kabelac S., Kamath A., Kedzierski M. A., Kieng L. G., Kim C., Kim J. H., Kim S., Lee S. H., Leong K. C., Manna I., Michel B., Ni R., Patel H. E., Philip J., Poulikakos D., Reynaud C., Savino R., Singh P. K., Song P., Sundararajan T., Timofeeva E., Tritcak T., Turanov A. N., Vaerenbergh S. V., Wen D., Witharana S., Yang C., Yeh W. H., Zhao X. Z., Zhou S. Q. (2009). J. Appl. Phys.94312, 109.

11. Lee J. H., Hwang K. S., Jang S. P., Lee B. H., Kim J. H., Choi S. U., Choi C. J. (2008). Int J Heat Mass Transfer. 51, 2651.

12. Zuolian Cheng, Annie Lai Kuan Tan, Yong Tao, Dan Shan, Kok Eng Ting, and Xi Jiang Yin. (2012). *Synthesis and Characterization of Iron Oxide Nanoparticles and Applications in the Removal of HeavyMetals fromIndustrialWastewater.* International Journal of Photoenergy. DOI: 10.1155/608298.

13. Acharya J., Sahu J. N., Mohanty C. R., and Meikap B. C. (2009). *Removal of lead (II) from wastewater by activated carbon developed from Tamarind wood by zinc chloride activation*. Chemical Engineering. Journal, vol. 149, pp. 249–262.

14. Sone H., Fugetsu B., and Tanaka S. (2009). *Selective elimination of lead (II) ions by alginate/polyurethane composite foams.* Journal of Hazardous Materials, vol. 162, pp. 423–429.

15. Reis M.T.A., and Carvalho J.M.R. (2004). *Modelling of zinc extraction from sulphate solutions with bis (2-ethylhexyl) thiophosphoric acid by emulsion liquid membranes.* Journal of Membrane Science. 237, pp. 97-107.

16. XinX., SiW., YaoZ., FengR., DuB., YanL., (2011). *Adsorption of benzoic acid from aqueous solution by three kinds*. J. Colloid Interface Sci. 359 (2) 499–504.

17. Sawsan A.M. Mohammeda, Nasser Zoulib, Muthanna Al-Dahhan. (2017). *Removal of benzoic acid from wastewater by pickering emulsion liquid membrane stabilized by magnetic Fe2O3*. J. Desalination and Water Treatment. doi:10.5004/dwt.2017.

18. Bouranene S., Samar M. E. H., and Abbaci A. (2003). *Extraction of cobalt and lead from wastewater using a liquid surfactant membrane emulsion*. Acta Chim. Slov. 50, 663–675.

19. Juang R.S., and Wang Y.Y. (2002). *Amino acid separation with D2 EHPA by solvent extraction and liquid surfactant membranes*. Journal Membrane Science. 207- 241–252.

20. Li Y., Wang A., Loon J.C.V., and Borefoot R.R. (1992). *Extraction and enrichment of cadmium and manganese from aqueous solution using a liquid membrane.* Talanta, 39(10) 1337–1341.

21. Bart H. J., Ramaseder C., Haselgrubler T., and Marr R. (1992). *The investigation of osmosis in the liquid membrane technology. Influence of key parameters*. Hydrometallurgy, 253–267.

22. Mortaheb H., Amini M., Sadeghian F., Mokhtarani B., and Daneshyar H. (2008). J. Hazard. Mater. 160,582.

23. Sawsan A.M. Mohammeda, Nasser Zoulib, Muthanna Al-Dahhanb. (2018). *Removal of phenolic compounds from synthesized produced water by emulsion liquid y the combination of surfactant and ionic liquid.* J. Desalination and Water Treatment. doi: 10.5004/dwt.22232.

24. Levent GU¨ REL, and Hanife BU¨ YU¨ KGU¨ NGO¨ R. (2007). *Investigation of Organic Matter Release in Emulsion Liquid Membrane Treatments.* Turkish J. Eng. Env. Sci. 31, 265 – 272.

25. Elsayed Fouad, Farooq Ahmad, and Khaled Abdelrahman. (2017). *Optimization of Emulsion Liquid Membrane for Lead Separation from Aqueous Solutions. Engineering.* Technology & Applied Science Research. Vol. 7, No. 5, 2068-2072.

26. Ahmad, A.L., Kusumastutia, A., Dereka, C.J.C., Ooi, B.S. (2011). *Emulsion liquid membrane for heavy metal removal: an overview on emulsion stabilization and destabilization.* Chem. Eng. J. 171, 870–882.

27. Benyahia, N., Belkhouche, N., Jönsson, J.A., (2014). *A comparative study of experimental optimization and response surface methodology of Bi(III) extraction by emulsion organophosphorus liquid membrane.* J. Environ. Chem. Eng. 2, 1756–1766.

28. Meryem Mesli, Nasr-Eddine Belkhouche. (2018). *Emulsion ionic liquid membrane for recovery process of lead. Comparative study of experimental and response surface design.* Chemical Engineering Research and Design.129.160-169.

29. Grue L., Altas L. and Buyukgungor H. (2005). *Removal of lead from wastewater*. Environ. Eng. Sci. 22, 411–420. Electronic Age, E-Publishing Inc., New York, 1999, pp. 281–304.

V. A NOVEL EMULSION LIQUID MEMBRANE (ELM) ENHANCED BY FE2O3 NANOPARTICLES AND IONIC LIQUID FOR EXTRACTING HEAVY METALS FROM WASTEWATER RECOVERING OF A VANADIUM COMPOUND AS AN EXAMPLE

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ABSTRACT

Emulsion Liquid Membrane for the first time was enhanced by NPs in the W1 phase, and ionic liquid in the O phase is being investigated for recovering/extracting vanadium as heavy metals example from wastewater synthetic and for improving emulsion stability. The efficient extraction/recovery of vanadium has been enhanced noticeably to 99.6 % in 3 min by using 5% (V/V) ionic liquid 1-Methyl-3-octyl-imidazolium-hexafluorophosphate ([OMIM][PF6) and modification surface 0.01% (W/W) superparamagnetic iron oxide nanoparticles (Fe_2O_3) of 20-50 nm in size. The emulsion stability was enhanced significantly, giving 16% of the leakage for three days. This study outcome can be applied further to extract/recover heavy metals from water and industrial wastewater.

1. INTRODUCTION

Different industries usually produce wastewater with heavy metal compounds as pollutants. Such heavy metal compounds are also found in groundwater and other water resources. Vanadium is taken as a sample to be recovered among the other toxic heavy metal pollutants found in industrial wastewater generated from mining and mineral, petroleum, chemical, and other processing industries, spent catalysts treatment, etc. [Qusay J. Rasheed et al.,2012]. Furthermore, vanadium and its compounds have been used as catalyst active sites for many chemical reactions, and hence its efficient recovery has the advantage to be recycled and reused as a valuable element for catalyst manufacturing [Zhang et al., 2011]. The vanadium level was set to be maximum 35 (mg/m^3) as recommended by the United States Environmental Protection Agency (USEPA) and according to Occupational of Safety and Health [EPA. 2011f]. USEPA has considered vanadium among the toxic aqueous heavy metals in the human body due to its ability to cause damage to the blood cells, liver, the system's main nerve, and kidneys [Christopher. 2012]. Therefore, the wastewater that contains this heavy metal compound needs an effective treatment to extract it and possibly reuse it before the wastewater is released into the environment. [FEDRIP. 2012].

Many methods and studies are described in the literature on extracting/recovering vanadium and heavy metals in general from water and industrial wastewater. Amongst these treatment methods are "precipitation, carbon adsorption, ion exchange, and solvent extraction" [Archana. 2015]. Separation by liquid membrane has been developed over the recent years as an emerging technology to treat wastewater, where liquids as membrane barriers between phases have been used [Al-Obaidi et al., 2019]. The method of the liquid membrane has three types: Supported Liquid Membrane (SLM), Bulk Liquid Membrane (BLM), and Emulsion Liquid Membrane (ELM). ELM method has emerged as a new technology to treat wastewater or to remove and extract the heavy metals from it [Al-Obaidi et al., 2020].

In general, the ELM that was introduced first by Li, N. (1968) refers to the aqueous (W1) phase and Oil (O) phases (W1-O emulsion), which are mixed with the wastewater (W2) phase to form (W1/O/W2), or Oil (O) phase and aqueous (W) phases (O1-W emulsion), which are mixed with organic waste oil (O2) phase to form (O1-W-O2) ELM [Li. 1968]. The W1-O emulsion consists of tiny droplets (0.1-10 µm) of receiving inner phase solution (W1) that contain the stripping agent (reactant) dispersed in the organic phase (O). When this emulsion (W1-O) is mixed with the wastewater (W2) phase, it creates globules of the spherical shape of about (0.1-10 mm) [Chakraborty. 2010] of emulsion accommodating the tiny droplets of W1. In this work, ELM (W1-O-W2) has been further developed to recover vanadium from aqueous synthetic wastewater (W2). Hydro sulfuric acid (H_2SO_4)) has been used as the stripping agent in W1 to react with the vanadium-forming soluble vanadyl sulfate. Vanadium is insoluble in the globules' organic phase, and hence, it needs an agent called the carrier, (Di-(2-Ethylhexyl) phosphoric acid in this case (D2EHPA), to transport it through the O phase from W2 to W1. The carrier reacts with vanadium to create a complex compound soluble in the organic (O) phase. Once this complex compound reaches the surface of the droplets of W1, it releases the vanadium ion to be reacted with the stripping agent H_2SO_4 forming aqueous soluble vanadyl sulfate. This is a key advantage of ELM by maintaining maximum transport driving force of concentration gradient during the whole treatment time, as shown in Figure 1 as the schematic diagram of transport in ELM [Bjorkegren et al., 2012].

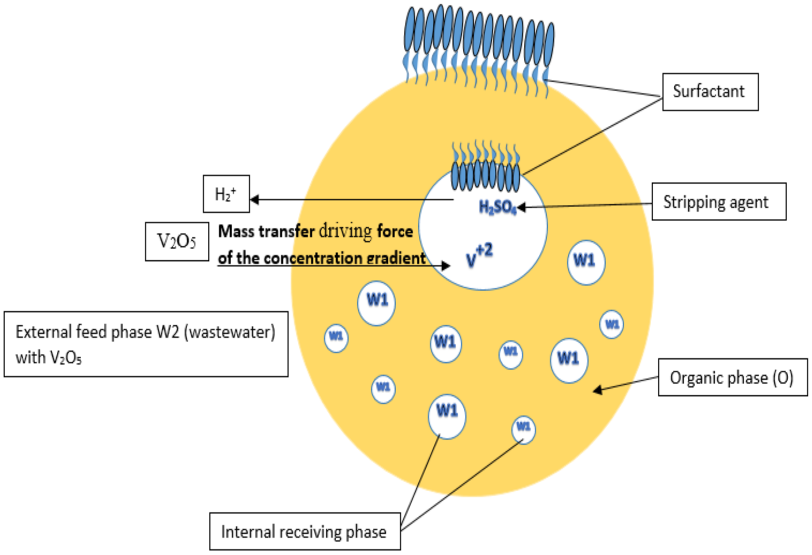


Figure 1. Schematic of the Emulsion Liquid membrane (ELM).

ELM has encountered critical technical issues that hinder its scale-up and industrial applications. These are related to the following: 1) not achieving high percentage or near-complete removal (~100%); 2) encountering swelling leakage and breakage of the emulsion that reduces its stability and lowers the extracting/recovery efficiency; 3) confronting a long batch time (long residence time) to achieve a maximum percentage of extraction/recovery that is not very high, and 4) using an ineffective demulsification method to separate phases and recycle the organic phase [Al-Obaidi et al., 2021]. One measure taken so far was using surfactant Span 80 in the organic phase

(O) to enhance the stability of emulsion and reduce swelling leakage and breakage of the emulsion [Badgujar et al., 2011].

To further enhance the emulsion stability, an ionic liquid used as a stabilitate has been illustrated. Al-Obaidi pointed in their study of recovering Pb^{+2} from synthetic wastewater that the emulsion (W1/O) stability was enhanced by incorporating in the O phase the ionic liquids of $[BMIM]^{+}[NTf2]^{-}$ and [OMIM]PF6. The results showed that when the concentration of ([OMIM]PF6) increased up to 5% (V/V) in the O phase gave an enhancement in the emulsion stability to three days extended and improved extraction efficiency of Pb(II) from 43% to 70.4% in 30 minutes in a batch operation [Al-Obaidi et al., 2020].

Studies have not been reported nor investigated of the effect NPs (in W1 phase) & studied the impact of the combination of the NPs (in W1 phase) and ionic liquid (in O phase) on the ELM stability, enhancement of the extract (increased removal percentage), and the reduction of the batch time for the recovery of the heavy metals' pollutants. These represent the key performance indicators (KPIs) for enhanced ELM. Accordingly, this work focuses on addressing the effect of the superparamagnetic iron oxide nanoparticles (Fe_2O_3 size of 20-50 nm) in W1 alone and with the combination of ionic liquid ([OMIM]PF6) in the O phase on the mentioned ELM KPIs indicators for vanadium recovery wastewater.

2. MATERIALS AND METHODS

2.1. CHEMICALS

The chemicals that have been used were: The organic solvent was kerosene (Boiling Point 175 – 325 °C), Span-80 as a surfactant, di-2-Ethylhexyl phosphoric acid (D2EHPA) as a carrier to transport the vanadium from the wastewater (W2) through the O phase to W1 phase, 0.5 N sulfuric acids (H_2SO_4) in the W1 phase as the stripping agent, hydrochloric acid (HCl), 1-Methyl-3-octylimidazolium hexafluorophosphate ([OMIM]PF6) as an ionic liquid. These chemicals were obtained from Sigma Aldrich (St. Louis, MO 63103, USA). In addition, the superparamagnetic iron oxide nanoparticles (Fe_2O_3) were used and obtained from Alfa Aesar (Ward Hill, MA 01835, USA). A 20-50 nm size range was selected, as the cost is essential for large-scale applications.

2.2. PREPARATION OF THE MIXTURE OF NANOPARTICLES AND W1

Superparamagnetic iron oxide nanoparticles (Fe_2O_3) were mixed with the stripping agent (W1) solution (IKA ULTRA-TURRAXR T-25 Digital Homogenizer at 5000 rpm for 45 min to ensure complete dispersion and suspension of the NPs in the W1 phase. Then, an ultrasonic bath (manufactured by Fisher Scientific, USA) was used to break down the finer aggregated NPs for 60 min [Qusay Jaffer Rasheed et al., 2011].

3. EXPERIMENTAL WORK

The ELM is formed by mixing the O phase with the W1 phase of the 0.5 H_2SO_4 reactant stripping agent solutions at a high emulsification speed (rpm) to produce globules emulsion of tiny aqueous droplets (W1) phase (0.1-10 µm) in the membrane O phase. The O phase contains the solvent kerosene, surfactant Span 80, and carrier di-2-Ethylhexyl phosphoric acid (D2EHPA). Then (W1/O) emulsion globules (0.1-2 mm) are dispersed in the external wastewater (W2) phase, where the heavy metal of vanadium pollutant was present [Liu et al., 2017]. In the ELM, the vanadium pollutants are removed from the wastewater by mass transfer with the chemical reaction of the pollutant compounds with the stripping agent H_2SO_4 (reaction agent) in the aqueous droplets (W1) of the emulsion globules as per the reactions 1 to 4 [Al-Obaidi et al., 2020 and Liu et al., 2017]. To maintain the maximum driving force of the concentration gradient of the pollutant from the concentration in W2 to zero concentration in W1 until about the completion of the extraction during a particular time. Figure 2 [Hossein et al., 2015].

$V_2O_5 + 2H_2O = H_4V_2O_7$ (1)

$H_4V_2O_7$ (W2) + 4HR (carrier) $\leftrightarrows$ $H_4V_2O_72R_2$ [interface (external\membrane)] + $2H_2$ (external) (2)

$H_4V_2O_72R_2 + 14H^+ \leftrightarrows 2V^{+2} + 4HR + 7H_2O$ (3)

$V^{+2} + 3H_2SO_4 \rightarrow VOSO_4 + 3H_2O + 2SO_2$ (4)

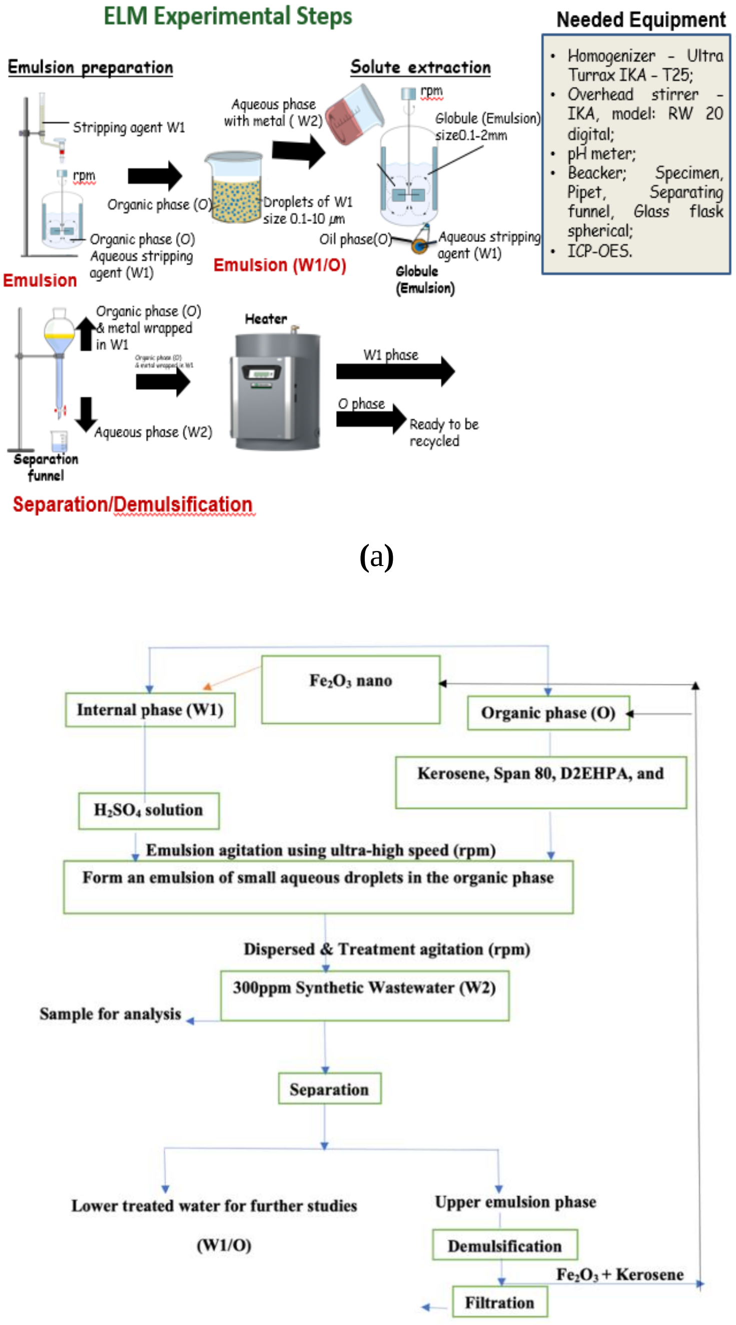
Many variables that affect the extraction of the vanadium using ELM that has been studied in literature are Span 80 concentration (W/V), D2EHPA carrier concentration (V/V), W1/O volume ratio (V/V), emulsification agitation speed to create an emulsion (rpm), ELM (W1/O)/W2 (V/V), treatment agitation mixing speed of W2 (rpm), and pH of W2 [Al-Obaidi et al., 2020]. Hence, the first step in this work was to assess the best combination values of these variables to extract/recover vanadium before studying the impacts of NPs and ionic liquid on ELM's key performance indicators

(KPIs) of 1. Extraction/recovery efficiency (percentage separation or removal), 2. duration of the extraction/recovery, and 3. enhanced stability. It is worth mentioning that the concentration of sulfuric acid needs to be assessed compared to the concentration of vanadium ion in W2 and the carrier concentration in O to ensure enough sulfuric acid and carrier to achieve the desired recovery or removal.

Therefore, in this study, the values of these variables have been checked first for the best values listed above by varying one variable at a time as outlined below, while the others are kept unchanged at the best value. The variation made on these variables are: the volume ratio of the W1 phase to the O phase of 1/1 (V/V), 1/2 (V/V), 1/3 (V/V), 1/4 (V/V), 1/5 (V/V), and 1/6 (V/V); Span 80 surfactant concentrations of 1% (W/V), 2% (W/V), 3% (W/V), 4% (W/V), and 5% (W/V); D2HAPA carrier concentrations were 1% (V/V), 2% (V/V), 3% (V/V), 4% (V/V), and 5% (V/V); emulsification speed (Turrax IKA-T25) 4000 (rpm), 5000 (rpm), 6000 (rpm), 7000 (rpm), and 8000 (rpm) to 10 minutes is producing a liquid membrane with a milky white color; the treatment volume ratio of ELM to W2 phase 1/8 (V/V), 1/10 (V/V), 1/12 (V/V), and 1/15 (V/ V); treatment mixing speed (IKA overhead stirrer: RW20 digital) 250 (rpm), 300 (rpm), and 400 (rpm) for 30 minutes; pH of W2 phase of 1, 2, 3, 4, 5, and 6. The emulsion (W1/O) was dispersed and mixed with the W2 phase that contains vanadium shown in Figure 2.

From the agitated solution, samples were taken at various times by using a nylon syringe filter of 0.2 µm (Simsii Inc. USA) to ensure sampling only W2. The syringe filter is used to prevent emulsion globules from mixing with W2 samples or in case of their breakage due to sampling from mixing W1 with W2 samples. Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) was applied to analyze vanadium ions

[Reis et al., 2004]. The concentration of vanadium was obtained from the calibration curves established first with known concentration samples [Al-Obaidi et al., 2020].



(b)

Figure 2 .(a) Schematic diagram of the Emulsion Liquid membrane (ELM) process. (b) Block diagram of the ELM process.

Using these best variables value, the effects of the superparamagnetic iron oxide nanoparticles (Fe_2O_3) alone in the W1 phase of 0.01% (W/W), 0.05% (W/W), 0.1% (W/W), 0.15 (W/W), and 0.2% (W/W) and the [OMIM]PF6 ionic liquid alone in the O phase of 1%(V/V), 2%(V/V), 3%(V/V), 4%(V/V), 5%(V/V), and 6% (V/V) on the ELM key performance indicators for the recovery of vanadium have been investigated. That allows identifying the best value of NPs alone and [OMIM]PF6 alone to vary them around these values to study the effects of their combination on the emulsion key performance indicators and to determine the best values with a consideration to use the lowest possible amounts a combination of nanoparticles and ionic liquid for economic benefits.

It is noteworthy that a shorter batch operation time will facilitate the transformation of the ELM process from batch to continuous operation for industrial applications. Every experiment was repeated three times for all the conditions investigated, where the error bars were estimated, which are within the points; therefore, they were not plotted in the figures.

At the end of the experiment, the solution is set in a separation funnel to separate the upper emulsion phase with the vanadium ion and the lower treated aqueous phase. The demulsification occurs when the aqueous phase is separated from the organic phase by heating 80^oC for 1hr in a closed vessel for final vanadium extraction. The solvent (kerosene) from the broken emulsion is collected to be reused if needed to prepare a new ELM experiment [Spas et al., 2009].

The percentage of the vanadium extracted/recovered was calculated by the following Vintequation (5).

$$\text{Extraction } \% = \frac{\text{initial concentration} - \text{final concentration}}{\text{initial concentration}} \text{ X } 100 \quad (5)$$

The stability of the ELM was examined by the following Equation:

$$\text{Leakage rate } \% = \frac{Vr}{Vint} \text{ X } 100 \quad (6)$$

$$\text{Vr} = Vext * [\frac{(10^{pHo}) - (10^{pH})}{(10^{pH}) - (H^{+})i}] \quad (7)$$

where Vext = initial external phase volume, pH0= initial pH of the emulsion,

pH= pH of emulsion after a certain time,

$[H^+]$i= protons initial concentration in the internal phase.

Vint= left volume of the emulsion.

4. RESULTS AND DISCUSSION

4.1. ASSESSING THE BEST VALUES OF THE ELM OPERATING VARIABLES COMBINATIONS REPORTED IN THE LITERATURE FOR VANADIUM EXTRACTION USING ELM WITHOUT NANOPARTICLES AND IONIC LIQUID

Experiments were implemented to assess the best desirable combined values of the operating variables for the ELM to study the effects of nanoparticles and ionic liquid on vanadium extraction/recovery. Our finding has been consistent with the best value of the ELM operation variables that have been reported in the literature. For these best values, the extraction of vanadium was found to be 69.7% within 5 min, and the extraction decreased to 33.1% after 30 min of batch operation, as shown in Figure 3. The reduction in percentage recovery could be attributed to the leakage of the emulsion, which means W1 was leaked to W2. The leakage was calculated to be 72% after 6 hours. Such percentage recovery of ELM and the needed batch time of the experiment is within the range of heavy metals recovery by ELM without nanoparticles and ionic liquid reported in the literature [Al-Obaidi et al., 2020, Kumbasar. 2008, and Norela et al., 2016].

In such assessment, reducing the concentration of Span 80 affected the vanadium extraction negatively and decreased the emulsion's surface tension, which produces small globules containing a small number of droplets of W1. However, adding more of the surfactant of Span 80 increases the leakage causing a decrease in the emulsion stability, and hence a reduction in the efficiency extraction due to the formation of thicker emulsion globules [Liu et al., 2017, Hossein et al., 2015, and Garcia et al., 2013].

Carrier D2EHPA has an essential impact on heavy metal extraction because heavy metal compounds are usually insoluble in the O phase. Therefore, vanadium transport from the W2 phase to the W1 phase through the O phase by the carrier [Reis et al., 2004]. Increasing the concentration of D2EHPA decreases the extraction/recovery efficiency of the vanadium and, decreasing emulsion stability efficiency, which needs to be studied in separate effect experiments [Rania et al., 2007, Mortaheb et al., 2008, Spas et al., 2009, and Othman et al., 2012]. However, excessive amounts of the D2EHPA may affect the carrier's interfacial properties, which favors oil-in-water emulsions and could counter affecting the surfactant Span 80 [Avinas et al., 2014].

The ratio of W1 phase volume to O phase volume has an essential function in the emulsion vanadium ion reacts with the stripping agent (H_2SO_4) [Kumbasar. 2008, Norela et al., 2016, and Lelin. 2015]. The W1/O ratio can be adjusted by varying either volume of the W1 phase or the volume of the O phase. Increasing the volume of the W1 phase creates more W1 droplets, decreasing the thickness between the O phase and W1 droplets that improve the transfer of the metal from W2 through O to W1. While increasing the volume of the O phase causes a large thickness between the O phase and the W1 droplets, which decreases the vanadium transferred from W2 to W1 through O. The W1/O volumes ratio of 1 gives better extraction and less leakage [García et al., 2013, Mortaheb et al., 2008, Lelin. 2015, and Levent et al., 2007].

The emulsification speed rpm produces crucial emulsion to increase extraction/recovery efficiency [Hossein et al., 2015 and García et al., 2013]. The emulsification speed of 6000 rpm was convenient for forming an emulsion “mayonnaise-like,” resulting from generating more droplets while decreasing the interfacial tension between the W1 and O phases. The droplet form increases in a highly viscous emulsion, where the droplets coalesce due to rapid mixing. In contrast, the increase beyond that limit causes lower diffusion capability (diffusivity) of the obtained vanadium -D2EHPA complex [Reis et al., 2004, and Motaheb et al., 2008].

The treatment volume ratio (ELM/W2) plays an essential function in ELM's performance [19 and 25]. The volume ratios were other than 1/10 decrease the extraction/recovery efficiency attributed to increased emulsion thickness around the globules. Moreover, the mechanical resistance of the emulsion increases when a higher organic fraction is presented, which prevents the coalescence of the dispersed globules and reserves the size within the range of standard globules of 0.1−2 mm [Al-Obaidi et al., 2020]. In general, the increased sizes of the globules increased the ELM instability because of rapid coalescence.

The mixing treatment intensities (rpm) affect the ELM stability and the ELM leakage. They produce a greater shear force on the globules by more significant agitation intensity that considerably decreases the emulsion globules size where the contact area for mass transfer increases [Rania et al., 2007 and Bouranene et al., 2003]. Despite this, increasing the mixing treatment intensity can decrease the ELM stability due to the globules' rupture, creating a leakage of the W1 phase into the W2 phase [Kumbasar. 2008 and Avinash et al., 2014]. However, increasing the rpm may also lead to ELM breaking [Lelin. 2015]. Thus, the best value of 300 rpm produces small globules enough to have high surface area exposure to provide higher extraction/ recovery efficiency [García et al., 2013 and Levent et al., 2007].

The pH of the treated phase (W2) performs a vital role in the surface charges of the W2 phase [Mortaheb et al., 2008]. It has been shown that the percentage extraction/recovery of vanadium was efficient and more stable when the pH value of the W2 phase was 5 [Othman et al., 2012 and Ahmad et al., 2011]. At the higher pH of the W2 phase, an increase in the hydrogen ion concentration of the W2 phase increased the extraction rate and affected the vanadium's transport by affecting the reaction with the carrier at the interface of the globules. At higher pH (as pH 5 in this study), the surface of the globules was considerably surrounded by an increase in the hydrogen ion [Mortaheb et al., 2008, Bouranene et al., 2003, Ahmad et al., 2011, and Benyahia et al., 2014].

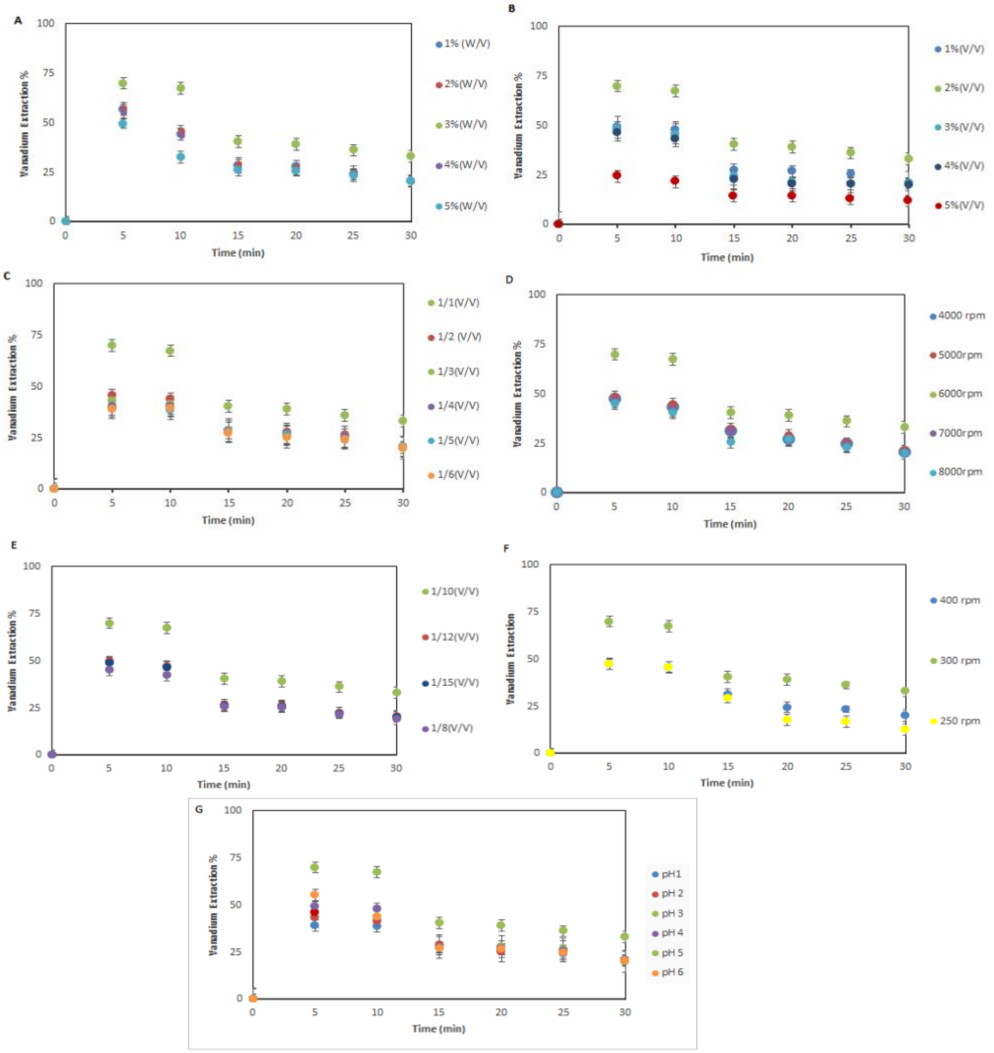


Figure 3. The effect of the ELM variables on the extraction of the vanadium using the following values when a designated variable is changed: A. Variation of the surfactant concentration of Span 80 in the organic phase, B. Variation of the carrier concentration of di(2-ethylhexyl)phosphoric acid (D2EHPA) in the organic phase, C. Variation of the volume ratio of W1/O phase D. Variation of the agitation intensity (rpm) to create emulsification (emulsion agitation), E. Variation of the volume ratio (V/V) of (W1/O) globules to W2 phase, F. Variation of the agitation intensity (rpm) of the mixing of (W1/O) globules and W2 phase (treatment agitation), and G. Variation of the pH of the W2 phase

4.2. THE EFFECT OF NANOPARTICLES ALONE ON THE EXTRACTION /RECOVERY OF VANADIUM

The effect of 0.01%, 0.05%, 0.1%, 0.15%, and 0.2% (W/W) of superparamagnetic iron oxide (Fe_2O_3) in the W1 phase on the extraction/recovery of vanadium was studied. At the same time, the ELM operating variables are kept at the best values mentioned and discussed above (Figure 3). The results demonstrate that the ratio of 0.15 % (W/W) of superparamagnetic iron oxide Fe_2O_3 NPs alone in the W1 phase enhances the recovery from 69.7% to 87.3 % after five minutes of batch operation, and the leakage was 73% for 78 hrs.

The presence of the superparamagnetic iron oxide nanoparticles (Fe_2O_3) in the W1 phase improves vanadium's mass transfer from the O phase's interface to the W1 phase. Therefore, the nanoparticles would improve the extraction/recovery of the vanadium by forming a protective film at the interface inside W1 droplets and increasing the binding sites on the W1 phase droplets' surface. However, further increasing the concentration of nanoparticles causes full coverage of the internal surface of W1 droplets that could hinder the mass transfer of vanadium ions to be reacted. Also, in this case, the left-over superparamagnetic iron oxide nanoparticles (Fe_2O_3) would affect the availability of the reactants because as it will pack the droplets, they might produce aggregates on the W1/O interface also be leaked and dispersed in the organic phase (O). Hence, these could cause decreasing in the extraction efficiency.

It is noteworthy that Figure 4 shows a reduction in the extraction percentage with time up to the time duration of the experiment, which is 30 minutes, and for all the concentrations of W/W percentages of nanoparticles used, including without nanoparticles experiments (see Figure 3). The reduction in the percentage extraction in

W2 (i.e., increasing the concentration of vanadium ion in W2) is steeper for the 0.15% W/W nanoparticles addition than the other concentrations. As mentioned earlier, their leakage and emulsion breakage will release the heavy metal ion from the inner W1 phase to the W2 phase.

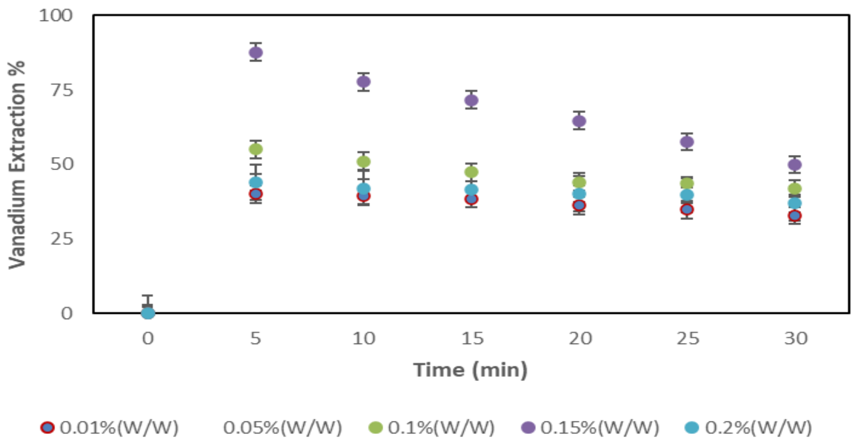


Figure 4. The effect of Fe_2O_3 nanoparticles alone in W1 phase on the ELM extraction for vanadium: Span 80 concentration of 3% (W/V), D2EHPA carrier concentration of 2% (V/V), W1/O volume ratio of 1/1 (V/V), emulsification agitation speed to create emulsion of 6000 rpm, ELM (W1/O)/W2 volume ratio of 1/10, treatment agitation mixing speed of W2 of 300 rpm, and pH of W2 of 5.

4.3. THE EFFECT OF THE IONIC LIQUID ALONE IN THE ORGANIC PHASE (O) ON THE EXTRACTION OF VANADIUM

The ionic liquid in the organic phase (O) has been used to enhance the emulsion stability. Thus, the ionic liquid ([OMIM]PF6) was selected in this study because Al-Obaidi et al., 2020 showed that this ionic liquid gives better extraction efficiency besides enhancing stability. Figure 5 presents the effect of ionic liquid on the percentage extraction of vanadium ions. Ionic liquid ([OMIM] PF6) concentration increase up to 5% (V/V) will increase the stability time [Bjorkegren et al., 2012 and Al-Obaidi et al., 2020]. As shown in Figure 5, at 5% (V/V) [OMIM] PF6 concentration, the vanadium extraction improved from 69.7% at five minutes batch time when there is no ionic liquid to 78.8 % at five minutes of batch time. As a result, the emulsion stability improves from leakage of 72% for 6 hours to 49% for 78 hrs. At a high [OMIM] PF6 concentration of 6% (V/V), the time of maintaining emulsion reduced because of increased ELM sedimentation due to could be a higher density of the [OMIM]PF6. The increase in the ELM stability could be attributed to Coulombic interactions of the [OMIM]PF6 and charges on the H_2SO_4. This strong interaction enhances the ELM stability by lowering the internal droplets' coalescence [Bjorkegren et al., 2012 and Al-Obaidi et al., 2020]. In addition, the hydrogen bond may cause strong protection around the inner droplets to avoid coalescence [Al-Obaidi et al., 2020]. Increasing the ([OMIM] PF6) concentration would further decrease the interfacial tension through a bonding on the W1-O interface and thus reduce the repulsion of hydrophilic head groups of Span 80 at the interface and reducing droplet size for W1.

4.4. THE EFFECT OF COMBINING OF FE2O3 NANOPARTICLES AND IONIC LIQUID ON THE EXTRACTION OF VANADIUM

The concentration of 0.01% (W/W) of superparamagnetic iron oxide Fe_2O_3 NPs in the W1 phase has been found to provide the best percentage extraction of 99.6% in 3 minutes, as shown in Table 1 when it was combined with the ionic liquid ([OMIM]PF6) concentration of 5% (V/V) in the O phase. These concentrations represented the least amounts to be used for Fe_2O_3 NPs & [OMIM]PF6 and are beneficial for large-scale economic applications. This also gives the additional advantage of achieving the highest extraction/recovery percentages in the shortest time without allowing more time for the leakage to reduce the extraction/recovery percentage with time, as shown and discussed above.

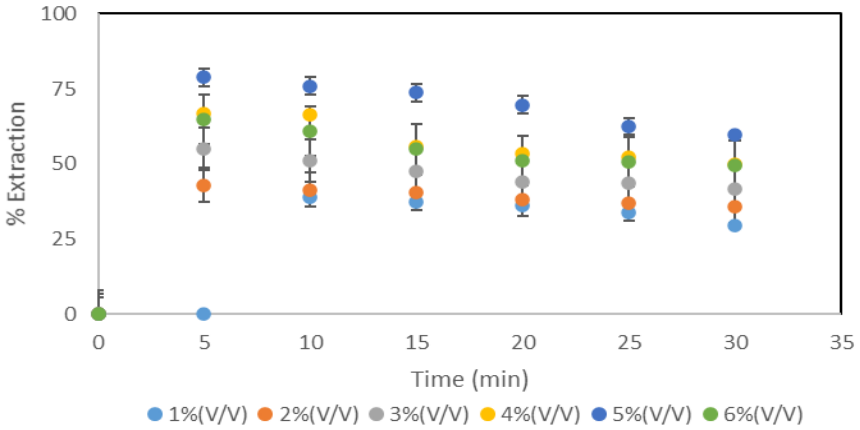


Figure 5. The effect of ionic liquid ([OMIM]PF6) alone in organic phase on the ELM extraction for vanadium: Span 80 concentration of 3% (W/V), D2EHPA carrier concentration of 2% (V/V), W1/O volume ratio of 1/1 (V/V), emulsification agitation speed to create emulsion of 6000 rpm, ELM (W1/O)/W2 volume ratio of 1/10, treatment agitation mixing speed of W2 of 300 rpm, and pH of W2 of 5.

Furthermore, the combination of Fe_2O_3 NPs and [OMIM]PF6 has been found to increase the emulsion stability, as shown in Figures 6 and 8, where the percentage leakage was estimated by Equations 6 and 7. The lower leakage and higher ELM stability time were achieved and maintained with the combination of the superparamagnetic iron oxide Fe_2O_3 NPs and [OMIM]PF6 of 16% for 78 hours during the experiments. This represents a much longer time after completing the recovery of 3 minutes. Additionally, the stabilization of ELM with nanoparticles and ionic liquid improves the strength between ELM droplets and prevents collisions and coalescence of the droplets. This confirms that the combination of Fe_2O_3 NPs and [OMIM]PF6 enhanced the ELM stability compared with ELM alone, and ELM + ionic liquid alone decides to improve the extraction efficiency.

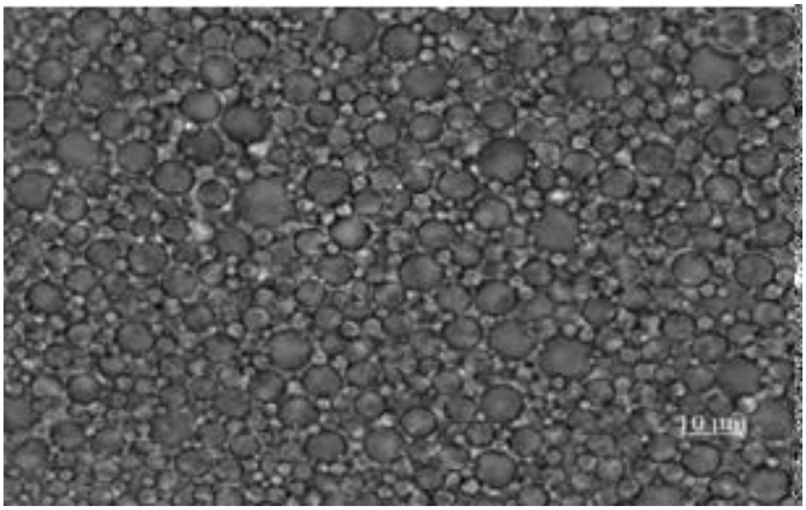


Figure 6. Microscope emulsion droplet stabilized at best condition for ELM process for vanadium extraction/recovery.

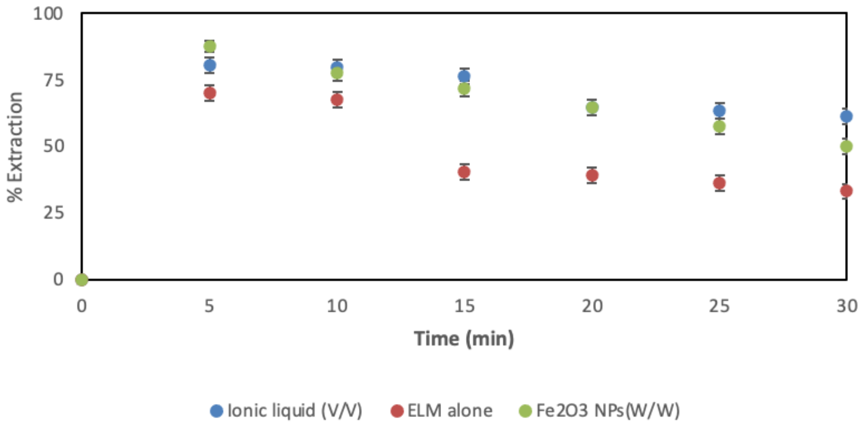


Figure 7. Effect of the 0.01% (W/W) magnetic Fe_2O_3 nanoparticles in W1 phase alone and 5% (V/V) ionic liquid ([OMIM]PF6) in O phase alone on the vanadium extraction: W1:O volume ratio of 1/3 (V/V), surfactant concentration of 2%, emulsification speed of 8000 rpm, ELM (W1/O)/W2 volume ratio of 1/2 (V/V), treatment agitation mixing speed of W2 of 300 rpm, and pH of W2 of 1.5.

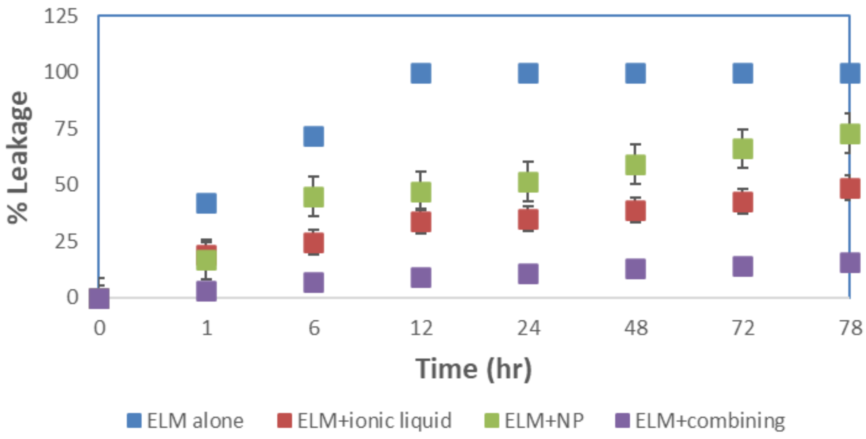


Figure 8. Effect of the combination 0.01% (W/W) magnetic Fe_2O_3 nanoparticles in W1 phase and 5% (V/V) ionic liquid ([OMIM]PF6) in O phase on the ELM emulsion stability: W1:O volume ratio of 1/3 (V/V), surfactant concentration of 2%, emulsification speed of 8000 rpm, ELM (W1/O)/W2 volume ratio of 1/2 (V/V), treatment agitation mixing speed of W2 of 300 rpm, and pH of W2 of 1.5.

Table 1. The effect of combination 0.01% (W/W) superparamagnetic Fe_2O_3 nanoparticles (20 nm to 50 nm) in W1 phase and 5% (V/V) ionic liquid ([OMIM]PF6) in organic phase on the ELM extraction for vanadium: Span 80 concentration of 3% (W/V), D2EHPA carrier concentration of 2% (V/V), W1/O volume ratio of 1/1 (V/V), emulsification agitation speed to create emulsion of 6000 rpm, ELM (W1/O)/W2 volume ratio of 1/10, treatment agitation mixing speed of W2 of 300 rpm, and pH of W2 of 5.

Time (min)	**Fe_2O_3 NP in W1 phase+([OMIM]PF6) in O phase**
1	**98.3**
2	**98.4**
3	**99.6**

5. CONCLUSION

For the first time, the enhanced ELM (W1/O/W2) has been developed and studied by combining the superparamagnetic iron oxide nanoparticles (Fe_2O_3) of 20-50 nm in the

W1 phase and [OMIM]PF6 ionic liquid in the O phase of 0.01% (W/W) and 5% (V/V), respectively. The following is a summary of the findings.

The vanadium extraction percentage and ELM stability were greatly improved by combining Fe_2O_3 NPs in the W1 phase and [OMIM]PF6 in the O phase.

The concentration of combination obtained was 0.01% (W/W) of Fe_2O_3 NPs in the W1 phase and 5% (V/V) [OMIM]PF6 in the O phase, which gave high vanadium extraction efficiency of 99.6 % in about 3 minutes, and the leakage of 16% for more than three days. This proves the capability of the composition comprising to increase the ELM stability and vanadium extraction. When Fe_2O_3 NPs were applied in the O phase and in the W2 phase did not achieve any extraction/recovery of the vanadium and block the reactions. Therefore, we changed the position of the NPs to the W1 phase, and then we studied the vanadium recovery rate.

The vanadium extraction efficiency was improved to 87.3 % after the first five minutes of running time via adding Fe_2O_3 NPs alone in the W1 phase of 0.15% (W/W). After five minutes of batch operation, the percentage of vanadium extraction drops due to the ELM leakage.

The ELM stability has been enhanced with the addition of 5% (V/V) of [OMIM]PF6 in the O phase, which might be due to the Coulombic interaction of hydrogen bonding present between the H_2SO_4 and [OMIM]PF6. The vanadium extraction efficiency with 5% (V/V) of [OMIM]PF6 concentration was 78.8 % after 30 min of batch operation with leakage of 49% for three days.

The best variables values for ELM performance indicators have been confirmed in this study for the extraction/recovery of vanadium, which is: Surfactant concentration of 3% (W/V), the attention of D2HEPA carrier of 2% (V/V), a volume ratio of W1 to O phase of 1/1 (V/V), emulsification speed of 6000 rpm, treatment (ELM/W2) volume ratio of 1/10 (V/V), the treatment mixing speed of 300 rpm, and W2 of pH 5. Vanadium was extracted of 69.7% from the W2 phase after five minutes of batch operation and the leakage of 72% for six hours. Such recovery is not high, and its time duration is high. Such percentage recovery of ELM and batch time for vanadium is within the range of heavy metals percentage recovery by ELM without nanoparticles and ionic liquid.

REFERENCES

1. Ahmad, A.L., Kusumastutia, A., Dereka, C.J.C., Ooi, B.S., 2011. *Emulsion liquid membrane for heavy metal removal: an overview on emulsion stabilization and destabilization.* Chem. Eng. J. 171, 870–882.

2. Archana Saily P. 2015. *Separation and recovery of vanadium from spent vanadium pentaoxide catalyst by Cyanex 272.* Environmental systems research 4/7. DOI: 10.1186/s40068-015-0032-3.

3. Avinash B. Lende, Manish K. Dinker, Vikas K. Bhosale, Sanjay P. Kamble, Pawan D. Meshramc and Prashant S. Kulkarni. 2014. *Emulsion ionic liquid membranes (EILMs) for removal of Pb(II) from aqueous solutions.* The Royal Society of Chemistry. 4, 52316–52323.

4. Badgujar V., Rastogi, Desalin N.K. 2011. *Water Treat.* 36-187.

5. Bjorkegren S., Karimi R.F. 2012. *A Study of the Heavy Metal Extraction Process using Emulsion Liquid Membrane*s. Chalmers University of Technology, Sweden.

6. Benyahia, N., Belkhouche, N., Jönsson, J.A., 2014. *A comparative study of experimental optimization and response surface methodology of Bi(III) extraction by emulsion organophosphorus liquid membrane*. J. Environ. Chem. Eng. 2, 1756–1766.

7. Bouranene S., Samar M. E. H., and Abbaci A. 2003. *Extraction of cobalt and lead from wastewater using a liquid surfactant membrane emulsion.* Acta Chim. Slov. 50, 663–675.

8. Chakraborty M., Bhattacharya C., and Datta S. 2010. *Chapter 4 - Emulsion Liquid Membranes: Definitions and Classification, Theories, Module Design, Applications, New Directions and Perspectives, in Liquid Membranes.* V.S. Kislik, Editor. Elsevier: Amsterdam. 141–199.

9. Christopher J. Portier, Ph.D. 2012. *TOXICOLOGICAL PROFILE FOR VANADIUM U.S. Agency for Toxic Substances and Disease Registry Division of Toxicology and Human Health Sciences (proposed) Environmental Toxicology Branch (proposed) 1600 Clifton Road NE Mailstop F-62 Atlant.,* Georgia 30333.

10. EPA. 2011f. *Designation of hazardous substances. U.S. Environmental Protection Agency. Code of Federal Regulations 40 CFR 116.4.* CFR-2011-title40-vol22/pdf/CFR¬2011-title40-vol22-part116.pdf.

11. FEDRIP. 2012. *Vanadium. Federal Research in Progress database. Springfield, VA:* National Technical Information Service.

12 García, M.G., Acosta, A.O., Marchese, J., 2013. *Emulsion liquidmembrane pertraction of Cr(III) from aqueous solutions usingPC-88A as carrier.* Desalination 318, 88–96.

13. 24- Mortaheb H., Amini M., Sadeghian F., Mokhtarani B., and Daneshyar H. 2008. J. Hazard. Mater. 160,582.

14. Hossein Tavallali and Rozita Nejabat. 2015. *Developing Fast and Facile Method for Speciation Analysis of Vanadium (V/IV) Ions with Calmagite Immobilization on Triacetyl Cellulose Membrane in Water Samples.* Journal of the Brazilian Chemical Society. Print version ISSN 0103-5053.

15. Kumbasar, R.A., 2008. *Studies on extraction of chromium(VI)from acidic solutions containing various metal ions byemulsion liquid membrane using Alamine 336 as extractant.* J.Membr. Sci. 325, 460–466.

16. Lelin Zeng, L. Y. 2015. *Influences of axial mixing of continuous phase and polydispersity of emulsion drops on mass transfer performance in a modified rotating disc contractor for an ELM system*. Ind. Eng. Chem. Res., 54, 9832 - 9843.

17. Levent GU¨ REL, and Hanife BU¨ YU¨ KGU¨ NGO¨ R. 2007. *Investigation of Organic Matter Release in Emulsion Liquid Membrane Treatments*. Turkish J. Eng. Env. Sci. 31, 265 – 272.

18. Li N.N. 1968. *Separation hydrocarbons with the liquid membrane.* U.S. Patent 3,410,794.

19. Liu Honga, Zhang Yimina, Huang Jinga, Liu Taoa, Xue Nannana, Wang Kuia. 2017. *Selective separation and recovery of vanadiumfrom a multiple impurity acid leaching solution of stone coal by emulsion liquid membrane usingdi-(2-ethylhexyl) phosphoric acid.* Chemical engineering research and design 1 2 2-289–297.

20. Norela Jusoh, Norasikin Othman. 2016. *Stability of water-in-oil emulsion in liquid membrane prospect.* Malaysian Journal of Fundamental and Applied Sciences Vol. 12, No. 3, 114-116.

21. Othman N., Mili N., Idris A., Zailani S.N., Sustain. Membr. 2012. Technol. Energy Water Environ. 221.

22. Qusay Al-Obaidi, Jasmine Monroe, Hannah Smith, Zaid Haha, and Muthanna Al-Dahhan. 2020. *Assessing the Removal of Heavy Metals using Emerging and Intensifying Technology of Emulsion Liquid Membrane with Ionic Liquid.* Available at SSRN: https://ssrn.com/abstract=

23. Qusay Al-Obaidi, Malak Alabdulmuhsin, Alice Tolstik, Jacob G Trautman, Muthanna Al-Dahhan. 2021. *Removal of hydrocarbons of 4-Nitrophenol by emulsion liquid membrane (ELM) using magnetic* Fe_2O_3 *nanoparticles and ionic liquid.* Journal of Water Process Engineering. Volume 39. Pages 101729.

24. Qusay Al-Obaidi, Muthanna Al-Dahhan. 2019. *Advanced Removal/Extraction of the Hydrocarbons by Emulsion Liquid Membrane Enhanced by Nanoparticles.* AIChE Annual Meeting.

25. Qusay Al-Obaidi, Muthanna Al-Dahhan. 2020. *Advanced Removal of 4-Nitrophenol by Emerging and Intensifying Technology of Emulsion Liquid Membrane with Magnetic Nanoparticles*. Elsevier Journal. SSRN. 3601736.

26. Qusay Jaffer Rasheed, Kannaiyan Pandian, Karuppan Muthukumar. 2011. *Treatment of petroleum refinery wastewater by ultrasound-dispersed nanoscale zero-valent iron particles. Ultrasonics Sonochemistry.* Volume 18, Issue 5, Pages 1138-1142.

27. Qusay J. Rasheed, Karuppan Muthukumar. 2012. *Studies On Treatment Of Petroleum Refinery Wastewater*. LAP LAMBERT Academic Publishing. ISBN-10 3659247138, ISBN-13 978-36592471.

28. Rania Sabry, Azza Hafez, MaalyKhedr, Adel El-Hassanin. 2007. *Removal of lead by an emulsion liquid membrane Part I. Science Direct.* Desalination 212, 165–17521-

29. Reis M.T.A., and Carvalho J.M.R. 2004. *Modelling of zinc extraction from sulphate solutions with bis (2-ethylhexyl) thiophosphoric acid by emulsion liquid membranes.* Journal of Membrane Science. 237, pp. 97-107.

30. Spas D. Kolev, Yoshinari Baba, Robert W.Cattrall, TsutomuTasaki, NataliePereira, Jilska M.Perera, Geoffrey W.Stevens. 2009. *Solid phase extraction of zinc(II) using a PVC-based polymer inclusion membrane with. di(2-ethylhexyl)phosphoric acid (D2EHPA) as the carrier. Elsiver.* Talanta journal. Volume 78, Issue 3, Pages 795-799.

31. Zhang, Y.M., Bao, S.X., Liu, T., 2011. *The technology of extracting vanadium from stone coal in China: history, current status and future prospects.* Hydrometallurgy 109, 116–124.

VI. SIMULTANEOUS EXTRACTION/RECOVERY OF MIXED HEAVY METALS BYENHANCED EMULSION LIQUID MEMBRANE (ELM) WITH VARYIN NANOPARTICLES AND IONIC LIQUID

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ABSTRACT

The new enhanced emulsion liquid membrane with the combination of MgO & Al_2O_3 NPs in the W1 phase and ionic liquid ([OMIM][PF6) in the O phase has been applied for extracting mixed heavy metals (Pb^{+2} & V^{+5}) from synthetic wastewater. The duration of time for the batch extracting was reduced and the stability of the emulsion was improved. Pb^{+2} extracting efficiency has been enhanced noticeably to 95.8% in 3 min for 0.01% (W/W) of MgO NPs and 5% (V/V) ([OMIM][PF6), and 94.6 % in 3 min for 0.01% (W/W) of Al_2O_3 NPs and ([OMIM][PF6). However, the V^{+5} extracting efficiency has been enhanced noticeably to 98.6 % in 3 min by using 0.01% (W/W) of MgO NPs and 5% (V/V) ([OMIM][PF6), and 97.7 % in 3 min by using 0.01% (W/W) of Al_2O_3 NPs and 5% (V/V) ([OMIM][PF6). The stability of the emulsion was improved significantly which give the lowest leakage to 16% for more than 78 hours. The outcomes of this work can be exyended to the extraction of pollutants from industrial wastewater and water.

1. INTRODUCTION

Every year, large amounts of wastewater with contaminants heavy metals are generated by industry which are serious to the environment’s concern because they are highly toxic and no-biodegradable. Heavy metal compounds are significant, for example, lead and vanadium, which are exist in many wastewaters of industrial processes such as mining and mineral processing industries [1]. USEPA has deliberated heavy metals as a severe health hazard due to its ability to ground significant issues, such as damaged kidneys, organs, nervous system, and reproductive system in the human body [2, and 3]. For that reason, the wastewater from these industries needs to require effective treatment to extracting the contaminants before releasing them into the environment [4].

Several studies and methods in the literature have been defined heavy metal removal from water and industrial wastewater; these processing methods are "chemical precipitation, electrochemical techniques, ion exchange, and liquid membrane techniques" [5]. The membrane process was too accessible for water and wastewater treatment, impacting either nonporous or porous polymeric and ceramic membranes with several types of improvement to treat the contaminated water [6]. The liquid membrane is introduced and developed as a bulk liquid membrane (BLM), supported liquid membrane (SLM), an emulsion liquid membrane (ELM).

The emulsion liquid membrane (ELM) has been emergedas new technology by Li. N. (1968) to remove pollutants from the wastewater [7&8] with high removal rate and high selectivity with low cost [9].

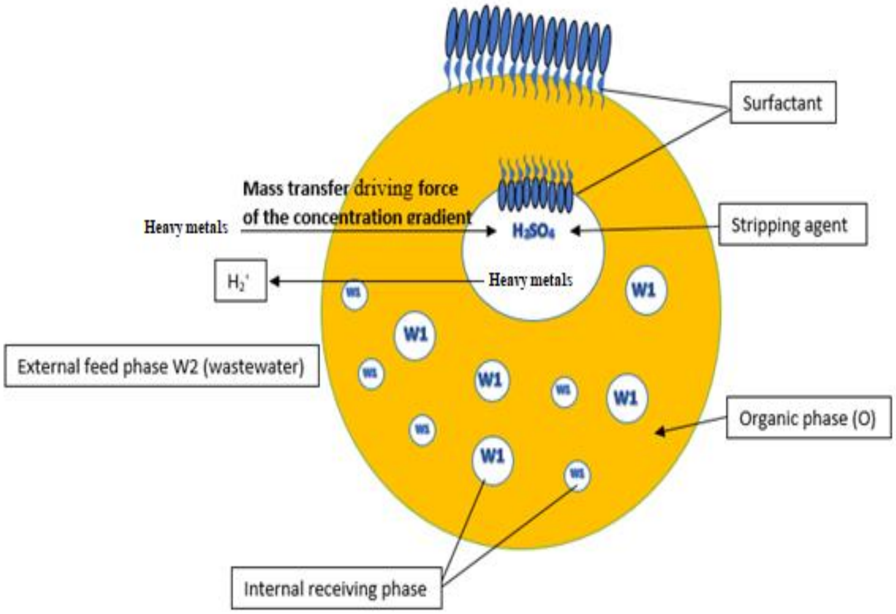


Figure 1. Schematic of the Emulsion liquid membrane

In this study, the W1-O-W2 type used in the ELM method is considered to remove the mixed heavy metals of Pb^{+2} & V^{+5} compounds from aqueous synthesis wastewater. The emulsion consists of tiny droplets of an aqueous phase solution that contains the stripping agent (W1) dispersed in the organic membrane phase (O), creating globules via mixing with the external wastewater feed phase (W2) [10]. Globules are spheres of emulsion that accommodate many tiny droplets of W1 that contained the stripping to react with the contaminant.The mixed heavy metals compounds of Pb^{+2} & V^{+5} in the W2 are insoluble in the emulsion globules, and they need an agent called the carrier to transported them through the O phase to the W1 phase. The carrier reacts with the heavy metals to create complexes, which are also soluble in the organic phase (O) to transfer them to the W1 phase, which reacts with the stripping agent (reactant). Figure 1 shows the schematic of the transport in ELM [11].

As reported in the literature, the capable results of (ELM) have not progressed extensively to industrial applications because the ELM method is suffering from low emulsion stability due to breakage and swelling, which affects reducing the extraction efficiency.

Long duration of time (residence time) to achieve a high percentage of extracting and an inefficient process of demulsification to separates phases and to recycle the solvent [12].

The extracting efficiency of ELM and the emulsion stability have been considered to detect the relationship between the emulsion membrane's properties and operating variables [13]. Al-Obaidi et al. (2020) studied ionic liquids' role in improving emulsion and mass transfer rate stability. He used $[BMIM]^+[NTf2]^-$ and ([OMIM]PF6) ionic liquid in the O phase during the emulsion process for the extraction/recovery of Pb^{+2}. The results showed that 5% (V/V) of ionic liquid ([OMIM]PF6) in the O phase gave an improvement in the stability of the emulsion and the extraction/recovery efficiency of 70.4% after 5 min in a batch operation [14].

The current work motivations are studying the emulsion's stability, extracting/ removing mixed Pb^{+2} & V^{+5} efficiency rate from the synthesis wastewater in a batch operation using ELM with nanoparticles in the W1 phase alone and ELM combination nanoparticles in the W1 phase and ionic liquid in the O phase.

Nanoparticles of MgO and Al_2O_3 were used and the effect of nanoparticles type was studied.

2. EXPERIMENTAL METHODS

2.1. CHEMICAL REAGENTS

The used chemicals in this work were used carrier di-2-ethylhexyl phosphoric acid (D2EHPA), surfactant (Span 80), and kerosene, whose boiling points range from (175-325) ˚C, as solvents (O). 1-Methyl-3-octylimidazolium hexafluorophosphate ([OMIM]PF6), lead (II) nitrate $Pb(NO_3)_2$, vanadium pentoxide (V_2O_5), sodium hydroxide pellets (NaOH), and hydrochloric acid (HCl) were obtained from Sigma Aldrich (USA). The other chemicals used in this study were, 0.5 N sulfuric acid (H_2SO_4) as internal aqueous phase as stripping agent to react with the $Pb(NO_3)_2$ and V_2O_5. Aluminum oxide (Al_2O_3) and magnesium oxide (MgO) nanoparticles with the size range between 20 nm to about less than 50 nm were used and obtained from Fisher Scientific.

2.2. NANOPARTICLES (NPs) IN W1 PHASE

0.01% (W/W) of MgO NPS and Al_2O_3 NPs with a size range of 20nm to 50 nm were suspended separately with a stripping agent (W1) using IKA ULTRA-TURRAXR T-25 Digital Homogenizer at 5000 rpm for 45 min ensure complete dispersion of the nanoparticles in the base fluid. An ultrasonic bath (manufactured by Fisher Scientific, USA) was used to break down the finer nanoparticle aggregates for 60 min.

2.3. ELM PROCESS

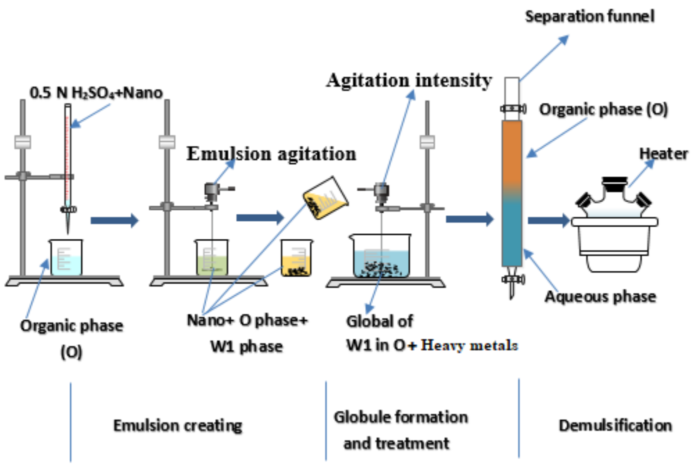
Several variables impact the extracting of the pollutants using ELM methods, such as the volume ratio of the W1 to O phase (V/V), emulsification speed (rpm), Span 80 concentration (%W/V), D2EHPA concentration (%V/V), a treatment volume ratio

(ELM/W2 ratio (V/V)), treatment mixing speed (rpm), pH of W2, and MgO NPs & Al_2O_3 NPs and ionic liquid concentrations. Accordingly, the initial step is to detect the best variables values to extract the mixed Pb^{+2} & V^{+5} before studying the effects of MgO Nps & Al_2O_3 NPs and ionic liquid on the emulsion stability and efficiency extraction rate and extraction duration time.

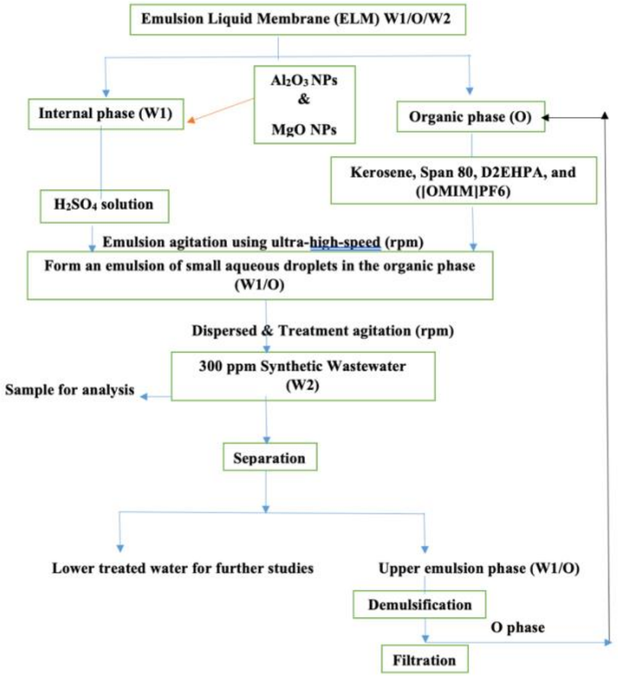
The emulsion (W1/O) was dispersed and mixed (IKA overhead stirrer Model: RW20 digital) with the W2 phase contains Pb^{+2} & V^{+5}, as shown in Figure 2. The sample was taken from the mixing solution at different times and then separated by a nylon syringe filter of 0.2 µm (Simsii Inc. USA). The Pb^{+2} & V^{+5} was analyzed using an inductively coupled plasma - optical emission spectrometry (ICP-OES) [17]. The effects of MgO Nps & Al_2O_3 NPs alone in the W1 phase of 0.01% (W/W), 0.05% (W/W), 0.1% (W/W), 0.15% (W/W), and 0.2% (W/W) and ionic liquid ([OMIM]PF6) alone in the O phase of 1%, 2%, 3%, 4%, 5%, and 6% (V/V) on extracting rate of heavy metals and the batch extracting time were invistegated.

The main aim is to determine the lowest amount possible of nanoparticles and ionic liquid with the best ELM performance in terms of the stability of the emulsion, high percentage extracting, and shorter duration time of the batch operation for extracting. Each experiment was repeated three times for all the investigated conditions, where the error bars were evaluated.

At the end of the extraction of the heavy metals, the solution is placed in a separation funnel to separate the upper emulsion phase and the lower aqueous feed phase. The aqueous phase will be separated from the organic phase by heating 80°C for 1hr in a closed vessel to finally recover the internal receiving phase with heavy metals and separately collected oil from the broken emulsion.



(a)



(b)

Figure 2 (a) Schematic diagram of the Emulsion liquid membrane process. (b). Block diagram of the Emulsion liquid membrane process

2.4. CALCULATION OF ELM STABILITY

ELM stability determined by the following Equation:

Breaking rate %= (Vr/Vint) X 100 (1)

$Vr = Vext *[(10^{pH0})-(10^{pH})]/[(10^{pH})-(H^{+}) i]$

Where Vext = initial emulsion volume, pH0= pH initial of the emulsion,

pH= pH of the emulsion after certain time ,

$[H^{+}]$i = protons initial concentration in the internal phase.

Vint= left volume of the emulsion.

2.5. ANALYTICAL METHODS

The percentage extraction was calculated by the following equation.

Extraction %= [(initial concentration-final concentration)/ initial concentration] X100. (2)

3. RESULTS AND DISCUSSION

To investigate the effects of the nanoparticles (MgO NPs & Al_2O_3 NPs) and the ionic liquid ([OMIM]PF6) on the ELM stability, the simultaneous extraction/recovery efficiency of mixed heavy metals compounds, and the extracting duration, the following steps have been performed.

1. First studied the effects of each variable's best value by varying that examined variable and keeping the other variables constant. These variables are volume ratio of the W1 to O (V/V), Span 80 concentration (W/V), D2EHPA concentration (V/V), emulsification speed (rpm), a treatment volume ratio (V/V), mixing treatment speed (rpm), and pH of W2.

2. Investigated the effect of ionic liquid ([OMIM]PF6) only on the Elm performance of extracting/recovering mixed heavy metals compounds by varying the ionic liquid concentration while maintaining the values of the variables outlined in Step (1). It has determined the best value of the ionic liquid concentration that provides the best ELM performance in this step.

3. Studied the effects of only the MgO NPs & Al_2O_3 NPs (20-50 nm) on the ELM performance of extracting/recovering mixed heavy metals compounds by varying the nanoparticles concentration while maintaining the same values of the variables mentioned in Step (1) above. We determined the best value of the nanoparticle concentration in this step that provides the best ELM performance (improved emulsion stability, highest % extracting, and shortest time of extraction).

4. Studied the effects of combining the MgO NPs & Al_2O_3 NPs with ([OMIM]PF6) around the best values obtained in Step (1) on the ELM performance of extracting/recovering mixed heavy metals compounds. In this investigation, determined the best concentrations of a combination of nanoparticles and ionic liquid with the consideration to seek to define the least nanoparticles amount and ionic liquid that can provide the desirable and best performance of ELM in terms of the parameters mentioned above.

In the ELM method, the pollutants are extracted by mass transfer with the chemical reaction of the pollutant compounds' reaction agent in the W1 phase. This means that the driving force of the gradient concentration for the pollutants transfer from the W2 phase to the W1 phase through the O phase remains at its maximum, and then the transport of pollutants continues until the extraction is complete (Al-Obaidi and Aldahhan 2020).

3.1. THE EFFECTS OF NANOPARTICLES AND IONIC LIQUID ON THE SIMULTANEOUS EXTRACTION/RECOVERY OF THE MIXED HEAVY METALS

The Pb^{+2} extracting of 43.1% and V^{+5} of 69.9% at the first 5 minutes of the batch operation and leakage of 72% for 6 hrs with the earlier mentioined best values and defined below which is confirmed and agrees with what has been listed in the literature (Al-Obaidi et al., 2020). These best values used in our experiments of extracting/recovering simultaneously mixed heavy metals compounds are as follows:

The volume ratios of the W1 to the O phase of 1/1 (V/V).

Span 80 concentration of 3% (W/V).

D2EHPA concentration 2% (V/V).

Emulsification speed of 6000 rpm.

The volume treatment ratio (ELM/W2) of 1/10 (V/V).

Treatment mixing speed of 300 rpm.

The pH of W2 of 5.

Experiments were conducted to evalute these best values of the variables that have been used to investigate the effects of nanoparticles (MgO NPs & Al_2O_3 NPs) and ionic liquid ([OMIM]PF6) on the simultaneous extracting of Pb^{+2} & V^{+5}, its duration, and the stability of the emulsion.

3.2. THE EFFECT OF THE NANOPARTICLES ALONE ON THE SIMULTANEOUS EXTRACTION/RECOVERY OF THE MIXED HEAVY METALS

Figures 3 and 4 shows the results of the simultaneous extraction of Pb^{+2} & V^{+5} using 0.01%, 0.05%, 0.1%, 0.15%, and 0.02% (W/W) of MgO NPs & Al_2O_3 NPs in the W1 phase. The results show that the concentration of 0.15 % (W/W) of MgO NPs in the W1 phase promotes 75.97% exctraction of Pb^{+2} and 85.73% extraction of V^{+5} at the first 5 minutes in one batch of operation.

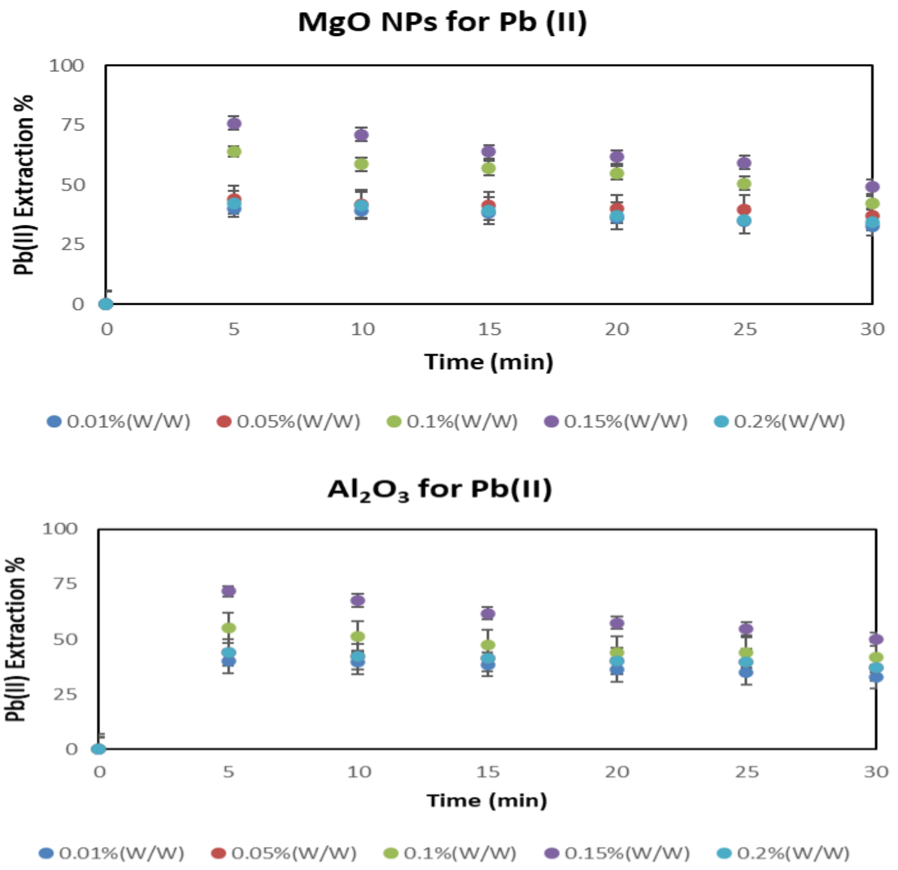


Figure 3. The effect of MgO and Al_2O_3 nanoparticles alone in W1 phase on the ELM extraction/recover for Pb(II): Span 80 concentration of 3% (W/V), D2EHPA carrier concentration of 2% (V/V), W1/O volume ratio of 1/1 (V/V), emulsification agitation speed to create emulsion of 6000 rpm, ELM (W1/O)/W2 volume ratio of 1/10, treatment agitation mixing speed of W2 of 300 rpm, and pH of W2 of 5.

However, 0.15% (W/V) of Al_2O_3 NPs in the W1 phase gave 73.73% and 81.70% extraction of Pb^{+2} and V^{+5} respectively at the first 5 minutes in one batch of operation. The nanoparticles in the W1 phase enhance the emulsion stability since the leakage reduces from 72% to 45% for 6 hrs.

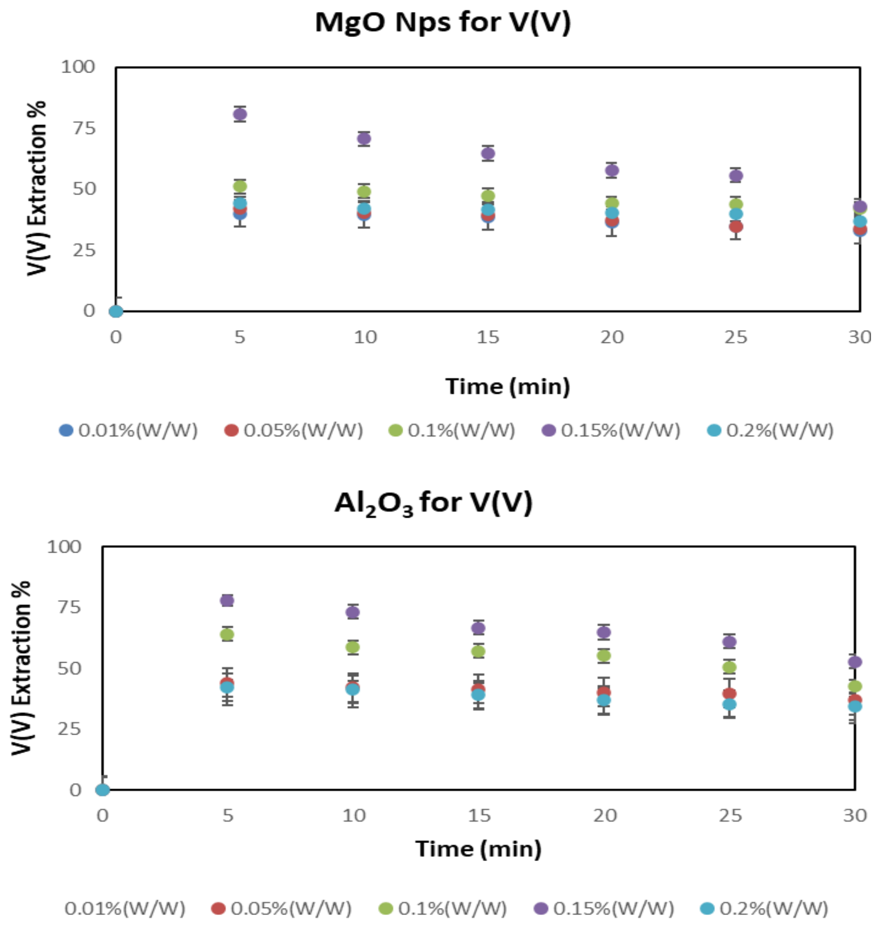


Figure 4. The effect of MgO and Al_2O_3 nanoparticles alone in W1 phase on the ELM extraction/recover for V(V): Span 80 concentration of 3% (W/V), D2EHPA carrier concentration of 2% (V/V), W1/O volume ratio of 1/1 (V/V), emulsification agitation speed to create emulsion of 6000 rpm, ELM (W1/O)/W2 volume ratio of 1/10, treatment agitation mixing speed of W2 of 300 rpm, and pH of W2 of 5.

Increases in the contaminant extracting are because of theis ability of nanoparticles to form a protective film at the emulsion interface which increases the binding sites on the surface of internal phase droplets. Nevertheless, with increasing the concentration of nanoparticles further than the full coverage of the internal phase droplets, other nanoparticles will be dispersed in the W2 phase, and some of the particles might form aggregates on the emulsion interface. Furthermore, the stabilization of ELMs with nanoparticles enhances the strength between emulsion droplets and prevents collision or coalescence of the droplets.

3.3. THE EFFECT OF IONIC LIQUID ONLY IN THE ORGANIC PHASE (O) ON THE SIMULTANEOUS EXTRACTION/RECOVERY OF THE MIXED HEAVY METALS

The ionic liquid in the O phase is an alternative method to enhance the ELM stability. The ([OMIM]PF6) ionic liquid concentrations of 1 % (V/V) to 6% (V/V) experimented, as shown in Figures 5 and 6. The concentration of 5% (V/V) gives extracting of Pb^{+2} of 71.55% and V^{+5} of 80.37% of 30 minutes in one batch of operation of mixed heavy metals compounds with leakage of 49% for 78 hours according with the results achieved by Al-Obaidi et al., 2020. At the same time, the ELM extraction and stability decreased with the ionic liquid concentration of 6% (V/V) because sedimentation of ELM increased by considering the high density of the ([OMIM]PF6). The ELM stability was raised due to the Coulombic interactions of the charges on the stripping agent (H_2SO_4) and ([OMIM]PF6). This intense interaction promotes ELM stability by lower coalescence internal droplets [14]. Hydrogen is bonding between the [OH] group of striping gents (H_2SO_4) and ([OMIM]PF6) and may produce adequate protection surrounding the internal droplets to avoid coalescence (Qusay et al., 2020).

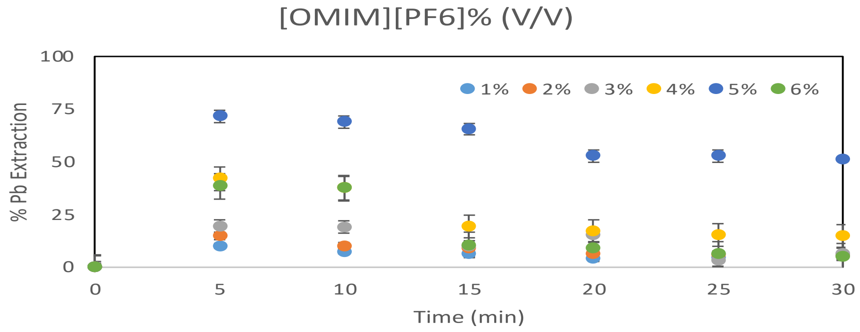


Figure 5. The effect of ionic liquid ([OMIM]PF6) in organic phase on the ELM extraction/recover for Pb(II): Span 80 concentration of 3% (W/V), D2EHPA carrier concentration of 2% (V/V), W1/O volume ratio of 1/1 (V/V), e mulsification agitation speed to create emulsion of 6000 rpm, ELM (W1/O)/W2 volume ratio of 1/10, treatment agitation mixing speed of W2 of 300 rpm, and pH of W2 of 5.

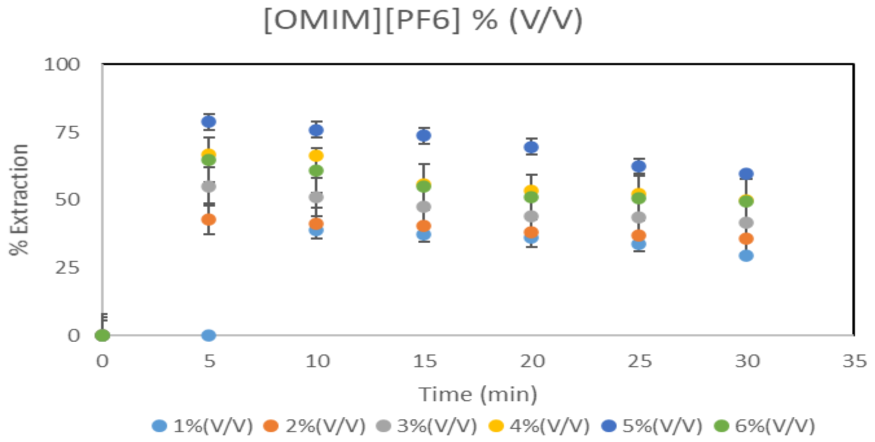


Figure 6. The effect of ionic liquid ([OMIM]PF6) in organic phase on the ELM extraction/recover for V(V): Span 80 concentration of 3% (W/V), D2EHPA carrier concentration of 2% (V/V), W1/O volume ratio of 1/1 (V/V), emulsification agitation speed to create emulsion of 6000 rpm, ELM (W1/O)/W2 volume ratio of 1/10, treatment agitation mixing speed of W2 of 300 rpm, and pH of W2 of 5.

([OMIM]PF6) can further decrease the interfacial tension through adsorbing in the W1-O interface, thereby minimizing the repulsion of the hydrophilic head-groups of the Span 80, which contributes to a more efficient packing of the Span 80 at the interface and reduces the droplet size of W1. This clarifies the ability to increase the emulsion stability and extraction. The ionic liquid will disperse in the aqueous feed phase with further increasing the concentration after emulsion droplets covering totally.

3.4. THE EFFECT OF COMBINING NANOPARTICLES AND IONIC LIQUID ON THE SIMULTANEOUS EXTRACTION/RECOVERY OF THE MIXED HEAVY METALS

Enhanced ELM combines nanoparticles in the W1 phase and ionic liquid in the O phase which improves the ELM stability, extracting efficiency of the mixed heavy metals (Pb^{+2} & V^{+5}), and duration of the extraction. The results are illustrated in Table 1 & 2 and Figures. 7 & 8. The ionic liquid concentration of 5% (V/V) in the O phase and the 0.01% (W/W) concentration of MgO NPs & Al_2O_3 NPs in the W1 phase have been found to provide the best ELM performance of Pb^{+2} extracting of 95.8% & 94.6% and V^{+5} 98.6% and 97.7% in about 3 minutes of batch operating time were obtained respectively as they represent a minuscule amount used for nanoparticles and ionic liquid which is desirable from an economic point of view for large scale applications.

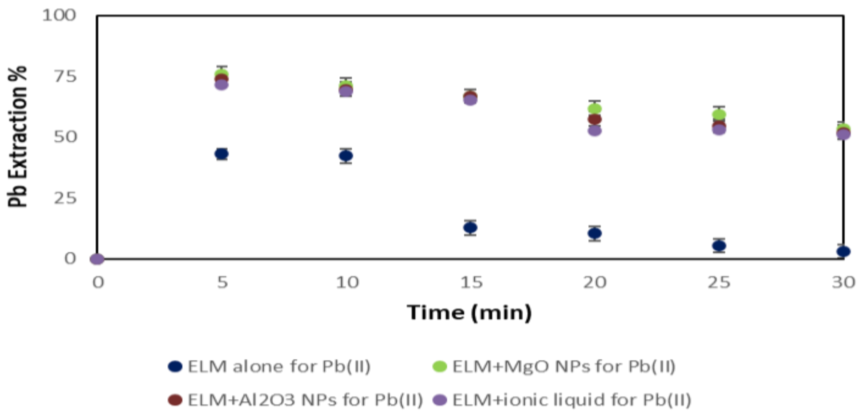


Figure 7. The effect of MgO and Al_2O_3 nanoparticles alone in W1 phase on the ELM extraction/recover for Pb(II): Span 80 concentration of 3% (W/V), D2EHPA carrier concentration of 2% (V/V), W1/O volume ratio of 1/1 (V/V), emulsification agitation speed to create emulsion of 6000 rpm, ELM (W1/O)/W2 volume ratio of 1/10, treatment agitation mixing speed of W2 of 300 rpm, and pH of W2 of 5.

The lowest leakage and higher stability time were obtained using the nanoparticles in the W1 phase and ionic liquid in the O phase after 1hr, which sustained during the study.

Table 1. The effect of combination 0.01% (W/W) Al_2O_3, and MgO nanoparticles (20 nm to 50 nm) in W1 phase and 5% (V/V) ionic liquid ([OMIM]PF6) in organic phase on the ELM extraction for lead: Span 80 concentration of 3% (W/V), D2EHPA carrier concentration of 2% (V/V), W1/O volume ratio of 1/1 (V/V), emulsification agitation speed to create emulsion of 6000 rpm, ELM (W1/O)/W2 volume ratio of 1/10, treatment agitation mixing speed of W2 of 300 rpm, and pH of W2 of 5.

Time (min)	**Al_2O_3 NP**	**MgO NP**
1	**75.9**	**78.3**
2	**80.1**	**82.5**
3	**94.6**	**95.8**

Table 2. The effect of combination 0.01% (W/W) Al_2O_3, and MgO nanoparticles (20 nm to 50 nm) in W1 phase and 5% (V/V) ionic liquid ([OMIM]PF6) in organic phase on the ELM extraction for vanadium: Span 80 concentration of 3% (W/V), D2EHPA carrier concentration of 2% (V/V), W1/O volume ratio of 1/1 (V/V), emulsification agitation speed to create emulsion of 6000 rpm, ELM (W1/O)/W2 volume ratio of 1/10, treatment agitation mixing speed of W2 of 300 rpm, and pH of W2 of 5.

Time (min)	**Al_2O_3 NP**	**Mgo NP**
1	**94.91333**	**93.97**
2	**95.40667**	**94.39**
3	**97.7**	**98.6**

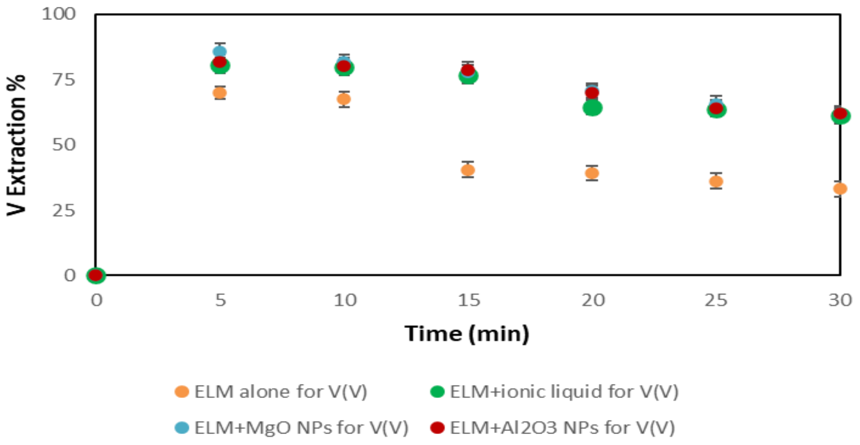


Figure 8. The effect of MgO and Al_2O_3 nanoparticles alone in W1 phase on the ELM extraction/recover for V(V): Span 80 concentration of 3% (W/V), D2EHPA carrier concentration of 2% (V/V), W1/O volume ratio of 1/1 (V/V), emulsification agitation speed to create emulsion of 6000 rpm, ELM (W1/O)/W2 volume ratio of 1/10, treatment agitation mixing speed of W2 of 300 rpm, and pH of W2 of 5.

The emulsion becomes more stable with this concentration of the nanoparticles and ionic liquid by covering more of the emulsion droplet interface, and increasing the extraction efficiency.

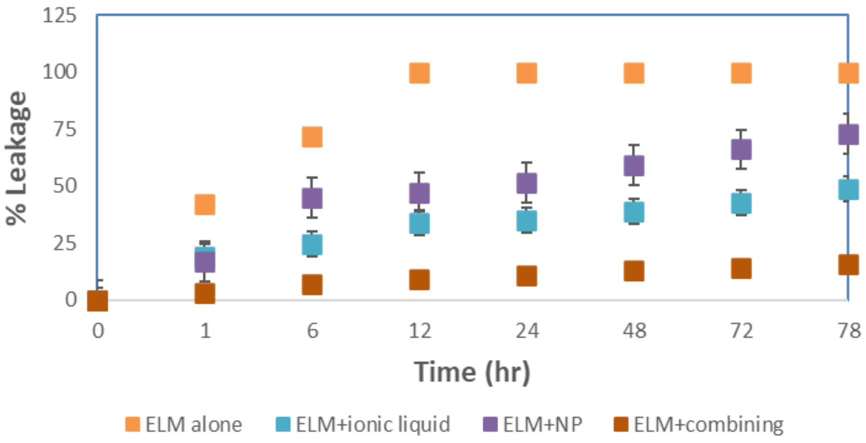


Figure 9. Effect of the combination 0.01% (W/W) nanoparticles in W1 phase and 5% (V/V) ionic liquid ([OMIM]PF6) in O phase on the ELM emulsion stability: W1:O volume ratio of 1/3 (V/V), surfactant concentration of 2%, emulsification speed of 8000 rpm, ELM (W1/O)/W2 volume ratio of 1/2 (V/V), treatment agitation mixing speed of W2 of 300 rpm, and pH of W2 of 1.5.

This confirms that the combination enhanced the ELM stability compared with ELM alone and ELM + ionic liquid, as shown in Figures 9. Hence, the combination enhances the stability and forms droplets that are exceptionally stable in the emulsion. Extraction time is considered as the target to determine the ELM effectiveness, which represents the time for the concentration of lead and vanadium to reach to close to zero.

4. CONCLUSION

In this work the following have been demonstrated and noticed:

The effective ability of the enhanced ELM (ELM with the combination of nanoparticles and ionic liquid) to extract/recover simultaneously of mixed heavy metals compounds of Pb^{+2} and V^{+5}.

The best operating conditions obtained for the simultaneous extraction of the mixed heavy metals were, the volume ratio of W1/O was 1/1 (V/V), D2HEPA concentration was 2% (V/V), Span 80 concentration was 3% (W/V), the emulsification speed was 6000 rpm, treatment ratio was 1/10 (V/V), mixing speed was 300 rpm, and pH was 5. Simultaneous extracting of Pb^{+2} achieved was of 43.1% within 5min and decreased the extraction rate to 3% for 30 min with leakage of 72% for 6 hours. While for the V^{+5} was 70% within 5 min, and the extraction rate decreased 33% for 30 min with leakage of 72% for 6 hours.

Extracting efficiency of the mixed heavy metals compounds was enhanced to 75.97% for Pb^{+2} & 85.73% V^{+5} at the first 5 minutes in one batch of operation by adding MgO NPs alone in the W1 phase and 73.73% for Pb^{+2} & 81.7% for V^{+5} at the first 5 minutes in one batch of operation by adding Al_2O_3 NPs alone in the W1 phase increasing the nanoparticles to 0.15% (W/W) with the leakage of 72% for 6 hrs.

The ionic liquid [OMIM][PF6] enhances the ELM extraction and the stability. The results indicated that the ratio of 5 % (V/V) of [OMIM][PF6] to the O phase promotes the simultaneous Pb^{+2} extraction to 71.55 % within 5 min and extraction decrease to 51.2% and V^{+5} was 80.37% within 5 min, and the extraction rate decreased 61.2% for 30 min with leakage of 49% for three days.

When the nanoparticles were added in the organic phase (O) phase or in the external feed wastewater (W2) phase, we don't get any extraction which could be due to blocking the reaction. Hence, we used the nanoparticles in W1 phase for this work.

The obtained concentration of the combination were 0.01% (W/W) of MgO NPs and Al_2O_3 NPs in the W1 and 5% (V/V) ionic liquid ([OMIM]PF6) in the O phase, which give higher simultaneous extraction/recovery efficiency of Pb^{+2} of 95.8% and 94.6% and of V^{+5} of 98.6 %, and 97.7 % in about 3 minutes of batch operating time for MgO and Al_2O_3 NPs, respectively with leakage of 16% for more than three days. This clarifies the ability of composition comprising to increase the emulsion stability and simultaneous extraction.

REFERENCES

[1] Meryem Mesli, Nasr-Eddine Belkhouche. 2018. *Emulsion ionic liquid membrane for recoveryprocess of lead. Comparative study of experimental and response surface design.* Chemical Engineering Research and Design 129-60-169.

[2] Hou, H., Jing, Y., Wang, Y., Wang, J., Xu, J., Chen, J., 2015. *Solvent extraction performance of Ce(III) from chloride acidic solution with 2-ethylhexyl phosphoric acid-2-ethylhexyl ester (EHEHPA) by using membrane dispersion micro-extractor*. J.Rare Earths 33, 1114–1121.

[3] Li N.N. 1968. *Separation hydrocarbons with the liquid membrane*. U.S. Patent 3,410,794.

[4] Kebiche-Senhadji. O., Mansouri. L. and Benamor M. 2015. *Consideration of Polymer Inclusion Membranes Containing D2EHPA for Toxic Metallic Ion (Pb2+) Extraction Recovery*. 2015 5th International Conference on Environment Science and Engineering. Volume 83 of IPCBEE (2015). DOI: 10.7763/IPCBEE. 2015. V83. 30.

[5] Avinash B. Lende, Manish K. Dinker, Vikas K. Bhosale, Sanjay P. Kamble, Pawan D. Meshramc and Prashant S. Kulkarni. 2014. *Emulsion ionic liquid membranes (EILMs) for removal of Pb(II) from aqueous solutions*. The Royal Society of Chemistry. 4, 52316–52323.

[6] Amiri A., Shanbedi M., Chew B. T., Kazi S. N., Solangi K. H.2016. Chem. Eng. J. 289, 583.

[7] Lee J. H., Hwang K. S., Jang S. P., Lee B. H., Kim J. H., Choi S. U., Choi C. J..2008. Int J Heat Mass Transfer. 51, 2651.

[8] Acharya J., Sahu J. N., Mohanty C. R., and Meikap B. C. 2009. *Removal of lead (II) from wastewater by activated carbon developed from Tamarind wood by zinc chloride activation*. Chemical Engineering. Journal, vol. 149, pp. 249–262.

[9] Sone H., Fugetsu B., and Tanaka S. 2009. *Selective elimination of lead (II) ions by alginate/polyurethane composite foams*. Journal of Hazardous Materials, vol. 162, pp. 423–429.

[10] Bouranene S., Samar M. E. H., and Abbaci A. 2003. *Extraction of cobalt and lead from wastewater using a liquid surfactant membrane emulsion*. Acta Chim. Slov. 50, 663–675.

[11] Bourenane S., Samar M.E.H., and Abbaci A. 2003. *Extraction of cobalt and lead from wastewater using a liquid surfactant membrane emulsion*. Ac. Chem. Solv. 50-663–675.

[12] Juang R.S., and Wang Y.Y. 2002. *Amino acid separation with D2 EHPA by solvent extraction and liquid surfactant membranes*. Journal Membrane Science. 207- 241–252.

[13] Li Y., Wang A., Loon J.C.V., and Borefoot R.R. 1992. *Extraction and enrichment of cadmium and manganese from aqueous solution using a liquid membrane*. Talanta, 39(10) 1337–1341.

[14] Bart H. J., Ramaseder C., Haselgrubler T., and Marr R. 1992. *The investigation of osmosis in the liquid membrane technology.* Influence of key parameters, Hydrometallurgy, 253–267.

[15] Mortaheb H., Amini M., Sadeghian F., Mokhtarani B., and Daneshyar H. 2008. J. Hazard. Mater. 160,582.

[16] Qusay Al-Obaidi, Jasmine Monroe, Hannah Smith, Zaid Haha, Muthanna Al-Dahhan. (2020), "*Assessing the Removal of Heavy Metals using Emerging and Intensifying Technology of Emulsion Liquid Membrane with Ionic Liquid"*. Elsevier Journal. SSRN. 3601713.

[17] Qusay Al-Obaidi, Muthanna Al-Dahhan. (2020), *"Advanced Removal of 4-Nitrophenol by Emerging and Intensifying Technology of Emulsion Liquid Membrane with Magnetic Nanoparticles".* Elsevier Journal. SSRN. 3601736.

SECTION

3. CONCLUSIONS AND RECOMMENDATIONS

3.1. CONCLUSIONS

Described herein are novel emulsion liquid membranes useful for extracting pollutants from water industrial wastewater. The emulsion liquid membranes include, in various phases, at least one of nanoparticles, an ionic liquid, and combinations of nanoparticles and ionic liquids. Use of the present emulsion liquid membranes enhances the separation and the stability of the emulsion liquid membrane method for pollutant extraction and recovery from wastewater and water.

3.1.1. The First Disclosure. First use of the combination of nanoparticles (in W1 or O) and ionic liquids in O phase to enhance the separation and the stability of the ELM for the hydrocarbon extraction and recovery from wastewater and water. Enhancing the separation of hydrocarbons by combining magnetic nanoparticles and ionic liquid for emulsion liquid membrane has wide commercial applications.

3.1.2. The Second Disclosure. First use of nanoparticles in W1 to enhance the separation and the stability of the ELM for heavy metals extraction and recovery from wastewater and water. Enhancing the separation of heavy metals by combining nanoparticles in W1 phase and ionic liquid in O phase with emulsion liquid membrane has wide commercial applications.

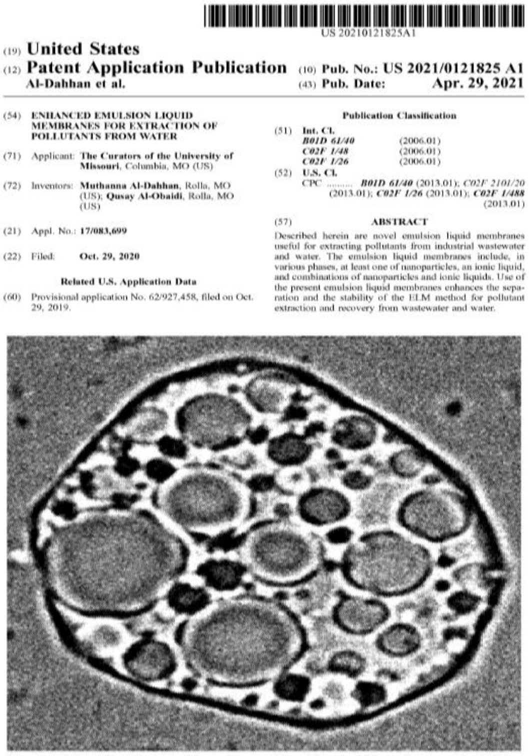
3.2. RECOMMENDATIONS

Emulsion Liquid Membranes (O1/W/O2) for extracting pollutants from water and industrial wastewater.

APPENDIX

UNITED STATES PATENT APPLICATION PUBLICATION

Described herein are noval emulsion liquid membranes useful for extracting pollutants from industrial wastewater and water. The emulsion liquid membranes include, in various phases, at least on of the nanoparticles, an ionic liquid, and combinations of nanoparticles and ionic liquid. Use of the present emulsion liquid membrane enhance the separation and the stability of the ELM method for pollutant extraction and recovery from wastewater and water.



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(54) **ENHANCED EMULSION LIQUID MEMBRANES FOR EXTRACTION OF POLLUTANTS FROM WATER**

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C02F 1/26 (2006.01)

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CPC ***B01D 61/40*** (2013.01); *C02F 2101/20* (2013.01); ***C02F 1/26*** (2013.01); ***C02F 1/488*** (2013.01)

(57) **ABSTRACT**

Described herein are novel emulsion liquid membranes useful for extracting pollutants from industrial wastewater and water. The emulsion liquid membranes include, in various phases, at least one of nanoparticles, an ionic liquid, and combinations of nanoparticles and ionic liquids. Use of the present emulsion liquid membranes enhances the separation and the stability of the ELM method for pollutant extraction and recovery from wastewater and water.

Figure A.1.United State Patent Application Publication.

REFERENCES

[1] Meryem Mesli, Nasr-Eddine Belkhouche. 2018. *Emulsion ionic liquid membrane for recoveryprocess of lead. Comparative study of experimental and response surface design.* Chemical Engineering Research and Design 129-60-169.

[2] Hou, H., Jing, Y., Wang, Y., Wang, J., Xu, J., Chen, J., 2015. *Solvent extraction performance of Ce(III) from chloride acidic solution with 2-ethylhexyl phosphoric acid-2-ethylhexyl ester (EHEHPA) by using membrane dispersion micro-extractor.* J.Rare Earths 33, 1114–1121.

[3] Li N.N. 1968. *Separation hydrocarbons with the liquid membrane.* U.S. Patent 3,410,794.

[4] Kebiche-Senhadji. O., Mansouri. L. and Benamor M. 2015. *Consideration of Polymer Inclusion Membranes Containing D2EHPA for Toxic Metallic Ion (Pb2+) Extraction Recovery*. 2015 5th International Conference on Environment Science and Engineering. Volume 83 of IPCBEE (2015). DOI: 10.7763/IPCBEE. 2015. V83. 30.

[5] Avinash B. Lende, Manish K. Dinker, Vikas K. Bhosale, Sanjay P. Kamble, Pawan D. Meshramc and Prashant S. Kulkarni. 2014. *Emulsion ionic liquid membranes (EILMs) for removal of Pb(II) from aqueous solutions.* The Royal Society of Chemistry. 4, 52316–52323.

[6] Amiri A., Shanbedi M., Chew B. T., Kazi S. N., Solangi K. H.2016. Chem. Eng. J. 289, 583.

[7] Lee J. H., Hwang K. S., Jang S. P., Lee B. H., Kim J. H., Choi S. U., Choi C. J..2008. Int J Heat Mass Transfer. 51, 2651.

[8] Acharya J., Sahu J. N., Mohanty C. R., and Meikap B. C. 2009. *Removal of lead (II) from wastewater by activated carbon developed from Tamarind wood by zinc chloride activation*. Chemical Engineering. Journal, vol. 149, pp. 249–262.

[9] Sone H., Fugetsu B., and Tanaka S. 2009. *Selective elimination of lead (II) ions by alginate/polyurethane composite foams.* Journal of Hazardous Materials, vol. 162, pp. 423–429.

[10] Bouranene S., Samar M. E. H., and Abbaci A. 2003. *Extraction of cobalt and lead from wastewater using a liquid surfactant membrane emulsion*. Acta Chim. Slov. 50, 663–675.

[11] Bourenane S., Samar M.E.H., and Abbaci A. 2003. *Extraction of cobalt and lead from wastewater using a liquid surfactant membrane emulsion*. Ac. Chem. Solv. 50-663–675.

[12] Juang R.S., and Wang Y.Y. 2002. *Amino acid separation with D2 EHPA by solvent extraction and liquid surfactant membranes.* Journal Membrane Science. 207- 241–252.

[13] Li Y., Wang A., Loon J.C.V., and Borefoot R.R. 1992. *Extraction and enrichment of cadmium and manganese from aqueous solution using a liquid membrane*. Talanta, 39(10) 1337–1341.

[14] Bart H. J., Ramaseder C., Haselgrubler T., and Marr R. 1992. *The investigation of osmosis in the liquid membrane technology.* Influence of key parameters, Hydrometallurgy, 253–267.

[15] Mortaheb H., Amini M., Sadeghian F., Mokhtarani B., and Daneshyar H. 2008. J. Hazard. Mater. 160,582.

[16] Qusay Al-Obaidi, Jasmine Monroe, Hannah Smith, Zaid Haha, Muthanna Al-Dahhan. (2020), “*Assessing the Removal of Heavy Metals using Emerging and Intensifying Technology of Emulsion Liquid Membrane with Ionic Liquid”*. Elsevier Journal. SSRN. 3601713.

[17] Qusay Al-Obaidi, Muthanna Al-Dahhan. (2020), *“Advanced Removal of 4-Nitrophenol by Emerging and Intensifying Technology of Emulsion Liquid Membrane with Magnetic Nanoparticles”.* Elsevier Journal. SSRN. 3601736.

VITA

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