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Qusay Al-Obaidi

Jasmine Monroe

Hannah Smith

Zaid Haha

et. al. For a complete list of authors, see https://scholarsmine.mst.edu/che_bioeng_facwork/921

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Assessing the Removal of Heavy Metals using Emerging and Intensifying Technology of Emulsion Liquid Membrane with Ionic Liquid.

Qusay Al-Obaidi[ab], Jasmine Monroe[a], Hannah Smith[a], Zaid Haha[a], and Muthanna Al-Dahhan[a]

[a]*Multiphase Flows Reactor and Engineering & Applications Laboratory (mFReal), Department of Chemical and Biochemical Engineering, Missouri University of Science and Technology, Rolla, MO 65409, USA.*
[b]*Department of Chemical Engineering Department, University of Technology, Iraq*
e-mail : qja54d@mst.edu, jrmgt9@mst.edu, hs94c@mst.edu, zhhcqp@mst.edu, and aldahhanm@mst.edu

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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.

Keywords: Emulsion liquid membrane technique; lead removal; industry wastewater, D2EHPA extractant, ionic liquid ({[BMIM]$^+$ [NTf2]$^-$), and [OMIM][PF6] .

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 (0.01 ppm).

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 Type 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, 0.5 N 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 in to the organic phase (Fig.1). The H_2SO_4 solution (0.5 N) 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 H_2SO_4 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 (H2SO4) 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) and lead(II) sulfate, 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 80 oC for 1hr in a closed vessel for final recovery of the internal receiving phase with Pb (II) ion, and oil from the broken emulsion was separately collected. Finally, the W1 and Pb were washed with alcohol to extract the Pb(II).

2.3.1. Calculation of ELM Stability.

To measure the ELM stability by the percentage of leakage (%) determined by the following Equation:

$$Breaking\ rate\ \% = \frac{Vr}{Vint}\ X\ 100 \qquad (1)$$

Vr = Vext *[(10^-pHo)-(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

2.3.2. Analytical Methods

The extraction remaining was calculated by the following equation.

$$Extraction\ \% = \frac{initial\ concentration - final\ concentration}{initial\ concentration}\ X100 \qquad (2)$$

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 transport 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 Fig.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 [12]. The higher viscosity affects the extraction of solute and reduces membrane stability, resulting in a low mass transfer efficiency [13].

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. [14].

It was illustrated by Reis et al. [15] 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 Fig.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.

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 [16], and [17].

3.3. The Effect of the Emulsification Speed on the Extraction Efficiency

The efficiency of extraction increases with an increase in the emulsification agitation [16], and [18]. 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 Fig.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).

3.4. The Effect of the Volume Ratio of the Internal Receiving Phases (W1) to the Organic Phase (O), (W1O)

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 H_2SO_4 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 investigated the effect of the internal receiving phase (W1) to organic phase (O) as proposed by [19] and shown in Fig.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].

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 Pb(II), variable speeds were tested such as 250, 300, and 400 rpm.

The mixing speed was first ran at (250) rpm, and then increased to (300) rpm and eventually to (400) rpm in the third experiment. The results (Fig.6) shows 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].

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 Fig.7, and which will provide an increase in overall surface area for mass transfer and extraction capacity.

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 Fig.8. From the results the practical Pb(II) removal from wastewater was at pH 5 because Pb(II) [25, 26, 27, and 28]. 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, and 30].

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.

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

$$Pb(OH)_2(\text{ extrenal }) + 2HR \leftrightarrows Pb(OH)2R2\ [\text{ interface (external} \setminus \text{membrane)}] + 2H_2\ (\text{ external }) \quad (4)$$

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.

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

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.

$$Pb^{+2} + H2SO_4 \rightarrow PbSO4 + H_2 \quad (6)$$

The ionic liquid enhance 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 Fig.9. This result is indicate 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 Fig.10. [36].

Extraction time is considered as the target to determine the ELM effectiveness which represents the period of time 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 Fig.9, and 10. at above optimum operating conditions which were 2% carrier D2EHPA, 3% surfactant Span 80 and 0.05 N H_2SO_4 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 .

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.

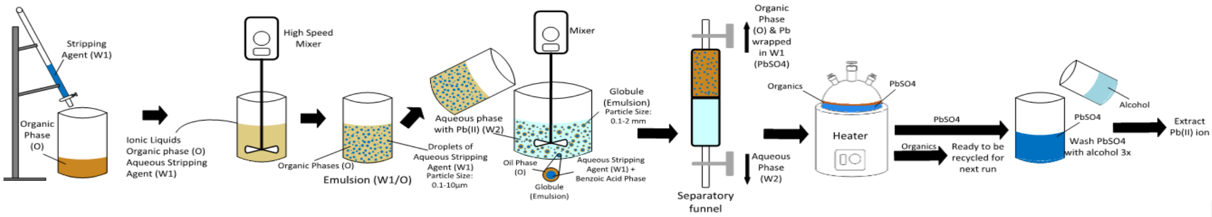
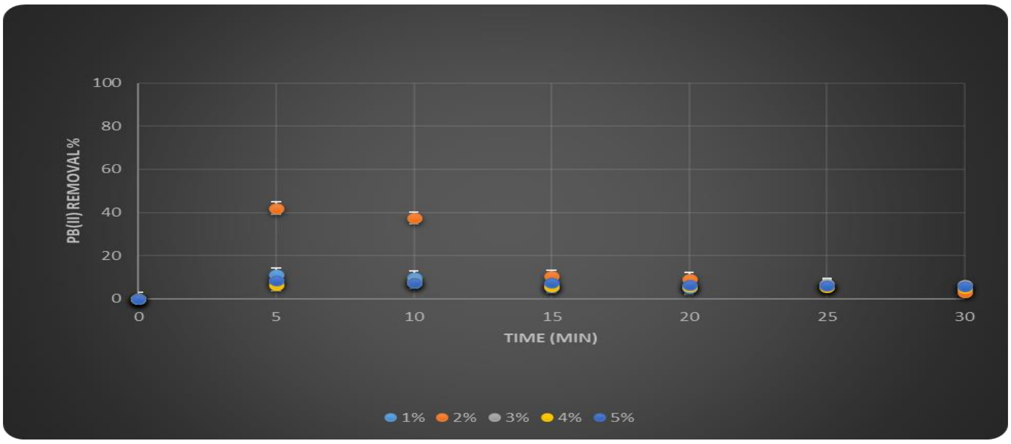
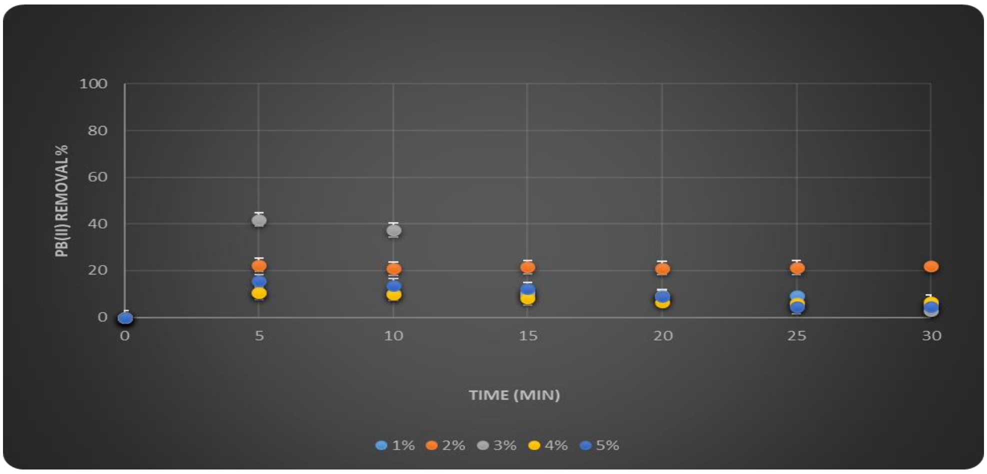


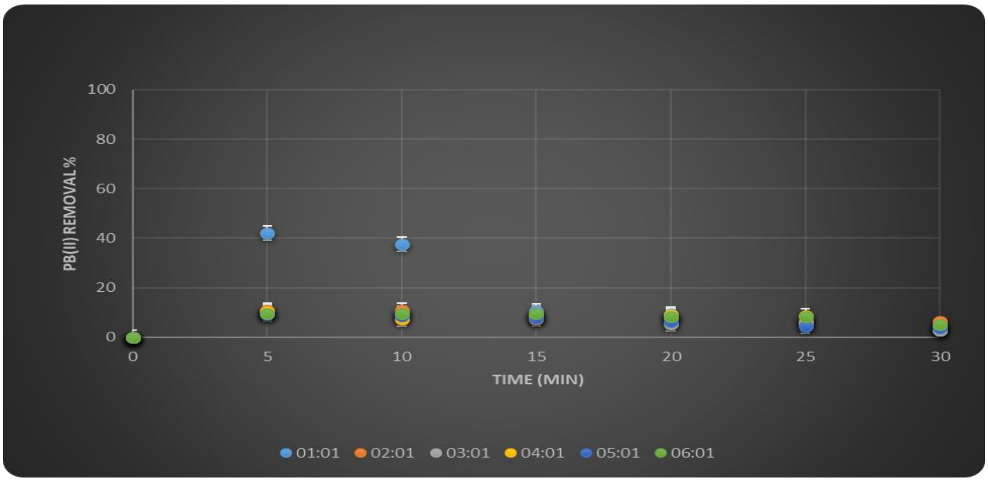
Fig. 1. ELM process.



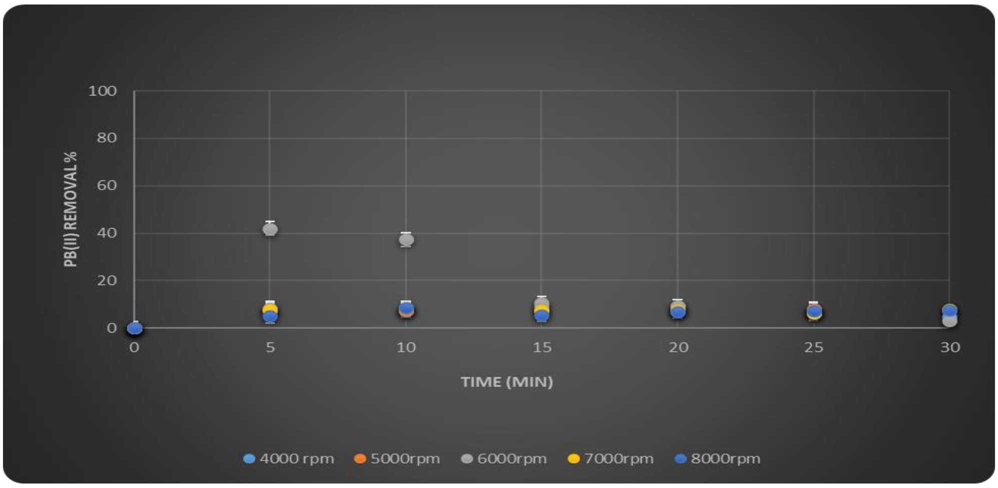
2The effects of carrier concentration (V/V)



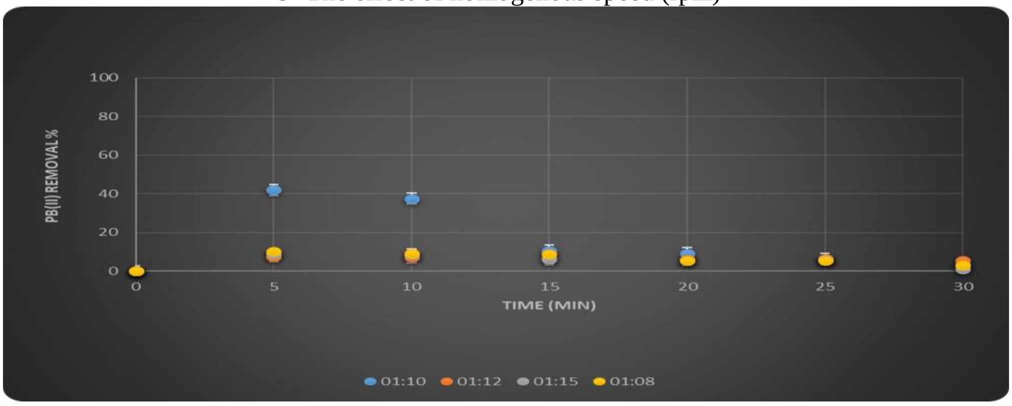
3The effects of Span 80 concentration (W/V)



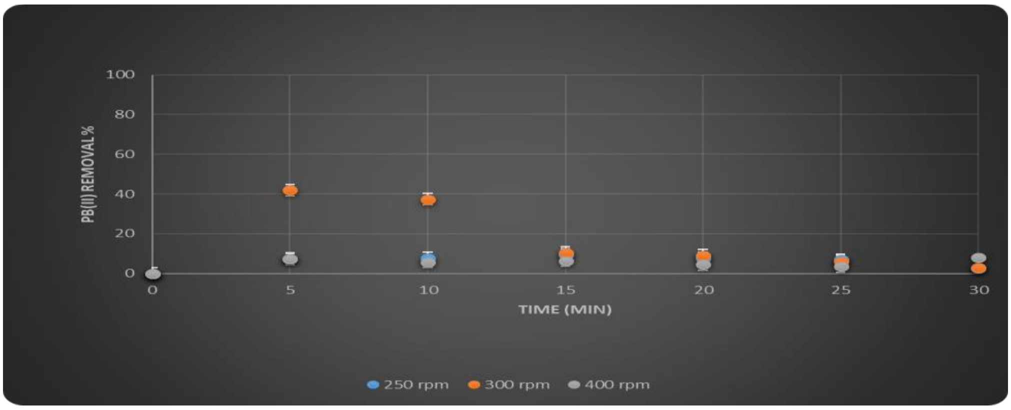
4The effects of Volume ratio of W1: O (V/V)



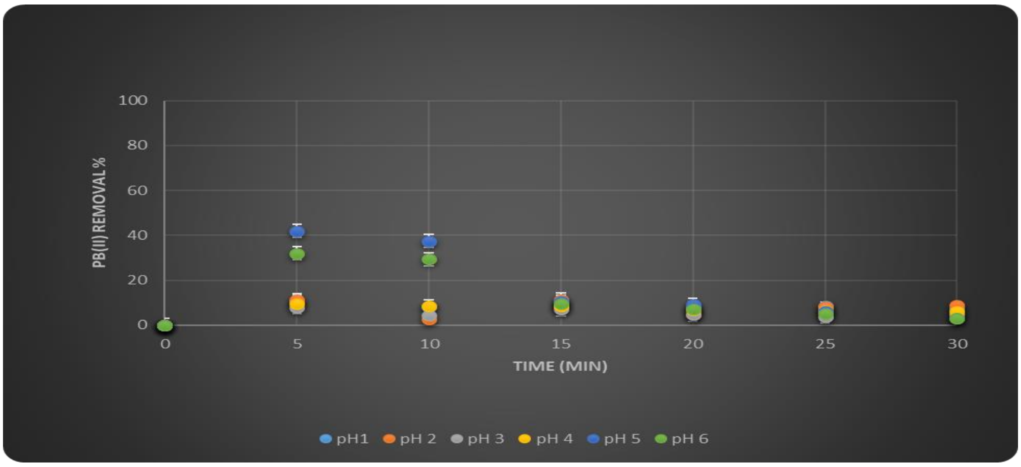
5- The effect of homogenous speed (rpm)*



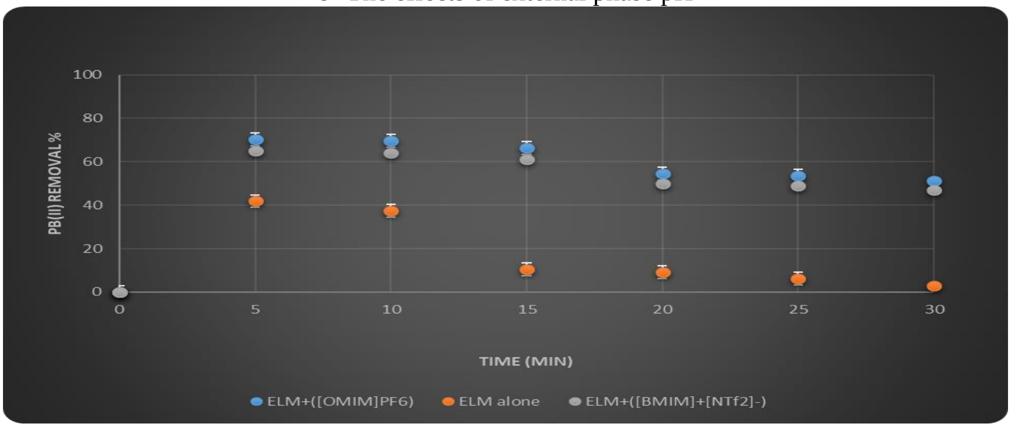
6The effects of volume treatment ratio (V/V)



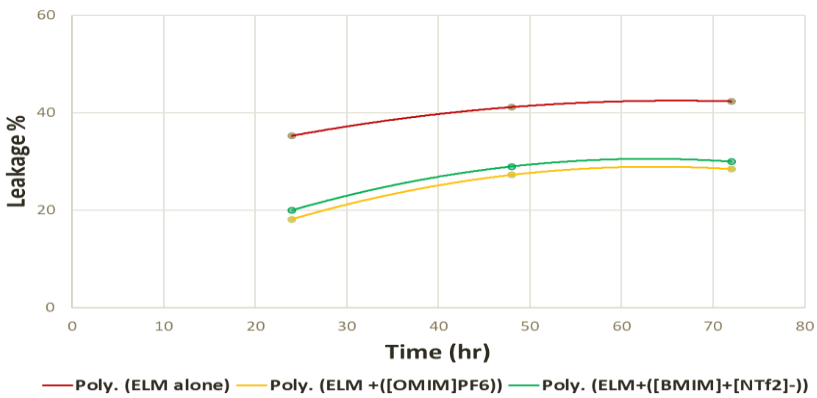
7- The effects of sped of treatment ratio (rpm)



8- The effects of external phase pH



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



10- ELM Stability

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