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Simultaneous Extraction of Lead, Copper, and Cadmium from Aqueous Solution using Emulsion Liquid Membrane Technique

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ABSTRACT

A simultaneous extraction study of lead, copper, and cadmium from diluted aqueous solution through Emulsion Liquid Membrane (ELM) technique was conducted and extensive investigations of the impact of the pH of the feed phase, homogenizer speed, surfactant (Span 80) and carrier (D2EHPA) concentrations, and ratio of external to membrane phase on the system stability (breakage) and removal efficiencies of Pb^{2+}, Cu^{2+}, Cd^{2+} ions were experimentally carried out. Kerosene was used as the membrane and stabilized by Sorbitan monooleate (Span 80) as the emulsifier. Bis-2-Ethylhexyl phosphoric acid (D2EHPA) as an extractant and H_2SO_4 as a reagent (internal phase) were utilized. Lead, Copper, and Cadmium extraction efficiencies of 100%, 100%, and 98% were obtained respectively under specific operating conditions. The emulsion stability of the system was studied, and breakage of 1.8% under the best operating condition was obtained. High reagent (H_2SO_4) concentration (0.5 M) maintained the simultaneous extraction of the three heavy metals (lead, copper, and cadmium) and minimizes the probable interaction and competing mechanism between them in the extraction stage.

1. Introduction

Large quantities of wastewater containing heavy metals are annually dumped in the environment H. Ma et al. [1]. Heavy metals have dangerous effects on health and environment. If wastewater containing heavy metals is directly disposed to surface water, sea, and groundwater, it strongly affects the lives of organisms Begum et al. [2]. Heavy metals such as; lead, copper, cadmium, zinc, nickel, Mercury, silver, iron, Chromium, gold, Arsenic, cobalt, Molybdenum, aluminum and Manganese can be absorbed and cumulative inside body of human causing dangerous health problems Mahakal et al. [3] .Cancer, organ harm, and harm for the nervous system are examples of health problems caused by heavy metals.

In particular, Copper, Cadmium, and Lead are considered to be highly toxic minerals. Copper results in liver and kidneys damage S. N. H. D. et al. [4], Cadmium as carcinogen for humans, also affects kidneys [5][6]. Lead causes major damage to immune and nervous systems Salman et al. [7] . It also hinders children's growth.

Therefore, the removal of heavy metals from wastewaters becomes very important and several separation processes have been developed for this purpose, such as precipitation Swain et al. [8], adsorption [9][10], ion-exchange Khanmohammadi et al. [11], reverse osmosis Li et al. [12], Electrodialysis and electrochemical [13][14].

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Emulsion Liquid Membrane (ELM) has emerged as an effective separation process used to remove heavy metals from wastewater Nemati et al. [13].

ELM mainly depends on concentration difference between external and internal phases through flexible membrane surrounding the internal phase. ELM is considered as an easy operation and low energy consumption separation process in comparison with other traditional processes such as reverse osmosis, ultrafiltration, and semi-permeable membrane techniques Hussein et al. [15].

The simplicity of ELM systems is reflected on its low operating and maintenance costs. Extraction and stripping of heavy metal are happened simultaneously when ELM is used for the removal of heavy metals from wastewaters resulting in high efficiency process Goyal et al. [16]. ELM processes can select a component from a solution containing a mixture of minerals [17][18], or remove more than one element at the same time Ammar et al. [19].

However, ELM's instability is considered as a major challenge of the process. Membrane breakage (leakage) is the main reason of the membrane instability and directly affects the overall ELM efficiency Mohammed et al. [20]. Breakage is defined as the process of leaking the internal phase of the globules, which reduces the stripping agent and consequently reduces the extraction and destabilizes the system Pfeiffer et al. [21].

ELM consists of two aqueous phases (external and internal) separates by a thin membrane of organic phase. ELM assumed as a "bubble within a bubble" the internal bubble represents the internal phase and external bubble represents external phase, where membrane (skin) separates the contents of the two bubbles (phases) from merging. External phase is treated as the feed phase [22][23] .

Choosing the appropriate membrane components determines the success of the ELM which includes the right selection of the organic composition, surfactant composition, carrier/extractant composition, and internal phase composition, These are the most important factors on which the success of the ELM system depends Abbassian et al. [24] .

Carriers/extractants like D2EHPA Yanlin et al. [25] , TBP Mohammed et al. [26] or Aliquat336 Rosly et al. [27] must suitable to form complexes with the target pollutant and then extract it. The Internal phase like H_2SO_4 Chiha et al. [28], HCl Kusumastuti et al. [29] or NaOH Das et al. [30], and surfactants like span80 Zarandi et al. [31] or ECA 4360J Kumbasar et al. [17] should also choose carefully because it is the most important part of the system that is related to the stability of the emulsion. When properly selected, it leads to less breakage and swelling. In the ELM process, diluents are treated as one of the main components of the organic phase and have a critical function in ELM stability. Kerosene is one of the most used diluents by researchers because of its easy access to it and the appropriate viscosity, but it remains an environmentally unfriendly component Kumar et al. [22].

Using ELM for removing more than one or two metal ions is rarely found in the literature. This research focuses on extracting three toxic elements (Pb, Cu, and Cd) from an aqueous solution, which mimics the wastewater of the Ad Diwaniyah refinery. The study was extended to investigate system stability and defining the best operating conditions for it. Literature shows that the Pb removal from wastewaters was studied by [31][32][7], the Cu removal from wastewaters was studied by [33][28][1], and the Cd removal from wastewaters was studied by [34][35][25].

2. Chemicals and experimental methods

2.1. Chemicals

Di-(2-Ethylhexyl) phosphoric acid (D2EHPA) as the extractant which was purchased from Sigma-Aldrich (Merck, Darmstadt, Germany). and Sorbitan monooleate (Span 80) was the non-ionic. surfactant and sulfuric acid (H_2SO_4) was the stripping agent and both were obtained from Thomas beaker (Mumbai, India). The kerosene procured from Al-Wasat Refineries Company/Al-Diwaniya Refinery (Iraq, Al-Qadisiyah) behaved as a diluent.

The aqueous solutions were formed using the solid form of lead nitrate, Cadmium sulphate and Cupric sulphate were obtained also from Thomas beaker (Mumbai, India).

2.2. Emulsion preparation

The W/O emulsion was formed through two main steps; starting with adding certain ratios of span 80 and D2EHPA acid to kerosene oil and then mixing it for a short time on a magnetic mixer without heating to maintain the viscosity of the mixture, then transfer the mixture to a suitable glass beaker (use here a 200 ml beaker) to mix with H_2SO_4 solution prepared according to certain molarity using a high-speed SR30 homogenizer. A cold-water bath used when speed higher than 12700 rpm, the speed and time are changed to obtain the best conditions.

2.3. Procedure and mechanism extraction

During the emulsion preparation process, the outer phase is prepared. In this study, concentrations of 10 ppm of lead, copper and cadmium ions are taken with the pH setting. The emulsion phase is added to the aqueous phase to be mixed by digital mixer for 8 minutes at a speed of 250rpm, after which the samples are drawn and filtered using a filter syringe of 0.22 μm.

Adding carries Which is di-2-ethyl hexyl phosphoric acid (D2EHPA) in this study to the organic phase works to increase the effectiveness and selectivity of separating dissolved ions, as this extractant works on forming a complex with target metal ions to increase extraction. the process of forming complexes is the intermediary of transporting ions from the external phase to the internal phase passing through the organic phase as **Fig. 1**.

The extraction and stripping reactions for metals transfer through the oil phase by acidic carriers can be displayed as follows:

$$M^{+2} + 2HR \Rightarrow MR_2 + 2H^+ \tag{1}$$

$$MR_2 + 2H^+ \Rightarrow 2HR + M^{+2} \tag{2}$$

Where HR is the protonated form of acidic extractants, M^{2+} is the metal ions and H^+ the hydrogen ion.

Eq.(1) represents the extraction process that takes place by the interaction of the extracted carrier with metal ions to form complexes. As for Eq.(2), it refers to the abstraction process that takes place in the inner stage to separate the ion from the complex, while the carrier returns to form other complexes.
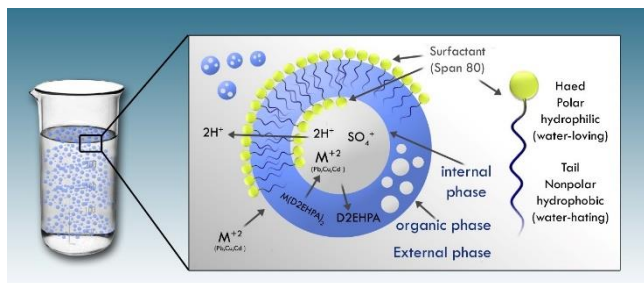
Figure 1. Extraction mechanisms of ELM system.

2.4. Analysis and calculations

The concentration of metal ions is measured by an atomic absorption spectrometer (Japanese 2000) where acetylene gas is used with clean and dry air. The lead element is measured with a wavelength of (283.3 nm) while the wavelength of copper (324.7 nm) and cadmium (228.8 nm).

The efficiency of the extraction calculated by the following equation:

$$\%E = \frac{C_i - C_f}{C_i} * 100 \qquad (3)$$

Where; C_i : initial concentration of (Pb^{2+}, Cu^{2+}, Cd^{2+}) in aqueous external Solution, C_f : concentration of (Pb^{2+}, Cu^{2+}, Cd^{2+}) in aqueous external Solution after treatment.

Instability is one of the disadvantages of this technique, which reduces the extraction efficiency of the solvents. The breakage emulsion (%B) indicates instability, as can be verified using the following equation [20][26][7] [36][28] :

$$\%B = \frac{VI}{VII} * 100 \qquad (4)$$

where VII: initial volume of internal phase

VI: volume of internal phase leaked into the external phase and can be find from this equation:

$$VI = Vext. \; \frac{10^{-pHi} - 10^{-pHf}}{10^{-pHf} - C_{H+}^{int}} * 100 \qquad (5)$$

$Vext$: initial volume of external phase

pHi : pH of external phase before treated

pHf : pH of feed phase after a certain time of treated

C_{H+}^{int} : the initial concentration of H^+ in stripping phase

The operational conditions and ranges used in this study, which affected stability and removal efficiency, are included in the **Table 1**.

Table 1. Range of the variation of the operating factors during the ELM study.

Variation range	Parameter
5800 – 24000	Emulsification rotating speed, rpm
2 – 8	D2EHPA concentration, % v/v
0 – 6	Span 80 concentration, % v/v
2 - 6	pH of external phase
100:2 – 100:15	external: membrane phase ratio

3. Results and discussion

3.1. Effect of homogenizer speed on system stability and extraction efficiency of lead, copper, and cadmium

The speed of the homogenizer has shown a considerable impact on the ELM system stability and the extraction efficiency. It was noticed that the extraction efficiency of Pb^{2+}, Cu^{2+}, Cd^{2+} increases as the speed of the homogenizer increases up to a certain limit. Beyond that limit, breakage took place and extraction efficiency declined as a function of homogenizer speed as shown in **Fig. 2**.

Increasing the homogenizer speed from 5800 rpm to 16200 rpm demonstrated a considerable decrease of the breakage from 3.8 to 1.8, and the extraction efficiencies of Pb^{2+}, Cu^{2+}, Cd^{2+} were found to be 100%, 100%, 98.7% respectively. Both breakage improvement and the increase of the extraction efficiencies of Pb^{2+}, Cu^{2+}, Cd^{2+} were attributed to the formation of smaller droplets size as the speed of the homogenizer increased, which resulted in an increase of the surface area available for solute transport. When the speed of the homogenizer exceeded 16200 rpm, the extraction efficiency of Pb^{2+}, Cu^{2+}, Cd^{2+} started to decrease and 80% efficiency was attained at 24000 rpm. At the same time, an increase of breakage from 1.8 to 12 was demonstrated at 24000 rpm to indicate that higher speeds of homogenizer would cause droplets collision and coalescences, through which breakage increased and system instability was evidenced.

Through a review of previous studies, it was found that the optimum speed for each research varied based on the working conditions and the extracted pollutant and its concentration, where Salman et al. [7] said that the best speed is 12,700 within 10 min of lead with a concentration pouring to 200 ppm, and 20000 rpm at 4 min in another study Chaouchi et al. [37] .

A maximum of extraction efficiency at a certain value of homogenizer speed followed by a noticeable decrease was reported in both researcher's works, and a minimum of breakage value was obtained during their course of work at the same points corresponding to the maximum extraction efficiencies .
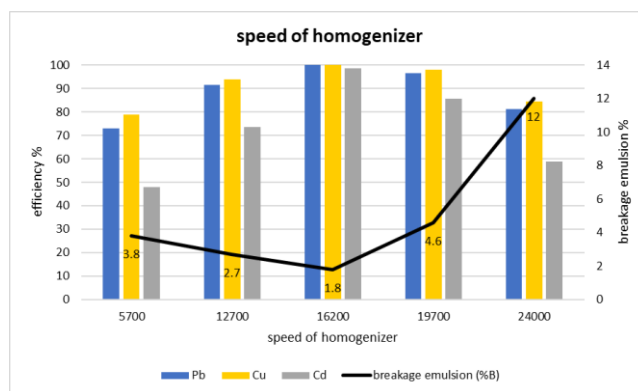

Figure 2. Effect of homogenizer speed on the extraction efficiency and membrane breakage (time of homogenizer : 10 min, span80:4%(v/v), 0.5M H₂SO₄, internal to organic ratio: 1, D2EHPA: 4% (v/v), feed pH:4, 8 min and 250 rpm in digital mixer , feed to emulsion ratio: 100/10).

3.2. Effect of extractant concentration on system stability and extraction efficiency of lead, copper, and cadmium

Di-(2-ethylhexyl) phosphoric acid (D2EHPA) was used as a carrier to facilitate the transport of organic and inorganic pollutants. D2EHPA has high ability to form complexes with Pb^{2+}, Cu^{2+}, Cd^{2+} ions Hussein et al. [15] and consequently increases the extraction efficiency. A range of 2-8% D2EHPA to Kerosene volume ratio was investigated to determine the best value of it. As shown in **Fig. 3**, increasing the D2EHPA to Kerosene volume ratio from 2% to 4% resulted in a considerable increase of the extraction efficiencies of Pb^{2+}, Cu^{2+}, Cd^{2+} from 75%, 75%, 41% to 100%, 100%, 98% respectively. The breakage dropped from 3.8 to 1.8 to indicate better system stability. However, when we continued increasing the volume ratio, a decrease in extraction efficiencies was observed and an increase of breakage value was noticed to indicate system instability.

Increasing the volume ratio led to an increase of the extractant increased to contribute to membrane viscosity increase and the formation of larger globules which promote swelling phenomenon Sengupta et al. [33].

The percentage of the volume ratio of 4% was found to outperform in the extraction of Pb^{2+}, Cu^{2+}, Cd^{2+} ions from the feed phase at the same time, while different volume ratios were reported when those ions were treated

separately[7][28][25] . For Pb^{2+} ions, it was reported to be 4% using D2EHPA as a carrier Salman et al. [7]. For Cu^{2+} ions, it was reported to be 20% Chiha et al. [28], and for Cd^{2+} ions, the volume ratio was reported to be 4.4% Yanlin et al. [25].
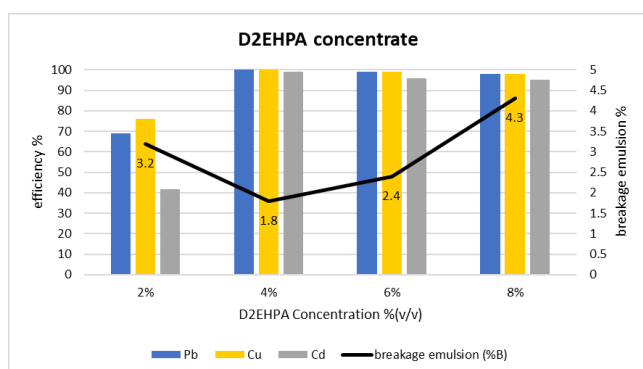

Figure 3. Effect of extractant concentration on the extraction efficiency and membrane breakage (time of homogenizer: 10 min, span80:4%(v/v), 0.5M H_2SO_4, internal to organic ratio: 1, homogenizer speed:16200 rpm, feed pH:4, 8 min and 250 rpm in digital mixer , feed to emulsion ratio: 100/10).

3.3. Effect of surfactant concentration on system stability and extraction efficiency of lead, copper, and cadmium

The effect of the surfactant (Span 80) concentration on the breakage and the extraction efficiencies of Pb^{2+}, Cu^{2+}, Cd^{2+} ions from the feed phase were examined. The surfactant concentration was varied between 0-6% (v/v %). **Fig. 4** shows that the breakage exhibited a value of 62% for 0% surfactant (Span 80) concentration to indicate high system instability. The high instability of the system was reflected in the extraction efficiencies of the Pb^{2+}, Cu^{2+}, Cd^{2+} ions to demonstrate low extraction efficiencies of 44%, 55%, and 13% respectively. When the surfactant (Span 80) concentration was increased to 2% (v/v %), a significant drop of the breakage value was

noticed and a value of 4.9% was obtained. However, the value of the breakage of 4.9% raised the extraction efficiencies of the Pb^{2+}, Cu^{2+}, Cd^{2+} ions to 82%, 85%, 63% respectively. The maximum extraction efficiencies of the Pb^{2+}, Cu^{2+}, Cd^{2+} ions were observed at 4% Span 80 concentration. Both Pb^{2+} and Cu^{2+} ions showed 100% extraction efficiency, while Cd^{2+} ions showed 98% extraction efficiency, and the breakage of the system dropped to the value of 1.8 for 4% surfactant concentration. Having continued increasing the Span 80 concentration to 6% (v/v %) resulted in a decline in the extraction efficiencies of the Pb^{2+}, Cu^{2+}, Cd^{2+} ions to demonstrate 76%, 78%, and 71% extraction efficiencies respectively. The breakage also witnessed small increase to a value of 2.3 to indicate slight deterioration of system stability.

Some studies have reached the same conclusion but lead ions only that the surfactant concentration must not exceed 4% v/v to obtain 99% removal efficiency Sabry et al. [32] and also 4% for extraction copper ions only Chiha et al. [28].

others offered 6.6 vol% Span 80 the optimal choice for the liquid membrane system for extraction cadmium(II) Yanlin et al. [25] .

Although the increase of the surfactant concentration enhances the system stability and hence increases the extraction efficiency, further increase of Span 80 concentration resulted in increasing the membrane phase viscosity and a difficult transport of the Pb^{2+}, Cu^{2+}, Cd^{2+} ions through the membrane would be occurred.
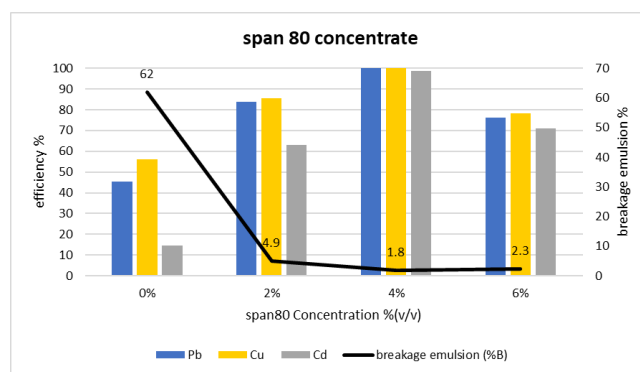

Figure 4. Effect of surfactant concentration on the extraction efficiency and membrane breakage (time of homogenizer: 10 min, D2EHPA:4%(v/v), 0.5M H_2SO_4, internal to organic ratio: 1, homogenizer speed:16200 rpm, feed pH:4, 8 min and 250 rpm in digital mixer , feed to emulsion ratio: 100/10).

3.4. Effect of external phase pH on system stability and extraction efficiency of lead, copper, and cadmium

Fig. 5 shows the weak dependence of the extraction efficiency of the Pb^{2+}, Cu^{2+}, Cd^{2+} ions on the pH change of the external phase within the range of 2-6. The low effect of the pH on the extraction efficiency of the Pb^{2+}, Cu^{2+}, Cd^{2+} ions may be due to small difference between the pH of the internal and external phases, and the poor performance of removal solute at low pH result from the contest of hydrogen ions that released from the acidic extractant in the feed phase as explained Noah et al. [38].

It is shown in **Fig. 5** that the extraction efficiencies of the Pb^{2+}, Cu^{2+}, Cd^{2+} ions were 85.3%, 87.4%, and 76.6% respectively at pH 2, while the breakage was as high as 12.7 indicating considerable system instability.

However, increasing pH value to 4 resulted in better performance of extraction and stability.

The extraction efficiencies of the Pb^{2+}, Cu^{2+},Cd^{2+} ions were 100%, 100%, and 98% respectively. The breakage of 1.8 was obtained at pH of 4 indicating good stability of the system. When the value of pH exceeded 4, the extraction efficiency decreased due to an increase of the difference of osmotic pressure which consequently stimulated the transport of water molecules to the internal phase and caused the swelling phenomenon of the membrane Laki et al. [39]. The system continued showing lesser breakage values indicating better system stability as shown in **Fig. 5**.
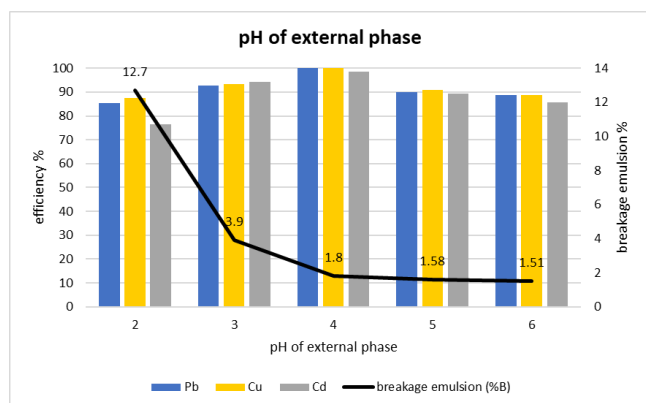

Figure 5. Effect of pH of external phase on the extraction efficiency and breakage (time of homogenizer: 10 min, D2EHPA:4%(v/v), 0.5M H_2SO_4, internal to organic ratio: 1, homogenizer speed:16200 rpm, span80:4%(v/v), 8 min and 250 rpm in digital mixer , feed to emulsion ratio: 100/10).

3.5. Effect of external:emulsion phase ratio on system stability and extraction efficiency of lead, copper, and cadmium

The volume ratio of the external to emulsion phases is called Treat Ratio (TR). TR was found to affect the mass transfer of the ELM system, so a range of 100:2 – 100:15 was studied to evaluate the TR effect on the system performance. As shown in **Fig. 6**, lower TR values gave lower extraction efficiencies of the Pb^{2+}, Cu^{2+}, Cd^{2+} ions and as TR increased to the value of 100:10, maximum extraction efficiencies for the Pb^{2+}, Cu^{2+}, Cd^{2+} ions were obtained (100%, 100%, and 98% respectively).

Beyond the value of the TR of 100:10, the efficiency decreased to lower values. System stability followed the same trend of extraction efficiency. The system stability was getting better as the TR increased from 100:2 to 100:10 to show a minimum value of 1.8, but it slightly increased to 2.2 when the TR was increased to 100:15. The obtained results matched that reported in Salman et al. [7] .

The drop in the extraction efficiencies of the Pb2+, Cu2+,Cd2+ ions beyond the value of TR of 100:10 may be attributed to the swelling phenomenon of the internal globules, and consequently the decrease of the surface area available for mass transfer Mahakal et al. [3].
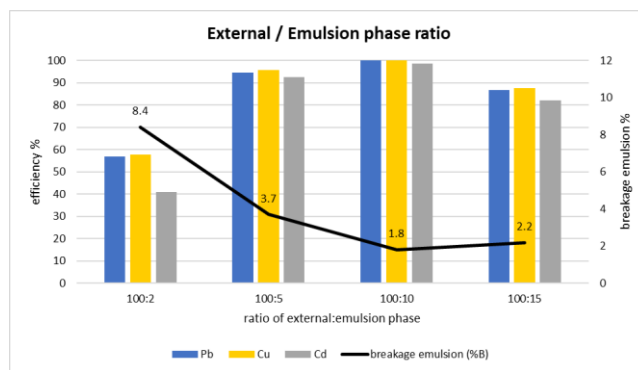

Figure 6. Effect of treat ratio on the extraction efficiency and breakage (time of homogenizer: 10 min, D2EHPA:4%(v/v), 0.5M H_2SO_4, internal to organic ratio: 1, homogenizer speed:16200 rpm, span80:4%(v/v), 8 min and 250 rpm in digital mixer , feed pH:4).

4. Conclusions

A successful extraction of three toxic heavy metal ions (Pb^{2+}, Cu^{2+},Cd^{2+}) from an aqueous solution using ELM technique was carried out. The extraction efficiencies were as high as 100% for both Pb^{2+} and Cu^{2+}, and 98% for Cd^{2+}. The system had shown good stability of 1.8 values for 8 minutes period of extraction.

The system has two distinguished features other than published research; the low concentrations of the Pb^{2+}, Cu^{2+}, Cd^{2+} ions (10 ppm each) and the simultaneous extraction of the three ions. Best operating conditions for the system were found to differ from best operating conditions of each ion when extracted separately

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