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# Effective W/O emulsion performance to extract the antibiotic co-trimoxazole from wastewater

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## ABSTRACT

Recently, the increased concentrations of co-trimoxazole (C-TMZ) in wastewater have gained significant concerns for their persistent input and possible risk to human health and the ecological environment. In this work, the separation of C-TMZ from wastewater by the emulsion liquid membrane (ELM) method was investigated. The W/O emulsion phase consists of xylene as the main solvent, di-(2-ethylhexyl)phosphoric acid (D2EHPA) as a carrier, Span80 as a stabilizer agent, and $H_2SO_4$ solution as the stripping (internal) phase. The influence of several effective conditions on the extraction efficiency and emulsion stability were examined, including homogenization time, membrane to internal phase volume ratio, stabilizer and carrier concentration, $H_2SO_4$ concentration, pH of the external phase, emulsion to external ratio, and stirring speed. It was found that after 10 min of mixing time between the emulsion and the external phases, more than 98% of C-TMZ is removed from the external phase with the highest membrane stability of 99.5%. The determination of mass transfer coefficients and extraction kinetics were also investigated in this study. Four recycling processes of the organic liquid membrane phase were successfully applied to extract C-TMZ in a new ELM process.

*Keywords:* Emulsion; Liquid membrane; Surfactant; Co-trimoxazole; Stability; Extraction

## 1. Introduction

Since the beginning of the new century, World Health Organization has recommended co-trimoxazole (C-TMZ) in breastfeeding HIV-exposed, HIV-uninfected infants from 6 weeks age till breastfeeding has stopped and the infants are definitely not to be infected with HIV [1]. In developing countries, C-TMZ history back to the late 1960s, in which the combination of sulfamethoxazole and trimethoprim was introduced into clinical practice and used to treat many infectious diseases, like respiratory infections, urinary tract infections, Gram-negative sepsis, sexually transmitted diseases, typhoid fever, and enteric infections. C-TMZ is considered an important compound that offers an additional choice in the conflict against many pathogens, due to its low-cost, toxicity profile is acceptable, available in both oral and intravenous routes, and bactericidal activity [2].

C-TMZ is one of the most frequently used antibiotics to treat infections caused by bacterial activities such as bronchitis (tube infections leading to the lungs), pneumonia (infection of a lung), and infections of the urinary tract, intestines, and ears. C-TMZ which has a molecular weight of 543.60 g/mol and a molecular formula of $C_{24}H_{29}N_7O_6S$ is widely spotted in the aqueous environment due to its

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high mobility and broad-spectrum antibacterial property, thus it could have a potential risk to the human health and living organisms by improving the resistance for the bacterial drug. The removal of C-TMZ from wastewaters is problematic and incomplete by the present water treatment processes and has not yet been investigated. This paper is aimed to study the removal and separation of C-TMZ from simulated wastewater by emulsion liquid membrane (ELM). ELM which was first founded in 1968 by Li [3], offers significant features, like low capital and operating costs, no sludge production, two processes of extraction and re-extraction (stripping) in one stage, and short mixing time [4,5]. These features make ELM overcome other similar wastewater treatment methods which have their own inherent limitations such as high capital and operating costs, high quantities of sludge production, high energy consumption, and long operation time [6,7].

ELM method is an easy system of three dispersion phases [8], external and internal miscible liquid phases, and membrane which is the immiscible oil phase [9,10]. The internal phase is encapsulated within the organic liquid membrane phase by a homogenizing process in the existence of surfactant to stabilize the water-inside-oil emulsion, followed by dispersing this W/O emulsion phase into the external solution for the extraction process. In general, a liquid membrane is a non-porous and uniform organic film, in which the target solute is transported by concentration gradient from the external water phase towards the internal water phase. The target solute in the external phase reacts with the carrier present in the organic liquid membrane solvent and forms a solute-carrier complex at the external-membrane interface. While at the internal-membrane interface, the solute-carrier complex is a breakdown, and the target solute is liberated into the internal solution, and thus the carrier is regenerated and goes back into the organic liquid membrane phase.

There are four common solute transport mechanisms available in ELM systems. Type(I) is termed passive transport, the movement of atoms/ions/molecules that are readily soluble in the organic membrane phase is driven by the entropy growth of the system and does not need any additional chemical energy. The phenomenon of component diffusion is the concentration gradient from higher to lower concentration zone, and the solute transport continues until the gradient is eliminated [11]. Type(II) is known as facilitated diffusion, in which the transport of chemical solutes through the membrane phase occurs via extractant (carrier agent) in the membrane solvent. The extractant reacts with the solute present in the feed phase and makes a complex that diffuses into the stripping phase. The transport continues until the stripping agent in the internal solution is saturated with the solute. Type(III) is the coupled transport, in which two species are present in the aqueous solution and the transport of both species occurs at the same time. If the transport of solutes in the same direction is called a co-transport process, and if the solutes are transported in opposite direction is termed a counter-transport process. And the last type(IV) is known as active transport, in which the solute is transported against the concentration gradient (i.e., from low to high concentration area), this phenomenon is identified as the non-equilibrium mass transfer. Two chemical reactions occur in this case and are known as the oxidation–reduction (redox) reaction. These reactions supply the energy for the non-equilibrium mass transfer process [12].

To our knowledge, the extraction of C-TMZ from wastewater by ELM technique has not yet been considered by any works. This work is intended to estimate ELM stability and extraction ability to remove C-TMZ from wastewater via different process parameters. Also, recycling of the organic liquid membrane constituents was investigated in this study.

## 2. Experiments

### 2.1. Chemicals

Di-(2-ethylhexyl)phosphoric acid (D2EHPA) was used as carrier and Sorbitan-monooleate (Span80) as an emulsion stabilizer (Merck Co., Germany). Hydrochloric acid (HCl), sulfuric acid ($H_2SO_4$), and sodium hydroxide (NaOH) for changing pH and as the stripping phase; while xylene as a diluent was prepared from chemical pure compounds (Thomas-Beaker). The initial concentration of 100 ppm in the external solution was prepared by dissolving certain quantities of the antibiotic C-TMZ in deionized water (Samarra Pharmaceutical Industry, Iraq).

### 2.2. Experimental procedure

For preparing the organic liquid membrane phase, suitable volumes of Span80 and D2EHPA were dissolved into the diluent xylene so that the total volume is 20 mL. The same amounts of $H_2SO_4$ solution were dissolved into distilled water to formulate the internal phase and then added drop-by-drop to the oil (membrane) phase while the homogenizing process was done by a high-speed homogenizer (SR30, Korea) to create the milky white water-in-oil emulsion. The external phase and the milky white emulsion were then stirred into a beaker at specific times and speeds. In order to increase the process applicability from point of economic view, the organic and aqueous solutions were separated by using a separating funnel followed by demulsification of the W/O emulsion phase by applying heat and a centrifugal force at 6,000 rpm for 15 min to reuse emulsion phase in another extraction process. The total experimental procedure is shown in Fig. 1. All the samples were filtrated by using a 0.22 μm pore size filter-syringe (hydrophilic PVDF membrane, supplied from Merck, Sigma-Aldrich). Table 1 summarizes the all experimental condition used throughout this work.

### 2.3. Calculations methodology

An ultraviolet spectrophotometer (UV) device was used to analyze the concentration of C-TMZ (Wavelength of 238 nm) in the external phase and the extraction percentage is calculated according to the following formula:

$$\%E = \frac{C_{Ef_0} - C_{Ef}}{C_{Ef_0}} \times 100 \tag{1}$$

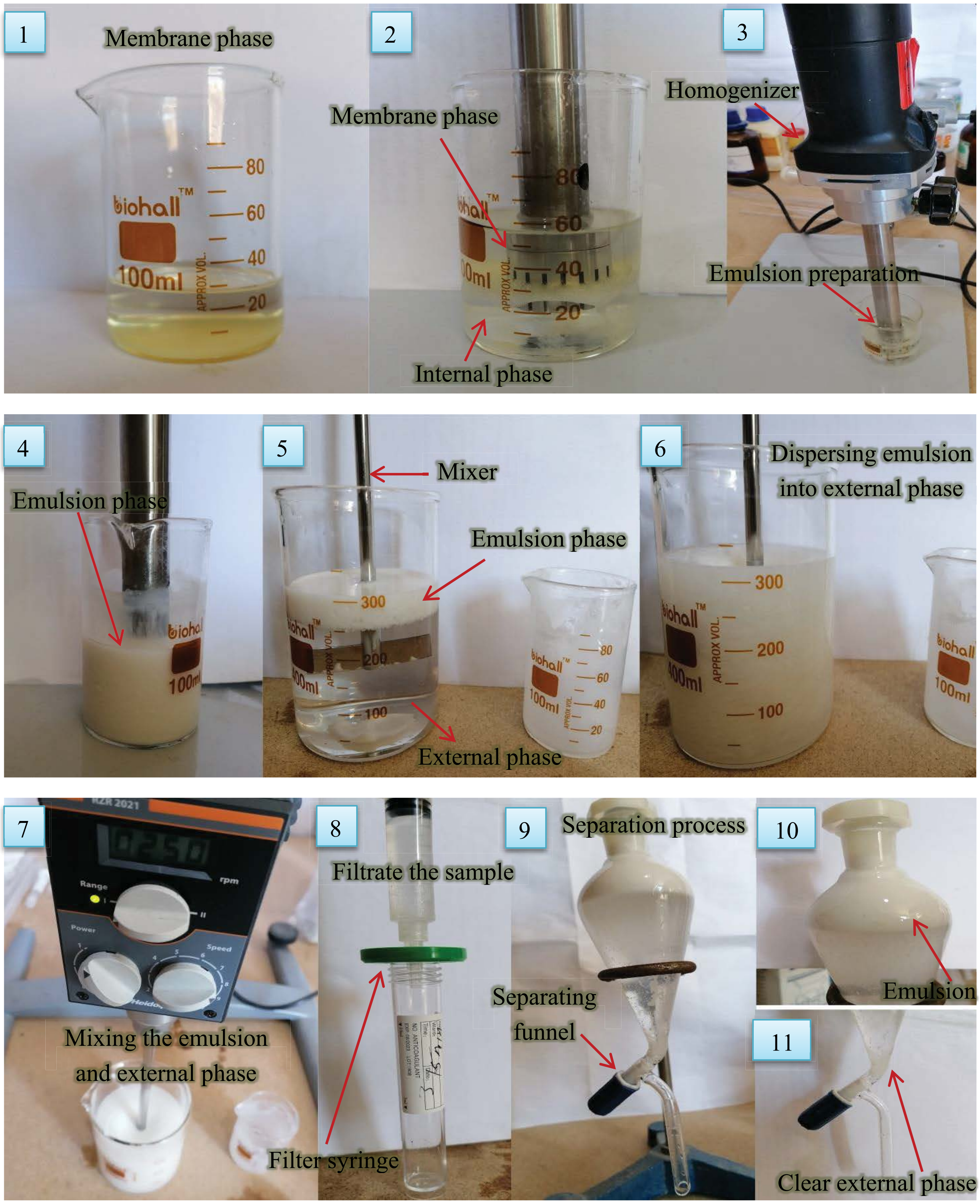


Fig. 1. Total ELM process.

where $C_{E_0}$ and $C_{E_f}$ represents the initial concentration of C-TMZ and the concentration of C-TMZ after a specific time in the external phase, respectively.

The stability (%S) is the opposite of the emulsion breakage (%ξ). Breakage is defined as the percentage of internal phase volume leaked into the external solution ($V_I$) to the initial internal phase volume ($V_{\text{int}}$), however, $V_I$ is

Table 1
Operating parameters for ELM system

| Parameter | Ranges |
|---|---|
| Emulsification time (min) | 3, 5, 8, 10 |
| Span80 % (v/v) | 2, 4, 6, 8,10 |
| $H_2SO_4$ (M) | 0.01, 0.05, 0.1, 0.25, 0.35, 0.5 |
| Membrane/Internal ratio | 1, 1.5, 2, 2.5, 3 |
| D2EHPA % (v/v) | 0, 2, 4, 6, 8, 10 |
| External pH | 2, 3, 4, 5, 6, 8 |
| Stirring speed (rpm) | 200, 250, 300, 350, 400 |
| Emulsion to external ratio | 20:50, 20:75, 20: 100, 15:100, 10:100 |

calculated from the mass balance of external phase pH before and after contact [13,14].

$$\%S = 100 - \%\xi \tag{2}$$

$$\%\xi = \frac{V_I}{V_{\text{int}}} \times 100 \tag{3}$$

$$V_I = V_{\text{ext}} \frac{10^{-\text{pH}_0} - 10^{-\text{pH}}}{10^{-\text{pH}} - C_{H^+}^{\text{int}}} \tag{4}$$

where $V_{\text{ext}}$ signifies the initial external phase volume, $C_{H^+}^{\text{int}}$ signifies the initial internal phase concentration, $\text{pH}_0$ is the initial external solution pH, and pH is the external solution pH at a certain time.

## 3. Results and discussion

### 3.1. Effect of emulsification (homogenization) time

The stability and C-TMZ extraction percentage were studied at various emulsification times (ETs) from 3 to 10 min. Fig. 2 displays that low W/O emulsion stability happened for insufficient homogenization time (<8 min) because of the formulation of large droplet size, in which the coalescence phenomenon takes place in a short time [8,15]. The highest C-TMZ extraction efficiency of 81% occurs within 8 min, which gives the maximum W/O emulsion stability of 98%. Mohammed et al. [15] also found that a stable emulsion could be created within 10 min of emulsification time for the extraction of the antibiotic tetracycline. Further rising the ET (>8 min), led to decreases the emulsion stability (94.7%) and C-TMZ extraction efficiency (80%). This is due to the high internal shearing led to the creation of a high number of milky-white droplets per unit-volume that facilitates their dispersion towards the feed solution [16]. For further experiments, 8 min was chosen to be the best emulsification time.

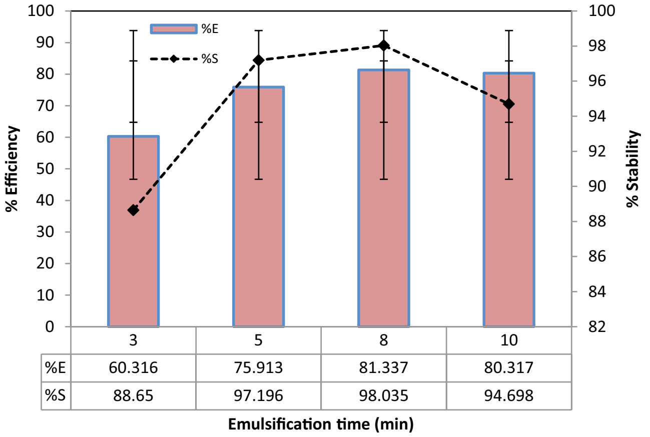


Fig. 2. Emulsification time vs. the emulsion stability and extraction efficiency (homogenizer speed = 12,700 rpm; Span80 concentration = 4%; 0.25 M $H_2SO_4$; D2EHPA concentration = 4%; M/I phase ratio = 1; external pH = 6; emulsion to external ratio = 20:100; stirring speed = 250 rpm for 10 min).

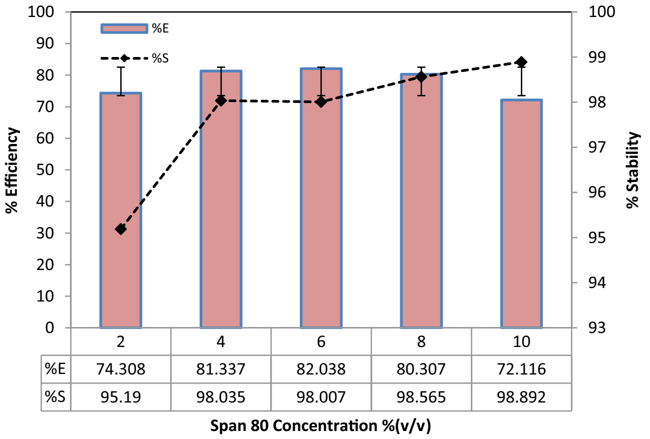


Fig. 3. Span80 concentration vs. the emulsion stability and extraction efficiency (homogenizer speed = 12,700 rpm; ET = 8 min; 0.25 M $H_2SO_4$; D2EHPA concentration = 4%; M/I phase ratio = 1; external pH = 6; emulsion to external ratio = 20:100; stirring speed = 250 rpm for 10 min).

### 3.2. Effect of Span80 concentration

Surfactants play a significant part in decreasing the tension between the surfaces of the organic phase by adsorbing the interface between the external and membrane phases. Without surfactants, the internal phase is impossible to be dispersed into the organic oil phase. Span80 was used in this work at concentrations from 2% to 10% (v/v) to investigate its influence on the emulsion stability and extraction capacity of C-TMZ. Fig. 3 demonstrates that the stability decreases by increasing the Span80 percentage from 2% (stability of 95%) to 4% (stability of about 98%) and the extraction efficiency increases from 75.3% to 81%, respectively. This is because of incremental raise in the Span80 percentage lowered the membrane surface tension, which definitely cause an increase in the surface contact area [17]. Further increasing Span80 concentration (beyond 4%), the emulsion stability increases due to the presence of an additional surface-acting agent at the interface, however; the extraction efficiency starts to decrease. This happened as a result of high mass transfer resistance occurring at the internal- membrane interface [7]. Similar behavior was also indicated by other literature [18–20], therefore; a surfactant percentage of 4% was recognized as an ideal value for further experiments.

### 3.3. Effect of $H_2SO_4$ concentration

Concentration of $H_2SO_4$ in the stripping (internal) solution was changed from 0.01 to 0.5 M. Fig. 4 downstate that the stability and the extraction percentage were significantly enhanced by increasing the $H_2SO_4$ concentration from 0.01 to 0.35 M. This is because the difference in the concentration of $H^+$ ions between the external and internal water phases, which is the main driving force for the solute transport in ELM system. The release of more internal phase constituents toward the external phase have been occurred by increasing the $H_2SO_4$ concentration above 0.35 M, in which the emulsion stability and extraction percentage start to decrease. This decrease occur as a result of the reaction between the surfactant (Span80) and carrier (D2EHPA) which led to a reduction in the stabilizer properties and consequently cause a destabilization phenomenon [21]. Hence, 0.35 M $H_2SO_4$ which gives the highest stability (98.7%) and extraction percentage (84.3%) was chosen throughout this work.

### 3.4. Effect of the membrane to internal phase volume ratio (M/I)

The organic liquid membrane stability and C-TMZ extraction efficiency were investigated at various ratios of the membrane to internal volumes as illustrated in Table 1. Fig. 5 shows that varying the ratio from 1 to 2 led to a decrease in the emulsion stability from 98.7% to 94.3% and declining in the extraction percentage from 84.3% to 70.6%. This occurs as a result of too much organic oil phase which causes a thicker and highly viscous membrane interface that obstructs the dispersing of stripping solute into the organic solvent. Also, the main reason for decreasing the extraction efficiency is less internal agents exist in the membrane phase to strip the solute. Continues varying the ratio from 2 to 3 led to reducing the emulsion stability, and the extraction percentage dropped to approximately 60%. In addition, the internal phase cannot be completely captured for the inadequate volume of the aqueous phase, and thus tends to escape outside the W/O emulsion globules. Similar behaviors were also reached by previous literature [8,22,23]. Therefore, a ratio of 1 was selected as an optimum value appropriate to achieve the highest stability and extraction efficiency.

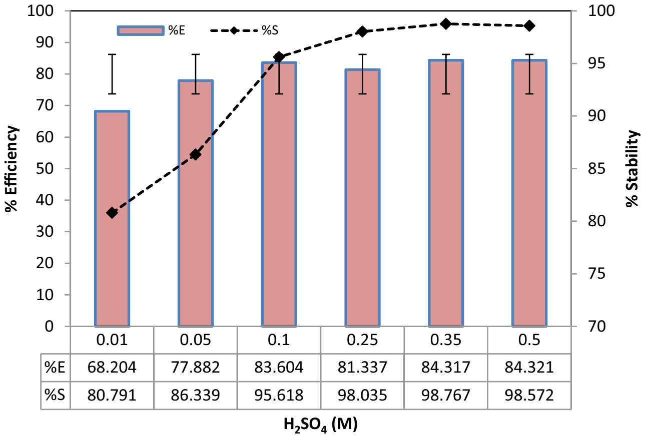


Fig. 4. $H_2SO_4$ concentration vs. the emulsion stability and extraction efficiency (homogenizer speed = 12,700 rpm; ET = 8 min; Span80 concentration = 4%; D2EHPA concentration = 4%; M/I phase ratio = 1; external pH = 6; emulsion to external ratio = 20:100; stirring speed = 250 rpm for 10 min).

### 3.5. Effect of carrier concentration

Di-(2-ethylhexyl)phosphoric acid (D2EHPA) was used as a capture agent in the ELM system. In order to study its influence on ELM stability and extraction capacity, the carrier percentage varied from 0% to 10% (v/v). Fig. 6 shows that the transported percentage of C-TMZ was less than 11% in the absence of D2EHPA which means that C-TMZ although it's an organic compound, cannot be

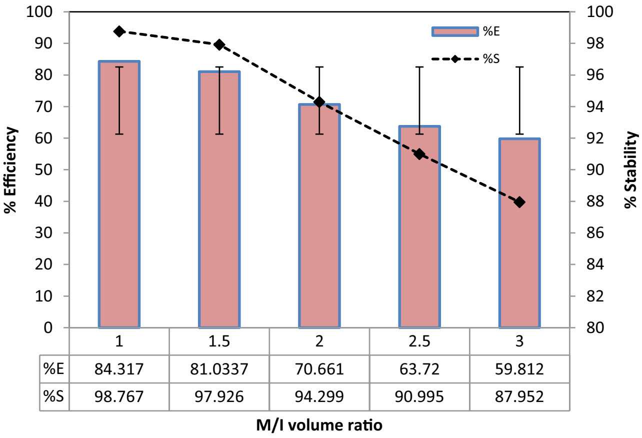


Fig. 5. Membrane to internal phase ratio vs. the emulsion stability and extraction efficiency (homogenizer speed = 12,700 rpm; ET = 8 min; Span80 concentration = 4%; 0.35M $H_2SO_4$; D2EHPA concentration = 4%; external pH = 6; emulsion to external ratio = 20:100; stirring speed = 250 rpm for 10 min).

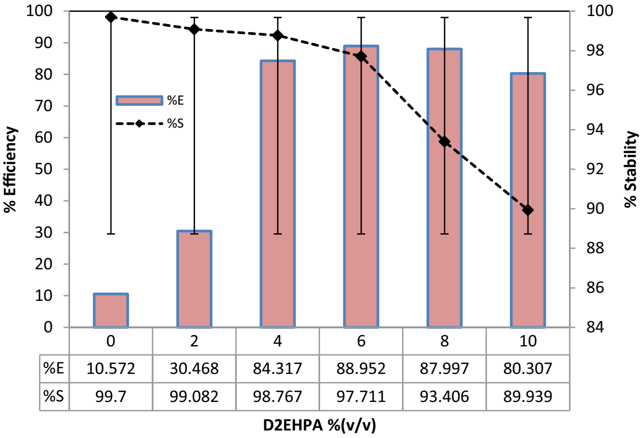


Fig. 6. D2EHPA concentration vs. the emulsion stability and extraction efficiency (homogenizer speed = 12,700 rpm; ET = 8 min; Span80 concentration = 4%; 0.35 M $H_2SO_4$; M/I phase ratio = 1; emulsion to external ratio = 20:100; external pH = 6; stirring speed = 250 rpm for 10 min).

transported efficiently without the presence of a carrier; while this absence of D2EHPA results in full ELM stability. Increasing D2EHPA concentration to 6% achieves an optimum extraction percentage of 89%, while the stability was not significantly influenced. Additionally increasing the concentration of D2EHPA results in an unstable ELM, and more of the internal aqueous phase leaked outside the W/O emulsion phase. This happens as a result of the competitive adsorption and reaction of D2EHPA with the stabilizer at the two interfaces as they have opposite actions. Furthermore, excess carrier percentage inside the W/O emulsion phase led to a rise in the interfacial surface-tension, and thus increased viscosity of the W/O emulsion phase, and led to create large sized milky-white droplets, which might cause the permeation swellings [24]. Zhao et al. [25] found the same performance in the extraction of $Cr^{3+}$ at a 7% concentration of D2EHPA. Hence, a 6% concentration of D2EHPA was used in this study.

### 3.6. Effect of external phase pH

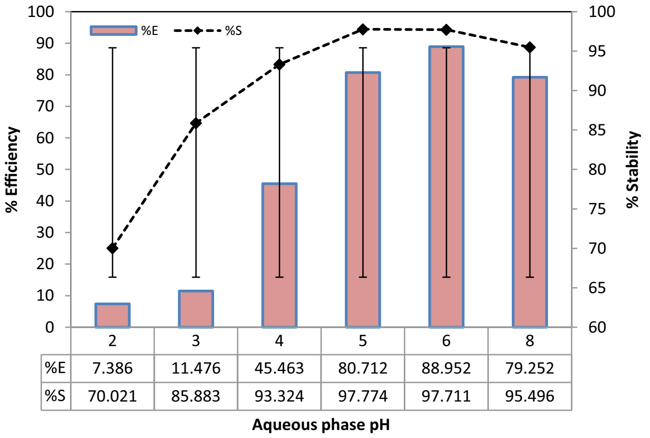
Results in Fig. 7 reveal that stability and extraction efficiency was highest at a pH value of 8. However, it is very obvious that extraction of C-TMZ is very influenced in acidic pH region in which the extraction efficiency was about 7% at pH of 2 and the stability decreased to 70% at this pH region. This could be due to that lower pH (higher $H^+$ concentrations) led to destabilizing the emulsion globules, while the extraction percentage decreased as a result of the neutral carrier (D2EHPA) which cannot sufficiently create the solute-carrier complex. While increasing the external pH to neutral conditions, the extraction percentage and the stability start to enhance. Additionally, at pH beyond a value of 6, the extraction percentage started to decrease slightly as a result of the protons that were released as a result of anion exchange-reaction at this pH region [26]. As a result, the pH value of 6 was very appropriate for further experiments.

### 3.7. Effect of stirring speed

Reactor hydrodynamics have a significant issue in ELM systems and must be controlled very carefully. The stirring speed has a key role in the transport of solute through the LM. Stirring or mixing speed was varied from 200 to 400 rpm within a contact time of 15 min. Fig. 8 demonstrates that the extraction performance declined by reducing the mixing speed from 250 to 200 rpm, whereas the stability was not greatly influenced. This is because at an agitation speed of 250 rpm, the dispersed emulsion droplet size is reduced and thus the interfacial-area for mass transfer is improved. Advancing the level of mixing to more than 250 rpm, the shear force acting on the emulsion droplet increased which led to producing a smaller emulsion droplet size and thus increasing the osmotic swelling that makes the W/O emulsion to be unstable [27,28]. The same behavior was obtained by Mohammed et al. [8] for removing >98% of ciprofloxacin, and Zabat [29] found that 90% of $Pb^{2+}$ can be extracted at 250 rpm mixing speed. As a result, the mixing speed of 250 rpm was selected to keep good emulsion stability and highest the extraction efficiency.

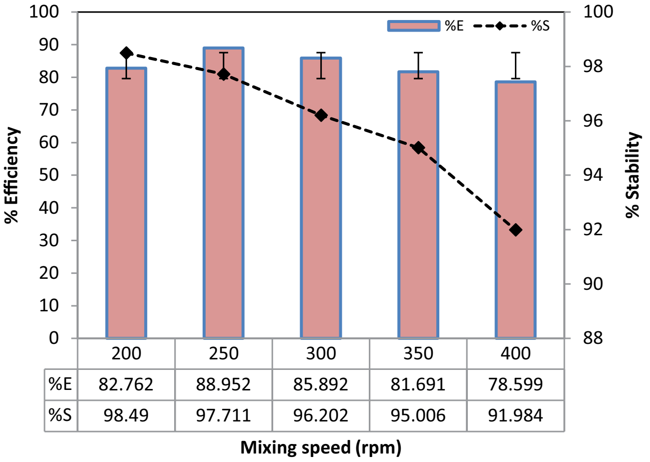
### 3.8. Effect of emulsion to external volume ratio

Controlling the interfacial mass transfer rate across ELM systems requires to study of one of the most important conditions in the ELM process which is the emulsion to external phase ratio. The ratio of emulsion to external volume was changed from 20:50 to 10:100 as in Table 1. Fig. 9 illustrates that a volume ratio of 20:100 yield the highest extraction of C-TMZ. While increasing the volume ratio to 20:50 result in inadequate mixing of the phases which decrease the extraction percentage, this is due to the higher percentage of the more viscous milky-white phase. Whereas decreasing the ratio to 10:100 causes a significant decline in extraction percentage, which is because fewer milky-white emulsion quantities will be available to attach the contaminant from the external aqueous phase. As the



| | 2 | 3 | 4 | 5 | 6 | 8 |
|---|---|---|---|---|---|---|
| %E | 7.386 | 11.476 | 45.463 | 80.712 | 88.952 | 79.252 |
| %S | 70.021 | 85.883 | 93.324 | 97.774 | 97.711 | 95.496 |

Fig. 7. External phase pH vs. the emulsion stability and extraction efficiency (homogenizer speed = 12,700 rpm; ET = 8 min; Span80 concentration = 4%; 0.35 M $H_2SO_4$; M/I phase ratio = 1; D2EHPA concentration = 6%; emulsion to external ratio = 20:100; stirring speed = 250 rpm for 10 min).



| | 200 | 250 | 300 | 350 | 400 |
|---|---|---|---|---|---|
| %E | 82.762 | 88.952 | 85.892 | 81.691 | 78.599 |
| %S | 98.49 | 97.711 | 96.202 | 95.006 | 91.984 |

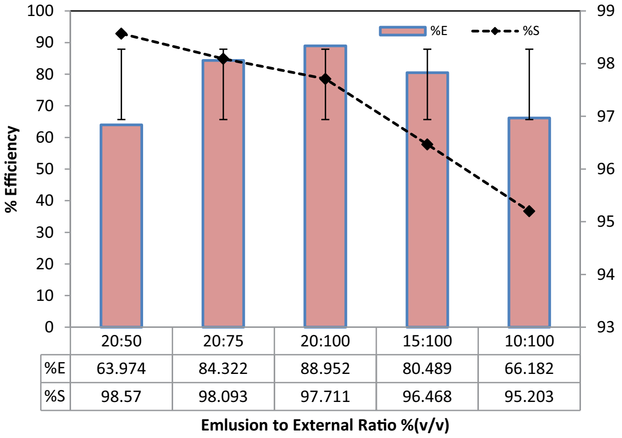
Fig. 8. Stirring speed vs. the emulsion stability and extraction efficiency (homogenizer speed = 12,700 rpm; ET = 8 min; Span80 concentration = 4%; 0.35 M $H_2SO_4$; external pH = 6; M/I phase ratio = 1; D2EHPA concentration = 6%; emulsion to external ratio = 20:100).

internal phase leakage outside the emulsion globules was very marginally with different emulsion to external ratios, the stability was not significantly affected. Definitely, by increasing emulsion to external ratio the occurrence of swelling phenomena becomes notable, fast, and accompanied by embrittlement following a more substantial coalescence of the stripping phase [30]. As a result, the emulsion to the external ratio of 20:100 was chosen in this work.

### *3.9. Determination of C-TMZ extraction kinetic and mass transfer coefficients*

Fig. 10 shows the extraction kinetic of C-TMZ by using the first-order rate equation (5) [31,32]. Since the slope of the curve is straight which is represented by ($k_{\text{obs}}$), thus it approves that the extraction C-TMZ followed the kinetics of first-order.

$$\ln\left(\frac{C_{Ef}}{C_{Ef_0}}\right) = -k_{\text{obs}}t \quad (5)$$



| | 20:50 | 20:75 | 20:100 | 15:100 | 10:100 |
|---|---|---|---|---|---|
| %E | 63.974 | 84.322 | 88.952 | 80.489 | 66.182 |
| %S | 98.57 | 98.093 | 97.711 | 96.468 | 95.203 |

Fig. 9. External to emulsion ratio vs. the emulsion stability and extraction efficiency (homogenizer speed = 12,700 rpm; ET = 8 min; Span80 concentration = 4%; 0.35 M $H_2SO_4$; external pH = 6; M/I phase ratio = 1; D2EHPA concentration = 6%; stirring speed = 250 rpm for 10 min).

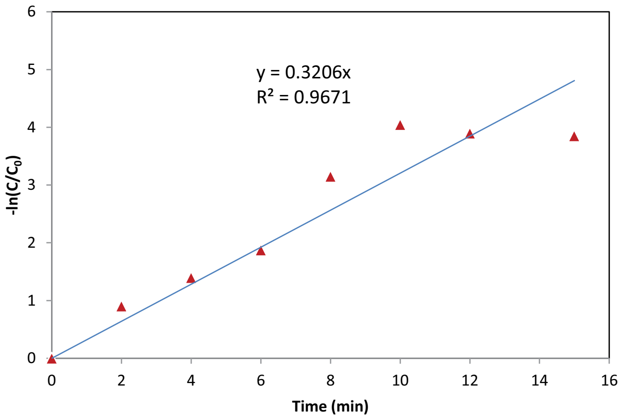


Fig. 10. Extraction kinetic of CIP.

where $t$ represents the time in minutes, while $k_{\text{obs}}$ represents the extraction rate constant (1/min) [33].

The total mass transfer coefficients $K_T$ (m/s) for the ELM system is shown in Eq. (6) [34]:

$$\frac{1}{K_T} = \frac{1}{K_M} + \frac{1}{K_F} \quad (6)$$

where $K_M$ (m/s) signifies the mass transfer coefficient of the external solution and is determined from Raji et al. [31] correlation given in Eq. (7):

$$\frac{K_M}{\sqrt{ND}} = 2.932\times10^{-7}\left(\frac{V_i+V_m}{V_i+V_m+V_e}\right)\left(\frac{d_I}{T}\right)^{0.548}\mathrm{Re}^{1.371} \quad (7)$$

where $N$ (rpm) signifies the agitating speed of the mixing tank; $D$ represents the diffusivity of the C-TMZ-D2EHPA complex in the membrane phase and is estimated from the correlation of Eq. (8) [35]: $V_e$, $V_i$, and $V_m$ represent the external, internal and membrane volumes, respectively; $T$ and $d_I$ refer to the mixing and impeller tank diameter, respectively; and Re refers to the Reynold number of the continuous phase and is estimated from Eq. (9):

$$D = \frac{\left(117.3\times10^{-18}\right)\left(M\varphi\right)^{0.5}T}{\mu_m\varphi_c^{0.6}} \quad (8)$$

where $M$ represents the solvent molecular weight for xylene (106.16 kg/kmol), xylene association factor ($\phi = 1$), $T$ is the temperature = 293 K, the membrane viscosity ($\mu_m$) = 0.387 × $10^{-3}$ kg/ms, and the molar volume of the C-TMZ-D2EHPA complex ($\phi_c$) is estimated by using the Schroeder method [36] and its value equal to 0.6931 $m^3$/kmol. The obtained $D$ from the above equation is equal to $1.391\times10^{-9}$ $m^2$/s, and thus the obtained $K_M$ value was $1.93\times10^{-3}$.

$$R_e = \frac{Nd_I^2\rho_C}{\mu_C} \quad (9)$$

where $\mu_C$ and $\varrho_c$ are the continuous phase viscosity (kg/ms) and density (kg/$m^3$). The obtained Re value is 62517.

$K_F$ (m/s) signifies the interfacial reaction rate constant, and is calculated from Eq. (10):

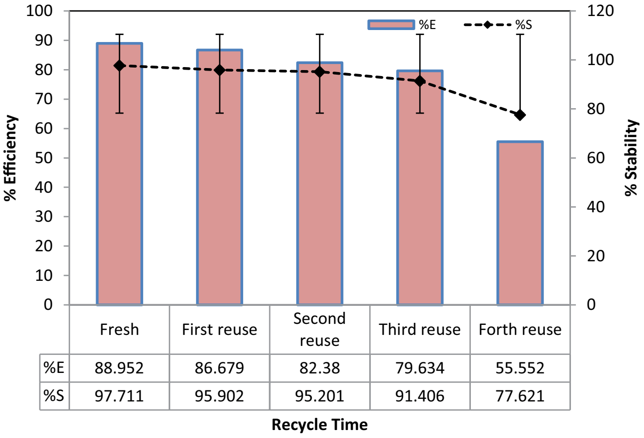
$$\ln\left(\frac{C_{Ef}}{C_{Ef_0}}\right) = -Ak_Ft \quad (10)$$

$K_F$ can be estimated by comparing Eqs. (10) and (5):

$$k_F = \frac{k_{\text{obs}}}{A} \quad (11)$$

where $A$ represents a specific interfacial area of the emulsion and is calculated from Eq. (12) [37]:

$$A = \frac{A_i}{V} = \frac{6\alpha}{d_{32}} \quad (12)$$



| | Fresh | First reuse | Second reuse | Third reuse | Forth reuse |
|---|---|---|---|---|---|
| %E | 88.952 | 86.679 | 82.38 | 79.634 | 55.552 |
| %S | 97.711 | 95.902 | 95.201 | 91.406 | 77.621 |

Fig. 11. The effect of various recycling process on emulsion stability and extraction efficiency (homogenizer speed = 12,700 rpm; ET = 8 min; Span80 concentration: = 4%; 0.35 M $H_2SO_4$; emulsion to external ratio = 20:100; M/I phase ratio = 1; external pH = 6; D2EHPA concentration = 6%; stirring speed = 250 rpm for 10 min).

where $V$ and $A_i$ are the emulsion unit volume and emulsion droplet interfacial area, respectively, while $\alpha$ and $d_{32}$ represent the volume fraction of the water phase and sauter mean diameter, respectively. The water volume fraction is 0.5 and the sauter mean diameter was calculated according to the procedure in the previous study [8].

The yield mass transfer coefficients were as follows: $K_M$, $K_F$ and $K_T$ were 1.93 × $10^{-3}$ (m/s), 8.81 × $10^{-9}$ (m/s) and 8.803 × $10^{-9}$ (m/s), respectively. These results reveal that the interfacial reaction rate constant ($K_F$) will be more dominant in the transport processes than the external phase mass transfer coefficient ($K_M$).

### *3.10. Recyclability of the membrane material*

After completing the extraction process, recycling processes were applied in order to reuse the organic membrane solvent in another ELM system. This process can be considered a significant feature in the ELM technique for environmental protection and economic point of view, since the oil phase, stabilizer, and carrier are expensive resources and can cause unwanted pollution when disposing them [38]. The organic and aqueous solutions were separated by using a separating funnel followed by de-emulsification of the W/O emulsion phase by applying heat and a centrifugal force at 6,000 rpm for 15 min. At the yield optimal experimental conditions, the obtained oil solvent was reused without consuming further carriers or surfactants in a new extraction process. Fig. 11 reveals that the extraction percentage was the same in the 1st and 2nd recycling processes and decreased slightly in the 3rd stage. While in the 4th process, the extraction percentage declined significantly to about 55% which might be because the membrane solvent and particularly the carrier materials are being saturated by more C-TMZ solutes and cannot carry the molecules efficiently anymore [8]. The milky-white emulsion stability was also dropped in the 4th reuse process, this could occur as a result of the property of surfactant (Span80) changed by more recycling process.

## 4. Conclusions

This article is aimed to extract co-trimoxazole (C-TMZ) from wastewater by ELM using xylene as a green diluent, D2EHPA as a carrier and Span80 as a surfactant. The following conclusions can be drawn from this study:

- ELM method is an actual operative and effective technology to eliminate C-TMZ from wastewater.
- The optimum operating condition that impacts the W/O emulsion stability and extraction efficiency are homogenizer speed (12,700 rpm), emulsification time (8 min), Span80 concentration (4%), membrane to internal phase ratio (1), $H_2SO_4$ concentration (0.35 M), D2EHPA concentration (6%), pH of external phase (6), emulsion to external phase ratio (20:100), and mixing speed (250 rpm).
- At the best operational parameters, it was clear that 89% could be extracted from the external solution containing an initial concentration of 100 ppm with a contact time of 10 min.
- The system ensured the highest emulsion stability of 98%.
- The total mass transfer coefficient in the ELM system was 8.57 × $10^{-9}$ (m/s).
- The organic phase (membrane) was reused efficiently to make a more stable milky-white emulsion to remove C-TMZ four times.

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