

# Dye removal from water using emulsion liquid membrane: Effect of alkane solvents on efficiency

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**Abstract.** Effect of different alkane based solvents on the stability of emulsion liquid membrane was investigated using normal alkanes (n-hexane, n-heptane, n-octane and n-decane) under various operating parameters of surfactant concentration, emulsification time, internal phase concentration, volume ratio of internal phase to organic phase, volume ratio of emulsion phase to external phase and stirring speed. Results of stability revealed that emulsion liquid membrane containing n-octane as solvent and span-80 (5 % (w/w)) as emulsifying agent presented the highest amount of emulsion stability (the lowest breakage) compared with other solvents; however, operating parameters (surfactant concentration (5% (w/w)), emulsification time (6 min), internal phase concentration (0.05 M), volume ratio of internal phase to organic phase (1/1), volume ratio of emulsion phase to external phase (1/5) and stirring speed (300 rpm)) were also influential on improving the stability (about 0.2% breakage) and on achieving the most stable emulsion. The membrane with the highest stability was employed to extract acridine orange with various concentrations (10, 20 and 40 ppm) from water. The emulsion liquid membrane prepared with n-octane as the best solvent almost removed 99.5% of acridine orange from water. Also, the prepared liquid membrane eliminated completely (100%) other cationic dyes (methylene blue, methyl violet and crystal violet) from water demonstrating the efficacy of prepared emulsion liquid membrane in treatment of dye polluted waters.

**Keywords:** Emulsion liquid membrane (ELM); alkane based solvents; stability; extraction; dye removal

## 1. Introduction

In general, dyes are defined as chemicals attaching surface or fabrics of materials to convey colour to the host structures. Having complicated and complex molecular organic patterns, dyes should be resistant to a multitude of circumstances, take for an example, the effects of detergents. Synthetic dyes are abundantly useful in a wide variety of advanced industrial disciplines including textile industry, paper, leather tanning, food processing, plastics, textiles, cosmetics, rubber, printing and dye manufacturing industries. By the same token, with reference to evident data, it should be noticed that more than 100,000 commercial dyes have been produced with an annual rate of about 700,000 tons per a year. As an illustrative example, in textile industries, the global dye consumption is more than 10,000 tons per a year such that around 100 ton/year of dyes are released into water (Abraham Reife 1996, Yagub, Sen *et al.* 2014). With regard to their particle charges upon dissolution in aqueous media, dyes can be categorized in three main groups: cationic (basic dyes), anionic (direct, acid and reactive dyes), and non-ionic (dispersed dyes) (Yagub, Sen *et al.* 2014). To put this process into perspective, it should be emphasized that covering an aquatic ecosystem with thick colorful layers (like dyes) can diminish the possibility of penetration of sunlight to benthic

organisms, thereby limiting photosynthesis. To add to that, this procedure also can influence the aesthetic value of an aquatic ecosystem as a result of coloration of water resources (Ngulube, Gumbo *et al.* 2017). Moreover, the photosynthetic activities in an aquatic life may be altered by the decrement in light penetration due to dye pollution, and dyes may be toxic to some aquatic life because of the presence of metals, aromatics, etc. (Yagub, Sen *et al.* 2014). It is worth mentioning that dyes are carcinogenic, mutagenic, or teratogenic in various microbiological species and can cause severe damages to human body including dysfunctions in kidneys, respiratory system, liver, brain and central nervous system (Kadirvelu, Kavipriya *et al.* 2003). Due to the aforementioned harmful consequences of presence of dyes in our ecosystem, applying a beneficial method which controls their influences and limits their release into the environment has attracted a great deal of attentions. In this regard, specific methods and technologies to remove dyes from different kinds of wastewater streams are highly desirable.

Notwithstanding the available methods to remove dye contaminants from water and wastewater including coagulation (Lee, Choi *et al.* 2006, Khayet, Zahrin *et al.* 2011, Tiaiba, Merzouk *et al.* 2018), chemical oxidation (Ghodbane, Nikiforov Anton *et al.* 2014), membrane separation (Ghaemi, Madaeni *et al.* 2015, Jegatheesan, Pramanik *et al.* 2016, Khan, Khan *et al.* 2017, Zeng, Ye *et al.* 2017), electro chemical processes (Soloman, Basha *et al.* 2009), aerobic and anaerobic microbial degradation (Yagub, Sen *et al.* 2014, Tan, Vakili *et al.* 2015), and adsorption methods (Khenifi, Bouberka *et al.* 2007, Kalmár, Lente *et al.*

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2016). Meanwhile, there is a great deal of potential in the application of liquid membrane processes as attractive alternative treatment for the removal of dyes from wastewater. Generally, emulsion liquid membrane (ELM) process is a feasible solution to eliminate various unwanted chemicals from water where conventional methods may not act efficiently. Take, for example, metals (Vasconcelos and Carvalho 1993, Ganesh Prasad, Venkatesan *et al.* 2007, Fouad 2008, Ahmad, Kusumastuti *et al.* 2012), weak acids (like phenol and cresol (Terry, Li *et al.* 1982, Balasubramanian and Venkatesan 2012, Othman, Noah *et al.* 2017)) and weak bases (like ammonium and amines (Cahn, Li *et al.* 1978)), inorganic species (Koby, Topçu *et al.* 1997, Lin and Long 1997), hydrocarbons, biochemical and dyes (Othman, Yi *et al.* 2013, Bahloul, Bendebane *et al.* 2016). Effectively, due to simultaneous steps of extraction and stripping in liquid membrane processes, these membranes have been considered as an improved solvent extraction. Some attractive characteristics of surfactant liquid membrane or emulsion liquid membrane process, in comparison with conventional processes, are their simpler operation, lower cost, higher efficiency, extraction and stripping in one stage, larger interfacial area and continuous operation (Hu, Li *et al.* 2003, Kislik 2009).

An ELM system consists of three different phases including an internal, intermediate, and external phase. The internal or receiving phase as well as the external or feed phase are usually aqueous, while the liquid membrane which acts as an intermediate phase is organic. Therefore, there would be two dispersed phases forming an emulsion with a continuous phase. In an extraction process, the considered solute in the outer feed phase moves across the membrane phase to reach the inner phase, and due to a much smaller volume of the interior aqueous phase in comparison with its external equivalent, both separation and concentration procedures of the solute can be achieved in one step (Patnaik 1995). In ELM, the concentration difference between the external and the internal phases leads to the solute mass transfer through the organic phase or membrane as a barrier (Kislik 2009). Table 1 introduces some research studies focusing on the use of emulsion liquid membranes to extract dye contaminants from water (Agarwal, Das *et al.* 2010, Othman, Yi *et al.* 2013, Bahloul, Bendebane *et al.* 2016). In this regard, it can be obviously inferred from the table that liquid membranes had a remarkable level of efficiency in removal of dyes. Based on an extensive review on the pertinent literature, it can be revealed that, heretofore, there has been no study to investigate the removal of acridine orange dye from water using liquid membrane. Notwithstanding the relevant information in literature discussing the use of hexane and heptane as solvents in preparation of ELM, the effect of other alkanes on the stability of emulsion and also extraction of dye from water has not been studied so far. As one of the parameters influencing the stability of emulsion, solvent viscosity may be effective on the performance of membrane. Moreover, due to the variety of diffusion coefficients in different solvents (membranes), it can affect the rate of solute diffusion through the membrane, thereby influencing extraction of solute from external phase (Erkey,

Rodden *et al.* 1990, Leahy-Dios and Firoozabadi 2007).

Hence, this study focuses on the preparation of emulsion liquid membrane including various alkanes (n-hexane, n-heptane, n-octane and n-decane), Span-80 as emulsifying agent and sodium hydroxide as stripping agent in the internal phase. By the same token, the stability of prepared emulsions was investigated under the effect of various parameters such as surfactant concentration, emulsification time, internal phase concentration, volume ratio of internal phase to organic phase, volume ratio of emulsion phase to external phase, and stirring speed. The Efficiency of ELM with the highest stability was evaluated in removal of acridine orange as a cationic dye using various types of solvents as well as different concentrations of external phase. Finally, other cationic dyes such as methylene blue, methyl violet and crystal violet were applied to assess capability of optimum ELM in the treatment of dye polluted waters.

## 2. Experimental

### 2.1 Chemicals

All chemicals were obtained with an analytical grade, and used without any further purification. To prepare liquid membrane, a surfactant and a diluent (solvent) are necessary. Span-80 (Merck, Germany), as a non-ionic material, was used as surfactant for stabilization of emulsion, and different organics (n-hexane ( $\geq 99\%$ ), n-heptane ( $\geq 99\%$ ), n-octane ( $\geq 99\%$ ) and n-decane ( $\geq 99\%$ )) purchased from Merck were applied as solvents (diluent). Sodium hydroxide ( $\geq 99.9\%$ ) (Merck, Germany) was utilized as a stripping agent in the internal phase. Performance of liquid membrane was evaluated in removal of various cationic dyes (acridine orange, methylene blue, methyl violet and crystal violet ( $\geq 99.9\%$ , Merck, Germany)) from water. Chemical structure of dyes is illustrated in Fig. 1.

### 2.2 Emulsion preparation

In order to prepare emulsion liquid membrane, a solution containing span-80 (5% (w/w)) in the solvent (diluent) was prepared under mixing (2000 rpm) by a high speed magnetic stirrer. Afterwards, the internal aqueous phase containing sodium hydroxide (0.05 M) was gently added to the membrane phase while mixing by a magnetic stirrer (300 rpm) for a constant mixing time (6 min).

### 2.3 Emulsion stability

Emulsion stability is one of the important parameters influential on the efficiency of emulsion liquid membrane. Emulsion breakage reduces the separation efficiency and causes the leakage of extracted dye from the internal phase to the external aqueous one. For this reason, different methods have been employed so far such as chemical (Dâas and Hamdaoui 2010, Chaouchi and Hamdaoui 2015) and high voltage methods (Othmana, Zing-Yia *et al.*, Salazar, Ortiz *et al.* 1992, Lu, Lu *et al.* 1997, Wan, Wang *et al.* 1997,

Table 1 A summary on the prepared emulsion liquid membranes to extract dye from water

External phase (dye solution)	Membrane (diluent)	Surfactant	Internal phase	Carrier	Extraction (%)	Ref
Acid Yellow 99	Cyclohexane	Span-80	Sulfuric acid	Aliquat 336	99.9	(Bahloul, Bendebane <i>et al.</i> 2016)
Methylene blue	Kerosene	Span-80	Sulfuric acid	Bis (2-ethylhexyl) phosphoric acid	98	(Othmana, Zing-Yia <i>et al.</i> )
Rhodamine 6G	Kerosene	Span-80	Sulfuric acid	Bis (2-ethylhexyl) phosphoric acid	100	(Othman, Yi <i>et al.</i> 2013)
Methylene blue	Hexane	Span-80	Sulfuric acid	Bis(2-ethylhexyl) phosphoric acid	98	(Bahloul, Ismail <i>et al.</i> 2013)
Red 3BS	Kerosene	Span-80	Sodium chloride	Tri-dodecyl amine	100	(Othman, Zailani <i>et al.</i> 2011)
Congo red and acid blue 25	Hexane	Span-80	Sodium carbonate	No carrier	>99	(Dâas and Hamdaoui 2010)
Methylene blue and crystal violet	n-Heptane	Span-80	Sodium hydroxide	No carrier	>90	(Agarwal, Das <i>et al.</i> 2010)
Methylene blue and crystal violet	n-Heptane	Span-80	Sodium hydroxide	No carrier	99	(Das, Rungta <i>et al.</i> 2008)
Methylene blue, rhodamine B, malachite green and basacryl red GL	Hexane	Span-80	Sulfuric acid	di(2-ethylhexyl) phosphoric acid	>98	(Djenouhat, Hamdaoui <i>et al.</i> 2008)
MB R 12 red reactive	Kerosene	Span-80	Hydrogen chloride	Trioctylamine	99	(Masu, Botau <i>et al.</i> 2005)

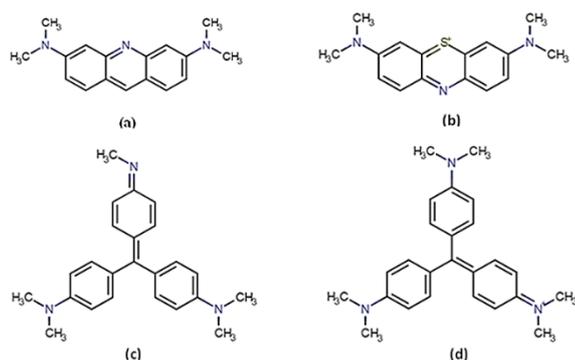


Fig. 1 Chemical structure of (a) acridine orange, (b) methylene blue, (c) methyl violet and (d) crystal violet

$$EB(\%) = \frac{V_s}{V_{int}} \times 100 \quad (2)$$

in which  $V_{int}$  is the initial volume of internal phase. In this research, effect of important parameters on the stability of emulsion were examined such as type of solvent (n-hexane, n-heptane, n-octane and n-decane), surfactant concentration (2, 5 and 8 wt.%), emulsification time (3, 6 and 9 min), internal phase concentration (0.01, 0.05 and 0.1 M), volume ratio of internal phase to organic phase (1/1, 1/2 and 2/1), volume ratio of emulsion phase to external phase (1/2, 1/5 and 1/8) and stirring speed (100, 300 and 500 rpm). It should be mentioned that this range of parameters were selected based on the relevant literature as well as primary experiments. It is also worth mentioning that each experiment was carried out at least twice, and an average amount was reported for each parameter as its final value. All experiments were conducted at room temperature ( $25 \pm 2$  °C).

#### 2.4 Extraction of dye

The liquid membrane with the highest stability was prepared under the experimental conditions obtained from the stability sections, and thereafter, the efficiency of membrane in the extraction of acridine orange dye from external phase was evaluated at room temperature. In this regard, 40 mL of emulsion solution was added to 200 mL of the prepared dye solution (external phase) in a cylindrical vessel equipped with a stirrer. The content of the vessel (external phase) was analyzed after 10 min of a steady condition using an UV-Vis spectrophotometer (PG Instruments, T80+, UK) at a definite wavelength relating to maximum absorbance of dye (acridine orange: 492 nm, methylene blue: 663 nm, methyl violet: 590 nm, and crystal violet: 590 nm). A schematic diagram illustrating both emulsion preparation and extraction process is provided in Fig. 2.

Ahmad, Buddin *et al.* 2017); however, a more feasible and applicable method may be a tracer method in which pH of the external phase is measured during time. Any increment in the concentration of hydroxyl ions in the external aqueous phase increases the pH indicating the break-up of emulsion. In this regard, a certain volume of the prepared emulsion was added to 200 mL of distilled water as the external aqueous solution, and  $V_s$  (volume of internal phase (sodium hydroxide solution) leakage to the aqueous external phase) was calculated using the following equation (Ahmad, Kusumastuti *et al.* 2012, Ahmad, Kusumastuti *et al.* 2014):

$$V_s = V_{ext,0} \frac{10^{pH_0-14} - 10^{pH_t-14}}{10^{pH_t-14} - C_{OH^-}^{int}} \quad (1)$$

where  $pH_0$ ,  $pH_t$  and  $C_{OH^-}^{int}$  and  $V_{ext,0}$  are the initial pH of external phase, the pH of external phase after mixing with emulsion phase at time  $t$ , the initial concentration of  $OH^-$  in the internal phase, and the initial volume of external phase, respectively. The percentage of emulsion breakage (EB (%)) was calculated using equation (2):

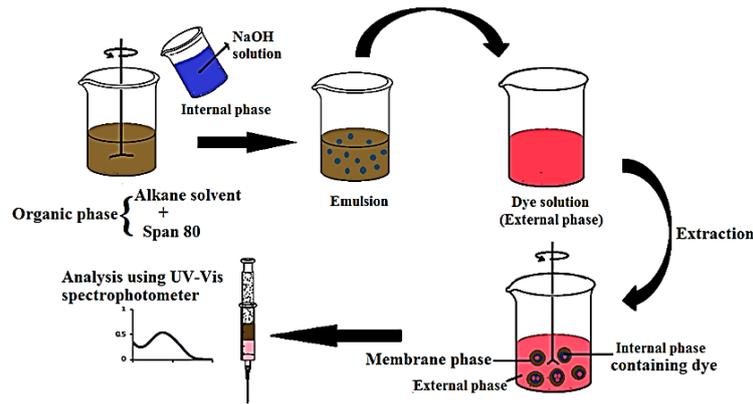


Fig. 2 Schematic of emulsion preparation and dye extraction process

Extraction (%) of dye using ELM was calculated using the following equation

$$\text{Extraction (\%)} = \frac{C_0 - C_t}{C_0} \times 100 \quad (3)$$

where  $C_0$  is the initial concentration of dye, and  $C_t$  is dye concentration at time  $t$ . Extraction tests were conducted for acridine orange with different concentrations (10, 20 and 40 mg/L), and all experiments were conducted using different solvents in order to reach the best efficiency. Diffusion coefficient of acridine orange as solute molecule in different alkane solvents was calculated by Wilke-Chang equation (Seader, Henley *et al.* 1998)

$$D_{AB} = \frac{7.4 \times 10^{-8} (\phi_B M_B)^{1/2} T}{\mu_B \nu_A^{0.6}} \quad (4)$$

where  $D_{AB}$  is diffusion coefficient of solute in each solvent ( $\text{cm}^2/\text{s}$ );  $M_B$  is molecular mass of solvent ( $\text{g}/\text{mol}$ );  $\mu_B$  is solvent viscosity (centipoises);  $T$  is temperature (K);  $\nu_A$  is liquid molar volume of solute at its normal boiling point ( $\text{cm}^3/\text{mol}$ ), and  $\phi_B$  is an association factor for the solvent which is 1.0 for unassociated solvents such as hydrocarbons (Schotte 1992, Demirel 2007).

Finally, the efficiency of ELM was evaluated in removal of other cationic dyes of methylene blue, methyl violet and crystal violet from aqueous external solution.

### 3. Results and discussion

#### 3.1 Influence of different parameters on emulsion stability

##### 3.1.1 Type of solvent

Type of solvent is one of the highly influential parameters on the efficiency of ELM. Based on the literature review, in many studies, up to now, n-hexane has been employed as solvents (Chiha, Hamdaoui *et al.* 2010, Dâas and Hamdaoui 2010, Lende and Kulkarni 2015); however, other alkane-based solvents with a higher viscosity have not been used so far in this regard. Thus, in this research, influence of various organic solvents of n-hexane, n-heptane, n-octane and n-decane on stability of membrane was investigated. In this case, an emulsification time of 6 min, a volume ratio of internal phase to organic

phase of 1/1, a volume ratio of emulsions to external pure water phase of 1/5, a stirring speed of 300 rpm, a concentration of Span 80 of 5% (w/w) and a concentration of internal phase of 0.05 M were selected as experimental conditions. Results of breakage percent versus time for various solvents are depicted in Fig. 3.

According to the literature, solvent viscosity plays a key role in the stability of emulsion; however, it should be noticed that an optimum amount of solvent should be used since a high viscosity creates a resistance against mass transfer, thereby reducing the speed of extraction. On the other hand, low viscosity of solvent may lead to instability and break-up of emulsion (Chakravarti, Chowdhury *et al.* 1995, Mokhtari and Pourabdollah 2012). According to the results, although the emulsion stability caused by the applied solvents is more or less the same during the first 3 to 4 min of experiment commencement, it decreased in the following order: n-octane > n-decane > n-hexane > n-heptane. It means that the emulsion prepared by n-octane as solvent presented the best stability in comparison with those prepared by other solvents. This behavior can be explained by a lower viscosity of n-hexane (0.31 cP) and n-heptane (0.41 cP) compared with n-octane (0.50 cP) leading to a more easily formation of emulsion (Thompson and Doraiswamy 1999). Based on the obtained results, n-octane was selected as the best solvent (diluent) for the preparation of emulsion in the next stages of stability tests.

##### 3.1.2 Concentration of span-80

In this stage, various concentrations of span-80 (2, 5 and 8% (w/w)) were applied to fabricate emulsion. As seen in Fig. 4, the emulsion prepared by 5% of span-80 offered the lowest amount of breakage (about 0.2%) during 10 min, while the higher (8%) and lower (2%) amounts of surfactant led to considerable increments of about 13 and 6.5% in the breaking-up of the emulsion, respectively. The surfactant concentration plays a crucial role in the liquid membrane stability. Surfactant with concentrations less than the optimum amount leads to breakage of emulsion because it is not able to surround all the internal phase. On the other hand, high amounts of surfactant create some aggregates which act like reservoirs promoting the water transport to the external (swelling phenomenon) or internal phase (breakage) (Chiha, Samar *et al.* 2006, Venkatesan and

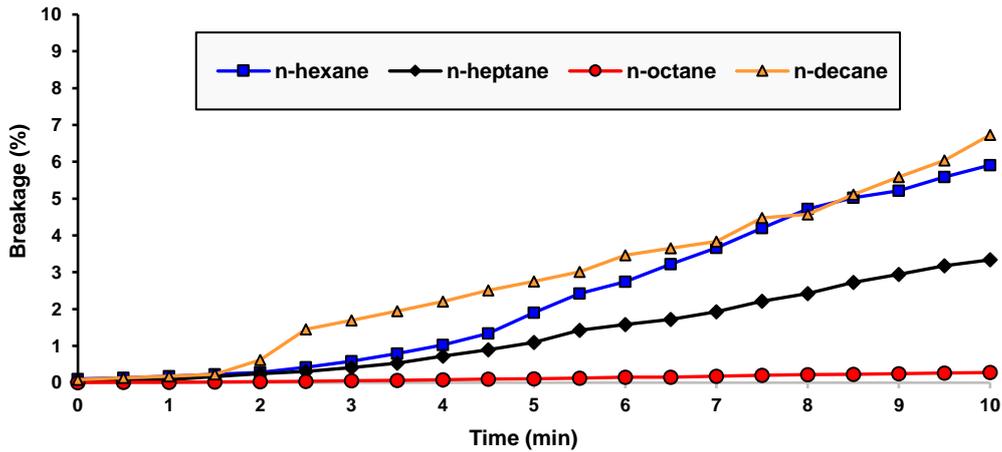


Fig. 3 Effect of solvent on the stability of emulsion (experimental conditions: 5% (w/w) concentration of surfactant, 0.05 M concentration of internal phase, stirring speed of 300 rpm, emulsification time of 6 min, volume ratio of internal phase to organic phase of 1/1 and volume ratio of emulsions to external pure water phase of 1/5)

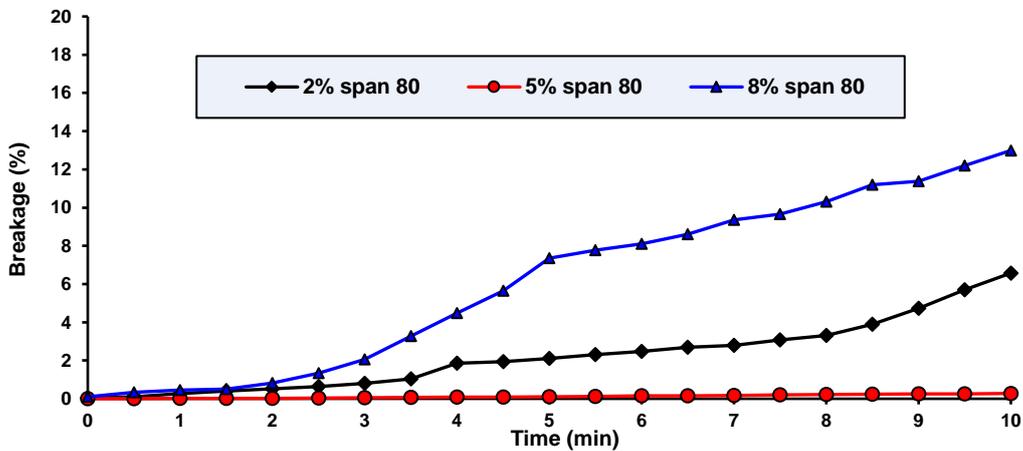


Fig. 4 Effect of surfactant concentration on the emulsion stability (experimental conditions: n-octane as solvent, 0.05 M concentration of internal phase, stirring speed of 300 rpm, emulsification time of 6 min, volume ratio of internal phase to organic phase of 1/1 and volume ratio of emulsions to external pure water phase of 1/5)

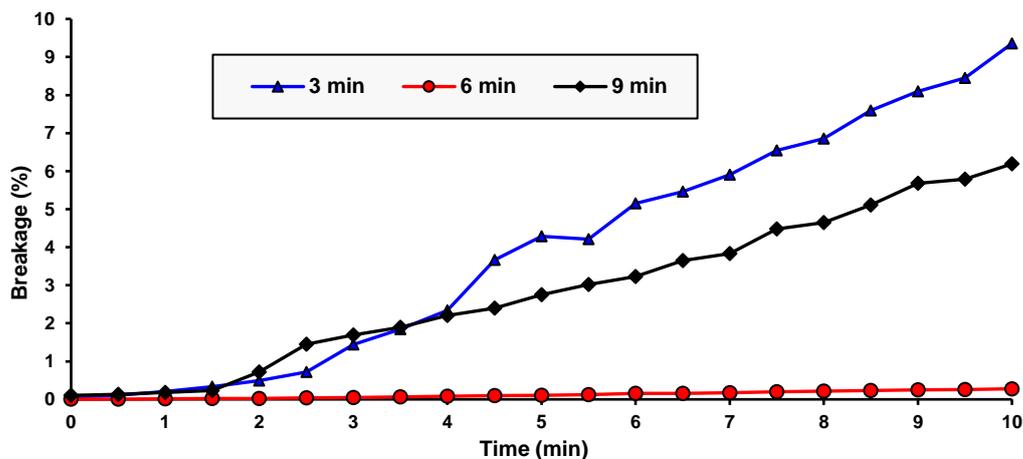


Fig. 5 Effect of emulsification time on the emulsion stability (experimental conditions: n-octane as solvent, 5% (w/w) concentration of surfactant, 0.05 M concentration of internal phase, stirring speed of 300 rpm, volume ratio of internal phase to organic phase of 1/1 and volume ratio of emulsions to external pure water phase of 1/5)

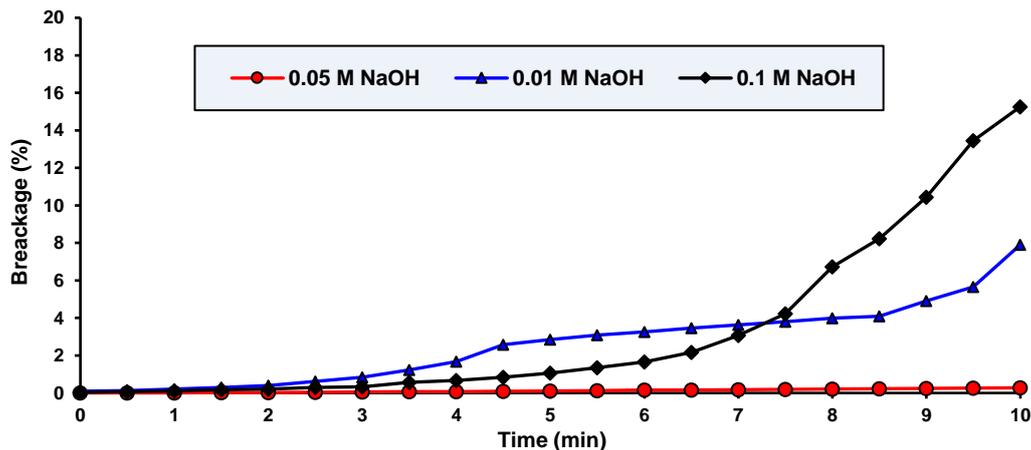


Fig. 6 Effect of concentration of internal aqueous phase on the emulsion stability (experimental conditions: n-octane as solvent, 5% (w/w) concentration of surfactant, stirring speed of 300 rpm, emulsification time of 6 min, volume ratio of internal phase to organic phase of 1/1 and volume ratio of emulsions to external pure water phase of 1/5)

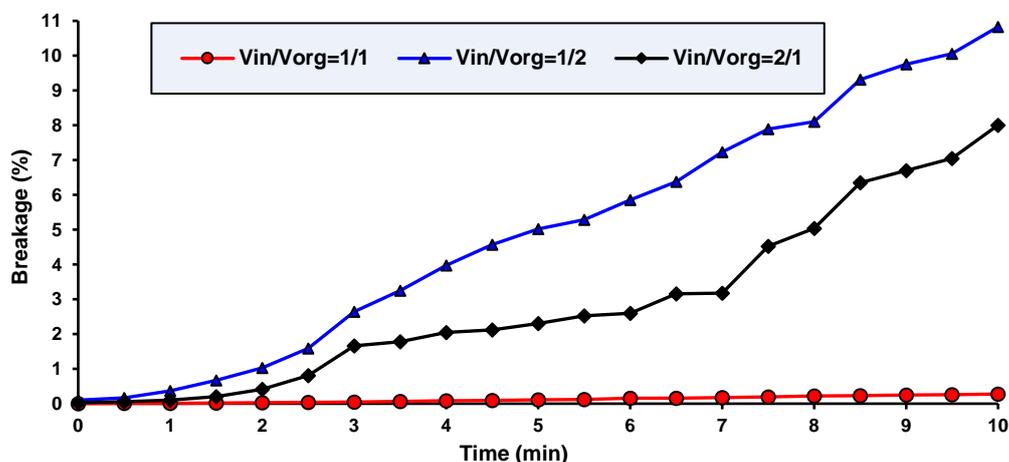


Fig. 7 Effect of volume ratio of internal phase ( $V_{in}$ ) to organic phase ( $V_{org}$ ) on the emulsion stability (experimental conditions: n-octane as solvent, 5% (w/w) concentration of surfactant, 0.05 M concentration of internal phase, stirring speed of 300 rpm, emulsification time of 6 min and volume ratio of emulsions to external pure water phase of 1/5)

Begum 2009). Hence, an exact caution must be taken in the employment of surfactant, and a suitable amount (minimum and adequate) must be used to reach the most stable emulsion. Based on the results, the concentration of 5% (w/w) of span-80 was selected as the optimum amount since it led to the highest stability of emulsion.

### 3.1.3 Emulsification time

To probe the influence of emulsification time on the stability, the emulsion was prepared during 3, 6 and 9 min, and experimental conditions were similar to the aforementioned circumstances using n-octane as solvent and 5% w/w of span-80. The results (Fig. 5) showed that increasing the emulsification time from 3 to 6 min considerably improved the emulsion stability, while a higher increment (from 6 to 9 min) led to a reduction in the stability and an increment in the emulsion breakage. The detected improvement in the emulsion stability observed at 6 min might be due to the reduction of droplets in the internal aqueous phase, thereby improving the homogeneity of emulsion phase. By increasing the emulsification time

more to 9 min, the breakage percent increased to about 6%, probably as a result of increasing the number of droplets and therefore, the attachment of droplets during the addition of emulsion to the external phase (Djenouhat, Hamdaoui *et al.* 2008, Chiha, Hamdaoui *et al.* 2010). Hence, the emulsification time of 6 min was chosen as the optimum time.

### 3.1.4 Concentration of internal aqueous phase

The influence of concentration of sodium hydroxide in the internal aqueous phase was investigated using various concentrations of 0.01, 0.05 and 0.1 M. The other experimental conditions were identical to the former section with an emulsification time of 6 min. Emulsion stability were almost similar for all prepared emulsions for the first 5 min (see Fig. 6); however, a considerable difference was observed by the passage of time. Increasing the sodium hydroxide concentration from 0.01 to 0.05 M significantly decreased the emulsion breakage (increased the stability) from about 8% to 0.3%, respectively. The application of an internal phase with a higher concentration (0.1 M) reduced

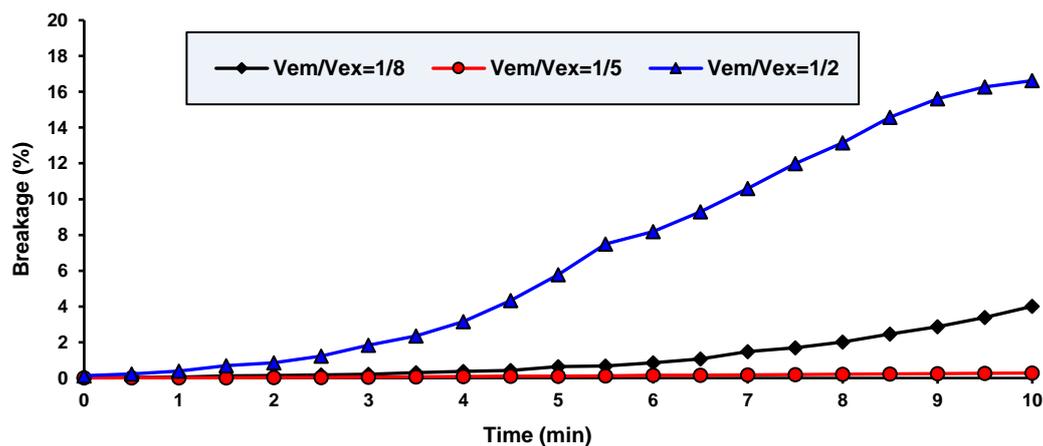


Fig. 8 Effect of volume ratio of emulsion phase ( $V_{em}$ ) to external pure water phase ( $V_{ex}$ ) on the emulsion stability (experimental conditions: n-octane as solvent, 5% (w/w) concentration of surfactant, 0.05 M concentration of internal phase, stirring speed of 300 rpm, emulsification time of 6 min and volume ratio of internal phase to organic phase of 1/1)

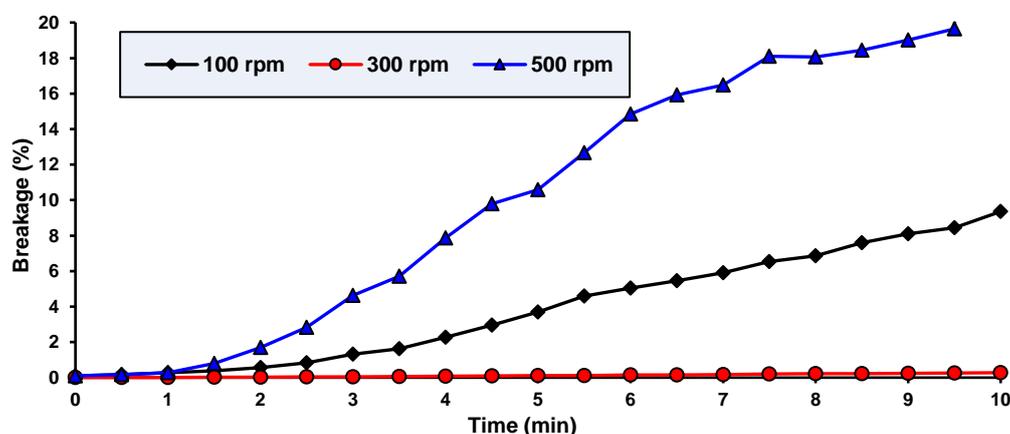


Fig. 9 Effect of speed of stirring on the emulsion stability (experimental conditions: n-octane as solvent, 5% (w/w) concentration of surfactant, 0.05 M concentration of internal phase, emulsification time of 6 min, volume ratio of internal phase to organic phase of 1/1 and volume ratio of emulsions to external pure water phase of 1/5)

the emulsion stability due to excess NaOH which caused swelling of emulsion (Agarwal, Das *et al.* 2010). and also due to the more interaction between sodium hydroxide and span-80 resulting in a decrement in span-80 proficiency (Chiha, Samar *et al.* 2006). According to the results, 0.05 M concentration of sodium hydroxide was selected as the best concentration of the internal phase leading to a higher stability of emulsion.

### 3.1.5 Volume ratio of internal phase to organic phase

The effects of various volume ratios of aqueous internal phase to organic phase (1/2, 1/1 and 2/1) on the emulsion stability were investigated under the experimental conditions of the previous section with 0.05 M concentration of the internal phase (see Fig. 7).

Emulsion stability considerably increased as the volume ratio rose from 1/2 to 1/1 because of the simplicity of the repelling of the internal phase in an emulsion with higher proportion. Therefore, in an emulsion with a volume ratio of 1/2, the breakage percent is higher. The breakage

amounts in Fig. 7 declare that a higher volume ratio of the internal phase to organic phase (2/1) offered a lower stability in comparison with the ratio of 1/1. In fact, due to the increment in the volume of internal phase, the volume of organic phase would not be sufficient surrounding all the internal aqueous phase which leads to instability of emulsion (Kumbasar 2008, Tang, Yu *et al.* 2010). Hence, the optimum volume ratio of internal phase to organic phase was selected as 1/1 due to higher stability of emulsion phase.

### 3.1.6 Volume ratio of emulsion phase to external pure water phase

Influence of volume ratio of emulsion phase to external phase with various ratios of 1/8, 1/5 and 1/2 was studied under optimum amounts obtained in the previous sections. Based on the results depicted in Fig. 8, an increment in the volume ratio from 1/8 to 1/5 remarkably improved the stability due to a reduction in swelling (Sulaiman, Othman *et al.* 2014); however, a higher increment to 1/2 caused a significant reduction in the stability. This behavior may be a result of coagulation and attachment of emulsion phase due

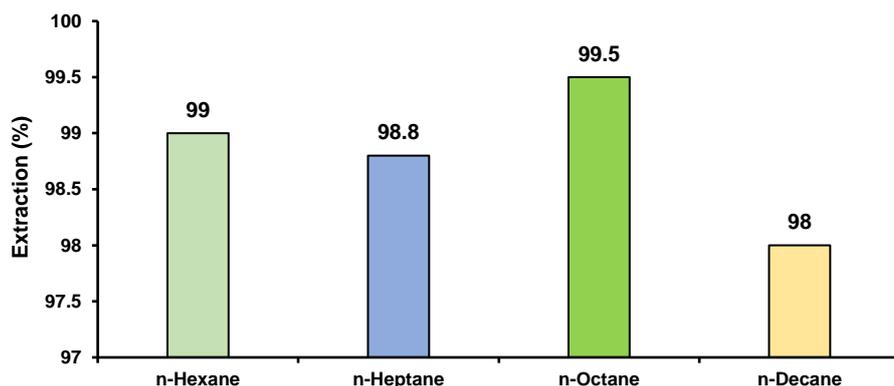


Fig. 10. Effect of solvent type on the removal of acridine orange from external phase (experimental conditions: 5% (w/w) concentration of surfactant, 0.05 M concentration of internal phase, stirring speed of 300 rpm, emulsification time of 6 min, volume ratio of internal phase to organic phase of 1/1 and volume ratio of emulsions to external phase of 1/5)

to the reduction of emulsion phase proportion relative to the external phase (Kageyama, Matsumiya *et al.* 2004, Tang, Yu *et al.* 2010). Accordingly, the volume ratio of 1/5 was taken as the optimum amount regarding the higher emulsion stability.

### 3.1.7 Speed of stirring

The speed of stirring is another parameter influential on the emulsion stability. Hence, various speeds of 100, 300 and 500 rpm were selected to prepare emulsion phase. At this stage, experimental conditions were based on the optimum amounts obtained previously. Generally, due to increments in shear force, increasing the stirring speed reduces the droplet size of emulsion, thereby improving the emulsion stability (Chiha, Hamdaoui *et al.* 2010). In this regard, it should be noticed that the obtained results of this study were in accordance with this claim (see Fig. 9). As the stirring speed rose from 100 to 300 rpm, the emulsion stability accordingly improved. However, the stability diminished in the higher speed of 500 rpm as a result of decrement of droplets resistance against shear force due to high reduction of droplet size at this speed. Similar trends were also reported in some relevant literature (Djenouhat, Hamdaoui *et al.* 2008, Dâas and Hamdaoui 2010). This phenomenon is due to the increment in the osmotic swelling of the organic phase (membrane) which makes the emulsion instable (Djenouhat, Hamdaoui *et al.* 2008). Therefore, the stirring speed of 300 rpm was selected as the optimum speed of agitation in this study.

### 3.2 Efficiency of ELM in acridine orange extraction

In this connection, 40 ML of emulsion solution was mixed with 200 mL of the external solution containing 20 mg/L of acridine orange under the optimum experimental parameters obtained in the stability section. Effects of solvent type using different organic solvents on the removal of acridine orange from external phase (feed solution) have been presented in Fig. 10. As it is observed, the employed solvents offered different behaviors in the removal of dye, and the efficiency of the prepared ELM increased with an order of n-octane>n-hexane>n-heptane>n-decane. Solvent

viscosity is a crucial parameter effective on the performance of liquid membrane because it controls the stability of emulsion, and also the performance of membrane in extraction of solute (Chakravarti, Chowdhury *et al.* 1995, Mokhtari and Pourabdollah 2012). Viscosity of the employed solvents changes with the following order: n-decane (0.84 cP)> n-octane (0.50 cP)> n-heptane (0.41 cP)> n-hexane (0.31 cP). Another influential parameter in transferring solute (dye) through a liquid membrane is diffusion coefficient of solvent (membrane).

Results of calculating the diffusion coefficients of acridine orange in all employed alkane based solvents are presented in Table 2. The results clearly exhibit that diffusion coefficient of acridine orange in alkane solvents decreases with increasing of the solvent molecular mass and viscosity (Erkey, Rodden *et al.* 1990). The mobility of each component is associated with Brownian motion as random movement of molecules as a function of diffusion coefficient and viscosity at a specific temperature. Although the mobility is improved by decreasing the viscosity as well as increasing diffusion coefficient (Leahy-Dios and Firoozabadi 2007), to reach the highest mass transfer, there should be a balance between solvent viscosity and diffusion coefficient. In this study, dye extraction improved by increasing the viscosity of solvent from n-heptane to n-octane; however, applying n-decane as solvent (diluent) led to the least efficiency in removal of acridine orange from the external phase as a result of significant resistance against mass transfer (high viscosity and low diffusion coefficient) which was created by this solvent in comparison with others. In fact, there should be an optimum amount of viscosity for a solvent in which the emulsion stability (impressed by solvent viscosity) and membrane capability in transferring of pollutants (diffusion coefficient of solvent) acts simultaneously to reach the best ELM.

To assess the external phase concentration, acridine orange solutions with different concentrations of 10, 20 and 40 mg/L were prepared. Based on the results (Fig. 11), the extraction was improved by increasing the concentration from 10 to 20 mg/L. This observation may be due to the enhancement of driving force so that an increment in solute transfer from the external solution towards the internal

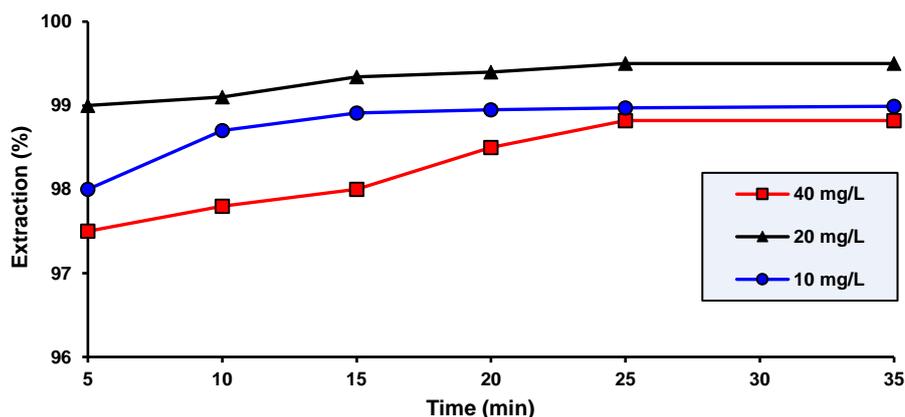


Fig. 11 Effect of concentration of acridine orange in the external phase on the extraction (experimental conditions: n-octane as the solvent, 5% (w/w) concentration of surfactant, 0.05 M concentration of internal phase, stirring speed of 300 rpm, emulsification time of 6 min, volume ratio of internal phase to organic phase of 1/1 and volume ratio of emulsions to external phase of 1/5)

Table 2 Diffusion coefficients of solute in solvents

Solvent	Molecular mass ( $M_B$ , g/mol)	Solvent viscosity ( $\mu_B$ , cP)	Diffusion coefficient ( $D_{AB}$ , $\text{cm}^2/\text{s}$ )
Hexane	86	0.31	$2.16 \times 10^{-5}$
Heptane	100	0.41	$1.76 \times 10^{-5}$
Octane	114	0.50	$1.54 \times 10^{-5}$
Decane	142	0.84	$1.02 \times 10^{-5}$

phase was achieved (Wan, Wang *et al.* 1997, Ahmad, Buddin *et al.* 2017). Dye extraction from an external phase with a higher concentration (40 mg/L) reduced due to the saturation of interface between membrane and droplets of the internal phase (Wan, Wang *et al.* 1997, Ahmad, Buddin *et al.* 2017). This phenomenon increases the resistance against the passage of dye, thereby decreasing the extraction efficiency of membrane.

### 3.3 Efficiency of ELM in removal of cationic dyes from water

Capability of emulsion liquid membrane in extraction of methylene blue, methyl violet and crystal violet from an aqueous phase was evaluated under the optimum conditions obtained in the previous sections. The experimental parameters were similar to the former section, and n-octane was utilized as solvent. As it is observed from the obtained extraction data (Fig. 12), the prepared liquid membrane revealed almost a perfect capability in the extraction of cationic dyes from water. All the applied dyes possessed almost similar structures comprising aromatic rings. Therefore, the prepared ELM membrane extracted almost completely all dyes from external phase. Meanwhile, the extraction amount of acridine orange was lower in comparison with the other tested cationic dyes, probably due to a higher positive charge of methylene blue, methyl violet and crystal violet dyes causing more interaction with stripping agent in the internal phase.

## 4. Conclusion

In this research, liquid surfactant membranes were prepared using n-alkanes (n-hexane, n-heptane, n-octane and n-decane) with different viscosities, span-80 as emulsifying agent and sodium hydroxide as stripping agent in the internal phase. The stability of membranes was evaluated under various operating conditions of surfactant concentration, emulsification time, internal phase concentration, volume ratio of internal phase to organic phase, volume ratio of emulsion phase to external phase, and stirring speed, and an emulsion liquid membrane with the best stability was employed in extraction of acridine orange from the external aqueous phase. The following results have been achieved: (1) Stability of emulsion was influenced by solvent viscosity, and the membrane prepared by n-octane as solvent offered the least breakage among the others due to an easier formation of cavitation bubbles. It was revealed that although viscosity of solvent played a positive role in improving the stability of emulsion, solvents with a high viscosity offered an unsuitable stability (i.e. n-decane). (2) The emulsion with the least breakage (0.2%) was prepared under the following experimental parameters: concentration of surfactant (5% (w/w)), concentration of internal phase (0.05 M), stirring speed (300 rpm), emulsification time (6 min), volume ratio of internal phase to organic phase (1/1) and volume ratio of emulsions to external phase (1/5). (3) The emulsion liquid membrane, which was prepared by n-octane, extracted more than 99% of acridine orange from external phase, and its efficacy was the best among the other liquid membranes prepared by other alkane-based solvents. It was concluded that viscosity and diffusion coefficient factors of a solvent are simultaneously influential on improving the efficiency of membrane, so an optimum amount should be practically determined. (4) The prepared emulsion liquid membrane in this endeavor was more successful in extraction (100%) of methylene blue, methyl violet and crystal violet from external phase compared with acridine orange. It was due to a higher positive charge of the tested cationic dyes in comparison with acridine orange and also more interactions with stripping agent in the internal phase.

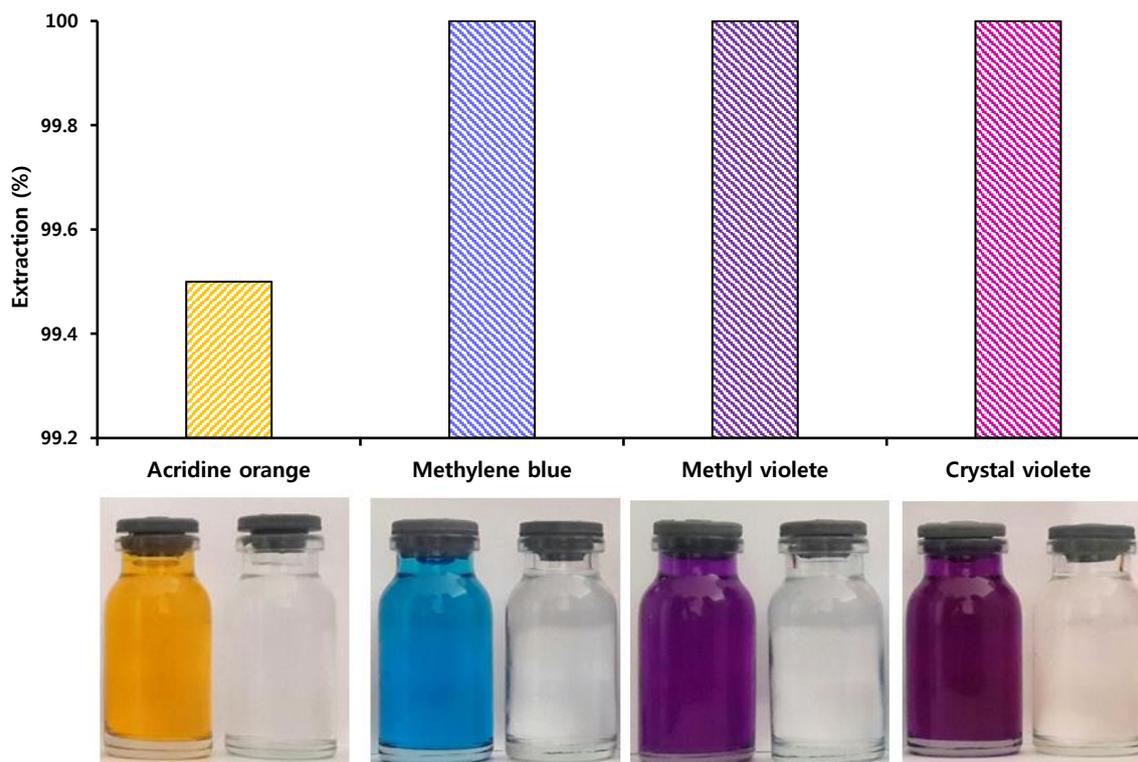


Fig. 12. Extraction of cationic dyes using prepared ELM (experimental conditions: n-octane as the solvent, 5% (w/w) concentration of surfactant, 0.05 M concentration of internal phase, stirring speed of 300 rpm, emulsification time of 6 min, volume ratio of internal phase to organic phase of 1/1 and volume ratio of emulsions to external phase of 1/5)

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