Emulsion Liquid Membrane for Textile Dye Removal: Stability Study

by Samsudin Anis

Submission date: 30-Aug-2019 08:54AM (UTC+0700)
Submission ID: 1165066490
File name: on_liquid_membrane_for_textile_dye_removal._Stability_study.docx (56.16K)
Word count: 2308
Character count: 12913

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Abstract. Although textile dyes is basically available in very low concentration; it should be removed due to the toxicity to human body and environment. Among the existing methods, emulsion liquid membrane (ELM) is a promising method by providing high interfacial area and the ability to remove a very low concentration of the solute. The optimal emulsions were produced using commercially supplied homogeniser. The drop size was measured by the aid of microscope and image J software. Initially, methylene blue in simulated wastewater was extracted using a stirrer. Methylene blue concentration was determined using spectrophotometer. The research obtained optimal emulsion at surfactant concentration of 4 wt. %, kerosene as diluent, emulsification time of 30 min, emulsification speed of 2000 rpm. The lowest membrane breakage and the longest stability time were about 0.11% and 150 min, respectively.

INTRODUCTION

Emulsion liquid membrane (ELM) method has been established for few decades. ELM is an alternative of conventional liquid/liquid extraction. Having high interfacial area, the system was able to selectively recover solute. The method has successfully extracted solute even in very low concentration by almost no loss of organic solution. The combination of extraction and stripping processes in one stage contributes to the economics of this method.

ELM involves the use of double emulsion, the most common is the water in oil in water system. The other type is oil in water in oil system. This double emulsion system is facing stability problem, especially towards the shear caused by mixing process during extraction. Membrane breakage and swelling are the most two common instability problem of ELM system.

Some researchers found that ELM processes suffered emulsion instability of membrane breakage in about 8% and emulsion swelling in about 35%. These facts needs further concern since the ELM tolerance for membrane breakage and emulsion swelling are about 0.1% and 10%, respectively.

The best performance of solute extraction could be achieved by employing optimallly stable emulsion. Theoretically, increasing surfactant concentration is helpful in maintaining emulsion stability. However, it can be detrimental to extraction performance. The improvement of extraction speed contributes to the enhancement of extraction efficiency, nevertheless, it ruins emulsion stability in term of membrane breakage. This phenomenon results in the release of entrapped solute to the external phase thus decreasing extraction efficiency.

Stable emulsion that determines emulsion performances included large mass transfer area resulted by tiny emulsion. Li et al. found that combination of rapid extraction rates and good stability are produced by emulsions with droplets size of 0.3 to 10 μm (preferably 0.8 to 3 μm). Emulsion is commonly produced by the aid of mechanical agitation included homogeniser, mixer, and stirrer. The appropriate emulsion formulation is inevitable to deliver optimally tiny and stable emulsion.

Been declared as world heritage by UNESCO, batik has attracted more people. The production capacity of batik home industry increased rapidly. Batik is produced by many areas in Indonesia. Pekalongan, one of the well-known city of batik, is economically depending on batik industry. In 2011, there were 1342 small industries in Pekalongan, in which about 83.1% of them were batik industry. About 202.4 m^3 of industrial wastewater was monthly released by home industry producing 6000-20000 pieces of fabric. Unfortunately, only about 0.6% of industries have their own wastewater treatment installation, while the others dispose the wastewater directly to the environment.

Although harmful to the living organisms, heavy metal is widely used in textile industry. Chromium is an essential metal in the dyeing of wool and nylon materials. While cobalt, chromium and copper are inevitable in the dyeing of leather, wool and nylon. In the dyeing process, heavy metal gives excellent colour fastness. Metals are present in industrial liquid waste as free ionic or complex metal. Mordanting agent in the dyeing of wool contains chromium. Chromium contained C.I. Mordant Black 11 is the most widely used in the textile dye processing. Copper salt is used as fixator agent in the dyeing of direct dyes to get good colour fastness. Cationic dyes contain zinc, mercury, cadmium and impurities as impurities. Oxidation process of the dyeing using vat and sulphur dyes involving heavy metal as well. Finishing process of direct dyes need the use of heavy metals. The most widely used dyes in the textile industry are acid, alkali, direct, disperse, reactive and vat dyes that contain chromium, arsenic, cadmium, mercury, copper, lead and zinc.

This research emphasize the existence of dyes in textile industrial liquid waste. Without any prior treatment, the disposal of textile dyes may result in serious health problems. Textile dyes recovery is of important to achieve environmental-friendly industrial process. Simple and economic but selective method is urgently required due to the high waste discharge in relatively low concentration of dye. Study of emulsification method involving selection of membrane phase solution as well as optimisation of emulsification speed and time was done. Emulsion characterisation was investigated in term of membrane breakage and stability time.

THEORY

ELM system involved the utilization of primary emulsion that consists of membrane and stripping phase. The both dispersed in the feed or effluent phase, which is the phase to be treated. Carrier acts as an organic soluble extractant, used for solute separation even in very low concentration. The mechanism of dye transport in ELM system is shown in Figure 1. The dye and carrier form a complex that is soluble in the membrane phase. Subsequently, this complex will permeate through the membranes from the outer to the inner interface. At the inner interface, the complex decomposes by reversal of the equilibrium reaction and the dye ion is released into the internal phase and the regenerated free carrier diffuse back into the membrane phase.

METHODS

This research offer the recovery of dyes from textile industrial liquid waste using emulsion liquid membrane. In the beginning, emulsion was produced by varying concentration of surfactant at 2-8 wt. %, diluent type of oxylene, kerosene, and n-heptane as well as volume ratio of membrane to internal phase of 2, 3, and 5. The operating condition to be varied are emulsification time of 20-45 min and speed of 1000-2500 rpm. The obtained emulsion was then allowed to stand to determine its stability time. Extraction process involving emulsion and feed phase at treatment ratio of 1:5 was executed in a stirred vessel. Sample was taken after 15 min of extraction. The raffinate was taken to test final concentration of textile dye.

The research employed reagents of analytical grade. All aqueous solutions were prepared with deionized water. The surfactant used was Span 80. Hydrochloric acid (HCl) was used as internal phase. Span 80, HCl, and kerosene were obtained from Sigma Aldrich. The aqueous feed solution was prepared of methylene blue diluted in the deionized water.

The droplet sizes of w/o emulsions were measured using Olympus optical microscope equipped with camera. The solution pH was measured using Fisher Scientific accumet AB15 pH meter. The concentration of methylene blue was determined spectrophotometrically using UV Vis Spectrophotometer.

RESULT AND DISCUSSION

The membrane and internal phase could be mechanically mixed by reducing the interfacial tension. Surfactant as surface active agent contributes to the decrease of interfacial tension of membrane and internal phase. Surfactant concentration was investigated at 2 wt. %, 4 wt. %, 6 wt. %, and 8 wt. %. The effects to membrane breakage and stability time were carefully examined. The membrane breakage and stability time of W/O emulsion obtained at different surfactant concentration is presented in Figure 2. The figure reveals that membrane breakage insignificantly increased by the increase of surfactant concentration from 2 wt. % to 4 wt. % on the contrary the stability time increased by the increase of surfactant concentration. The most stable emulsion was produced by emulsion prepared of surfactant concentration of 4 wt. %. Emulsion given by system with surfactant concentration of 2 wt. % resulted in acceptable membrane breakage, however, it experienced in shorter stability time. The phenomenon was due to the fact that at 2 wt. % of surfactant, the emulsion system suffered from insufficient concentration of surfactant, in which the membrane phase unable to completely cover the internal phase solution. The amount of surfactant was not enough to stabilise the emulsion thus the emulsion had separated into two phases in shorter times. This condition is not acceptable for practical application. On the other hand, increasing surfactant concentration beyond optimal value is also not favourable. The excess of surfactant or micelles was adsorbed to emulsion surface thus triggered droplets coalescence. Optimal stable emulsion could be produced by precisely considering surfactant concentration since increasing surfactant concentration beyond critical point only results in insignificant effect on the emulsion stability. Emulsion stability tends to be distracted by excessive surfactant concentration. The result confirmed that of Venkatesan and Begum which revealed the same trend.

The following study of emulsification involving the investigation of membrane breakage and stability time as results of diluent type. During the emulsification study, three types of diluent were utilized, i.e. oxylene, kerosene, and n-heptane. Each diluent was used by maintaining other variables constant. Figure 3 reveals the result given under variation of diluent type. It is seen that oxylene produced emulsion with the highest membrane breakage and the shortest stability time. The best condition was achieved by emulsion composed of kerosene in the membrane phase. Kerosene, as having moderate viscosity of 1.64 cP and grouped in the aliphatic diluent performed good stability. Othman and Goto found that emulsion produced by aliphatic diluent is more preferable because of its insolubility in water. Moreover, the high boiling point, low toxicity, and its commercially availability makes kerosene a promising diluent.

Obtaining optimal condition of surfactant concentration and diluent type, emulsification study was continued in the variation of volume ratio of membrane to internal phase. In this stage, volume ratio of membrane to internal phase was examined at 2, 3, and 5 as shown in Figure 4. It is depicted that the lowest volume ratio of 2 resulted in high membrane breakage. Less amount of membrane phase follows the lower volume ratio of membrane to internal phase. As is known, internal phase solution could not be completely covered by low volume of membrane solution thus it resulted in less stable emulsion. Optimal volume ratio of membrane to internal phase was obtained at 3 which performed the best stability time of about 150 min. Further increase in the volume ratio tends to thicken emulsion wall and enhance surface tension thus triggered complicate dispersion of emulsion droplets. The emersion of emulsions coalescence dropped stability time.

Figure 4 also depicts membrane breakage phenomenon as the effect of phase ratio. Commercially unacceptable membrane breakage of about 10 % was given by phase ratio 2. Phenomenon of membrane breakage was enhanced under the production of thin emulsion walls due to the lack amount of membrane solution. Acceptable membrane breakage of about 0.11% was successfully obtained by phase ratio of 3. Increasing phase ratio to be 5 sharply increased membrane breakage to be about 13%. Difficult emulsion droplets dispersion faced at this phase ratio. The incomplete process of emulsification led to higher membrane breakage during extraction process.

Emulsion diameter was examined at various emulsification times within the range of 20-45 min. Membrane breakage and stability time as a function of the emulsification time is displayed in Figure 5. The irradiation time was increased from 20 min to 45 min with 5 min steps. Longer stability time yielded by longer emulsification time is indicated by the figure. Longer emulsification time provided greater energy to the system thus ensured the homogeneity as well as the intensity of mixture solution. More tiny emulsion could be produced by the increase amount of shrunk and entrapped internal phase solution as theoretically finer droplets would be yielded at longer emulsification time. Nevertheless, excessive amount of fine droplets in turn facilitated coalescence, resulting in emulsion instability. Prolonging emulsification time beyond 30 min started to decrease stability time. Optimal

emulsification time was found to be 30 min that would be used for subsequent experiments. This results agreed with the investigation carried out by Djenouhat et al., in which excessive emulsification time triggered emulsions coalescence thus enhancing emulsion instability phenomenon.

Another study on emulsification is reported in Figure 5. It describes the membrane breakage as the effect of emulsification time. High membrane breakage of more than 60% inferred the occurrence of incomplete emulsification process. At the shortest emulsification time of 20 min, internal phase was not perfectly covered by membrane solution since it unable to homogenise the emulsion solution. Big and unstable emulsion suffered from low extraction efficiency and high membrane breakage. Extending emulsification time to be 25 min could enhance stability time, nevertheless membrane breakage percentage of about 8% was not acceptable for commercial use. The commercially feasible emulsion was successfully prepared at emulsification time of 30 min, which has membrane breakage of about 0. 11%. Slight increment of membrane breakage to be 0.14% was resulted by lengthening emulsification until 35 min. Although the membrane breakage was in the range to be acceptable, but for the sake of process efficiency, shorter emulsification time is more preferable. Further addition of emulsification time even gave emulsion with higher membrane breakage and shorter stability time.

Investigation on effect of emulsification speed to membrane breakage and stability time was done at speed variation of 1000, 1500, 2000, and 2500 rpm. Figure 6 depicts that membrane breakage decreased by the increase of emulsification speed of 1000 to 2000 process. After 2000 ppm, membrane breakage started to increase back. The size and number of emulsion droplets vary according to the agitation speed used in the emulsion preparation. Higher emulsification speed will produce smaller diameter and much more emulsion droplets than that of lower emulsification speed. On the contrary, for higher emulsification speed, the breakage is increased due to high internal shearing leading to a very high number of small droplets by volume unit.

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