Jurnal Teknologi

Full Paper

ENHANCING TEXTILE DYE REMOVAL IN EMULSION LIQUID MEMBRANE SYSTEM USING TAYLOR COUETTE COLUMN

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Article history
Received
15 March 2017
Received in revised form
18 November 2017
Accepted
15 January 2018
Published online
1 April 2018

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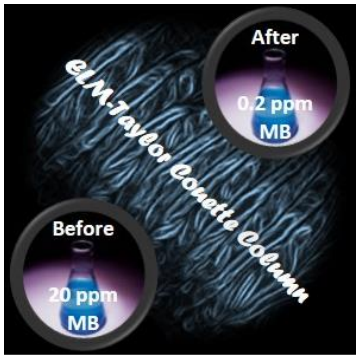
Graphical abstract



Abstract

Although textile dyes is basically available in very low concentration (10-200 ppm); 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. Initially, methylene blue in simulated wastewater was extracted using a Taylor-Couette column. Methylene blue concentration was determined using spectrophotometer. Complete extraction was performed in the designed column. The research obtained optimal extraction efficiency of about 99% at external phase pH of 10, carrier concentration of 9 wt. %, HCl concentration of 0.5 M, initial feed concentration of 20 ppm, volume ratio of emulsion to feed phase of 1:5, extraction time of 5 min, and extraction speed of 600 rpm.

Keywords: Emulsion liquid membrane, textile dye, methylene blue, extraction, Taylor-Couette column

Abstrak

Walaupun pewarna tekstil pada dasarnya terdapat dalam kepekatan yang sangat rendah (10-200 ppm); ia perlu dikeluarkan kerana ketoksikan kepada badan manusia dan alam sekitar. Antara kaedah yang sedia ada, membran emulsi cecair (ELM) adalah satu kaedah yang menjanjikan dengan menyediakan kawasan muka yang tinggi dan keupayaan untuk mengeluarkan kepekatan yang sangat rendah bahan larut. Emulsi optimum telah dihasilkan menggunakan homogeniser dibekalkan secara komersial. Pada mulanya, biru metilena dalam air sisa simulasi diekstrak menggunakan lajur Taylor-Couette. Kepekatan biru metilena telah ditentukan dengan menggunakan spektrofotometer. Pengekstrakan lengkap dilakukan dalam ruang yang direka. penyelidikan yang diperolehi kecekapan pengekstrakan optimum kira-kira 99% pada pH fasa luaran 10, kepekatan pembawa 9 wt. %; kepekatan HCl 0.5 M; kepekatan suapan permulaan sebanyak 20 ppm; nisbah jumlah emulsi untuk fasa suapan 1:5, masa pengekstrakan 5 min; kelajuan pengekstrakan 600 rpm.

Kata kunci: Membran cecair emulsi, pewarna tekstil, biru metilena, pengekstrakan, lajur Taylor-Couette

1.0 INTRODUCTION

Liquid-liquid extraction is a method used to extract compound from a solution into another liquid. The method also well-known as solvent extraction, which employs two separated chambers for extraction and stripping process. As an alternative of solvent extraction, emulsion liquid membrane (ELM) was developed to get more economical and efficient process. Unlike the original method, ELM combines extraction and stripping processes in a single container that makes the process more efficient, in terms of both cost and time. Involving the use of emulsion, this method offers high interfacial area to recover solute effectively. Another advantage of ELM method is that in this process, hardly can find any loss of organic solution. Many researchers have proved the capacity of ELM in recovering very low concentration of solute [1-4].

Transport mechanism in ELM occurs by the contribution of double emulsion, the most common is the water in oil in water (W/O/W) system. The other type of emulsion is oil in water in oil system. Emulsion instability problem threatens the effectiveness of overall ELM system. The most common instability problems take place in this system are membrane breakage and emulsion swelling. It was found that some researchers encountered membrane breakage and emulsion swelling in about 8% and 35%, respectively [5-10]. Based on the facts, in-depth study to overcome emulsion instability problem is important considering the ELM tolerance for membrane breakage and emulsion swelling are about 0.1% and 10%, respectively [11, 12].

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 rate, 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.* [13] 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.

Other than the formulation of emulsion, significant effect on the emulsion stability might arise from the operation parameters such as stirring speed and contact time. Many researchers applied the use of hight stirring speed to obtain optimal extraction efficiency [14, 15], nevertheless, accelerating mixing speed beyond certain values resulted in the degradation of emulsion quality. It is therefore an optimal stirring speed and contact time must be taken into account to obtain the optimum condition of emulsion. The conventional stirred vessel extraction process could be replaced by applying Taylor-Couette column as an alternative method to be maintain good emulsion stability as well as to reach high extraction rate [16]. This method provides relatively low and uniform fluid shear, and helps maintaining the stability of emulsion without compromising the extraction efficiency [16, 17]. The targeted compound is extracted within a Taylor Couette column in which the inner cylinder is rotated while the outer cylinder is fixed. The system provided high overall removal efficiencies in relatively short contact time. However, in general Taylor-Couette column with single inner cylinder rotation only works well in a small gap of the two cylinders for better fluid mixing thus impedes its working capacity [17]. The combination of using ultrasound emulsification and Taylor-Couette column permeation could minimise emulsion instability and increase extraction efficiency.

Batik is a resist-dyeing technique applied to textile. The patterns are reserved by applying wax using a copper stamp prior to dyeing. Once this process has done, the applied wax will be removed by boiling or scratching the cloth. The areas covered by wax keep their original colour; when the wax is removed the colour difference between the dyed and undyed areas forms the pattern. To obtain the desired colour, this process should be repeated as needed.

The demand of batik has been continuously increasing by the declaration of batik as world heritage by UNESCO. It trigerred the rapid increase of production capacity of batik home industry. In Indonesia, batik is produced by many areas. Pekalongan, one of the well-known city of batik, is economically depending on batik industry. Research by Fajri [18] showed that in 2011, there were 1342 small industries in Pekalongan, in which about 83.1% of them were batik industries. The home industry producing 6000-20000 pieces of fabric released about 202.4 m^3 of industrial wastewater monthly [19]. Unfortunately, due to the unavailability of wastewater treatment installation, about 99.4% of home industries directly disposed the wastewater to the environment without any prior treatment [18].

Despite its danger to the living organisms, the application of heavy metal in textile industry is inevitable. The dyeing of wool and nylon materials needs the addition of chromium (Cr). While cobalt (Co), copper (Cu) and Cr are inevitable in the dyeing of leather, wool and nylon. In the dyeing process, heavy metal contributes to the excellent colour fastness. Metals are present in industrial liquid waste as free ionic or complex metal. Mordanting agent in the dyeing of wool contains Cr. Cr contained C.I. Mordant Black 11 is the most widely used in the textile dye

processing. Cu salt is used as fixator agent in the dyeing of direct dyes to get good colour fastness. Cationic dyes contain zinc (Zn), mercury (Hg), and cadmium (Cd) 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 Cr, Cd, Hg, Cu, Zn, arsenic (As), and lead (Pb) [20]. In general, during dyeing process, 10-15% of the used textile dyes loss with the waste stream. It was reported that dye concentration in the water is in the range of 10-200 ppm [21, 22].

This research emphasizes the existence of dyes in textile industrial liquid waste. The disposal of textile dyes without any prior treatment may result in serious health problems. To achieve environmental-friendly industrial process, textile dyes recovery is important. To overcome environmental problem emerged by the relatively low concentration of dye in large quantity of waste water, a simple and economic as well as selective method is urgently required. Study of extraction method was done under Taylor-Couette column. The application of this column could solve instability problem which commonly occurs in conventional stirred vessel extractor. Permeation process was investigated in term of extraction efficiency. Previous study employed Taylor-Couette column equipped with belt as DC motor connector. Current research is done by developing Taylor-Couette column which is directly connected to DC motor.

2.0 METHODOLOGY

2.1 Material and Reagent

The non-ionic surfactant of sorbitan monooleate which is commercially known as Span 80 was used for stabilizing the emulsion. Bis(2-ethylhexyl phosphate) (D2EHPA) and kerosene were used as a mobile carrier and a diluent, respectively. Hydrochloric acid (HCl) was used as internal phase while Na_2CO_3 was used to adjust pH of external phase. Methylene blue was used as a textile cationic dye. Deionised water was used to prepare all aqueous solutions. The research employed reagents of analytical grade. Span 80, D2EHPA, kerosene, HCl, Na_2CO_3, and methylene blue were obtained from Sigma Aldrich. The aqueous feed solution was prepared of methylene blue diluted in the deionised water.

2.2 Experimental Procedures

This research offers the recovery of dyes from textile industrial liquid waste using emulsion liquid membrane. Emulsion liquid membrane produced in this work was a W/O/W emulsion. It basically consists of three liquid phases, namely, external, membrane, and internal phases.

In the beginning, the water in oil (W/O) emulsion was produced based on optimum condition reported in previous study [23]. It was prepared using surfactant concentration of 4 wt.%, D2EHPA diluted in kerosene volume ratio of membrane to internal phase of 3:1, emulsification time of 30 min, and emulsification speed of 2000 rpm. The obtained emulsion was then used to extract solute from external feed phase.

Feed phase solution was made by diluting certain methylene blue in the deionised water to make solution concentrations of 10-40 ppm. Extraction process was executed in a Taylor-Couette column by varying some parameters and operation conditions involving external phase pH, D2EHPA concentration, HCl concentration, volume ratio of emulsion to feed phase, extraction time, and extraction speed. In all experiments, the outer cylinder of Taylor-Couette column was rotated at various speeds whereas the inner cylinder was rotated in the opposite direction at a constant speed of 600 rpm. Table 1 provides detail parameters and operation conditions applied in this study. Once the extraction process completed, sample was taken. The raffinate was taken to test final concentration of textile dye.

Table 1 Extraction parameters and operation conditions

No	Parameters / Operation Conditions	Values
1	External Phase pH	8 – 12
2	Carrier Concentration (wt.%)	7 – 11
3	HCl Concentration (M)	0.1 – 0.6
4	Initial Feed Phase Concentration (ppm)	10 – 40
5	Volume Ratio of Emulsion to Feed Phase	1/9 – 1/3
6	Extraction Time (min)	1 – 30
7	Extraction Speed:	
	Inner cylinder rotation speed (rpm)	600
	Outer cylinder rotation speed (rpm)	0 – 600

Fisher Scientific accumet AB15 pH meter was used to measure pH of aqueous solutions. The concentration of remaining methylene blue in the raffinate phase and strip solution was determined spectro-photometrically using UV Vis Spectrophotometer.

3.0 RESULTS AND DISCUSSION

3.1 Effect of External Phase pH

Solute removal within ELM system is governed by pH of external feed phase. The formation of solute-carrier complex in the interface of external and membrane phase is affected by solution pH. The complex will only be built at suitable pH, which then they diffuse very

well through membrane phase towards internal stripping phase. Given by some literatures, complex formation rate is strongly affected by external phase pH [24]. Moreover, pH difference between external and internal phase might act as driving force for the extraction process. In the present study, effect of Na_2CO_3 concentration as the driving force for methylene blue extraction was investigated at pH of 8 - 12 while the internal phase concentration was kept constant at 0.5 M HCl solution. Figure 1 describes the performance of methylene blue extraction under different pH. It could be seen that extraction efficiency increased as the increase of solution pH from 7 to 10. However further increase of pH resulted in significant decrease of extraction efficiency. Although theoretically higher pH gradient is favourable for the extraction process, pH gradient may induce emulsion swelling. The decrease of extraction efficiency by the increase of external phase pH could be driven by emulsion swelling phenomenon. It involves transport of water from external feed phase towards internal stripping phase, leading to membrane leakage [25], resulting in the release of entrapped solute back to external feed phase. It is therefore, based on the result, further experiment would be done in external phase pH of 10.

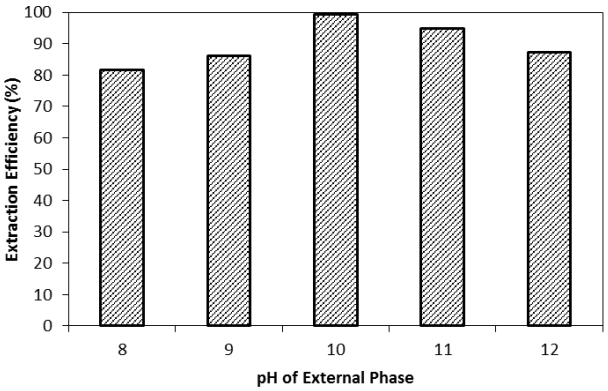


Figure 1 Effect of external phase pH to extraction efficiency (carrier concentration = 9 wt. %; HCl concentration = 0.5 M; initial feed concentration = 20 ppm; volume ratio of emulsion to feed phase = 1:5, extraction time = 5 min; extraction speed = 600 rpm)

3.2 Effect of Carrier Concentration

The following study of extraction process involving the investigation of extraction efficiency as results of extractant concentration. During the permeation study, carrier concentration were varied in the range of 7-11 wt. %. Each concentration was run by maintaining other variables constant. Figure 2 reveals the result given under variation of carrier concentration. It is seen that until extractant concentration of 9 wt. %, it was linearly proportional to the extraction efficiency. Further addition of D2EHPA concentration even dropped the system performance. This could be induced by the increase of membrane instability in line with the increase of carrier concentration. Naturally, D2EHPA promotes water transportation leading to serious emulsion swelling [26]. Another instability problem caused by excessive use of carrier comes from membrane rupture as also faced by Chiha *et al.* [27]. The formation of large emulsion that results in lower interfacial area became the possible cause of extraction rate decline [28].

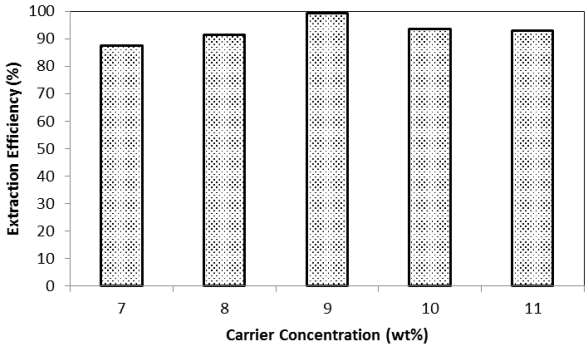


Figure 2 Effect of carrier concentration to extraction efficiency (external phase pH = 10; HCl concentration = 0.5 M; initial feed concentration = 20 ppm; volume ratio of emulsion to feed phase = 1:5, extraction time = 5 min; extraction speed = 600 rpm)

3.3 Effect of HCl Concentration

Study was continued to examine the effect of HCl concentration in the internal phase, i.e. from 0.1 M to 0.6 M on extraction efficiency. Figure 3 shows that the highest extraction efficiency was obtained using emulsion contained 0.5 M HCl. The pH gradient between stripping solution and external feed phase solution acted as driving force of the process thus ensure methylene blue permeation towards the internal stripping solution. At HCl concentration of 0.1 M to 0.4 M, the hydrogen ions chemical potential difference of internal and external phase was not enough to trigger solute transfer into internal phase, accordingly within the range of HCl concentration of 0.1 M – 0.4 M, the system could not reach optimal extraction efficiency. Higher HCl concentration resulted in higher extraction rate as also found by some other researchers [29-31]. However, higher concentration of 0.6 M resulted in lower extraction efficiency. Some researchers acquired swelling phenomena provoked by water permeation thru membrane phase due to excessive osmotic pressure difference between internal and external phase [31-33]. In addition, too high pH gradient also increase the potential of membrane breakage thus reduced extraction efficiency [34, 35].

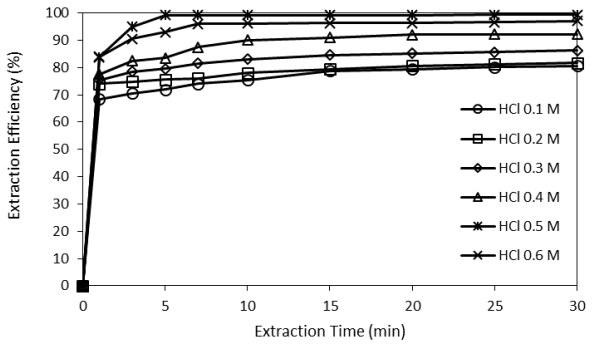


Figure 3 Effect of HCl concentration to extraction efficiency (external phase pH = 10; carrier concentration = 9 wt. %; initial feed concentration = 20 ppm; volume ratio of emulsion to feed phase = 1:5, extraction time = 5 min; extraction speed = 600 rpm)

3.4 Effect of Initial Feed Phase Concentration

The success of extraction process is also determined by initial solute concentration in the external feed phase. More concentrated feed solution leads to the decrease of degree of extraction. It can be explained that at higher solute concentration, the transport rate will be lower due to the fast saturation of internal droplets in the peripheral region, significantly increases the internal mass transfer resistance. This condition forces the complex of solute-carrier to diffuse deeper through the membrane phase toward internal phase.

Another significant driving force for diffusion process is imposed by the chemical potential due to concentration difference between feed and internal phase. Extraction efficiency of methylene blue was studied at initial feed concentrations of 10-40 ppm. Other parameters included concentration of carrier and internal phase were maintained constant. Both concentrations were enough to react with the highest methylene blue concentration of 40 ppm. The effect of initial feed concentration on extraction efficiency is shown in Figure 4.

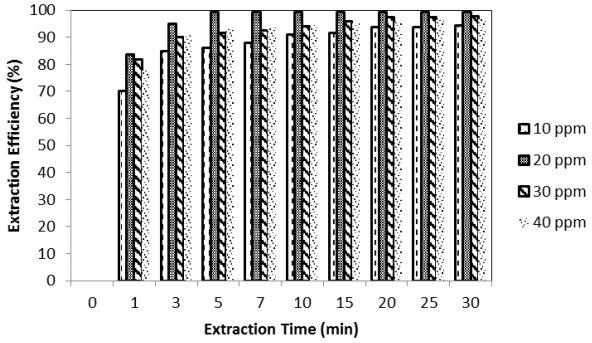


Figure 4 Effect of initial feed phase concentration to extraction efficiency (external phase pH = 10; carrier concentration = 9 wt. %; HCl concentration = 0.5 M; volume ratio of emulsion to feed phase = 1:5, extraction time = 5 min; extraction speed = 600 rpm)

As shown in Figure 4, extraction efficiency increased with an increase of initial feed concentration due to higher chemical potential between feed and internal phase. The highest extraction efficiency of 99% was achieved by system with initial concentration of 20 ppm. Beyond that concentration, extraction efficiency slightly decreased to be about 97%. At the beginning of extraction process, most of methylene blue has diffused into internal phase, occupying the outer portion of emulsion. Since the outer layer has been fulfilled, the rest of methylene blue must diffuse more deeply inside the emulsion globule. It meant that the latter complex pursued longer diffusional path [28, 36] which in turn reduced the extraction rate. In the study done by Basualto *et al.* [37] the amount of carrier was not enough to transport larger quantity of cadmium hence decreased extraction efficiency. Mathematically, Datta *et al.* [38] revealed that higher initial concentration is inversely proportional to percent removal that might be detrimental to extraction process, especially at limited concentration of carrier.

3.5 Effect of Volume Ratio of Emulsion to Feed Phase

Another operating condition investigated in this study was the effect of volume ratio of emulsion to feed phase. Observation was done at ratio of 1/9, 1/5, and 1/3. Diffusion process and extraction rate are related to this treatment ratio. Figure 5 shows extraction efficiency of methylene blue as a function of volume ratio of emulsion to feed phase.

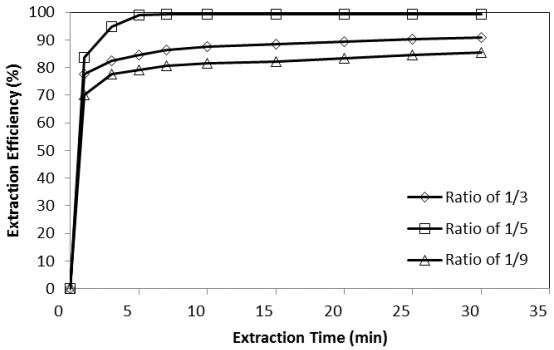


Figure 5 Effect of volume ratio of emulsion to feed phase to extraction efficiency (external phase pH = 10; carrier concentration = 9 wt. %; HCl concentration = 0.5 M; initial feed phase concentration = 20 ppm; extraction time = 5 min; extraction speed = 600 rpm)

It is observed in Figure 5, methylene blue removal increased with the increase of treatment ratio up to a certain value. The increase of extraction efficiency by enhancing treatment ratio from 1/9 to 1/5 could be explained as follows: increasing treatment ratio proportionally increased the amount of emulsion globules available for methylene blue per unit volume of reaction mixture. It is therefore increasing the interfacial surface area available for mass transfer

would directly increase the rate of mass transfer from feed to emulsion globule. The increase of extraction rate was also driven by larger amount of carrier as well as internal phase solution in emulsion. Significant increase in efficiency was observed by increasing the treatment ratio from 1/9 to 1/5, with efficiency of 80% and 99%, respectively.

In terms of emulsion size, high treatment ratio provides bigger size with smaller contact area thus it is not preferable [38]. This condition explains the phenomenon of extraction efficiency decrease at higher treatment ratio of 1/3. The possibility of membrane instability was also taken into account. Poor dispersion of emulsion phase in external feed solution was detrimental to extraction process. For higher amount of emulsion, globules interactions were also enhanced, led to the coalescence and re-dispersion of globules. Consequently, the membrane ruptured and the encapsulated solute was released into the feed phase [28].

3.6 Effect of Extraction Time

It is generally understood that longer residence time will increase extraction efficiency. More solute will be extracted from feed solution due to the increase of total mass transfer area of emulsion and feed phase. Investigation on effect of extraction time to extraction efficiency was done at time variation of 1, 3, 5, 10, 15, 20, 25, and 30 min. It is depicted in Figure 6 that extraction process occurred very fast, within 1 min almost 90% of methylene blue could be extracted from external feed phase solution. After 5 min, extraction efficiency seems to be plateau. Slight increment was found at the end of extraction process of about 99%. The remaining complex of methylene blue and D2EHPA was too low, the concentration gradient was not enough to drive the complex diffused into internal phase. Considering optimal value of extraction efficiency as well as membrane breakage, further experiment was done at 5 min.

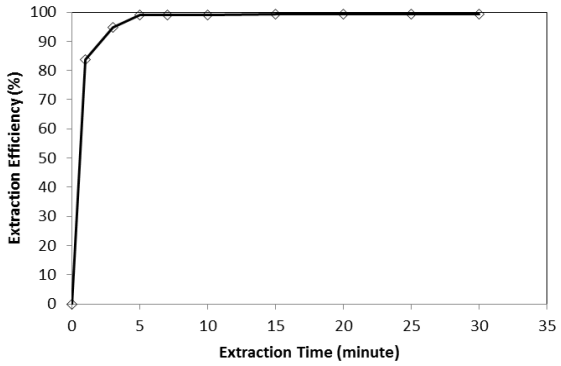


Figure 6 Profile of extraction efficiency along extraction process (external phase pH = 10; carrier concentration = 9 wt. %; HCl concentration = 0.5 M; initial feed phase concentration of 20 ppm; volume ratio of emulsion to feed phase = 1:5; extraction time = 5 min; extraction speed = 600 rpm)

3.7 Effect of Extraction Speed

Stirring rate is another parameter determines the success of extraction process. Effect of outer rotation speed on extraction efficiency was investigated at various stirring speeds of 0, 150, 300, 450 and 600 rpm. As shown in Figure 7, the highest extraction efficiency was attained at a stirring speed of 600 rpm. It is seen that even in the outer rotational speed of 0 rpm, the system able to remove about 85% of methylene dye. The extraction efficiency increased gradually until almost 100% at rotational speed of 600 rpm. The main difference among the varied rotational speed comes from the time for extraction. Shorter time was needed for the system done in higher rotational speed. It is therefore, stated in previous sub section, the process needed 5 min of extraction under rotational speed of 600 rpm.

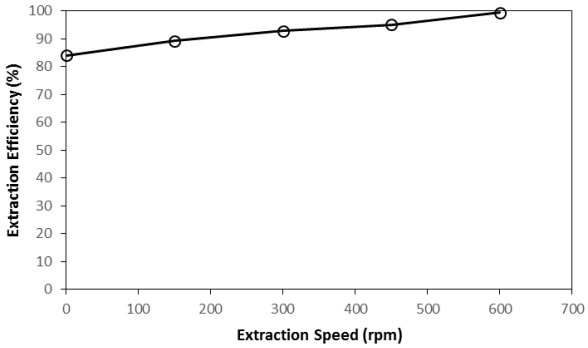


Figure 7 Effect of extraction speed to extraction efficiency (external phase pH = 10; carrier concentration = 9 wt. %; HCl concentration = 0.5 M; initial feed phase concentration = 20 ppm; volume ratio of emulsion to feed phase = 1:5; extraction time = 5 min)

4.0 CONCLUSION

A Taylor-Couette column has been successfully developed. The counter rotating system is directly connected to the DC motor that minimise mechanical loss. In this study, almost complete methylene blue removal of about 99% in 5 min extraction was achieved.

Acknowledgement

Penelitian Unggulan Perguruan Tinggi (No. 158/SP2H/LT/DRPM/III/2016) from Ministry of Research, Technology and Higher Education of the Republic of Indonesia is gratefully acknowledged.

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