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Study of Copper Recovery Using Emulsion Liquid Membrane under Taylor-Couette Column

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Abstract

High demand on batik fabric significantly increased wastewater volume from batik home industries. Copper, being used as mordanting agent, available in the highest concentration in industrial textile wastewater. Emulsion liquid membrane (ELM) is promising selective method to recover solute. Taylor-Couette column (TCC) was proposed to extract copper instead of using conventional reactor that disturbs emulsion stability. Experiment was done by varying volume ratio of emulsion to feed phase, carrier and internal phase concentration. Extraction efficiency of > 98% was obtained at volume ratio of emulsion to feed phase of 1:5, carrier concentration of 4 wt. %, and internal phase concentration of 0.1 M, respectively

Keywords: Taylor-Couette column, emulsion liquid membrane, recovery, copper

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1. Introduction

Since the establishment of batik as a world cultural heritage by UNESCO, the production capacity of batik home industries has significantly increased. Batik, produced by many areas in Indonesia, has their own characteristics in each region. Among regions in Indonesia whose economy is dominated by batik industries is Pekalongan. In 2011, there were 1342 small industries in Pekalongan in which around 83.1% were batik industries [1]. With a production capacity of 6000 to 20000 cloths per month [2], each industry has the potential to produce 202.4 m^3 of wastewater. What very worrying is the fact that only about 0.6% of industries have waste treatment units [1], while the rest dispose of waste water directly into the environment.

Around the last twenty years, the world has given great attention to environmental problems. Many efforts have been made to save the environment by implementing various regulations. Industry players are required to give a deep care for environmentally friendly production processes. With the issue of the quality and quantity of clean water, the textile industry is very much bound by government regulations regarding waste quality standards. Water is one of the main components needed in the textile industry which in the process also uses a variety of heavy metals.

Heavy metal is one of the important elements in biological systems, however, the deficiencies or excess of these elements can cause damage. Industrial textile wastewater generally contains heavy metals in the form of iron, zinc, lead, chromium, copper, nickel and cadmium [3, 4]. The wastewater can contaminate soil and surface water which eventually contaminates groundwater. As pollutants, heavy metal accumulation results in various organ disorders because heavy metals cannot be degraded [5]. Thus, industrial wastewater emerges various environmental problems with complex health threats not only in developing countries, but also in developed countries.

Despite the danger for living organisms, heavy metal is widely used in textile industries. Chromium is an essential metal for dyeing wool and nylon fabrics. While cobalt, chromium, and copper are inseparable from colouring leather, wool or nylon. The presence of heavy metals in dyes provides good fastness properties. Metals are present in textile industrial wastewater as free ions and complex metals. The mordant material for colouring wool fabrics contains chromium. C.I dye. Black Mordant 11 which contains chromium is one of the most widely used dyestuffs. Copper is used as a fixator in colouring with direct dyes so that it has good fastness. Cation dyes contain zinc, mercury, cadmium, and arsenic as impurities. Besides zirconium and aluminium, many other metals are used in the textile industry process. Dyeing of vessel dyes and sulphur dyes are inseparable from the role of heavy metals in the oxidation process. While the finishing process in dyeing with direct dyestuffs also requires the use of heavy metals. The most widely used dyes in the textile industry are acidic, basic, direct, disperse, reactive, and vessel dyestuffs. In these dyes contained chromium, arsenic, cadmium, mercury, copper, lead and zinc. The concentration of copper used in dyeing with acid dyes is the highest compared to other heavy metals [6]. Among the heavy metals, copper was available in the highest concentration of about 341 ppm [7], much higher than the permissible limit of 0.2 ppm [8]. It was found that copper ion was the best mordant in textile dyeing which able to enhance the shade depth of colour [9].

The process of heavy metals recovery from textile industrial wastewater is very important to achieve an environmentally friendly industrial process. A simple and economical but effective and selective method is of important in conjunction with the high volume of wastewater with relatively very low heavy metals concentrations. It is expected that the method is able to remove heavy metals from textile industrial wastewater.

So far membrane technology is considered capable of being an alternative to conventional textile wastewater treatment technology. Among the various types of membrane technology, liquid membranes are considered to play a major role in the separation process that has been applied in the biomedical and hydrometallurgical fields. The use of emulsion liquid membrane technology is able to recover dyes from wastewater, which in turn is expected to be able to be used again in the next dyeing process, thus saving production costs.

Emulsion liquid membranes are an alternative to liquid-liquid extraction methods. In the emulsion liquid membrane method, the combination of extraction and stripping processes encourages purification and solute concentration in one step. This combination of processes can significantly save equipment. Separate contactors for extraction and stripping processes as well as liquid-liquid extraction are not required. Thus, the liquid membrane emulsion method can save costs up to 40% compared to liquid-liquid extraction methods [10]. The application of liquid membrane emulsion method for heavy metal recovery along with studies on the stability and instability of emulsions has been published [11-14].

The principle of the liquid emulsion membrane method is the use of a three phase system. In this system, the emulsion formed from the membrane phase and stripping is dispersed in the feed phase, which is the phase to be restored. Carriers as organic extractants are used to separate solute, even in very small concentrations. Solute and carrier form a complex that can pass through the membrane phase. Then, the complex passes through the membrane phase to the inner interface. In that section, the complex will decompose so that the solute is released into the internal phase while the free carrier diffuses back into the membrane phase. The mechanism of metal transfer in the emulsion liquid membrane system is shown in Figure 1.

Although emulsion liquid membrane process offers many advantages to recover various contaminants in industrial wastewater, this method still has to be improved to overcome some technical limitations in its application. The success of the method application does not only depend on the selection of the right emulsification process, but also the emulsion formulation that corresponds to the solute to be recovered. Emulsion stability is the biggest challenge for the application of liquid membrane emulsion methods on an industrial scale. It was reported that in general, the instability of the emulsion that occurred in this process were membrane leakage and swelling respectively by 8% and 35% [15-20]. This information is interesting considering the tolerance for membrane leakage and maximum swelling emulsions are 0.1% and 10% respectively [21, 22].

Small diameter emulsions are believed to be more stable and have a larger surface area. Li et al. [23] suggested the use of emulsions in the range of 0.3 to 10 μm

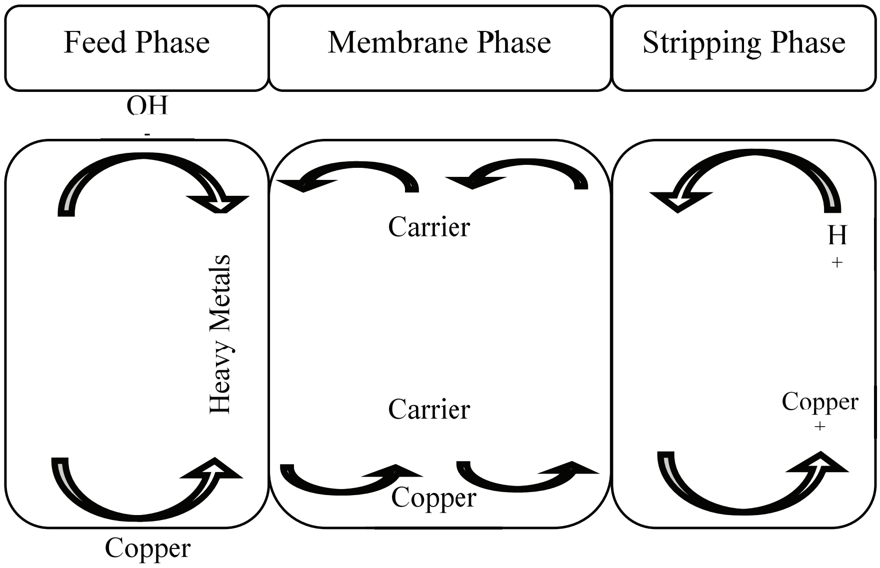

Figure 1: Transport mechanism of copper.

(best range 0.8 to 3 μm) because they have high extraction rates, good stability and resistance to stirring. Generally emulsions are made with homogenisers, mixers, stirrers. Emulsions preparation with the help of sonicator produces small diameter emulsions and is resistant to stirring forces [24].

Among the efforts to achieve a high extraction rate is the increment of stirring speed. However, this certainly disrupts the stability of the emulsion [25, 26]. The stirring speed and contact time must be determined to obtain optimal emulsion conditions. The use of Taylor-Couette columns (TCC) is an alternative to overcome the limitations of the extraction process with a stirred tank. In this method, the fluid shear is relatively low and uniform so as to maintain the emulsion stability without disturbing the efficiency of extraction process [27]. The target component is extracted within the columns in which inner cylinder is rotating and outer cylinder is constant. This system produced high efficiency in relatively short contact times [27]. The use of TCC is expected to maintain emulsion stability while increasing extraction process efficiency. Separation of textile dyes from synthetic waste using Taylor-Couette columns provides promising results [28, 29], however, its use for copper extraction has not been examined.

2. Theory

The results of cellulose-based fabric dyeing will be perfect after being added with copper compounds. The fabric has high fastness. This fastness property can be achieved by adding copper salts, namely copper sulphate. At the end of the process, a small portion of the copper salt will be left as residue. Therefore, the textile industry faces serious problems with the presence of copper in its waste.

Emulsion liquid membrane process has been studied by many researchers by utilising stirred vessel as contactor. However, some problems arise in the extraction process. In a stirred vessel, the emulsion liquid membrane system faces problems with emulsion stability. To achieve a better extraction rate, the process must be carried out at high speeds, which disrupts emulsion stability. Many researchers focused on membrane leakage and emulsions swelling on stirred vessels.

The Taylor-Couette column is designed to minimize the possibility of emulsion instability while maintaining good extraction performance. This system consists of two free cylinders, the solution is flowed between the two cylinders. To characterise the flow regime, Andereck et al. [30] map flow patterns for various internal and external cylinder rotation rates.

3. Methodology

3.1. Materials

Selection of liquid membrane components was done based on previous studies [31, 32]. The non-ionic surfactant of sorbitan monooleate which is commercially known as Span 80 was used as emulsion stabiliser. Low odour kerosene purchased from Sigma Aldrich was used as a diluent. Sulphuric acid (98%) from Merck was used as internal phase. TOA (>95%) from Merck was used as carrier. Copper sulphate (99.99%) from Sigma Aldrich was used in the external feed phase. Deionised water was used to prepare all aqueous solutions. The research employed reagents of analytical grade.

3.2. Procedures

Emulsion production was done using a ultrasonic probe. The solution was placed in a double glass beaker. Emulsion solution was placed in the inner glass, while cooling water was flowed in the outer glass to maintain temperature. Based on each parameter and operating conditions, the emulsion obtained was characterised based on the size and efficiency of emulsification process. The best conditions were used at next stage of extraction.

The feed solution was prepared by dissolving copper into deionised water. The emulsion was then poured into feed solution and the mixture was stirred. The volume ratio of emulsion to feed phase was varied to obtain optimal conditions. Extraction speed was varied to obtain the best efficiency with minimal emulsion instability. Extraction was carried out for 35 min, where the samples were taken in the 1/2, 1, 3, 5, 7, 10, 15, 20, 25 and 35 minutes. After extraction was complete, the solution was allowed to stand for 5 minutes. The bottom layer of solution was taken to determine the final copper concentration and test the magnitude of the membrane leakage.

4. Results and Discussion

4.1. Effect of volume ratio of emulsion to feed phase

Solute and carrier would form complex which is soluble in membrane phase. The complex diffuses towards internal phase. Extraction rate could be enhanced by increasing volume ratio of emulsion to feed phase. Mass transfer is affected by complex diffusion and interfacial reaction. Contact surface area of emulsion and feed phase is determined by treatment ratio. Capacity of emulsion in extracting solute is enhanced by higher treat ratio. However, economic feasibility is another factor to be considered. Study on effect of volume ratio of emulsion to feed phase was done at 1/9, 1/5, and 1/3. The result is depicted in Figure 2. It is shown that increasing treatment ratio from 1/9 to 1/5 resulted in the increase of extraction efficiency. At ratio 1/5, system efficiency was >98%. This is due to higher carrier was available in treatment ratio of 1/5, therefore, more complex was formed. More emulsion volume provided higher extraction capacity. However, further increase of treat ratio to be 1/3 gave significant decrease of extraction efficiency. This is due to the disruption of emulsion spread up in feed phase, that decrease contact area which in turn lowering extraction rate [33].

4.2. Effect of carrier concentration

Copper removal using ELM system was served by TOA as carrier. TOA acts as shuttle that carry copper from feed phase towards internal phase, as illustrated by Perera and Stevens [34]. Figure 3 reveals trend of extraction efficiency by the variation of carrier concentration. It is seen that low carrier concentration of 1 wt. % and 2 wt. % gave low extraction efficiency. It may due to at these low concentrations, there was mass transfer resistance in the interface of feed and membrane phases thus in turn inhibits copper diffusion. Moreover, these low carrier concentrations also unable to completely catch and transfer copper into internal phase thereby limits extraction rate [35, 36].

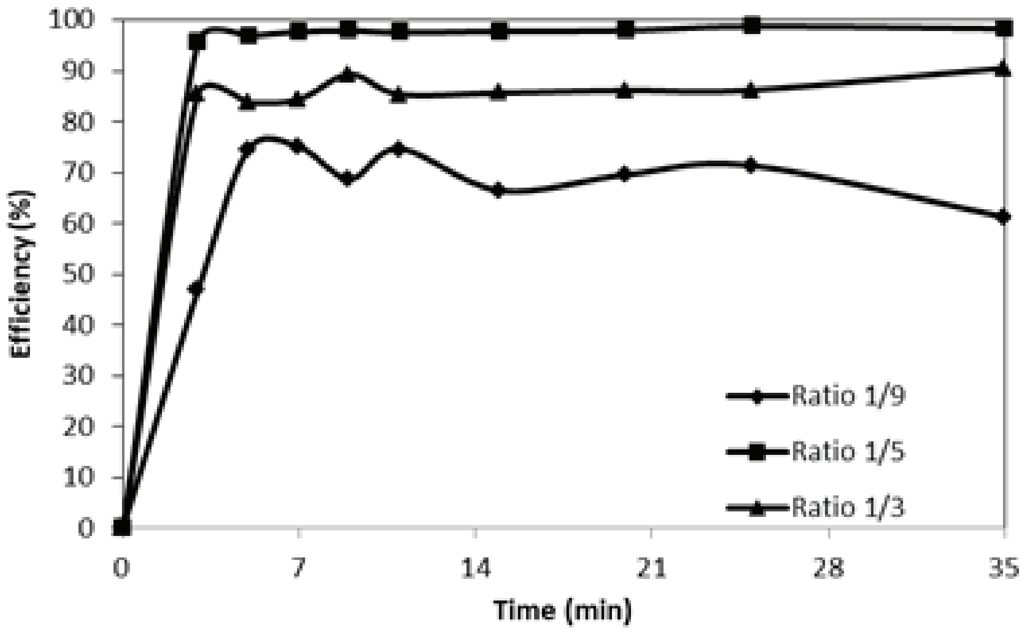

Figure 2: Effect of volume ratio of emulsion to feed phase on extraction efficiency.

Optimal carrier concentration was reached at 4 wt. % with extraction efficiency of >98%. However, increasing carrier concentration to be 6 wt. % resulted in the decrease of extraction efficiency. Interaction of carrier and surfactant in the interface of membrane phase leads to the decrease of ELM stability. Higher carrier concentration resulted in bigger emulsion diameter [24] whereas bigger emulsion diameter is not preferable for having low interfacial area that leads to lower capacity in extracting solutes [37-40]. Furthermore, considering economic feasibility of ELM process, application of lower carrier concentration is suggested [41, 42].

4.3. Effect of internal phase concentration

Optimisation study of copper extraction efficiency was also done to internal phase concentration. Utilising NH_3 as internal phase, study was done at concentration of 0.025 M – 0.25 M. Internal phase solution determines emulsion properties and stripping reaction. Theoretically, increasing internal phase concentration to certain point could increase emulsion stability. Driving force of extraction process could be determined by chemical potential difference of internal and external phases. On the other hand, beyond optimal concentration it could trigger emulsion swelling. Figure 4 shows the capability of emulsion in stripping copper at various NH_3 concentration. It indicates the increment of extraction efficiency by the increase of NH_3 concentration from 0.025 M to 0.1 M. The decrease of extraction efficiency as a result of NH_3 concentration increment

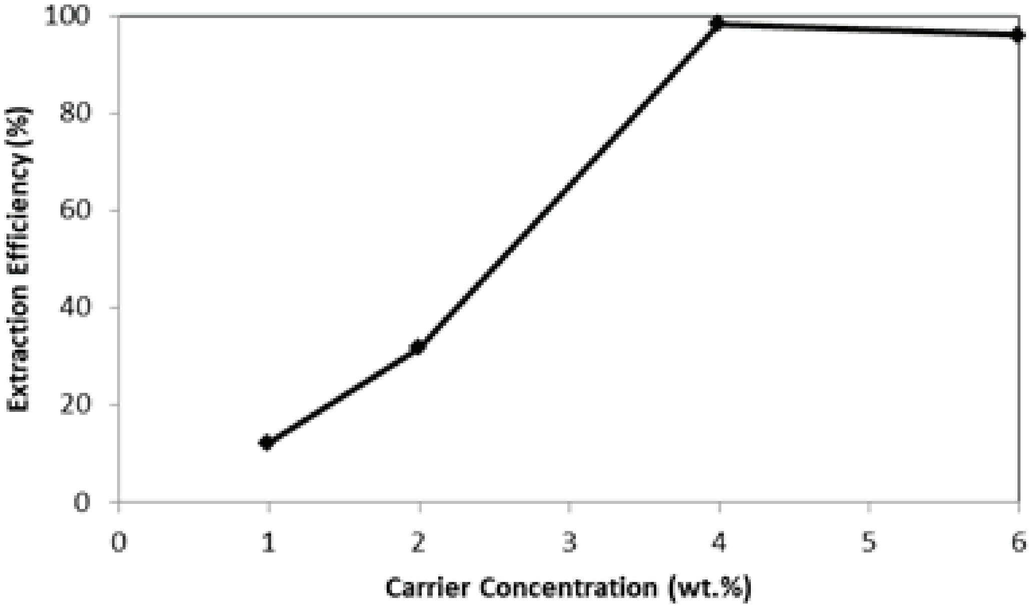

Figure 3: Effect of carrier concentration on extraction efficiency.

to be 0.25 M may be due to precipitation phenomenon. It is therefore NH_3 concentration of 0.1 M is recommended for copper extraction using ELM process under investigated conditions.

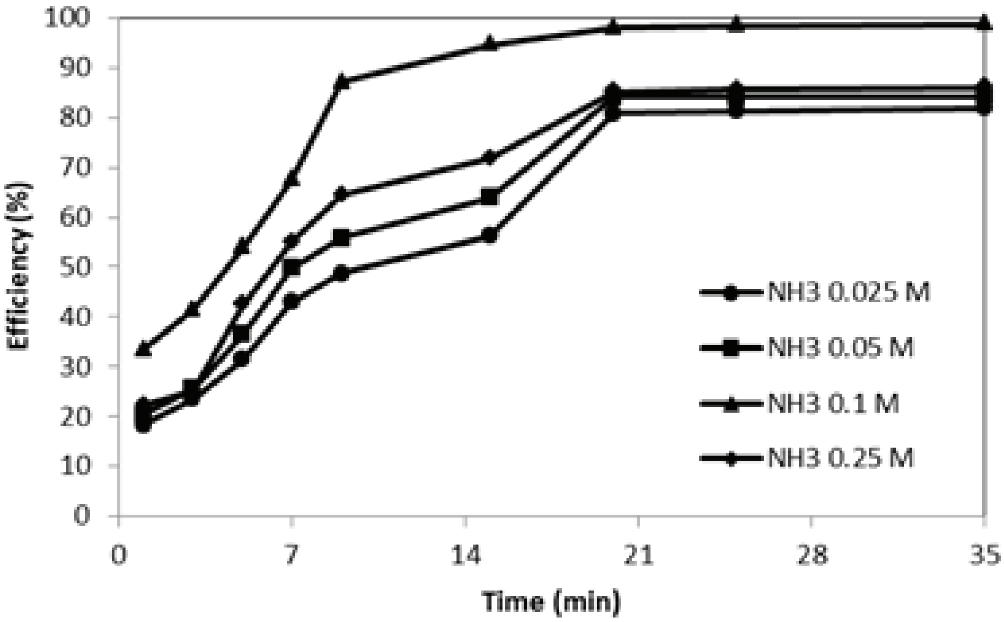

Figure 4: Effect of internal phase concentration on extraction efficiency.

5. Conclusion

ELM system for copper removal has been studied under TCC. Varying volume ratio of emulsion to feed phase, carrier concentration, and internal phase concentration, the study succeeded in determining optimal condition for each parameter. Minimising emulsion instability by maintaining extraction rate, the highest extraction efficiency of >98% was obtained at each parameter.

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