

Selection of Liquid Membrane Component for Lignosulfonate Removal from Liquid Waste Solution using Emulsion Liquid Membrane Process

N. Othman^{1*}, Z. Y. Ooi² & N. Harruddin³

^{1,2&3}Department of Chemical Engineering, Faculty of Chemical and Natural Resources Engineering, Universiti Teknologi Malaysia, 81310 UTM Johor Bahru, Johor, Malaysia

ABSTRACT

Removal of lignosulfonate from pulping process as an external biofuel and in specialty chemicals is growing such as in production of vanillin, animal feed pellets binder, pesticides, ect. Though lignosulfonate (LS) is nontoxic, it imparts brownish black colour to the water bodies and makes them unsuitable for usage in other processes. Therefore the removal and recovery of LS is needed. This study examined the liquid membrane component selection of lignosulfonate (LS) removal from liquid waste solution using trioctylamine (TOA) as a mobile carrier in batch process using mixer settler. Several parameters have been investigated such as choice of diluents, effect of pH, concentration of carrier, concentration of LS solution, organic to aqueous treat ratio, choice of stripping agent and concentration of stripping agent. The results show that at favorable condition of 0.1M concentration of TOA in kerosene, pH 3 of solution, treat ratio 1:15 and 0.7 M NaOH solution as stripping agent showed that almost 90 percent of lignin was extracted and recovered in receiving phase.

Keywords: Lignosulfonates, paper industry, wastewater, trioctylamine, extraction

1.0 INTRODUCTION

Nowadays, the pulp and paper plants are one of the most polluting industries. It consume a large volume of water in their processing stages and consequently discharge effluent that contains organic pollutants. The organic pollutants produced in kraft and sulfite pulping processes mainly comprise compounds of kraft lignin and lignosulfonate respectively along with a small percentage of sucrose. Lignosulfonate (LS) is a polydispersed macromolecule. It imparts brownish black colour to the water bodies and makes them unsuitable for usage in other processes. Nevertheless, when effluent discharge to river, the dark coloration of lignin will reduces oxygen availability and adversely affects aquatic flora and fauna [1].

Lignin is the second most abundant biopolymer on earth after cellulose [2]. Approximately fifty million tons of lignin are produced annually as a waste in paper and pulp industry alone [3]. Pulp and paper industries have chance to recover large quantities of lignin from their spent pulping liquor and then sell lignin as a biofuel to power companies, providing a new revenue source thereby reducing greenhouse gas emissions. In the scenario of future pulp mills, lignin can replace fossil fuels in other furnaces [4]. Furthermore, the solid product lignin fuel is similar to coal has lower ash, and can also replace more expensive fossil fuels on-site within the same mill, either in the power furnaces or lime kiln. Besides that, it also provides a new potential application consists of its use as an anti-oxidant, resin, co-polymer, and a resource for carbon fibers. It can be used in production of vanillin, animal feed pellets binder, pesticides ect. The chemical structure of lignosulfonates is shown in Figure 1 [5].

*Corresponding to: N. Othman (email: norasikin@cheme.utm.my)

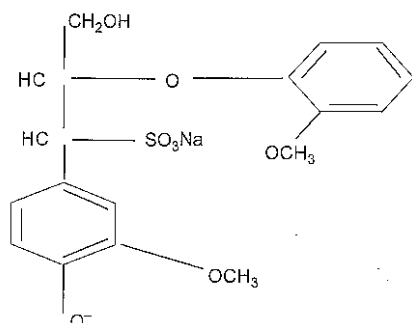


Figure 1 Chemical structure of lignosulfonate

Therefore, separation process of lignosulfonate from paper and pulp mill is significant due to many application of the final product while lowering the pollution of effluent streams. There were various methods developed for lignosulfonate removal and recovery from spent pulping liquor. These include methods like mineral acid precipitation, ultrafiltration [6], ion exchange, dialysis, electrolysis and extraction with amines [7]. These methods have advantages as well as drawbacks. The acid precipitation methods has some disadvantages such as handling of large amount of acid, and being corrosive and non-ecofriendly. In addition, these methods are expensive, and tedious especially when operated in large scale.

Much attention has been focused on LS removal techniques such as liquid-liquid-extraction (LLE) or solvent extraction and liquid membrane. Liquid-liquid extraction is used in numerous chemical industries to extract chemical compounds ranging from pharmaceuticals and biomedical to heavy organics and metals, in analytical chemistry and in environmental waste purification. Hence, the method that focuses in this research is liquid-liquid extraction. LLE is the preliminary study for screening the parameters which related to emulsion liquid membrane (ELM) process [8]. LLE is based on the principle that a solute can distribute itself in a certain ratio between immiscible solvents and extraction process depends on its mass transfer rate [9]. The advantages of LLE include high throughput, high purification, easy to scale up and ease of automatic operation [10]. Thus the main purpose of liquid-liquid extraction being applied in this research is to extract the lignin from aqueous

waste solution for emulsion liquid membrane process.

Separation using emulsion liquid membrane is one of the membrane technologies with considerable potential for a variety of applications. It is an accessible and easy way for the removal of pollutants from wastewaters and the transport them into desired phases, where the pollutants can be concentrated up to 10-100 times [11]. Furthermore, separation is achieved by using less consumption of chemicals. Using ELM, LS can be recovered in very concentrated solution in the recovery phase. In principal, the ELM is a three phase dispersion system, where primary emulsion consists of organic and stripping phase is dispersed in the feed or external phase, which is the phase to be treated. Even though the solute is in very low concentration in separation, the carrier is an organic soluble extractant, which is selectively combines with the solutes to form a solute-carrier complex. This complex will permeate through the membranes from the outer to the inner interface. At the inner interface, the complex decomposes by the reversal of the equilibrium reaction and the solutes ion is liberated into the internal phase and the regenerated carrier goes back into the membrane phase. The advantages of this process are extraction and stripping occurred simultaneously in one single step operation and equilibrium limitation can be removed. It also can reduce the amount use of expensive extractant, high fluxes and high selectivity is possible [12].

In this study, liquid membrane formulation of LS removal was studied through liquid-liquid extraction from liquid waste solution using TOA as an extractant. The percentage of LS extraction and stripping potential were investigated and operating conditions were optimized.

2.0 MATERIALS AND METHOD

2.1 Chemicals and Reagents

All the reagents were in analytical grade and used without further purification. The following reagents were used: trioctylamine, tridodecylamine, sodium hydroxide, sodium chloride and n-dodecane were procured from Merck (Germany),

sodium lignosulfonate was obtained from Aldrich-Sigma, kerosene, Cyanex 272 and Aliquat 336 were obtained from FLUKA, dichloromethane was obtained from Q-Rec.

2.2 Analytical Instruments

The LS concentration was determined spectroscopically by measuring the absorbance at 280 nm using a UV spectrophotometer (Jenway 6305). The pH measurement was carried out with a pH meter (DELTA 320).

2.3 Liquid-liquid Extraction

The experiments on the rate of forward extraction were carried out by mixing an equal volume (10 ml) of LS solution and organic solutions (TOA) using a mechanical shaker at 320 rpm for a period of 18 hours. Then, the mixture is carefully poured into separation funnel. After the phase separations (around 15-30 minutes), an aqueous phase was carefully separated from the organic phase. The amount of LS in the aqueous phase was determined by UV spectrophotometer while that in the organic phase was obtained from the material balance. The procedures were repeated for study for other parameters such as choice of diluents, effect of pH, concentration of carrier, concentration of LS solution, organic to aqueous treat ratio, choice of stripping agent and concentration of stripping agent. All experiments are carried in room temperature.

2.4 Stripping Process

This experiment is designed to identify the types and optimum strip agent concentration required to strip LS from LS loaded organic solution. Stripping process is the reverse extraction step. Therefore, organic phase (LS loaded organic phase) is taken from extraction process from Section B. An equal volume of strip agent and LS loaded organic phase were mixed by using mechanical shaker at 320 rpm for a period of 18 hours. Then, the mixture is carefully poured into separation funnel. After the phase separations (around 15-30 minutes), an aqueous phase was carefully separated from the organic phase. After

phase separation is completed, the aqueous phase was carefully separated to avoid any contamination by the organic phase and concentration of LS stripped were measure by UV spectrophotometer. The stripping procedures are repeated for other strip agents and concentrations.

3.0 RESULTS AND DISCUSSION

3.1 Choice of Diluents

Diluents should be chosen based on the immiscibility with the aqueous solution, viscosity, specific gravity, volatility and number of carbon. Different types of solvent have been chosen in the extractions which are kerosene, dichloromethane and n-dodecane. The rates of extraction in these solvents are reported in Table 1. It was observed that the extraction of LS was considered negligible in n-dodecane because of the less solubility of TOA in these organic diluents. Dichloromethane was proved as the best solvent due to high percentage of extraction. However, the volatility of dichloromethane is extremely high and it is not applicable in liquid-liquid extraction process. The diluents with lower dielectric constant were preferred for extraction [12].

Hence, kerosene is used as the diluents on this experiment which is high in dielectric constant in the range of 2.0-2.2 and low viscosity [14]. Besides that, kerosene is less toxic compared to other diluents [15].

Table 1 Effect of different diluents in liquid-liquid extraction. (Experimental conditions: [LS] = 100 ppm, [TOA] = 0.5 M, agitation speed = 320 rpm, duration = 18 hrs, T = 26 ± 1°C, pH = 8 ± 1, Treat ratio: 1:1)

Diluents	Extraction (%)	Distribution ratio (D)
Kerosene	51.5	1.0
Dichloromethane	88.5	7.7
n-dodecane	5.3	0.1

3.2 Effect of pH Feed Solution

Lignosulfonate is a polydispersed macromolecule which essentially affected by pH in extraction as the molar mass distribution of LS is greatly dependent on pH value in the solution [16]. The experiment was repeated with various pH in the range of 2-8. The results clearly show that the maximum extraction of LS occurs at pH 3 in Figure 2. It is indicate that the protonation of TOA is occur in acidic condition. At higher pH the distribution of LS is lower is due to the incomplete protonation of TOA during the liquid-liquid extraction. However, at much lower pH, the rate of extraction is decreased. The above fact could be attributed to the following two reasons which are in highly acidic condition LS is not ionized. Besides, in lower acidic condition chloride form will exhibit the formation of amine complex [8]. Thus, a pH 3 of feed solution is selected for the subsequent experiments.

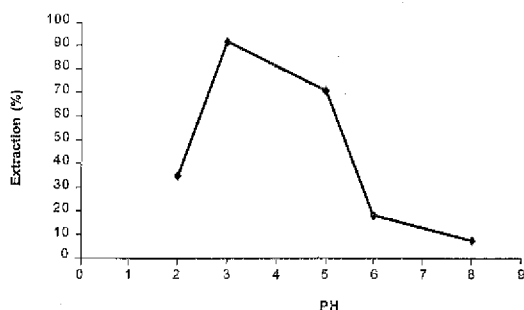


Figure 2 Effect of pH solution in liquid-liquid extraction. (Experiment conditions: [LS] = 100 ppm, [TOA] = 0.1 M, agitation speed = 320 rpm, duration = 18 hrs, $T = 26 \pm 1^\circ\text{C}$, diluents: kerosene, Treat ratio: 1:1)

3.3 Effect of Carrier Concentration

The effect of TOA concentration was studied in the range of 0.001 to 0.1 M. The results are showed in Figure 3. As the carrier concentration is increased from 0.001 to 0.1 M, the extraction increase. The LS extraction increases up to 90% from 0.001 to 0.03 M. Further increases the concentration of carrier the percentages of extraction almost plateau due to excess of carrier.

Percentage of extraction is maximum at 0.1 M TOA and then the extraction decrease with increase in TOA concentration up to 0.5 M. It presents that the saturation capacity of the organic phase for the complex reached at optimum 0.1 M TOA. The equilibrium of protonation TOA is occur when maximum extraction are achieved due to more number of TOA molecules get associated with LS and form complex. However, the decreasing rate of extraction may caused by the excess of extractant reacts with chloride ion that is soluble in aqueous phase. On the other hand, diffusivity is inversely proportional to viscosity, an increase of viscosity will cause reduction of diffusivity and eventually increases the organic phase resistance to transport [17]. Hence, it cause higher mass transfer resistance and does not favour the extraction kinetics. Thus, 0.1 M TOA is chosen for the subsequent experiments.

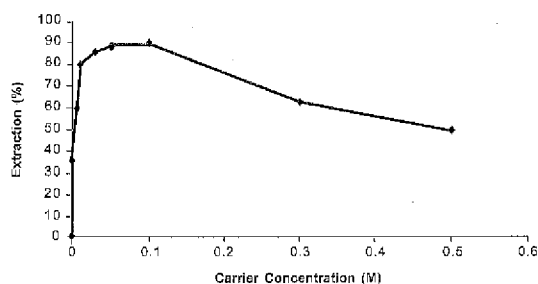


Figure 3 Effect of carrier concentration in liquid-liquid extraction. (Experiment conditions: [LS] = 100 ppm, agitation speed = 320 rpm, duration = 18 hrs, $T = 26 \pm 1^\circ\text{C}$, diluents: kerosene, pH = 3, Treat ratio: 1:1)

To determine the nature of extraction of LS, different concentration of TOA in organic solution was studied. The distribution ratio (D) of LS in organic solution was calculated. Based on the result from the present experiment, by assuming that all the TOA that existed in the system reacted with LS, at a constant pH. The nature of the extracted species was evaluated by the plot of $\log D$ versus $\log [R_3N]$ in Figure 4. The slope obtained for the plot is 1.2 which is nearly equal to 1.0. Hence, the LS to reagent ratio was found to be 1:1. Therefore, it indicates that one mole of LS requires one mole of TOA for extraction taken place.

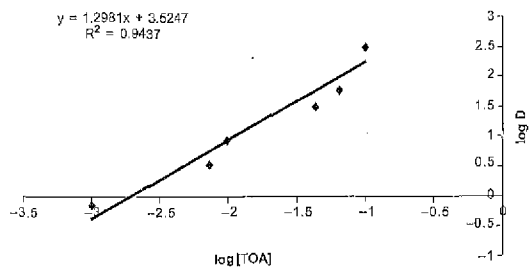


Figure 4 Stoichiometric plot for the equilibrium extraction of LS using trioctylamine as carrier and kerosene as solvent

3.4 Effect of Initial LS Concentration

The effect of initial concentration was studied in the range of 100 ppm to 5000 ppm of LS solution. From the Figure 5, there is a slightly increasing of extraction from 100 ppm to 2000 ppm. The highest extraction obtained at 2000 ppm. Further increases of LS concentration above 2000 ppm, percentage of LS extraction decreased. At higher initial LS concentration in aqueous solution, the extraction efficiency dropped. However, the absolute amount of LS extracted increased with increase in LS concentration [18]. Almost 100 percent of extraction rate was achieved from 100 to 2000 ppm while the percentage of LS extraction is 81 percent at 2500 ppm. Further increases of LS concentration, the percentage of extraction decreased due to the excess of LS in the solution that cannot react with the limited extractant in the solution. The decrease of extraction also caused by the precipitation which caused by the hydrolysis

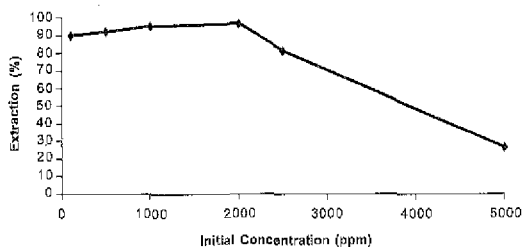


Figure 5 Effect of initial concentration in liquid-liquid extraction. (Experiment conditions: [TOA] = 0.1 M, agitation speed = 320 rpm, duration = 18 hrs, T = 26°C, diluents: kerosene, Treat ratio: 1:1)

phenomenon of LS at higher initial concentration. This was observed in the experiment. There is formation of brown precipitation in the LS solution during extraction. The increases of LS solution concentration need more carriers for the extraction. However, the contents of LS in waste liquid solution from the pulp industry are in the range of 93000-127000 ppm [19]. Therefore, further investigation needs to be considered in treating real concentration of LS from pulping industry.

3.5 Effect of Treat Ratio

The volume phase ratio of organic phase to aqueous phase is termed as treat ratio which plays an important role in determining the effectiveness of liquid membrane. The treat ratio varies from 1:1 to 1:20. Figure 6 shows that the performance of extraction almost the same from 1:1 to 1:15 where 94-96 percent of extraction was obtained. It yielded a higher percentage of LS removal from aqueous solution. This could be due to the higher free concentration of organic phase when the organic to aqueous phase ratio (O/A) is higher [20]. The performance of liquid membrane considered the best when treat ratio is 1:15. This may reduces the consumption of liquid membrane and eventually reduce the cost of expensive extractant for liquid membrane. The larger volume of LS solution can be extracted in lower treat ratio (1:15) is preferable. Eventually, treat ratio of 1:15 was chosen as the optimum treat ratio.

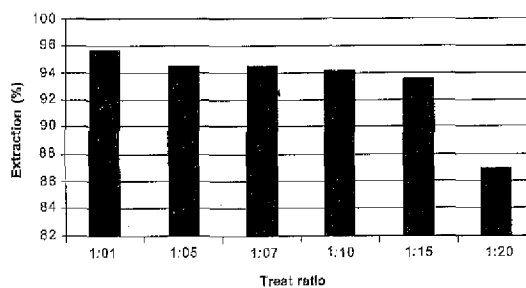


Figure 6 Effect of treat ratio in liquid-liquid extraction. (Experiment conditions: [LS] = 700 ppm, [TOA] = 0.1 M, agitation speed = 320 rpm, duration = 18 hrs, T = 26°C, diluents: kerosene, pH = 3)

3.6 Choices of Stripping Agent

In any extraction process, it is imperative to back extract the extracted LS from the organic phase and allow for recycling of the organic solvent without loss of efficiency in liquid-liquid extraction process. The type of stripping agent plays an important role in LS recovery and minimizing the co-transport of water in the extraction process [5]. LS loaded organic solution from liquid-liquid extraction was examined in stripping process by using two types of stripping agents which are NaOH and NaCl. The results presented in Table 2. It indicates that NaOH exhibits better performance in stripping LS from loaded organic phase compared to NaCl. Besides, from sight observation the aqueous solution after stripping in NaCl was cloudy. It may cause by some side reaction by salting out effect, which is defined as the aqueous solubility of various compounds in presence of inorganic salts [21]. Hence, NaOH was chosen as the best stripping agent.

Table 2 Effect of different stripping agents in stripping process. (Experimental conditions: [LS] = 700 ppm, [TOA] = 0.1 M, [stripping agent] = 1 M agitation speed = 320 rpm, duration = 18 hrs, T = 26°C, pH = 8, Treat ratio: 1:15)

Stripping agents	Stripping (%)
Sodium chloride (NaCl)	25.8
Sodium hydroxide (NaOH)	65.5

3.7 Effect of Stripping Agent Concentration

The influence of NaOH in the strip phase was studied in the range of 0.1-1.5 M. The results were reported in Figure 8. From the Figure 7, it can be seen that the stripping efficiency increased with increasing NaOH concentration up to 0.7 M. But, further increase in NaOH concentration it observed that a decreasing trend of stripping percentage. This phenomenon may cause by the increasing in difference of ionic strength between the feed and the strip phases. The increase of recovery of LS from 0.1 to 0.7 M NaOH shows

that the ionic concentrations in the two phases are balanced within the range. Hence, large amount of LS transport to strip phase. On the other hand, the decreasing trend of stripping process may due to the excess of stripping agent form complexes that is not soluble in aqueous phase. Hence, the optimum concentration of stripping agent is 0.7 M which achieves 89.3% stripping.

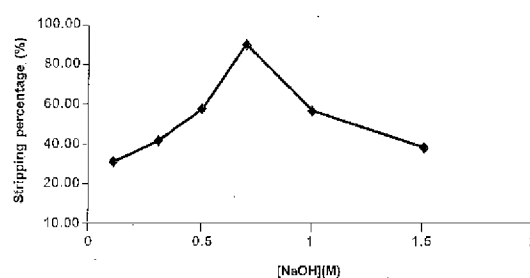


Figure 7 Effect of stripping agent concentration in stripping process. (Experimental conditions: [LS] = 100 ppm, [TOA] = 0.1 M, stripping agent = NaOH, agitation speed = 320 rpm, duration = 18 hrs, T = 26°C, pH = 8, Treat ratio: 1:7)

Based on the result from the present experiment, by assuming that all the NaOH that existed in the system reacted with TOA-lignin complex, the nature of the stripping species was evaluated by the plot of $\log D$ versus $\log [\text{NaOH}]$ in Figure 8. The slope obtained for the plot is 1.285 which is nearly equal to 1.0. Hence, the TOA-lignin complex to NaOH ratio was found to be 1:1. Therefore, it indicates that one mole of TOA-lignin complex requires one mole of NaOH for stripping taken place.

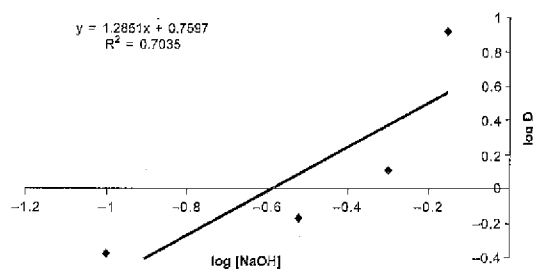


Figure 8 Stoichiometric plot for the equilibrium stripping of LS using NaOH as stripping agent

4.0 CONCLUSION

Based on this study, the developing of liquid-liquid extraction is possible to remove LS from its aqueous solution. Liquid membrane formulation of lignosulfonate removal from liquid waste solution was developed containing TOA as mobile carrier, kerosene as diluents and NaOH as stripping agent. It has been tested for the kinetic of lignin removal from aqueous waste solution. The maximum extraction occurs at feed phase pH of 3, TOA carrier concentration of 0.1 M, treat ratio 1:15, 0.7 M NaOH solution as stripping agent and diluents used is kerosene. Almost 93% and 89% of LS was extracted and recovered respectively.

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NOMENCLATURE

LS	lignosulfonate
TOA	trioctylamine
LLE	Liquid-liquid extraction
V _m	membrane/organic phase
V _f	feed phase
[TOA]	concentration of TOA
LS	sodium lignosulfonate
D	distribution ratio
[NaOH]	concentration of NaOH

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