Chemical Engineering Journal 95 (2003) 199–204

Chemical Engineering Journal

www.elsevier.com/locate/cej

Experimental studies on treatment of distillery effluent by liquid membrane extraction

T. Kumaresan[1], K.M. Meera Sheriffa Begum, P. Sivashanmugam, N. Anantharaman*, S. Sundaram

Department of Chemical Engineering, Regional Engineering College, Tiruchirapalli 620015, India

Abstract

Emulsion liquid membrane (ELM) as a technique for effluent treatment has received wide attention in recent years due to its ease of operation, lower power consumption and modular design. Odorous distillery effluent was treated for removal of acetic acid (solute) using ELM in a batch process. The effect of agitator speed, duration of agitation, xylene concentration in the membrane phase, membrane to external phase (M/E) ratio on the reduction of solute, concentration of biological oxygen demand (BOD) and chemical oxygen demand (COD) in the external phase has been studied. At 110 rpm, 4% xylene concentration and M/E ratio of 0.8, a maximum recovery of 44% solute and minimum values of BOD and COD of 96 and 927 ppm, respectively, in the external phase were observed. The experiment was also conducted in a York-Schiebel column at 110 rpm and the BOD and COD of treated effluent were 94 and 900 ppm, respectively, which is almost the same as that in a batch process.

Keywords: Distillery effluent; Emulsion liquid membrane; Extractor; M/E ratio; Agitator speed

1. Introduction

Emulsion liquid membrane (ELM) is a highly sophisticated but an energy-saving separation technique. Many studies have been carried out for separation of heavy metal ions, chemicals, organic acids, etc. by using this technique. In this technology, solutes are not only removed but also concentrated. The external phase to be treated is contacted with an emulsion dispersed in globules. Each emulsion globule consists of droplets of an aqueous internal stripping phase encapsulated in an organic membrane phase containing a surfactant as micelle interfacial layer. During this contact, solute transport occurs through the membrane phase into the internal stripping phase where it is concentrated. Since extraction and stripping are done in a single step, ELM technology is more preferred to treat effluents. Effluents from distilleries, tanneries and milk processing plants have been posing serious problems and extensive efforts to overcome them are in progress. Use of emulsion liquid membrane in effluent treatment has received wide attention due to its ease of operation, lower power consumption and modular design. A review of literature indicates that citric acid was extracted [1,2] using Shellsol oil in the organic phase, which, however, had the problem of swelling and leakage. ELM was used for extraction of lactic acid [3] and it is reported that 10% by volume of SPAN 80 in the membrane phase was required for stable emulsion. Citric acid was also extracted [4] using aqueous sodium hydroxide solution as internal stripping agent. Separation of mono-, di- and tri-valent metal ions was also tried with the aid of reversed micelles by Harada et al. [5]. The present paper is on batch extraction of acetic acid from distillery waste using ELM and optimizes agitator speed and M/E ratio on the performance of extraction. Further these optimum values obtained in batch studies were utilized on a rotary type, continuous York-Schiebel column to check its performance for future large scale applications.

2. Experimental

The ELM used in this work was water–oil–water (W/O/W) type of emulsion formed by mixing 50% by volume of distilled water as the internal stripping phase with 50% by volume of organic phase. The organic phase initially tried contained 2–5% xylene, 4–14% creslox emulsifier, an Indian glycol non-ionic surfactant obtained from Imperial Chemical Industries, India, and the rest was liquid paraffin. Xylene is the preferred solvent because of its high

* Corresponding author.
E-mail address: naraman@rect.ernet.in (N. Anantharaman).
[1] Present address: Department of Chemical Engineering, University Department of Chemical Technology, Mumbai, India.

1385-8947/$ – see front matter © 2003 Elsevier Science B.V. All rights reserved.
doi:10.1016/S1385-8947(03)00105-0

selectivity for organic compounds. The mixture was stirred at 4800 rpm for 15 min to produce an emulsion and stored for 24 h to check its stability. After several trials, it was found that stable emulsion should contain 2–5% xylene and 10% emulsifier and the rest liquid paraffin. After several trials an emulsion containing 2–5% xylene, 10% emulsifier and the rest liquid paraffin was very stable.

A one lit capacity batch extractor of 12.5 cm in diameter and 20 cm in height with a variable speed agitator of paddle type was charged with 300 ml of ELM and effluent (external phase) and stirred well. The quality of the effluent as obtained from the distillery is given in Table 1. The

Table 1
Properties of distillery effluent

S. no.	Effluent properties	Property value
1	Color	Dark brown
2	Odor	Rotten egg smell
3	COD	6800 ppm
4	BOD	3500 ppm
5	Absorbance	3.594
6	pH	3.64
7	Density	1000 kg/m^3
8	Boiling point	98 °C

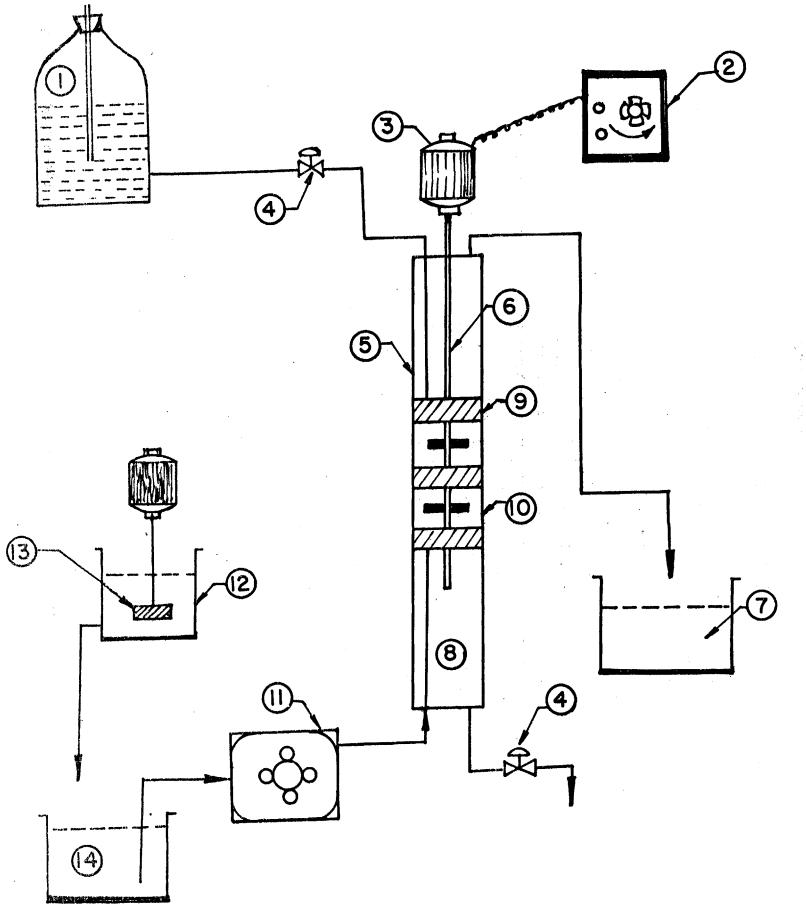

Fig. 1. Schematic diagram of York-Schiebel column.

Table 2
Results of continuous York-Schiebel column experiments at optimized conditions

S. no.	Parameter	Agitator speed at 110 rpm
1	pH	6.48
2	COD	900 ppm
3	BOD	94.3 ppm

external phase after agitation was separated and analyzed for acetic acid concentration in a UV Jasco spectrophotometer at 230 nm in the UV wavelength range. The pH was measured by a Mettler Delta pH meter. Biological oxygen demand (BOD) and chemical oxygen demand (COD) were determined by standard methods followed in APHA, 1992 [6]. The experiments were repeated for membrane to external phase (M/E) ratios of 0.33, 0.5, 1, 2, 2.3 and 2.5 and agitator speeds of 60, 80, 100, 110, 120 and 130 rpm. The experiments were repeated twice to check the reproducibility of the results.

The rotary type continuous York-Schiebel column, which has a better efficiency than plate and packed columns, and can handle larger capacity of effluents has also been used in this work. The column used in this study is shown in Fig. 1. Of the total height of 2.4 m, 0.4 m each at top and bottom was, respectively, used as settling zone, while the rest served for extraction. The effluent was fed from the top by gravity while the membrane phase with 4% xylene was pumped using a peristaltic pump to attain a M/E ratio of 0.8. After attaining steady state the treated effluent was collected and analyzed. The results are shown in Table 2 for an agitator speed of 110 rpm, which was optimized in the batch process.

3. Results and discussions

The Figs. 2–8 represent the various parameters studied for a batch extractor. Fig. 2 shows the effect of mixing time on the fraction of solute retained in external phase for various xylene concentrations. As the mixing time increases, there is a continuous drop in acetic acid concentration up to 8 min for xylene concentrations of 2, 3 and 4% and thereafter remains constant. For xylene concentration of 5%, the drop in acid concentration continues up to 10 min and remains constant.

Figs. 3 and 4 show the effect of agitator speed on pH and percentage solute (acetic acid) recovered from external phase. The percentage recovery of solute is defined as the ratio of difference in initial and final solute concentrations to that of the initial solute concentration. It is seen from the above figures that as the speed was increased from 60 to 110 rpm, the pH of the external phase increased up to 110 rpm and then decreased for all xylene concentrations. Similarly for the same range of speed, the percentage solute recovered from external phase increased and then decreased for all xylene concentrations. A maximum of 44.2% solute recovery in the external phase and a maximum pH of 6.39 were observed for 4% xylene concentration. The reason for the drop in percentage solute extracted from external phase beyond 110 rpm may be due to either de-emulsification induced by higher shear of the impeller or due to leakage from internal stripping phase.

Figs. 5–8 show the effect of M/E ratio on pH, COD (ppm), BOD (ppm) and percentage solute recovered from the external phase for an agitator speed of 110 rpm at 4% xylene concentration optimized earlier. It is observed from Figs. 5 and 6 that as M/E ratio was increased, the pH of external phase increased to a maximum of 6.4 for M/E ratio of 0.8 at

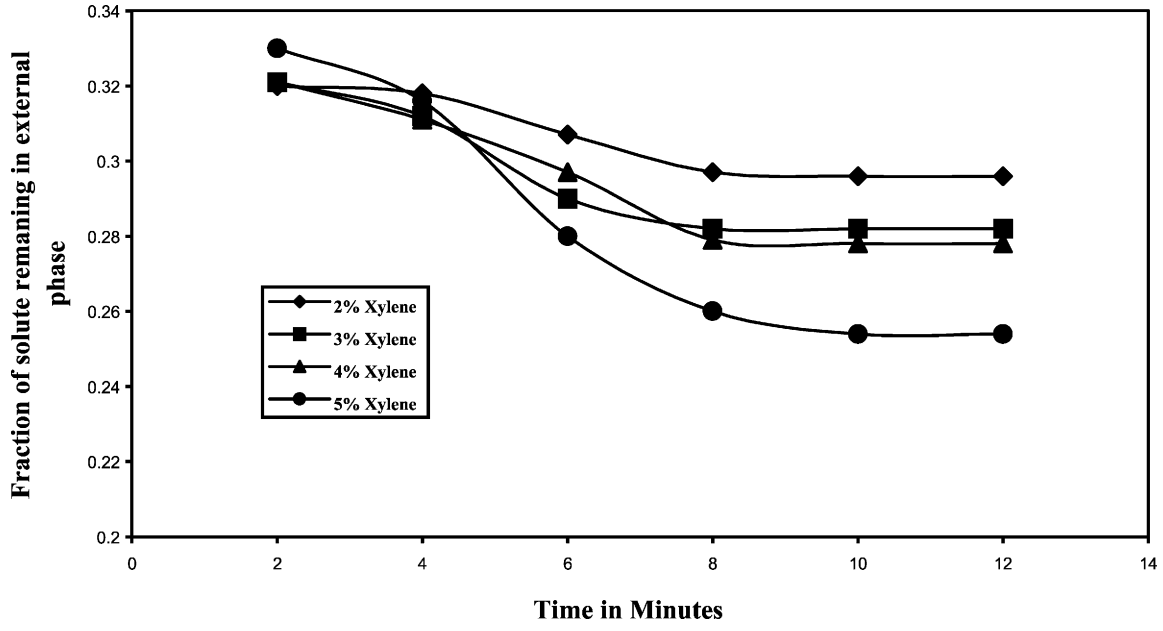

Fig. 2. Effect of agitation time on extraction (agitator speed: 100 rpm and M/E ratio: 1.0).

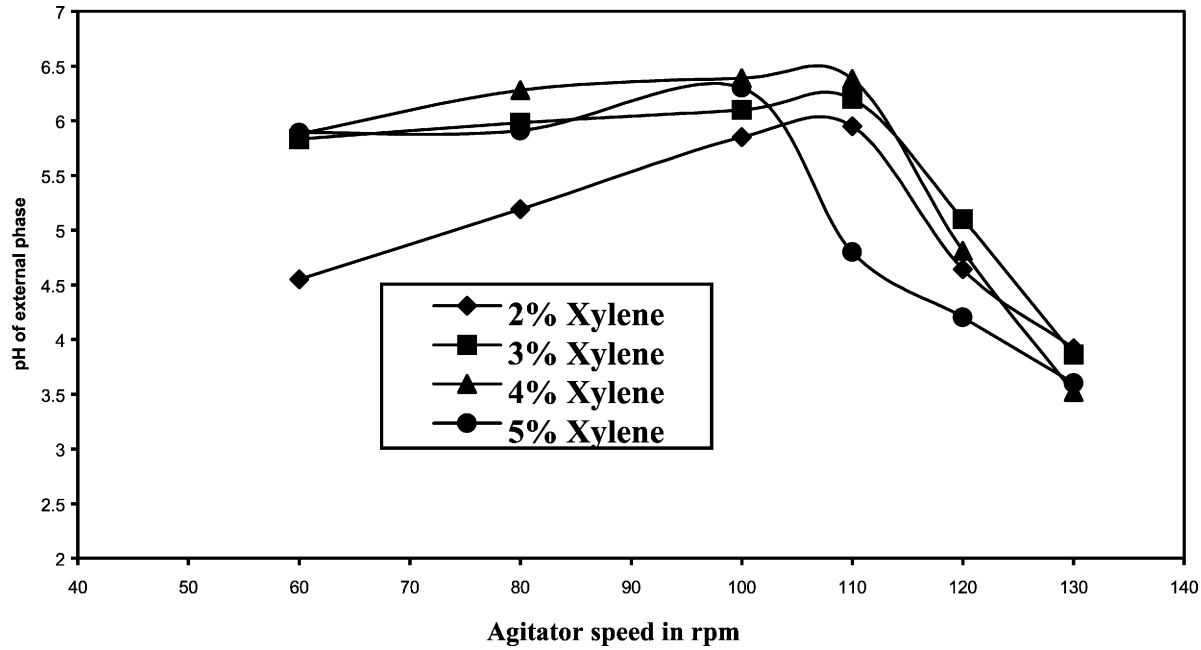

Fig. 3. Effect of agitator speed on pH of external phase (agitation time: 10 min and M/E ratio: 1.0).

110 rpm and then decreased. Similarly, the percentage solute extracted increased to a maximum of 44.2 for M/E ratio of 0.8 and then decreased. These observations clearly indicate that when M/E ratio was increased beyond 0.8, the interfacial area of contact between external phase and emulsion decreases due to the high intensity of micelle concentration, nothing but the dense micelle interfacial layer formed at the membrane phase which resists the solute transfer. A comparison between Figs. 3 and 4 and Figs. 5 and 6 reveals that there is an almost one-to-one correlation because of the increase in percentage solute recovery in external phase will improve the pH of treated effluent.

Figs. 7 and 8 reveal that when the M/E ratio was varied from 0.33 to 0.8, both COD and BOD decreased to minimum values and these values have been found from the plot as 927 and 96.5 ppm, respectively. For a M/E ratio >0.8, COD and BOD values started increasing. The drastic reduction of these values may be due to the extraction of other components such as acetic anhydride and ethanol along with acetic acid from the external phase. The maximum reduction of COD, BOD and the maximum increase of pH were obtained for an agitator speed of 110 rpm and a M/E ratio of 0.8 indicating that these were the optimum values for this extraction.

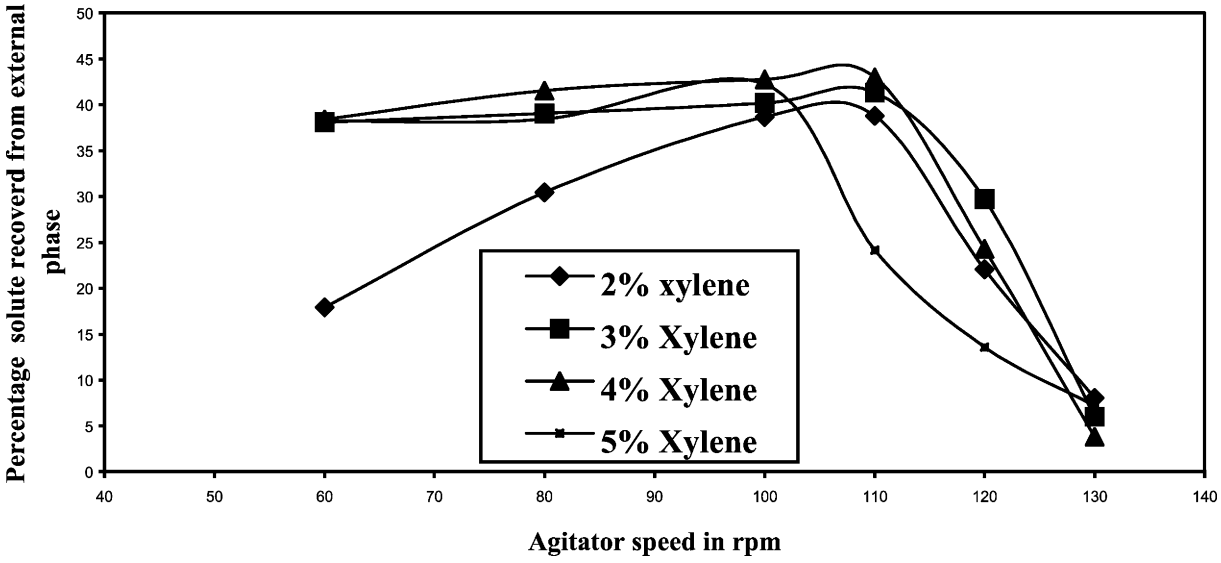

Fig. 4. Effect of agitator speed on percentage solute recovered from external phase (agitation time: 10 min and M/E ratio: 1.0).

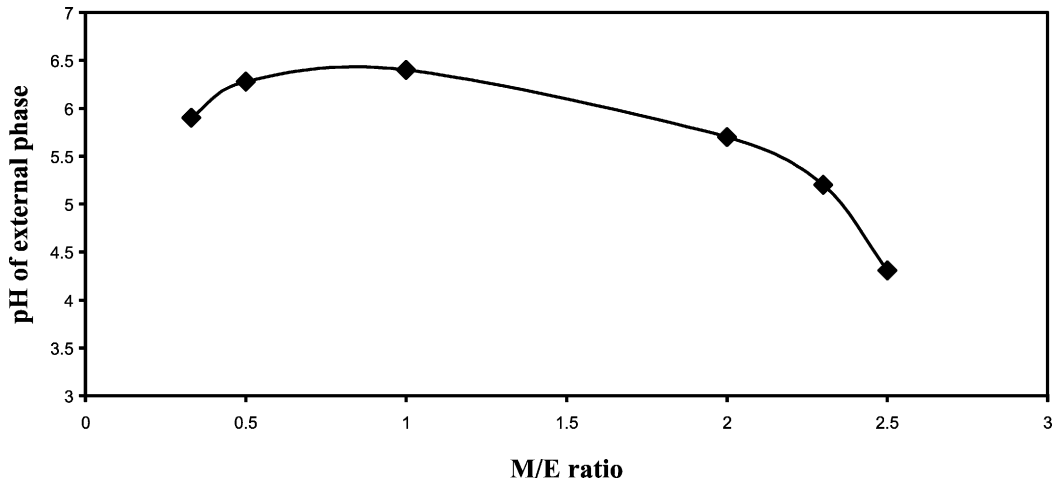

Fig. 5. Effect of M/E ratio on pH of external phase (agitator speed: 110 rpm and xylene concentration: 4%).

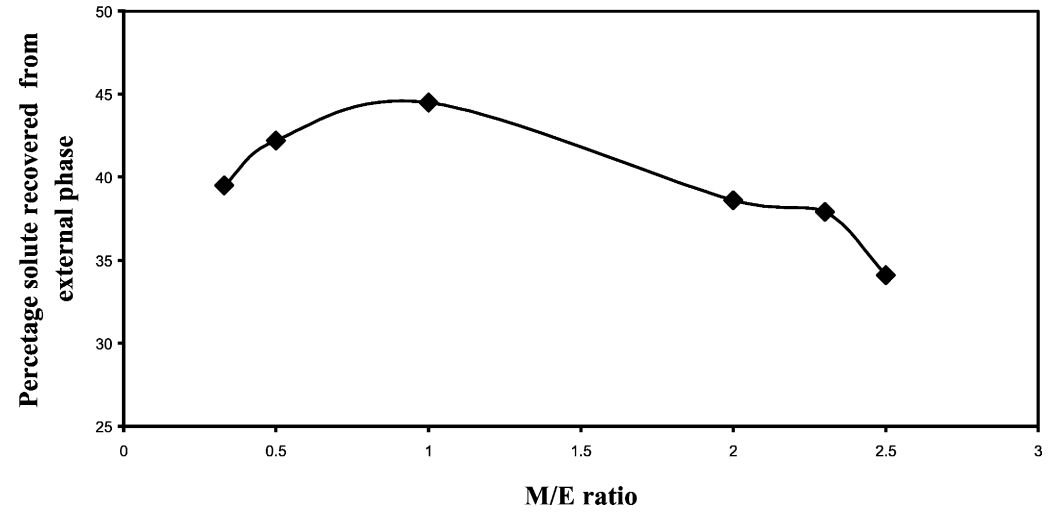

Fig. 6. Effect of M/E ratio on percentage solute recovered from external phase (agitator speed: 110 rpm and xylene concentration: 4%).

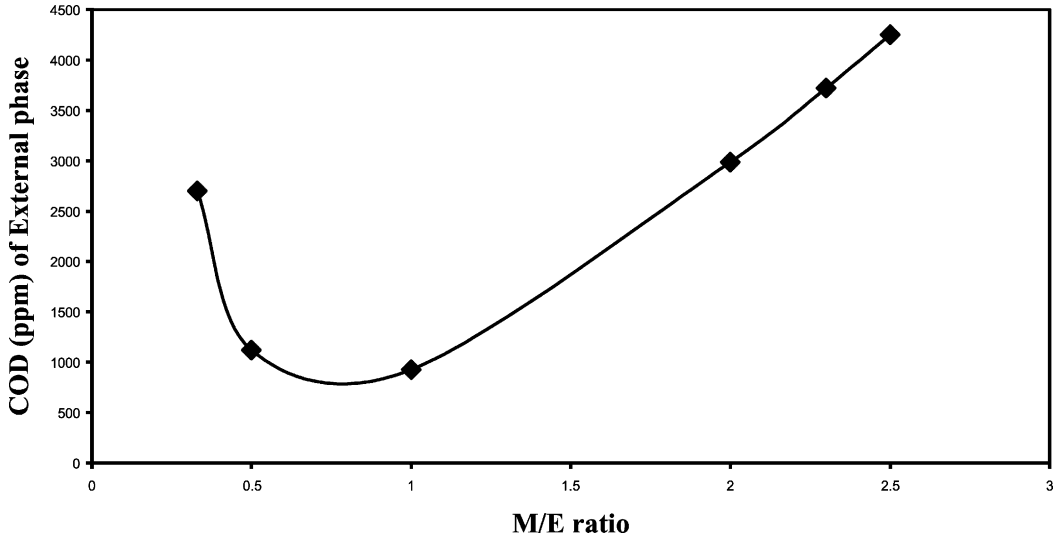

Fig. 7. Effect of M/E ratio on COD in external phase (agitator speed: 110 rpm and xylene concentration: 4%).

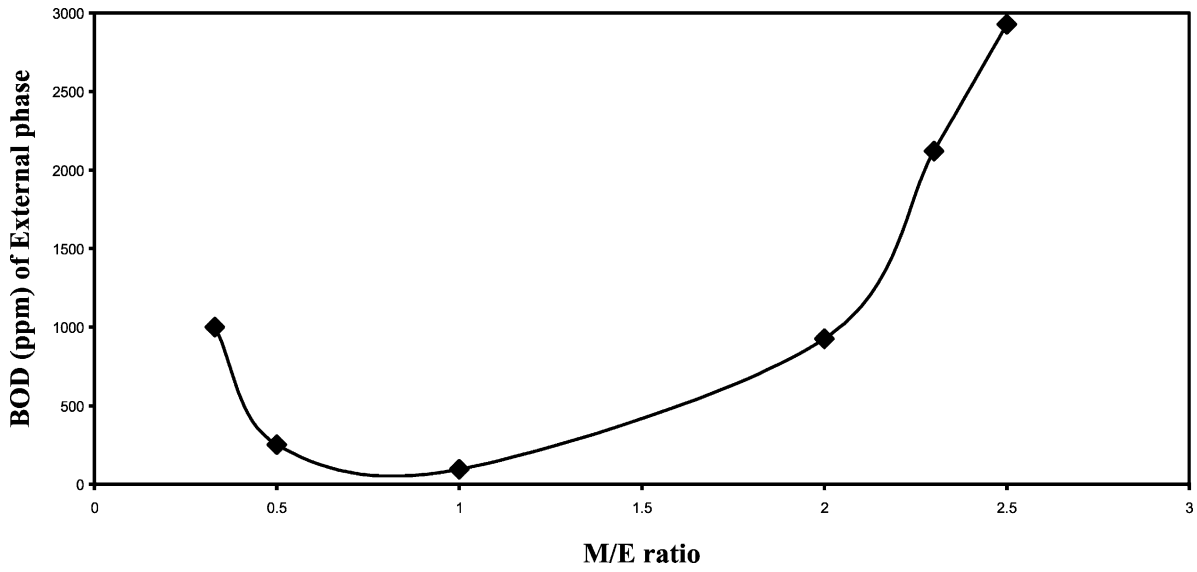

Fig. 8. Effect of M/E ratio on BOD of external phase (agitator speed: 110 rpm and xylene concentration: 4%).

The results in Table 2 show that the BOD, COD and pH of treated effluent are almost the same values as that obtained in batch operation at an agitator speed of 110 rpm and 4% xylene concentration indicating continuous treatment of distillery waste can be done efficiently in a York-Schiebel column.

4. Conclusion

In the ELM extraction technique for the removal of acetic acid, the maximum increase of pH and percentage solute recovered from external phase and the minimum BOD and COD values were obtained for an agitator speed of 110 rpm, 4% xylene concentration and M/E ratio of 0.8 and they were found to be 6.4, 44.2, 96.5 and 927 ppm, respectively. The experiment was also conducted in a continuous York-Schiebel column at the optimized experimental parameter conditions obtained earlier in batch operation. The pH, BOD and COD of treated effluent were 6.48, 94 and 900 ppm, respectively, which is almost the same as that in a batch process indicating that the continuous treatment of distillery waste can be done efficiently in a York-Schiebel column in future large scale applications.

References

[1] S.C. Boey, G.D.M.C. Cerro, D.L. Pyle, Extraction of citric acid by liquid membrane extraction, Inst. Chem. Eng. 65 (1987) 218–220.
[2] R. Basu, K.K. Srikar, Hollow fiber contained liquid membrane separation of citric acid, AICHE J. 37 (1991) 383–393.
[3] J.B. Chaudhuri, D.L. Pyle, Emulsion liquid membrane extraction of organic acids (Part I), Chem. Eng. Sci. 47 (1992) 41–49.
[4] S.B. Hu, J.M. Wiencek, Emulsion liquid membrane extraction of copper using a hollow fiber contactor, AICHE J. 44 (1998) 570–581.
[5] M. Harada, N. Shinbara, M. Adachi, Y. Miyake, Liquid membrane operation with acid of microemulsion—separation of metal ions, J. Chem. Eng. Jpn. 23 (1990) 50–57.
[6] Standard Methods for the Examination of Water and Waste Water, APHA, 18th ed., Washington, DC, USA, 1992.