International Journal of ChemTech Research
CODEN (USA): IJCRGG, ISSN: 0974-4290, ISSN(Online):2455-9555
Vol.11 No.10, pp 14-21, 2018

Recovery of Fumaric acid from Aqueous Solution Using Laboratory Prepared Nontoxic Diluent

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Abstract : The present work was done to check the ability of three laboratory-modified nontoxic diluents (made from sunflower, rice bran, & Sesame oil) for the extraction of fumaric acid (dicarboxylic acid) with Tri-n-octyl amine as an extractant. Physical extraction studies with fumaric acid showed that the three modified diluents are incapable of extracting fumaric acid The most effective Tri-n-Octylamine (TOA) extractant was dissolved in the three modified diluents (made from sunflower, rice bran, Sesame oil). Extraction efficiency increased with the increase in the percentage (V/V) of Tri-n-Octylamine (TOA) indicating a prominent role of the extractant. The extraction efficiency of 30% Tri-n-Octylamine (TOA) inall the 3 modified oils (diluent) is nearly 90%. The effect of higher percentages of Tri-n-Octylamine (TOA) extractant on extraction efficiency was also studied but the marginal increase in the extraction efficiency was found for all the three laboratory-modified oils.
Keywords : Fumaric acid, dicarboxylic acid, Tri-n-octyl amine (TOA), laboratory-modified nontoxic diluent, Reactive extraction.

1. Introduction:

Dicarboxylic acid like fumaric acid can be easily manufactured from petroleum feedstock via maleic acid (cis counterpart) through a series of steps like hydrolysis of anhydride to maleic acid and then isomerization to fumaric acid. It has low water solubility and high boiling point. The worldwide production of this acid is likely to touch 346-kilo tons by 2020 (5.9% increase from 2014 to 2020). The moderate growth in the demand of due to health consciousness among people to have a natural product like fumaric acid to be used as acidulants and flavoring agent in food and feed and also as a preservative. [1]

Fumaric acid founds application as buffering agent; precursor to acids like Glutaric acid, health drinks, cosmetics, manufacture of synthetic resins &biodegradable polymers(due to the presence of double bond favoring condensation and addition polymerization) and as an acid sizing agent in paper and pulp industry. Recently, a lot of focus is on the utilization of cheap abundant biomass generated due to humans into useful

DOI= http://dx.doi.org/10.20902/IJCTR.2018.111003

chemicals s by fermentation. Three strains of fungus bacterial strains have shown potential to produce fumaric acid using distillers' dried grains [2].

The high cost of recovery of products from fermentation is the biggest barrier in making this fermentation-based process an industrially viable option. Various methods such as ion-exchange, adsorption, nanofiltration, dialysis conventional electrodialysis, and bipolar electrodialysis are widely searched and proposed an alternative to traditional techniques such as extraction, precipitation and crystallizationcan for organic acid separation from fermentation broth and wastewater (low concentration).

Reactive extraction is regarded as the most probable method that can replace traditional methods due to high selectivity & high efficiency (effective extractant), the low temperature needed (efficiency is higher at low temperature), extractant can be recycled, and low operatingcost [3]. King [4]postulated that reactive extraction is one of the best and effective methods for separatingpolar organic substances with low concentration from wastewater or fermentation broth.

Now a day's researchers are working to integrate fermentation and extraction by replacing petroleum-based diluents with vegetable oils [5]-[15].

The reactive extraction when applied to the recovery of organic acids from fermentation broth often takes into account the toxicity of organic phase and only Uslu [6] have worked on nontoxic diluent for fumaric acid recovery so there is need to try other non-toxic options also. Here modified diluent (made from sunflower, rice bran, & sesame oil)is considered as an alternative process for the recovery of fumaric acid from fermentation broth or wastewater.

2.Materials and Methods:

Materials Procured

All the chemicals in the experiments were purchased through a local vendor and were used without any kind of treatment. The preparation of solutions(stock and diluted) were done using de-ionized water. Fumaric acid and Tri-n-Octyl amine (TOA) were supplied by SRL Pvt. Limited. The nontoxic diluentused in through the experiment was prepared through the chemical process on vegetable oils in the lab. A solution of phenolphthalein was purchased for using an indicator. Each time the determination of aqueous phase acid concentration was done through freshly prepared NaOH. The concentration of NaOH was determined by titrating it with 0.1 N Oxalic acid every time.

3. Experimental setup used and Procedure:

Firstly, a stock solution of concentration 0.5 kmols/m^3fumaric acid was prepared in de-ionized water. The desired concentrations to be used in extraction studies were prepared by diluting the stock solution with de-ionized water. The Tri-n-Octyl amine (TOA) extractant was dissolved in non-toxic diluent and solutions of 10%-50 % by volume of extractant (TOA) were prepared. A 10 ml each of aqueous and organic solutions were poured in conical flasks. These flasks were shaken in the Orbital shaking incubator at 150 rpm at 298K for 12 hours. The vigorously mixed phases were separated by Centrifuge (Make: REMI) by operating at 6,000 rpm for 10 minutes. The acid amount extracted by TOA into organic phase was determined by application of mass balance. A small number of runs were duplicated (observed accuracy was within ±2%)to check the reproducibility of the data.

4. Reactive extraction:

When the pH of the aqueous solution is smaller than p*K*a of the acid then carboxylic acid dissociates to a small extent only in the in aqueous solution. When the acid isweak the effect of the acid dissociation can be neglected. The equation given below can very well describe the extraction of the carboxylic acid by TBP in the natural non-toxic diluent.

$$[HA]_{aq} + p[E]_{org} \underset{<}{\overset{K_S}{\longrightarrow}}> [HA.(E)_p]_{org} \qquad (1)$$

According to the law of mass action, the interaction between the extractant and the extracted species can be written as:

K_s =[(HA).(E)$_p$]$_{org}$ /[HA]$_{aq}$ [E]$^p_{org}$ (2)

Where [HA]$_{aq}$ represents acid concentration in the aqueous phase and [E$_{org}$], [HA. (E)$_p$]$_{org}$ represents extractants concentration and acid extractant complex concentrations in the organic phase and the value of K_s depends upon properties of acids and of the diluent used and in particular the solvation(dissolving capacity)of diluent.

When pH is below pKa, acid consists of only the undissociated form is assumed by neglecting ionization so the extraction process can be analyzed by using the distribution coefficient (K_D). The Overall degree of extraction (E %) in terms of distribution coefficient canbe calculated as given below:

$$\% E= K_D \times 100/ (1+ K_D) \quad (3)$$

Model for Prediction Complexes based on Z values:

Loading ratio (Z) which represents the degree of loading of the organic phase (extractant + diluent) with acid can be described as:

$$Z = \frac{[\mathrm{HA}]_{\mathrm{org}}}{[\mathrm{E}]} \quad (4)$$

The nature of complexes can be described on the basis of values of the Z by applying fundamentals of chem. model. The 1:1, 2:1 and 3:1 types of complexes between acid and extractant seems to exist depending upon the values of Z. For low values of Z< 0.5, a complex of (1:1) between acid and extractant is assumed to be formed and for higher values of Z, 2:1 and 3:1 types of complexes are assumed to form.

5. Results and Discussion:

Physical extraction:

Recovery of fumaric acid with the help of modified oils *(made from sunflower, rice bran, & Sesame oil*) was carried out in the manner as described in the section: experimental setup used and procedure.The modified oils failed to extract fumaric acid from aqueous solution.Marti [13] also reported that sunflower oil could not extract formic acid so above observation is consistent with the results cited in the literature. The TOA was used as extractant to facilitate the process of extraction of fumaric acid from aqueous solution.

Reactive extraction with 10%-30% TOA in modified Sunflower Oil:

Table1: Experimental Results for the Extraction of Fumaric Acid by TOA in modified Sunflower Oil

The initial concentration of Acid [HA]$_{INI}$	Vol% of TOA (extractant)	[HA]$_F$	[HA]$_{Org.}$ =[HA$_{INI.}$-HA$_F$]	K_D=[HA]$_{Org.}$/ [HA]$_F$	E%=K_D/(1+K_D)*100	Z=[HA]$_{org.}$/[E]
.01	**10**	.0021	.0079	3.76	78.99	0.03
.02	**10**	.0033	.0167	5.06	83.49	0.07
.03	**10**	.0037	.0263	7.10	87.65	0.11
.04	**10**	.0046	.0354	7.69	88.49	0.15
.01	**20**	.0025	.0075	3.00	75.00	0.016
.02	**20**	.0029	.0171	5.89	85.48	0.037
.03	**20**	.0037	.0263	7.10	87.16	0.057
.04	**20**	.0046	.0354	7.69	88.49	0.077
.01	**30**	.0025	.0075	3.00	75.00	0.010
.02	**30**	.0033	.0167	5.06	83.49	0.024
.03	**30**	.0042	.0258	6.14	85.99	0.037
.04	**30**	.0050	.0350	7.00	87.50	0.05

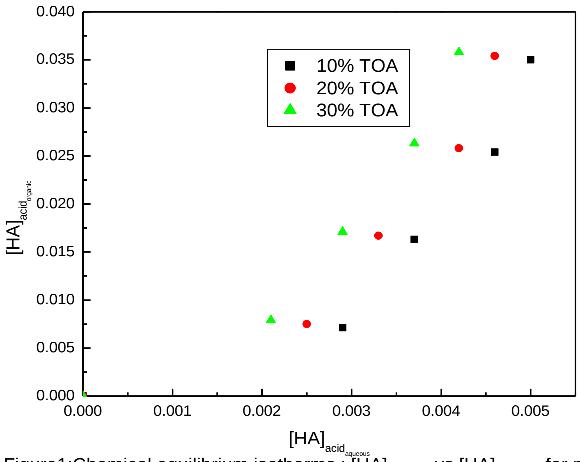

Figure1:Chemical equilibrium isotherms : $[HA]_{acid_{organic}}$ vs $[HA]_{acid_{aqueous}}$ for modified sunflower oil

Reactive extraction with 10%-30% TOA in modifiedRice Bran Oil:

Table2: Experimental Results for the Extraction of Fumaric Acid by TOA in modified Rice bran Oil

The initial concentration of Acid $[HA]_{INI}$	**Vol% of TOA (extractant)**	**$[HA]_F$**	**$[HA]_{Org.}$ $=[HA_{INI.}-HA_F]$**	**$K_D=[HA]_{Org.}/[HA]_F$**	**$E\%=K_D/(1+K_D)*100$**	**$Z=[HA]_{org.}/[E]$**
.01	**10**	.0025	.0075	3.00	75.00	0.032
.02	**10**	.0029	.0171	5.89	85.48	0.075
.03	**10**	.0033	.0267	8.09	88.99	0.117
.04	**10**	.0042	.0358	8.52	89.49	0.157
.01	**20**	.0021	.0079	3.76	78.99	0.017
.02	**20**	.0025	.0175	7.00	87.50	0.038
.03	**20**	.0029	.0271	9.34	90.32	0.05
.04	**20**	.0038	.0362	9.52	90.49	0.07
.01	**30**	.0016	.0084	5.25	84.00	0.012
.02	**30**	.0021	.0179	8.52	89.49	0.0261
.03	**30**	.0025	.0275	11.00	91.66	0.040
.04	**30**	.0029	.0371	12.79	92.74	0.054

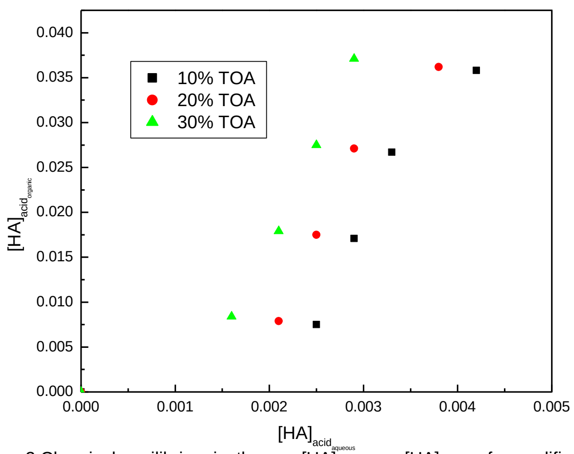

Figure2:Chemical equilibrium isotherms: $[HA]_{acid_{organic}}$ vs $[HA]_{acid_{aqueous}}$ for modified ricebran oil oil

Reactive extraction with 10%-30% TOA in modified Sesame Oil:

Table3: Experimental Results for the Extraction of Fumaric Acid by TOA in modified Sesame Oil

The initial concentration of Acid $[HA]_{INI}$	Vol% of TOA (extractant)	$[HA]_F$	$[HA]_{Org.} = [HA_{INI.} - HA_F]$	$K_D = [HA]_{Org.} / [HA]_F$	$E\% = K_D/(1+K_D)*100$	$Z = [HA]_{org.}/[E]$
.01	**10**	0.0029	0.0071	2.44	71.17	0.024
.02	**10**	0.0038	0.0162	4.26	80.98	0.056
.03	**10**	0.0046	0.0254	5.52	84.66	0.088
.04	**10**	0.0059	0.0341	5.77	85.22	0.118
.01	**20**	0.0025	0.0079	3.16	75.96	0.0173
.02	**20**	0.0029	0.0171	5.89	85.48	0.037
.03	**20**	0.0034	0.0266	7.82	88.66	0.058
.04	**20**	0.0042	0.0356	8.47	89.44	0.078
.01	**30**	0.0017	0.0083	4.88	82.99	0.012
.02	**30**	0.0025	0.0175	7.00	87.50	0.025
.03	**30**	0.0029	0.0271	9.34	90.32	0.039
.04	**30**	0.0034	0.0366	10.76	91.53	0.053

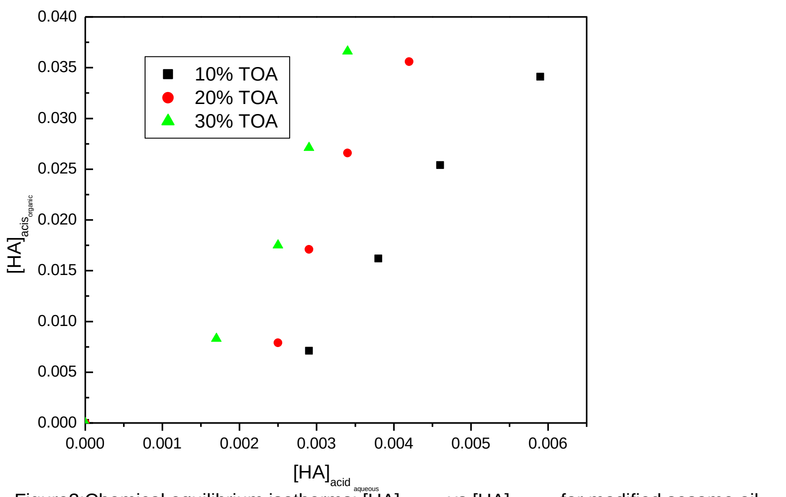

Figure3:Chemical equilibrium isotherms: $[HA]_{acid_{organic}}$ vs $[HA]_{acid_{aqueous}}$ for modified sesame oil

Reactive extraction with 40%-50% TOA in modified Sesame Oil, Rice Bran Oil and Sunflower Oil with 0.5 kmols/m^3 of initial fumaric acid

Table 4 : Experimental Results for the Extraction of Fumaric Acid by TOA in modified Sesame Oil, Rice Bran Oil and Sunflower Oil with 0.5 kmols/m^3 of initial fumaric acid.

Diluent	The initial concentration of Acid $[HA]_{INI}$	Vol% of TOA	$[HA]_F$	$[HA]_{Org.} = [HA_{INI.} - HA_F]$	$K_D = [HA]_{Org} / [HA]_F$	$E\% = K_D/(1+K_D)*100$	$Z = [HA]_{org.}/[E]$
Modified Sunflower oil							
	.05	**40**	0.0039	0.0461	11.82	92.19	0.040
	.05	**50**	0.0035	0.0465	13.28	93.03	0.032
Modified Rice Bran Oil							
	.05	**40**	0.0042	0.0458	10.90	91.60	0.048
	.05	**50**	0.0078	0.0421	11.50	92.00	0.029
Modified Sesame Oil							
	.05	**40**	0.0045	0.0454	10.08	90.97	0.039
	.05	**50**	0.0043	0.0457	10.62	91.39	0.041

The removal of fumaric acid by TOA dissolved in the modified nontoxic diluents sunflower oil, rice bran oil, and sesame oil in terms of distribution coefficient and extraction efficiency are tabulated in Tables 1-4. The extraction power of organic phase consisting of (TOA + diluent) mixtures changes with increasing initial concentration of amine in the organic phase. The following orders were obtained withmodified sunflower oil (13.28) > rice bran oil (11.50) > sesame oil (10.62) in TOA when the distribution coefficients (K_D) of the diluents were compared at 50% TOA. The following orders ofmaximum extraction efficiencies for removal of fumaric acid at 50% TOA in the diluents were obtained as sunflower oil (93.03%) > rice bran oil (92%) > sesame oil (91.39%) respectively. However, the efficiency increasesin all threecaseswith the increase in amine concentration and the increase were sharp till 30% but declined at higher TOA indicating a limitation of diluent to solvate the acid –extractant complex or it may be due to increased viscosity of organic phase due to increase in TOA%. These extraction efficiencies were raised by using reactive extractants so from an economical point of view 30% TOA as suggested for extraction. The following orders were obtained in terms of extraction efficiency at 30% sunflower oil (87.50%) > rice bran oil (92.74%) > sesame oil (91.53%) respectively.

Loading Ratios(Z)

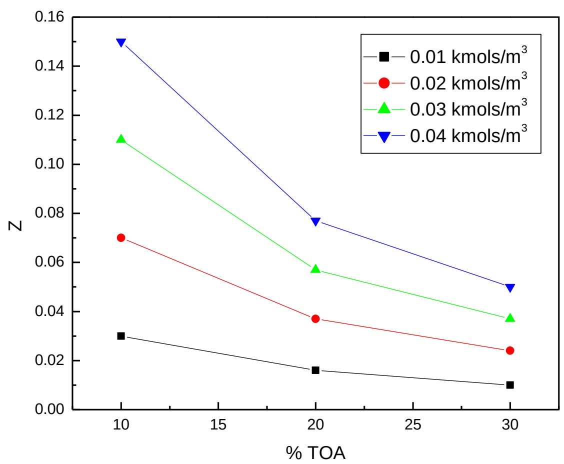

Figure 4:Loading ratios for the reactive extraction of fumaric acid using modified sunflower oil as organic phase diluent.

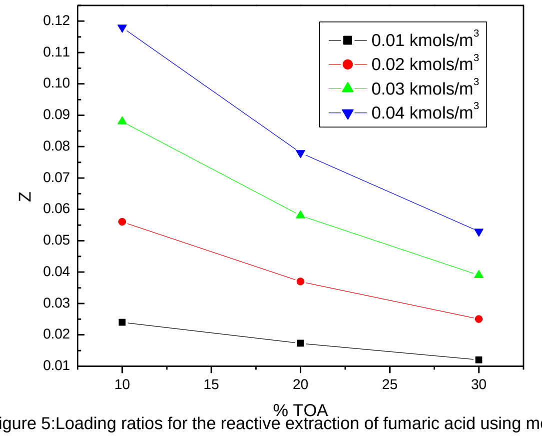

Figure 5:Loading ratios for the reactive extraction of fumaric acid using modified sesame oil as organic phase diluent.

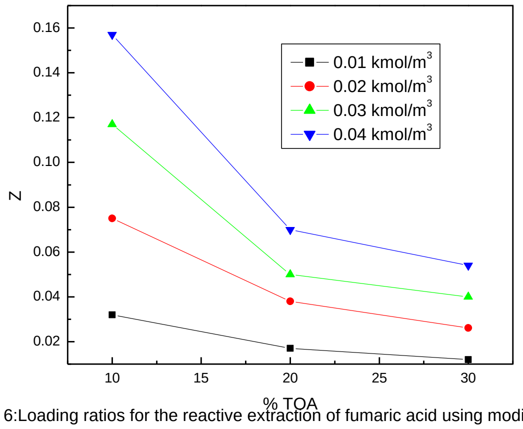

Figure 6:Loading ratios for the reactive extraction of fumaric acid using modified ricebran oil as organic phase diluent.

It can clearly be observed from figures4-6 that the loading factor values for the combination of TOA and all nontoxic diluents were lower than 0.5. The Z values were in the range from 0.010to 0.15 for sunflower 0.012to 0.157 for rice bran oil and 0.012 to 0.118 for sesame oil. No Overloading (Z > 1) was observed. The values of Z suggest that the complex formed (acid –extractant) contains one amine molecule and one acid molecule (1:1) for all diluents.Theliterature shows that the loading ratio depends on diluent also.The results also showed that Z values were markedly influenced by acid and extractant concentrations. The values of Z decrease with the increase in % TOA and are higher for higher acid concentration. Marti [13] and H Uslu [6] also obtained similar values of Z while using natural diluents.

6. Conclusions:

The laboratory prepared modified oils(sunflower oil, rice bran oil, sesame oil) proved to be excellent diluent at 30%TOA to extract fumaric acid.. The efficiency of extraction is comparable with the data available in the literature indicated the viability of results obtained. The values of Z(less than 0.5) confirm the formation of 1:1 acid-amine complexes in the present case. The maximum extraction efficiency (E) of as 92.59 % was obtained for a system consisting of TOA in Rice bran oil.

Symbols Used:

[E] = Extractant concentration in organic phase (kmol/m^3)
[HA]= Concentration of acid, (kmol/m^3)
(K_S)=Extraction equilibrium constant
D = Dimerization constant (m^3/kmol)

E% =Extraction efficiency
K_D = Acid distribution coefficient
Z= loading ratio

Subscripts

aq. = aqueous phase
org = organic phase

Superscript

diluent = for diluent only

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