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Acetic acid Extraction from Aqueous Solution using Tributyl phosphate in Modified Soyabean oil

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Abstract- Experimental study for extraction of acetic acid using tri-n-butyl phosphate (TBP) in non-toxic diluent (modified soyabean oil) from aqueous solution has been described here. The shaking time was optimized by performing extraction equilibrium studies for recovery of acetic acid from aqueous solution, the temperature effect on extraction efficiency and the effect of varying percentage of extractant on the extraction efficiency was determined. The experimental studies showed a marked influence of extractant (TBP) on the extraction of acetic acid from modified soyabean oil.

Index Terms- Acetic acid, modified soyabean oil, non-toxic diluent, TBP.

1. INTRODUCTION

These days acetic acid is an indispensable and most widely used aliphatic carbonic acid that finds application in chemical, food and pharmaceutical industries. The acetic acid can be used as reactant (in the production of acetic-acid esters) and it can also be employed as a solvent (in the production of cellulose acetate or in the manufacture of pharmaceutical products). The production of acetic acid by microbiological method (fermentation) in the past has been replaced by synthetic methods (petroleum resources) but currently the huge demand of acetic acid is largely met by extraction from wastewater (containing significant amount of acetic acid) to meet the water quality standards and fermentation (in spite of significant separation costs).

The various methods that can be used for recovery of acetic acid from wastewater are a distillation, membrane separations, precipitation, adsorption, reactive extraction, etc. [1]. Reactive extraction is showing a lot of promise over other methods due to ease in operation and ability to accommodate wastes containing a high concentration of toxic metals. Generally, reactive extraction requires the use of an extractant (organophosphorus-based and amine-based compounds) dissolved in a diluent (alcohol, hydrocarbons, ketone, etc.) for recovery of acids. The diluent may not be good at extraction but provide appropriate physical properties to extractant for use in the extraction process. The combination of solvating extractants and diluents opens a lot of new avenues in process development for extraction thus reduces energy and reagent consumption. A number of studies on the extraction of organic acids have been carried out using tri-n-butyl phosphate (TBP) [2-7] and also on acetic acid with various combinations of extractant and diluent. Recently, the toxicity of chemicals used in reactive extraction has drawn a lot of attention as it creates a hindrance for *in situ* recovery from fermentation broth; not only this, their solubility in water may affect the economics of wastewater treatment which is based on recycling of extractant. Vegetable oils can be a promising alternative as they are immiscible with water and non-toxic to microorganisms. Few citations using vegetable oils can be found in the literature [8-10]. The novelty of this work is the modification of soyabean oil without sacrificing immiscibility and toxicity.

2. MATERIALS AND METHOD

For the experimental studies on extraction, the extractant TBP and propionic acid were purchased from Thomas Baker. The soyabean oil purchased from the local market was modified prior to its use in the present study by one of the authors at UIET, CSJM University, Kanpur. Liquid phenolphthalein indicator was prepared in the laboratory and standardization of NaOH was done by titrating with oxalic acid. Distilled water was used for preparing an aqueous solution and other chemicals were used without any treatment.

The stock solution of acetic acid having concentration 0.6 gmol/litre was prepared using distilled water. This stock solution was further diluted for use in extraction experiments.

Both aqueous and organic phases (with extractant) were used in equal amounts (25 ml) and shaken for 4 hours (optimum time for shaking) in an orbital shaking incubator at 150 rpm. The centrifuge was used for separating the phases and then acid content was determined by titration with NaOH. The determination of acetic acid in the organic phase was done by using mass balance.

The extraction efficiency (*E* %) is determined using following formula:

$E\% = \{[HA],in - [HA],final/[HA],in\}*100$ …… (1)

Where,

[HA], in = Initial acid concentration

[HA], final = Initial acid concentration

[HA], org = Acid concentration in organic phase

A small number of experiments were also replicated to check the experimental error in the studies and were found to be within 3%.

3. RESULT AND DISCUSSION

3.1. *Effect of shaking time on extraction efficiency*

There is a lot of variation in the literature about shaking time, *i.e.*, 3-16 hours, so experiments were performed to optimize the shaking time by mapping the time required with extraction efficiency to obtain optimized time for shaking.

Table 1: Variation in extraction efficiency with shaking time at 32°C temperature, 0.5 gmol/litre acetic acid concentration and 50% TBP

Time (hrs)	[HA], final (gmol/litre)	[HA], org (gmol/litre)	Efficiency (%)
1	0.278	0.222	44
2	0.265	0.235	47
3	0.232	0.268	53
4	0.201	0.299	59
5	0.199	0.301	59.6

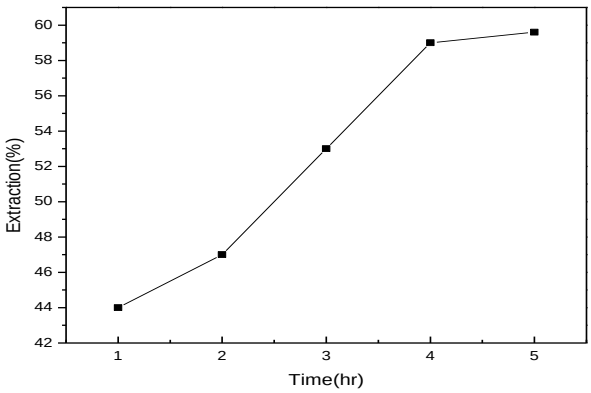

Figure 1: Variation in extraction efficiency with shaking time at 32°C temperature, 0.5 gmol/litre acetic acid concentration and 50% TBP.

The shaking time affects the economics of recovery process as it is an energy-intensive step and should be sufficient so that equilibrium stage is reached for maximum recovery, so the time of shaking in the orbital incubator shaker was varied from 1- 5 hours and extraction efficiency was calculated every time. The extraction efficiency showed no appreciable change between 4 and 5 hours (Table 1 and Fig. 1), hence 5 hours was taken as optimum shaking time for all reactive extraction experiments.

3.2. *Effect of temperature on extraction efficiency*

The extraction efficiency for recovery of acetic acid from aqueous solution decreases with the increase in temperature as tabulated in Table 2 and shown in Fig. 2. This drop in extraction efficiency may be due to exothermic reaction between acid and extractant as reported in the literature, shrinkage of two-phase region due to increase in the mutual solubility of two phases and increase in the ionization of acid due to decrease in ionization constant pKa (TBP is capable of extracting only unionised form of acid) [11-12].

Table 2: Variation in extraction efficiency with temperature at 0.5 gmol/litre acetic acid concentration and 50% TBP at 150 rpm

Temperature (°C)	[HA], final (gmol/L)	[HA], org (gmol/L)	Efficiency (%)
32	0.201	0.299	59
35	0.221	0.279	55
38	0.234	0.266	53
41	0.251	0.249	49

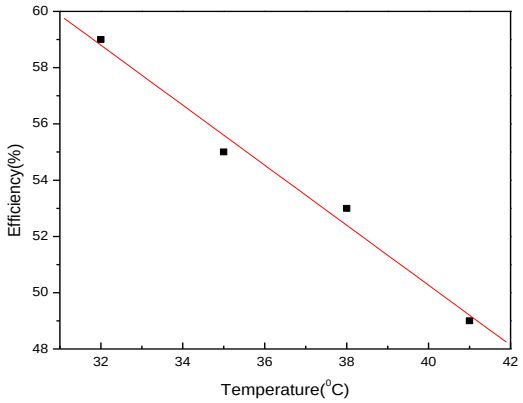

Figure 2: Variation in extraction efficiency with temperature at 0.5 gmol/litre acetic acid concentration and 50% TBP at 150 rpm.

3.3. *Effect of %TBP on extraction efficiency at a different initial acetic acid concentration*

Fig. 3 shows that the extraction efficiency of acetic acid with pure extractant TBP is lower than the 50% TBP in the oil because of better flow properties obtained when compared with viscous pure TBP. The viscosity of fluid plays an important role in mixing during shaking (high viscosity fluid show poor mixing). There is also a significant increase in the extraction efficiency when the percentage of TBP in oil is varied with initial concentrations of acetic acid. This is due to extractant TBP which forms an organic phase soluble complex via reversible complexion reaction. It also reflected the capability of the diluent (oil) in solvating the formed complex in the organic phase.

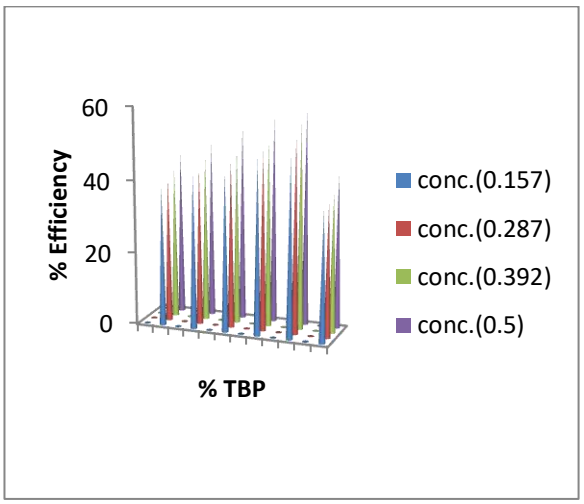

Figure 3: Variation in extraction efficiency with TBP% in oil for different initial acetic acid concentrations (gmole/litre)

4. CONCLUSIONS

The results of this study show that the present combination of TBP and modified soyabean oil is capable of extracting the acetic acid from aqueous solution. The combination of TBP and soyabean oil not only helps in reducing the toxicity (can be used for in-situ extraction from fermentation broth) but also the immiscibility (modified oil with water) is maintained. This ensures a negligible loss of extractant and diluent to an aqueous phase. The 50% TBP in oil was found to be the best for acetic acid recovery.

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