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Review Article

REACTIVE EXTRACTION A BOOM FOR ITACONIC ACID: A REVIEW

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ABSTRACT

The depletion of fossil fuels and need for sustainable development requires that fermentation Itaconic acid production replaces petroleum-based methods of Itaconic acid production. Itaconic acid is small organic acid with one or more carboxylic acid groups. Itaconic acid copolymers are used in packaging, substitutes for conventional plastics materials. Itaconic acid is also used for special lens and cut stone. Extraction of organic acids has been studied using tri-n-butyl phosphate. In this equilibrium study, a mixture of inert (1-Dodecanol, 1-Butanol & 1-Octanol) diluents is used to provide the appropriate physical properties of extractant (TBP) and improved extraction efficiency. Reactive Extraction with specific extractant and a proper combination of extractant and diluents provide the higher capacity and selectivity for Itaconic acid. The result of equilibrium experimental study is useful in extraction processes for recovery of Itaconic acids from fermentation broths.

INTRODUCTION

The itaconic acid production replaces petroleum-based methods of itaconic acid production. The high cost of downstream processing of biological production of itaconic acid is the only bottleneck which is preventing its commercialization. In 1837, Baup synthesized itaconic acid (IA) by thermal decomposition of citric acid. Itaconic Acid which is biodegradable in nature, it is small organic acid with one or more carboxylic acid groups. Figure 1 show the itaconic acid and their chemical structures. Itaconic acid is currently produced either from petroleum-based feed stocks through chemical synthesis or from carbohydrates via fermentation. Itaconic acid copolymers are used in packaging and have the advantage of being biodegradable and, both, substitutes for conventional plastics materials and new materials of specific uses, such as to prepare a water-soluble coating for food packaging to reduce bacterial contamination. Itaconic acid is also used in paint, ion-exchange resin, lubricant, binder, plasticizer, molding plastics and sealant. Its polymer has a special luster and transparency; it is fit for making synthetic special lens and cut stone. Exploitation of itaconic acid for production of biodegradable polymers is one among the recent applications.

However, the commercialization has not been done and the reason being the high cost of recovery and the difficult separation of the acid. In the present work, the reactive extraction of itaconic acid produced via fermentation, which is an intensified version of liquid-liquid extraction, is studied [1-2]. The traditional recovery process of itaconic acid from fermentation broth is quite complicated.

Generally, Organophosphorous-based and amine-based extractants are dissolved in diluents such as an alcohol, hydrocarbons, ketone etc. to provide appropriate physical properties for use in the extraction process. Polar diluents that enhance the extraction power of amines are more favorable than nonpolar diluents [3,4]. The solvating extractants open new avenues in process development and reduce energy and reagent consumption. Extraction of organic acids has been studied using tri-n-butyl phosphate (TBP)[5-10].

A biocompatible mixture of inert (1-dodecanol, 1-Butanol & 1-octanol) diluents is used to provide the appropriate physical properties of extractant (TBP) and improved extraction efficiency. 1-Dodecanol, 1-Butanol & 1-octanol as modifier are also useful if a third phase is formed during the extraction because of low solubility of acid extractant complex in the inert diluent.

Chemical Structure of Itaconic Acid

Its chemical formula is $HOOCCH_2C$ (=CH_2) COOH. Itaconic acid is a naturally occurring unsaturated 5-C dicarboxylic acid which is also known as methylenesuccinic acid or methylenebutanedioic acid. Its structural formula is given below:

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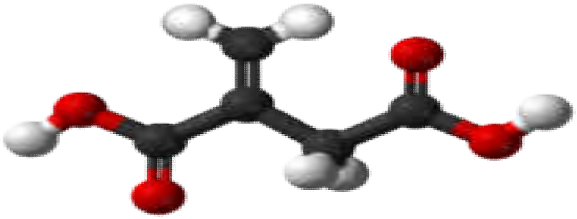

Figure 1 Structure of Itaconic Acid

Safety

The harmful effect of itaconic acid is irritation to eyes, skin, and gastrointestinal irritation with nausea, vomiting and diarrhea. For employees working in itaconic acid plants, the ventilation should be provided well. Personnel should wear impervious protective clothing, goggles, gloves, coveralls or apron to prevent skin contact.

In the case of accidental release of itaconic acid, the proper measures should be taken such as, the area of leak or spill should be well ventilated and spilled acid should be cleaned immediately and be swept to place in a suitable container for disposal.

Table 1 Rating of itaconic acid on safety chart **(**Source: www.inchem.org)

Mode	Rating
Flammability Rating	0-None
Health Rating	1-Slight (Life)
Reactivity Rating	0-None
Storage Color Code	Not available
Contact Rating	1-Slight (Corrosive)

Environmental Fate

When Itaconic acid is released into the water it creates acute toxicity for fish, aquatic invertebrates and plants.

Table 2 Health effects of itaconic acid (Source: www.inchem.org)

Skin Contact	Causes skin irritation
Inhalation	Causes respiratory tract irritation
Ingestion	Causes gastrointestinal irritation with nausea, vomiting and diarrhea
Chronic Exposure	Not available
Eye Contact	Causes skin irritation
Aggravation of Pre-existing Conditions	Not available

Uses

Itaconic Acid is used in greases, detergents, shampoos, herbicides and pharmaceuticals. Itaconic acid can also be used in the manufacture of emulsion paints, where it improves the adhesion of the paints and used as a hardening agent in organosiloxanes making in contact lenses.

The applications of itaconic acid and its esters in the field of plasticizers, lubricant oil, co-polymerizations, paper coating, carpets for better duration, coating, adhesives, thickener, surface active agents, paints, pharmaceuticals and printing chemicals.

Industrial Production

Itaconic acid is produce by various chemical methods: (1) Destructive distillation of citric acid. (2) The patented Montecatini method involving propargyl chloride; (3) the oxidation of mesityl oxide and subsequent isomerisation of the formed citric acid, (4) Fermentation of sugars by Aspergillus terreus.

Alternatives to conventional processes

Precipitation

The traditional product recovery method is based on the precipitation. This method consists of insoluble calcium salt of carboxylic acids with calcium hydroxides or calcium carbonates followed by re-acidification with sulphuric acid.

The disadvantage of this method is handling large amount of solid and slurry and production of equal amount of calcium sulphate as waste. Therefore a separation process is required to eliminate the generation of calcium sulphate as waste that includes solvent extraction and electro dialysis [22].

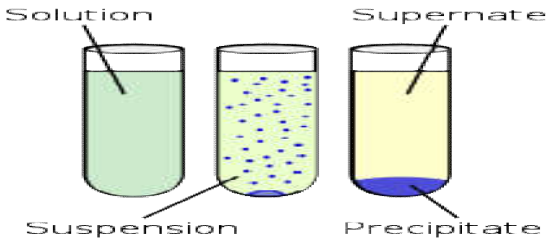

Figure 2 Precipitation Process

Adsorption

Itaconic acid may be recovered by the adsorption of itaconic acid on solid adsorbent or by the adsorption of itaconate on ion exchange resins. The polymer adsorbent showed good selectivity and high adsorption capacity for carboxylic acids even in the presence of inorganic salts.

The selected elutants were aliphatic alcohol, aliphatic ketone, and carboxylic ester. Separates the carboxylic acid by using a polymer adsorbent of pyridine skeletal structure and a cross-linked structure. Porous, solid sorbets with large surface areas, such as activated carbon and polymeric resins can be used in the recovery of the carboxylic acids. Although, sorption process is effective, the limited capacity for carboxylic acid on the solid surface is disadvantageous. [22], [23].

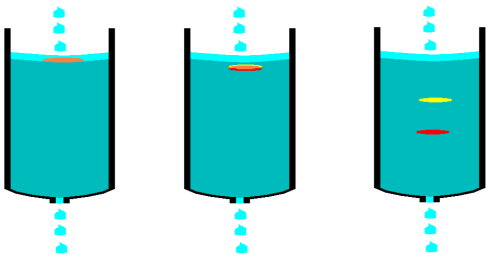

Figure 3 Adsorption of itaconate on ion exchange resins

Reverse Osmosis

The reverse osmosis could effectively concentrate itaconic acid from transmembrane pressure at energy use lower than multiple effect evaporators. Reverse osmosis has also studied for recovering itaconic acid from fermentation broths.

Electrodialysis

A special type of electrodialysis is water-splitting electrodialysis. Electrodialysis is a process where ion exchange

membranes are used for removing ions from an aqueous solution under the driving force of electrical field. Instead of anion exchange membranes in desalting, bipolar membranes are used in water-splitting electrodialysis. Electrodialysis is applied to remove salts from solutions or to concentrate ionic substances. Water-splitting electrodialysis is applied to electro conversion of salts to the corresponding acids. There are two different methods for recovery of itaconic acid.

A electrodialysis method in the first case and electrodialysis with double exchange reaction in the second case. In the first step of deasalting, sodium itaconate is recovered, purified and concentrated, in the water-splitting or acidification step, itaconic acid is regenerated from sodium itaconate, and sodium hydroxide is recovered and purified.

Liqid-Liquid Extraction

In liquid-liquid extraction the extracting solvent and feed after intimate mixing separates out into two layer viz enriched solvent liquid(extract) and rather depleted feed(raffinate)[23]. Liquid-liquid extraction is also widely used for separation of valuable chemical from waste water and fermentation broth. Liquid-liquid extraction show below,

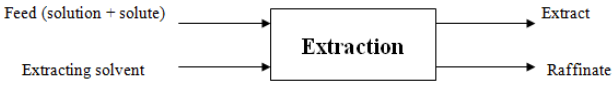

Figure 4 Liquid-Liquid Extraction

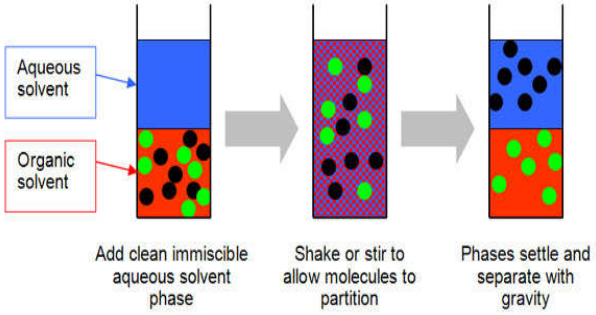

Figure 5 Liquid Liquid Extraction Mechanism

Liquid-liquid extraction is of two types:

1. Physical Extraction
2. Reactive extraction

Physical Extraction

It is a process in which separation of compounds based on their relative solubilities in two different immiscible liquids, usually water and an organic solvent occurs and no reaction take place. Extraction of itaconic acids by diluent alone was accounted for by three phenomena:

- ionization of acid in the aqueous phase (K_{HA});
- dimerization of acid in the organic phase (D).
- Partition of the undissociated acid in the organic phase (P).

Three factors to be considered for physical extraction

1. Ionization of the acid in aqueous phase
2. Partial dissociation of the acids between two phases
3. Dimerization of the acid in the organic phase.

Distribution coefficient (ratio of total acid in organic phase to aqueous phase) can be written in terms of partition coefficient and dimerization coefficient.

Reactive Extraction

In such processes itaconic acid is first being extracted from fermentation broth by the extractant and then recovered from the solvent by back extraction into another solvent. Although, conventional method is the most used technique on the large-scale processes, solvent extraction has been developed for the separation of itaconic acid. Itaconic acid can be readily extracted into a number of organic solvents with high molecular mass aliphatic amines; exhibiting particularly good selectivity. Many investigators have investigated the reactive extraction of itaconic acid into an immiscible extractant/solvent phase. Amine extractant has been found to be prospective method of seperation of carboxylic acids from aqueous solutions. Besides high capacity, high selectivity, low prices and non-toxic substance, because of the use in food industry, three important criteria have been established for solvent selection:

1. High distribution coefficient for itaconic acid,
2. Easy back extraction and regeneration, and
3. Low tendency to emulsion formation.

In this process, the solute present in an aqueous solution is extracted into an immiscible solvent containing a specific extracting agent. Reactive extraction is a process in which separation of compounds based on affinity of solvent for any compound present in feed and here solvation occurs due to a chemical reaction.

Reactive extraction is an efficient, economical, and environmental friendly method for separation of acids from waste water streams. Advantages of this system include the need for relatively small volumes of solvents. Low water miscibility in the system. High degree of phase separation in the system which allows for smaller extraction equipment; and stability and high boiling point of solvent. After the extraction of organic acids, solvents are regenerated by stripping the acids for recycle in the extraction process. So, cost of separation of these useful products is reduced by using recycled solvents.

The recovery of other low molecular weight acids suggested to make this method more economically attractive (Helsel, 1977).

The Several studies on reactive extraction of itaconic acid from dilute aqueous solution by use of extractants like TOPO, TBP, TOA etc has been reported.

Reasons for selection of a process for research

After studying the various processes for removal of itaconic acid from aqueous solution, Reactive extraction was chosen for treatment of aqueous solution of itaconic acid for several reasons as given below:

1. Extraction process is relatively insensitive to fluctuation in concentration of itaconic acid.
2. Extraction is not affected by toxic compound.
3. Availability of various solvents for extraction.
4. Recovered itaconic acid can be sold in the market, thus partially offsetting the cost of wastewater treatment.

5. Ease in reactor pH control without use of base addition.
6. Increased reactor productivity

The major objective of present research is to find out a system which can effectively remove itaconic acid from aqueous solution

Various research work that has been done so far on the Reactive Extraction of Itaconic Acid are as follows

Various studies has been carried out regarding the extraction of Itaconic Acid from aqueous solution by many researchers. The few studies in last 10 years related to extraction of Itaconic Acid are summarized here.

Uslu H. & Datta D, (2015)[10]- studied the experimental and theoretical investigations on reactive extraction of itaconic (2-Methylidenebutanedioic) acid using Trioctylamine (N,N-Dioctyloctan-1-amine). Maximum extraction efficiency of 94.80% with the value of K_D equal to 18.20 was obtained at 1.946 mol.kg^{-1} of TOA in octan-1-ol.

Guneet Kaur & Elst. K.,(2014)[11]-studied the extraction of itaconic acid with eight different amines with seventeen types of diluents (alcohols, esters, alkanes). Nine reactive extraction systems were found to be most suitable *i.e.* trioctylamine, dioctylamine and *N*-methyldioctylamine as amine extractants solved in 1-octanol, pentylacetate and methyloctanoate. The results of this study will form the basis for future investigations for large scale experiments with reactive extraction systems and development of appropriate ISPR configurations for itaconic acid.

Selim Y.A. & Ismail I,(2012)[12]- studied the reactive extraction by using trioctylamine (TOA), tridodecylamine (TDA) and mixtures of Amines in dimethyl phthalate (DMP), methyl isobutyl ketone (MIBK), 2-octanone, 1-octanol, cyclohexyleacetate (CHA), and 1-decanol to extract itaconic acid. The TOA–TDA mixture in DMP gave 98.39% extraction of itaconic acid.

Wasewar *et al*.,(2011)[13]-studied the Reactive extraction of itaconic acid using quaternary amine Aliquat 336 in ethyl acetate, toluene, hexane, and kerosene as diluents. The equilibrium complexation constants, loading ratios, and distribution coefficients were obtained for the reactive extraction of itaconic acid.

Datta *et al*., (2011)[14]-studied the reactive extraction of 2-methylidenebutanedioic acid (five initial acid concentrations in the range of 0.05 to 0.25 mol. dm^{-1}) from aqueous solution by N,N-dioctyloctan-1-amine (TOA, 0.115 and 0.229 mol.dm^{-3}) as extractants dissolved in six different diluents [heptane, kerosene, methyl benzene, decane-1-ol, 4-methylpentan-2-one (MIBK). The highest value of the K_D is found to be 32.478 at 0.05 mol. dm^{-3}.

Wasewar *et al*., (2010)[15]- studied the Reactive extraction of itaconic acid using tri-*n*-butylphosphate (TBP) (an organophosporous compound) and Aliquat 336 (a quaternary amine) in sunflower oil. Equilibrium complexation constant, K_E, values of 1.789 and 2.385 m^3 kmol^{-1}, respectively, were obtained for itaconic acid extraction using TBP and Aliquat 336 in sunflower oil.

Kyuchoukov *et al*., (2008)[16]-studied the extraction of itaconic acid from aqueous solution with Tributylphosphate dissolved in dodecane at different volume phase ratios. The prediction of acid extraction was possible only for a limited range of acid concentrations. The experimental results revealed that the concentration of the interaction product in the aqueous phase cannot be neglected.

Matsumoto *et al*., (2001)[17]- studied the Synergistic extraction equilibria of organic acid (itaconic acid) with tri-n-octylamine (TOA) and or tri-n-butylphosphate (TBP). The extraction equilibrium constants were roughly correlated with the hydrophobicity of the acid, except L-malic acid. The calculated results of the distribution ratio of organic acids based on the formation of three complexes explained well the experimental.

Bressler E., and Braun S., (1990)[18]- studied the selective separation of citric and itaconic acids by amine extractants. Tri-n-octyl amine in 1-octanol was selective for the stronger carboxylic, citrate. The role of amine salt, the diluent and of water-immiscible additives on the selectivity of the extraction. Itaconate is located in the polar envelope of the reverse micelle.

Hano *et al*., (1990)[19]- studied the extraction equilibria of organic acid (itaconic acid) with Tri-n-octylphosphineoxide (TOPO). The salvations' numbers of the acids were the same as the numbers of the carboxyl groups on each acids molecule. The extraction equilibrium was constant was controlled by the hydrophobicity of the acid when hexane was used as a diluents.

CONCLUSION

In this review paper extraction of itaconic acid using different extractants:- TBP and amines. thus suggesting TBP is the better extactant incomparable to amines. there are various processes for removal itaconic acid from aqueous solution but reactive extraction gives the best results. the studies on reactive extraction of itaconic acid with TBP and amines at a different acid concentration indicates that the reactive extraction occurs by mass of the interfacial formation of solvent between acid and TBP or amines. so in present time TBP is mostly used as a extractant for removing the itaconic acid from the aquous solution.

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