

# Impact on the effect of acetic acid in its aqueous forms on environments and its separations by solvent extraction method- A review

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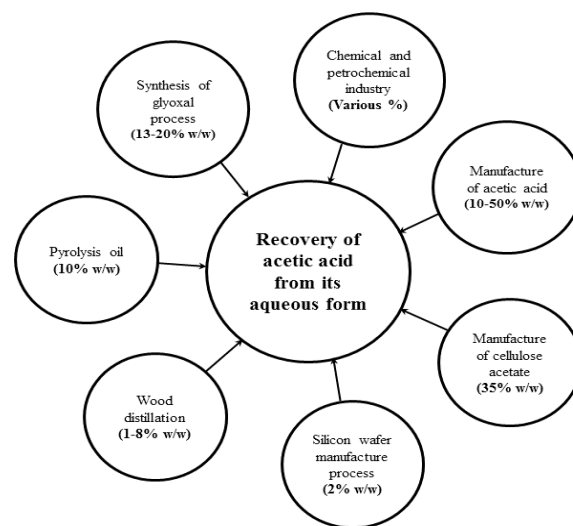
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**Abstract.** Acetic acid is one of the top twenty commodities used in various industrial processes. Removal of acetic acid in its aqueous forms is a significant problem, and it cannot be discarded directly to the environment because of its acidity nature. The separation of acetic acid from its aqueous phase is challenging because of the formation of azeotrope conditions. Several methods have been studied to recover the acetic acid in its aqueous phase, distillation, solvent extraction, membrane separation, pervaporation, etc. Out of which, solvent extraction is mainly used for feed concentration up to 50%. The efficiency of solvent extraction mostly depends on the solvent which is chosen for the extraction. The current study mainly focused on the review of extraction of acetic acid from aqueous phase using several organic solvents, single and combination of two solvents (dual solvents). The efficiency is studied in terms of distribution coefficient and separation factor. The model available in Aspen plus NRTL, UNIQUAC, UNIFAC was also discussed.

**Keywords:** Acetic acid; Solvent extraction; Single & Dual Solvent

## 1. Introduction

Acetic acid is one of the essential carboxylic acids extensively used in the process industries in two different roles, as chemical reagent and solvent in many processes, including production of polyethylene terephthalate, cellulose acetate, polyvinyl acetate, etc. The aqueous form of acetic acid is collected as a by-product and waste streams in many industries like food industries, the terephthalic acid plant, petroleum industries, etc. Additionally, the chemical reactions using the acetic anhydride either as a reactant or as an extractant can discharge a significant amount of acetic acid-containing water. The two methods of manufacture of acetic acid are synthetic methods and fermentation processes. From the two approaches, dilute form of acetic acid were obtained in its different concentrations. The details of industrial processes having acetic acid in their dilute phases (up to 50%) are represented in Figure 1. The primary concern of the process industries is to recover acetic acid from dilute streams either formed as a by-product or remaining in the spent streams whose concentrations could cover a wide range say from a few percent to ppm levels. The separation of acetic acid from its water phase is difficult; even though the boiling points are relatively distinct, the relative volatility is close to unity constraining the use of distillation processes.



**Figure 1. Industrial processes having acetic acid in its dilute phase**

Effluent continually leads many chemical methods for manufacturing required final products and intermediate products or recycling the acetic acid process itself. The resulting in the production of acetic acid in dilute forms that have to be removed to obtain the standards of glacial acetic acid.

Several physical and chemical separation methods include reverse osmosis, electrodialysis, liquid-liquid extraction, the liquid surface acting agent, membrane solvent extraction, anion exchange membranes, precipitation method, direct distillation, adsorption, and ion exchange, have been used to remove acetic acids from its aqueous phase. The conventional distillation process is used only for the acetic acid feed concentration above 50% (w/w). It leads to several drawbacks such as more energy consumption, phase separation, and many trays required. The adsorption and ion exchange process is applied only for low feed concentration, in which the regeneration and selection of adsorbent were found to be a significant problem. Therefore solvent extraction was established as an effective alternative method compared to other conventional methods. This paper concentrates on the recovery of acetic acid of 50% (w/w) and its below.

For an efficient solvent extraction process, solvent selection plays an important role, and research work was conducted towards the tuning of better solvent systems. The essential characteristics of the solvents are high partitioning coefficient, better selectivity toward solute,

and immiscibility with diluent phase. The other characteristics such as volatility, the density difference between the solvent and diluent, interfacial tension, viscosity of the solvent, corrosive nature, flammable condition, toxic nature, stability, and flexible compatibility with the product, availability, and economic value are to be considered while selecting the solvent. The valuable property to be considered while choosing a suitable solvent is the equilibrium distribution coefficient, where hydrocarbon had a very low distribution coefficient, alcohols having a high distribution coefficient, but it tends to esterify with acetic acid. Ketones had a high distribution coefficient but did not show the right azeotroping conditions for removing water in the recovery section. The solvents that are most preferably used are ethers and acetates. The current paper discussed acetic acid removal by solvent extraction method, and its overview was discussed.

## 2. Discussions

### 2.1. Methods of Separation

In general, the technology towards the development of separation and recovery of industrial ethanoic acid waste streams was started in the year 1954. Several physical separation techniques, such as solvent extraction, direct distillation, membrane extraction, adsorption, anion exchange, electrodialysis, precipitation, etc., have been employed to remove such ethanoic acid from its aqueous forms.

The most established technology for separating acetic acid from its aqueous phase is solvent extraction, also known as liquid-liquid extraction. The solvent extraction techniques are widely used on a large scale to separate acetic acid (concentration between 5-50%) even though its capital cost is high. A significant amount of organic solvents are utilized. The reactive extraction was found to be the favorite method for recovering acetic acid with a specified extractant, giving high distribution.

The use of membranes to remove and recover these acetic acid has been established in the year 1991; Siman et al. studied the effect of the liquid membrane to remove and recover the organic contaminants. Several membrane processes such as ultrafiltration, electrodialysis, nanofiltration, reverse osmosis, pervaporation, and polymeric supported liquid form membrane were suggested to remove the above said waste streams.

The most commonly used configuration of cellulose acetate membranes is spiral wound, hollow fiber, tubular or plate, or frame. In this process, the mass transfer of selected species occurs across the module placed between waste streams with a suitable solvent.

The use of solvent extraction or membrane solvent extraction processes for the low solute feed concentrations exhibits the solubility of solvent into the aqueous phase was more significant than the amount of solute recovered. In this situation, alternative methods of adsorption and ion exchange were required. Several adsorbents and ion-exchange resins were found to be used

in commercial-scale applications (Kentish and Stevens, 2001).

Kentish and Stevens (2001) stated that solvent extraction is a well-established process and economically feasible when the solute concentrations and flow rates are high. Still, this process becomes uneconomical when the solute concentration is low. Membrane technology is a recently developed process, and it is capable of extending the conditions under which the solvent extraction methods are economically feasible. In contrast, membrane fouling needs continuous cleaning, but it can produce a better separation of acids with high power and energy consumption.

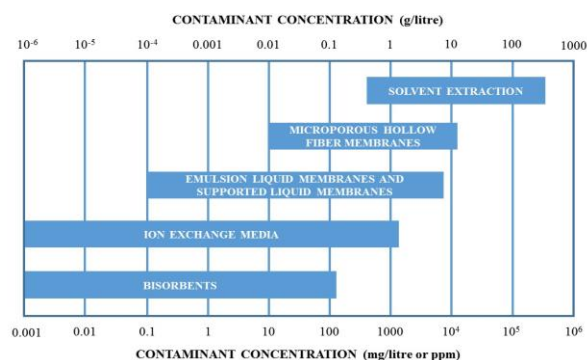


Figure 2. Solute concentration ranges for separation technologies (Kentish & Stevens, 2001)

The industrial streams contain the separation of ethanoic acid from its aqueous phase of three categories, namely, 0-2%, 2-20%, and 20-40% (vol%). Figure 2 indicates that the selection of the separation process depends on its concentration of solute present in the streams. It also concludes that the separation process for acetic acid separation mainly depends on its concentration.

### 2.2. Single Solvent studied

Several solvents studied in the literature, the efficiency of the solvents mainly expressed in terms of distribution coefficient and separation factor. The main concern about selecting a solvent extractant is whether choosing a solvent with high or low volatility refers to the acetic acid boiling point. The benefit of a low volatility extractant generally reduces the steam consumption for the reboiler while regenerating all the extractant are taken into the overhead. When choosing a high volatility solvent, the acetic acid is obtained as a top product. In contrast, with a lower boiling point than acetic acid, it comes as a bottom residue, consisting of some heavy contamination. The low volatility solvent can be used to increase the purity of acetic acid in the overhead product. The benefit of a common volatile solvent also prevents the combination of water separation and solvent regeneration in a single tower.

The distribution coefficient should be considered a second important property in selecting a solvent, which is indicated as the ratio between the concentration of acetic acid in the solvent phase to the concentration of acetic acid in the aqueous phase at equilibrium conditions. While

selecting a solvent, it is necessary to achieve a high distribution coefficient value as viable to minimize the quantity of the solvent required. As a further consideration, the solvent should also have a high selectivity for the separation process of acetic acid from the water phase to reduce the amount of water that must be taken out from the acetic acid after the extraction process. The distribution and separation factors are collected and studied. Based on the literature, the hydrocarbons n-Hexane, m-xylene, o-xylene, benzene, and toluene showed a distribution coefficient range of 0.05 to 0.9 (less than one), but these hydrocarbons given the separation factor range of 4 to 100. The ketones MIAK (Methyl IsoAmyl ketone), MIBK (Methyl Iso Butyl Ketone), MIPK (Methyl ISO propyl Ketone), cyclohexanone, and 3,3,-dimethyl-2-butanone given the distribution coefficient range of 0.1 to 0.9 and the separation factor range of 2 to 50. The esters amyl acetate, ethyl acetate, butyl acetate, propyl acetate, 2-methyl propyl acetate, cyclohexyl acetate, sec-butyl acetate, isopropenyl acetate, dibutyl phthalate, dimethyl and diethyl phthalate, and 2-methyl ethyl acetate were studied in the literature. They gave the distribution coefficient range of 1 to 15 and the separation factor range of 1 to 90. The ethers also produce the distribution coefficient above one and the separation factor around 40 to 50. The alcohols 1-pentanol, 2-pentanol, 1-heptanol, 1-undecanol, 1-decanol, tridecanol, and 2-ethyl 1-hexanol always showed a high distribution coefficient ranging from 1 to 60. Among these, the decanol and tri decanol showed a high distribution coefficient. All the alcohols showed the separation factor range of 1 to 25.

### 2.3. Mixed Solvent extraction

The mixtures of solvent were used instead of using a single solvent as an extractant to improve the combined synergism. Solvents of reciprocal characteristics were combined to get an increased distribution coefficient or separation factor. The combined solvents acetone and chloroform gave better results than the individually used one. Diisopropyl ether and isopropyl ether were used as a mixed solvent to study the combined synergism. This study concluded that using various compositions of mixed solvent would increase the area and the size of the heterogeneity region for the mentioned system (Ozmen & Imge, 1995). The solvents methyl ethyl ketone and cyclohexane have different solubility with water were taken, the solubility surface obtained was very high when compared with the single solvent extraction (Gomis et al.,

1995). For the mixed solvent tri-n-octyl phosphine oxide and tri-n-octyl phosphate (Matsumoto et al., 2001), acetic acid does not give any remarkable synergism. The dual solvent p-xylene and methyl acetate were taken to increase the area of the heterogeneous phase area. The mixed solvent gave a better heterogeneity area (Harvianto et al., 2016), but sometimes the combinations fail to provide better synergism. It mainly depends on the characteristics of the solvents used.

### 2.4. Effect of Temperature

The liquid-liquid extraction of acetic acid and water mainly affected by the temperature in some systems. The increase in temperature will increase the solubility of acetic acid in its organic phase. The study on 2-octanol with acetic acid and water showed very little impact on the distribution coefficient (Feng et al., 2020). For the case of Methyl isopropyl ketone system, at the higher range of temperature, it increased the solubility of solute in solvent phase (Correa et al., 1989). The study on butyl acetate, 2-methyl propyl acetate and 2-ethyl hexyl acetate at different temperatures showed that, the temperature did not affect the system that much (Wang et al., 2007) (Ince and Lalikoglu, 2014). The temperature effect study on the cyclohexane system also showed no improvements in the influence of temperature on the solubility of the solute (Lei et al., 2013). In some systems, the temperature affected the heterogeneity area, a work on the solvent CPME at different temperature showed the decrease in solubility of the acetic acid in the solvent phases (Zhang & Zhang, 2012). Most of the study concluded that no significant effect with respect to the changing of temperature, but few system had impact on it.

### 2.5. Models Studied

The excess activity models such as NRTL (Non Random Two Liquids Models), UNIQUAC (Universal Quasi Chemical), and UNIFAC (Universal function group activity coefficient) are frequently used to predict the equilibrium data in liquid-liquid extraction, and it was compared with the experimental results. Out of these three models the NRTL and UNIQUAC used to compare the experimental results (Ajimaz et al., 2000). The NRTL and UNIQUAC gave the least RMSD (Root Mean Square Deviation) with the experimental data for few studies (Liu et al., 2015) (Shen et al., 2016). Most of the study concludes that NRTL obtained low RMSD value than the UNIQUAC (Hu et al., 2010).

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