

NAVEEN PRASAD B. S. 1,  
SELVARAJU SIVAMANI<sup>1</sup>  
AZUCENA CUENTO<sup>1</sup>  
SENTHILKUMAR  
PACHIYAPPAN<sup>2</sup>

<sup>1</sup> Chemical Engineering  
Section, Engineering  
Department, University College  
of Technology and Applied  
Sciences- Salalah, Salalah,  
Oman

<sup>2</sup> Department of Chemical  
Engineering, Sathyabama  
Institute of Science &  
Technology, Chennai, India

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## CHEMICAL ROUTE FOR SYNTHESIS OF CITRIC ACID FROM ORANGE AND GRAPE JUICES \*

### Article Highlights

- Chemical route was attempted to synthesize citric acid from orange and grape juices
- Process parameters were optimized for maximum citric acid yield
- FTIR and XRD characterization was performed for purified citric acid crystals

### Abstract

*Citrus fruits contain sufficient citric acid, which is the main tricarboxylic acid. The properties of citric acid make it an important additive in various process industries. This experimental study aims to produce citric acid from orange and grape juices. The chemical route for the synthesis of citric acid from citrus juices involves three steps: (i) neutralization to adjust pH (9-11) with a 2.8 M NaOH solution, (ii) addition of CaCl<sub>2</sub> solution (40.3-41.1% w/v), and (iii) acidification with an H<sub>2</sub>SO<sub>4</sub> solution (1.5-2.3 M) to produce citric acid. In this study, the fruits were peeled, crushed, filtered, neutralized, added CaCl<sub>2</sub> solution, and acidified to obtain citric acid. The experiments were carried out by varying the final pH of the solution and the concentrations of CaCl<sub>2</sub> and H<sub>2</sub>SO<sub>4</sub> solutions, maintaining the total volume constant. A maximum citric acid yield of 91.1% and 79.8% were achieved from orange and grapefruits, respectively, at the optimum final pH of the solution and the concentrations of CaCl<sub>2</sub> and H<sub>2</sub>SO<sub>4</sub> solutions at 10, 40.7% w/v, and 1.9 M, respectively. Finally, the purified citric acid crystals were characterized using FTIR and XRD. Thus, it could be concluded that orange fruit would be a promising source for citric acid production than grape.*

*Keywords: orange juice, grape juice, neutralization, calcium chloride, acidification, citric acid.*

Citric acid (IUPAC: 2-hydroxy-1,2,3-propane tricarboxylic acid), a natural ingredient, is a common versatile metabolite (organic acid) of plants and animals used in the food sector (60%) and pharmaceuticals (10%) [1]. It was first crystallized from lemon juice. It finds its role in the metabolism of all aerobic organisms that Krebs did not announce in the late 1930s. The production of citric acid from lemon reached a peak of 17,500 tons between 1915 and 1916. In the 19th century, citric acid was extracted di-

rectly from the concentrated lemon juice, mainly in Sicily [2]. The worldwide production of this acid by fermentation is increasing rapidly. Today over 99% of global citric acid production is from green citrus fruits by South America, Mexico, and Greece. In 1934, Yuill and Bennett discovered the XRD pattern of the crystal structure of anhydrous citric acid obtained by cooling a hot concentrated solution of the monohydrate [3].

Citric acid is used due to its remarkable physicochemical properties and environmentally friendly nature. Citric acid was previously produced using three methods: extraction from citrus fruits, chemical synthesis, and fermentation. In the chemical route of synthesis, three methods are used to synthesize citric acid: (i) the addition of lime (CaO) to citrus juice, and the acidification with dilute sulfuric acid; (ii) the addition of limestone (CaCO<sub>3</sub>) to citrus juice, and the acidification with dilute sulfuric acid; and (iii) the addition of caustic soda (NaOH), followed by calcium

Correspondence: B.S.N. Prasad, Chemical Engineering Section, Engineering Department, University College of Technology and Applied Sciences- Salalah, Salalah, Oman.  
E-mail: [bsnaveenprasad@gmail.com](mailto:bsnaveenprasad@gmail.com)  
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chloride to citrus juice, and the final acidification with dilute sulfuric acid [4]. In the biochemical or fermentation route, fungi (particularly molds), such as *Aspergillus niger*, *A. awamori*, *A. aculeatus*, *A. wentii*, *A. carbonarius*, *A. factidus*, *Penicillium janthinelum*, *Saccharomycopsis lipolytica*, *Candida oleophila*, *C. tropicalis*, *C. parapsilosis*, *C. guilliermondii*, *C. citroformans*, *Corynebacterium sp.*, *Arthrobacter paraffinens*, *Bacillus licheniformis*, etc. were used to ferment glucose to citric acid through Kreb's cycle by solid-state or submerged fermentation [5]. Mainly *Aspergillus* species are used in studies because of their relatively high yield, ease of harvesting, and ability to use various raw materials [6].

The first industrial fermentation of citric acid was initially carried out as surface cultures. The introduction of submerged fermentation has been a significant improvement. Among the works examined before the commercial implementation of submerged fermentation was that of Perquin in 1938; it should be mentioned first for its skill and precision, comparable to Currie's work in the surface process [7]. In 2012, Ray *et al.* cleared that an enhanced efficient fermentation process and genetically modified organisms are required for higher yield and purity. Although many citric acid suppliers use molasses from genetically modified corn and genetically modified sugar beets, other manufacturers only produce citrate products formed from carbohydrates obtained from non-genetically modified crops and without the involvement of recombinant microorganisms, rDNA technology [8].

Seligra *et al.* (2016) investigated the cross-linked citric acid with starch using glycerin as a plasticizer by heating a mixture of starch, glycerin, water, and citric acid to 75-85 °C. The resulting citric acid films treated at 75 °C showed a significant decrease in moisture absorption and water vapor permeability. These two main parameters affect the barrier properties of packaging films. Crosslinking starch-glycerin films with citric acid also dramatically improves starch films' poor thermal degradation and mechanical properties [9]. Citric acid is an excellent and harmless disinfectant against various viruses, including the human norovirus. For example, citrate, added to norovirus-like particles, binds precisely to the binding pocket of histo-blood group antigens involved in binding to host ligands, thereby preventing the transmission of these viruses and preventing symptoms in people already infected with norovirus [10].

In the present study, citric acid was synthesized through a chemical route by adding caustic soda and calcium chloride and final acidification with dilute sulfuric acid. In the production process, three steps are involved: neutralization, reaction with calcium chloride,

and acidification. During neutralization, sodium hydroxide was added to citrus juice to neutralize the pH from <4 to 10. As a result, citric acid in fruits reacts with sodium hydroxide to form trisodium citrate and water (Figure 1(a)). During the addition of calcium chloride, sodium citrate reacts with calcium chloride to produce tricalcium dicitrate and sodium chloride (Figure 1(b)). During acidification, tricalcium dicitrate reacts with sulphuric acid to form citric acid and calcium sulfate (Figure 1(c)) [11].

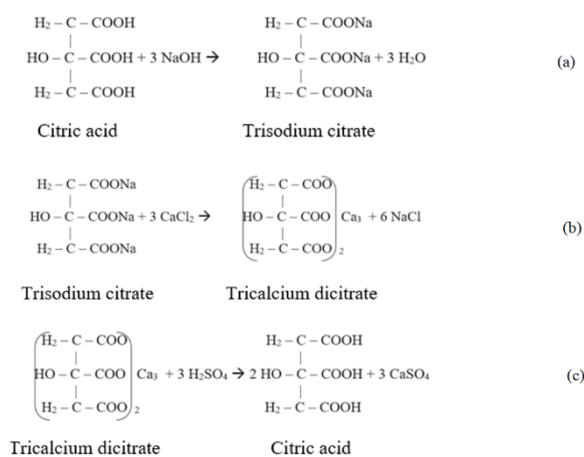


Figure 1. Chemical reactions involved in citric acid production from citrus fruit juices.

Even though the biochemical synthesis route is being used commercially to produce citric acid, the chemical route is used for production on a small scale in a few countries. Many papers are available on the biochemical route of citric acid synthesis compared to the chemical route [12,13]. Hence, the present study aims to evaluate the citric acid yield from citrus fruits' chemical route for the synthesis of citric acid from citrus (orange and grape) fruits. The objectives of the study are to study the effects of pH during neutralization, the concentration of  $\text{CaCl}_2$  during the second step, and the concentration of sulfuric acid during acidification on the citric acid yield.

## MATERIALS AND METHODS

### Materials

Fresh citrus fruits (orange and grape) were purchased from the local commercial market, Salalah, Sultanate of Oman. They were washed thoroughly before use. The fruits were peeled, crushed, and filtered twice to remove seeds and other insoluble impurities. The extracted fruit juices were used for the synthesis of citric acid. Sodium hydroxide, calcium chloride, and sulfuric acid of analytical grade were used in the experiments without processing.

## Methods

The fruit juices of 10 mL ( $V_a$ ) were titrated with a 0.1 M NaOH solution using phenolphthalein as an indicator to calculate the mass of citric acid in the feed. The remaining total volume of juice ( $V_f$ ) was measured. The pH of fresh juice was measured and found to be 3.3 for orange and 3.7 for grape. For neutralization, a 2.8 M NaOH solution (10% w/w) was added to fruit juices drop-by-drop, mixing properly to 10 pH. During neutralization, Na atoms in NaOH displace H atoms in carboxylic groups of citric acid based on  $pK_a$  value in steps. Sodium citrate produced is soluble in solution, and the remaining products except water are insoluble. Hence, the resultant mixture was filtered using filter paper to remove the insoluble part. The filtrate containing an aqueous sodium citrate solution and an aqueous sodium citrate solution was filtered thrice using filter paper again before proceeding to the second step.

In the second step, a known volume of  $\text{CaCl}_2$  (calculated in section 2.3) of 40.7% w/v was added to the sodium citrate solution and heated in a boiling water bath for 30 min. A double displacement reaction takes place between sodium citrate and  $\text{CaCl}_2$ . Calcium citrate is insoluble in water and precipitated at the bottom. So, the resultant mixture containing calcium citrate was filtered using vacuum filtration. The residue was washed with 100 mL of hot water in 4 steps to remove the impurities and byproducts. During the addition of hot water, the residue was stirred well. A neutral pH of 7 was ensured in the filtrate. If the pH of the filtrate is higher than 7, then more hot water should be added with stirring; if the pH value is less than 7, proceed to acidify. The resultant residue was dried to constant weight in a hot air oven.

Dried calcium citrate was acidified with a known volume of dilute  $\text{H}_2\text{SO}_4$  (calculated in section 2.3) of 1.9 M and heated at 60 °C with simultaneous mixing with a glass rod. Calcium citrate and calcium sulfate are insoluble in water, whereas citric acid is soluble. So, when calcium citrate and sulfuric acid were mixed, calcium sulfate precipitated at the bottom, leaving behind the citric acid solution at the top. Again, the mixture was vacuum filtered. Finally, citric acid was crystallized from its aqueous solution by evaporative crystallization; the yield of citric acid crystals was estimated gravimetrically and characterized using XRD and FTIR.

## Calculations involved in the experimental methods

### Orange juice

Total volume of fresh orange juice ( $V_f$ )=330 mL. From literature [14], concentration of citric acid in fresh

orange juice ( $C_o$ )=9.1 g/L. Mass of citric acid in orange juice =  $(330 \times 9.1)/1000 = 3$  g. According to stoichiometry, 192 g of citric acid produces 258 g of sodium citrate, 3 g of citric acid produces  $258/192 \times 3 = 4$  g sodium citrate. 258 g of sodium citrate requires 333 g of  $\text{CaCl}_2$ . 4 g of sodium citrate requires  $333/258 \times 4 = 5.2$  g of  $\text{CaCl}_2$ . Concentration of  $\text{CaCl}_2 = 40.7\%$ (w/v) = 407 g/L. Volume of  $\text{CaCl}_2$  solution required =  $5.2/407 = 0.0128$  L = 12.8 ml. 498 g of calcium citrate requires 294 g of  $\text{H}_2\text{SO}_4$ . 5.4 g of dried calcium citrate requires =  $294/498 \times 5.4 = 3.2$  g of  $\text{H}_2\text{SO}_4$ . Density of  $\text{H}_2\text{SO}_4$  solution = 1.84 g/mL. Volume of 100%  $\text{H}_2\text{SO}_4$  required =  $3.2/1.84 = 1.7$  mL. Volume of commercially available 98% (18.4 M)  $\text{H}_2\text{SO}_4$  required =  $1.7/98 \times 100 = 1.8$  mL. Volume of 10.2% (1.9 M)  $\text{H}_2\text{SO}_4$  required =  $18.4/1.9 \times 1.8 = 17.4$  mL.

### Grape juice

Total volume of fresh grape juice ( $V_f$ ) = 330 mL. From literature [14], concentration of citric acid in fresh grape juice ( $C_o$ ) = 0.2 g/L. Mass of citric acid in grape juice =  $(330 \times 0.2)/1000 = 0.066$  g = 66 mg. According to stoichiometry, 192 g of citric acid produces 258 g of sodium citrate. 66 mg of citric acid produces  $258/192 \times 66 = 89$  mg sodium citrate. 258 g of sodium citrate requires 333 g of  $\text{CaCl}_2$ . 89 mg of sodium citrate requires  $333/258 \times 89 = 114$  mg of  $\text{CaCl}_2$ . Concentration of  $\text{CaCl}_2 = 40.7\%$ (w/v) = 407 g/L. Volume of  $\text{CaCl}_2$  solution required =  $114/1000 \times 407 = 0.0003$  L = 0.3 mL. 498 g of calcium citrate requires 294 g of  $\text{H}_2\text{SO}_4$ . 0.12 g of dried calcium citrate requires =  $294/498 \times 0.12 = 0.07$  g of  $\text{H}_2\text{SO}_4$ . Density of  $\text{H}_2\text{SO}_4$  solution = 1.84 g/mL. Volume of 100%  $\text{H}_2\text{SO}_4$  required =  $0.07/1.84 = 0.04$  mL. Volume of commercially available 98% (18.4 M)  $\text{H}_2\text{SO}_4$  required =  $1.7/98 \times 100 = 0.04$  mL. Volume of 10.2% (1.9 M)  $\text{H}_2\text{SO}_4$  required =  $18.4/1.9 \times 0.04 = 0.38$  mL.

## Calculations for citric acid yield

### Orange juice

(Moles of NaOH in fresh orange juice) = (Molarity of NaOH solution)  $\times$  (Volume of NaOH solution (mL)). (Moles of NaOH in fresh orange juice) =  $0.1/1000 \times 15.5 = 0.00155$  mol. According to stoichiometry, 1 mole of citric acid requires 3 mol of NaOH. 0.00155 mol of NaOH requires  $1/3 \times 0.00155 = 0.00052$  mol of citric acid. Total volume of fresh grape juice ( $V_f$ ) = 330 mL. Moles of citric acid for total volume of juice =  $(330 \times 0.00052)/10 = 0.017$  mol. Mass of citric acid in feed = (Moles of citric acid)  $\times$  (Molecular weight of citric acid). Mass of citric acid in feed =  $0.017 \times 192 = 3.3$  g. Mass of citric acid in product found by gravimetry = 3 g. Percentage yield of citric acid = (Mass of citric acid in product)/(Mass of citric acid in feed)  $\times 100$ . Percentage yield of citric acid =  $3/3.3 \times 100 = 90.9\%$ .

### Grape juice

(Moles of NaOH in fresh grape juice) = (Molarity of NaOH solution) × (Volume of NaOH solution (mL)).  
 (Moles of NaOH in fresh grape juice) =  $0.1/1000 \times 5.2 = 0.00052$  mol. According to stoichiometry, 1 mole of citric acid requires 3 mol of NaOH. 0.00155 mol of NaOH requires  $1/3 \times 0.00052 = 0.00017$  mol of citric acid. Total volume of fresh grape juice ( $V_f$ ) = 330 mL. Moles of citric acid for total volume of juice =  $(330 \times 0.00017)/10 = 0.0057$  mol. Mass of citric acid in feed = (Moles of citric acid) × (Molecular weight of citric acid). Mass of citric acid in feed =  $0.0057 \times 192 = 1.1$  g. Mass of citric acid in product found by gravimetry = 0.88 g. Percentage yield of citric acid = (Mass of citric acid in product)/(Mass of citric acid in feed) × 100. Percentage yield of citric acid =  $0.88/1.1 \times 100 = 79.67\%$ .

### Statistical analysis

Treatments were organized with three replicates in randomized block design. The data were analyzed for statistical significance using ANOVA with a p-value < 0.05.

## RESULTS AND DISCUSSION

### Effect of process parameters on citric acid yield

Figure 2 shows the effect of final solution pH during neutralization on citric acid yield from the orange fruit. The effect of pH on citric acid yield was studied by varying the values from 9 to 11 in the steps of 0.5 at constant  $\text{CaCl}_2$  and  $\text{H}_2\text{SO}_4$  concentrations of 40.7% (w/v) and 1.9 M, respectively. The variation in pH exhibited an inverted parabolic curve. As the pH increased from 9 to 10 and then further to 11, the citric acid yield increased from 60.1 to 90.0 and then decreased to 87.8%, respectively. Figure 2 illustrates that the variation in pH between 9 and 10 is significant, whereas the variation between 10 and 11 is minimal. This may be because the mass of NaOH used for neutralization was insufficient to achieve maximum citric acid yield when pH was increased from 9 to 10 [15]. Nevertheless, when the pH was increased from 10 to 11, the maximum citric acid yield was achieved at pH 10. Citric acid undergoes a decomposition reaction at a slower rate at pH 11.

For grapes, the effect of final solution pH during neutralization was studied on citric acid yield. As the pH increased from 9 to 10 and then further to 11, the citric acid yield increased from 44.1 to 79.5 and then decreased to 60.6%, respectively. The variation in pH between 9 and 11 is most significant. This showed that the variation in pH is an essential factor to maximize the citric acid yield from grapes.

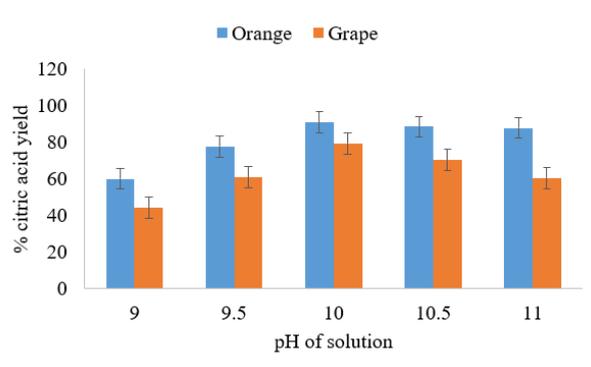


Figure 2. Effect of final pH of solution on citric acid yield during neutralization.

Figure 3 shows the effect of the concentration of  $\text{CaCl}_2$  on citric acid yield. The effect of  $\text{CaCl}_2$  concentration on citric acid yield was studied by varying the values from 40.3 to 41.1% (w/v) in the steps of 0.2% (w/v) at constant pH and  $\text{H}_2\text{SO}_4$  concentration of 10 and 1.9 M, respectively. The variation in  $\text{CaCl}_2$  concentration exhibited a flattened curve. As the  $\text{CaCl}_2$  concentration increased from 40.3 to 40.7 and then further to 41.1% (w/v), the citric acid yield increased from 83.5 to 90.6 and then decreased to 88.2%, respectively. Figure 3 illustrates that the variation in concentration of  $\text{CaCl}_2$  between 40.3 and 41.1 is minimal. For grapes, the effect of  $\text{CaCl}_2$  was studied on citric acid yield. As the concentration of  $\text{CaCl}_2$  increased from 40.3 to 40.7 and then further to 41.1% (w/v), the citric acid yield increased from 70.5 to 79.1 and then decreased to 77.8%, respectively. The variation in concentration of  $\text{CaCl}_2$  between 40.3 and 41.1% (w/v) is minimal, like orange fruit. This showed that the variation in the  $\text{CaCl}_2$  concentration does not significantly impact the citric acid yield from orange and grapefruits.

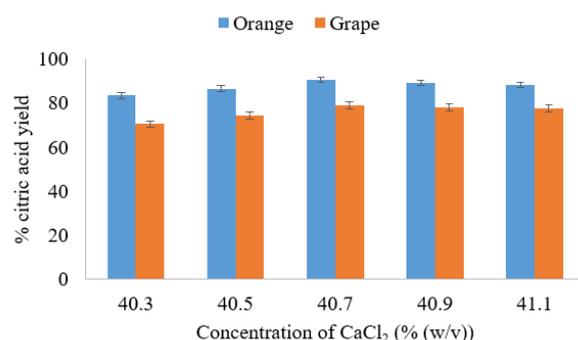


Figure 3. Effect of concentration of  $\text{CaCl}_2$  solution on citric acid yield.

Figure 4 shows the effect of the concentration of  $\text{H}_2\text{SO}_4$  on citric acid yield from orange during acidification. The impact of the concentration of  $\text{H}_2\text{SO}_4$  on citric acid yield was studied by varying the values from 1.5 to 2.3 M in the steps of 0.2 M at constant pH and  $\text{CaCl}_2$  concentration of 10 and 40.7% (w/v), respectively.

tively. The variation in concentration of  $\text{H}_2\text{SO}_4$  exhibited a bell-shaped curve. As the concentration of  $\text{H}_2\text{SO}_4$  increased from 1.5 to 1.9 and then further to 2.3 M, the citric acid yield increased from 72.5 to 91.1 and then decreased to 87.9%, respectively. Figure 4 illustrates that the variation in the concentration of  $\text{H}_2\text{SO}_4$  between 1.5 and 1.9 M is significant, whereas the variation between 1.9 and 2.3 M is minimal.

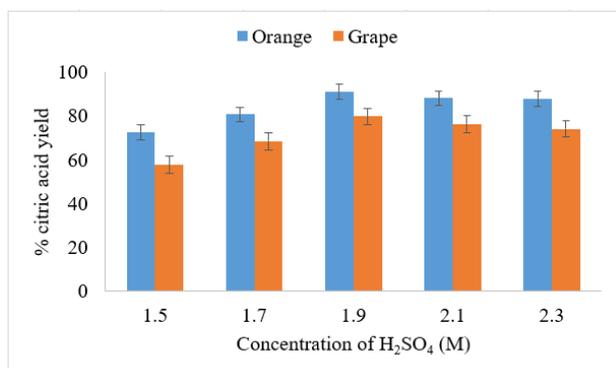


Figure 4. Effect of concentration of  $\text{H}_2\text{SO}_4$  on citric acid yield during acidification.

For grapes, the effect of the concentration of  $\text{H}_2\text{SO}_4$  during acidification was studied on citric acid yield. As the concentration of  $\text{H}_2\text{SO}_4$  increased from 1.5 M to 1.9 M and then further to 2.3 M, the citric acid yield increased from 57.6% to 79.8% and then decreased to 74.2%, respectively. The variation in concentration of  $\text{H}_2\text{SO}_4$  between 1.5 M and 1.9 M is most significant. This showed that the variation in concentration of  $\text{H}_2\text{SO}_4$  between 1.5 M and 1.9 M is substantial, whereas the variation between 1.9 M and 2.3 M is minimal. The citric acid recovery from orange is better than grape because of its high citric acid content.

### Characterization of citric acid crystals

#### FTIR

FTIR spectra of citric acid crystals revealed major peaks at 3300, 2600, 1730, and 1200  $\text{cm}^{-1}$  depict stretching of -OH, C-H, C-C, and C=O, respectively. A peak at 3300  $\text{cm}^{-1}$  represents the presence of moisture [16]. The peaks at 2600, 1730, and 1200  $\text{cm}^{-1}$  represent the vibrational motions of the functional group stretching in the citric acid molecule [17]. However, the characteristic absorption band at 1274  $\text{cm}^{-1}$  corresponds to the  $\text{CH}_2$  stretching vibration in citric acid crystals (Figure 5).

#### XRD

XRD spectra of citric acid crystals revealed major peaks at 2 $\theta$  values of 14°, 17°, 19°, 24°, 26°, and 29°, corresponding to the humps of pure citric acid (Figure 6). A peak at 24° indicates that the material starts gain-

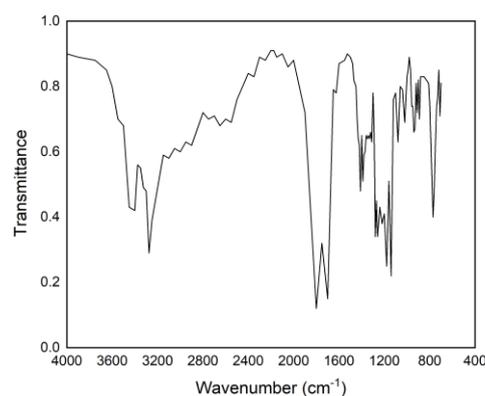


Figure 5. FTIR spectra of citric acid crystals.

ing short-range order or becomes a little bit more crystalline [18]. A peak at 26° corresponds to the reflections of the (002) lattice planes [19]. A peak at 29° is due to the presence of a carbon atom [20]. The diffraction pattern strongly affects heavier elements and contains more electrons. Since hydrogen is the lightest atom with only one electron, it is difficult to detect the presence of hydrogen atoms by XRD [21].

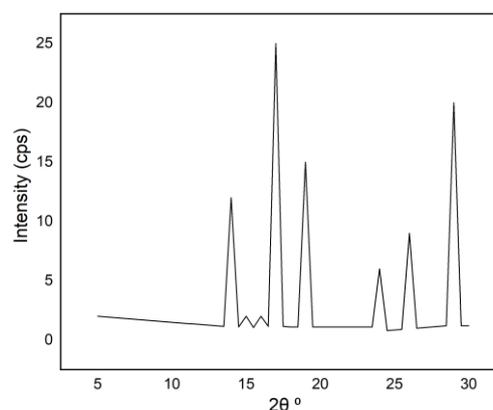


Figure 6. XRD spectra of citric acid crystals.

### CONCLUSION

The present study aims to optimize the final pH of the solution (9 - 11), the concentration of  $\text{CaCl}_2$  (40.3 - 41.1% (w/v)), and the concentration of  $\text{H}_2\text{SO}_4$  (1.5 - 2.3 M) to maximize the citric acid yield. The citric acid yield increased when the final pH of the solution, the concentration of  $\text{CaCl}_2$ , and the concentration of  $\text{H}_2\text{SO}_4$  were 10, 40.7% (w/v), and 1.9 M, respectively, and decreased after that. FTIR and XRD spectra revealed the presence of functional groups and crystalline nature, respectively, corresponding to citric acid crystals. Thus, it could be concluded that orange fruit would be a promising source for producing citric acid.

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NAVEEN PRASAD B. S.<sup>1</sup>,  
SELVARAJU SIVAMANI<sup>1</sup>  
AZUCENA CUENTO<sup>1</sup>  
SENTHILKUMAR  
PACHIYAPPAN<sup>2</sup>

<sup>1</sup> Chemical Engineering  
Section, Engineering  
Department, University College  
of Technology and Applied  
Sciences- Salalah, Salalah,  
Oman

<sup>2</sup> Department of Chemical  
Engineering, Sathyabama  
Institute of Science &  
Technology, Chennai, India

NAUČNI RAD

## HEMIJSKA SINTEZA LIMUNSKE KISELINE IZ SOKOVA POMORANDŽE I GREJFRUTA

*Citrusno voće sadrži dovoljno limunske kiseline, koja je glavna trikarbonska kiselina. Svojstva limunske kiseline čine je važnim dodatkom u raznim procesnim industrijama. Ova eksperimentalna studija ima za cilj proizvodnju limunske kiseline iz sokova pomorandže i grejfruta. Hemijski sinteza limunske kiseline iz sokova citrusnog voća uključuje tri koraka: (i) neutralizaciju radi podešavanja pH (9-11) sa 2,8 M rastvorom NaOH, (ii) dodavanje rastvora CaCl<sub>2</sub> (40,3-41,1% v/v), i (iii) zakišeljavanje rastvorom H<sub>2</sub>SO<sub>4</sub> (1,5-2,3 M). U ovoj studiji, da bi se dobila limunska kiselina, plodovi su oguljeni, usitnjeni, filtrirani, neutralizovani, tretirani rastvorom CaCl<sub>2</sub> i zakišljeni. Eksperimenti su izvedeni variranjem konačnog pH rastvora i koncentracija rastvora CaCl<sub>2</sub> i H<sub>2</sub>SO<sub>4</sub>, održavajući ukupnu zapreminu konstantnom. Maksimalni prinos limunske kiseline je 91,1% iz pomorandže i 79,8% iz grejfruta pri optimalnom konačnom pH rastvora od 10 i koncentracijama rastvora CaCl<sub>2</sub> i H<sub>2</sub>SO<sub>4</sub> od 40.7% ml/v and 1,9 M, redom. Konačno, prečišćeni kristali limunske kiseline su okarakterisani korišćenjem FTIR i XRD analiza. Dakle, može se zaključiti da je pomorandža bolja sirovina izvor za proizvodnju limunske kiseline od grejfruta.*

*Ključne reči: sok od pomorandže, sok od grejfruta, neutralizacija, kalcijum hlorid, zakišeljavanje, limunska kiselina.*