Int. J. Adv. Eng. Pure Sci. 2020, 1: 33-41
DOI: 10.7240/jeps.578285

RESEARCH ARTICLE / ARAŞTIRMA MAKALESİ

Effects of Mandelic and Propane-1,2,3-Tricarboxylic Acids on Calcium Oxalate Monohydrate Crystallization

Mandelik Asit ve Propan-1,2,3-Trikarboksilik Asitin Kalsiyum Oksalat Monohidrat Kristalizasyonuna Etkisi

Sevgi POLAT [1], **Perviz SAYAN** [1]

[1]*Department of Chemical Engineering, Faculty of Engineering, Marmara University, 34722, İstanbul, Turkey*

Abstract

The effects of mandelic and propane-1,2,3-tricarboxylic acids as additives on calcium oxalate monohydrate (COM) crystals were investigated in this study. The physicochemical properties of the COM crystals prepared with and without these additives were characterized using X-ray powder diffraction (XRD), scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FTIR), and zeta potential analysis. The XRD and SEM results showed that the crystals prepared in pure medium were monohydrates and consisted primarily of hexagonal crystals, respectively. The additives mandelic acid and propane-1,2,3-tricarboxylic acid in the crystallization media significantly changed the size and morphology of the COM crystals, the effects of which were more pronounced with higher concentrations of the additives. The results of FTIR suggested that both carboxylic acids were adsorbed onto the surface of the COM crystals. The zeta potential analysis showed a negative charge on the surface of the COM crystals in the mandelic acid medium, while the surface became more positive in the medium containing increasing concentrations of propane-1,2,3-tricarboxylic acid. In addition, an analysis was conducted to evaluate the thermal characteristics of the COM crystals prepared with and without the additives. The data obtained were used to calculate the kinetic parameters, such as the activation energy and pre-exponential factor, using the Coats-Redfern method. The calculated activation energies for stages I, II, and III in pure medium were 98.76, 270.69, 258.55 kJ/mol, respectively, which were lower than that of COM crystals prepared in the two media containing the additives.

Keywords: Calcium oxalate monohydrate, crystallization, morphology, thermal kinetics, carboxylic acids.

Öz

Bu çalışmada, katkı maddesi olarak kullanılan mandelik ve propan-1,2,3-trikarboksilik asidin, kalsiyum oksalat monohidrat (COM) kristalleri üzerindeki etkileri incelenmiştir. Saf ve katkı ortamında üretilen COM kristallerinin özellikleri, X-Işını Kırınımı (XRD) metodu, taramalı elektron mikroskobu (SEM), Fourier dönüşümlü kızılötesi spektroskopisi (FTIR) ve zeta potansiyeli analizi kullanılarak karakterize edilmiştir. XRD ve SEM sonuçları saf ortamda üretilen kristallerin monohidrat formunda ve genel olarak hegzaganol yapıda olduğunu göstermiştir. Kristalizasyon ortamında mandelik ve propan-1,2,3-trikarboksilik asitin varlığı, COM kristallerinin hem morfolojisinin hem de tane boyutunun önemli ölçüde değişmesine neden olmuştur. Bu etki, yüksek katkı konsantrasyonlarında daha belirgin hale gelmiştir. FTIR sonuçları, çalışmada kullanılan her iki karboksilik asitin de COM kristallerinin yüzeyine adsorplandığını göstermiştir. Zeta potansiyeli analiz sonuçları, mandelik asit ortamında kristallerin yüzey yükünün negatif olduğunu, bu değerin propan-1,2,3-trikarboksilik asit varlığında ise katkı konsantrasyonunun artmasıyla birlikte daha pozitif hale geldiğini göstermiştir. Ayrıca, saf ve katkı maddeleri varlığında üretilen COM kristallerinin termal özelliklerini değerlendirmek için analiz yapılmıştır. Elde edilen veriler kullanılarak aktivasyon enerjisi ve frekans faktörü Coats-Redern modeli kullanılarak hesaplanmıştır. Saf ortamda üretilen kristallerin I, II ve III. bozunma bölgeleri için hesaplanan aktivasyon enerjileri katkı maddesi ortamında üretilen kristallerin aktivasyon enerjilerinden düşük olup sırasıyla 98,76, 270,69, 258,55 kJ/mol olarak belirlenmiştir.

Anahtar Kelimeler. Kalsiyum oksalat monohidrat, kristalizasyon, morfoloji, kinetik, karboksilik asit.

Sorumlu yazar/Corresponding Author: Sevgi POLAT, **Tel:** 0216 3480292/1719, **e-posta:** sevgi.polat@marmara.edu.tr
Gönderilme/Submitted: 15.06.2019, **Düzenleme/Revised:** 26.10.2019, **Kabul/Accepted:** 11.12.2019

I. INTRODUCTION

Calcium oxalate, the most common calcium salt of oxalic acid, is found naturally in fossils, plants, and human kidney and bladder stones and can exist in three forms—monohydrate (COM, $CaC_2H_4{\bullet}H_2O$), dihydrate (COD, $CaC_2H_4{\bullet}2H_2O$), and trihydrate (COT, $CaC_2H_4{\bullet}3H_2O$,)—of which COM is the most stable under normal atmospheric conditions. The other forms are created under more specific solution conditions (e.g., supersaturation) and temperatures [1,2].

Calcium oxalate is a byproduct in some industrial processes such as paper and food production. In water-related industries, particularly in those using hard water, this mineral can form harmful scale deposits on heat exchangers, boilers, and reverse-osmosis membranes and resulting in heat-transfer inefficiency during evaporation processes, increases in energy use, and losses in production time [3,4]. Previous studies have shown that different types of carboxylic acids such as acetic acid, tartaric acid, citric acid and succinic acid [5-9] can prevent scale formation when added to the crystallization medium, and several studies [10,11] have been conducted that identified the mechanisms of this effect; however, studies on using specific carboxylic acids, such as mandelic acid ($C_8H_8O_3$) and propane-1,2,3-tricarboxylic acid ($C_6H_8O_6$), have been limited.

The aim of the current study was to investigate the crystalline structures and morphologies of the COM crystals synthesized in media containing these two carboxylic acids, which were chosen for their ease of handling and nontoxic properties, and compare these with crystals synthesized in pure medium. We also investigated the thermal decomposition behavior of the crystals using the Coats-Redfern model. We believe that the results of our study can be used as a guide for controlling the morphology and thermal properties COM crystals.

II. MATERIALS AND METHODS

Analytical grade calcium chloride dihydrate ($CaCl_2{\bullet}2H_2O$), sodium oxalate ($Na_2C_2O_4$), mandelic acid ($C_8H_8O_3$), and 1,2,3-propanetricarboxylic acid ($C_6H_8O_6$), were purchased from Merck & Co., Inc.. Distilled water was used throughout the experiments.

To examine COM crystallization, the experiments were conducted at 40 °C and pH 8 in a cylindrical, jacketed, glass crystallizer with a maximum working capacity of 0.5 L. The constant temperature was maintained in the crystallizer using a thermostat. A stirring mechanism comprised a spiral propeller blade and mechanical stirrer and the rate was maintained at a rate of 400 rpm. The pH in the crystallizer was kept constant at 8 using 0.1 M hydrochloric acid or calcium hydroxide solution.

Calcium chloride and sodium oxalate were used to create the solutions for synthesizing the COM crystals. First, calcium chloride solution was poured into the crystallizer and left to reach thermal equilibrium, after which sodium oxalate solution was fed into the crystallizer using a peristaltic pump at 5 mL/min. To investigate the effects of mandelic and propane-1,2,3-tricarboxylic acids on COM crystallization, we fed these additives into the crystallizer using an infusion pump. The experiments were conducted at three different additive concentrations—50, 100, and 200 ppm. All experimentation was performed in triplicate.

At the end of the experiments, the entire suspension in the crystallizer was removed, and the solution and solids were separated using the pressure filtration method. The filter cake was washed with distilled water to remove the chloride ions. Silver nitrate solution was added to the washing solution to check for any remaining chloride ions. The solid sample was put into an Erlenmeyer flask and kept in a water bath 25°C for 3 months to determine any structural transformations, after which the sample was used for characterization analyses.

X-ray powder diffraction (XRD) was used to identify the structures of the crystals (Bruker D2 Phaser tabletop diffractometer) using Cu Kα radiation ($\lambda = 1.5418$ Å) and performed for 2θ values of 10–70°. Additional structural analyses were conducted using the Shimadzu IR Affinity-1 spectrometer at a resolution of 4 cm^{-1} and a wavenumber from 4000 to 600 cm^{-1}. Scanning electron microscopy (SEM; Zeiss EVO LS 10) was used to characterize the morphology of the products. The surface electrical charge and particle size of the crystals were examined using the Malvern Zeta Sizer Nano Series Nano-ZS. The thermal properties of the COM crystals were determined using the Setaram LABSYS Evo instrument in which 15 ± 0.1 mg sample was placed in an aluminum oxide crucible and heated from 30 to 900 °C at a rate of 10 ºC/min under a constant nitrogen flow rate of 25 mL/min.

III. RESULTS AND DISCUSSION

3.1. XRD Analyses

Three forms of calcium oxalate crystals—COM, COD, and COT—can be synthesized depending on the conditions. To determine the forms and lattice parameters of these crystals and determine the reliability of the results, a Rietveld analysis was conducted using MAUD (http://maud.radiographema.com/). The XRD patterns along with the Rietveld refined data for the crystals prepared in pure medium are provided in Figure 1.

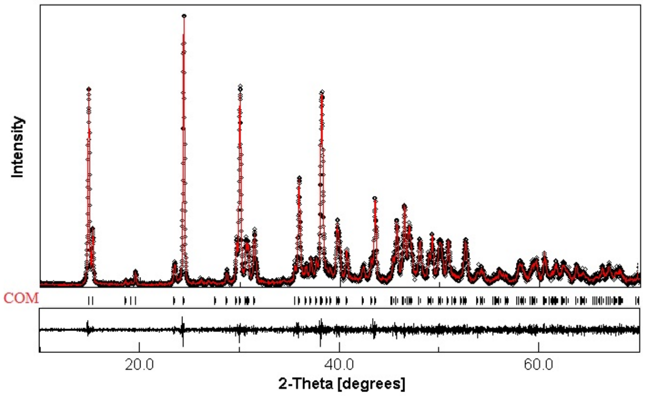


Figure 1. Rietveld refined X-ray powder diffraction (XRD) pattern of calcium oxalate monohydrate (COM) crystals prepared in pure medium.

In Figure 1, the black curve is the observed XRD pattern of the samples prepared in pure medium, and the red curve is the calculated XRD pattern, which were well-matched with each other. The major diffraction peaks detected at 2θ of ~15º, ~25º, ~30º, and ~38º for calcium oxalate crystals prepared in pure medium were compatible with the peaks of the monohydrate form and consistent with the Joint Committee on Powder Diffraction Standards (JCPDS) (No: 00-020-0231). The unit cell parameters were detected as a = 9.991 Å, b = 7.297 Å, and c = 6.309 Å, which agreed with those in the literature [12].

Figures 2 and 3 illustrate the XRD patterns of the crystals prepared using different concentrations of mandelic and propane-1,2,3-tricarboxylic acids, respectively.

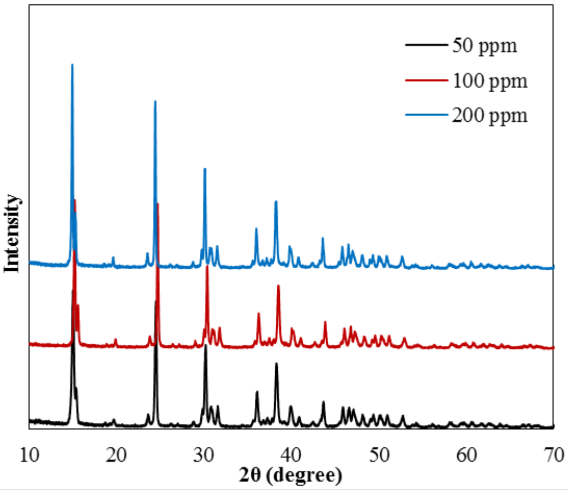


Figure 2. XRD pattern of calcium oxalate monohydrate (COM) crystals prepared in mandelic acid medium.

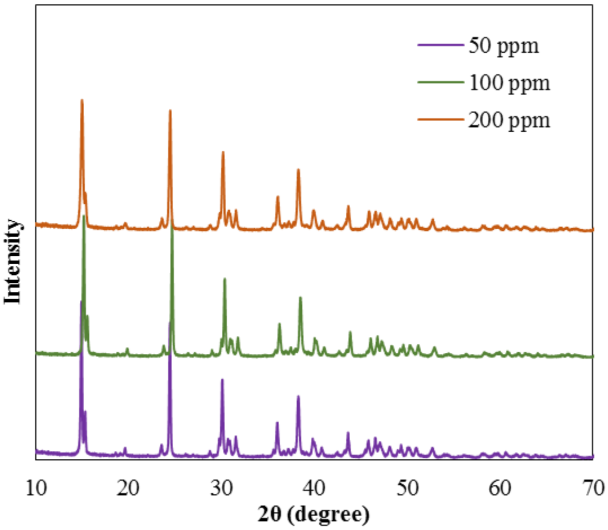


Figure 3. XRD pattern of calcium oxalate monohydrate (COM) crystals prepared in propane-1,2,3-tricarboxylic acid medium.

We determined that the studied concentration range of the additives in the crystallization medium did not lead to any changes in the crystal structure, and that all the crystals kept the monohydrate form. On the other hand, by increasing the concentration of both additives, the intensities of the diffraction peaks increased and shifted slightly, resulting from the lesser amounts of additives adsorbed onto the crystal surfaces.

3.2. SEM Analyses

Figure 4 displays the SEM image and corresponding energy-dispersive X-ray spectroscopy (EDX) spectrum for the COM crystals prepared in pure medium. Consistent with the literature [13], the uniform hexagonal prismatic crystals with smooth surfaces were those synthesized without the additives. The monohydrate samples were obtained beginning with the nuclei stage and were preserved during the growth process. The mean particle size of the crystals was ~1.0 µm. To determine the chemical composition of the COM crystal surface, an EDX was conducted; the resulting spectrum is shown in Figure 4b. We observed from EDX analysis that calcium, carbon, and oxygen were detected on the surface of the COM crystals.

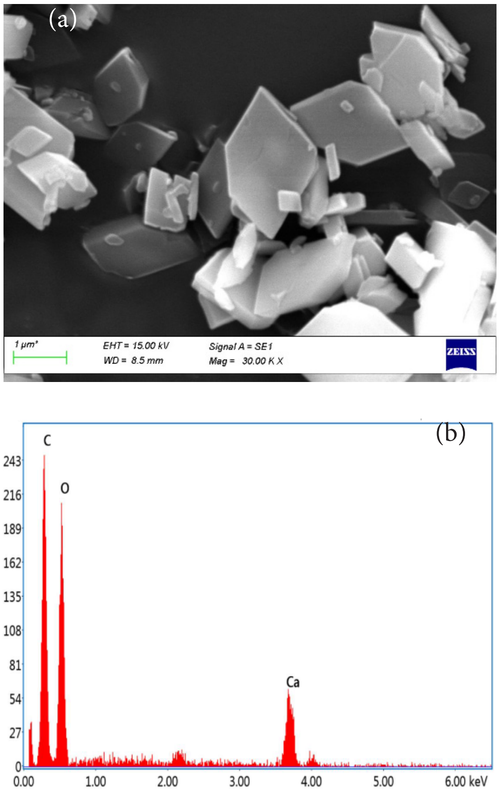
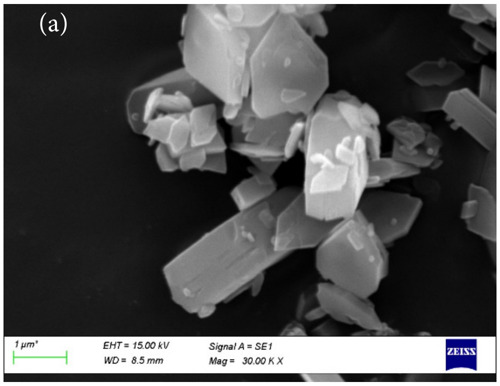
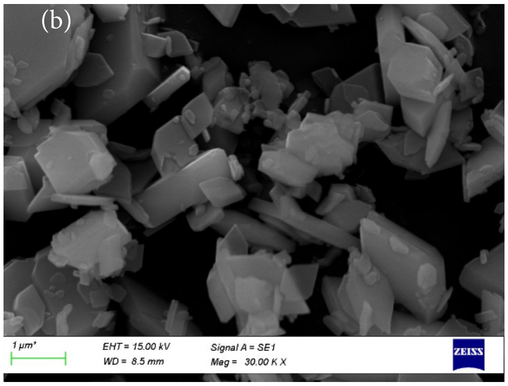


Figure 4. (a) SEM image and (b) energy-dispersive X-ray spectroscopy (EDX) spectrum of the calcium oxalate monohydrate (COM) crystals prepared in pure medium.

To investigate the effect of the mandelic and propane-1,2,3-tricarboxylic acids on the morphology of the COM crystals, the experiments were conducted using different additive concentrations of 50, 100, and 200 ppm. Figure 5 shows the SEM images of the COM crystals prepared using various mandelic acid concentrations.





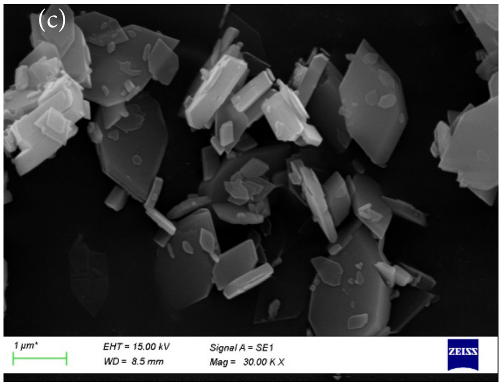


Figure 5. SEM images of calcium oxalate monohydrate (COM) crystals prepared in (a) 50 ppm (b) 100 ppm, and (c) 200 ppm mandelic acid.

The crystals synthesized in 50 ppm mandelic acid were similar to those synthesized in the pure medium, although their surfaces showed deformations because of disruptions in growth. Moreover, surface nucleation began by adding 50 ppm mandelic acid into the medium and this nucleation became more effective when the additive concentration was increased to 100 ppm, resulting in the formation of crystal agglomerates. As a result of the growth of nuclei that formed independently from surface nucleation of the main crystal structure, we observed a certain extent of overlapping growths on the crystal surface. At the same time, the morphology of the crystals began to change. The crystals prepared with 200 ppm mandelic acid had no distinctive form. These crystals lost their hexagonal appearance and exhibited a more rectangular form. Moreover, they were thicker than those in either the pure medium or in additive concentrations of 50 and 100 ppm, and exhibited a more compact structure, with several defects on the crystal surfaces. The ratios of length to width of the crystals were different from those synthesized in pure medium and the other mandelic acid concentrations. As a result, the presence of 200 ppm mandelic acid resulted in the formation more rectangular COM crystals.

Figure 6 shows the morphological features observed after adding propane-1,2,3-tricarboxylic acid to the crystallization medium. As seen from the figures, the surface properties and morphology of the COM crystals were directly related to the additive concentrations.

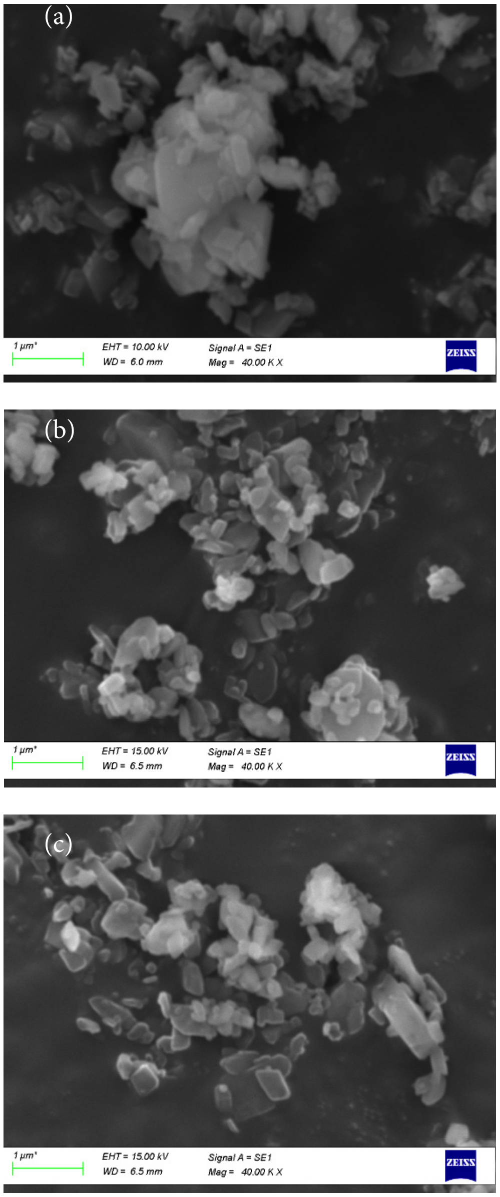


Figure 6. SEM images of calcium oxalate monohydrate (COM) crystals prepared in (a) 50 ppm (b) 100 ppm, and (c) 200 ppm propane-1,2,3-tricarboxylic acid.

The COM crystals prepared in propane-1,2,3-tricarboxylic acid were much smaller than those synthesized in pure medium and formed compact overlapping aggregates. These crystals lost a significant level of their hexagonal morphology and had no distinctive or regular shape. Surface nucleation was present and effective, and the crystals had a tendency toward overlapping growth. The crystals prepared in 100 ppm propane-1,2,3-tricarboxylic acid medium were even smaller than those synthesized in 50 ppm additive and nearly lost their hexagonal form. The sharp corners of the crystals disappeared, which led to rounder crystals. Similar to the crystals synthesized in 100 ppm mandelic acid, those formed in 100 ppm propane-1,2,3-tricarboxylic acid led to surface nucleation, resulting in a tendency to aggregate. In the presence of 200 ppm additive, the crystals nearly lost their appearance, and crystal defects were more noticeable. As these growth defects emerged, the crystal form became more irregular. The SEM images clearly showed that the surface of the crystals became rough, which suggested that adding propane-1,2,3-tricarboxylic acid led to the formation of smaller crystals with more defects.

3.3. FTIR Analyses

The FTIR spectra of the COM crystals prepared in both pure and additive media were analyzed to determine their chemical structures. Figure 7 displays the FTIR spectra of the COM crystals in the pure medium and in media containing 200 ppm mandelic acid and 200 ppm propane-1,2,3-tricarboxylic within a range of 600–4000 cm^{-1}, respectively.

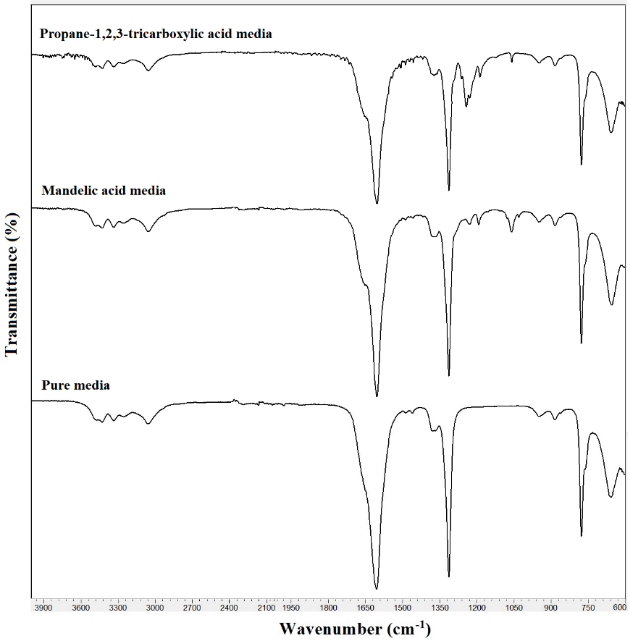


Figure 7. FTIR spectra of calcium oxalate monohydrate (COM) crystals prepared with and without additives to the medium.

The five transmittance bands, which are characteristic peaks of a monohydrate form, between 3000 and 3500 cm^{-1} represents the O–H stretch of the water molecules. The peaks at 1606 and 1315 cm^{-1} were assigned to the vibrations of carbonyl stretching, and the peaks at 950 and 883 cm^{-1} denoted the vibrations of C–C stretching [14,15]. On the other hand, very few functional groups were detected on the surface of the COM crystals prepared in either medium containing an additive. The most significant absorbance peaks were observed between 1250 and 1050 cm^{-1} assigned to the C-O stretching vibrations, which indicated the presence of the additives. Thus, the presence of characteristic bands provided a vivid explanation of the differences in the surface charge of the crystals prepared with mandelic and propane-1,2,3-tricarboxylic acids.

3.4. Zeta Potential Analyses

Zeta potential measurements were conducted to investigate the effects of different concentrations of mandelic and propane-1,2,3-tricarboxylic acids on the surface electrical charge of COM crystals. In the analyses, each measurement was repeated at least 10 times, and the mean value was calculated. All experiments were conducted at 25°C. The zeta potential profiles of the crystals based on the additive concentrations are shown in Figure 8.

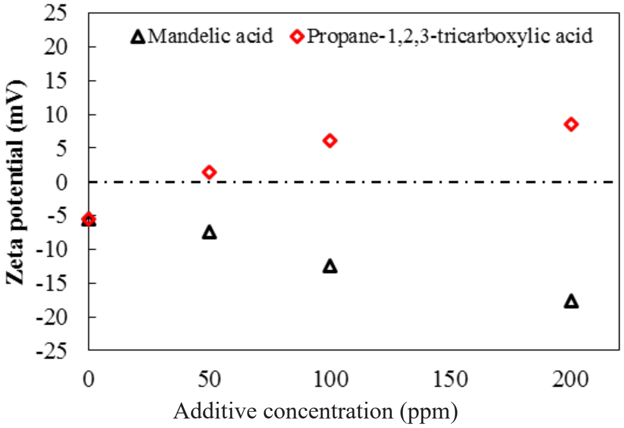


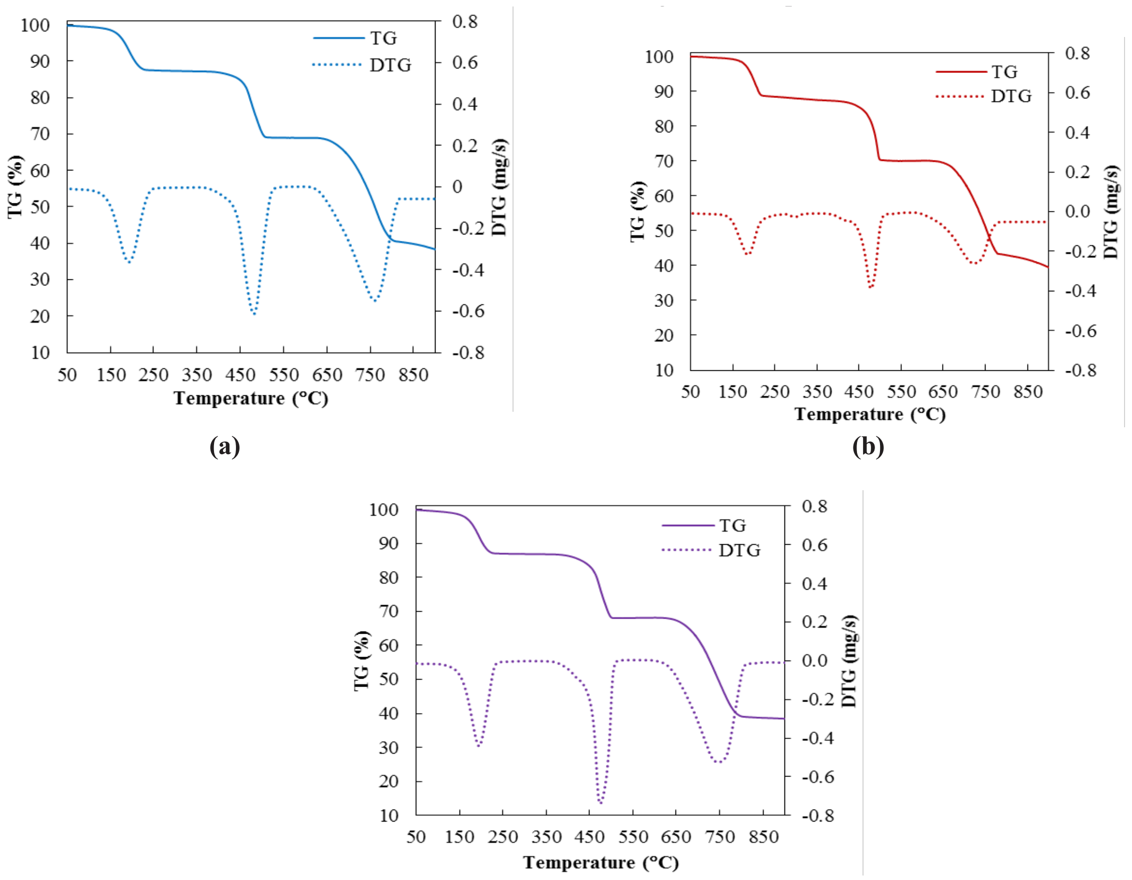
Figure 8. Changes in the zeta potential values of the calcium oxalate monohydrate (COM) prepared in pure medium and in medium containing different concentrations of additives.

Zeta potential measurements showed that COM crystals have a – 5.6 ± 1.4 mV zeta potential, and that the surface of the crystals in 100 ppm mandelic acid medium became more negative than that synthesized in pure medium with an increase in negativity to – 12.5 ± 0.9 mV. In addition, the surface became more negative by increasing the additive's concentration, which is an indication of the inhibitory effect of the additive on COM crystal aggregation.

In the presence of propane-1,2,3-tricarboxylic acid, the zeta potential passed the isoelectric point and reached a positive value, which increased even further by increasing the concentration of the additive. At 50 ppm propane-1,2,3-tricarboxylic acid, the zeta potential was 1.4 ± 1.1 mV. This result indicated that crystal agglomeration tended to increase, which supported the results of the SEM analysis. The variations in the zeta potential values showed that the carboxylic acids were adsorbed onto the surface of the COM crystals with weak van der Waals bonds.

3.5. Thermogravimetric Analyses

The thermal degradation behavior of the COM crystals was determined using thermogravimetric analysis (TGA). The TG and differential thermal analysis (DTG) curves of the COM crystals synthesized in the pure medium and in the presence of 200 ppm additives are shown in Figure 9. Thermal degradation of the prepared samples showed three weight loss regions—dehydration, decarbonylation, and decarbonation—respectively [14,16]. The first stage occurring from ~116 to 236°C represents dehydration of the COM crystal, and the second decomposition corresponds to the splitting of carbon monoxide. The final stage was the splitting of carbon dioxide. The DTG curves were used to determine the zone of degradation in which various reaction steps occurred over the entire temperature range. The maximum peak temperatures of the first, second, and third regions were 194, 482, and 761°C, respectively. A similar degradation tendency was also detected for the two media containing the additives; however, the COM crystals synthesized in mandelic and propane-1,2,3-tricarboxylic acids were thermally more stable than those synthesized in pure medium and decomposed more slowly over a broader temperature range of from 30 to 900 °C because of traces of the additives remaining in the samples.



(a)

(b)

(c)

Figure 9. Thermogravimetric (TG) and differential thermal analysis (DTG) curves of calcium oxalate monohydrate (COM) crystals prepared in pure medium (a), with mandelic acid (b), and with propane-1,2,3-tricarboxylic acid (c).

3.6. Kinetic Analyses of Thermal Decomposition

The kinetics of the thermal degradation of COM crystals were studied using thermogravimetry at a constant heating rate of 10°C/min. The kinetic parameters, activation energy, and pre-exponential factor of the COM crystals prepared with and without additives were determined using the Coats-Redfern method [17]. The degradation rate of the solid sample is given as the following formula:

$$\frac{dx}{dt} = A \exp\left(-\frac{E}{RT}\right)(1-x) \qquad (1)$$

where A is the pre-exponential factor, E is the activation energy, T is the temperature, t is time, and x is weight loss fraction, which can be calculated by Equation (2)

$$x = \frac{W_o - W_t}{W_o - W_f} \qquad (2)$$

where W_0 is the initial mass of the sample, W_t is the mass at time t, and W_f is final mass at the end of degradation. For a constant heating rate β during thermal degradation, $\beta = dT/dt$, rearranging Equation (1) and integrating give

$$\ln\left[-\frac{\ln(1-x)}{T^2}\right] = \ln\left[\frac{AR}{\beta E}\right] - \frac{E}{RT} \quad (n=1) \qquad (3)$$

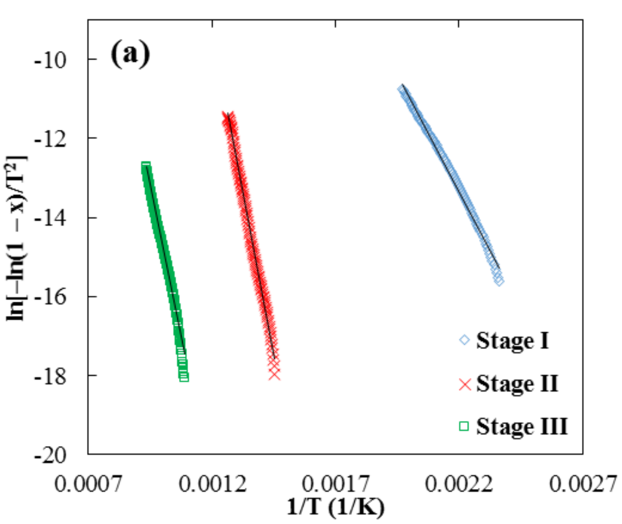
Plotting the left side of Equation (3) against $1/T$ gives a straight line and is presumed to be a first-order reaction. E can be determined from the slope of $-E/R$, and A can be calculated from the ln $[AR/\beta E]$ intercept [18].

Figure 10 shows the typical plot of $\ln[-\ln(1-x)/T^2]$ versus $1/T$ for 10 °C/min, which indicates that for the degradation of COM crystals, three independent first-order reactions fit well with the data. This linear fit was observed for each degradation stage. The results computed using the Coats-Redfern model assuming first-order reactions are presented in Table 1. The activation energies for the COM crystals synthesized in pure medium were 98.76, 270.69, and 258.55 kJ/mol for stages I, II, and III, respectively.

The calculated activation energy values were similar to those reported in previous studies [19], the highest of which represented the second stage and the lowest of which represented the first stage. In addition, the pre-exponential factors of the COM crystals synthesized in pure medium were 4.28×10^{10}, 2.70×10^{18}, and 3.99×10^{12} min^{-1}, respectively.

Table 1. Kinetic results for calcium oxalate monohydrate (COM) crystals prepared with and without additives to the medium.

Stage	Fitted equation	E (kJ/mol)	A (min^{-1})	R^2
		Pure media		
Stage I	y= – 11879x+12.794	98.76	4.28×10^{10}	0.9940
Stage II	y= – 32558x+29.745	270.69	2.70×10^{18}	0.9971
Stage III	y= – 31098x+16.368	258.55	3.99×10^{12}	0.9885
		Mandelic acid media		
Stage I	y= – 16091x+22.266	133.78	7.53×10^{14}	0.9904
Stage II	y= – 40785x+41.066	339.09	2.79×10^{23}	0.9825
Stage III	y= – 32867x+18.817	273.26	4.89×10^{13}	0.9835
		Propane-1,2,3-tricarboxylic acid media		
Stage I	y= – 13211x+15.665	109.84	8.40×10^{11}	0.9922
Stage II	y= – 33408x+31.215	277.75	1.20×10^{19}	0.9762
Stage III	y= – 32235x+17.727	268.00	1.61×10^{13}	0.9876



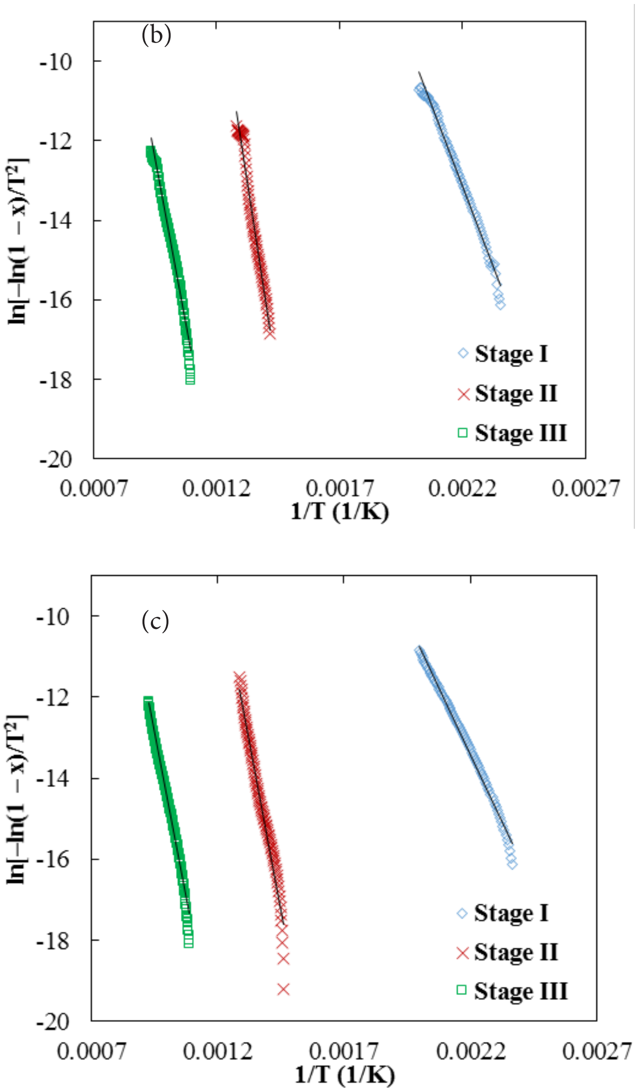


Figure 10. Plot of ln[-ln(1-x)/T^2] versus 1/temperature (T) for the three degradation stages of the calcium oxalate monohydrate (COM) crystals prepared in pure medium (a), in the presence of mandelic acid (b), and in the presence of propane-1,2,3-tricarboxylic acid (c).

The activation energies of the COM crystals were 133.78, 339.09, and 273.26 kJ/mol for mandelic acid and 109.84, 277.75 and 268.00 kJ/mol for propane-1,2,3-tricarboxylic acid in stages I, II, and III, respectively. The pre-exponential factors were 7.53×10^{14}, 2.79×10^{23}, and 4.89×10^{13} min^{-1} for mandelic acid and 8.40×10^{11}, 1.20×10^{19}, and 1.61×10^{13} min^{-1} for propane-1,2,3-tricarboxylic acid in stages I, II, and III, respectively. The linear correlation coefficient R^2 for these calculations was >0.9762, which supports the reliability of the model and resulting experimental data. The results of the thermal kinetic evaluation showed that the activation energy increased in both additive media, which meant that the energy requirement for the degradation of COM crystals was higher than that in pure medium.

IV. CONCLUSION

COM crystals synthesized in pure medium and in the presence of mandelic and propane-1,2,3-tricarboxylic acids were assessed for their characteristics. XRD, SEM, FTIR, and zeta potential analyses were successfully used to characterize the COM crystals prepared with and without additives. In addition, the Coats-Redfern model was applied to determine the activation energy of the COM crystals during the thermal degradation process that included three reaction steps. A lower average activation energy was observed in the COM crystals synthesized in pure medium than that synthesized in the additives. The activation energies of the COM crystals prepared in mandelic acid medium were 133.78, 339.09, and 273.26 kJ/mol for stages I, II, and III, respectively.

Our results will provide additional perspectives for studies in this area and experimental evidence for the modification of the shape of COM crystals. The calculated kinetic parameters can also be beneficial to interpreting and modelling studies on COM crystals.

Acknowledgements

This work was supported by the Marmara University Scientific Research Projects Commission under the funding FEN-A-110.718.0396.

REFERENCES

[1] Li, S., Tang, W., Li, M., Wang, L., Yang, Y., Gong, J., (2019). Understanding the Role of Citric Acid on the Crystallization Pathways of Calcium Oxalate Hydrates. *Cryst. Growth Des.,* 19(6), 3139-3147.

[2] King, H.E., Mattner, D.C., Plümper, O., Geisler, T., Putnis, A., (2014). Forming Cohesive Calcium Oxalate Layers on Marble Surfaces for Stone Conservation. *Cryst. Growth Des.,*14(8), 3910-3917.

[3] Akyol, E., Öner, M., (2014). Controlling of morphology and polymorph of calcium oxalate crystals by using polyelectrolytes. *J. Cryst. Growth.,* 401(1), 260-265.

[4] Akın, B., Öner, M., Bayram, Y., Demadis, K.D., (2008). Effects of Carboxylate-Modified, "Green" Inulin Biopolymers on the Crystal Growth of Calcium Oxalate. *Cryst. Growth Des.,*8(6), 1997-2005.

[5] Ruiz-Agudo, E., Burgos-Cara, A., Ruiz-Agudo, C., Ibañez-Velasco, A., Cölfen, H., Rodriguez-Navarro, C., (2017). A non-classical view on calcium oxalate precipitation and the role of citrate. *Nat Commun.,* 8, 768.

[6] Ouyang, J.M., Duan, L., Tieke, B., (2003). Effects of Carboxylic Acids on the Crystal Growth of Calcium Oxalate Nanoparticles in Lecithin-Water Liposome Systems. *Langmuir*, 19(21), 8980-8985.

[7] Li, S., Tang, W., Li, M., Wang, L., Yang, Y., Gong, J., (2019). Understanding the Role of Citric Acid on the Crystallization Pathways of Calcium Oxalate Hydrates. *Cryst. Growth Des.,* 19(6), 3139-3147.

[8] Ouyang, J.M., (2006). Effects of temperature on growth and aggregation of calcium oxalate in presence of various carboxylic acids in silica gel systems. *Mat. Sci. Eng. C-Mater.,* 26(4), 679–682.

[9] Grases, F., Millan, A., Garcia-Raso, A., (2010). Formation of Thermodynamically Unstable Calcium Oxalate Dihydrate in Sugar Mill Evaporators. *Proc. Aust. Soc. Sugar. Cane Technol.,* 32, 522-533.

[10] East, C.P., Doherty, W.O., Fellows, C.M., Yu, H., (1988). Polyhydroxycarboxylic acids as inhibitors of calcium oxalate crystal growth; Relation between inhibitory capacity and chemical structure. *J. Cryst. Growth.,* 89(4), 496-500.

[11] Akyol, E., Öner, M., (2007). Inhibition of calcium oxalate monohydrate crystal growth using polyelectrolytes. *J. Cryst. Growth.,* 307(1), 137-144.

[12] Izatulina, A.R., Gurzhiy, V.V., Krzhizhanovskaya, M.G., Kuz'mina, M.A., Leoni, M., Frank-Kamenetskaya, O.V., (2018). Hydrated Calcium Oxalates: Crystal Structures, Thermal Stability, and Phase Evolution. *Cryst. Growth Des.,* 18, 5465−5478.

[13] Zhang, Y., Tao, J., Feng, N., Han, X., (2008) Crystal growth of calcium oxalate induced by the extracts of Semen Plantaginis and Folium Pyrrosiae. *Cryst. Res. Technol.,* 43, 931-934.

[14] Ihli, J., Wang, Y.W., Cantaert, B., Kim, Y.Y., Green, D.C., Bomans, P.H.H., Sommerdijk, N.A.J.M., Meldrum, F.C., (2015). Precipitation of Amorphous Calcium Oxalate in Aqueous Solution. *Chem. Mater.,* 27, 3999−4007.

[15] Duan, C.Y., Xia, Z.Y., Zhang, G.N., Gui, B.S., Xue, J.F., Ouyang, J.M., (2013). Changes in urinary nanocrystallites in calcium oxalate stone formers before and after potassium citrate intake. *Int. J. Nanomedicine,* 8, 909–918.

[16] Frost, R.L., Weier, M.L., (2004). Thermal treatment of whewellite—a thermal analysis and Raman spectroscopic study. *Thermochim. Acta,* 409, 79-85.

[17] Coats, A.W., Redfern, J.P., (1964). Kinetic parameters from thermogravimetric data. *Nature,* 201, 68–69.

[18] Naqvi, S.R., Tariq, R., Hameed, Z., Ali, I., Naqvi, M., Chen, W.H., Ceylan, S., Rashid, H., Ahmad, J., Taqvi, S.A., Shahbaz, M., (2019). Pyrolysis of high ash sewage sludge: kinetics and thermodynamic analysis using Coats-Redfern method. *Renew Energy,* 131, 854-860.

[19] Vlaev, L., Nedelchev, N., Gyurova, K., Zagorcheva, M., (2008). A comparative study of non-isothermal kinetics of decomposition of calcium oxalate monohydrate. *J. Anal. Appl. Pyrolysis.,* 81, 253–262.