International Journal of Scientific Engineering and Research (IJSER)
ISSN (Online): 2347-3878
Impact Factor (2020): 6.733

Synthesis of Calcium Oxalate Particles via Precipitation Stripping: Effect of Molar Ratio Affect Morphological Changes

Harsh Bharatkumar Shukla

Chemical Engineering Department, Shri K J Polytechnic, Bharuch, Gujarat, India
Email: *Shuklahb22[at]gmail.com*

Abstract: ***Calcium oxalate (CaOx), a biomineral occurs in both plant and the animal kingdom. There are three hydrate forms of Calcium oxalate which are crystallized in different morphologies and the natural occurrence is connected with the three minerals whewellite as (COM) monoclinic monohydrate, (COD) weddilite as orthorhombic dehydrate and (COT) caoxite as triclinic trihydrate. Calcium oxalate used as filler and a pigment in coated paper and the cardboard industry to impart brightness. Many parameters like relative super saturation, pH, precipitation time, stirring, presence of inhibitors and surfactants affect the calcium oxalate hydrate forms and their morphology.***

Keywords: Calcium Oxalate, COM, COD, COT, Concentration Precursor, Precipitation stripping

1. Introduction

Calcium oxalate (CaOx), a biomineral occurs in both plant and the animal kingdom. Calcium oxalate is the most abundant mineral present in the human kidney stones and is therefore widely studied by urologists in an effort to understand the onset of the disease and prevent kidney stones.

There are three hydrate forms of Calcium oxalate which are crystallized in different morphologies and the natural occurrence is connected with the three minerals whewellite as monoclinic monohydrate (COM), weddilite as orthorhombic dehydrate (COD) and caoxite as triclinic trihydrate. Of the three hydrates (COM, COD, COT) only the monohydrate form is thermodynamically stable. The dihydrate and trihydrate are not stable and when left in contact with the supernatant liquid get transformed to COM.

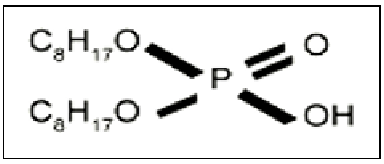
Calcium oxalate also has a commercial importance; it is used as filler and a pigment in coated paper and the cardboard industry to impart brightness.

Literature indicates that many parameters like relative super saturation, pH, precipitation time, stirring, presence of inhibitors and surfactants affect the calcium oxalate hydrate forms and their morphology.

2. Synthesis of Calcium Oxalate Particles:

Precipitation stripping under agitated conditions

1) *Calcium Salts:* Calcium Nitrate Tetra hydrate (minimum assay 99%) of AR grade supplied by S. D. fine chem. Ltd., Calcium Chloride dihydrates (minimum assay 97%) of AR grade supplied by Merck specialties private Ltd., was used as a precursor to synthesis the particles.
2) *Oxalic Acid:* AR grade with a minimum assay 99.8% from S.D. fine chem. Ltd. was used to precipitate the oxalate salt from their respective precursors.
3) *Sorbitane Monooleate (Span 80):* Span 80, nonionic surfactant used for the preparation of W/O emulsion was of S. D. fine chem. Ltd. make with saponification value of 145-160, hydroxyl value of 190-215, water content <1.0%, acid value < 8.0 and density of 0.9944 g/cc.
4) *Extractant:* D2EHPA (di-(2ethylhexyl) phosphoric Acid) ($C_{16}H_{35}PO_4$) having structural formula as shown below and a boiling point of 48 ºC at 12 mm Hg, flash point 137 ºC and density 0.97 g/cc supplied by FLUKA Chemicals Private limited was used as extractant.



5) *Kerosene:* Kerosene having boiling point range 152-271 ^{0}C with viscosity of 1.6 cP and specific gravity 0.8 at 30 ^{0}C, supplied by Indian Oil Corporation Limited Vadodara was used as the oil phase for preparation the emulsion.
6) *Sodium Hydroxide:* Sodium hydroxide pellets of AR grade with minimum assay 98.0% from S.D. fine chem. Ltd. were used to prepare NaOH of different molarities and adjust the pH of external aqueous phase.
7) *Buffer solutions:* Buffer tablets of pH 4.0 and pH 7.0 from Merck Specialties Private Ltd were used to calibrate digital pH meter.
8) Acetone and ethanol (AR grade from Merck specialties private Limited), were used to demulsify the emulsion and wash the synthesized particles.

Precipitation stripping under agitated conditions:

The precipitation reaction for formation of calcium oxalate proceeds via a simple ionic double decomposition reaction.

$$Ca\,(NO_3)_2 4H_2O + H_2C_2O_{4(aq)} \rightarrow CaC_2O_4xH_2O_{(s)} + 2\ HNO_{3\,(aq)}$$

Calcium oxalate particles were also synthesized by extracting the alkali earth metal from aqueous phase into an oil phase which had a suitable extractant. The extracted Ca^{2+} ions were then stripped from the oil phase to another aqueous phase containing a strippant so as to precipitate the particles in the bulk aqueous phase.

Equal volumes of feed containing 500 mg/L calcium salt (7.537×10^{-3} moles) and an organic phase (kerosene) containing 1-10% v/v extractant (D2EHPA) were contacted for 30 minutes. The pH values of the aqueous phase were adjusted with sodium hydroxide. The loaded oil phases were stripped with equal volume of strippant (oxalic acid, 0.075 - 0.3 M) for 30 minutes on a magnetic stirrer. The precipitates obtained were separated from aqueous phase by centrifuging at 5000 rpm washed using acetone and dried.

3. Results and Discussion

Calcium oxalate particles were also synthesized using the precipitation stripping technique. In comparison to precipitation in homogeneous quiescent media and in ELM, where the internal droplets are stagnant resembling quiescent conditions and there is phase and transport restriction. Stripping / precipitation were carried out on a magnetic stirrer where there was no phase restriction. Stripping took place at a continuous rate where both the phases (oil and aqueous) were well mixed).

Precipitation stripping experiments were conducted by first loading the oil phase with the alkali metal in first stage by taking equal volumes of feed and oil containing 10% v/v extractant. The loaded oil phases were then stripped by taking equal volumes of the oil and stripping phase (oxalic acid) for 30 minutes on a magnetic stirrer. The oxalic acid concentration was varied so as to obtain a Ca/OA molar ratio of 0.5, 1.0 and 2.0 respectively that which was identical to that used for homogeneous precipitation and also for synthesizing particles in ELM's. The precipitates obtained in the aqueous phase were separated by centrifugation washed with acetone and dried prior to characterization.

Characterization of the synthesized particles:
Hydromorphs and crystallites phases of the precipitated oxalate were determined by XRD studies. (Fig. 3.1.1) shows the XRD spectra of particles synthesized by precipitation stripping at Ca/OA molar ratio = 0.5, 100% COM monoclinic structure was obtained having d-spacing at 5.948, 3.649 and 2.972

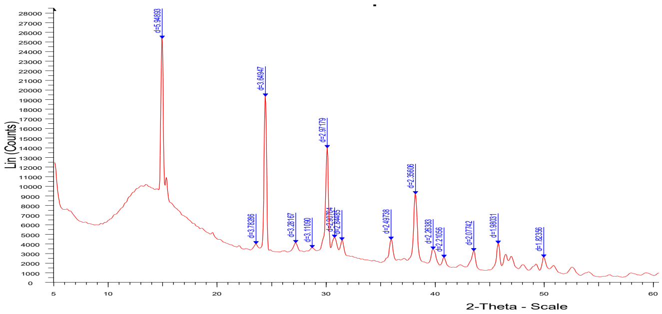


Figure 3.1.1: XRD spectra of calcium oxalate for particles synthesized at Ca/OA molar ratio 0.5 using precipitation stripping.

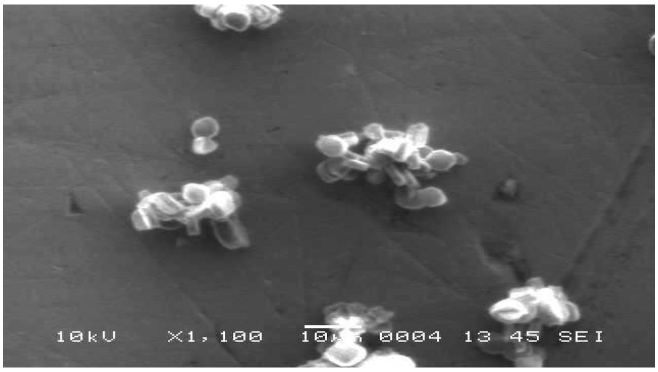


Figure 3.1.2: SEM picture of calcium oxalate monohydrate hexagons at Ca/OA molar ratio 0.5 using precipitation stripping

SEM analysis (Fig.3.1.2) showed that hexagonal flat COM aggregates were formed. The particle size closely resembled that obtained using the particle size analyzer (Fig.4.26). The results obtained were further supported by the FT-IR spectra (Fig. 4.27) where the antisymmetric stretching occurred at 1315.5 and which is very close to the reported value of 1317 for pure COM (Table 4.3). The sharp peak at 781.2 cm^{-1} attested the presence of COM.

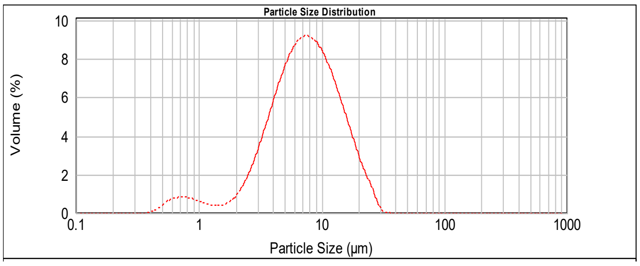


Figure 3.1.3: Particle size distribution of calcium oxalate particles synthesized by precipitation stripping at M.R. = 0.5

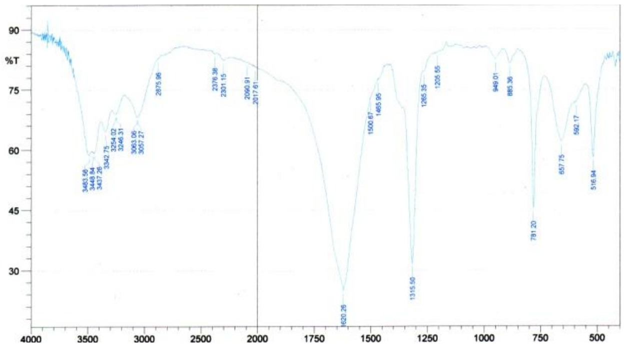


Figure 3.1.4: FT-IR spectra of calcium oxalate particles synthesized by precipitation stripping at M.R. = 0.5.

Increasing the molar ratio of Ca/OA to 1.0 decreased the % of COM to 92.7% and 7.3% anhydrous calcium oxalate was present (Table 4.6).

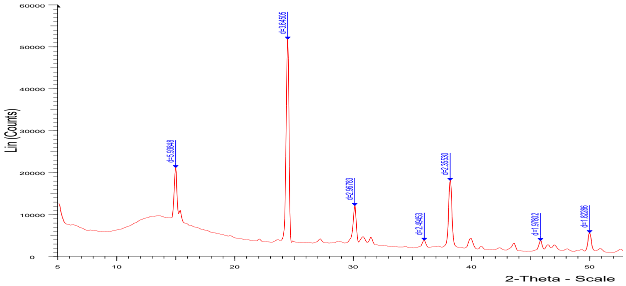


Figure 3.1.5: XRD spectra of calcium oxalate for particles synthesized at Ca/OA molar ratio 1.0 using precipitation stripping.

Fig. 3.1.5 shows the XRD plot. The d-spacing for anhydrous calcium oxalate being close to that of COM. All the three measured d-spacing for COM matched with the result obtained.

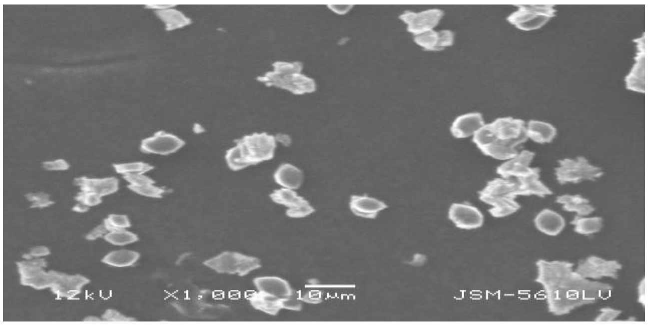


Figure 3.1.6: SEM picture of calcium oxalate monohydrate hexagonal at Ca/OA molar ratio 1.0 using precipitation stripping.

SEM pictures (Fig.3.1.6) showed presence of flat hexagonal COM and also same plate like structure representative of anhydrous CaOx. Size distribution obtained by particle size analysis (Fig.3.1.7) was similar to that observed from the SEM analysis.

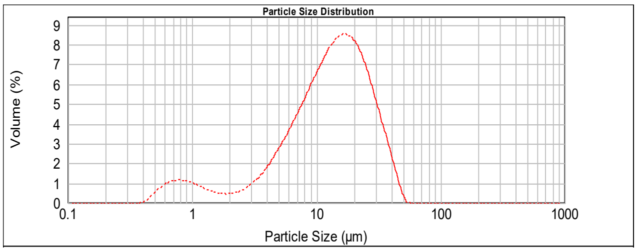


Figure 3.1.7: Particle size distribution of calcium oxalate particles synthesized by precipitation stripping at M.R. = 1.0.

Fig.3.1.8 shows the FT-IR spectra for CaOx particles obtained using precipitation stripping at molar ratio = 1.0. there was a shift observed in the antisymmetric stretching band and it was found to be at 1610 instead of 1618 for pure COM which could be due to small amount of anhydrous oxalate present, metal carboxylate was observed at 1315

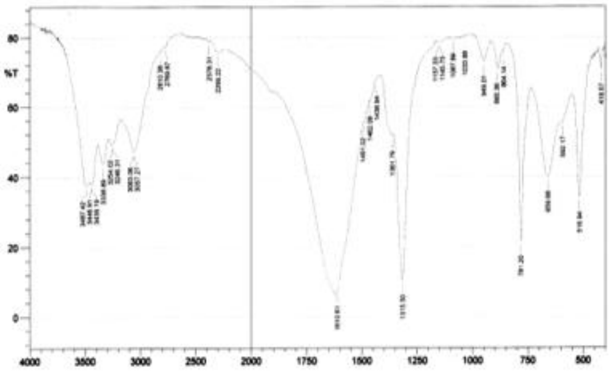


Figure 3.1.8: FT-IR spectra of calcium oxalate particles synthesized by precipitation stripping at M.R. = 1.0

Increasing the molar ratio of Ca/OA to 2.0 further decreased the % COM (67%) and increased anhydrous calcium oxalate (33.1%) (Table 3.1). This is probably due to the decrease in oxalic acid concentration. In both the cases when molar ratio = 1.0 and 2.0. The 100% peak intensity was obtained at d2 values rather than d1 (Table 3.1).

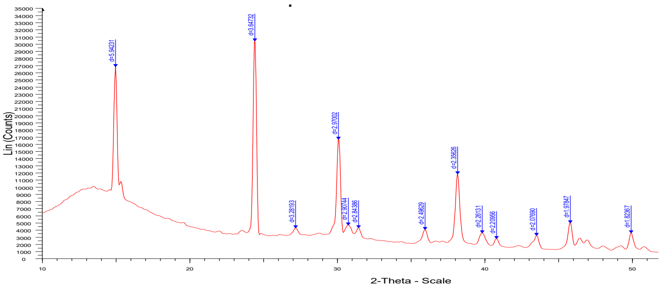


Figure 3.1.9: XRD spectra of calcium oxalate for particles synthesized at Ca/OA molar ratio 2.0

Figure 3.1.10: SEM picture of calcium oxalate monohydrate hexagonal at Ca/OA molar ratio 2.0

The SEM picture (Fig.3.1.10) showed more plate like structures this was due to he increased in anhydrous CaOx. Fig.3.1.11 shows the particle size distribution obtained, these are well in the range as observed from the SEM pictures.

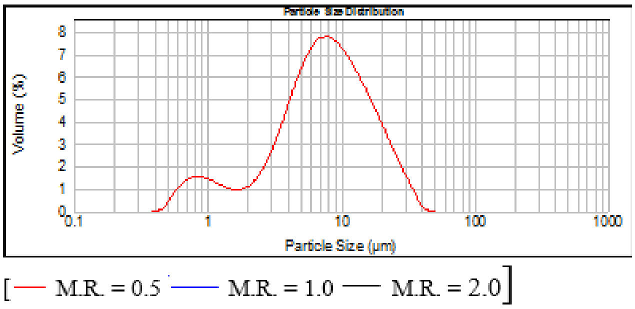


Figure 3.1.11: Particle size distribution of calcium oxalate particles synthesized by precipitation stripping at M.R. = 2.0

Thermal analysis of the particles obtained at MR = 0.5 exhibit the same 3 steps of decomposition with the first stage weight loss 12.98%, 2nd stage of 23% and 3rd of 30.55% leaving behind a residue of 33.37%. The sharp decrease in the peaks is indicative of the high crystallanity of the particles obtained.

It can be concluded that for precipitation of calcium oxalate particles using precipitation stripping techniques.

- Increasing molar ratio from 0.5 to 2.0 resulted in decrease of % COM.
- Scherrer crystallite sizes obtained for all 3 cases are listed in Table 4.5. Increasing concentration of oxalic acid decreased scherrer crystallite sizes.
- Comparative XRD spectra for a varying Molar ratio shows shift in 100% intensity peaks at d2 values when M.R. = 1 and 2.

Table 3.1: Comparison of hydrates, crystallite sizes and major d-spacing Obtained from XRD data for varying molar ratios: (calcium nitrate 0.15 M).

Oxalic acid Concentration (M)	Molar ratio	Hydrates obtained	Crystallite Size (scherrer)	Measured d-spacing				Standard d-spacing				
				d1	d2	d3	d4		d1	d2	d3	d4
0.30	0.5	100%COM (Monoclinic)	319.2 A	5.948	3.649	2.972	2.356	COM	5.97	3.64	2.98	5.77
0.15	1.0	92.7%COM, (Monoclinic) 7.3% CaOx,	362.7 A 457.7 A	3.645	5.938	2.355	2.967	COD	6.18	4.42	2.77	2.24
0.075	2	67.0%COM, 33.1% CaOx	528.8 A 81.5 A	3.647	5.942	2.97	2.356	COT	2.84	5.52	5.48	4.99

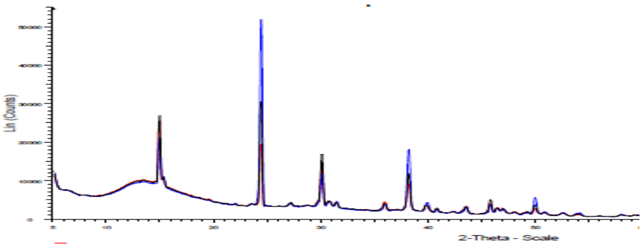


Figure 3.1.12: Comparative XRD spectra at varying molar ratios for precipitation stripping.

- At M.R. = 0.5 COM aggregates were obtained increasing M.R. from 0.5 to 1.0 presence of plate like structures which are representative to anhydrous CaOx were obtained.
- Size distributions obtained were in cognizance to that observed in the SEM pictures.

References

[1] A.M. Cody, R.D. Cody. "Calcium oxalate trihydrate phase control by structurally-specific carboxylic acids", *Journal of Crystal Growth*, 135, 235-245, (1994)

[2] A.M. Cody, R.D. Cody. "Contact and penetration twinning of calcium oxalate monohydrate (CaC_2O_4 H_2O)", Journal of Crystal Growth, 83, 485-498, (1987)

[3] Angel Millan. "Crystal Growth Shape of Whewellite Polymorphs: Influence of Structure Distortions on Crystal Shape", *Crystal Growth & Design*, 2001, 1 (3), 245-254.

[4] Donald J. White and George H. Nancollas., "The iunetics of dissolution of calcium oxalate monohydrate; a constant composition study", Journal of Crystal Growth, 57, 267-272, (1982)

[5] J G. L. Gardner. "Nucleation and crystal growth of calcium oxalate trihydrate", *Journal of Crystal Growth*, 30, 158-168, (1975)

[6] Mauricio Carvalho, Marcos A. Vieira. "Change in calcium oxalate crystal morphology as a function of supersaturation", *International Braz J Urol,* 30 (3), 205-209, (2004).

Author Profile

Harsh Shukla received the B.E. and M.E. degrees in Chemical Engineering from SVMIT and M.S. University in 2006 and 2009, respectively. After 2010, I am working as a Lecturer in Chemical Engineering Department in Shri K J Polytechnic, Bharuch