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RESEARCH ARTICLE

SYNTHESIS OF CALCIUM OXALATE PARTICLES: EFFECT OF VARIOUS FACTORS AFFECT MORPHOLOGICAL CHANGES

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ABSTRACT

The Calcium oxalate (CaOx), a biomineral occurs in both plant and the animal kingdom. 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. 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. A study based on homogeneous precipitation indicates that many parameters like relative super saturation, pH, precipitation time, stirring affect the calcium oxalate hydrate forms and their morphology.

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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. In plants calcium oxalate exists in a wide range of morphologies as prismatic crystals, styloids, sand, raphite crystals and druses. 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 affect the calcium oxalate hydrate forms and their morphology.

Although considerable work has been done on the precipitation of calcium oxalate in bulk solution at pH (4-6) simulating human like environments, precipitation of the oxalate under acidic conditions has been largely ignored.

Synthesis of Calcium Oxalate Particles

Materials and Reagents

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.

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.

Buffer solutions: Buffer tablets of pH 4.0 and pH 7.0 from Merck Specialties Private Ltd were used to calibrate digital pH meter.

Acetone and ethanol (AR grade from Merck specialties private Limited), were used to demulsify the emulsion and wash the synthesized particles.

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Table 1 (a). Effect of precursor concentration on morphology and size of CaOx particles (calcium nitrate concentration 0.1 M, precipitation time 60 min)

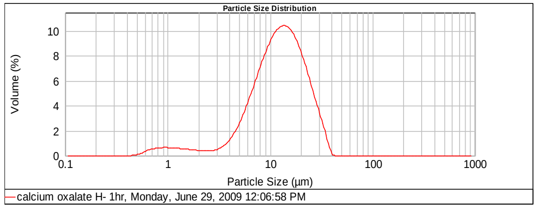
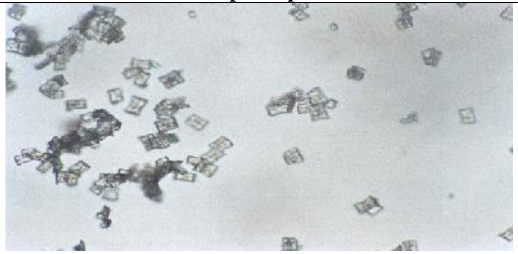
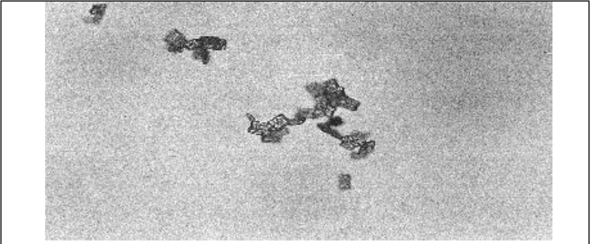
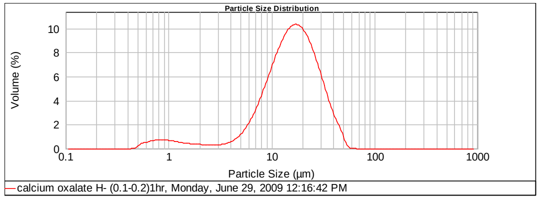
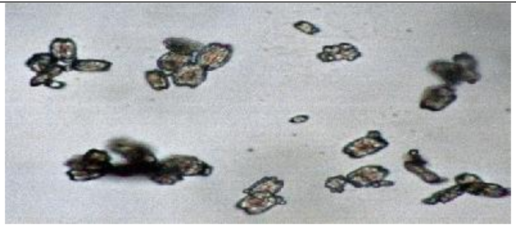
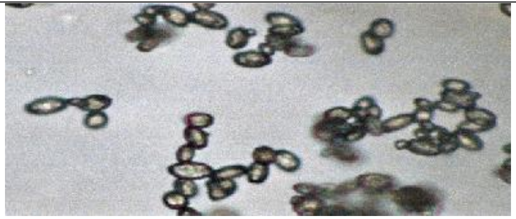
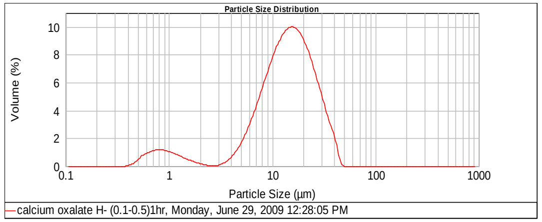
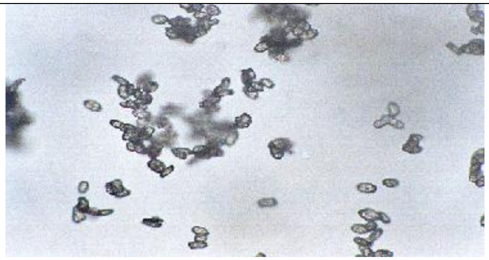
Sr. no.	Oxalic acid Conc.(M)	M.R. Ca/OA	Particle size dist. (µm)	Microscope snap at 600x	Morphology
1	0.05	2.0	 D[3,2]=5.905 µm, d(0.5)=11.052 µm		COM-twins prismatic
2	0.1	1.0			COM-twins Prismatic
3	0.2	0.5	 D[3,2]=7.869 µm, d(0.5)=15.801 µm		COM-twins
4	0.4	0.25			COM-Ovals
5	0.5	0.2	 D [3, 2] =6.083 µm, d (0.5) =14.024 µm		COM-Ovals

Table 1 (b). Effect of precursor concentration on morphology and size of CaOx particles (calcium nitrate concentration 0.2 M, precipitation time 60 min)

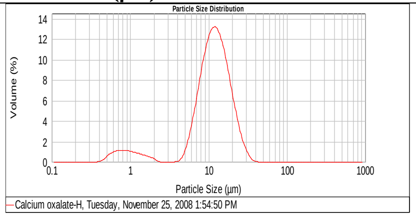
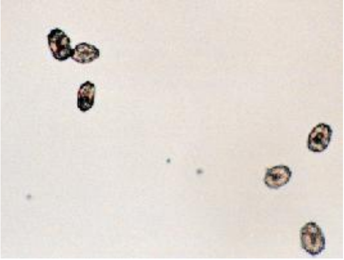
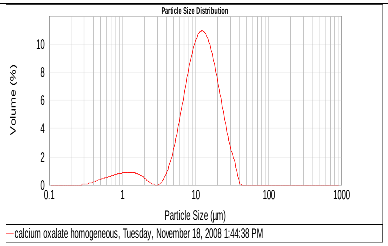
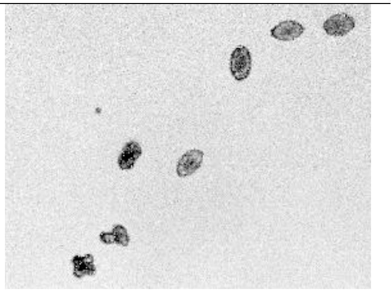
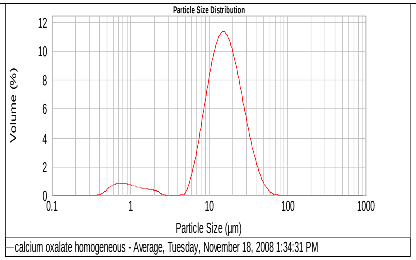
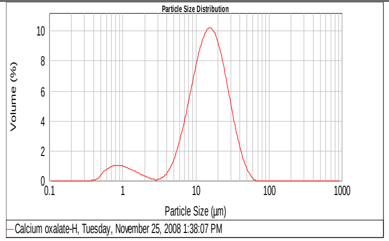
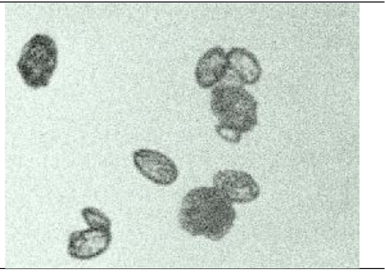
Sr. no.	OA Conc.(M)	M.R. Ca/OA	Time (min.)	Particle size dist. (μm)	Microscope snapshots at 600x	Morphology
1	0.1	2	10	 D [3, 2] =5.66 μm, d (0.5) =11.565 μm		• COM- twins, • COM-oval shape
2	0.2	1.0	10	 D [3, 2] =6.214 μm, d (0.5) =11.812 μm		• COM- twins, • COM-oval shape
			20	 D [3, 2] =7.328 μm, d (0.5) =15.264 μm		
3	0.4	0.5	10	 D [3, 2] =6.659 μm, d (0.5) =14.548 μm		• COM aggregates, (oval shape)

Table 1 (c). Effect of precursors concentration on morphology and size of calcium oxalates particles grown in presence of ethanol (Calcium nitrate concentration = 0.1 M, precipitation time 30 min)

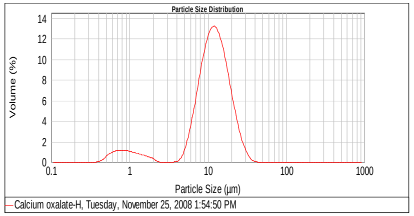
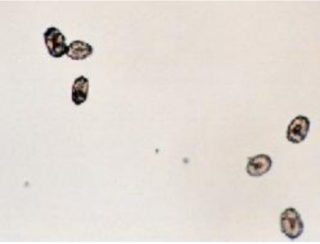
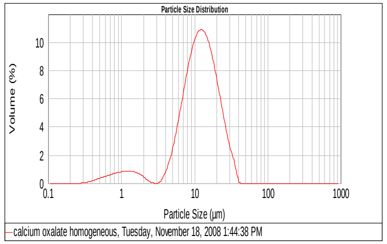
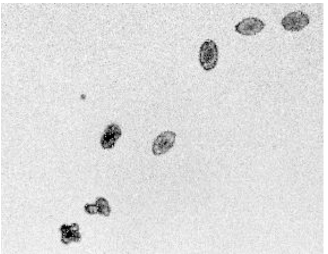
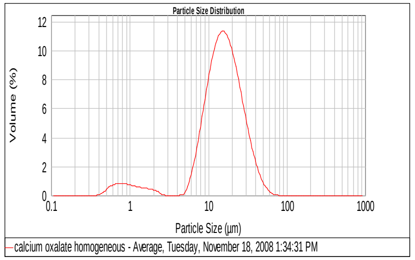
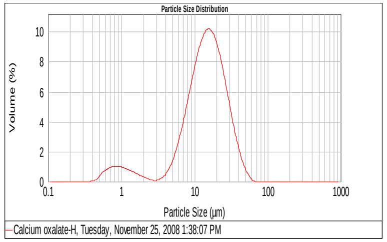
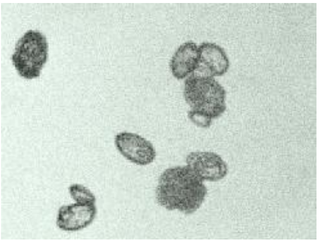
Sr. no.	OA Conc.(M)	M.R. Ca/OA	Time (min.)	Particle size dist. (µm)	Microscope snapshots at 600x	Morphology
1	0.1	2	10	 D [3, 2] =5.66 µm, d (0.5) =11.565 µm		- COM- twins, - COM-oval shape
2	0.2	1.0	10	 D [3, 2] =6.214 µm, d (0.5) =11.812 µm		- COM- twins, - COM-oval shape
			20	 D [3, 2] =7.328 µm, d (0.5) =15.264 µm		
3	0.4	0.5	10	 D [3, 2] =6.659 µm, d (0.5) =14.548 µm		- COM aggregates, (oval shape)

Table 1 (c). Effect of precursors concentration on morphology and size of calcium oxalates particles grown in presence of ethanol (Calcium nitrate concentration = 0.1 M, precipitation time 30 min).

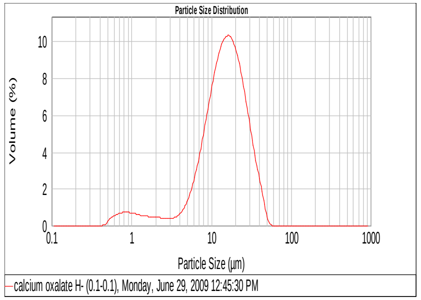
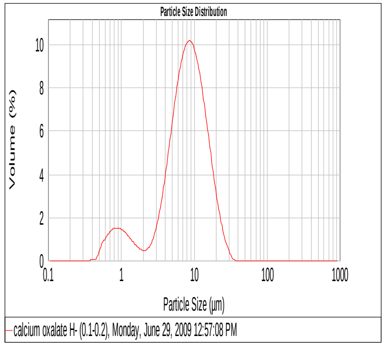
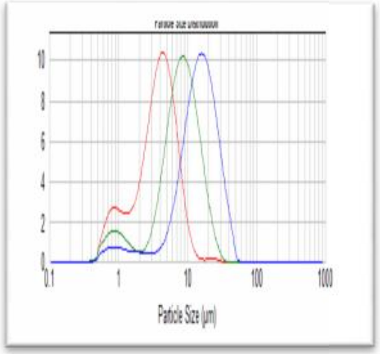
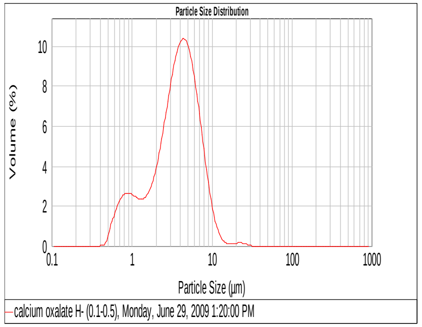
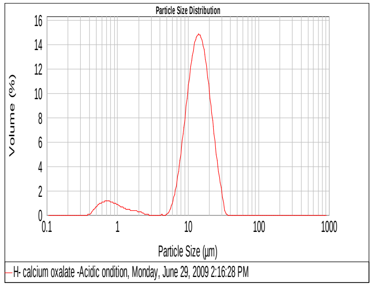
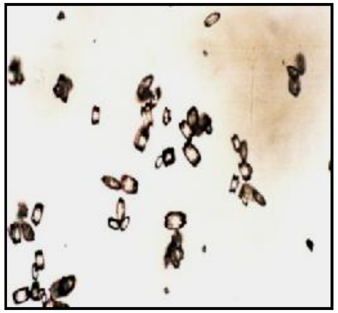
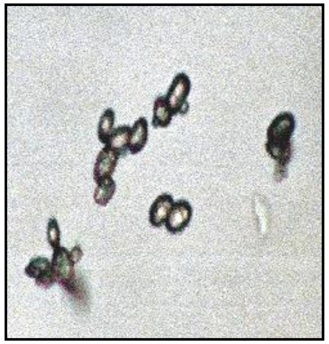
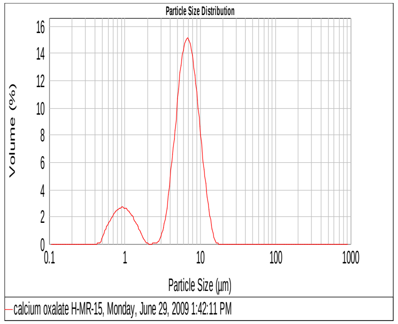
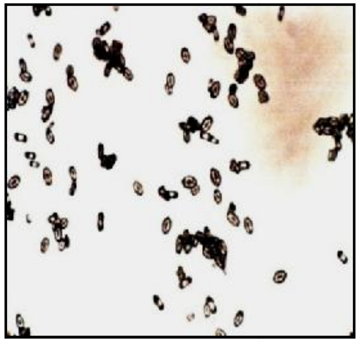
Sr. No.	OA Concentration (M)	Molar ratio Ca/OA	Particle size distribution (µm)	Particle size distribution Comparison	Microscope snapshots at 600x
1	0.1	1.0	 D [3, 2] =7.657 µm,d (0.5) =14.946 µm		
2	0.2	0.5	 D [3, 2] =4.359 µm, d (0.5) =8.017 µm		
3	0.5	0.2	 D [3, 2] =2.406 µm, d (0.5) =3.718 µm	Blue 0.1-0.1 M Green 0.1-0.2 M Red 0. 1-0.5 M	

Table 1(e). Effect of supersaturation ratio on morphology and size of calcium oxalates (Precipitation time 30 min)

Sr. No.	CN Conc.	OA Conc.	M.R. Ca/OA	Particle size distribution (µm)	Microscope snapshots at 600x	Morphology
1	0.025 (SS=8.9)	0.025	1.0	 D [3, 2] =6.172 µm, d (0.5) =13.660 µm		COM- Hexagona, COM-Ovalshape, COM-Prismatic twins, COD-tetragonal.
2	0.1 (SS=35.7)	0.5	0.2			COM-Oval aggregate, COT- needle shape.
3	0.01875 (SS=134)	0.00125	15	 D [3, 2] =3.328 µm, d (0.5) =6.349 µm		COM- Hexagonal oval, COM-Prismatic

Homogeneous precipitation (Louis Gordon, 1952)

In this method, equal volumes of calcium nitrate solution (0.1-0.5 M) and oxalic acid (0.1-0.5 M) were mixed under stagnant as well as stirring condition for varying times (5min-1hr). The initial and final pH was recorded using Systronics pH meter with calibrated glass combination electrode assembly. The calcium oxalates precipitates obtained were separated by centrifuging at 5000 rpm. The precipitates were washed 3 times with acetone and dried in desiccator. Particle morphology was observed using an OLYMPUS microscope (model BHS) equipped with a PM-10AD Olympus photo micrographic system.

RESULTS AND DISCUSSION

Synthesis of calcium oxalate particles in literature is based on considering the environmental conditions in the human body, since most of the investigations are directed towards the understanding of inhibition of growth of stones in the kidneys and urinary tract. The precipitation reaction for formation of calcium oxalate proceeds via a simple ionic double decomposition reaction.

$$Ca(NO_3)_2\ 4H_2O + H_2C_2O_{4\,(aq)} \longrightarrow CaC_2O_4\ x\ H_2O_{(s)} + 2\ HNO_{3\,(aq)}$$

Calcium oxalate exists as three different hydromorphs and depending on the precipitation conditions, concentration of the precursors, different hydrates and morphologies are obtained. This work is preliminary addressed to determine the effect of the precipitation conditions on the type of hydrates obtained the morphology, and the particle size and particle size distribution obtained.

Exploratory investigations on precipitation of calcium oxalate (Ljerka Brecevic and Damir Kralj, 1989)

Studies were conducted to study the effect of variation in precursor concentration, mode of stirring, pH condition and the time of precipitation on the morphology of the CaOx hydrate particles obtained. Precipitation experiments were carried out using 0.1 M and 0.2 M calcium nitrate as the alkali metal precursor and oxalic acid (0.05-0.5 M) as the precipitating agent. In many experiments the time allowed for precipitation was varied and precipitations were carried out in presence of ethanol.

Effect of concentration of precu-rsors

When the calcium nitrate concentration was 0.1 M and oxalic acid concentration was varied from 0.05-0.5 M in all the cases the thermodynamically stable phase COM was obtained but with different morphologies (Table 1 a). Increasing the oxalic acid concentration changed the morphology from COM prismatic (0.05M) to COM oval twins (0.2M). When the oxalic acid concentration was further increased to 0.5M COM ovals were obtained (Table 1 a). The size distributions changed with D [3, 2] of 5.905 µm at 0.05 M and concentration to 6.083 µm at 0.5 M acid concentration. When the calcium nitrate concentration was increased 0.1 to 0.2 M all the particles showed COM oval morphology (Table 1 b). In 10 minutes of precipitation time particles almost had the same distribution as that obtained in 30 minutes in the previous case.

Effect of concentration of precursors in presence of ethanol

It has been reported that presence of ethanol arrests the growth of crystals and crystals of smaller size are obtained. In view of objective of fine particle synthesis experiments were conducted to prepare calcium oxalate particles in the presence of ethanol. The oxalic acid solutions were prepared in water/ ethanol solution containing 50% ethanol. When precipitation of CaOx was carried out in presence of ethanol for 30 minutes of precipitation time the particles were very small in comparison to that obtained in absence of ethanol. The D [3, 2] and d (0.5) values were 4.36 µm and 8.017 µm in comparison to 7.86 µm and 15.80 µm in absence of ethanol when calcium nitrate concentration was 0.1 M and oxalic acid concentration 0.2M (Table 1 c). Comparing the three cases when oxalic acid concentration varied from 0.1M-0.5M at lower values of MR (<1) the particle size distribution shifted to smaller sizes but d (0.5) and D[3,2] values remained the same sizes. Since the particles were very small it was difficult to predict the morphology from the microscope snapshots at 600x magnification.

Effect of stirring

To study the effect of stirring on morphology of particles the precipitation of calcium oxalate were studied under three different conditions, unstirred, magnetically stirred and mechanically stirred conditions. There is a lot of controversy regarding the existence of different morphologies under different stirring conditions (Louis Gordon et al., 1952; Ljerka Brecevic and Damir Kralj, 1989 and Gardner1975). Poor mixing causes different morphologies. In this work it was observed that stirred/ unstirred condition did not affect the morphology of calcium oxalate particles. Only the sizes and particle size distribution were affected (Table 4.1 d) shows the effect of stirring the particle size and size distribution. It can be seen that particle sizes were larger under mechanical condition followed by unstirred conditions. Magnetic stirring yielded the smallest size of D [3, 2] = 3.14 µm.

Effect of supersaturation ratio (SS) (Mauricio Carvalho *et al.*, 2004 and El-Shall, 2004)

Table 1 (e) shows the effect of SS on the crystal morphology and size distribution. When the molar concentration of calcium nitrate was 0.025 M and the oxalic acid concentration was 0.025M the SS ratio was 8.19. Particle morphology observed was COD and COM. Low SS leads to the formation of dihydrates. This was the only case when CaOx dihydrate was observed. Carvalho and Vieira (Mauricio Carvalho, Marcos, 2004) reported that SS < 10 exhibited COD morphology. Increasing the SS from 8.19 to 35.71 (calcium nitrate 0.1M) and oxalic acid (0.5M) resulted in the formation of COM oval aggregates. Higher concentration of oxalic acid results in formation of COM. Further increasing the SS ratio to 134 (calcium nitrate 0.375 M) (oxalic acid 0.025M) high MR of 15, resulted in the formation of small crystals with COM hexagonal and oval morphology. Carvalho and Vieira (Mauricio Carvalho, Marcos, 2004) reported that SS >50 produced hydrates 0f different shapes.

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