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Synthesis of Calcium Oxalate Particles Using Emulsion Liquid Membrane (ELM): Effect of Extractant Concentration on Morphology

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Abstract: ***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. Emulsion Liquid Membrane (ELM) systems is a useful tool for quick and selective removal of metals from dilute aqueous streams. Calcium oxalate used as filler and a pigment in coated paper and the cardboard industry to impart brightness.***

Keywords: Calcium Oxalate, COM, COD, COT, Concentration Precursor, ELM, extractant concentration

1. Introduction

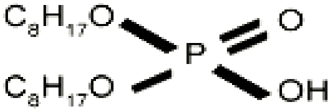
There are three hydrate forms of Calcium oxalate which are crystallized in different morphologies and the natural occurrence is connected with the three minerals whewellite as monoclinic monohydrate (COM), weddilite as orthorhombic dehydrate (COD) and caoxite as triclinic trihydrate. Of the three hydrates (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 precipitation time, stirring, presence of inhibitors and surfactants affect the calcium oxalate hydrate forms and their morphology.

2. Reagents for Synthesis of Calcium Oxalate Particles

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.

3. Synthesis of Calcium Oxalate Particles

Precipitation using facilitated transport in confined spaces (Emulsion Liquid Membranes):
The precipitation reaction for formation of calcium oxalate proceeds via a simple ionic double decomposition reaction.

$$Ca(NO_3)_2 4H_2O + H_2C_2O_{4(aq)} \longrightarrow CaC_2O_4 xH_2O_{(s)} + 2\ HNO_{3\ (aq)}$$

3.1 Emulsion Characterization:

<u>Internal drop size measurement:</u>
Internal droplet sizes of the emulsion were observed under an OLYMPUS microscope (model BHS) equipped with a PM-10AD Olympus photo micrographic system. Emulsions were diluted with kerosene (1:45) and the diluted emulsions were mounted on a slide and covered with a 0.5 mm thick cover slip.

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Droplet sizes were measured at 600x magnification using an ocular micrometer (graduated scale) (Erma make) and a stage micrometer, a 3”x1” glass slide on which a millimeter scale is imprinted, graduation of this scale is in hundredths of millimeter. The measurement of drop sizes by this method required the calibration of the ocular micrometer with the stage device. The value of single ocular meter unit (O) was calculated as,

$$O = \frac{\text{Distance of 10 stage divisions (mm)}}{\text{Number of eyepiece divisions}}$$

$$= \frac{0.1}{30} = 3.33\ \mu\text{m}$$

On calibrating the ocular, the stage micrometer was removed and the prepared slide was placed. Once the slide was focused, the number of division (N) covered by the droplet was counted and size of the droplet was calculated by multiplying the number of division (N) with the calculated value of O that is 3.33 μm.

Viscosity Measurement:

Emulsion viscosity was measured using a Brookfield cone and plate rheometer, LVDV- Ⅲ using CPE-52(cone angle 3 degree, and radius 1.2) at varying shear rates.

3.2 Preparation of calcium oxalate particles in ELMs

The experimental set up consisted of a glass baffled reactor (4 baffles) of 9.82 cm I.D. and 14.0 cm height equipped with a six bladed turbine agitator assembly. The agitator was driven by a fractional HP (1/8) variable speed motor (REMI make 0.95 Amp, with 12 HP, 220-230 V). A rheostat from MAGGSTAT ELECTRICALS was provided to control the input voltage to the motor driven the agitator, so that the speed could be maintained constant. The dimensional specification of the assembly is shown in Figure 3.2.1.

600 ml of feed solution (initial calcium concentration 500 mg/L (7.537×10^{-3} moles) was contacted with 100 ml of the cured emulsion at 160 rpm and 30 ± 2 ^{0}C so, as to give a treat ratio of 1:6. After 30 min of mixing, the W/O emulsion was separated from the external feed solution and demulsified by adding definite amount of acetone/ethanol. The particles, formed in the internal phase of emulsion, were then separated by centrifuging at 5000 rpm, washed with acetone/ethanol, and dried.

Precipitation in ELMs is based on the principal of facilitated transport II wherein the alkali metal ions bind with a suitable extractant to get transported through the oil phase membrane to the internal phase membrane interface to get precipitated in the internal droplets of the emulsion containing the precipitating agent.

In comparison to homogeneous precipitation which is instantaneous there is a time gap for precipitation in ELMs. The precursor is in the bulk phase which is the stirred phase has to get transported to the internal phase and the particles are precipitated in the internal droplets which are stagnant droplets. This behavior is identical to precipitation in homogeneous quiescent media. There is no restriction in homogeneous phase but there is phase and transport restriction in ELMs.

Synthesis of particles is an ELM offers a distinct advantage of producing particles of controlled sizes. The size selectivity of an ELM is obtained because precipitation takes place within the internal droplets of a W/O emulsion. Under normal emulsification conditions the internal drop size in an emulsion range from 1-10 μm with an average size of ~3 μm. Hence, the particles synthesized within an ELM would yield sizes < 3 μm.

Before carrying out precipitation in an ELM the mechanism needs to be developed wherein the Ca^{+2} ions can be transported and precipitated in the internal phase droplets. Since cation transport necessitates the addition of an extractant in the oil membrane phase which would selectively bind the cation at the external oil- water interphase. Ca ion transfer into ELM follows facilitated type – II mechanisms.

$$2RH + Ca^{2+} \leftrightarrow R_2Ca + 2H^+ \text{ ---------------------------- } (1)$$

$$R_2Ca + 2H^+ \leftrightarrow 2RH + Ca^{2+} \text{ ---------------------------- } (2)$$

The internal phase reaction (2) will free the extractant and strip the Ca ions from the extractant and seed the particle making the extractant free to bind more cations to be transported to external phase. In this system D2EHPA was used as the extractant due to its commercial availability. Extractants are highly sensitive to feed phase pH. Fig.4.12 shows the extraction isotherms for divalent cations using D2EHPA as extractant. It can be seen that D2EHPA extracts calcium at wide range of pH values from 1.5 to 2.8. The pH of the feed was maintained at 6.

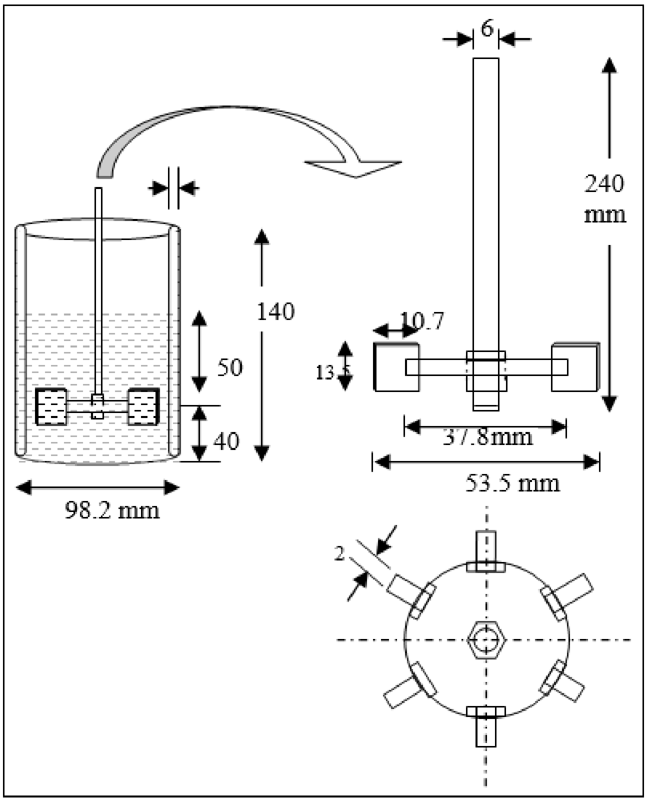


Figure 3.2.1: Dimensional assembly of agitator vessel

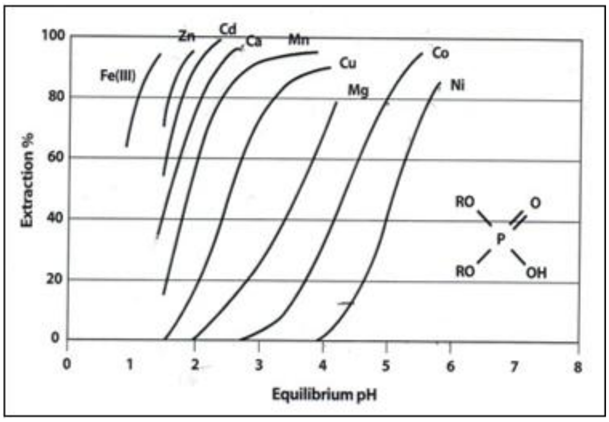


Figure 3.2.2: Metal extraction by Di-2- ethylhexyl phosphoric acid as a function of pH.

Emulsions were prepared as per method discussed in section 3.2.3. The emulsions contained 1 and 10% v/v of extractant, 5% wt of oil phase surfactant, oxalic acid (0.075 M- 0.3 M) and the ratio of the oil to aqueous phase Φ = 0.5 and 0.64. Fig. 3.2.3 shows the drop size distributions. It can be seen that D [3, 2] = 3.364 μm for emulsion having Φ = 0.5 and acid concentration = 0.15 M. Increasing the value of Φ to 0.64 resulted in a wider size distribution with D [3, 2] = 4.84 μm.

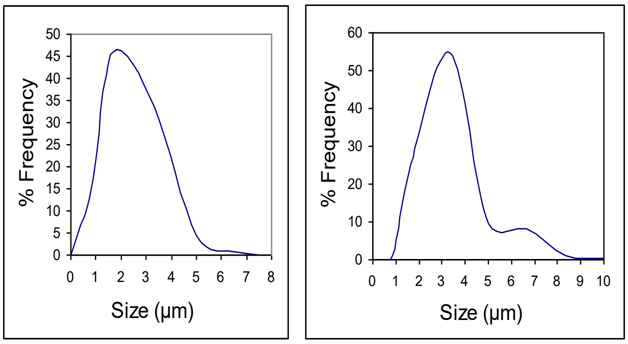


Figure 3.2.3: Internal drop size distributions of emulsions

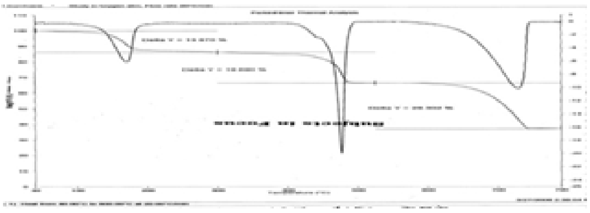
100 ml of these prepared emulsions were dispersed in 600 ml feed containing calcium nitrate (0.0125 M) so as to get a treat ratio of 1:6. The stirring speed was maintained at 160 rpm since, pilot studies showed that the emulsion was not will dispersed at 150 rpm at speeds higher than 160 rpm stability of emulsion was a question. Hence, in all the experiments speed of 160 rpm with surfactant concentration of 5% wt of oil phase was maintained. The feed and emulsion were contacted for 30 minute of time. The emulsion was separated from the feed phase washed with water and than demulsified using acetone to recover the precipitated CaOx particles formed in the internal phase of the emulsion. The particles were washed with acetone and dried.

3.3 Effect of extractant concentration:

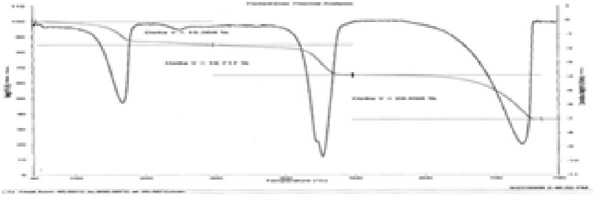
Reducing the extractant concentration from 10% to 1% keeping Φ = 0.5. M.R. = 0.5 did not affect the hydromorphs obtained except that there was a slight increase in the % COT obtained.

Thermal analysis of synthesized particles:

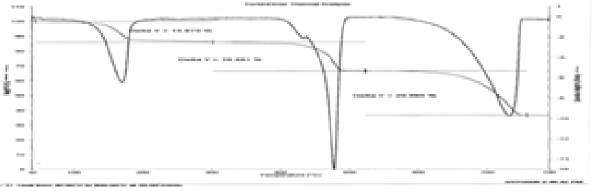
Thermal analysis of all the synthesized particles was conducted in oxygen atmosphere at heating rate of 20^0/min.



(a) Extractant 10%, Φ = 0.5.



(b) Extractant 1%, Φ = 0.5.



(c) Extractant 10%, Φ = 0.64.

Figure 3.3.1: Thermal analysis for calcium oxalate particles synthesized in an ELM system.

Fig. 3.3.1 shows the TGA, DTG plots obtained for various parametric variations at MR = 0.5. Calcium oxalate is a standard material used for TGA, DTG analysis and it is well known that the CaOx decomposition takes place in three stages, the formation of the dehydrated oxalate, calcium carbonate formation and finally the corresponding oxide formation. The dehydration curves are endothermic, when the carbonate is formed and then its decomposition also endothermic. In 1st stage calcium oxalate hydrate is converted into calcium oxalate anhydrous at temperate 150 - 200^0C. The first loss of sample weight is due to the dehydration of water (12.32 % for COM).The loss of sample weight is equal to the quantity of one mole of crystal water.

Table 3.3.2 shows the % loss obtained and the theoretical calculated loss and residue obtained in all the 3 steps when M.R. = 0.5 for varying extractant concentration and internal phase volume fraction Φ.

Table 3.3.2: TGA calculations for varying extractant and internal phase volume fraction.

Sr. no.	Condition	1st stage			2nd stage			3rd stage			Residue
		Theoretical loss = 12.33%			Theoretical loss = 19.18%			Theoretical loss = 30%			
		Initial	Final	Loss	Initial	Final	Loss	Initial	Final	Loss	
1	(Extractant =10%, Φ=0.50)	2.514	2.1653 86.13%	0.3486 13.87%	2.165	1.6703 66.44%	0.495 19.69%	1.6703	0.9336 37.14%	0.7366 29.30%	37.14%
2	Extractant =10%, Φ=0.64	2.474	2.1307 86.13%	0.34326 13.88%	2.131	1.6485 66.63%	0.4822 19.49%	1.6485	0.9091 36.75%	0.7394 29.89%	36.75%
3	(Extractant =1%, Φ=0.50	2.255	1.9152 84.93%	0.3397 15.07%	1.915	1.4706 65.21%	0.446 19.72%	1.4706	0.8234 36.52%	0.6471 28.70%	36.52%

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Author Profile

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