crystals

MDPI

Supporting Information

1. Other Methods Explored for COM Solubility

Accurate solubility of Calcium Oxalate Monohydrate (COM) is needed to extend the current knowledge of nephrolithiasis. The COM solubility is determined as a function of temperature and pH. The temperature dependent solubility is done by a mixture of COM and ultrapure water. To identify the most suitable method to measure solubility, explored different methods.

Firstly, we discuss the gravimetric method. In this method, 200 mg COM is suspended in 1000 ml solution volume to minimize the weighing error. Once the volatiles are evaporated, the amount of dry material; CaC_2O_4 was determined. The weighted amounts showed large variations hence error bars. We suspect these large error bars originate from material sticking in vessels where evaporation occurs. Hence we concluded that gravimetric method is not the most suitable approach for measuring solubility of this a sparely soluble compound.

Then we explored polythermal method based on turbidity with multiple reactor systems Crystal16 and Crystalline (Avantium Technologies). Volumes of one and eight milliliters respectively were tested. The vials with concentrations ranging between 0.1mg/ml and 1.6 mg/ml were placed in the setup at a stirring speed of 400 rpm. The heating and cooling rates were chosen as 0.1 °C /min and 1.0 °C /min respectively. The temperature profile was chosen from 5 to 90 °C. This temperature cycle was repeated three times for each sample. Following, we used different concentrations, temperatures profiles and heating cooling rate to find solubility curve. In such turbidity-based measurements, we expect to see significant changes in transmittivity across the scanned temperature range. However, observed 100 % transmittivity at all times indicating that the turbidity did not change throughout the measurements. We hypothesize that, due to low solubility of COM, the amount of crystals forming was not sufficient to alter transmittivity. We also explored UV-Vis (Hach DR 6000) spectroscopy with measurements to quantify the COM solubility. Samples with a concentration ranging between 0.1mg/ml and 1.6 mg/ml at 25, 37, 60 and 90 °C. were tested at 620nm [4]. However, there were not significant peaks regarding at 620 nm. We have also explored Focused Beam Reflectance Measurement (FBRM, Mettler Toledo D600L). The probe was inserted in Easymax reactor at experimental temperature and concentration ranges. We could not get any reproducible results with this method as well. We hypothesize that the small change in COM crystal size was beyond the detection limit FBRM. ReactIR iC10 (Mettler Toledo) was used to measure different oxalate concentrations. There were sharp drops in the absorbance. Yet repeated measurements under identical experimental conditions, produced irreproducible results.

2. Supporting Information on Reported Measurements

In this section, we provide raw data for each ICP-OES and ICP-MS measurement in Tables S8 to S11. In addition to the all raw data provided, information relevant to buffer solutions (Table S1–S5), material list (Table S6) and equipment list (Table S7) is provided below. We hope these details listed below will make it easier for other experimentalist to reproduce our results.

Table S1. The amounts of materials used in buffer solution preparation [1,2].

Compound	Volume of Ultrapure Water (mL)	Weight of the Compound (g)
Citric acid ($C_6H_8O_7$)	658.320	12.648
Disodium phosphate (Na_2HPO_4)	781.920	22.200
Glycine ($C_2H_5NO_2$)	240.000	3.603
Sodium hydroxide *(NaOH)*	138.000	1.104

Table S2. pH values for two different buffer solutions [1,2].

pH	Buffer Solution
3.2, 5.36, 6.0, 7.55	Citric Acid – Disodium phosphate
9.0, 10.6	Sodium hydroxide – Glycine

Table S3. Desired Buffer solution calculation for pH 3.0, 5.0, 6.0 and 7.4 [1,3].

pH	x ml 0.1 M - Citric Acid ($C_6H_8O_7$)	x ml 0.2 M - Disodium Phosphate (Na_2HPO_4)
3.0	381.36	98.64
5.0	233.04	247.20
6.0	184.25	315.75
7.4	43.92	436.08

We could not reach the same pH values for 3.0, 5.0, 7.4. We obtained 3.2, 5.36, 6.0, 7.55 values which are in Table S3.

Table S4. Desired Buffer solution calculation for pH 9.0 and 10.6 [1,3].

pH	× ml 0.2 M - Glycine ($C_2H_5NO_2$)	x ml 0.2 M - Sodium Hydroxide ($NaOH$)	Ultrapure Water
9.0	120.0	28.8	331.20
10.6	120.0	109.2	250.80

Table S5. Weight of the needed compounds during the buffer solution preparation [1,3].

Compound	Volume Ultrapure Water (ml)	Weight of the Compound (g)
Citric acid ($C_6H_8O_7$)	658.32	12.656
Disodium phosphate (Na_2PO_4)	781.92	22.20
Glycine ($C_2H_5NO_2$)	240.00	3.60
Sodium hydroxide ($NaOH$)	138.00	1.10

Table S6. Material list for Solubility Experiment.

Materials	Chemical Formula	CAS Number	Vendor
Citric Acid	$C_6H_8O_7$	77-92-9	MERCK
Disodium phosphate	Na_2HP_4	7558-79-4	Sigma-Aldrich
Sodium hydroxide	$NaOH$	7558-79-4	Sigma-Aldrich
Ultrapure water	H_2O	-	ELGA PURELAB Resistivity:18.2 MΩ·cm at 23.6 °C) -
Glycine	$C_2H_5N_2$	1310-73-2	Sigma-Aldrich
Calcium oxalate monohydrate	$CaC_2O_4{\cdot}H_2O$	563-72-4	Sigma-Aldrich

Table S7. Equipment list for Solubility Experiment.

Equipment	Equipment Name	Brand
Scale	Mettler PM2000	Mettler Toledo
Scale	Precision Balance MS4002TSDR/00	Mettler Toledo
Ultrasonic bath	Branson 2510 Ultrasonic Cleaner	Branson
Oven	-	Binder
Reactor	EasyMax 102 Advanced Synthesis Workstation	Mettler Toledo
pH-meter	914 pH/Conductomer	Metrohm

At least seven repetitions were done for each temperature point for ICP-OES and ICP-MS measurements. Measurements at three different wavelengths for ICP-OES at given in Table S8. The average of the measured values at 317.9 nm is converted to molarity considering dilution factor and presented in Figure 2 and Figure 4 in main text.

Table S8. The raw results of ICP-OES measurements (in ultrapure water) for different temperatures at 317.9, 393.4 and 396.8 nm.

T (°C)	Ca [ppm] 317.9	Ca [ppm] 393.4	Ca [ppm] 396.8
25	0.4056	0.4016	0.4055
	0.4968	0.5010	0.4913
	0.4219	0.4269	0.4244
	0.4255	0.4266	0.4261
	0.4560	0.4587	0.4598
	0.5306	0.5300	0.5195
	0.4234	0.4287	0.4211
	0.4112	0.4167	0.4126
	0.5088	0.5206	0.5039
	0.3898	0.4069	0.3941
	0.4200	0.4305	0.4234
	0.4404	0.4646	0.4458
	0.4348	0.4488	0.4411
	0.4447	0.4610	0.4509
	0.4174	0.4276	0.4199
	0.3572	0.3590	0.3559
	0.4316	0.4280	0.4239
	0.3718	0.3670	0.3666
	0.3925	0.4020	0.3904
	0.3852	0.4021	0.3866
	0.5200	0.5324	0.5140
37	0.5085	0.5032	0.4967
	0.5112	0.5138	0.5027
	0.5267	0.5390	0.5288
	0.5363	0.5386	0.5291
	0.5165	0.5251	0.5142
	0.5220	0.5187	0.5080
	0.4398	0.4457	0.4384
	0.4516	0.4529	0.4538
	0.4963	0.4955	0.4934
60	0.4820	0.4722	0.4737
	0.4567	0.4628	0.4665

	0.5139	0.5308	0.5145
	0.4683	0.4792	0.4728
	0.5687	0.5683	0.5506
	0.5353	0.5408	0.5297
	0.5386	0.5337	0.5229
	0.5620	0.5620	0.5506
	0.5019	0.5264	0.5098
	0.4994	0.5155	0.4999
	0.4307	0.4581	0.4368
	0.4810	0.4846	0.4935
90	0.5581	0.5352	0.5426
	0.5419	0.5348	0.5444
	0.5129	0.5122	0.5222
	0.5627	0.5525	0.5638
	0.4995	0.5122	0.4983
	0.4701	0.4745	0.4746
	0.4389	0.4465	0.4382
	0.5154	0.5156	0.5038
	0.5253	0.5191	0.5072
	0.5529	0.5582	0.5451
	0.4986	0.5085	0.5002
	0.5085	0.5215	0.5128
	0.5769	0.5801	0.5709
	0.5203	0.5300	0.5207
	0.5699	0.5688	0.5595
	0.5325	0.5363	0.5244
	0.5459	0.5506	0.5378
	0.5318	0.5346	0.5228
	0.5551	0.5597	0.5483
	0.5439	0.5376	0.5261

Table S9. The raw results of ICP-MS measurements (in ultrapure water) for different temperatures.

T (°C)	Ca44 ppm	T (°C)	Ca44 ppm
25	0.3607	60	0.5364
	0.3573		0.5263
	0.4426		0.5092
	0.4380		0.4737
	0.4007		0.4376
	0.3547		0.4126
	0.4030		0.4977
	0.4613		0.4620
	0.4311		0.4604
	0.4031		0.4620
	0.4256		0.5038
	0.3954		0.4911
	0.4307	90	0.4795
	0.4464		0.6030
	0.4390		0.4645
	0.3939		0.4443

	0.3886	0.4595
	0.4228	0.6168
37	0.4781	0.7694
	0.4685	0.6210
	0.4730	0.7528
	0.5202	2.4830
	0.5176	0.5325
	0.5365	0.5192
	0.6372	0.4841
	0.5201	0.4691
	0.4915	0.5304
	0.4853	0.5013
	0.5214	0.4711
	1.2615	0.5009
		0.5631
		0.4781
		0.5267

Table S10. ICP-OES measurements for calcium in two different buffer solutions at different pH values at 317.9 nm.

pH	[10^{-4}M]Ca	pH	[10^{-4}M]Ca	pH	[10^{-4}M]Ca
3.20	6.9643	6.00	9.0308	9.0	1.5217
	6.6891		8.7389		1.2382
	7.5778		8.8617		1.1448
	7.1229		8.8143		1.3272
	6.8283		8.7908		1.4097
	6.9428	7.55	6.6807		1.5232
	6.5506		6.8234		1.6705
	6.5964		6.5193		1.5810
	6.9645		6.6901		1.4909
5.36	8.8569		6.3096	10.6	1.8360
	8.7473		6.2740		1.7147
	8.7014		6.8890		2.1585
	8.0327		7.3478		2.0182
	7.9405		7.2781		2.1788
	8.3122				2.1189
	8.5062				2.3200
	8.5010				2.5504
	8.5546				

At body temperature condition, nine replicate samples were analyzed for each pH; namely, 3.2, 5.36, 7.55, 9.0, 10.6 and five replicate samples were analyzed for pH 6.0.

Table S11. The average calcium values at different pH values using ICP-OES.

ICP-OES [10^{-4} M]		
pH	**[Ca_tot]**	st dev.
3.2	6.929	0.277
5.36	8.478	0.101
6.0	8.847	0.112
7.55	6.770	0.210
9.0	1.437	0.128
10.6	2.152	0.158

The average values of Calcium molarity in two different buffer solutions at different pH values using ICP-OES are used in Figure 5 in manuscript.

3. Detailed Information on Various Reactions used in Modelling

3.1. The reactions of Titration

Oxidation $C_2O_4^{2-} \rightarrow 2CO_2 + 2e^-$

Reduction $8H^+ + MnO_4^- + 5e^- \rightarrow Mn^{2+} + 4H_2O$

Net $16H^+ + 2MnO_4^- + 5C_2O_4^{2-} \rightarrow 2Mn^{2+} + 10CO_2 + 8H_2O$

Molecular balance

$2KMnO_4 + 5CaC_2O_4 \cdot H_2O + 8H_2SO_4 \rightarrow 2MnSO_4 + K_2SO_4 + 5CaSO_4 + 10CO_2 + 13H_2O$ [4–6].

The titration is completed with a certain amount of potassium permanganate solution.

3.2. Ultrapure Water and COM

The reactions for the mixture of COM and water,

$CaC_2O_4(aq) \leftrightarrow Ca^{2+} + C_2O_4^{2-}$

$C_2O_4^{-2} + H^+ \leftrightarrow HC_2O_4^-$

$HC_2O_4^- + H^+ \leftrightarrow H_2C_2O_4$

$2C_2O_4^{2-} + Ca^{2+} \leftrightarrow Ca(C_2O_4)_2^{2-}$

3.3. Citric acid-Disodium Phosphate Buffer Solution and COM

The reactions for the citric acid,

$H_3C_6H_5O_7(aq) \leftrightarrow H_2C_6H_5O_7^-(aq) + H_3O^+(aq)$

$H_2C_6H_5O_7^+(aq) \leftrightarrow HC_6H_5O_7^{2-}(aq) + H_3O^+(aq)$

$HC_6H_5O_7^{2-}(aq) \leftrightarrow C_6H_5O_7^{3-}(aq) + H_3O^+(aq)$

The reactions for the disodium phosphate,

$Na_2HPO_4 \leftrightarrow 2Na^+ + HPO_4^{2-}$

$HPO_4^{2-} \leftrightarrow H^+ + PO_4^{3-}$

$HPO_4^{2-} + H^+ \leftrightarrow H_2PO_4^-$

$H_2PO_4^- + H^+ \leftrightarrow H_3PO_4(aq)$

3.4. Glycine-Sodium Hydroxide Buffer Solution and COM

The reaction for the glycine,

$NH_2CH_2COOH \leftrightarrow H^+ + NH_2CH_2COO^-$

The reactions for the sodium hydroxide,

$NaOH \leftrightarrow Na^+ + OH^-$

$Na^+ + NH_2CH_2COO^- \leftrightarrow NH_2CH_2COONa(aq)$

4. Procedure for Checking for pH Change in Solubility Measurements

To ensure that the pH of ultrapure water did not change during solubility measurements due to added COM or carbon dioxide dissolving in water at elevated temperatures, we measured pH in only ultrapure water and in a suspension of COM. For both cases, we reproduced identical conditions as ICP-OES and ICP-MS measurements detailed in main text. The measurements are conducted in triplicates and given in Table S12.

Table S12. Measuring pH before and after adding of COM in ultrapure water at measured temperatures.

T (°C)	pH for Ultrapure Water	Average	St. dev.	pH for the Mixture of Ultrapure Water and COM	Average	St. dev.
25	7.12			7.09		
	7.15	7.07	0.109	7.17	7.08	0.101
	6.95			6.97		
37	6.88			6.91		
	6.8	6.82	0.049	6.85	6.83	0.086
	6.79			6.74		
60	6.2			6.1		
	6.55	6.47	0.248	6.68	6.493	0.341
	6.68			6.7		
90	6.2			6.33		
	6.4	6.26	0.118	6.3	6.26	0.096
	6.19			6.15		

5. Modelling: Detailed list of Association Constants

In this section, we provide detailed list of association constants used in modelling.

Table S13. Association reactions and their equilibrium constants at 37 °C from literature. .

Parameters	Reaction	Source	K value
K_{H_3Cit}	$H_3Cit \rightleftarrows H^+ + H_2Cit^-$	7	1348
$K_{H_2Cit^-}$	$H_2Cit^- \rightleftarrows H^+ + HCit^{2-}$	7	57544
$K_{HCit^{2-}}$	$HCit^{2-} \rightleftarrows H^+ + Cit^{3-}$	7	2.51E6

$K_{H_3PO_4}$	$H_3PO_4 \rightleftarrows H^+ + H_2PO_4^-$	8	141.3
$K_{H_2PO_4^-}$	$H_2PO_4^- \rightleftarrows H^+ + HPO_4^{2-}$	8	1.58E7
$K_{HPO_4^{2-}}$	$HPO_4^{2-} \rightleftarrows H^+ + PO_4^{3-}$	8	2.4E12
K_{Gly}	$Gly \rightleftarrows H^+ + Gly^-$	9	6.03E9
$K_{\mathrm{NaCit}^{2-}}$	$NaCit^{2-} \rightleftarrows Na^+ + Cit3^-$	7	8.5
K_{CaCit^-}	$CaCit^- \rightleftarrows Ca^{2+} + Cit3^-$	8	4.76E4
K_{CaHCit}	$CaHCit \rightleftarrows Ca^{2+} + HCit^{2-}$	8	2860
$K_{\mathrm{NaC_2O_4^-}}$	$NaC_2O_4^- \rightleftarrows Na^+ + C_2O_4^{2-}$	10	1.035
K_{CaGly^+}	$CaGly^+ \rightleftarrows Ca^{2+} + Gly$	11	25.1

Table S14. Dissolved COM in ultrapure water measured by ICP-OES and simulated values**.**

	Streit *et al.*	**ICP-OES**	**Simulation**
T	[Ca]	[Ca]	[Ca]
25	4.85E-05	0.000105	0.000108
37	5.09E-05	0.000124	0.000113
60	5.54E-05	0.000125	0.000124
90	6.11E-05	0.000133	0.000138

Dissolved COM concentrations in ultrapure water were measured by ICP-OES as a function of temperature. Simulated values using the K_{sp} values of Sreit *et al.*[12] and the fit of the ICP-OES results with the simulated total soluble Calcium concentration after estimation of $K_{sp,0}$ and ΔH_r using the Van 't Hoff equation. These values are used in Figure 4 in manuscript.

6. Characterization of Suspended Crystals via Raman and XRD

To check the polymorph purity, we performed Raman and PXRD measurements of our samples before and after the solubility measurements.

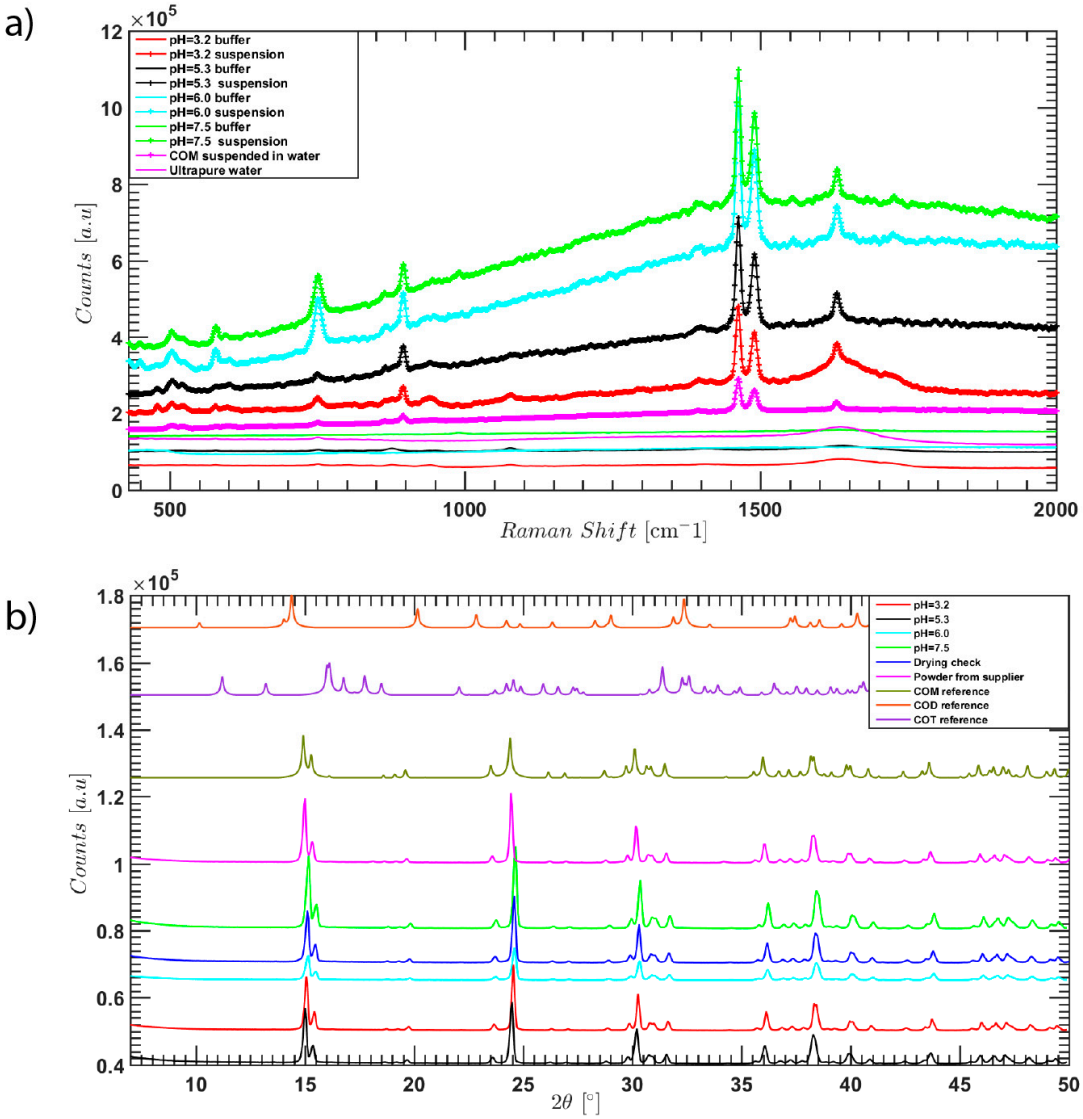

Figure 2. Characterization of suspended crystals in a citric acid-disodium phosphate buffer for pH values of 3.2, 5.36, 6.0, and 7.55. **a**) The results of Raman measurements include just buffer (-), just water (-) or the suspension (+) of COM in buffer. pH = 3.2; red, pH = 5.3; black, pH = 6.0; cyan pH =7.55; green, ultrapure water; magenta (-), the suspension of COM in water; magenta (+). **b**) The results of XRD measurements. pH = 3.2; red, pH = 5.3; black, pH = 6.0; cyan, pH = 7.55; green, mixture of COM in water; blue, COM reference; dark green, COD; orange and COT; purple.

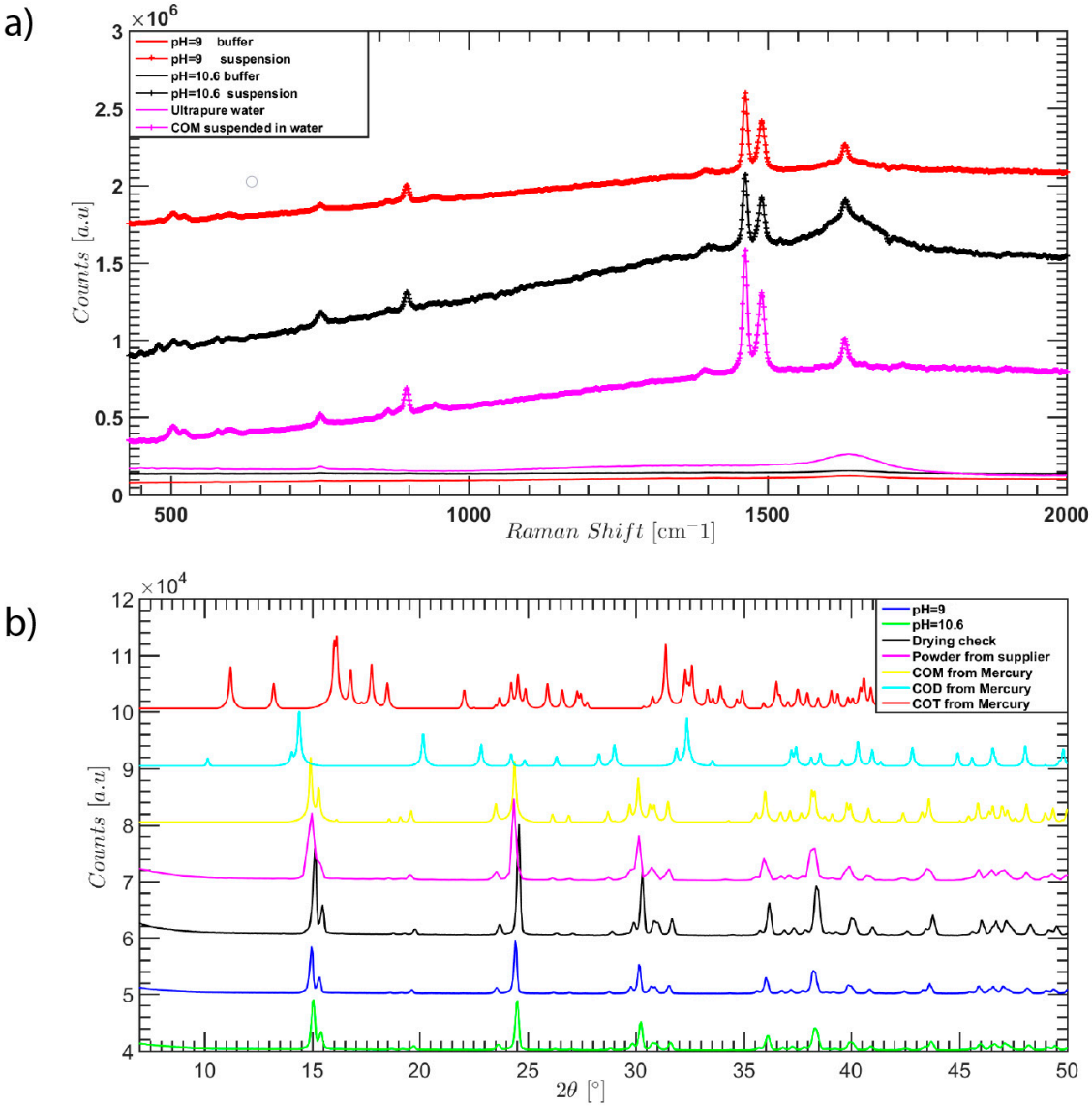

Figure S3. Characterization of suspended crystals in a Sodium hydroxide (NaOH) and for pH values of 9.0 and 10.6 **a**) The results of Raman measurements include just buffer (-), just water (-) or the suspension (+) of COM in buffer. pH=9.0; red, Ph =10,6; black, ultrapure water; magenta (-), the suspension of COM in water; magenta (+). **b**) The results of XRD measurements. ph = 9.0; blue, pH=10.6; green, mixture of COM in water; black, COM from supplier; magenta, COM reference; yellow, COD; cyan and COT; red.

Figure 2.a and 3.a show that the characteristic COM Raman bands were obtained at 504, 508 (O–C–O), 897 (C–C), 1463, 1490 (C–O), and 1629 (C–O) cm^{-1} [14–16]. The peak values show that crystals stayed always as COM in different conditions. pH experimental conditions did not lead transition from COM to another CaOx hydrate form. Figure 2.b and 3.b verify that tuning pH values did not cause phase transformation from COM to Calcium Oxalate Dihyrate (COD) or Calcium Oxalate Trihyrate (COT) [13]. Crystal structure of COM (CALOXM03), COD (CAOXAL) and COT (ZZZUOQ01) data were taken from the Mercury database. COM crystals from Mercury are showing as high peak intensity as at the same plane positions at different pH values.

7. Characterization of Suspended Crystals via Microscope and Scanning Electron Microscopy

The crystals placed on the glass cover slip were visualized with an optical microscope (Nikon TE) and a scanning electron microscope (SEM) for different temperatures and pH values.

Microscope Images

50 µl COM suspension were taken from Easymax reactor and put in two thin microscope slides for characterization. Unfortunately we could not identify different hydrate forms with optical and scanning electron microscopy measurements.

Microscope Images at Different Temperatures

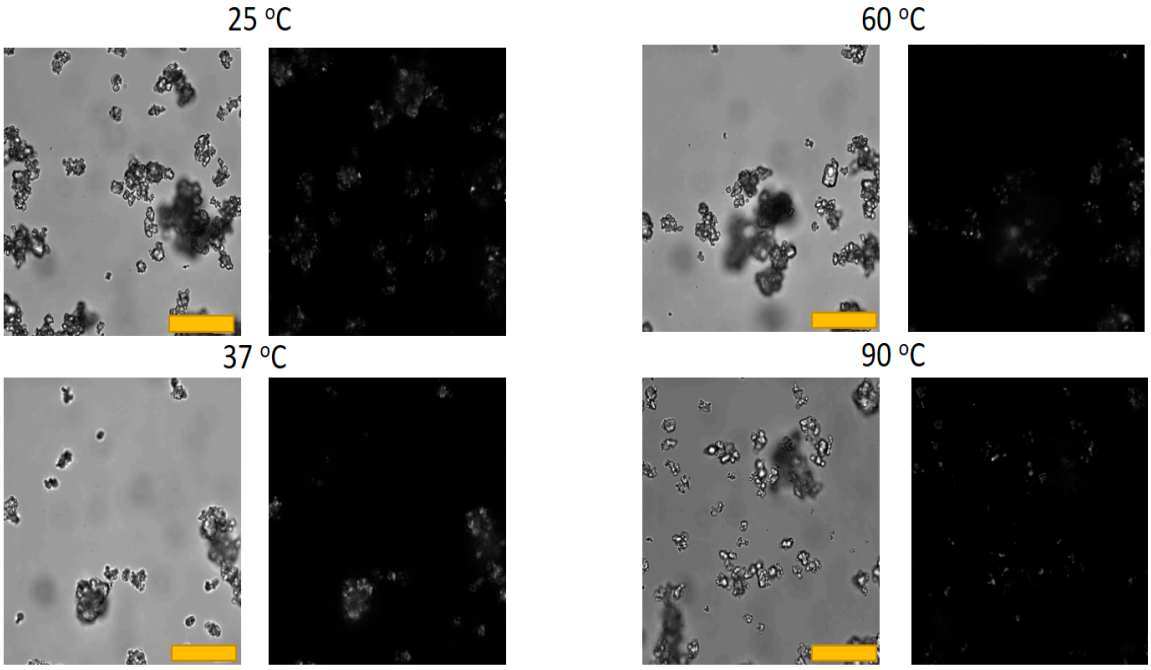

Figure 4. Characterization of CaOx forms via optical microscope at different temperatures. Left hand side images were taken in bright field mode (all the scalebars are 30µm), right ones were taken with crossed-polarised light at the same positions.

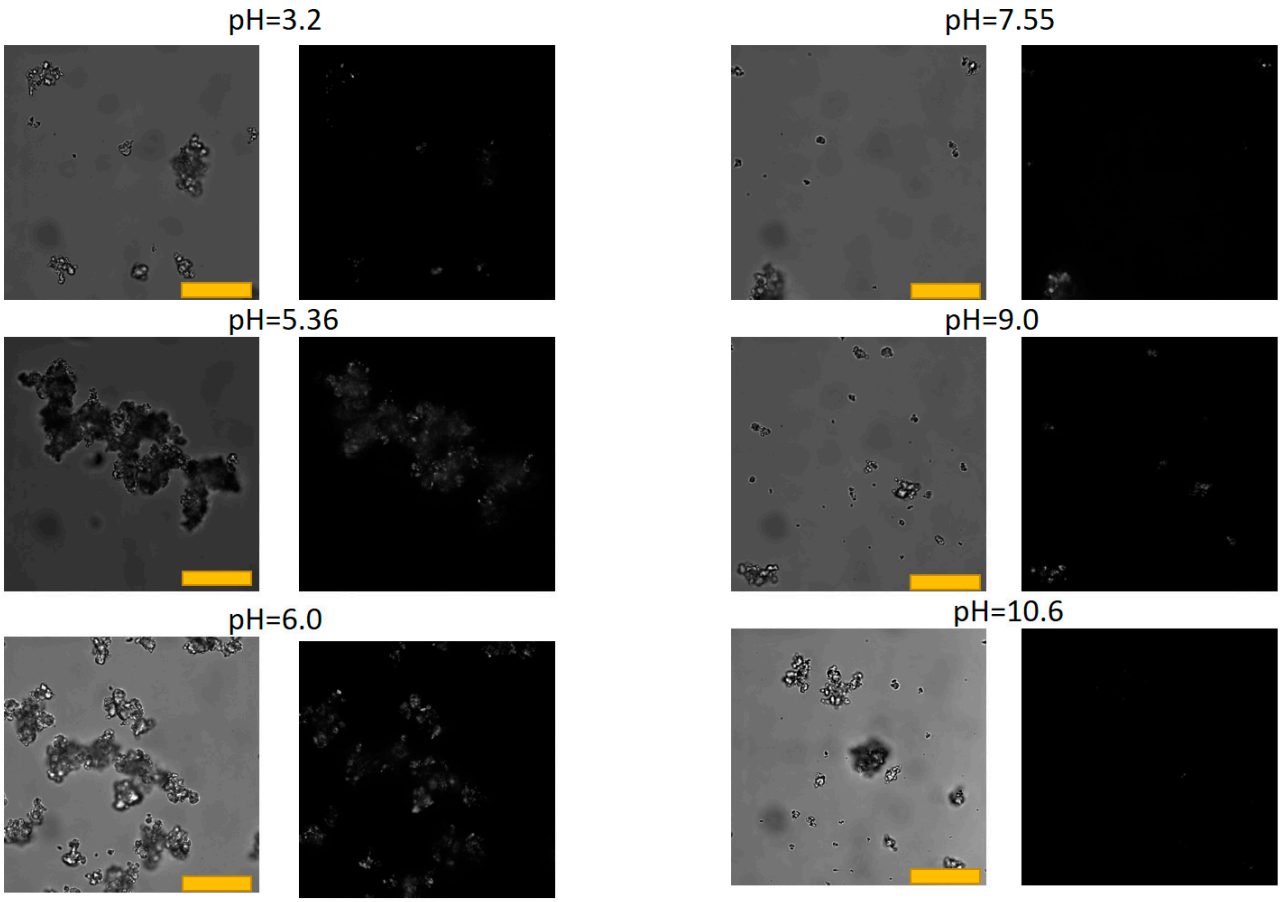

Figure 5. Characterization of CaOx forms via optical microscopy at different pH values. Left images were taken via at brightfield mode (all the scalebars are 30μm), right ones were taken with crossed-polarised light at the same positions.

Scanning Electron Microscopy (SEM)

SEM Images were taken for different temperatures, pH and without treatments of COM crystals

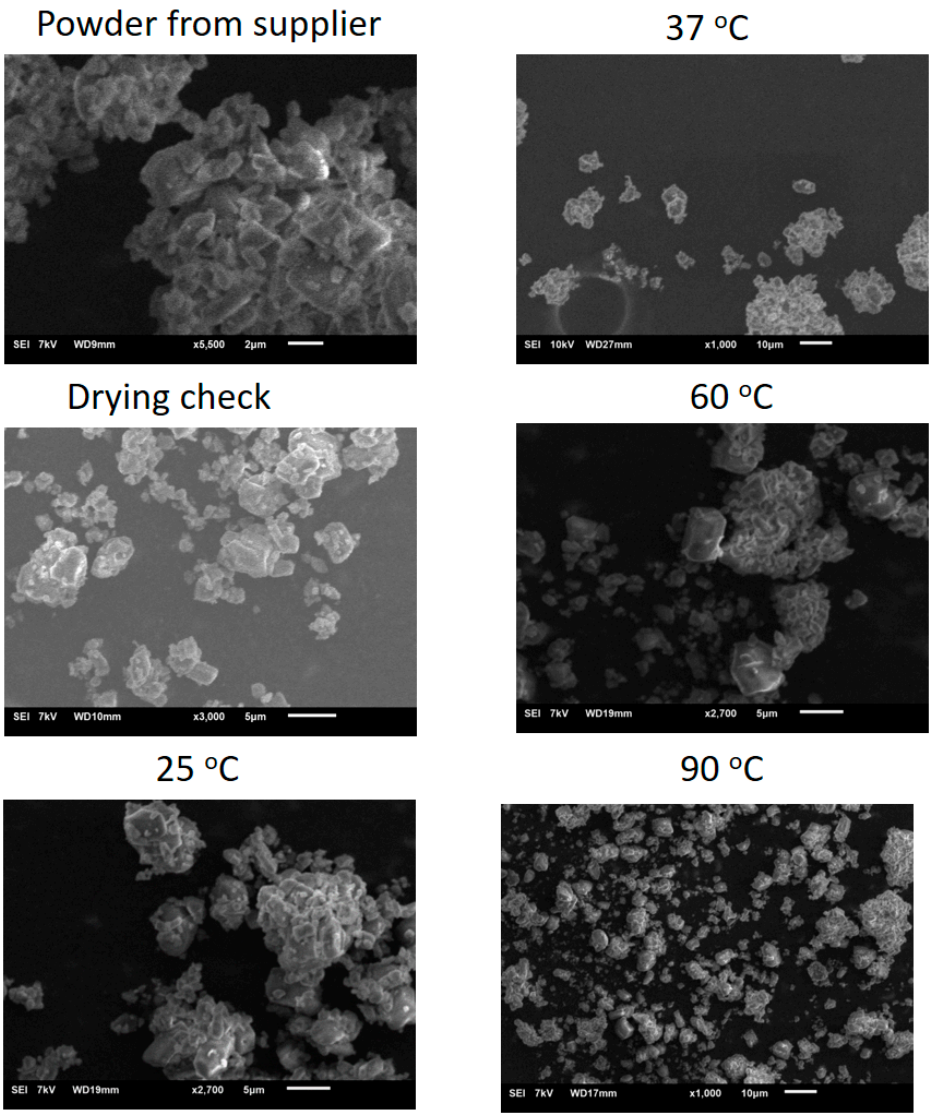

Figure 6. Characterization of CaOx forms via SEM images at different temperatures.

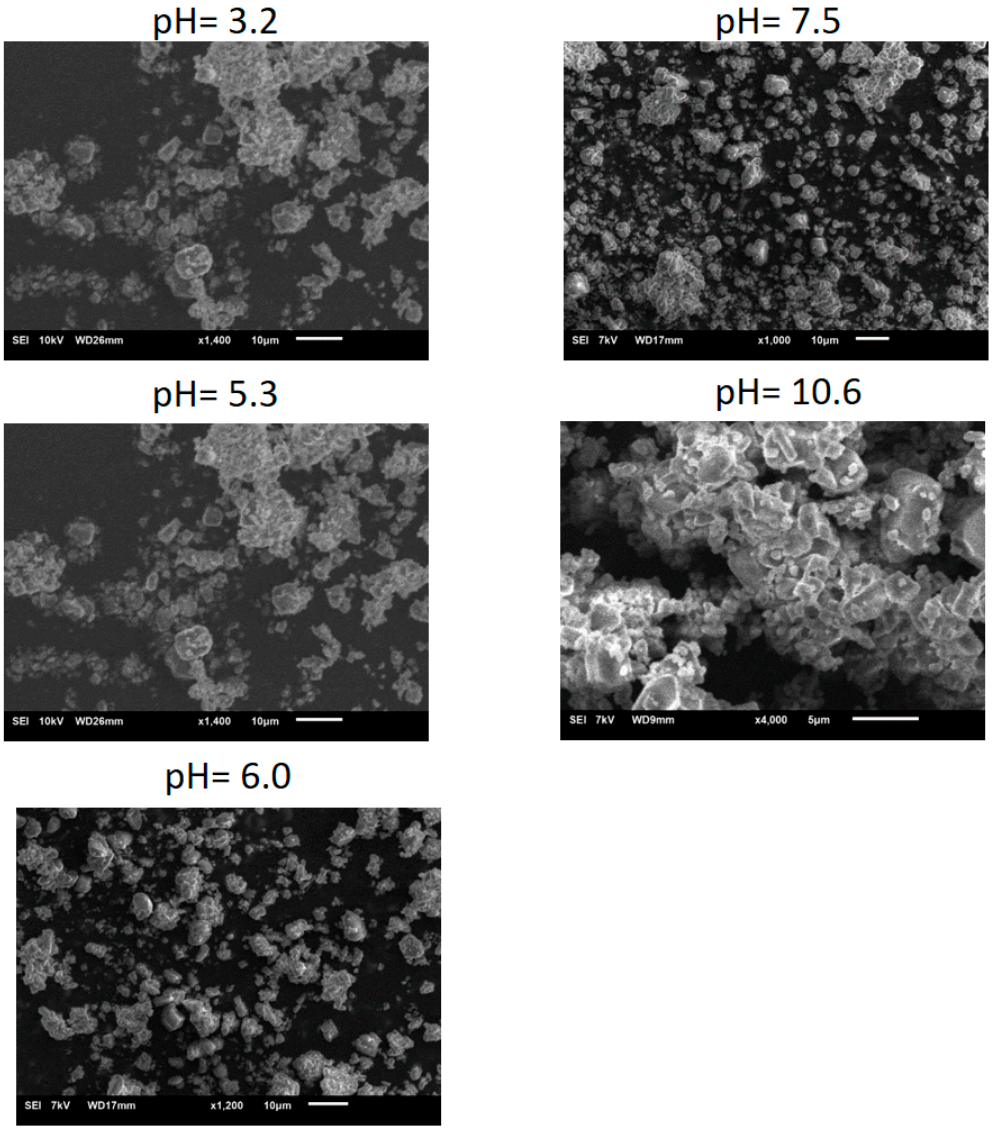

Figure 7. Characterization of CaOx forms via SEM images at different pH values.

Based on the shape of the crystals we can guess of the crystal phases as COM, COD, and COT. The shape of our crystals was compared to literature to determine the crystal phase. Some crystals appear to be COM [15,16]. But we could not draw conclusions on most crystals hence we can not rule out existance of other hydrates COD and COT.

8. Calibration for ICP-OES

ICP-OES is using an external calibration. A multi-element standard (Merck chemicals), containing 1000 [ppm] Ca was used. From this solution, the dilutions to the proper range of calibration is done . Dilutions in 3 [m%] HNO3. Calcium is calibrated for different wavelengths, 315.887[nm], 317.933[nm], 393.366[nm], and 396.847 [nm]. The certain amount of Calcium Chloride, Sodium Oxalate, and COM are dissolved in ultrapure water to check calibration of ICP-OES. The solutions were dissolved in Easymax during 1 hour at 400 rpm using the same solution preparation methods. Besides that, water and diluted calcium solution were used. All samples were measured via ICP-OES at 317.9 nm. The results at chosen wavelenght are presented in Table S15. Each values represent the average of three replications.

Table S15. Different types of samples were measured via ICP-OES at 317.9 nm.

Solutions	Average [Ca] 10^{-4} M	std. dev
0.2 × 10^{-4} M COM	0,206	0,005
1*10^{-4} M COM	0,998	0,041
1.5*10^{-4} M COM	1,495	0,078
15*10^{-4} M Calcium Solution	14,729	0,281
10. 10^{-4} M Calcium Solution	9,973	0,111
5*10^{-4} M Calcium Solution	4,941	0,072
1.5*10^{-4} M Calcium Solution	1,501	0,009
0.5*10^{-4} M Calcium Solution	0,503	0,0118
0.2*10^{-4} M Calcium Solution	0,198	0,005
0.2*10^{-4} M $CaCl_2$	0,199	0,045
1*10^{-4} M $CaCl_2$	1,055	0,034
1.5*10^{-4} M $CaCl_2$	1,519	0,012
Ultrapure water	0,006	0,000
0.2*10^{-4} M NaOx	0,000	0,000
1.5*10^{-4} M NaOx	0,001	0,001
1*10^{-4} M NaOx	0,005	0,001

Known initial Calcium concentrations are in agreement with ICP-OES results. We can conclude that calcium measurement at 317.9 nm by using ICP-OES were fully calibrated successfully.

References

1. Available from: http://microscopy.berkeley.edu/Resources/instruction/buffers.html. (accessed on 15 June 2019).
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