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Supporting Information

Modulation of $CaCO_3$ Phase and Morphology by Tuning the Sequence of Addition: An Insight into the Formation of Monohydrocalcite

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Materials and Instruments: All the materials for synthesis and experiments were purchased from Sigma-Aldrich and used without further purification.

The FT-IR spectra of the dried compounds were recorded on a PerkinElmer-Spectrum One FT-IR spectrometer with KBr pellets in the range 1800−400 cm^{-1}. The Powder XRD and the quantitative analysis results of the samples were obtained from the Rigaku Smartlab X-ray Spectrophotometer with Cu-Kα (λ=1.54 Å), source running at a power of 9 KW. The particle sizes and zeta potential were measured by dynamic light scattering (DLS) experiments at pH 7 and temperature 20 ^{o}C on Anton Paar Litesizer 500 instrument. The morphology of the particles was investigated by using FESEM imaging studies using Sigma 300 FESEM (Carl Zeiss). The EDX elemental analysis and mapping were performed in Sigma (Zeiss). The TGA analysis was performed in Netzsch, STA449F3A00.

Methods

Preparation of Tulsi extract in methanol and water

Fresh leaves were collected in their blooming stage from several spots at IIT Guwahati campus. The leaves were thoroughly washed with water so as to remove the external impurities and dried at room temperature for 48 hours. The dried leaves were then powdered, and in each extraction process, 2 grams of the dried powder was subjected to reflux in 50 ml of methanol and water, respectively. The extracts were then collected by filtering through regular filter paper.

Preparation of Green tea extract in methanol and water

Green tea in its purest form and of the finest quality was obtained from the local tea gardens of Assam. The powdered leaves, 3 grams, were subjected to reflux as such in 50 ml of methanol and water, respectively, followed by filtration through regular filter paper to obtain the pure extracts.

Reusability of tulsi extract in methanol and the effectiveness of the mixture of tulsi and green tea extracts in methanol

In the reusability experiment, the crystallization process using tulsi extract in methanol was studied to observe whether the template retains its effectiveness even after several cycles. In this experiment, the filtrate that was obtained on filtering the suspension after the crystallization process was used to perform the templating role for the next cycle, all other steps in the procedure were kept the same. A total of three cycles were performed to study the effects of reusing the extract. In another experiment, both the tulsi and the green tea extracts in methanol were mixed in a ratio of 1:1 (2.5 ml each). They used as a template in the crystallization process to observe their role in a mixture.

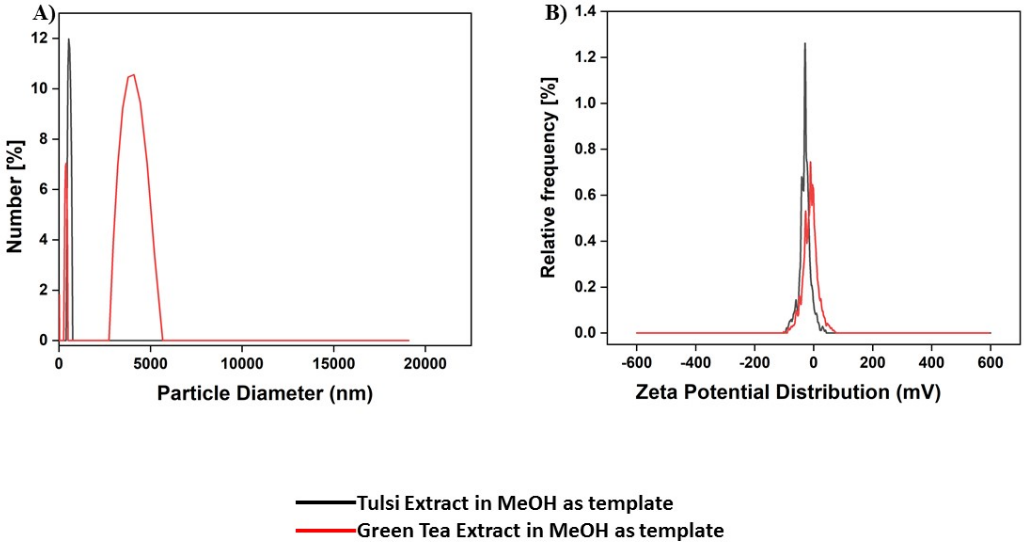


Figure S1: A) DLS-based particle size analysis; B) Zeta Potential of $CaCO_3$ particles synthesized in the presence of the tulsi and green tea extract in methanol.

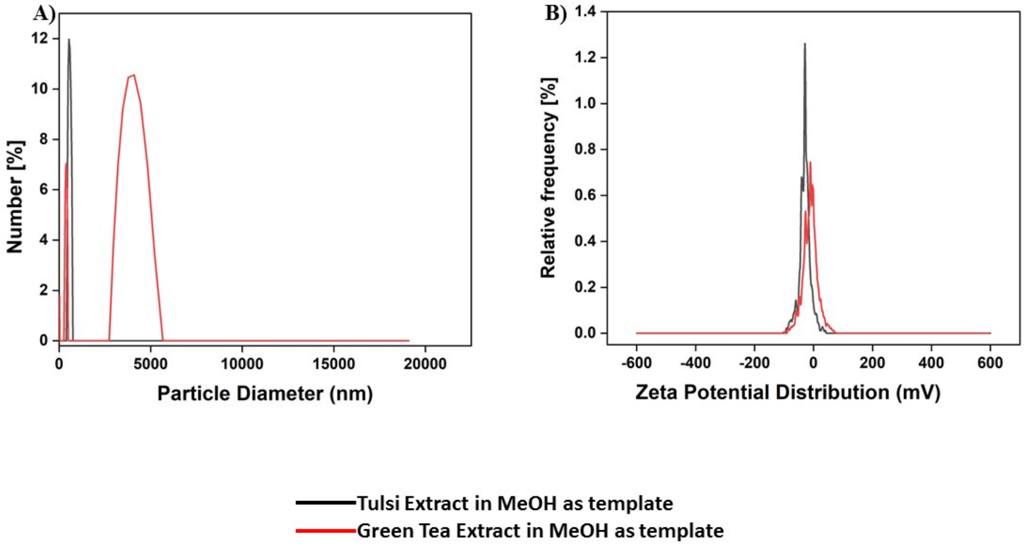


Figure S2: A) DLS-based particle size analysis; B) Zeta Potential of $CaCO_3$ particles synthesized in the presence of the tulsi and green tea extract in water.

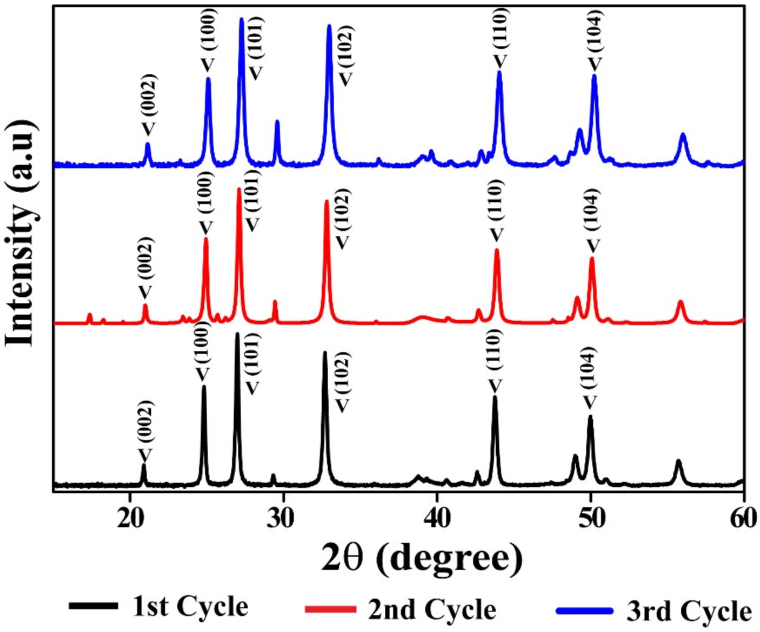


Figure S3: PXRD pattern showing the formation of vaterite after using the tulsi extract (in methanol) for three consecutive cycles.

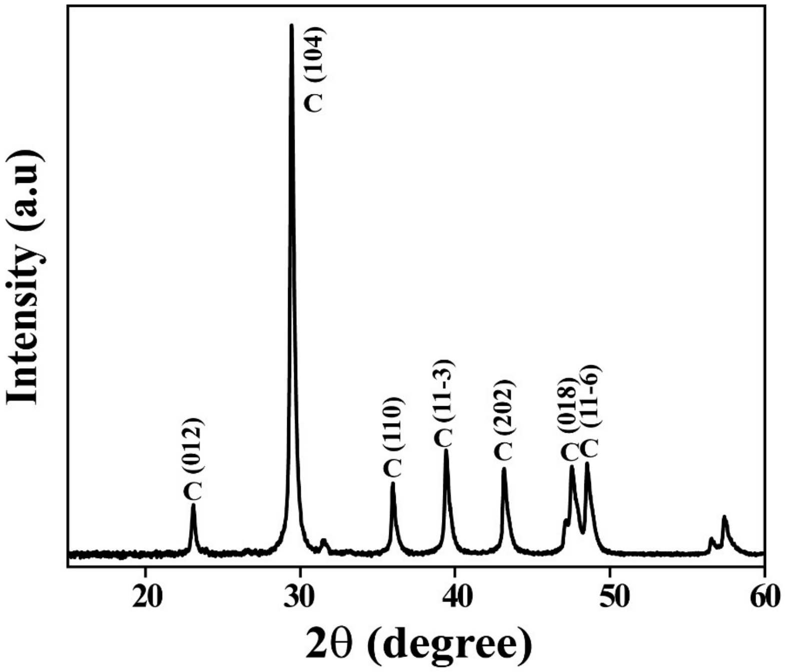


Figure S4: PXRD pattern showing the formation of calcite on using both the templates (tulsi and green tea in methanol) in the ratio 1:1.

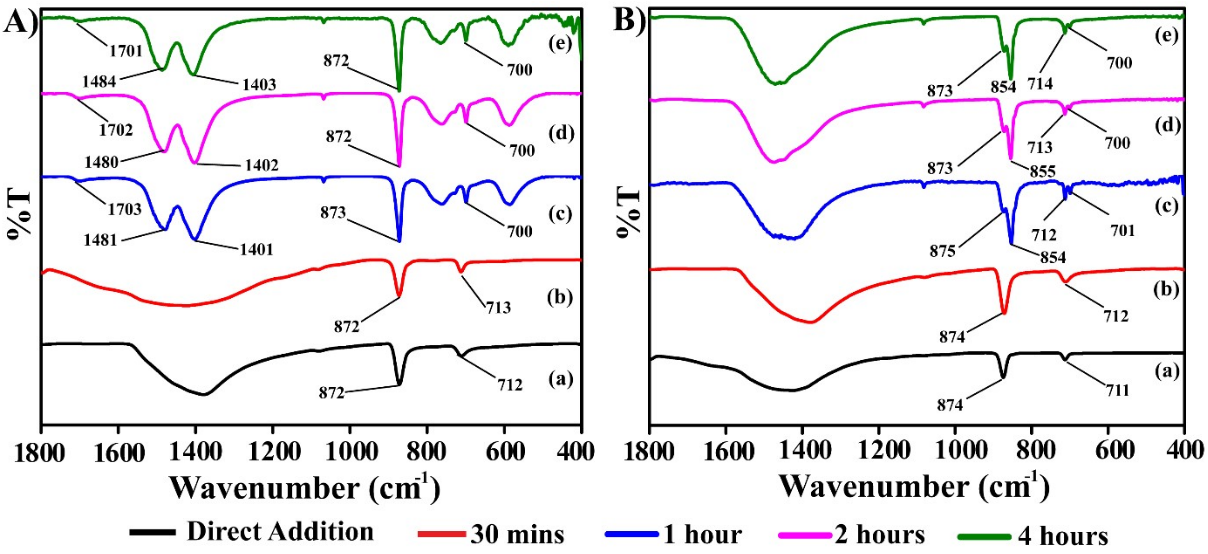


Figure S5: FT-IR spectra of $CaCO_3$ particles precipitated by reverse sequence of addition at different addition rates in presence of tulsi extract in methanol followed by (A) Maturation of the particles in solution at room temperature; (B) Heating the particles in solution at 80 ^{o}C.

Stability of ACC in solution and in the isolated state

The stability of the ACC particles in solution was studied by obtaining the FT-IR spectrum, Fig. S7 of the particles by isolating them every hour by vacuum filtration. On isolation immediately after the precipitation, it was observed that a split signal at 1475 cm^{-1} and 1415 cm^{-1} and a signal at 864 cm^{-1}, which are characteristics of the ACC phase were present. The particles isolated after hour 1 and 2 also showed similar patterns with split signals at 1481 cm^{-1} and 1418 cm^{-1} and at 1473 cm^{-1} and 1420 cm^{-1}, respectively, and the signal at 864 cm^{-1} being common in both the cases. These being the characteristics of the ACC phase, suggested the stabilization of the unstable phase in aqueous solution at least for 2 hours. The particles isolated after 3 hours showed characteristic of the calcite phase with signals at 1440 cm^{-1}, 872 cm^{-1} and 713 cm^{-1}, suggesting the conversion of the amorphous precursor to the stable crystalline phase.

However, the isolated particles showed great stability even when stored under ambient conditions. The particles were subjected to PXRD analysis, after days 1, 4 and 7, where in each case a similar pattern with no sharp peaks but a pattern with a broad hump at 2θ equal to 32, Fig. S8(A) characteristic of the amorphous phase suggested the stability of the ACC phase. The FESEM images, Fig.S8(B), S8(C) and S8(D), of the particles were also obtained and it could be seen that the particles remained as stable nanospheres with no change in morphology even after 7 days.

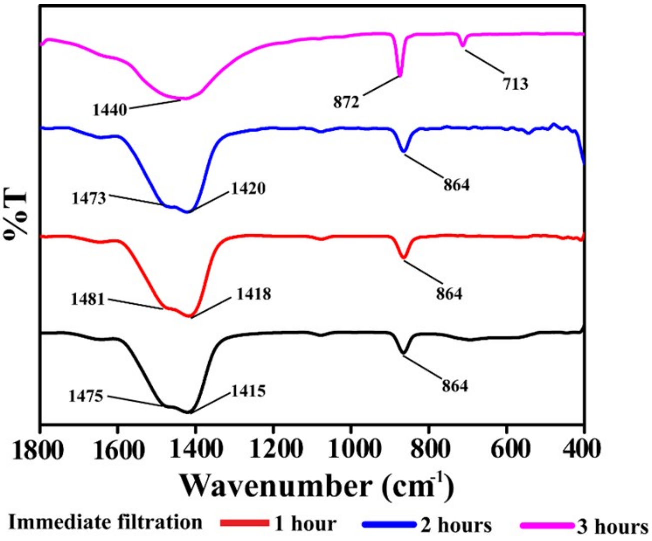


Figure S6: FT-IR spectra of the ACC particles isolated at 1 hour interval of time.

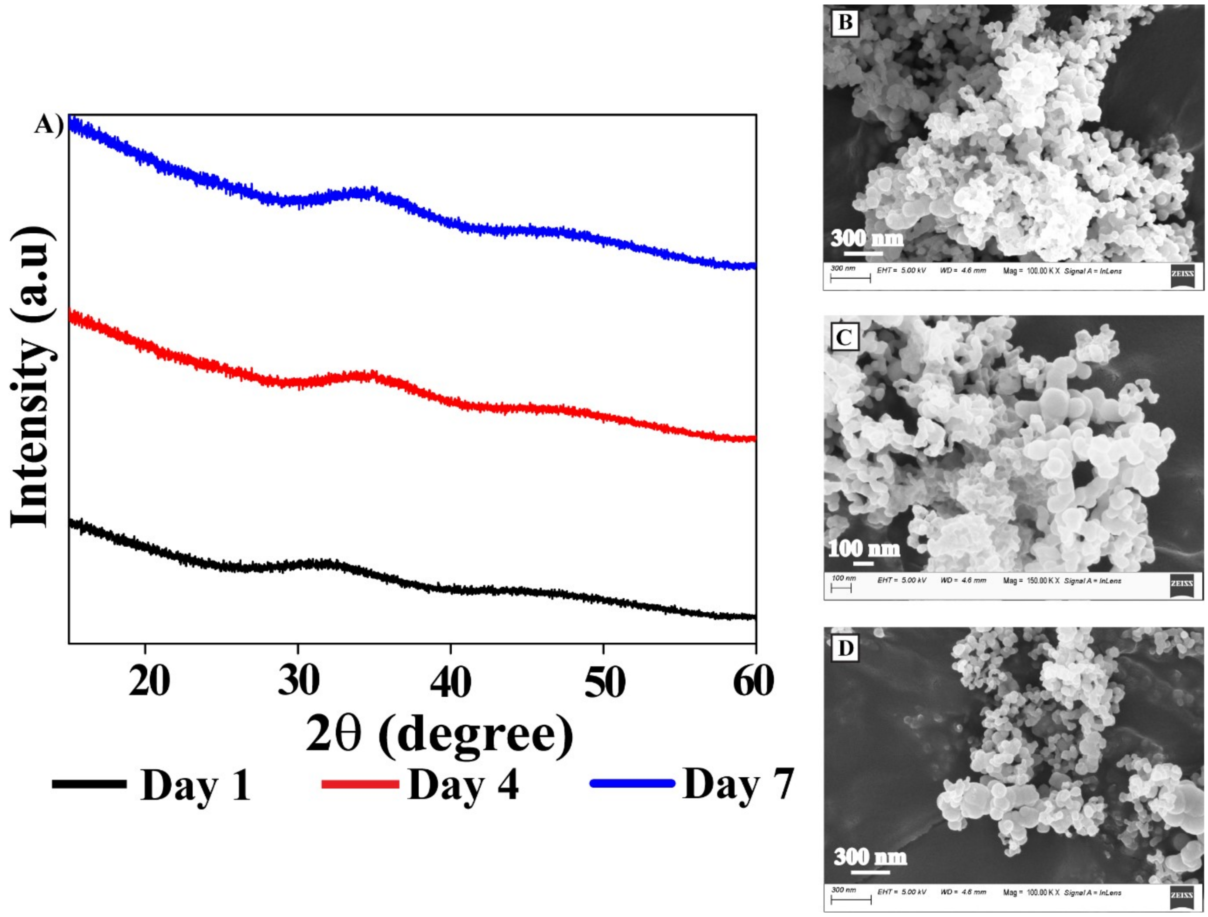


Figure S7: (A) PXRD pattern of the ACC particles synthesized by the reverse sequence of addition in the presence of the tulsi extract in methanol after day 1, 4 and 7; FESEM image of the ACC particles after (B) Day 1; (C) Day 4; (D) Day 7.

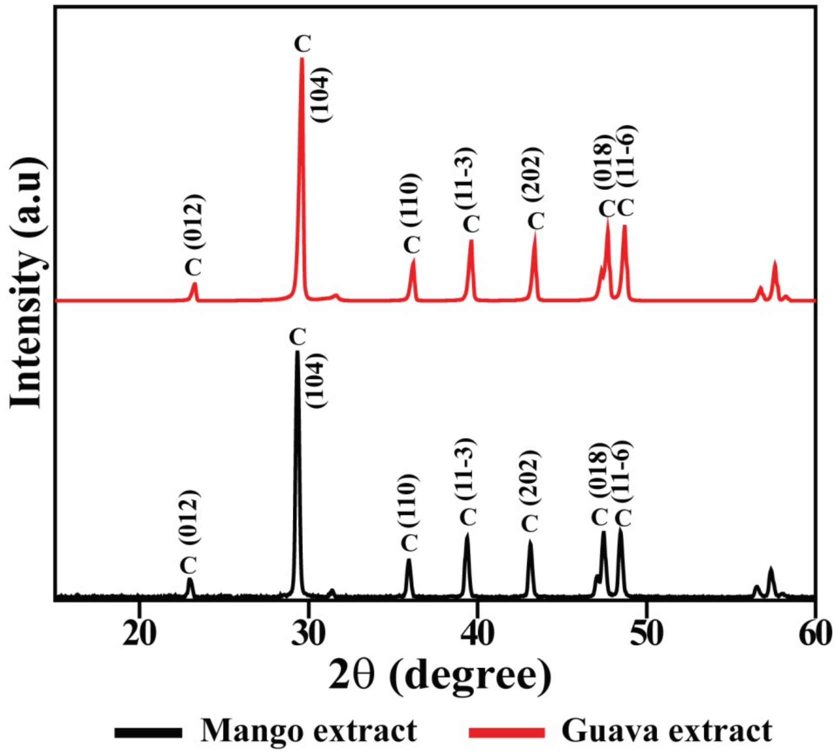


Figure S8: PXRD pattern of $CaCO_3$ particles precipitated in the presence of mango and guava extracts in methanol.

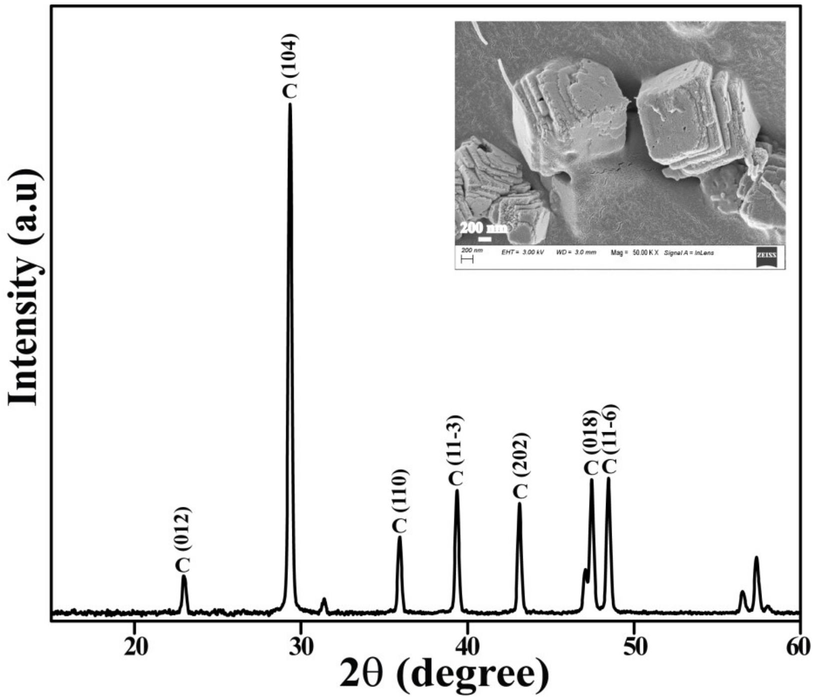
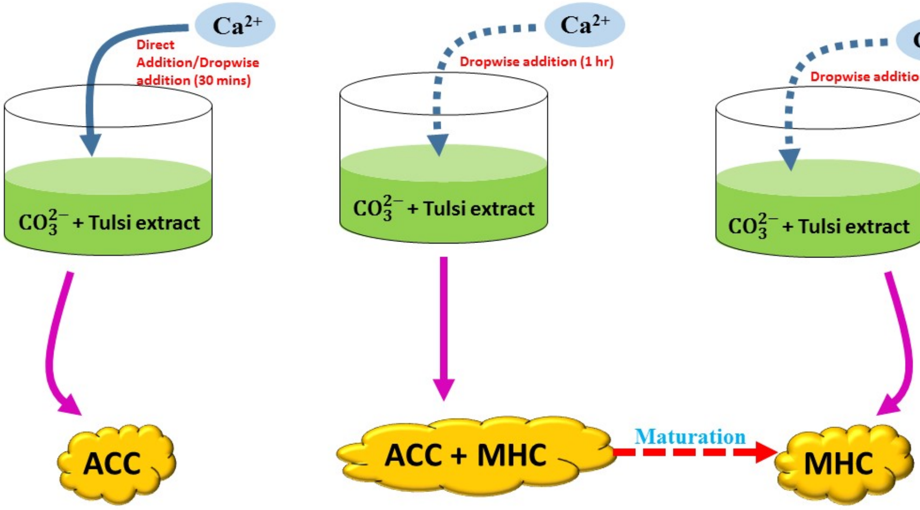


Figure S9: PXRD pattern and FESEM image of $CaCO_3$ particles precipitated by the reverse sequence of addition in the presence of the green tea extract in methanol.



Scheme S1: Illustration of the reverse sequence of addition in the presence of tulsi extract (in methanol) to obtain the MHC phase via the amorphous precursor.

Table S1: Phytochemical constituents of Tulsi and Green Tea

Tulsi (Ocimum sanctum)	***Green Tea (Camellia sinensis)***
Proteins	Proteins
Amino acids	Amino acids
Carbohydrates	Carbohydrates
Phenolic compounds	Phenolic compounds
Flavonoids	Flavonoids (Catechin)
Glycosides	Alkaloids (Caffeine)
Tannins	Fibers
Steroids	Vitamins
Sterols	Sterols
Terpenoids	Minerals and Trace elements
Minerals and Trace elements	
Organic acids	
Essential oils and Fatty acids	

Table S2: Phytochemical constituents in Methanol and Aqueous extracts of Tulsi

Phytochemicals	***Methanol extract***	***Aqueous extract***
Proteins	-	-
Carbohydrates	+	-
Phenols	+	+
Flavonoids	+	+
Tannins	+	-
Glycosides	+	+
Steroids	-	-
Terpenoids	+	-
Essential oils and Fatty acids	+	-

Table S3: Percentage concentration of the major phytochemical constituents in Methanol extract of Tulsi

Phytochemicals	***Concentration***
Proteins	~21%
Carbohydrates	~40%
Phenols (mg/g)	~2 mg/g
Flavonoids (mg/g)	~29 mg/g
Glycosides	~3.50%
Essential oils and Fatty acids	~3.60%

Table S4: Acids and Essential oils and Fatty acids present in the methanol extract of Tulsi

Acids	***Essential oils and Fatty acids***
Oleanolic acid	Eugenol
Ursolic acid	Methyl Eugenol
Rosmarinic acid	Carvacrol
Tuberonic acid	Lauric acid
4-Hydroxypelargonic acid	Myristic acid
5-Phenylaleric acid	Palmitic acid
Usnic acid	Palmitoleic acid
Pteroyl-D-glutamic acid	Stearic acid
Undecylic acid	Oleic acid
3-Phenoxypropionic acid	Linoleic acid
5-Phenylvaleric acid	Linolenic acid
6-Methyl caprylic acid	

Table S5: Phase obtained on performing the reverse sequence of addition with varying time of dropwise addition

Time taken for addition	***Initial phase obtained***	***On maturation (3 hours)***	***On heating (at 80 ^{o}C)***
Direct addition	ACC	Calcite	Calcite
30 mins	ACC	Calcite	Calcite
1 hour	MHC + ACC	MHC	MHC + Calcite
2 hours	MHC	MHC	MHC + Calcite
4 hours	MHC	MHC	MHC + Calcite