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Effect of the Experimental Parameters on Calcium Carbonate Precipitation

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In this study, calcium carbonate crystals were obtained by mixing of calcium chloride and sodium carbonate in the presence of biopolymer, carboxymethyl inulin (CMI). The effect of the feed rate of reactant and the initial [Ca^{+2}] concentration was investigated. The produced calcium carbonate ($CaCO_3$) crystals were characterized by scanning electron microscopy (SEM), Fourier transform infrared spectrometer (FT-IR) and X-ray diffraction (XRD). In the presence of additive (0.5 g/L), the polymorph of the obtained calcium carbonate crystals changed from pure calcite to the mixture of vaterite and calcite. With adding of biopolymer, the crystal structure of calcite changed from cubic to dumbbell shape.

1. Introduction

Calcium carbonate is known as the cheapest commercially available inorganic mineral (Wang et al. 2007). It is used in many industrial applications, such as paper, paint, cosmetic, rubber, pigment (Xiang et al. 2004). In nature, calcium carbonate has different crystal polymorphs such as calcite, aragonite and vaterite (Berger et al. 2009)., . The three polymorphs have different characteristic properties. Vaterite and aragonite are thermodynamically unstable and can be stabilized kinetically or biochemically (Spanos and Koutsoukos 1998). The metastable vaterite transforms easily to stable calcite when it is kept in its solution for several hours (- Nancollas et al. 1981). Although vaterite is rare in nature as natural mineral, it can nucleate and growth in biologic system. It was found that vaterites crystal lattice can be stabilized In the presence of amino acids (Shen et al. 2007). Calcite polymorph having different crystal structures is the most important phase in industrial applications due to its thermodynamic stability. While scalenohedral calcite is applied in the paint and paper industry, ultrafine rhombohedral calcite is used in the plastic and sealant industry. The properties of calcium carbonate crystals such as morphology, phase, size and size distribution should be modified according to the application areas such as paper, food processing and sensor applications (-, Gorna et al. 2008). The morphological forms and phases of calcium carbonate are related with the synthesis conditions, such as the concentration of reactants, temperature, aging time and nature of additives (Sangwal 2007). Synthesis of precipitated calcium carbonate (PCC) with specific polymorphs can be provided in the presence of additive at room temperature. The process parameters could be effective on the morphology of calcium carbonate phases (Kirboga and Oner 2012). The presence of additives especially polyelectrolytes may influence the polymorph selection, growth mechanism, nucleation, shape and size of the crystal (Oner and Calvert 1994).

In the present work, the effect of carboxymethylinulin (CMI) on the precipitation of calcium carbonate was investigated. The biodegradability and non-toxicity of CMI allows a wide application possibility in industries (Kirboga and Oner 2012). In this work, calcium carbonate crystals were synthesised by mixing of calcium chloride and sodium carbonate with using a peristaltic pump. Produced crystals were characterized by XRD, FT-IR and SEM analysis.

2. Materials and Methods

Calcium chloride ($CaCl_2$) and sodium carbonate (Na_2CO_3) were from Merck. Sodium hydroxide (NaOH) was purchased from J.T. Baker. CMI-20 was from thermPhos, Switzerland as Dequest DPB-116AB (where

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AB = 20 for CMI-20). The number AB indicates the degree of substitution (DS). DS is defined as the average number of carboxylate moieties per fructose unit (for CMI-20, DS = 2.0).

The common method to produce calcium carbonate in a laboratory experiment is mixing aqueous solutions of two soluble salts such as Na_2CO_3 and $CaCl_2$. Peristaltic pumps (MasterFlex L/S) were used to add the reactant to the solution. The experiments were conducted in a 0.5 dm^3 water-jacketed reactor providing a constant-temperature at 25 ± 0.1 ºC. The stock solutions of calcium chloride and sodium carbonate were prepared as 20, 60 and 100 mmol/L with calcium/carbonate molar ratio of 1. Calcium carbonate was always precipitated by mixing equal volumes of $CaCl_2$ and Na_2CO_3 solutions. Reaction solution was prepared by adding calcium solution to the reactor first. The biopolymer was added to the Na_2CO_3 solution. To study the effect of addition rate of carbonate stock solution, the feeding rate was ranged 1, 3 and 5 mL/min. At the end of each crystallization experiment, the product suspension was filtered through a 0.2 µm cellulose nitrate membrane filter, washed with small portions of water, dried at 100 ºC for 24 h.

3. Results and Discussions

Samples were coded to include the information about the synthesis conditions. The first number in the code of samples indicates initial $[Ca^{+2}]$ concentration (mmol/L). The second number coming after short line shows the biopolymer concentration (g/L), the last number coming after shows the feeding rate of Na_2CO_3 (mL/min). While S20-0/1 denotes sample is synthesized at 20 mmol/L initial $[Ca^{+2}]$ concentration in the absence of biopolymer with 1 mL/min of Na_2CO_3 feeding rate, S20-0.5/1 denotes sample is synthesized at 20 mmol/L initial $[Ca^{+2}]$ concentration in the presence of 0.5 g/L biopolymer with 1 mL/min of Na_2CO_3 feeding rate.

In order to eliminate the possible existence of amorphous and metastable phases of $CaCO_3$, reaction solution was incubated 24 h. X-ray diffraction, FTIR and SEM were used in order to characterize $CaCO_3$ crystals. The amount of the polymorphs was calculated from XRD results. X-ray diffraction analysis of the samples was carried out by means of Panalytical X'pert Pro PW 3040/60 powder diffractometer operating with Cu Kα radiation in operating at 40mA and 45 kV. The 2θ range was from 5° to 90° at scan rate of 0.026° $step^{-1}$. The samples were analyzed using FT-IR spectral analysis (Bruker Alpha-P) in the 4000 – $400cm^{-1}$ region at a resolution of $4cm^{-1}$.

Obtained calcium carbonate crystals were analysed by FT-IR spectral analysis (Figure 1). The bands at ~1420, ~874 and ~712 cm^{-1} could be attributed to vibrations of calcite (Chen and Xiang 2009). These characteristic peaks of calcite were obtained in the all samples (Figure 1). The peaks at ~1070 and ~745 cm^{-1} which are the characteristic peaks of vaterite (Wang et al. 2010) were only observed in the presence of biopolymer. The characteristic peaks of both calcite and vaterite were observed in the presence of biopolymer. It is clear that the mixture of calcite and vaterite was obtained with the addition of biopolymer.

The characterization of calcium carbonate crystals were analysed by the X-ray diffraction. The characteristic peaks of calcite at 2θ of 29.4°, 35.9° and 39.5° (Shen et al. 2007) were obtained both in the presence and absence of biopolymer (Figure 2). The diffraction peaks at 24.92°, 26.99° and 32.78° which are corresponding to vaterite (Tai and Chen 2008) were observed only in the presence of biopolymer. X-ray diffraction confirmed the existence of mixture of calcite and vaterite polymorphs in the presence of CMI-20. The crystal morphology was changed with the addition of biopolymer. The addition of additive is a general method which is used to control the morphology of crystals (Yu et al. 2004, Kirboga and Oner 2010, Oner et al. 1998, Akyol et al. 2006, Oner and Dogan 2005). Vaterite can be thermodynamically stable because the negatively charged biopolymer can be adsorbed onto the positively charged vaterite crystal faces (Tong et al. 2004). The addition of biopolymer can successfully induce the formation of mixing of vaterite-calcite phase instead of calcite. The amount of vaterite in the samples was calculated from XRD data using Rao's equation (Wei et al. 2003):

$$f_V = \frac{I_{V(110)} + I_{V(112)} + I_{V(114)}}{I_{V(110)} + I_{V(112)} + I_{V(114)} + I_{C(104)}} \tag{1}$$

where I_C and I_V are the intensity of calcite and vaterite respectively, three suffixes are Miller indexes of each phase, and f_V is the content of vaterite in the samples. The percent of vaterite in calcium carbonate samples was given in Figure 3. The maximum content was obtained at 20 mmol/L initial $[Ca^{+2}]$ concentration. It is known that calcite is obtained at high supersaturation, so maximum vaterite formed at minimum initial $[Ca^{+2}]$ concentration. In addition, the feed rate of Na_2CO_3 affected the percent of vaterite in the samples. The amount of vaterite at the addition rate of 1 mL/min was higher than that at 5 mL/min at all initial [Ca^{+2}] concentrations. The ratio of vaterite in samples decreased with increasing of addition rate of reactant. The results related with the effect of feed rate of sodium carbonate on the portion of vaterite are agreement with earliest report in literature (Kitamura 2002).

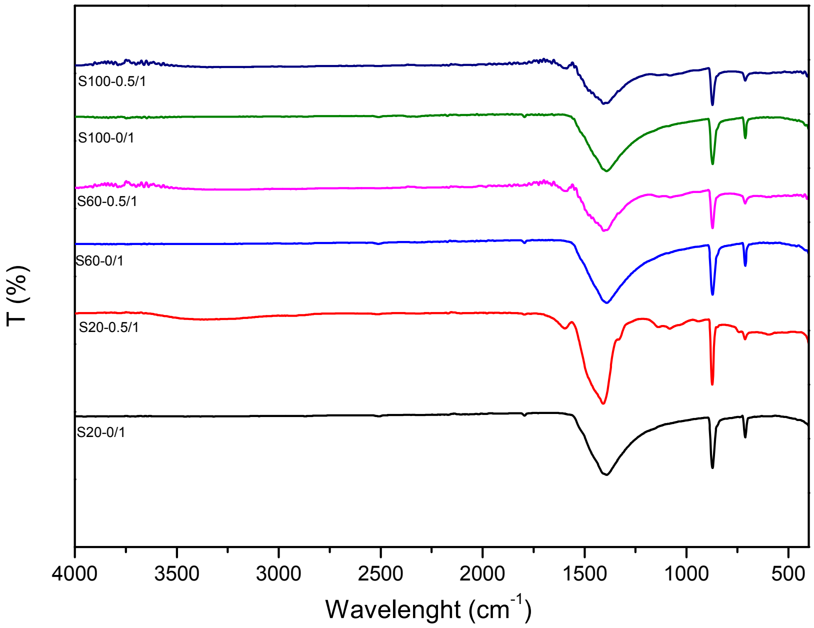

Figure 1: FT-IR spectrum of obtained calcium carbonate crystals at 25 °C

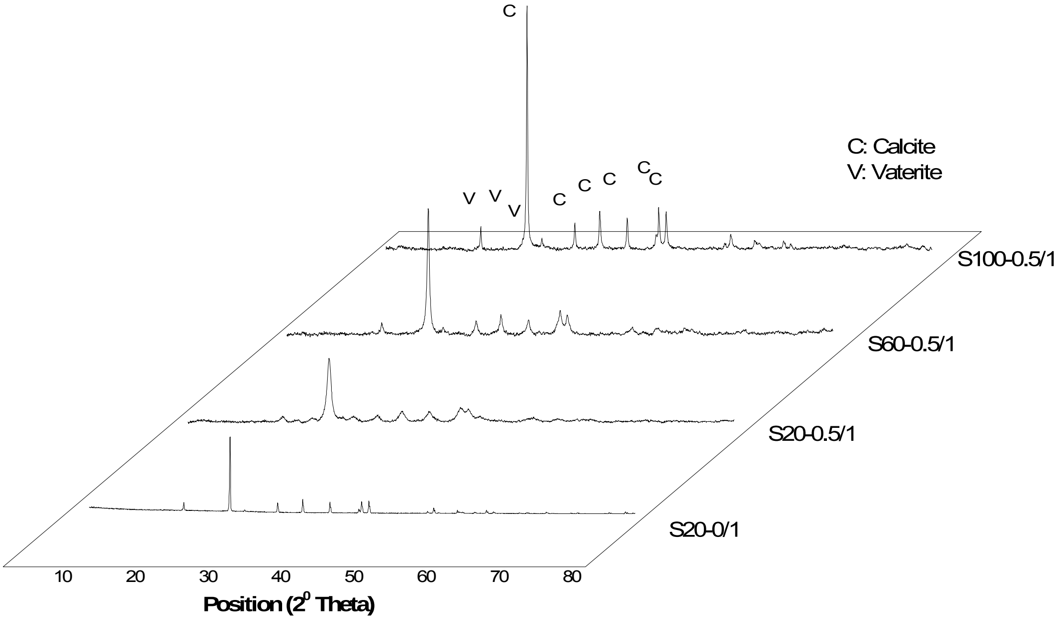

Figure 2: XRD analysis of obtained calcium carbonate crystals at 25 °C

It appeared that initial [Ca^{+2}] concentration and the feed rate of reactant influence on the crystallization behaviours of polymorphs. The fraction of vaterite can be increased in the presence biopolymer at minimum initial [Ca^{+2}] concentrations with minimum flow rate of sodium carbonate.

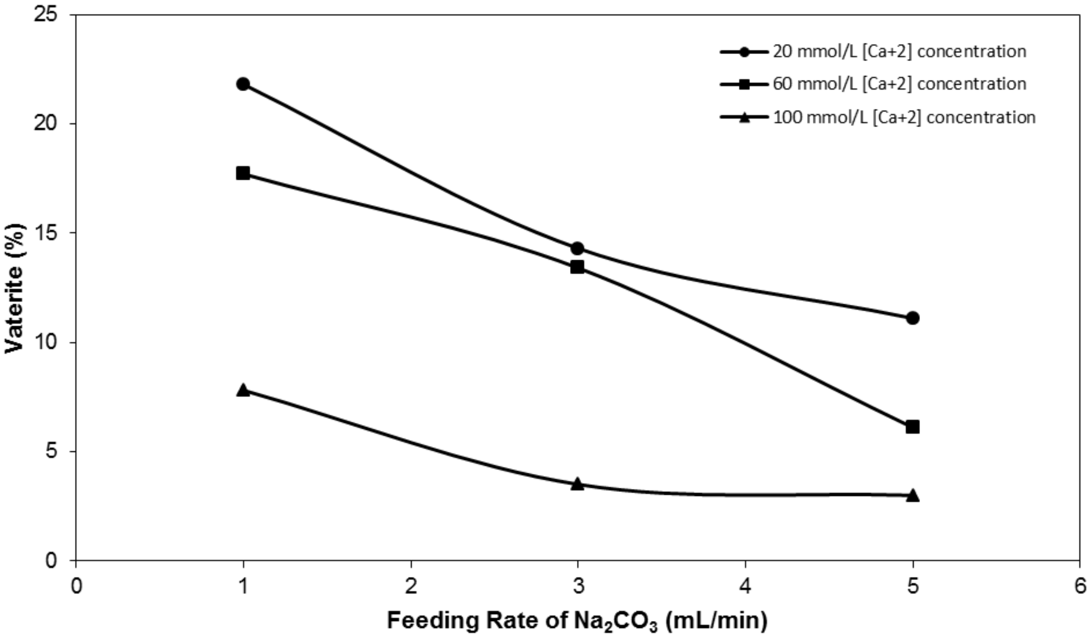

Figure 3: The percent of vaterite in obtained calcium carbonate crystals in the presence of biopolymer

The samples crystallite morphology was analyzed by scanning electron microscopy (JEOL JSM 6335F). The SEM photographs of the calcium carbonate particles were given in Figure 4. In the absence of biopolymer the structure of calcite was rhombohedral (Figure 4a). Rhombohedral calcite changed to dumbbell form with addition of biopolymer. In addition spherical vaterite crystals were obtained in the presence of CMI (Figure 4b-4c). It can be seen that CMI is an effective additive to control the morphology of calcium carbonate. The dumbbell and spherical morphology of calcium carbonate was also obtained by Cölfen and Qi for calcite and vaterite, respectively (Cölfen and Qi 2001).

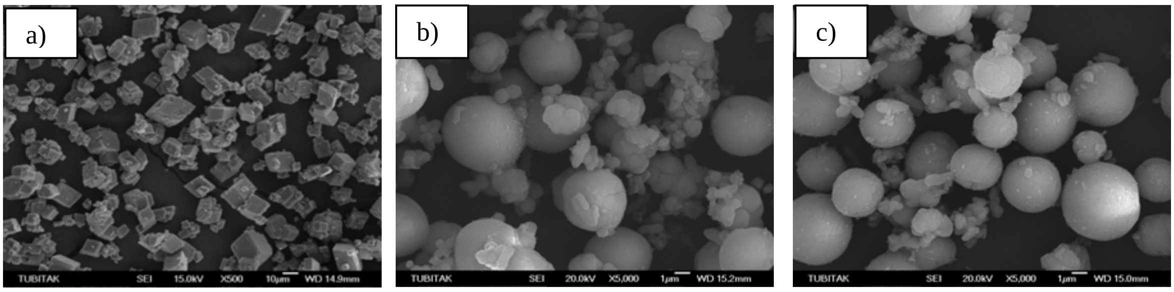

Figure 4: SEM photograph of obtained calcium carbonate crystals at 25 ^{o}C (a) S2-0/1, (b) S60-0.5/1 and (c) S100-0.5/1

4. Conclusion

In the presence of additive (0.5 g/L), the polymorph of the synthesized calcium carbonate crystals changed from pure calcite to the mixture of vaterite and calcite. The maximum vaterite content was obtained at 20 mmol/L initial [Ca^{+2}] concentration. The amount of vaterite was inverse proportional with initial [Ca^{+2}] concentration. In addition, the percent of vaterite in the samples decreased with the feed rate of Na_2CO_3. The amount of vaterite at the addition rate of 1 mL/min was higher than that at 5 mL/min. The results showed that the fraction of vaterite can be increased in the presence of minimum initial [Ca^{+2}] concentration with minimum flow rate of sodium carbonate. Vaterite has become stable with biopolymer.

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