Clinica Chimica Acta 418 (2013) 12–16

Contents lists available at SciVerse ScienceDirect

Clinica Chimica Acta

journal homepage: www.elsevier.com/locate/clinchim

Chemical modulation of crystalline state of calcium oxalate with nickel ions

Khalida Akhtar *, Ikram Ul Haq

National Centre of Excellence in Physical Chemistry, University of Peshawar, Peshawar-25120, Khyber Pakhtoonkhwa, Pakistan

ARTICLE INFO

Article history:
Received 24 September 2012
Received in revised form 21 December 2012
Accepted 21 December 2012
Available online 7 January 2013

Keywords:
Calcium oxalate
Calcium oxide
Fine particles
Chemical precipitation

ABSTRACT

Background: We explored that the presence of nickel ions in the precipitation medium affected size, shape and crystalline phase of the precipitated particles of calcium oxalate, whereas the applied synthesis conditions strongly influenced their uniformity.
Methods: Aqueous solutions of oxalic acid and calcium chloride, containing varying amounts of nickel sulfate, were mixed at room temperature and allowed to sonicate for various periods of time. The obtained particles were characterized by SEM, XRD, TG/DTA, and FTIR.
Results: Results revealed that particle morphology of calcium oxalate and their hydration states were dependent upon the chemical composition of the reactant solutions. For instance, the particles precipitated out in the form of dihydrate and having prismatic, and discs shaped particle morphology, when nickel ions were introduced in the starting reactant solution in different amounts. In contrast, the calcium oxalate particles precipitated under identical conditions in the absence of nickel ions were in the form of flakes with corrugated edges. Obvious variations were also found in the XRD patterns and crystallite size of these three solids. Heat treatment produced changes in the surface morphology of these particles due to loss of material and converted them calcium oxide.
Conclusions: Gentle mixing of aqueous solutions of calcium chloride and oxalic acid in the absence and presence of nickel ions produced precipitated particles of calcium oxalate. Chemical composition of the reactant solutions and their order of mixing were found to be the key parameters in controlling the particle morphology and their hydration/crystalline state. Heat treatment at the elevated temperature transformed the as-prepared calcium oxalate to calcium oxide with visible changes in surface features of the particles.

1. Introduction

Calcium oxalate is the major constituent of kidney stone [1–3] and higher plants [4–6] and exists there in three different crystalline forms, i.e. calcium oxalate monohydrate (COM), calcium oxalate dehydrate (COD), and calcium oxalate trihydrate (COT) in variable proportions and in different morphologies. Among these, COM is considered the most insoluble state among the mentioned three states. In order to explore the factors responsible for the formation of calcium oxalate in different forms, a number of investigators have made attempts to synthesize calcium oxalate in laboratories in the presence of various types of chemical compounds, such as carboxylic acids [7], surfactants [8], polyelectrolytes [9], water soluble macromolecules [10], other additives [11,12] etc. Those studies have shown that the reported chemical compounds affected morphology and phase composition of calcium oxalate to different extent.

In this study, we explored the effect of nickel ions on the morphology and phase composition of the calcium oxalate particles, produced by reacting calcium chloride with oxalic acid in aqueous solutions under various experimental conditions. Nickel ions were selected for this study because (i) traces of nickel ions are always there in human body as well as in plants, and (ii) to our knowledge, no such type report is available in the literature. It is hoped that our findings would provide supporting data for establishing mechanisms for the emergence of calcium oxalate in different hydrated/crystalline forms and morphologies in human kidneys and plant kingdom.

2. Experimental

2.1. Materials

Reagent grade calcium chloride ($CaCl_2$), nickel sulfate ($NiSO_4 \cdot H_2O$) and oxalic acid ($H_2C_2O_4$) were purchased from Merck and used as received. All the solutions were made with doubly distilled water using Pyrex glass vessels. The stock and working solutions were filtered through 0.2 μm pore size membrane filter before use in order to remove any insoluble impurities.

2.2. Particles synthesis

Calcium oxalate particles were prepared by mixing aqueous solutions of calcium chloride (0.001–0.03 mol/l) and oxalic acid (0.001–0.03 mol/l) in appropriate ratio at room temperature in the absence and presence of nickel sulfate (0.0002–0.00425 mol/l). The experiments were performed in a stoppered reactor, sonicated under controlled frequency and were

* Corresponding author.
E-mail address: khalida_akhtar@yahoo.com (K. Akhtar).

0009-8981/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.cca.2012.12.027

aged for various intervals of times (3–30 min). The precipitated solids were isolated from the mother liquor by vacuum filtration using membrane filters. After aqueous and ethanolic washings, the residues were dried and stored in a desiccator before subjected them to various characterization techniques.

2.3. Heat-treatment

Samples of the above mentioned synthesized dry powders were heated in a tube furnace up to 700 °C at the heating rate of 10 °C/min and then kept them at this temperature for 1 h. The samples were cool down to room temperature inside the furnace by turning it off and then stored in a desiccator.

2.4. Characterization

Selected batches of the as-prepared and heat-treated solids were characterized by various physical methods. Particle morphology was analyzed with scanning electron microscope (JSM-5910, JEOL, Tokyo, Japan). For this purpose, the sample was prepared by mounting small quantity of the desired powder on aluminum stub with the help of a double-stick conducting tape and then coated with gold in an auto fine coater (JEOL, JFC-1600). IR spectra of the same solids were recorded with FTIR (Shimadzu, IR Prestigue-21, Kyoto, Japan) in the range 400–4000 cm^{-1}. Before each run, the sample was thoroughly mixed with KBr in appropriate ratio and then transferred to the sample holder of the diffuse reflectance accessory (DRS-800A), installed in the same instrument. Similarly, the crystallinity of these powder samples was assessed from the XRD patterns, obtained with x-ray diffractometer (JEOL JDX-3532) using Cu-Kα radiation. The accelerating voltage and the applied current were 40 kV and 20 mA, respectively. The sample was scanned in a 2θ range 5–80° with the step angle of 0.02°. The energy dispersive x-ray analyzer (EDX Inca-200) was employed for the qualitative composition of the powder samples with respect to metals, whenever desired. Thermal behavior of the samples was evaluated with a simultaneous TGA/ DTA analyzer (Diamond TGA/ DTA Perkin Elmer, Waltham mA) at the heating rate of 10 °C/min in the flow of air.

3. Results and discussion

Precipitation of calcium oxalate particles was carried out by varying the experimental conditions, such as concentration of the reactants, aging time, sonication, etc. SEM analysis indicated that morphology of the precipitated particles was dependent upon relative amounts and order of mixing of the starting chemicals in the reactant mixtures, and aging time. In most of the cases, irregular shaped particles were obtained. Uniformity in particles shapes and size was achieved under a narrow set of the applied experimental conditions.

SEM images shown in Fig. 1 are of the calcium oxalate particles obtained under the described experimental conditions. It is mentioned that in this paper, the batches of the particles shown in Fig. 1A, B, and C have been designated as S1, S2, and S3, respectively. As can be seen, all the three batches of the precipitated solids composed of monosize particles, but in different shapes and sizes, which showed that composition of the starting reactant solution strongly affected the precipitation process since its inception till the full growth of the particles. Especially,

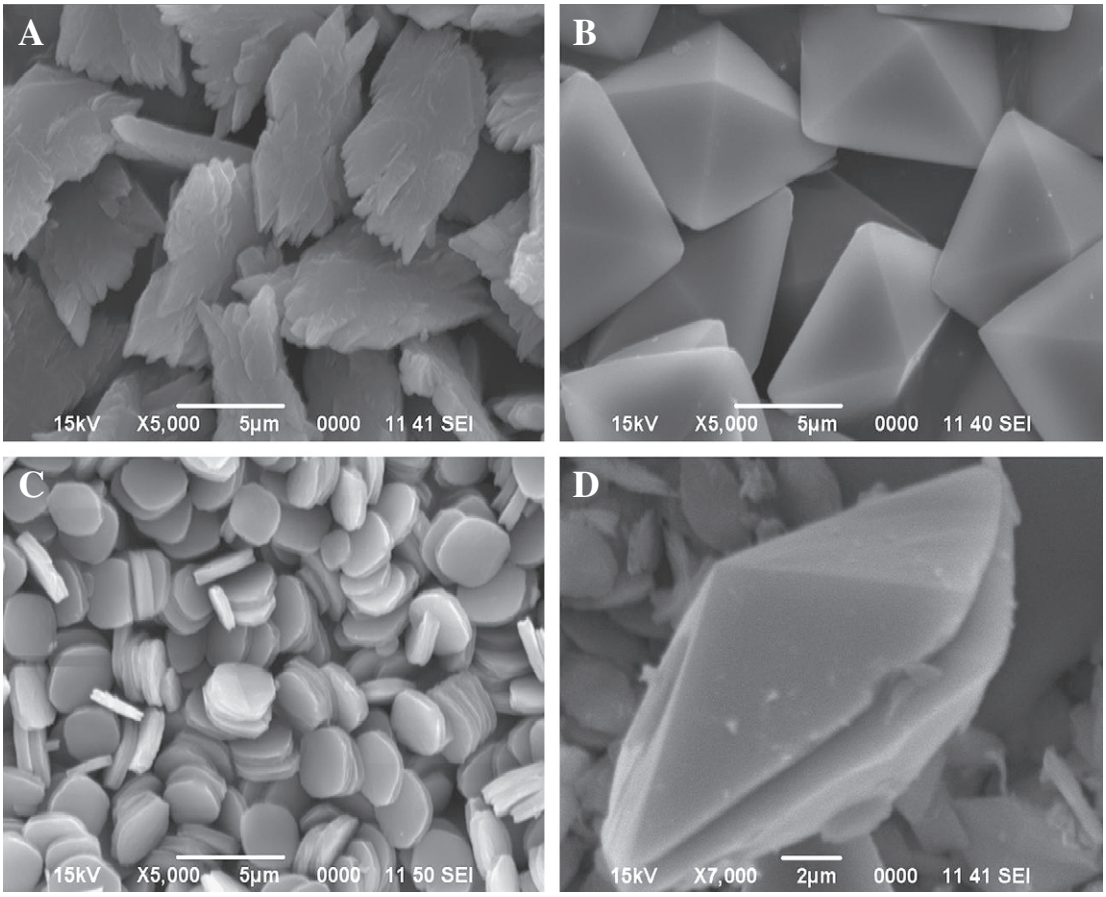

Fig. 1. Scanning electron micrographs (SEM) of calcium oxalate particles obtained by aging under sonication at room temperature for 20 min, aqueous solutions containing 0.0125 mol/l calcium chloride and 0.0125 mol/l oxalic acid (A), 0.0125 mol dm^{-3} calcium chloride, 0.0125 mol/l oxalic acid and 0.00123 mol/l nickel sulfate (B), and 0.0075 mol/l calcium chloride, 0.0125 mol/l oxalic acid and 0.0002 mol/l nickel sulfate (C). (D) Incidentally captured in the batch in B.