



# Adsorption and precipitation of fluoride on calcite nanoparticles: A spectroscopic study



Sukanto Budyanto<sup>a</sup>, Yu-Lin Kuo<sup>b</sup>, J.C. Liu<sup>a,\*</sup>

<sup>a</sup> Department of Chemical Engineering, National Taiwan University of Science and Technology, Keelung Road, Section 4, Taipei 106, Taiwan

<sup>b</sup> Department of Mechanical Engineering, National Taiwan University of Science and Technology, Keelung Road, Section 4, Taipei 106, Taiwan

## ARTICLE INFO

### Article history:

Received 3 April 2015

Received in revised form 1 July 2015

Accepted 8 July 2015

Available online 10 July 2015

### Keywords:

Adsorption

Calcite

Fluoride

Fluorite

Precipitation

## ABSTRACT

Adsorption and precipitation of fluoride on the surface of calcite ( $\text{CaCO}_3$ ) nanoparticles was investigated. Results from X-ray photoelectron spectroscopy (XPS) showed that calcium fluoride (fluorite,  $\text{CaF}_2$ ) precipitated on the surface of calcite nanoparticles at  $\text{pH } 7.2 \pm 0.1$  and fluoride concentration of 100 mg/L, while no precipitate was found at 10 mg/L. Analysis by high resolution transmission electron microscopy (HRTEM) of calcite nanoparticles reacted with 40 mg/L of fluoride showed a thin layer of fluorite on the surfaces. Interaction of calcite nanoparticles with 100 mg/L of fluoride resulted in damage of single calcite nanoparticle, and more grains of precipitate were observed. Transition from adsorption to precipitation was confirmed by zeta potential of calcite nanoparticles that shifted to negative values when at fluoride concentration of 5 mg/L, and then increased with fluoride concentration. Fluoride at low concentration is mainly removed by surface adsorption via electrostatic interactions, while surface precipitation of calcium fluoride begins at higher fluoride concentration (ca.  $\geq 10$  mg/L), and surface precipitation becomes dominant at higher concentration (ca.  $\geq 40$  mg/L).

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## 1. Introduction

Fluoride naturally presents in most types of soil, sediments, rocks, and groundwater [1]. It can also be found in wastewater discharged from agricultural and industrial activities, such as semiconductor manufacturing, metal processing, fertilizer production, electroplating, production of high-purity graphite, electrolysis of alumina, ceramic, and glass manufacturing [2]. Fluoride is known as an essential micronutrient for the human body which is beneficial for the calcification of dental enamel and bone formation. However, fluoride contamination of groundwater has become a major concern worldwide because long-term ingestion of high fluoride content drinking water can cause serious health problems [3]. Several studies have demonstrated that its accumulation can alter DNA structure, cause neurological damage, and lesions of the endocrine glands, thyroid, liver, and other organs [4].

Many methods have been developed for removal of fluoride from water and wastewater, including coagulation–precipitation, adsorption, ion exchange, membrane, electrochemical, and nanotechnology [2]. Precipitation of fluoride is primarily used for concentrated wastewater. It is done by addition of chemicals, mainly

calcium salts, such as  $\text{CaCl}_2$  and  $\text{Ca}(\text{OH})_2$  for calcium fluoride (fluorite,  $\text{CaF}_2$ ) precipitation [5]. Fluoride can also be recovered as cryolite [6,7]. Adsorption is effective for dilute systems and various adsorbents have been examined for fluoride removal, such as aluminum modified natural materials [3], hydrated cement [8],  $\text{CaO}$  [9], and  $\text{CaO}$  loaded  $\text{Al}_2\text{O}_3$  [10].

Limestone and calcite have been shown effective for fluoride removal [11,12]. A fixed bed packed with calcite ( $\text{CaCO}_3$ ) could remove fluoride effectively from wastewater, in which the process is considered as a replacement of calcite by fluorite [13]. Reardon and Wang [11] designed a two-column reactor of limestone in which fluoride concentrations of 109 mg/L is reduced to below 4 mg/L. In addition, calcite has been used for removal of phosphate and fluoride simultaneously from optoelectronic wastewater [14]. Adsorption of fluoride using calcite mainly depends on initial concentration, pH, and temperature. The amount of fluoride removed is also dependent on the particle size and the surface area of the adsorbent. Decreasing particle size to the nanometer range results in an increase of adsorption capacity [9]. Aluminum modified calcite did not show high adsorption capacity when compared with zeolite, probably due to its low specific surface area [3].

Both adsorption and precipitation reactions are involved for fluoride removed by calcite surfaces. Turner et al. [15] utilized atomic force microscopy (AFM) and X-ray photoelectron spectroscopy (XPS) to examine fluoride removal by calcite. Direct evidence of

\* Corresponding author.

E-mail address: [liu1958@mail.ntust.edu.tw](mailto:liu1958@mail.ntust.edu.tw) (J.C. Liu).

calcium fluoride precipitation at fluoride concentration of 700 mg/L was found by XPS, and a conceptual model combining surface adsorption and precipitation was proposed. Yang et al. [16] used X-ray diffraction (XRD) and AFM to examine dissolution of calcite and formation of fluorite at pH 3 and 7. Spherical fluorite rods formed around nucleation centers at pH 3. However, the transition between adsorption and precipitation as fluoride concentration increases is still not fully understood. In this study, calcite nanoparticles are used for fluoride removal with fluoride concentrations from 5 mg/L to 100 mg/L. Instrumental analysis, including zeta potential analysis, XPS, and high resolution transmission electron microscopy (HRTEM) were used to develop an in-depth examination on the reactions between fluoride and calcite.

## 2. Materials and methods

### 2.1. Reaction of calcite nanoparticles with fluoride

Stock solution of 1000 mg/L fluoride was prepared by dissolving 2.210 g of reagent grade sodium fluoride (NaF, Merck) in 1 l of deionized water. Calcite nanoparticles (99.9% purity) were purchased and used without further treatment (American Element). The experiments of reaction kinetics started by placing 1 g of calcite nanoparticles in the 200 mL of fluoride solution of 10 and 100 mg/L, respectively. The initial pH was adjusted by 2 M hydrochloric acid (HCl, Fisher Scientific), so that desired pH ( $7.2 \pm 0.1$ ) was obtained throughout the reaction. The reaction proceeded under continuous stirring at 100 rpm under room temperature for 2 h. At each time interval of 0, 1, 3, 5, 10, 15, 30, 60, and 120 min, 1 mL of sample was taken using a syringe (Pall Co.), and directly filtered with 0.20  $\mu\text{m}$  mixed cellulose ester membrane (Advantec). The filtrate was diluted and analyzed using the ion selective electrode (Thermo Scientific, Orion 4 Star). Total ionic strength adjustment buffer (TISAB) was added to the samples and standard solutions. The amount of fluoride adsorbed onto calcite nanoparticles at a given time  $t$ ,  $q_t$  (mg/g), was defined as:

$$q_t = \frac{(C_0 - C_t)V}{m} \quad (1)$$

where  $C_0$  is the initial concentration of fluoride (mg/L),  $C_t$  the concentration of fluoride at a given time (mg/L),  $V$  the volume of liquid (L), and  $m$  the mass of adsorbent (g).

### 2.2. Characterization of calcite nanoparticles

Brunauer–Emmett–Teller (BET) surface area was determined from  $\text{N}_2$  adsorption–desorption isotherms over a range of relative pressure ( $P/P_0$ ) at 196 °C by an instrument (Quantachrome Autosorb-1). Prior to the measurements, calcite nanoparticles were degassed at 200 °C under vacuum for at least 24 h. The BET surface area was determined to be 20.5  $\text{m}^2/\text{g}$ . It is higher than the value of 9.15  $\text{m}^2/\text{g}$  of commercial calcite [14].

Zeta potential was measured using a zeta meter (Malvern, Zetasizer 2000). Firstly, the pH of several 10 mL solutions of various fluoride concentration (5–100 mg/L) was adjusted by 0.05 N NaOH, so that equilibrium pH of  $9.3 \pm 0.1$  was obtained. Fixed amount of calcite nanoparticles was added to each solution. After 24 h, the final pH was measured. Before measurement, samples were sonicated to provide a better dispersion. Each loaded sample was measured at least three times and the average value was taken.

The size and surface morphology of calcite nanoparticles were assessed using a high resolution transmission electron microscopy (HRTEM, FEI Tecnai G2 F30 300 kV), while its composition was examined by energy-dispersive X-ray spectroscopy (EDX). Results

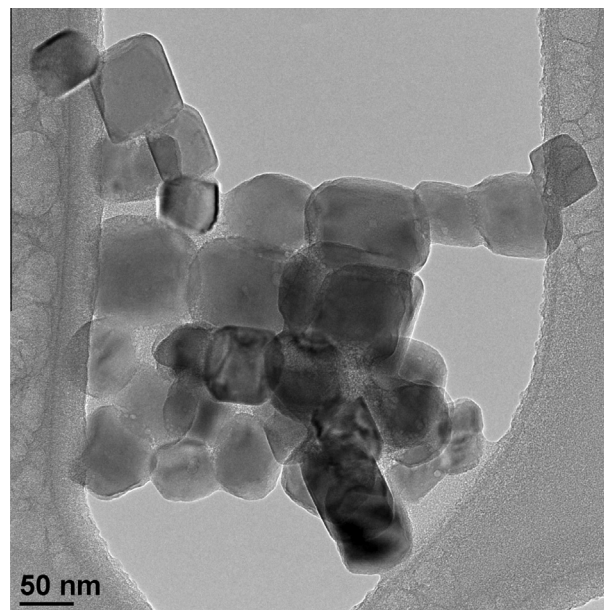


Fig. 1. HRTEM image of calcite nanoparticles.

showed that the calcite nanoparticles had size around 50–80 nm with a tendency to aggregate, and they were not porous (Fig. 1). Calcite nanoparticles after reacting with fluoride were examined using HRTEM to reveal atomic structures of crystalline defects, such as the two boundaries. Ethanol was used as a solvent to prepare suspension of calcite nanoparticles. A drop of suspension (solvent and calcite nanoparticles) was placed on specimen support (copper grid) and the solvent evaporated. This specimen was then irradiated with an electron beam of uniform current density. Emitted electrons illuminated the specimen through a condenser lens system, and formed an image of the specimen that can be recorded digitally.

The composition of calcite nanoparticles before and after reacting with fluoride was assessed by X-ray photoelectron spectroscopy (XPS, Thermo VG Scientific Theta Probe) using monochromatic  $\text{Al K}\alpha$  (1486.6 eV) as excitation sources, with pass energy of 50 eV. Argon ion was employed with 3 kV and 1 mA current. The characteristics of samples were examined under take-off angle of 53°, with X-ray spot size of 400  $\mu\text{m}$ . After reacting with fluoride, loaded calcite nanoparticles were filtered and washed with deionized water. They were then dried and stored in a desiccator until analysis. XPS deconvolution was carried out by using Peak fit® software. The fitting was performed by applying Gauss–Lorentzian fitting.

## 3. Results and discussion

### 3.1. Spectroscopic analysis

#### 3.1.1. X-ray photoelectron spectroscopy (XPS)

Fig. 2A shows the wide-scan XPS spectra of calcite nanoparticles after reacting with fluoride. Calcium, carbon, oxygen, and fluorine were the major constituents as expected. The presence of  $\text{Ca}2s$ ,  $\text{Ca}2p$ ,  $\text{C}1s$ , and  $\text{O}1s$  represented original calcite nanoparticles, while  $\text{F}1s$  in loaded sample indicated surface process of fluoride on the surface of calcite nanoparticles [17]. However, high resolution spectra from XPS, especially  $\text{Ca}2p$  spectra,  $\text{C}1s$  spectra, and  $\text{F}1s$  spectra are needed to reveal chemical bondings between each constituent.

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