



# Sequential precipitation of a new goethite–calcite nanocomposite and its possible application in the removal of toxic ions from polluted water

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## HIGHLIGHTS

- ▶ A simple and innovative synthesis route for goethite–calcite nanocomposite.
- ▶ Nanosized goethite particles adhered onto sub-micrometric calcite.
- ▶ Goethite–calcite composite has a well sequestration capacity for toxic ions.

## ARTICLE INFO

### Article history:

Received 13 July 2012

Received in revised form 26 October 2012

Accepted 27 October 2012

Available online 2 November 2012

### Keywords:

Goethite

Calcite

Nanocomposite

Precipitation

Removal

Metalloids

Heavy metals

## ABSTRACT

This study proposes a simple and innovative synthesis route for a goethite–calcite nanocomposite. This synthesis is summarised by three sequential precipitation reactions: (1) precipitation of nanosized acicular goethite ( $\alpha$ -FeOOH) using a high OH/Fe molar ratio ( $\approx 5$ ); (2) instantaneous precipitation of portlandite ( $\text{Ca}(\text{OH})_2$ ) by adding  $\text{CaCl}_2$  salt to a goethite alkaline suspension ( $2\text{NaOH} + \text{CaCl}_2 \rightarrow \text{Ca}(\text{OH})_2 + 2\text{NaCl}$ ) and; (3) sub-micrometric calcite precipitation by injection of  $\text{CO}_2$  into a goethite–portlandite alkaline suspension ( $\text{Ca}(\text{OH})_2 + \text{CO}_2 \rightarrow \text{CaCO}_3 + \text{H}_2\text{O}$ ). The XRD patterns have confirmed the goethite and calcite mineral composition in the composite precipitated at 30 and 70 °C. FESEM and TEM observations have revealed the formation of nanosized goethite particles well dispersed with sub-micrometric calcite particles, leading to an orange–brown colour nanocomposite with high specific surface area of around 92 m<sup>2</sup>/g for a composite synthesized at 30 °C and 45 m<sup>2</sup>/g for a composite synthesized at 70 °C. Both values were determined using the conventional BET method on N<sub>2</sub> sorption isotherms. Finally, a goethite/calcite weight ratio equal to 0.8 in the composite was determined by Thermogravimetric Analysis (TGA). Additionally, some adsorption experiments carried out at two different pH values revealed that the goethite–calcite composite has a good sequestration capacity for  $\text{Cu} > \text{Cd} > \text{As(III)} > \text{Se(IV)} > \text{As(V)}$ . Conversely, the Se(VI) did not show any chemical affinity with the goethite–calcite composite under the physico-chemical conditions studied. In practice, the goethite–calcite composite can neutralise acidic wastewater by slight calcite dissolution, enhancing the removal of heavy metals (e.g. Cu and Cd) at the calcite–solution interfaces.

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## 1. Introduction

Goethite and calcite are two inorganic compounds that are widely studied due to their abundance in nature as minerals (abiotic origin) and biominerals (biotic origin). Both minerals can co-exist in several terrestrial environments such as deep geological formations, water aquifers, soils and aerosols, and play a major role

in the fate and transport of several metalloids and heavy metal trace elements and organic molecules at the mineral–fluid interfaces [1–5]. Goethite and calcite minerals have also been identified in several extraterrestrial environments. For example, calcite has recently been discovered in Martian soils by the Phoenix Mars exploration mission [6] and goethite has been suspected as a constituent of Martian dust and dark asteroids [7,8]. Moreover, goethite and calcite minerals are technologically important materials and widely applied as components in various industrial products, e.g., pigments in the building industry, inorganic dyes, pigments and adsorbents in the paper industry, lacquers or plastics, sorbents

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