Journal of Colloid and Interface Science 398 (2013) 88–94

Contents lists available at SciVerse ScienceDirect

Journal of Colloid and Interface Science

www.elsevier.com/locate/jcis

The effect of hydroxyl groups and surface area of hematite derived from annealing goethite for phosphate removal

Haibo Liu [a,b], Tianhu Chen [a,*], Jin Chang [b], Xuehua Zou [a], Ray L. Frost [b,*]

[a] School of Resources & Environmental Engineering, Hefei University of Technology, China
[b] School of Chemistry, Physics and Mechanical Engineering, Science and Engineering Faculty, Queensland University of Technology, Australia

ARTICLE INFO

Article history:
Received 19 December 2012
Accepted 8 February 2013
Available online 21 February 2013

Keywords:
Goethite
Hematite
Hydroxyl group
Surface area
Phosphate removal

ABSTRACT

Synthetic goethite and thermally treated goethite at different temperatures were used to remove phosphate from sewage. The effect of annealing temperature on phosphate removal over time was investigated. X-ray diffraction (XRD), transmission electron microscopy (TEM), N_2 adsorption and desorption (BET), and infrared emission spectrum (FT-IES) were utilized to characterize the phase, morphology, specific surface area, pore distribution, and the surface groups of samples. The results show that annealed products of goethite at temperatures over 250 °C are hematite with the similar morphology as the original goethite with different hydroxyl groups and surface area. Increasing temperature causes the decrease in hydroxyl groups, consequential increase in surface area at first and then experiences a decrease (14.8–110.4–12.6 m^2/g) and the subsequent formation of nanoscale pores. The variation rate of hydroxyl groups and surface area based on FT-IES and BET, respectively, are used to evaluate the effect of annealing temperature on phosphate removal. By using all of the characterization techniques, it is concluded that the changes of phosphate removal basically result from the total variation rate between hydroxyl groups and surface area.

1. Introduction

Phosphate adsorption on soils and sediments plays a crucial role in regulating the transport, mobility, enrichment, and bioavailability, which affects water quality and soil fertility [1,2]. Among all adsorbents, iron (hydroxy) oxides are usually considered as active sorbents as well as some waste materials reported recently [3–11]. In the past decades, adsorption of phosphate by iron (hydroxy) oxides has been extensively researched. Goethite is regarded as the most frequent and abundant of the iron (hydroxy) oxides [11–13].

As is well-known, surface complex formation as well as surface precipitation has been proved to be the most likely adsorption mechanism between phosphate and surface hydroxyl groups researched by using IR, XPS, Zetaplus, etc. [2,3,14–17]. Surface complex is easy to understand, namely monolayer ligand exchange between phosphate and hydroxyl groups. In contrast, surface precipitation is defined as ternary adsorption of phosphate on the surface of adsorbents which was confirmed by Ler and Stanforth [14]. To obtain the detailed adsorption mechanism, spectroscopic methods have been used to qualitatively investigate the inner-sphere phosphate species adsorbed on the surface of goethite [1,2,13,18–22]. These results demonstrated that this kind of surface complex belongs to binuclear or monodentate; it mainly depends on the reaction parameters including pH and surface coverage. The previous research of Zhong et al. [2] suggested that, from pH 3.5 to 8.0, the dominant phosphate surface species is a bidentate complex and the monodentate complex increases with increasing pH values and decreasing phosphate surface coverage. A mixture of different phosphate complexes was found at the hematite surface by Elzinga and Sparks using an in situ ATR-FTIR [23]. Whatever kinds of complex formations are involved in the adsorption process, the hydroxyl group is consistently regarded as the adsorption site. However, the decrease in hydroxyl group will necessarily result in the decrease in phosphate over hematite. In addition, as is widely known, the surface area affects the number of adsorption sites. However, the effect of the joint effect of hydroxyl groups and surface area on the removal phosphate has not been reported.

In the present paper, goethite and thermally treated goethite are used to evaluate the role of hydroxyl groups and the effect of surface area on the adsorption of phosphate. The main difference between goethite and experimental synthetic hematite is the number of hydroxyl groups and subsequent surface area. Thus, it is easy to discuss the role of hydroxyl groups and the effect of surface area on the coordinating phosphate. The aim is to make it clear whether hematite with larger specific area has a high phosphate removal and how hydroxyl groups and the surface area affect the phosphate removal using goethite and hematite.

---

* Corresponding authors. Fax: +61 7 3138 1804 (R.L. Frost).
E-mail addresses: chentianhu168@vip.sina.com, chentianhu1964@126.com (T. Chen), r.frost@qut.edu.au (R.L. Frost).

0021-9797/$ - see front matter © 2013 Elsevier Inc. All rights reserved.
http://dx.doi.org/10.1016/j.jcis.2013.02.016

2. Experimental

2.1. Material preparation

Goethite used in this study was sourced from Zhenjiang city, Jiangsu province, China. The powdered goethite annealed at different temperature (200, 250, 300, 350, 400, 500, 600 °C) for 2 h was used for adsorption experiments and further characterization.

2.2. XRD

XRD patterns were recorded using Cu Kα radiation (λ = 1.5406 Å) on a Philips PANalytical XPert Pro multi purpose diffractometer. The tube voltage is 40 kV and the current 40 mA. All XRD diffraction patterns were taken in the range of 10–70° at a scan speed of $2^\circ\ \mathrm{min}^{-1}$ with 0.5° divergence slit size. Phase identification was carried out by comparison with those included in the Inorganic Crystal Structure Database (ICSD).

2.3. TEM

Transmission electron microscope (TEM) measurements were performed on JEM-1010. The sample was mixed with alcohol and deposited on a Cu grid. Images of the microstructure are acquired using an analytical electron microscope.

2.4. BET

Thirteen-point BET-nitrogen isotherms were used to quantify changes in the specific surface area. All samples were degassed at 110 °C for 12 h before analysis was conducted. The multi-point BET surface area of each sample was measured at atmospheric pressure using TriStar II 3020 Surface Area and Pore Size Analyzer. The adsorption isotherms achieved a p/p_o range of 0.009–0.25. Pore size distribution was evaluated by BJH desorption pore distribution report between 1.7 nm and 20 nm.

2.5. Infrared emission spectroscopy

FTIR emission spectroscopy was carried out on a Nicolet spectrometer equipped with a TGS detector, which was modified by replacing the IR source with an emission cell. A description of the cell and principles of the emission experiment have been published elsewhere [15–19]. A thin layer (approximately 0.2 μm) on a platinum surface with 6 mm diameter held in an inert atmosphere within a nitrogen-purged cell during heating. The spectra were acquired by coaddition of 1024 scans at the temperature of 100, 150, 200, 512 scans at 250, 256 scans at 300, 350, and 128 scans at temperature from 400 to 900 °C. Spectral manipulation such as baseline adjustment, smoothing, and normalization was performed using the Grams® software package (Galactic Industries Corporation, Salem, NH, USA). Band component analysis was undertaken with the Jandel "Peakfit" software package, and fitting was undertaken until reproducible results were obtained with squared correlations of R^2 greater than 0.995.

2.6. Adsorption experiments

Phosphate-enriched sewage was prepared by addition of 0.1097 g KH_2PO_4 to 4.5 L deionized water. Then, 0.1 mol/L NaOH was used to regulate the pH up to a neutral condition; then, some deionized water was added up to 5 L. Finally, a desired phosphate concentration (5 mg P/L) was achieved with a pH of 6.8.

All of the adsorption experiments were carried out by a batch method at ambient temperature (23 ± 2 °C). The phosphate removal from the prepared KH_2PO_4 was determined by stirring a known amount of adsorbent in a given volume of solution in conical bottle. Synthetic goethite annealed at different temperature (25, 200, 250, 300, 350, 400, 500, 600 °C) for 2 h was used to adsorb phosphate at the same experimental conditions. Kinetic adsorption results were obtained by stirring known amounts of the adsorbents with a known volume of solution for 5 min, 10 min, 0.5, 1, 2, 4, 6 h to obtain the equilibrium. 30 ± 0.2 mg of adsorbent was added into 100 mL conical bottle, and then, 50 mL phosphate-enriched sewage was added. The conical bottle was put on magnetic stirrer and stirred by a magnetic bar with a rotate speed of 360 rpm to ensure the good mixing. Meanwhile, a blank with the same volume of phosphate-enriched sewage was also prepared at different adsorption time without any adsorbent to compensate the possible loss via adsorption on the plastic. When desired adsorption time was reached, the mixture was migrated into plastic centrifuge tube and then was centrifuged with a rotate speed of 3500 rpm for 20 min. After this, the phosphate concentrations in the supernatant solutions were measured by the method proposed by Murphy and Riley [24], using an Agilent diode array spectrophotometer equipped with several 1 cm quartz cell. The detection limit was about 0.05 mg P/L. The uptakes of phosphate were calculated from the decreases in phosphate concentrations relative to those of the initial concentrations. Each data point was the result of one individual experiment.

3. Results and discussion

3.1. XRD

Fig. 1 shows the XRD patterns of goethite and annealed goethite at different temperatures. All the reflections are found on the XRD patterns of goethite and annealed goethite at 200 °C and are indentified as goethite as compared with the standard reference pattern (ICSD (96-900-2159)). The intensity of the characteristic reflections of goethite shows a significant increase after annealing at 200 °C. This is attributed to the dehydration which results in the high crystallinity of goethite. Previous report [25] indicates that a mass loss of absorbed water is observed over the ambient to 150 °C from the TG curve of goethite. These reflections of annealed goethite over 300 °C are indentified as hematite when compared with the standard reference pattern (ICSD (96-900-0140)). Obviously, the goethite is completely transformed into hematite as annealing temperature is over 300 °C. The reflection intensity of hematite increases with an increase in annealing temperature ranging from 300 to 600 °C. In addition, the XRD pattern of transient formation from goethite to hematite is found after annealing at 250 °C. To the best of our knowledge, goethite can be transformed into hematite after annealing over 200 °C. Gualtieri and Venturelli [26] have studied this transformation by in situ synchrotron XRD using pure, synthetic goethite. The results showed the dehydration of goethite started at 200 °C and ended at about 270 °C, and the resultant phase is with non-stoichiometric composition called protohematite which was eventually converted into hematite at around 800 °C. Previous reports [27,28] also have the similar conclusions.

3.2. TEM

The TEM images of goethite and annealed goethite at 300, 400, 500, 600 °C were presented in Fig. 2. About 1 nm-wide longitudinal pores array was observed in Fig. 2b, a magnification of square in Fig. 2a, after annealing at 300 °C, which was ascribed to the dehydroxylation of goethite and was consistent with previous reports based on TEM observation. The dehydration of goethite to hematite has been the subject of numerous TEM studies [29,30]. It is proved