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Low temperature hydrothermal synthesis and characterization of iron oxide powders of diverse morphologies from spent pickle liquor

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ABSTRACT

Iron oxide nanoparticles (goethite and hematite) of various shapes have been synthesized through a simple hydrothermal reaction from the stripped solution of Fe(III) obtained after extraction and separation of Zn and Fe from spent pickle liquor. The influence of pH and synthesis time on the structure and morphology of the as-prepared α-Fe_2O_3 are investigated. It was possible to control the particle size and shape by adjusting the pH (2–12) of the starting solutions and time of synthesis (1–6 h). Under the appropriate conditions, rod-like α-FeOOH (goethite) and hexagonal α-Fe_2O_3 (hematite) materials of the uniform nano-crystalline structure were selectively synthesized in large quantities. The morphology and structure of the final products were investigated in detail by X-ray powder diffraction pattern (XRD), transmission electron microscopy (TEM), Raman spectroscopy and vibrational sample magnetometer (VSM). The probable mechanism of formation of uniform α-FeOOH and α-Fe_2O_3 nano-particles is discussed on the basis of the experimental results and characterization studies. The evaluation of the magnetic property has established the weak ferromagnetism characteristics of both goethite and hematite at room temperature.

1. Introduction

Iron oxide-particles are important for the preparation of magnetic recording materials, pigments, catalysts, and sorbent for the removal of heavy metals from wastewater and soil. There are several types of iron oxide particles, namely goethite (α-FeOOH), maghemite (γ-Fe_2O_3), magnetite (Fe_3O_4) and hematite (α-Fe_2O_3). The methods for the synthesis of iron oxide particles reported in the literature include sol–gel, combustion, high energy ball milling, solvothermal, thermal decomposition, hydrothermal processes, etc. [1–5]. Among these techniques synthesizing high value iron oxides or ferrites for advanced applications by a hydrothermal process is considered to be the most effective method due to its economical and eco-friendly nature. Above all, morphology, crystallinity, particle size, properties, etc. can be easily tuned by varying reaction conditions such as temperature, pressure, solution pH, reaction time, reactant concentration, surfactant, solvent, etc. [6–9].

Cubic α-Fe_2O_3 (hematite) microparticles (side lengths = 0.3–1.3 μm) were recently synthesized using glycine and ferric chloride in a simple one-step hydrothermal reaction [10]. An increase in the duration of hydrothermal reaction from 10 to 24 h increased the yield of α-Fe_2O_3 by almost 8% on the surface of the micro-particles so synthesized. Tadic et al. [9] reported the hydrothermal synthesis of single phase α-Fe_2O_3 with a plate like structure by adding oleic acid and NaOH into the solution of iron nitrate in ethanol/water (1:1) at 200 °C. The α-Fe_2O_3 so produced had coercivity (H_{ci}), remnant magnetization (M_r) and saturation magnetization (M_S) values as 1140 Oe, 0.125 emu/g and 2.15 emu/g, respectively. Subsequently Tadic et al. [11] also reported the thermal decomposition synthesis of α-Fe_2O_3 particles at 800 °C for 4 h and examined its morphology and magnetic properties. The values of the H_{ci}, M_r and M_S at room temperature of the thermally synthesized particles were found to be 4350 Oe, 0.731 emu/g and 6.83 emu/g, respectively. Monodispersed ellipsoidal and spherical α-Fe_2O_3 particles were synthesized at 120 °C and 200 °C for 12 h by the hydrothermal route [12] using $FeCl_3$, NaOH and $C_2H_2O_4$ as the raw materials. The ellipsoidal and spherical particles thus produced exhibited a ferromagnetic behavior with H_{ci} values of 3815.0 and 1543.34 Oe, respectively depending upon the temperature of the synthesis. The precipitation of hematite from ferric chloride solution in an autoclave was systematically investigated by Riveros and Dutrizac [13]. The minimum temperature required to form hematite in the absence of hematite seed was ~125 °C whereas, akaganeite (β-FeO·OH) was precipitated at lower temperatures in <6 h. In the presence of hematite seed, Fe_2O_3 was precipitated at temperatures as low as 100 °C. Lu et al. [14] reported the synthesis of hexagonal pyramidal columnar hematite particles by a hydrolysis method using iron sheets and nitric acid of mildly acidic pH (1.95 < pH < 3.50) at 90 °C. The α-Fe_2O_3 produced, showed weak ferromagnetic behavior, with a M_r of 0.051 emu/g, a H_{ci} of 94.64 Oe and a M_s of 0.511 emu/g at room temperature.

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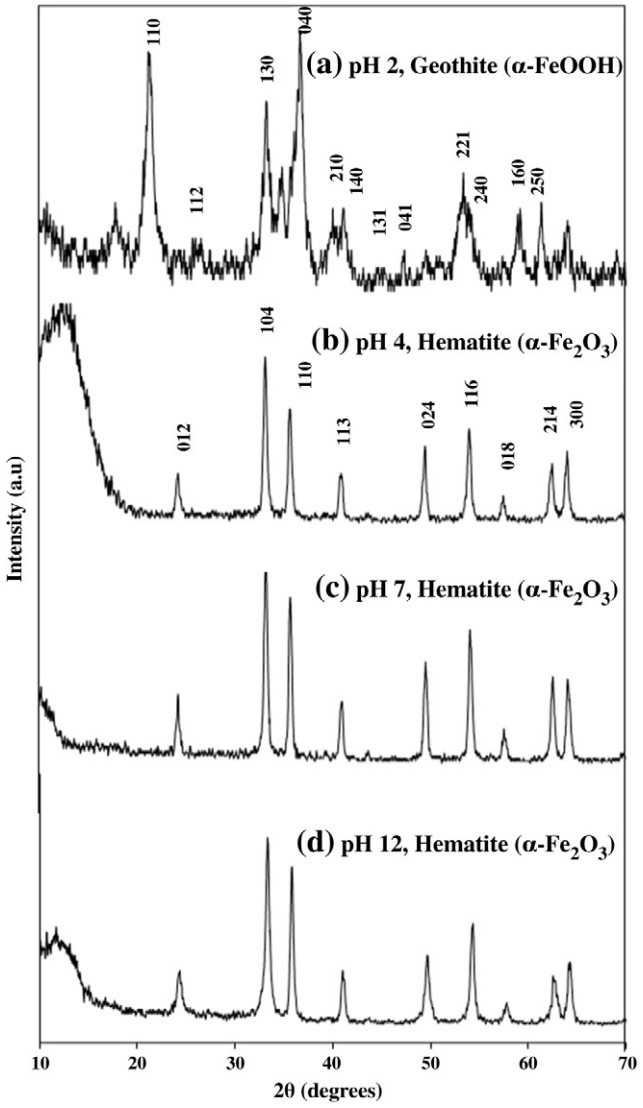

Fig. 1. XRD patterns of iron oxide particles obtained at different pH in 2 h. (a) pH 2, (b) pH 4, (c) pH 7 and (d) pH 12.

Recently a simple process was developed to produce hierarchical α-Fe_2O_3 nanostructures of different morphologies like peanuts, capsule, cantaloupe and almond by simply varying silicate anions and other inorganic reagents [15]. The particle size of α-Fe_2O_3 decreased with an increase in pH (1.2 to 8) and temperature (200 to 220 °C). It was also found that all the α-Fe_2O_3 products exhibited ferromagnetic behavior showing higher M_r and H_{ci} values (2.5 emu/g and 3.5 kOe). The rod-like goethite (α-FeOOH) and porous fusiform hematite (α-Fe_2O_3) of uniform nano-crystallinity using sodium dodecyl sulfate as surfactant were synthesized [16]. At 140 °C poorly crystallized goethite (α-FeOOH) was produced in just 4 h. With the increase in reaction time to 8 and 24 h, nano-rod-like α-FeOOH with adequate crystallinity and uniform porous fusiform nanocrystalline hematite (α-Fe_2O_3) particles were produced.

Albeit in most of the above investigations high value iron oxides were synthesized using pure solutions of iron. Use of industrial waste solutions containing a high concentration of iron for the preparation of high value products of iron, is very limited [17–19]. Spent pickle liquor generated in galvanizing plants of steel industry is a high iron containing waste solution. The general practices adopted for treatment of such solutions include either neutralization followed by disposal of generated sludge as land fill or recovery of iron oxide as a by-product by pyro-hydrolysis [20]. However, both the practices are associated with economic and environmental issues. Therefore, it is imperative to develop an efficient process to recover value added products of iron from the spent pickle liquor which meets the waste management strategy and offers economic returns.

In our continuing efforts [21] of processing the HCl based spent pickle liquor of steel plants, the stripped solution of Fe(III) obtained as precursor after extraction and separation of Zn(II) and Fe(II)/Fe(III), was investigated for the hydrothermal synthesis of iron oxide particles of nano-size at different pH and a moderate temperature (150 °C) in contrast to the higher temperature (~220 °C) generally used [15]. The effect of reaction time on the morphology and size of iron oxide at a particular pH during hydrothermal synthesis is also reported without using any precursor or surfactant. The obtained iron oxide particles have been characterized by using different techniques.

2. Experimental

2.1. Reagent and materials

From a model pickle solution containing 90 g/L HCl, 117 g/L Zn, 30 g/L Fe(II) and 1 g/L Fe(III), different components were separated while applying the optimized conditions as elaborated elsewhere [21]. Zn was extracted with TEHA (Aldrich Chemicals) and HDEHP (Dihachi Chemical Industry Co.) diluted in kerosene (Indian Oil Ltd.) along with 10% isodecanol as the phase modifier. Fe(III) was extracted with Versatic 10 acid from the Zn(II) free pickle liquor after microbial

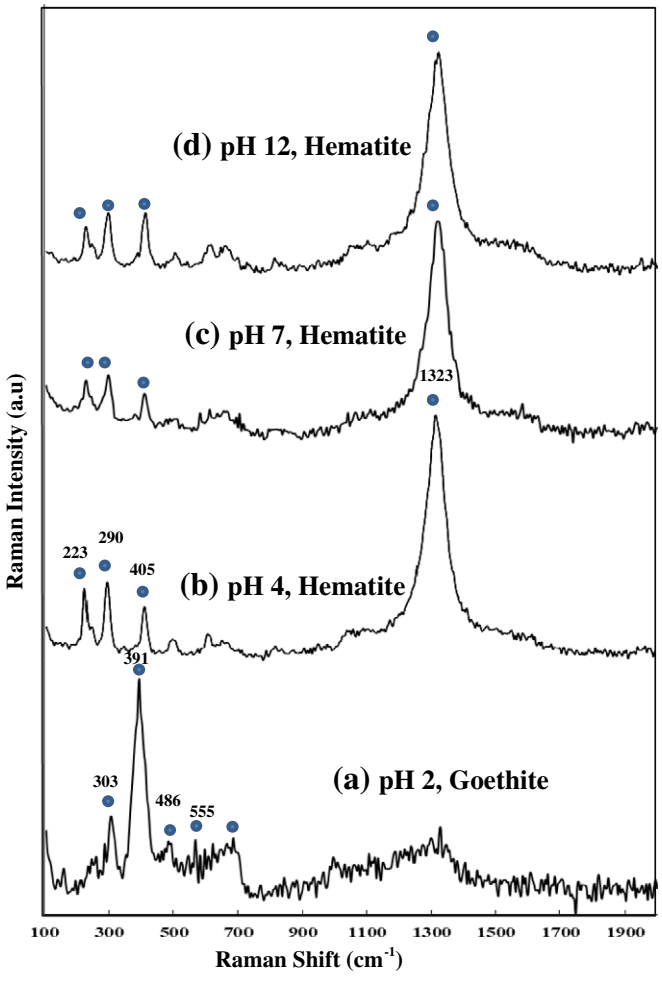

Fig. 2. Raman spectra of iron oxide particles obtained at different pH in 2 h. (a) pH 2, (b) pH 4, (c) pH 7 and (d) pH 12.