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Synthesis and characterization of magnetite and activated carbon binary composites

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ABSTRACT

Magnetite and its composite materials with activated carbon were prepared using a co-precipitation method with Fe^{2+}/Fe^{3+} at 60 °C under anaerobic conditions. Iron oxyhydroxide (goethite, α-FeOOH) was synthesized at a 5/1 OH^-/Fe^{3+} molar ratio. Characterization of these composite materials and goethite was established using powder X-ray diffraction (PXRD), Raman spectroscopy, diffuse reflectance infra-red Fourier transform spectroscopy (DRIFTS), thermogravimetric analysis (TGA), scanning electron microscopy (SEM), transmission electron microscopy (TEM), and N_2 adsorption–desorption analysis. Inhomogeneous growth of magnetite in the activated carbon was revealed by electron microscope images, N_2 adsorption–desorption isotherm analysis, and the total Fe content in the composites were determined. Composite materials of activated carbon and iron oxide possess modified pore structure and oleophilicity relative to activated carbon and the iron oxide starting materials. The tunable adsorption properties of such materials were reported by Kwon et al. [53] for an organo-arsenical in aqueous solution and an independent kinetic study of selenite anion species. The unique behaviour of the composite materials were related to their relative composition and hydrophile–lipophile characteristics.

1. Introduction

Inhomogeneous chemical reactions involving nanoparticles (NPs) for large-scale practical applications require that NPs be supported in a matrix that allow for flow and interaction with the NPs. The surfaces of iron oxide-based bulk materials and NPs have a relatively high affinity for metal cations and their oxyanions. Wastewater treatment employs bulk iron oxides and oxyhydroxides such as magnetite, Fe_3O_4; maghemite, γ-Fe_2O_3; hematite, α-Fe_2O_3; goethite, α-FeOOH, and other oxides of iron. Treatment processes are generally not regenerative by design, thus, the use of smaller quantities of materials with chemical selectivity is more desirable. The increased surface area presented by NPs allows for the use of smaller quantities in water treatment applications. For example, iron-oxide composite NPs would enable optimization adsorption process of specific ions such as arsenate [1] and organic dyes [2–4].

The high surface area (>1000 m^2/g) of activated carbon (AC) and its surface reactivity allows for further surface treatment [5] such as metal impregnation [6], acid–base treatment [7], oxidation, and grafting to afford a modular support material [8–13]. As well, AC is commercial available, cost effective, available in reasonable purity, and amenable to relatively low-cost manufacturing of composite materials [14–16]. Other support matrices are metal–organic frameworks [17], tea waste [18], polyacrylonitrile/iron (III) acetylacetonate [19], chitosan polymer [20,21], multiwall carbon nanotubes (MWCNTs) [22,23], microcrystalline cellulose [24,25], carbon nanofibers [19] and sawdust [26]. Chitosan/magnetite composites consist of an inorganic metal oxide and chitosan to enhance adsorption rate and high adsorption efficiency. Composite materials are suitable for the uptake of contaminants such as heavy metals and organic materials in aqueous solutions with relatively facile recovery and reuse properties for the treatment of water [20,27,28].

Embedding nanomaterials in a high surface area support include embedded magnetite particles within carbon nanofibers obtained by electrospinning a solution of polyacrylonitrile (PAN) containing the iron oxide precursor, iron (III) acetylacetonate (AAI), followed by heating at 850 °C under argon [19]. The use of a non-aqueous ferrofluid allows for the distribution of oleic acid-based magnetite nanoparticles onto a microporous and microfibrous silicate

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substrate [16]. Magnetic carbon nanotube composites may be prepared by three general strategies: (i) physical encapsulation, (ii) chemical incorporation within the walls, or (iii) chemical deposition on the outer surface of the nanotube [22,23]. Microcrystalline cellulose composites comprising cellulose fibres with a length scale of 20 mm and inorganics are of interest due to their utility in forming hybrid materials. Such composites possess properties inherent of the fibre substrate (stiffness and strength, non-toxic nature and biocompatibility, variable ionic permeability and hydrophilicity) which share the magnetic properties of the NPs [16,24]. Examples of cellulose materials are carboxymethyl-cellulose [24,29], carrageenan [30], α-amylase [31], and microcrystalline cellulose with polyurethane prepolymers.

NPs of iron oxide composites containing AC would provide enhanced adsorptive properties and the possibility of selective removal of waterborne pollutants [32]. The tendency to remove oxyanions and metal cations is attributed to the unique Lewis acid–base characteristics, and the oleophilicity of activated carbon, including iron oxide NPs. Supported NPs on AC are anticipated to display reduced iron leaching into solution and facile separation of the sorbent phase from wastewater by virtue of the magnetic susceptibility of the composite in an electromagnetic field.

Although synthetic methods for the oxides of iron are well established, it is essential to characterize the synthetic iron oxides and composites since different phases have variable reactivity. Thus, the various synthetic phases of materials require multi-instrumental characterization such as powder X-ray diffraction, Raman and energy-dispersive X-ray spectroscopy (EDS). Characterization of the size and shape are achieved by Scanning electron microscopy (SEM) and transmission electron microscopy (TEM); whereas, dynamic laser scattering (DLS) provide estimates of particle size distribution, magnetometry provides an estimate of the magnetic moment, and BET analysis is used to evaluate the porosity and textural properties of such materials [33]. An evaluation of the sorption properties of the composite materials was carried out, as reported elsewhere [34,35] for selenium and organic arsenic species.

2. Experimental

2.1. Synthesis of magnetite (denoted as Mag-P)

Magnetite was prepared by co-precipitation methods shown by Eq. (1) [36].

$$2FeCl_{3(aq)} + FeCl_{2(aq)} + 8NH_{3(aq)} \rightarrow Fe_3O_{4(aq)} + 8NH_4Cl_{(aq)} \quad (1)$$

Briefly, 10 mL of 2.0 M $FeCl_2{\cdot}4H_2O$ (98%; Alfa Aesar) (3.976 g $FeCl_2{\cdot}4H_2O$ in 2.0 M HCl) and 10 mL of 1.0 M $FeCl_3{\cdot}6H_2O$ (98%; Alfa Aesar) (2.703 g $FeCl_3{\cdot}6H_2O$ in 2.0 M HCl) solutions were prepared as starting materials. A dropping funnel containing 50 mL of 1.45 M NH_4OH (ACS grade from EDM) was fitted to a 500 mL three-neck round bottom flask containing 200 mL Millipore water was stirred and maintained at 50–60 °C with an oil bath. The reaction system was oxygen free by purging with argon (99.999%). One mL of 2.0 M $FeCl_2{\cdot}4H_2O$ was added and then followed by 4.0 mL of 1.0 M $FeCl_3{\cdot}6H_2O$ (molar ratio of Fe^{2+}:Fe^{3+} is 1:2) whilst stirring and maintaining an argon gas purge. After stirring the mixture for 5 min. with continued stirring and purging, the NH_4OH was added drop-wise for about 45 min. The final solution (pH 10–11) was stirred vigorously for 1 h. Thereafter, the reaction was stirred without heating for 1 h. The magnetic material (magnetite) was washed with Millipore water at ambient pH, followed by methanol washing, with subsequent air-drying, and final treatment with vacuum oven drying at ambient temperature overnight. The overall product yield was 97.0%.

2.2. Synthesis of activated carbon-based magnetite composites

A similar synthetic procedure of preparing magnetite was applied as above (*cf.* Section 2.1). In the case of impregnation of magnetite onto activated carbon, 1.0 g of NORIT ROX 0.8 (as received from NORIT America: denoted as AC) was added in the flask with Millipore water before addition of $FeCl_2{\cdot}4H_2O$ and $FeCl_3{\cdot}6H_2O$ solution. By adjusting the molar ratio of $FeCl_2{\cdot}4H_2O$ and $FeCl_3{\cdot}6H_2O$ solution relative to the amount of AC, the magnetite-based composite with variable loading of AC was prepared. The ratio of magnetite in the AC (w/w%) was 32% (CM-32), 19% (CM-19), and 10% (CM10); where the sample ID is denoted in parentheses. The average overall product yield was 97.5%.

2.3. Goethite

Synthesis of nanoscale acicular goethite (α-FeOOH) was achieved by employing a 5/1 OH^-/Fe^{3+} molar ratio according to Eq. (2) [37].

$$3NaOH_{(aq)} + FeCl_{3(aq)} \rightarrow FeOOH_{(s)} + 3NaCl_{(aq)} + H_2O_{(l)} \quad (2)$$

10 mL of 4.0 M NaOH was added to 170 mL of Millipore water followed by 20 mL of 0.4 M $FeCl_3{\cdot}6H_2O$. The mixture was stirred vigorously at 30 °C for 24 h. Finally, the product was rinsed with Millipore water until the filtrate washings reached neutral pH. The material was air dried overnight before drying in a vacuum oven for 2 h at 55 °C.

2.4. Characterization of magnetite and its composites

2.4.1. Powder X-ray diffraction (PXRD)

PXRD measurements were conducted on a PANalytical instrument (Model: Empyrean, manufacturer: PANalytical, The Netherlands) fitted with Cu Kα and Co Kα X-ray irradiation sources. Data obtained from the iron oxides and the composite materials were compared to simulated data obtained from the X'Pert Highscore Plus software (Ver. 3.0b (3.0.2), PANalytical, Almelo, The Netherlands). PXRD was obtained and compared for synthesized samples of magnetite and its composites (CM-32, CM-19, and CM-10); whereas, a physical mixture of AC/magnetite 19% (w/w) were prepared by mixing commercial magnetite from Aldrich or goethite with NORIT ROX 0.8.

2.4.2. Raman spectroscopy

Raman spectra were acquired with a Renishaw Invia Raman Microscope. Raman shifts were obtained at ambient temperature by using a 514 nm Argon ion laser (optimized at 1 mW to prevent sample burning), 50× objective lens and 50 scans with a 10 s integration time. Raman spectra of magnetite, magnetite composites (CM-32, CM-19, and CM-10), NORIT ROX 0.8, the commercial magnetite (Aldrich, nanopowder <50 nm), and goethite were measured and compared.

2.4.3. Diffuse reflectance infra-red Fourier transform spectroscopy (DRIFTS)

Diffuse reflectance infrared Fourier transform (DRIFT) spectra were obtained with a Bio RAD FTS-40 spectrophotometer. Samples were diluted with KBr (FTIR grade; Alfa Aesar) by 10% and scanned (n = 256) from 4000 to 400 cm^{-1} (resolution of 4 cm^{-1}). DRIFTS spectra of magnetite, magnetite composites (CM-32, CM-19, and CM-10), NORIT ROX 0.8, commercial magnetite (Aldrich, nanopowder <50 nm), and goethite were measured and compared.

2.4.4. Thermogravimetric analysis (TGA)

TGA data was obtained with a TGA Q50 from TA Instruments using the procedure and mass flow control settings outlined in