Adsorption of arsenate on synthetic goethite from aqueous solutions

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Abstract

Goethite was synthesized from the oxidation of ferrous carbonate precipitated from the double decomposition of ferrous sulfate doped with sodium lauryl sulfate (an anionic surfactant) and sodium carbonate in aqueous medium. The specific surface area and pore volume of goethite were $103\,\mathrm{m^2\,g^{-1}}$ and $0.50\,\mathrm{cm^3\,g^{-1}}$. Batch experiments were conducted to study the efficacy of removal of arsenic(V) using this goethite as adsorbent for solutions with $5\text{–}25\,\mathrm{mg\,l^{-1}}$ of arsenic(V). The nature of adsorption was studied by zeta-potential measurements. The adsorption process followed by Langmuir isotherm and diffusion coefficient of arsenate was determined to be $3.84 \times 10^{11}\,\mathrm{cm^2\,s^{-1}}$. The optimum pH of adsorption was found to be 5.0. The kinetics of adsorption was evaluated with $10\,\mathrm{mg\,l^{-1}}$ and $20\,\mathrm{mg\,l^{-1}}$ of As(V) solutions and activation energy of adsorption, as calculated from isoconversional method was in the range of $20\,\mathrm{kJ\,mol^{-1}}$ to $43\,\mathrm{kJ\,mol^{-1}}$. This suggests that the adsorption process is by diffusion at the initial phase and later through chemical control. FT-IR characterization of arsenic treated goethite indicated the presence of both As—O—Fe and As—O groups and supported the concept of surface complex formation.
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1. Introduction

Arsenic is known to cause various ailments to humans ranging from skin rashes to carcinoma and its presence in exceedingly higher concentrations in drinking water poses threat to millions of people in West Bengal of India and Bangladesh [1]. United States Environmental Protection Agency (USPEA) has revised the maximum contaminant level for arsenic in drinking water from $50\,\mathrm{\mu g\,l^{-1}}$ to $10\,\mathrm{\mu g\,l^{-1}}$ because of its proven toxic effects on human health. Under reducing conditions, arsenic occurs in trivalent form (arsenious acid species) whereas the pentavalent state (arsenic acid species) is common in oxidizing conditions in aqueous systems [2]. In order to combat the problem of arsenic contamination, various treatment methods are proposed. The most common methods include the application of aluminum and iron salts that are used in water purification [3]. The removal of arsenic is accomplished by adsorption techniques wherein adsorbents such as amorphous ferric hydroxide [4], ferrihydrite [5], natural iron ores [6], ferruginous manganese ores [7], iron oxide coated polymers [8], lanthanum compounds [9], zero valent iron [10], silica containing iron oxide [11], activated carbon [12], have been recommended. In another study, it has been demonstrated that arsenic in the form of arsenate could be removed up to 95% by adsorption on to hardened paste of Portland cement [13]. Iron filings (40 mesh) immersed in water was used to remove arsenic in batch type adsorption and a removal efficiency of 90% was reported [14]. The arsenic uptake from aqueous solutions by iron bearing minerals such as goethite, lipidocrocite, mackinawite and pyrite was studied and found to be better [15]. In a comparative study [16], that evaluated the arsenic removal from water using a variety of adsorbents, viz., zirconia-impregnated activated carbon, AM3 (a commercial adsorbent comprising calcite, fluorite and iron oxide) and granules iron hydroxide (GIH), the sorption capacity was found to be 2.8 mg, 2.0 mg and 2.3 mg of arsenic per gram of adsorbent. It is observed that in most of these cases, the adsorption efficiency is dependent on the surface properties of the adsorbent such as specific surface area, surface charge, pore volume and pore sizes.

Among the various adsorbents, iron bearing minerals especially goethite was observed to be more effective and economically viable. Various synthesis methods of goethite [17] were reviewed and found that the particle size, shape and

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Nomenclature

a	amount adsorbed ($mg\,g^{-1}$)
a_s	amount of adsorbed at equilibrium ($mg\,g^{-1}$)
A	pre-exponential factor
C_e	equilibrium concentration of adsorbate
C_o	initial concentration of adsorbate
C_∞	concentration of adsorbate at infinite time
D	diffusion coefficient ($cm^2\,s^{-1}$)
E_a	activation energy ($kJ\,mol^{-1}$)
k	rate constant
K	adsorption coefficient
R	universal gas constant
x/m	adsorbate: adsorbent ratio ($mg\,g^{-1}$)
α	degree of adsorption or conversion fraction

surface area of goethite depend on the Fe(III):OH ratio, the rate of base titration of iron salt, temperature of neutralization and time of crystallization. Most of the synthesis methods were based on neutralization of ferric nitrate with an alkali and subsequent aging spanning from 20 h to 336 h. The specific surface area of goethite specimens obtained by the above method ranges from $11\,m^2\,g^{-1}$ to $150\,m^2\,g^{-1}$. In another method, goethite nano crystals with mean size ranging from 1 nm to 10 nm and specific surface area around $300\,m^2\,g^{-1}$ by hydrolysis of aqueous solutions of ferric salts followed by membrane purification and freeze drying was reported [18].

In the present investigation, the synthesis of goethite was carried out by oxidation of ferrous carbonate precipitated from ferrous sulfate solution doped with sodium lauryl sulfate and sodium carbonate solution, wherein CO_3^{2-}/Fe^{2+} molar ratio of the resultant solution was maintained at 1.0. The interaction of arsenate with goethite surface, the kinetics of adsorption process and the activation energy of adsorption by isoconversional method were also studied. An attempt was made to elucidate the mechanism of arsenic(V) adsorption on goethite synthesized from the oxidation of ferrous carbonate.
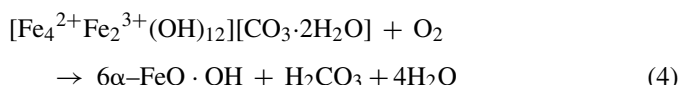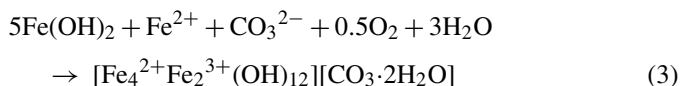
2. Experimental

2.1. Reagents

Electrolytic grade (99.9% purity) iron powder was treated with sulphuric acid to prepare 0.5 M ferrous sulfate solution. 2.0 M stock solutions of sodium carbonate and sodium hydroxide were prepared by using analar grade chemicals obtained from E. Merck sodium lauryl sulfate obtained from British Drug House (BDH) was used to prepare 1% (w/v) solutions. Arsenic(V) test solutions were prepared from H_3AsO_4 (E. Merck-NIST Certified: 1000 ppm As) standard reference solution. The test solutions were freshly prepared from the stock solution using double distilled water.

2.2. Preparation of goethite and its characterization

One hundred milliliters of sodium lauryl sulfate solution was added to 0.5 M ferrous sulfate under continuous stirring. Sodium carbonate (2.0 M) was added to ferrous sulfate solution through a burette under stirring conditions, till the slurry pH of 10.0 was obtained. At this juncture, ferrous ions were precipitated as ferrous carbonate in the form of a pale green precipitate. An aliquot portion of sodium hydroxide (2.0 M) was further added to the slurry to raise the pH to 12.0. Oxygen was passed through the solution using a perforated glass impinger and the rate of scrubbing was maintained at $2.0\,l\,min^{-1}$. The ferrous carbonate precipitated, dissolves partially to produce ferrous hydroxide and the oxidation triggers the formation of another compound known as Green Rust Carbonate (GRC1). With the onset of further oxidation, GRC1 was oxidized to iron oxy hydroxide (α-FeO·OH). The scrubbing time of oxygen was maintained for a period of 12 h. The precipitate was filtered and washed with copious amounts of double distilled water to get rid of excess alkali. The wet cake was dried at 90 °C for 6 h and a fine iron oxy hydroxide powder was obtained and preserved for adsorption studies. The sequence of reactions underlying the synthesis method can be written as follows:

$$FeCO_3 + OH^- \rightarrow FeOH^+ + CO_3^{2-} \tag{1}$$

$$FeOH^+ + OH^- \rightarrow Fe(OH)_2 \tag{2}$$

Green Rust Carbonate 1:

$$5Fe(OH)_2 + Fe^{2+} + CO_3^{2-} + 0.5O_2 + 3H_2O$$
$$\rightarrow [Fe_4^{2+}Fe_2^{3+}(OH)_{12}][CO_3 \cdot 2H_2O] \tag{3}$$

$$[Fe_4^{2+}Fe_2^{3+}(OH)_{12}][CO_3 \cdot 2H_2O] + O_2$$
$$\rightarrow 6\alpha\text{–FeO} \cdot OH + H_2CO_3 + 4H_2O \tag{4}$$

The Green Rust Carbonates are widely studied because of their occurrence in nature in hydromorphic soils and corrosion products of iron in carbonate/bicarbonate media. The specific surface area and pore volume of goethite were estimated by using ASAP-2020 Micromeritics BET Surface Analyzer and the same were found to be $103\,m^2\,g^{-1}$ and $0.50\,cm^3\,g^{-1}$, respectively. The particle size of goethite was measured using CILAS-1180 particle size analyzer. The mean size of goethite particles was found to be 8.77 μm. The iron oxide prepared was subjected to X-ray diffraction and the d values obtained were found to match with that of goethite.

2.3. Adsorption experiments

Known quantity of arsenic test solution was taken in 250 ml conical flask and its pH was adjusted to the desired value by using dilute NaOH/HCl. Known weight of goethite was added to the test solution and equilibrated for 1 h with the help of laboratory shaker at constant temperature. After the equilibration time of 1 h, the solutions were filtered through 0.2 μm membrane filter and filtrates were analyzed for arsenic.