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Synthesis of Mg(II) doped goethite and its cation sorption behaviour

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ABSTRACT

Modified goethite samples were prepared with Mg(II) content varying in the range of 0–1.36%. A typical TEM of Mg(II) doped sample showed needle shaped goethite particles having 10–30 nm width and 100–400 nm length. Sorption studies of cations namely Pb(II), Cu(II), Cd(II), Zn(II) and Fe(III) were conducted onto the Mg(II) doped modified goethite surface. Goethite doping with 0.18 M Mg (GMg_2) showed better sorption capacity for Pb(II), Cu(II) and Cd(II). Therefore, the effect of contact time, solution pH, sorbate and sorbent concentrations on the sorption of various metal ions was studied on this sample in batch experiments. The time data fitted to pseudo-second-order kinetics for all the metal ions. Sorption on GMg_2 sample for the metal ions increased with the increase in pH from 2 to 4. The isothermic data showed good fit to both Langmuir and Freundlich isotherms except for Cd(II) which followed only the later model. The sorption capacities with respect to Pb(II), Cd(II), Zn(II), Cu(II) and Fe(III) were found to be 87.7, 153.25, 86.25, 33.4 and 72.5 mg/g respectively. The results of sorption studies on GMg_2 from binary and ternary solutions have also been presented. The XRD patterns of metal ion loaded GMg_2 samples confirmed that metal ion adsorption resulted in shifting of *d*-values/altering of relative intensity (RI) of major planes of goethite.

1. Introduction

Goethite (α-FeOOH) is one of the most important iron oxides in terrestrial soils. It is found under a broad range of climatic and hydrologic conditions and is thermodynamically a stable oxide. Goethite has double bands of FeO(OH) octahedra which share edges and corners to form 2 by 1 octahedra tunnels (only large enough to accommodate the passage of protons) partially bonded by H bonds [1–3]. It is also one of the most important iron oxide surfaces, which incorporates a range of geo-chemically and environmentally important oxy-anions and cations in its complex matrix. Goethite is considered an important material which can control the sorption capacity of soils for toxic metals. The sorption of heavy metals on the outer surfaces of goethite is strongly influenced by their hydrolytic properties. Metals like Pb, Mn, Ni, Cu, Cd, Co with a high affinity for hydroxyl ions in solution also have a high affinity for the hydroxyl groups of the goethite. Due to this nature of goethite, considerable amount of research related to heavy metal sorption has been carried out on synthetic goethite [4–9], modified goethite [10], and goethite containing ore bodies/overburden materials [11,12]. Goethite can be modified by doping small amounts of metal ions such as Cu, Ni, Co [13]. In this paper modified goethite samples were prepared by doping different % ages of Mg(II) and the adsorptive behaviour with respect to Pb(II), Cd(II), Cu(II), Zn(II) and Fe(III) ions was evaluated. Heavy metal ion adsorption of Mg(II) doped goethite has not been reported earlier.

2. Experimental

2.1. Reagents and glassware

All chemicals used were of "AnalaR" reagent grade. Nitrate salts of Pb(II), Cd(II), Cu(II), Zn(II) and Fe(III) of E Merck, India were used to prepare stock solutions.

3. Synthesis, analysis and characterization of Mg(II) doped goethite samples

Mg(II) doped goethite samples were prepared using 1 M ferric nitrate and 10 M sodium hydroxide solutions under controlled conditions. Required quantities of ferric nitrate solution and $MgSO_4$ solution were vigorously stirred at room temperature and 10 M sodium hydroxide solution was added until the pH of the solution reached 12. The suspension so obtained was kept in a polythene bottle at 343 K for 24 h. The doped goethite samples were filtered and washed with water until the filtrate was free of nitrate and sulphate. The prepared products were dried at 373 K in an air oven for 24 h.

Known amounts of the samples were digested in hydrochloric acid and the solutions obtained thereof were analyzed volumetri-

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Table 1
Physico-chemical analysis.

Sample	% Fe	% Mg	pH_{PZC}
G	62.8	0	6.48
GMg_1	61.09	0.09	6.7
GMg_2	61.43	0.18	7.01
GMg_3	60.98	0.27	7.08
GMg_4	60.64	0.37	7.13
GMg_5	60.24	1.36	7.17

cally for iron [14]. The metal ions such as Pb, Cd, Zn, Fe, Cu and Mg, were estimated by atomic absorption spectrophotometer (AAS PerkinElmer AA 200 Model) after making proper dilutions.

The X-ray diffraction (XRD) measurements were taken over a range of 20–70° using Phillips Powder Diffractometer Model PW 1830 with CoK_α radiation at a scan speed of 1.2°/min. The surface morphology of a typical sample was studied using electron microscope (FEI Technai^{G2} 20 TWIN TEM).

3.1. Sorption experiment

Individual stock solutions containing 1000 mg/L of Cd(II), Pb(II), Cu(II), Zn(II) or Fe(III) were prepared from their nitrate salts. Metal ion solutions of required concentrations were prepared by diluting the stock solutions. Batch sorption experiments were carried out by shaking weighed amount of sample with 100 mL aqueous solution having desired initial concentration of the cation in a series of reagent flasks at different pH and constant speed of 165 RPM in a mechanical horizontal water bath shaker (Sonar, Delhi, India). A suitable volume of hydrochloric acid or sodium hydroxide solution was added to adjust pH that was measured with a digital pH meter (Systronic—pH System 361). The contents were then filtered and the metal ion concentration was estimated in the filtrate by atomic absorption spectrophotometer. Some of the experiments were carried out in duplicate for reproducibility.

4. Results and discussion

4.1. Chemical analysis and characterization of samples

The chemical analysis of prepared samples are summarized in Table 1. The pH_{PZC} of the samples have also been listed in the same Table 1. It is observed that the pH_{PZC} of the sample shifted to higher pH as the % Mg(II) increased in the goethite matrix. The XRD patterns of all Mg(II) doped synthetic samples along with pure goethite are shown in Fig. 1. All the diffraction peaks match well with the reported *d*-values of goethite (α-FeOOH—file number 81-0464). The peaks of Mg(II) loaded samples are sharper than the pure goethite and peak heights increased with the increase in % Mg(II) in the goethite matrix indicating higher crystallinity of goethite phase due to magnesium doping. Major plane of goethite (1 1 0) shifts by +0.008, +0.016, −0.012, −0.03, and −0.03 Å for samples containing 0.09, 0.18, 0.27, 0.37 and 1.36% Mg respectively. The +ve/−ve shift shows structural imbalance due to magnesium doping. Typical TEM micrograph of Mg doped goethite (GMg_2) is shown in Fig. 2. Needle shaped goethite particles having 10–30 nm width and 100–400 nm length were observed.

4.2. Comparative study of sorption behaviour of Pb(II), Cd(II), Zn(II), Cu(II) and Fe(II) on Mg(II) doped goethite samples

Fig. 3 shows the loading capacities of different Mg(II) doped goethite samples with respect to metal ions. During the sorption study the experimental conditions maintained were: contact time 60 min, sorbent concentration 2 g/L, temperature 308 K, metal ion concentration 100 mg/L and pH 4 except for Fe(III) where the pH maintained was 2.25 to avoid iron precipitation. Since Fe(III) hydrolyzes, polynuclear species such as $Fe_2(OH)_2^{4+}$, mononuclear species $FeOH^{2+}$, and $Fe(OH)_2^+$ are formed in acidic medium, while $Fe(OH)_3$ (aq) and $Fe(OH)_4^-$ are formed in neutral and basic medium [15]. Thus to correlate removal with sorption rather than precipitation, an initial pH chosen for the sorption of Fe(III) was 2.25.

It is observed that for Pb(II), Cd(II) and Cu(II) sorption, the loading capacities of Mg(II) doped goethite pass through maxima for the sample containing 0.18% Mg (GMg_2). On either side of this, the loading capacities decrease. Whereas in case of Fe(III) sorption, the loading capacity increased from 31 to 42.56 mg/g by increasing % Mg(II) from nil to 0.27 in goethite matrix and further increase in Mg content has only marginal effect. In case of Zn(II) sorp-

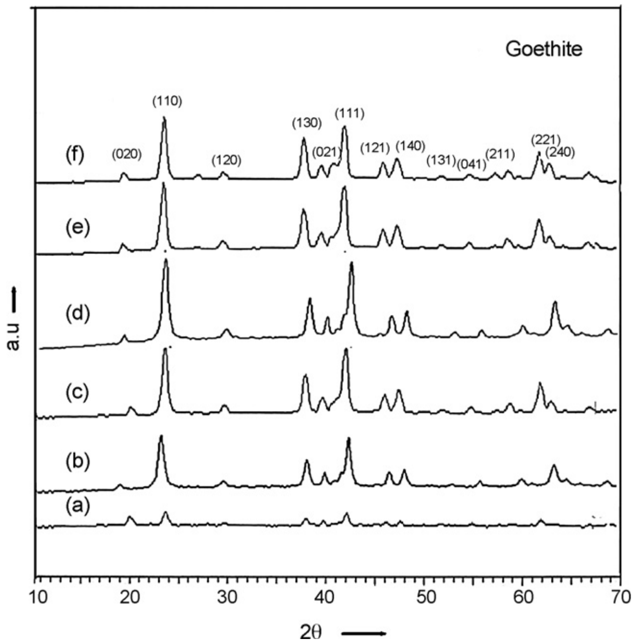

Fig. 1. XRD patterns of (a) G, (b) GMg_1, (c) GMg_2, (d) GMg_3 (e) GMg_4 and (f) GMg_5.

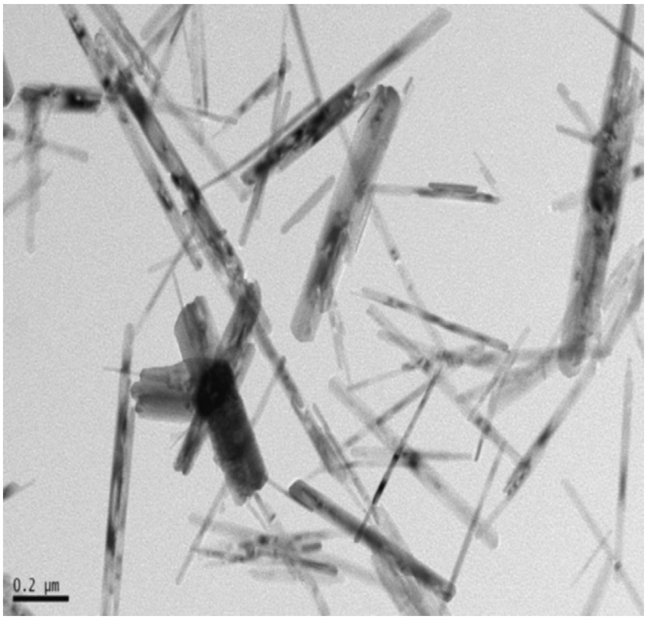

Fig. 2. TEM of GMg_2 sample (0.18% Mg).