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.

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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$_\alpha$ 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
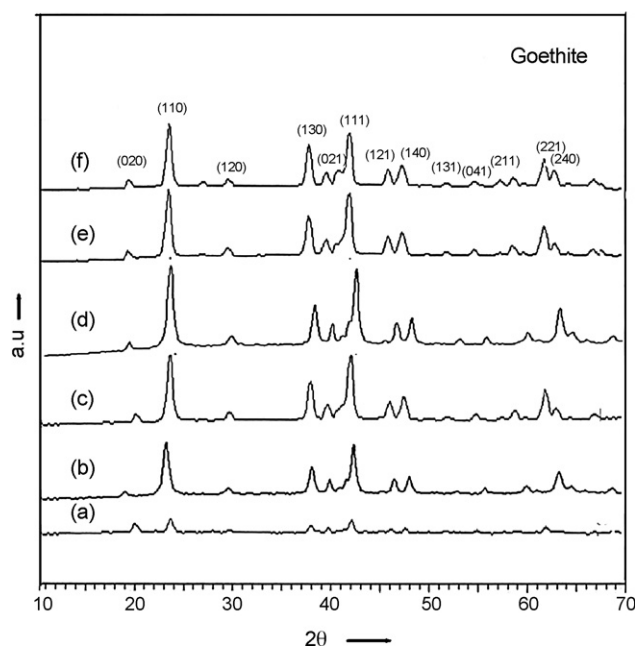
Fig. 1. XRD patterns of (a) G, (b) GMg$_1$, (c) GMg$_2$, (d) GMg$_3$ (e) GMg$_4$ and (f) GMg$_5$.

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-
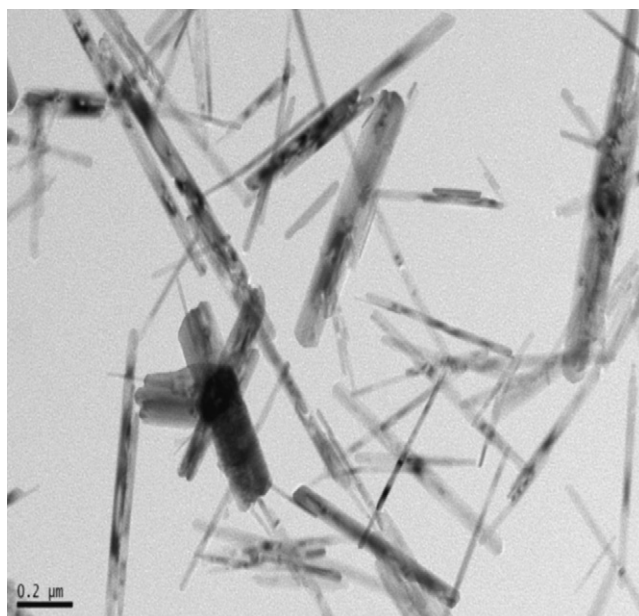
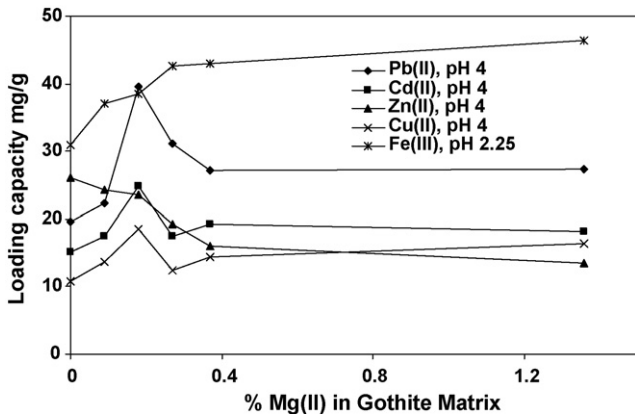**Fig. 2.** TEM of GMg$_2$ sample (0.18% Mg).

Fig. 3. Sorption capacities of Mg(II) doped goethite samples for Pb(II), Cd(II), Cu(II), Zn(II) and Fe(III).

tion the loading capacity decreased from 26 mg/g to 13.4 mg/g by increasing Mg(II) percentage from nil to 1.37 in goethite matrix. The solutions were tested for Mg after adsorption. At pH of 4 taking GMg$_5$ maximum Mg dissolution of 0.57 mg/L was observed for Cu(II) adsorption and for all other metal ions it was $\leq$0.15 mg/L. It has been reported that the magnesium loading on goethite increase the particle charge considerably and affects the electro static potential of 1-plane [16] which may be responsible for enhanced metal ion adsorption in general for doped samples. The maximum adsorption for Pb(II), Cd(II) and Cu(II) for sample GMg$_2$ could be due to maximum +ve shift observed at the major (1 1 0) plane of goethite. Ankomah [17] reported that Zn(II) sorption to goethite between pH 5.4 and 8.5 decreased in the presence of Mg(II) by as much as 31% in terms of surface coverage. During doping of Mg(II), Zn(II) sorption sites will be adversely affected thereby decreasing the Zn(II) sorption with increase in Mg content of the sample.

Since GMg$_2$ sample with 0.18% Mg(II) in goethite sample shows good loading capacity with respect to many metal ions, further sorption studies were carried out by taking GMg$_2$ sample as the sorbent.

4.3. Sorption studies on GMg$_2$ sample

4.3.1. Kinetic study

Figs. 4 and 5 show percentage Pb(II), Cd(II), Zn(II) and Cu(II) sorption vs. time plots for GMg$_2$ sample under the following conditions: sorbate concentrations 100 mg/L, sorbent concentrations 2 g/L, temperature 308 K and pH 4 and 5.25 respectively. The % Pb(II), Cd(II) and Zn(II) show rapid increase with the increase in contact
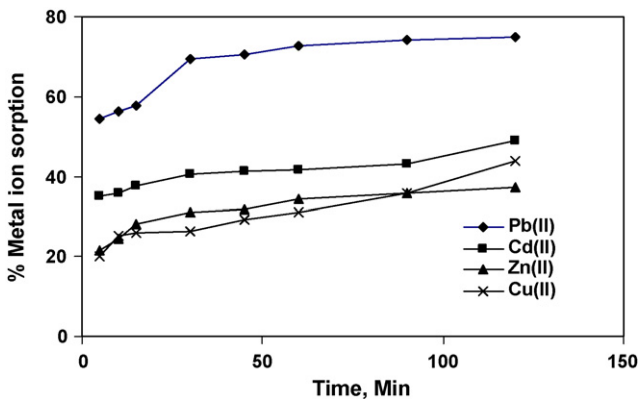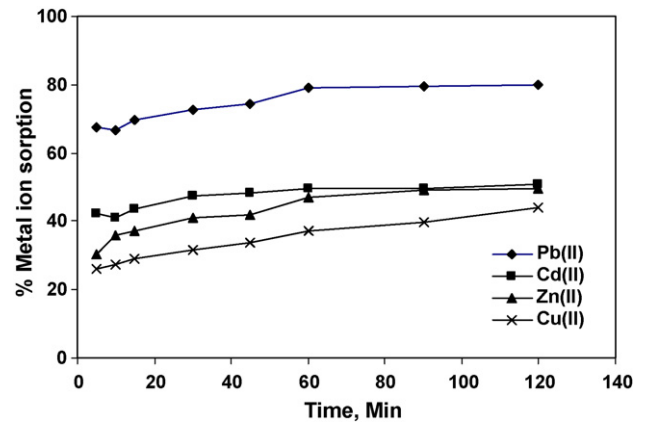

Fig. 5. Effect of contact time on metal ion sorption on GMg$_2$ sample. Conditions: sorbent concentration 2 g/L, temperature 308 K and pH 5.25.

time up to 30 min followed by only marginal increase up to 60 min. It indicates attainment of quasi equilibrium state in 30 min. However, in case of Cu(II) the % sorption increases with the increase in time up to 120 min. All the rest of experiments were conducted with a contact time of 30 min for comparison purposes. Fig. 6 shows % age Fe(III) sorption vs. t plots for GMg$_2$ sample under the same conditions as mentioned above except the initial pH of 2.25. The % Fe(III) sorption shows rapid increase with the increase in contact time up to 15 min followed by only marginal increase till 120 min.

Pseudo-second-order equation was employed to model the sorption data over the entire time range. The pseudo-second-order kinetic rate equation is generally expressed as follows [18]:

$$\frac{dq}{dt} = k(q_e - q)^2 \tag{1}$$

where k is the pseudo-second-order rate constant (g/mg/min). Integrating and applying boundary conditions as $t = 0$ and $q = 0$ to $t = t$ and $q = q_e$, Eq. (1) becomes:

$$\frac{t}{q} = \frac{1}{q_e}2k + \frac{t}{q_e} \tag{2}$$

The rate constant k can be obtained from the intercept of the linearised pseudo-second-order rate equation. The t/q_t vs. t plots shown in Figs. 7–9 give regression coefficient, r^2 values varying from 0.95 to 0.99. The kinetic parameters are given in Table 2. It is observed that the calculated values of q_e match well with the experimentally obtained values.
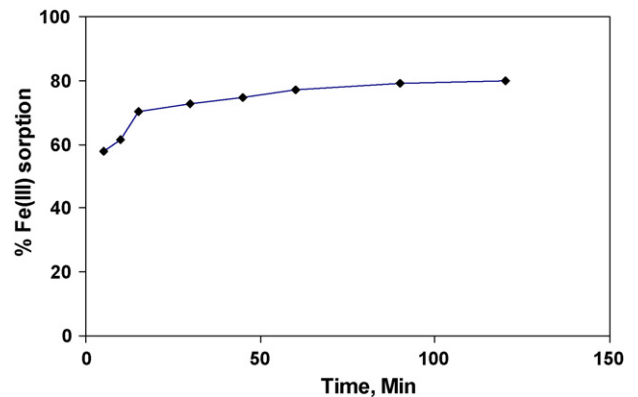

Fig. 4. Effect of contact time on metal ion sorption on GMg$_2$ sample. Conditions: sorbent concentration 2 g/L, temperature 308 K and pH 4.

Fig. 6. Effect of contact time on Fe(III) sorption on GMg$_2$ sample. Conditions: initial Fe(III) concentration 100 mg/L, sorbent concentration 2 g/L, temperature 308 K and pH 2.25.
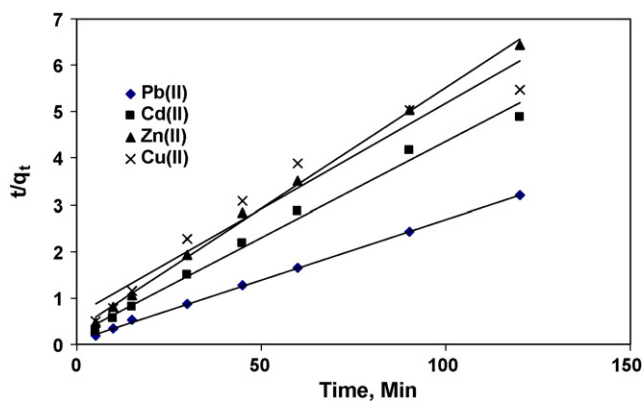
Fig. 7. Pseudo-second-order kinetic plot for GMg$_2$ sample (data correspond to Fig. 4).
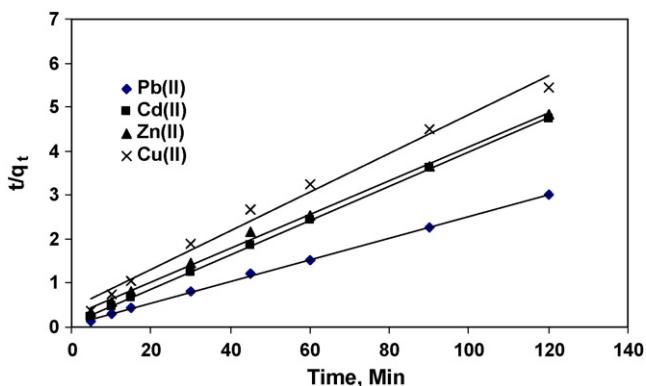

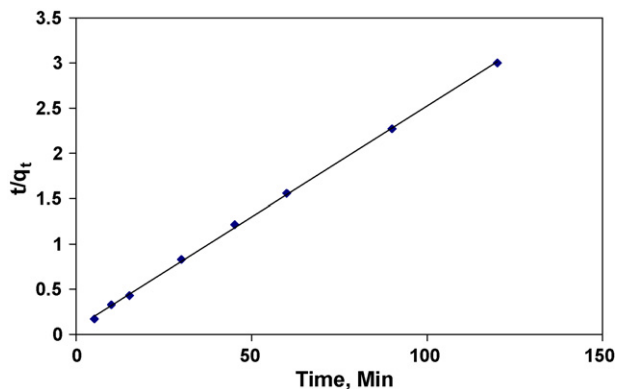**Fig. 8.** Pseudo-second-order kinetic plot for GMg$_2$ sample (data correspond to Fig. 5).

Fig. 9. Pseudo-second-order kinetic plot on GMg$_2$ sample (data correspond to Fig. 6).

Table 2
Kinetic data for adsorption of Pb(II), Cd(II), Zn(II), Cu(II) and Fe(III) on GMg$_2$.

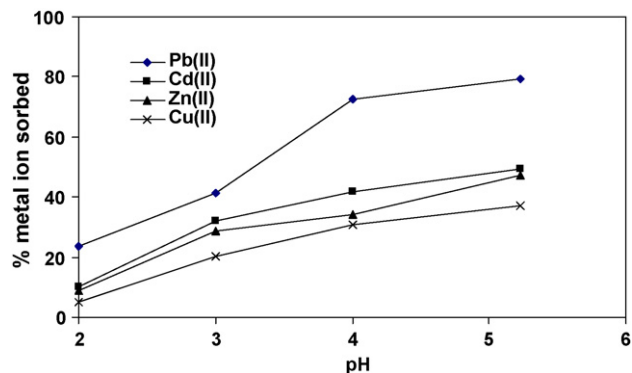|	Pb(II)	Cd(II)	Zn(II)	Cu(II)
pH	4.00			
q_{exp}	37.4	24.5	18.65	21.9
$k\,10^{-3}$ (g/mg/min)	7.3	8.03	8.14	3.25
q_e	38.46	24.15	19.26	21.9
r^2	0.99	0.99	0.99	0.95
pH	5.25			
q_{exp}	39.97	25.37	24.85	21.98
$k\,10^{-3}$ (g/mg/min)	10.06	16.81	6.39	4.76
q_e	40.65	25.70	25.90	22.57
r^2	0.99	0.99	0.99	0.98
Kinetic parameters for Fe(III) at pH 2.25				
q_{exp}	39.97			
$k\,10^{-3}$ (g/mg/min)	7.90			
q_e	40.81			
r^2	0.99			

Fig. 10. Effect of pH on sorption of Pb(II), Cd(II), Cu(II) and Zn(II) on GMg$_2$. Condition: sorbate concentration 100 mg/L, sorbent concentration 2 g/L, temperature 308 K and time 60 min.

4.3.2. Effect of pH

Metal uptake was studied at pH ranging from 2.0 to 5.25 (where chemical precipitation is avoided, so that metal removal could be related to the sorption process) at a temperature of 308 K. Pb(II), Cd(II), Zn(II) and Cu(II) sorption increased with the increase in pH from 2 to 4.0 (Fig. 10) and thereafter only marginal increase was observed with the increase in pH values to 5.25. Depending on the nature of metal ion adsorbed the Mg(II) concentration in solution after adsorption at initial pH of 2 was only 2.4–3.7 mg/L and at pH 3, it varied from 1.3 to 3 mg/L. At higher pH there was practically no dissolution of Mg(II) during adsorption.

4.3.3. Effect of sorbent dosage

The effect of the dosage of GMg$_2$ on the removal of Pb(II), Cd(II), Zn(II), Cu(II) and Fe(III) is shown in Fig. 11. Increasing the amount of sorbent at a constant pH and initial metal concentration, led to an increase in the percentage removal of Pb(II), Cd(II), Cu(II) and Fe(III) and then almost saturated with 3 g/L sorbent concentration (Fig. 11). In general % age adsorption would increase with the increase in adsorbent dose due to higher surface availability for the adsorbate [8] till all the metal ion from solution is completely adsorbed. In case of Zn(II), % age sorption passes through a maxima at 1 g/L sorbent dose without complete uptake of Zn(II) from solution. Decrease in % adsorption or constant % age adsorption without nearly 100% adsorption has not been observed earlier. It is difficult to explain the trend observed in the present studies though the results were confirmed by triplicate experiments.
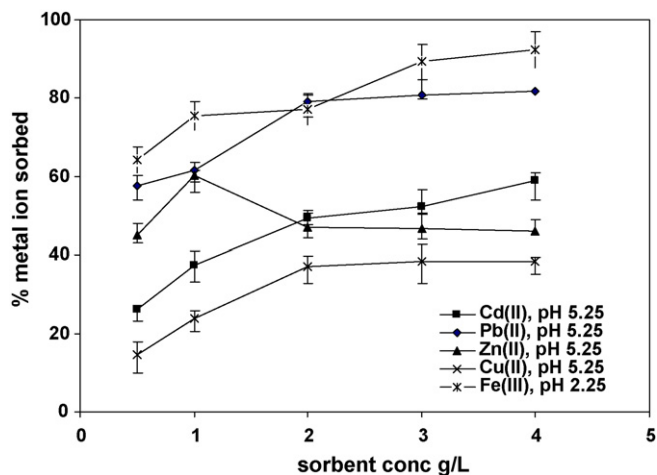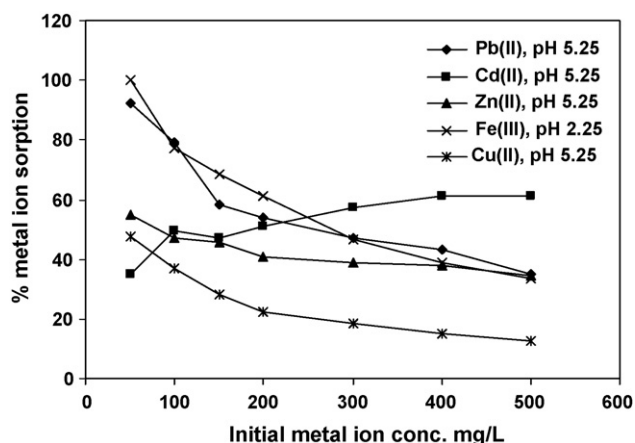

Fig. 11. Effect of sorbent dose on sorption of Pb(II), Cd(II), Cu(II) Zn(II) and Fe(III) on GMg$_2$. Condition: sorbate concentration 100 mg/L, temperature 308 K and time 60 min.

Fig. 12. Effect of sorbate concentration on sorption of Pb(II), Cd(II), Cu(II), Zn(II) and Fe(III) on GMg$_2$. Condition: sorbent concentration 2 g/L, temperature 308 K, pH 5.25 and time 60 min.

### 4.3.4. Effect of metal ion concentration

The effect of initial metal concentration on the amount of metal ions sorbed on GMg$_2$ at a fixed sorbent dose of 2 g/L and pH 5.25 (except Fe(III) where pH was maintained as 2.25) are depicted in Fig. 12. The results show that for Pb(II), Cu(II), Zn(II) and Fe(III) percentage of metal ion sorbed decrease with increasing initial metal concentration (Fig. 12). This behaviour was attributed to the existence of a range of intensities of binding between the metal ions and solid surface sites, as well as the more efficient utilization of the sorption capacities of the sorbent due to a higher concentration gradient pressure. However, in case of Cd(II) sorption there is increase in % age adsorption till initial metal ion concentration of 300 mg/L and then remains more or less constant. Consequently the loading capacities for Cd(II) would keep on increasing with increase in initial metal ion concentration and will not reach the maxima, hence this trend is observed for Cd(II) adsorption. From Fig. 12, the maximum sorption capacity with respect to Pb(II), Cd(II), Zn(II), Cu(II) and Fe(III) metal ions are found to be 87.7, 153.25, 86.25, 33.4 and 72.5 mg g^{-1} respectively. Converting the sorption capacities in mg/g to mmol/g, the sorption order is established as: Cd(II) > Zn(II) > Fe(III) > Cu(II) > Pb(II). However, Kooner [19] investigated the comparative sorption of copper, lead, and zinc by goethite and found that the affinity order was Cu(II) > Pb(II) > Zn(II) at pH 6.0. Other researchers have also reported that metal affinity for goethite is generally, with slight variations, found to follow the order Cu > Pb > Zn > Cd [7,9,20]. Schwertmann and Taylor [9] observed their trend to be consistent with electronegativity, while Christophi and Axe [21] found it to be in agreement with the hydrated radii of the cations.

Langmuir-type and Freundlich-type sorption isotherms have commonly been used to model data obtained in sorption studies. The sorption equations are:

Langmuir $$\frac{C_e}{q_e} = \frac{1}{(bq_m)} + \left(\frac{1}{q_m}\right)C_e \qquad (3)$$

Freundlich $$q_e = K_f C_e^n \qquad (4)$$

where q_m, is the monolayer sorption capacity (mg/g) and 'b', the constant related to the energy of sorption (L/g), K_f indicates sorption capacity (mg/g) and 'n' an empirical parameter related to the intensity of sorption, which varies with the heterogeneity of the sorbent. For 'n' values in the range 1–10 ($0.1 < 1/n < 1$), sorption is favorable. The greater the values of 'n' better is the favorability of sorption. The Langmuir and Freundlich parameters (Figs. 13 and 14 respectively) for Pb(II), Cd(II), Cu(II), Zn(II) and Fe(III) are given in Table 3 with their correlation coefficients. It is clear from Table 3
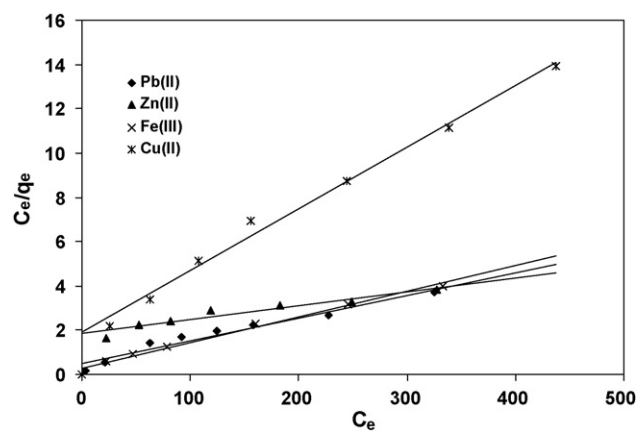
Fig. 13. Langmuir sorption isotherm (data correspond to Fig. 12).
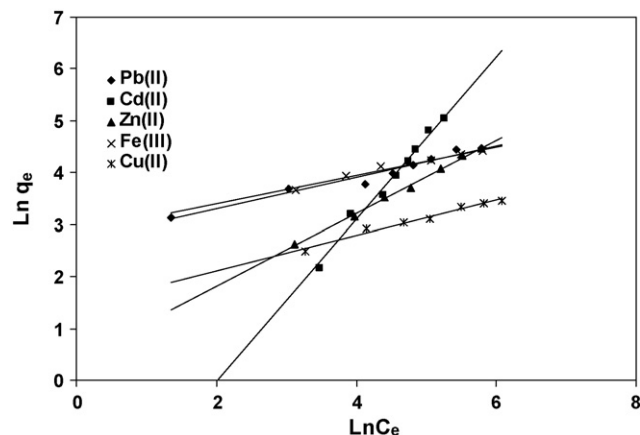
Fig. 14. Freundlich sorption isotherm (data correspond to Fig. 12).

that except in case of Cd(II) sorption (which shows good fit only to Langmuir model), the data fit very well to both the isothermic models.

4.3.5. Sorption from binary and ternary solutions

To study the effect of presence of Cu(II), Cd(II) or Zn(II) on Pb(II) sorption, binary solutions of metal ions keeping the concentration of each metal ions 100 mg/L were taken as the sorbate. The results are shown in Table 4. It is observed that % Pb(II) sorption is adversely affected in the presence of Cu(II) and Zn(II) whereas in the presence of Cd(II), lead sorption increases. Presence of Pb(II) is highly detrimental to the sorption of three metal ions namely Cu(II), Cd(II) and Zn(II) with their sorption decreasing from 37 to 22.5%, 49.5 to 18.05% and 47 to 0% respectively. From the ternary solutions containing Pb(II), Cd(II) and Zn(II), Pb(II) sorption was only 39.27% with absolutely no uptake of Cd(II) or Zn(II). Presence of Cd(II) increased Pb(II) adsorption. These studies are indicative of selective uptake of lead from mixed solutions which can be applied

Table 3
Langmuir and Freundlich parameters for adsorption of cations on GMg$_2$.

Cations	Langmuir coefficients				Freundlich coefficients		
	q_m (mg/g)	b (L/g)	r^2	R_L	K_f (mg/g)	n	r^2
Pb(II)	98.03	0.02	0.95	0.33	14.64	3.28	0.96
Cd(II)	–	–	–	–	23.93	0.638	0.98
Zn(II)	158.73	0.003	0.91	0.65	1.5	1.42	0.99
Cu(II)	35.97	0.014	0.99	0.65	4.179	2.94	0.97
Fe(III)	90.9	0.026	0.99	0.29	17.04	3.6	0.98

Table 4
Results on sorption from binary and ternary solutions on GMg₂.

System	% Pb(II) sorption	% Cu(II) sorption	% Cd(II) sorption	% Zn(II) sorption
Pb(II) + Cu(II)	18.75	22.5	–	–
Pb(II) + Cd(II)	87.95	–	18.05	–
Pb(II) + Zn(II)	36.25	–	–	Nil
Pb(II) + Cd(II)+Zn(II)	32.97	–	Nil	Nil

Sorption from single metal ion solutions with initial concentration as $100\,mg\,L^{-1}$. Pb(II) 79.2%, Cd(II) 49.5%, Cu 37% and Zn 47%.

Table 5
Relative intensities and shifting of peaks XRD data of Fig. 15.

Sample	(1 1 0)		(1 1 1)		(1 3 0)		(2 2 1)	
	% RI	Shift (Å)	% RI	Shift (Å)	% RI	Shift (Å)	% RI	Shift (Å)
GMg₂ [a]	100	–	83	–	54	–	36	–
GMg₂ (Pb loaded)	100	(+0.08)	83	(+0.006)	56	37		
GMg₂ (Cd loaded)	100	–	90	–	53	–	35	–
GMg₂ (Zn loaded)	100	(+0.06)	89	(+0.02)	53	(+0.016)	35	(+0.026)
GMg₂ (Cu loaded)	100	–	91	–	46	–	31	–
GMg₂ (Fe loaded)	100	–	60	(−0.014)	40	(−0.01)	29	(−0.008)

[a] GMg₂ has been taken as reference for comparing shift.
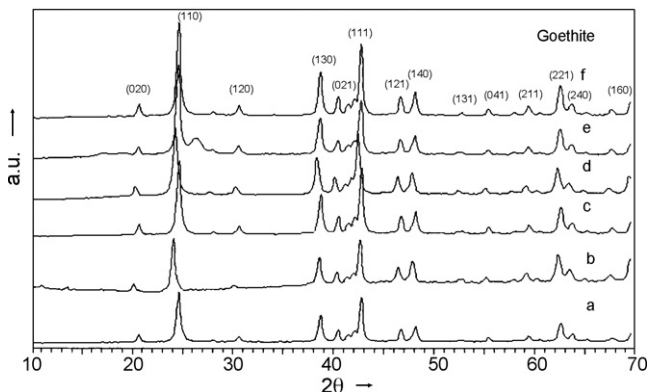
Fig. 15. XRD patterns of (a) original GMg₂ and metal ions loaded GMg₂ sample (b) Pb (II), (c) Cd(II), (d) Zn(II), (e) Fe(III) and (f) Cu(II).

for removal of Pb(II) from aqueous solutions containing Pb(II), Cd(II) and Zn(II).

4.3.6. XRD studies of the metal ions sorbed GMg₂ samples

The XRD patterns of original GMg₂ sample along with metal ion loaded sample are shown in Fig. 15. The XRD analysis shows the presence of goethite phase in all the metal loaded samples. The shifting of various major peaks and their relative intensities are given in Table 5. It is observed that during adsorption either the shift in d-values of certain planes takes place or the relative intensities are altered. In case of Pb(II) adsorption +ve shifts in (1 1 1) and (1 1 0) planes are observed. For Zn adsorption shifts in all the four major planes are observed. Pb(II) and Cd(II) adsorption takes place with altering of % RI values whereas −ve shifts in d-values of three planes are observed for Fe(III) adsorbed GMg₂ sample.

5. Conclusions

Six samples of crystalline goethite with % Mg as 0, 0.09, 0.18, 0.27, 0.37 and 1.36% were synthesized. Comparative studies on sorption of Pb(II), Cd(II), Cu(II), Zn(II) and Fe(III) on various samples showed that the sample having 0.18% Mg gave maximum loading capacities for all the cations except for Fe(III) and Zn(II). In case of Fe(III) sorption, loading capacity increased with the increase in Mg content whereas reverse trend was observed for Zn(II) sorption. The time data for GMg₂ sample fitted to pseudo-second-order kinetics for all the cations. Sorption of all metal ions on Mg(II) (0.18%) sample increased with the increase in pH from 2 to 4. The isothermic data fitted well to both Langmuir as well as Freundlich models except for Cd(II) sorption which showed good fit only to the later model. Sorption from aqueous solutions containing two or three cations at a time gave interesting results. Pb(II) adsorption increased in the presence of Cd(II) while presence of Zn(II) or Cu(II) exhibited adverse effect on Pb(II) sorption. From a solution containing Pb(II), Zn(II) and Cd(II) only lead ion was sorbed indicating selectivity of the sample. The XRD patterns of metal ion loaded samples showed that during adsorption either the d-values of major planes are shifted or the relative intensities alter.

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