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A comparative study on Pb(II), Cd(II), Cu(II), Co(II) adsorption from single and binary aqueous solutions on additive assisted nano-structured goethite

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Abstract

Development of low cost adsorbents for mitigation of toxic ions is one of the most important areas of research and development. Iron oxides especially in nano form have the potential for removing cations due to their structural properties. In the present work additive assisted nano structured goethite was synthesized at pH 3.0 and its cation adsorption behaviour was studied for Pb(II), Cd(II), Cu(II) and Co(II) from single and binary aqueous solutions. The contact time data for single cation adsorption followed pseudo second order kinetic model for all the four cations. The isothermic data was fitted to Langmuir and Freundlich models. The experimentally obtained maximum loading capacities were estimated as 109.2, 86.6, 29.15 and 37.25 mg/g of goethite for Pb(II), Co(II), Cd(II) and Cu(II) respectively from single cation containing solutions. Thermodynamic parameters were evaluated for the four metal ions. Adsorption behaviour from binary solutions was studied by keeping the concentration of Pb(II) at saturation concentration (500 mg/L) for its maximum uptake and varying the concentration of other metal ions (one at a time) in the range of 25 to 200 mg/L. The Pb(II) loading capacity increased in the presence of Cd(II) or Co(II) while it decreased in the presence of Cu(II) in the studied range of concentration variation. Maximum Pb(II) uptake was observed from Pb(II)-Cd(II) binary system (222 mg/L) with Pb(II) and Cd(II) concentration as 500 and 200 mg/L respectively. An increase in the combined uptake capacities for Pb(II)-Cd(II) and Pb(II)-Co(II) binary systems were observed whereas a decrease was observed for Pb(II)-Cu(II) binary system. The synthesized goethite can be used effectively for cation removal from single/binary cation containing aqueous solutions.

Keywords: Nano goethite; TEM, adsorption; cations; binary; kinetics

1. Introduction

The rapid growth of industrial activities during the last few decades is one of the major reasons for pollution of water, air and soil. Effluents from metallurgical, chemical, ceramics, electro-galvanization and textile industries are the main sources of water contamination. According to the World Health Organization (WHO, 1984), the metals of most immediate concern are lead, cadmium, copper, cobalt, aluminium, chromium, manganese, iron, nickel, zinc and mercury. Various treatment techniques including adsorption, precipitation, ion exchange and reverse osmosis have been employed to eliminate or reduce the toxic ion concentrations in wastewaters. Adsorption on solid surfaces is the most common one and efforts are being made continuously to develop new, low cost and efficient adsorbents for removal of heavy metals. Several low cost adsorbents such as agriculture wastes (Sud *et al.,* 2008), natural clay, soils, low grade ores (Huang and Fuerstenau, 2000; Babel and Kurniawan, 2003; Dong *et al.*, 2007; Mohapatra and Anand, 2007; Mohapatra *et al*., 2007; Samir Abu-Eishah, 2008; Mohapatra *et al.,* 2009a; Serrano *et al.,* 2009) and industrial wastes (Gupta and Sharma, 2002; Agrawal and Sahu, 2006; Wang *et al*., 2008; Xue *et al.,* 2009; Mohapatra *et al*., 2009b) have been projected as potential adsorbents for mitigation of toxic cations from aqueous streams.

Iron oxides/hydroxides/oxyhydroxides form an important category of low cost adsorbents for removal of heavy metals and organic compounds form wastewater (Venema *et al*., 1998; Fendorf *et al.,* 1997; Heijman *et al*., 1999, Sen *et al.,* 2002; Glover *et al.*, 2002; O'reilly and Hochella , 2003; Pan *et al.,* 2010). Goethite, α-FeOOH, one of the most important iron oxyhydroxide, having double bonds of FeO(OH) octahedra which share edges and corners to form 2 by 1 octahedra tunnels partially bonded by H

bonds (Schwertmann and Cornell, 1991; Grossl and Sparks, 1995; Cornell and Schwertmann, 1996) possesses the capability of incorporating a range of environmentally important oxy-anions and cations in its complex matrix. Hence, it can be used as an adsorbent. Mohapatra and Anand (2006) synthesized goethite and studied kinetic and thermodynamic aspects of cadmium adsorption. Khatun *et al.* (2007) reported Pb(II) adsorption on goethite. In another publication (Mustafa *et al.,* 2004), synthetic goethite prepared by ageing a ferric hydroxide gel at high pH and room temperature was used for Cd adsorption and desorption studies in presence of sodium and calcium ions. Forbes *et al.* (1976) synthesized goethite to study adsorption of Cd, Co, Cu, Pb and Zn. Amorphous iron oxide was used by Benjamin and Leckie (1981a). Improved adsorption capacities could be achieved by modifying goethite either by pre treating or by doping with other metal ions. Phosphate pre-treated goethite enhanced metal ion adsorption (Venema *et al.,* 1997; Collins *et al.,* 1999; Wang and Xing, 2002). With the increase of phosphate higher Zn adsorption (Jie *et al.,* 2000) has been reported. Depending on the way goethite was pretreated with oxalic acid, affinity for Cd(II) varied (Zhang *et al.,* 2001). Mamata *et al.* (2009c) succeeded in doping synthetic goethite with Mg(II) and studied its effectiveness in removing cations. In the present work nano structured goethite prepared by a novel technique using hydrazine sulphate as an additive (Mohapatra *et al.,* 2010) has been used as an adsorbent for Pb(II), Cd(II), Cu(II), Co(II) removal.

Further, it is observed that usually the effluents and contaminated waters contain more than one toxic cation. It is therefore important, to investigate the adsorption characteristics from single and binary cation containing solutions. Recently, a number of studies have appeared dealing with adsorption of heavy metals from binary or tertiary cation containing aqueous systems (Lee and Allen 2001; Jeon *et al.,* 2003; Juang and Chung, 2004; Vılar *et al.,* 2008; Kongsuwan *et al.,* 2009; Swayampakulaa *et al*., 2009). The present investigations also address the adsorption behaviour of cations from binary aqueous solutions.

2. Materials and Methods

The surface modified goethite was synthesized by taking 100 mL of 1M iron nitrate solution in a conical flask followed by addition of 7.5 g of $N_2H_6SO_4$ with continuous stirring (Mohapatra *et al.,* 2010). The colour of the solution changed from reddish brown to yellowish brown. The clear solution was heated at 363 K for one hour in a closed reactor and cooled followed by pH adjustment to 3.0 by drop-wise addition of 1M NaOH solution. The precipitate was filtered and washed with distilled water till free of sulphate and nitrate and was dried for 24 h at 373 K. Samples were prepared in five batches, mixed and used for chemical analysis, characterization and adsorption studies.

The initial metal ion stock solutions were prepared from their respective nitrate salts. The pH of the initial metal ion solutions was adjusted, when needed, by addition of hydrochloric acid (0.1N) or sodium hydroxide solution (0.01 M) and was measured with a Systronic pH instrument. A known weight of goethite sample was taken in 100 mL conical flask and predetermined volume of cation stock solution was added at required pH. The contents were agitated in a PID controlled (temperature controller system offering adjustable proportional, integral and derivative) horizontal shaker (160 rpm) for desired time period. After the adsorption experiment the suspension was filtered through a 0.45µm membrane filter. The residual metal ions in the filtrate were analyzed after proper dilutions by Atomic Absorption Spectrophotometer Perkin- Elmer Model AA 200 (AAS).

Transmission Electron Microscopy (TEM) of the typical sample was studied using electron microscope (FEI Technai^{G2} 20 TWIN TEM). Infrared spectra of the synthesized samples were measured from 400 to 4000 cm^{-1} using a JASCO Model 5300 spectrometer in a KBr matrix. A pH-meter (Model: LI-127, ELICO India) was used for pH measurements.

3. Results and Discussion

3.1 The physico chemical characteristics of the adsorbent

The chemical analysis of the prepared sample showed that it contains 61.78% of iron as Fe(III) with no ferrous iron. The XRD pattern of the synthetic material corresponded to α-FeOOH (Mohapatra *et al.,* 2010). The formation of pure goethite phase is also supported by IR studies. A very strong and broad band at 3150 cm^{-1} with a shoulder at 3390 cm^{-1} (Figure 1) correspond to OH stretching mode in goethite and to the stretching mode of surface water molecules or to the hydrogen-bonded surface OH groups (Ruan *et al.,* 2002). The 1627 cm^{-1} sharp band can be ascribed to the bending mode of H_2O molecules (Gotic *et al.,* 2008). The characteristic sharp bands at 799 cm^{-1} and 890 cm^{-1} can be assigned to the Fe−O−H bending vibration of goethite. The 608 cm^{-1} and 470 cm^{-1} band are ascribed to Fe−O stretching vibrations of goethite lattice (Parida and Das, 1996). This band is affected by the shape of the goethite particles (Parida and Das, 1996; Ruan *et al*., 2002). The FT-IR spectrum showed bands at 1140, 1090 and 1017 cm^{-1}which can be assigned to sulphate (Music *et al.,* 2000). The TEM micrograph (Figure 2) confirms the nano particles with size variation in the range of 2 to 10 nm.

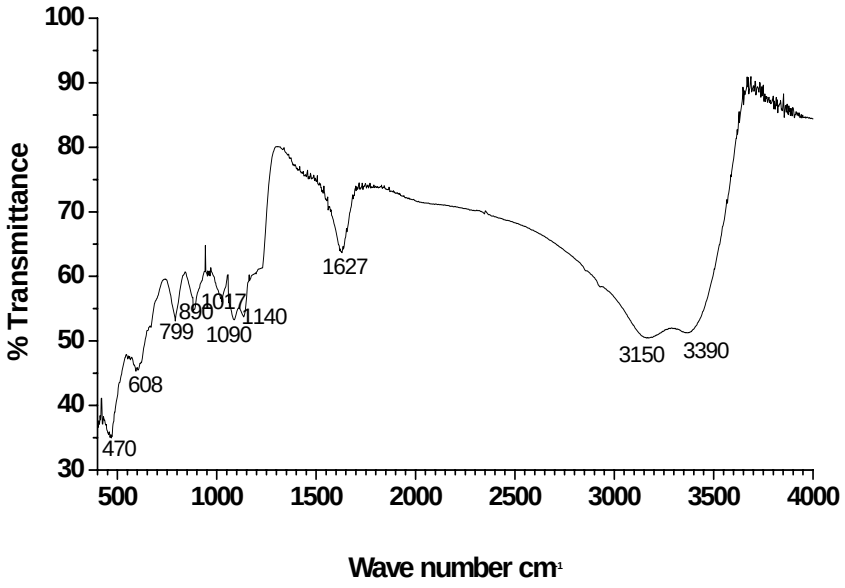

Figure 1. FTIR spectra of goethite sample

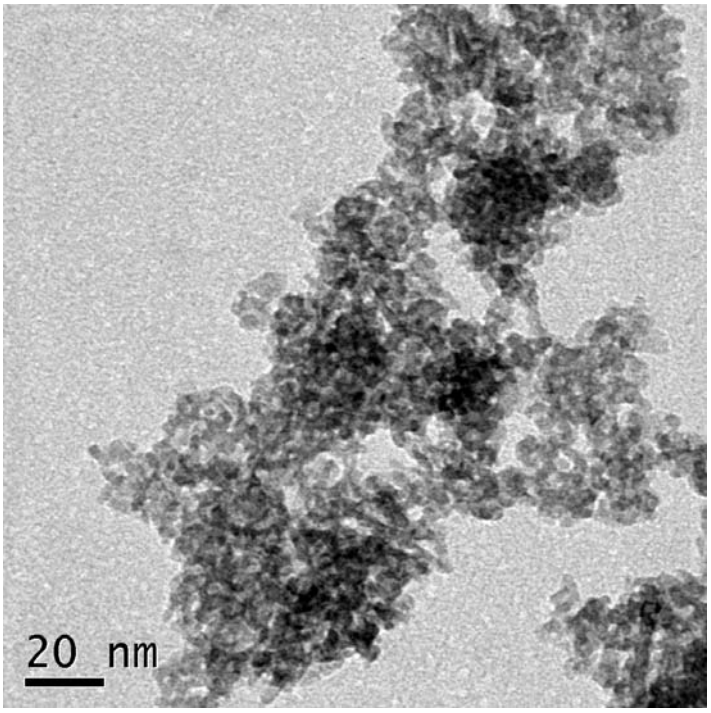

Figure 2. TEM of goethite sample dispersed in methanol for sonicating.

3.2 Pb(II), Cd(II), Cu(II) and Co(II) adsorption from single cation system

3.2.1 Adsorption kinetics

The adsorption of Pb(II), Cd(II), Cu(II) and Co(II) on the synthesized goethite as a function of time was investigated (Figure 3) under the conditions: adsorbent concentration 2 g/L, adsorbate concentration 100 mg/L and temperature 308 K. Within one hour maximum adsorption takes place for all the four cations indicating achievement of quasi equilibrium within one hour. Further increase in contact time has no significant effect on percentage adsorption.

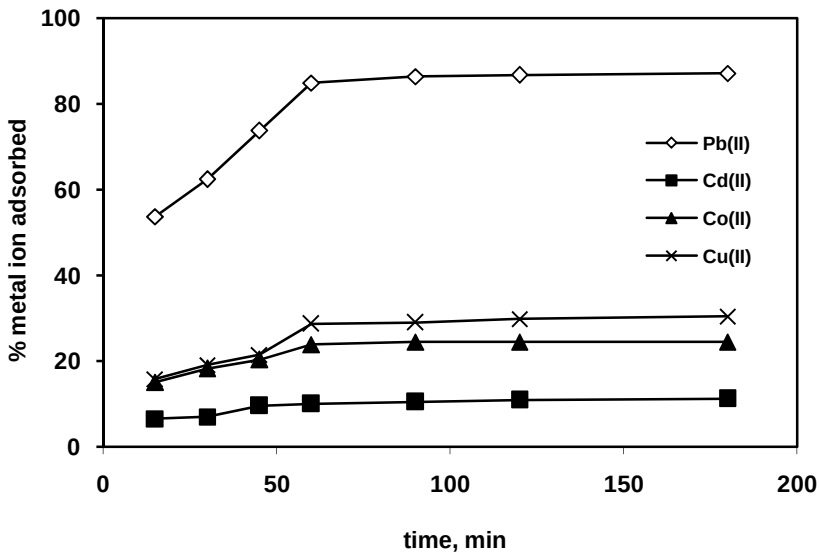

Figure 3. Effect of contact time on cation adsorption. Conditions: adsorbent dose 2 g/L, initial cation concentration 100 mg/L, temperature 303 K and pH 5.0.

The time data upto 180 minutes was tested for the following two kinetic models:
Pseudo-first-order rate equation of Lagergren

$$log(q_e-q_t) = logq_e - k_1/2.303 \times t \quad (1)$$

Pseudo-second-order rate equation

$$t/q_t = 1/k_2q_e^2 + 1/q_e \times t \quad (2)$$

where q_e and q_t are the amounts of the metal ions adsorbed (mg/g) at equilibrium and at time t (min), respectively. k_1 is the adsorption rate constant (L/min) for 1st order kinetic, k_2 (g/mg. min) is the rate constant of pseudo-second-order adsorption reaction. The plots of first order kinetics [log ($q_e - q_t$) vs. t], and 2nd order kinetics [t/q_t vs. t] are given in Figures 4 and 5 respectively.

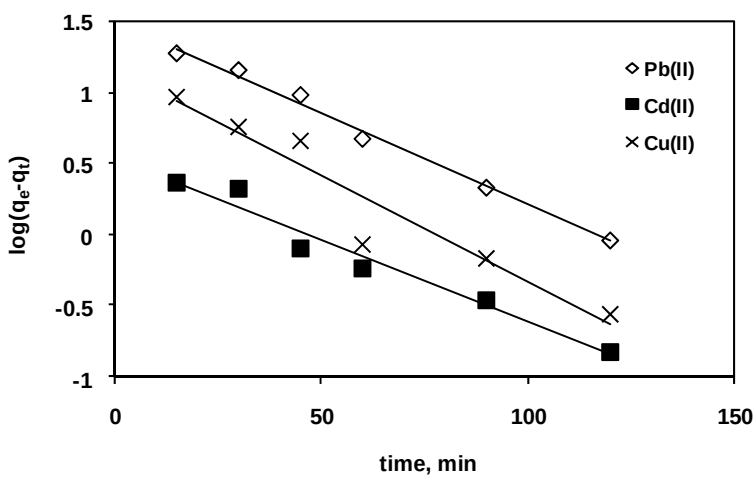

Figure 4. Pseudo first order kinetic plot of cation adsorption for goethite. (data correspond to Figure 3)

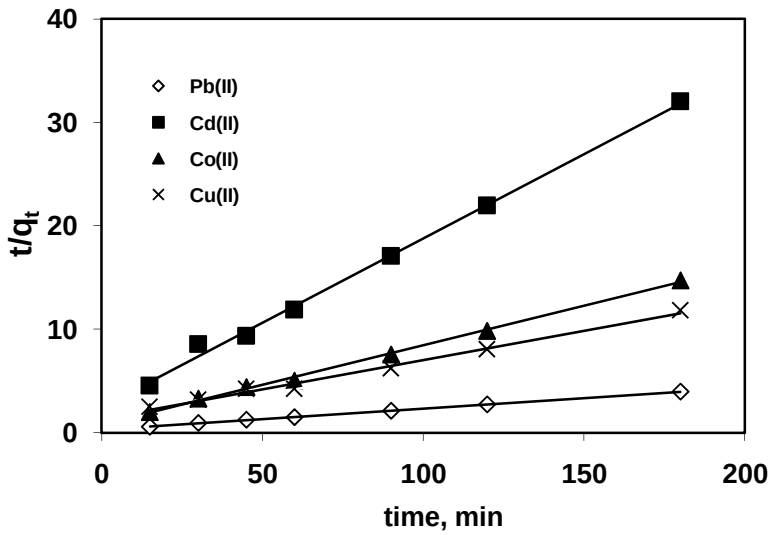

Figure 5. Pseudo second order kinetic plot of cation adsorption for goethite (data correspond to Figure 3)

The kinetic parameters for two kinetic models and correlation coefficients of metal ions were calculated from these plots and are listed in Table 1. It is observed that (i) r^2 values for the first order kinetics for Pb(II), Cd(II), Cu(II) vary in the range of 0.92 to 0.99 but in case of Co(II) r^2 value was only 0.41 (plot not shown in Figure 4) and the predicted loading capacities especially for Pb(II) and Cd(II) show wide variations when compared with the experimental values, (ii) r^2 values of >0.99 for all the four cations are obtained from pseudo second order reaction plots and the q_e values are comparable with the experimental values which suggest the applicability of this kinetic model. A number of studies on adsorption of cations on iron oxide/hydroxide surfaces have reported kinetics being controlled by pseudo second order model and chemisorption nature of the adsorbed species (Zhang *et al.,* 2001; Mohapatra and Anand, 2006; Mohapatra and Anand, 2007; Mohapatra *et al.,* 2007; Samir Abu-Eishah, 2008; Serrano *et al*., 2009; Mohapatra *et al.,* 2009a; Mohapatra *et al.,* 2009c).

Table 1. Kinetic parameters for adsorption of various cations on goethite from single cation containing solutions

	Pb(II)	Cd(II)	Cu(II)	Co(II)
q_{exp}, mg /g	45.28	5.66	15.2	12.23
pseudo 1 st order				
$k_1.10^{-2}$ (/min)	2.97	2.64	3.43	2.00
q_e, , mg/ g	31.44	3.42	14.29	-
r^2	0.99	0.96	0.92	0.41
pseudo 2 nd order				
$k_2.10^{-3}$ (g/mg/min)	1.40	10.89	2.40	7.314
q_e, , mg/g	46.26	6.12	17.60	13.10
r^2	0.998	0.996	0.991	0.997

3.2.2 Effect of initial pH

The effect of pH on the removal of all four cations is studied over a pH range of 2 to 5.25. As shown in Figure 6, a general increase in adsorption with increasing pH of solution was observed for all the metal ions up to a pH value of 5.25.A similar behaviour has been reported by many authors (Zhang *et al.,*2001; Angove *et al.,* 1999; Mohapatra *et al.,* 2007; Benjamin and Leckie, 1981a) for the uptake of metal ions on various adsorbents. At low pH, the percentage adsorption is low for these metal ions, as large quantities of protons compete with metal cations for the adsorption sites. According to Low *et al.* (1995), at low pH value the surface of the adsorbent, would be closely associated with hydronium ions (H_3O^+) and hold mainly protonated sites as a result, the surface maintains a net positive charge. Hence it hinders the access of the metal ions to the surface functional group.

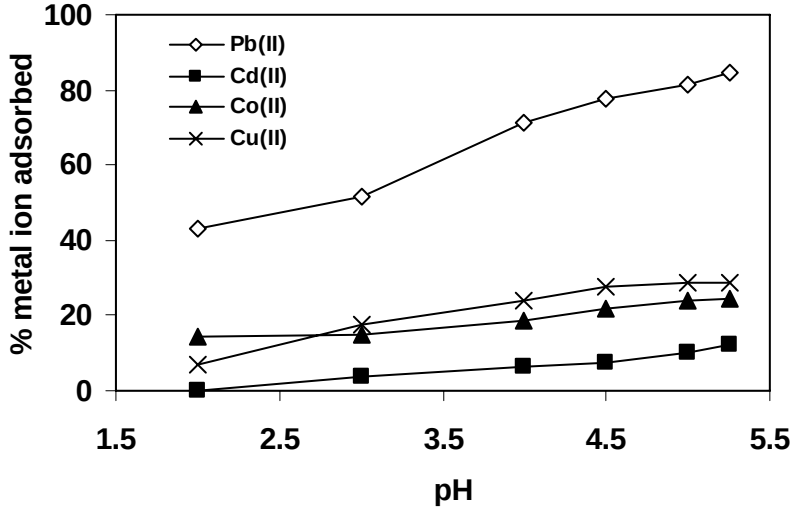

Figure 6. Effect of pH on metal ion adsorption. Conditions: adsorbent dose 2 g/L, initial cation concentration 100 mg/L, temperature 303 K, contact time 1 h.

Consequently the percentage of metal ion removal may decrease at low pH. The positive charge on adsorbent surface, however, gradually decreases as pH increases, thus reducing the electrical repulsion between sorbing surface and cations. Moreover, lower H^+ concentration also favors cation sorption by mass action. For example, the adsorption of bivalent cations such as M^{2+} on iron oxide can be written as:

$$FeOH_2^+ + M^{2+} \longrightarrow FeOM^+ + 2H^+ \quad (3)$$

Lowering H^+ concentration will drive this reaction toward the right-hand side and favor the sorption of M^{2+} by increasing pH.

3.2.3 Effect of metal ion concentration and adsorption isotherms

50 mL of metal ion solutions of different concentrations ranging from 50 to 500 mg/L were contacted with 2g/L of adsorbent at a pH of 5.0, at 303K for a period of 1 h. The results given in Figure 7 show that the loading capacities were in the order Pb(II)>Co(II)>Cu(II)> Cd(II) within the studied range of initial metal ion concentrations. From the figure it is observed that the amount of Cd(II) and Cu(II) adsorbed were 29.15 and 37.25 mg/g respectively with the initial concentration of 300 mg/L. After that the saturation was observed as the loading capacities did not increase with further increase in initial concentration. In case of Pb(II) and Co(II), loading capacity increased as the metal ion concentration increased. The amounts of Pb(II) and Co(II) adsorbed per gram of material were ~109 and 86.6 mg respectively for the metal ion concentration of 500 mg/L and did not achieve saturation.

The isothermic data of Figure 7 was treated using Langmuir and Freundlich Isotherm Models. The linearised forms of Langmuir and Freundlich isotherms are expressed by Eq. (4) and (5) respectively:

$$C_e/q_e = 1/bq_m + C_e(1/q_m) \quad (4)$$

$$\log q_e = \log K_F + 1/n \log C_e \quad (5)$$

where C_e is the equilibrium concentration of substrates in the solution (mg/L), q_e is the adsorption capacity at equilibrium (mg/g), q_m is the maximum amount of adsorption (mg/g), 'b' is the adsorption equilibrium constant (L/mg). K_F is the constant representing the adsorption capacity, and 'n' is the constant depicting the adsorption intensity. The Langmuir and Freundlich adsorption isotherms for all the cations taken up for the present studies are shown in Figures 8 and 9 respectively. The isothermic data are given in Table 2. The values of regression coefficients point towards better fit of Freundlich model. The data shows highest K_f value for Pb(II) adsorption (Table 2) and lowest K_f value for Cd(II) adsorption indicating the greatest binding of lead ion on goethite. Empirically, K_f values may be used to predict differences in the abilities of adsorbents to adsorb a particular adsorbate. In case of Co(II) adsorption, the data did not fit at all to the Langmuir isotherm. Studies on adsorption of Pb(II), Cd(II), Cu(II) and Co(II) from single metal ion containing solutions show that the goethite synthesized by modified method exhibit high metal uptake for Pb(II) and Co(II).

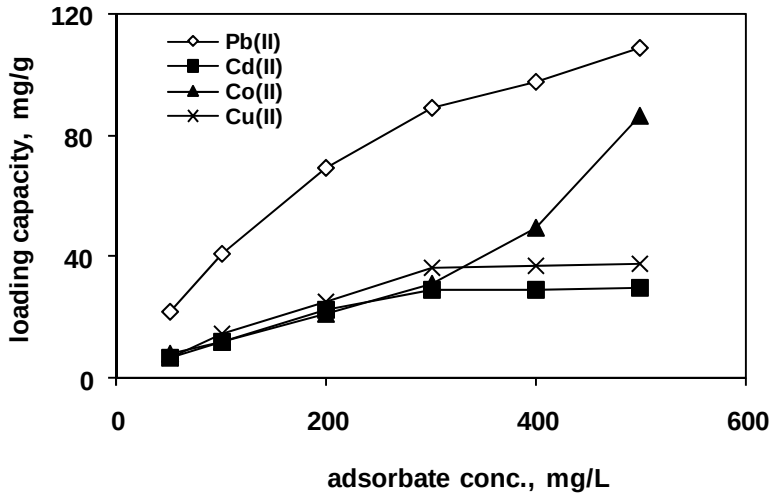

Figure 7. Effect of metal ion concentration on their adsorption. Conditions: Adsobent dose 2 g/L, initial cation conc. 100 mg/L, pH 5.0, temp. 303 K and time 1h.

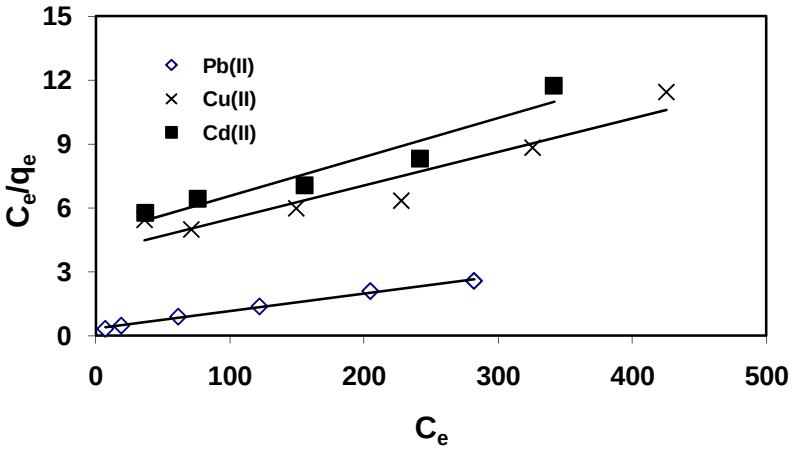

Figure 8. Langmuir plots for Pb(II), Cu(II) and Cd(II). (Data correspond to Figure7).

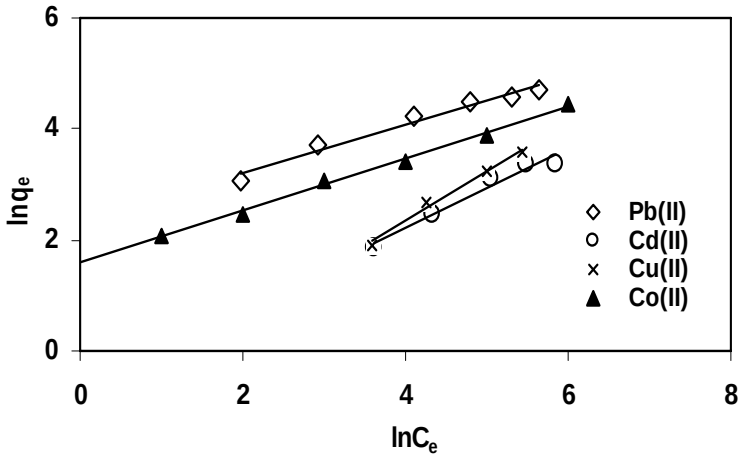

Figure 9. Freundlich plots for Pb(II), Cd(II), Cu(II) and Co(II). (data correspond to Figure 7)

Table 2 Langmuir and Freundlich parameters for adsorption of cations on goethite sample

Cations	Langmuir coefficients			Freundlich coefficients		
	q_m (mg/g)	b (L/g)	r^2	K_f	n	r^2
Pb(II)	120.48	0.025	0.99	10.33	2.304	0.97
Cd(II)	54.64	0.003	0.92	1.933	1.390	0.967
Co(II)	-	-	-	4.836	2.11	0.997
Cu(II)	63.69	0.004	0.899	3.559	1.11	0.99

3.2.4 Effect of temperature

The effect of temperature on % adsorption of metal ions onto goethite was studied. The *%* adsorption for all metal ions except Co(II) increased with the increase in temperature (Figure 10.) indicating the process to be endothermic in nature (Ho., 2006). This effect is characteristic of a chemical reaction or bond being involved in the adsorption process (Aksu, 2002). However from Figure 10, it is observed that the adsorption of Co(II) decreased at higher temperature due to the exothermic adsorption of this bivalent cation.

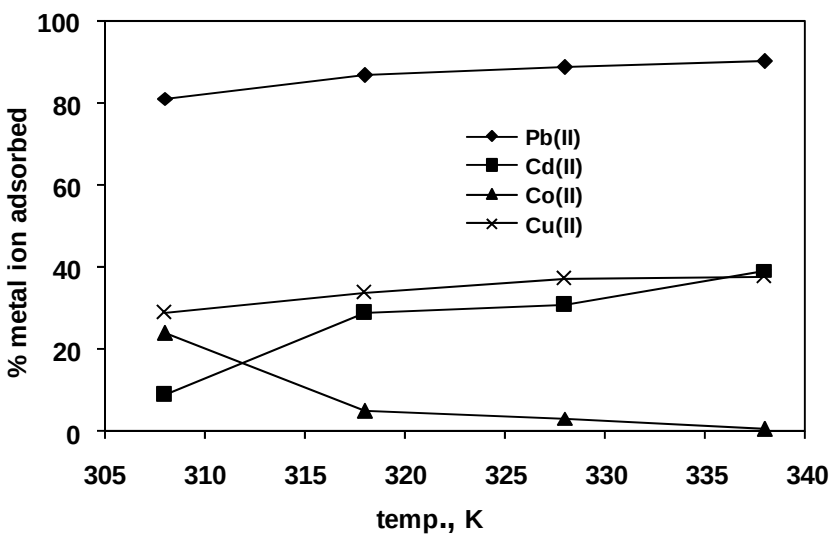

Figure 10. Effect of temperature on % adsorption of cations. Conditions: Adsorbent dose 2 g/L, initial cation concn.100 mg/L, pH 5.0, time 1h.

3.2.5. Thermodynamic parameters

The mechanism of adsorption may be determined through the thermodynamic quantities such as change in free energy ΔG^0, change in enthalpy of adsorption ΔH^0 and change in entropy ΔS^0. Thermodynamic parameters were calculated at pH 5 at various temperatures and initial metal ion concentrations of 100 mg/L.

The free energy of adsorption reaction is given by the following equation:

$$\Delta G^0 = -RT \text{ Ln } K_c \quad (6)$$

where R is the gas constant, T is the temperature (in Kelvin) and K_c is distribution coefficient which is determined as:

$$K_c = q_e/C_e \quad (7)$$

The values of ΔH^0 and ΔS^0 were determined from the van't Hoff equation as given below.

$$\text{Log } K_c = \Delta S^0 / 2.303R - \Delta H^0/2.303RT \quad (8)$$

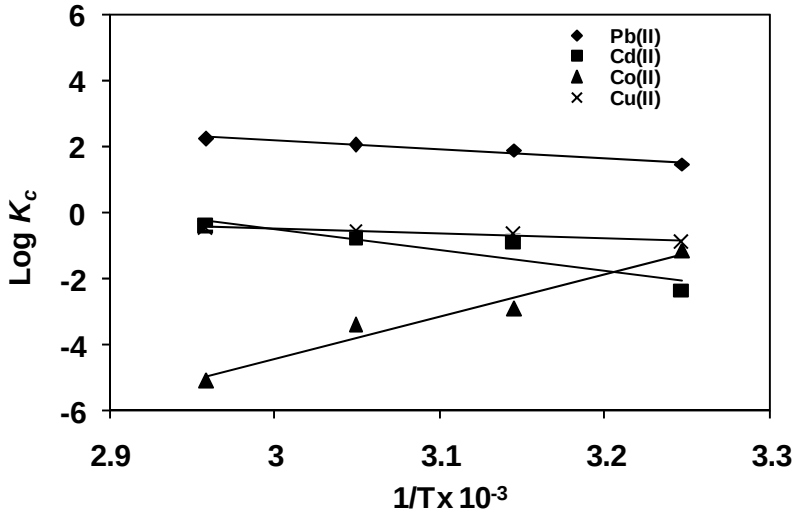

Figure 11. van't Hoff plots. (Data corresponding to Figure 10).

From the slopes and intercepts of the plots between Log K_c and 1/T, ΔH^0 and ΔS^0 were calculated and are given in Table 3. Typical van't Hoff plots for the three metal ions are shown in Figure 11. The positive value of ΔH^0 confirms the endothermic (Singh and Rawat, 1994) adsorption of all the three metal ions except Co(II). The positive ΔS^0 values reflect that significant change occur. The positive ΔH^0 and ΔS^0 values have been reported for the adsorption of cations on iron oxide minerals, such as Co(II)/goethite and Cd(II)/goethite (Angove *et al.,* 1999; Mohapatra *et al*., 2006), and Cd(II)/hematite (Pivovarovw *et al.,* 2001).

Table 3. Thermodynamic parameters for adsorption of cations on goethite sample

Metal ion	ΔH^0 (kJ /mol)	ΔS^0 (J/deg/mol)
Pb(II)	48.92	188.18
Cd(II)	117.88	343.6
Cu(II)	27.00	71.11
Co(II)	-245.5	-821.8

3.3 Adsorption from solutions containing binary cations

During these studies the metal ion concentration of Pb(II) was kept at saturation point i.e 500 mg/L while the concentrations of other metal ions were varied from 25 to 100 mg/L. Effect of variation of Cu(II), Cd(II) or Co(II) concentrations on adsorption of Pb(II) while keeping its concentration as 500 mg/L is shown in Figure 12. The presence of Cu(II) had an adverse effect on Pb(II) adsorption as the loading capacity decreased from 109 mg/g to 49.4 mg/g by increasing Cu(II) concentration from nil to 200 mg/L. Similar observation was also made while studying Pb(II)-Cu(II) binary system for adsorption onto 6-line ferrihydrite (Mohapatra *et al.,* 2010 communicated). With the increase in Cd(II) concentration from nil to 200 mg/L, Pb(II) loading capacity increased from 109 mg/g to 222.2 mg/g. The increase in Pb(II) loading capacity in presence of Cd(II) was also observed in our earlier work on Pb(II)-Cd(II) binary system using 6-line nano structured ferrihydrite as the adsorbent (Mohapatra *et al.,*2010 communicated). Saha *et al*., 2002 have also reported that in the Cd-Pb binary system, Pb adsorption on Hydroxyaluminum- and Hydroxyaluminosilicate-Montmorillonite complexes clearly exceeded Cd adsorption throughout the studied pH range. With the increase in Co(II) concentration from nil to 200 mg/L , Pb(II) loading capacity increased from 109 mg/g to 177 mg/g. Such an increase in Pb(II) uptake capacity in binary systems containing Co(II) has not been reported earlier.

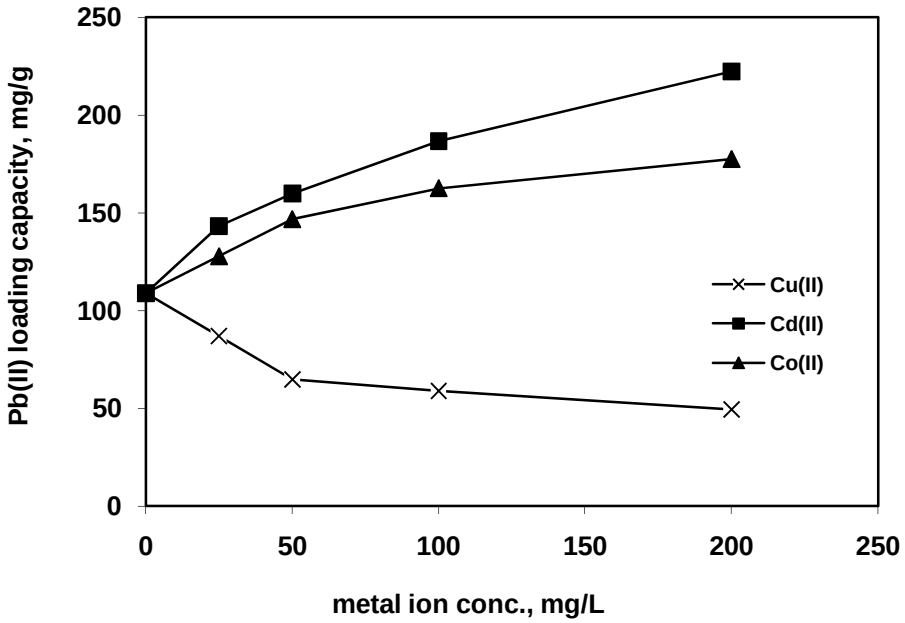

Figure 12. Effect of metal ion concentration on Pb(II) loading capacity. Conditions: adsorbent concentration 2 g/L, time 1 h, pH 5.0, Pb(II) concentration 500 mg/L.

Figure 13 shows the effect of Cu(II), Cd(II) or Co(II) concentration on their loading capacities in presence of 500 mg/L Pb(II). When these capacities are compared in absence of Pb(II) i.e single metal ion sorption (Figure 8), it is observed that Cd(II) adsorption capacity increased (except 25 mg/L) at all studied concentrations in the presence of Pb(II) and for 200 mg/L Cd(II), the capacity had increased from 22.1 to 57.87 mg/g. Similar observation was made by Serrano *et al.,* (2005) during the adsorption of cadmium and lead in acid soils of Central Spain. They explained that, the increment in the initial Cd adsorption rate in binary solutions could indicate that the competitive Pb adsorption forces Cd retention on adsorption sites with greater affinity or more specific for this metal. However at low concentration, no competition between Pb and Cd was observed in other studies (Benjamin and Leckie, 1981b; Saha *et al*., 2002). Cu(II) uptake capacity had only marginal effect while Co(II) loading capacities decreased in the presence of Pb(II) when compared to their capacities in absence of Pb(II).

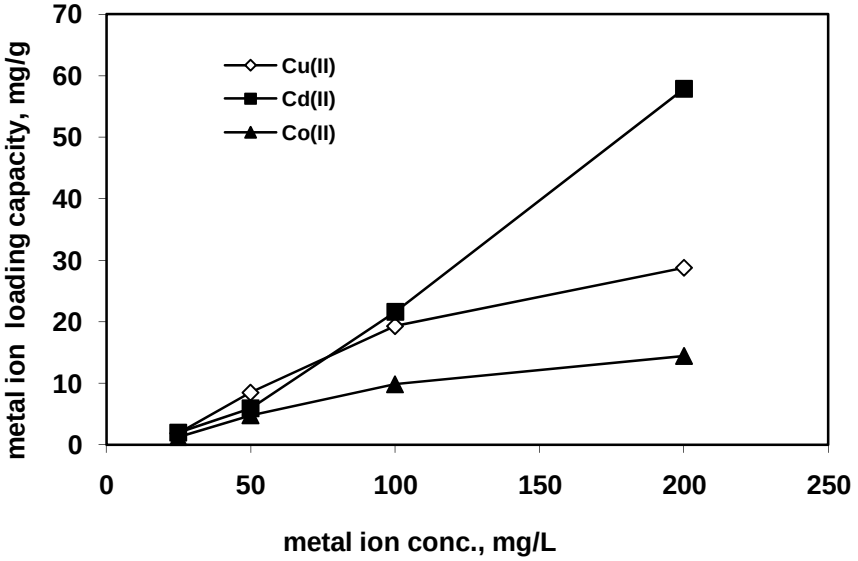

Figure 13. Effect of presence of 500 mg/L Pb(II) on loading capacities of Cu(II), Cd(II) and Co(II) at their various initial concentrations in binary system. Conditions: adsorbent concentration 2 g/L, time 1 h, pH 5.0

From the foregoing results it can be concluded that the adsorption behaviour becomes complicated in binary solutions. In order to find a correlation between the metal ion uptake and metal ion properties, several parameters are considered. Mainly, factors like (i) electro negativity of the metal ion (ii) electrostatic attraction due to charge to radius ratio (iii) hydroxo complex formation abilities and (iv) preferred adsorption site on the adsorbent are responsible for the preferential adsorption of one metal ion over other. The metals with higher electro negativity adsorb more readily. Considering the metal ions electro negativity, the adsorption selectivity of metal ion in the present study may be Pb^{2+}(2.33) > Cu^{2+} (2.00) > Co^{2+} (1.8)> Cd^{2+} (1.69). Also, with an increase of the ionic size, the absolute value of enthalpy of hydration decreases. Accordingly order of enthalpy of hydration as Pb^{2+}> Cd^{2+}> Co^{2+}, ions have accessibility to the adsorbent surface. Again, adsorption in multi-component systems is complicated because of the fact that solute–surface interactions are involved. The specific adsorption of bivalent Cd, Co, Cu, Pb, and Zn on goethite were measured as a function of pH by Forbe *at al.* (1976). They reported, the intrinsic affinities of the metal ions for the oxide surface increase in the order, Cd < Co < Zn < Pb < Cu. The second metal ion present in the water solution competes with the single metal ions adsorption. In our binary systems Pb(II) uptake had decreased in Pb(II)-Cu(II) system. It has been reported that in case of Pb-Cu system, Cu (II) adsorption will be enhanced as Cu, forms most stable monohydroxo complex and least soluble hydroxide which has a tendency to adsorb more preferably than Pb(II) thereby inhibiting the Pb(II) adsorption (Avena, 2006). Cu(II) which shows stronger binding replaces the other metal ion, thereby increasing its own uptake (Juang and Chung, 2004). Though in the present Pb-Cu system, Pb(II) uptake capacity was adversely affected but Cu(II) uptake remained unaffected. There is no available literature on Pb(II)-Co(II) binary system adsorption but considering the intrinsic affinities of the metal ions for the oxide surface (Forbes *et al.,* 1976) it is expected the adsorption of Co(II) as a secondary metal ion would decrease as observed in our study.

It has been reported that the total loading capacities of the adsorbent remains more or less same in a binary system and the metal ions compete to occupy the active adsorption sites (Swayampakulaa *et al.,* 2009). In the present study it has been observed that in the binary systems, the total metal uptake may exceed the saturation levels observed with single cation containing solutions. The total metal uptake in mg/g or in mmole/g from the single metal ion containing and corresponding binary systems are compared in Table 4.

Table 4 Comparison of total metal ion uptake from single and binary solutions with Pb(II) as the primary metal ion and Cd(II), Cu(II) or Co(II) as the secondary metal ions

System	Total metal uptake from			
	Single metal ion system		Binary metal ions system	
	(mg/g)	(mmole/ g)	(mg/g)	(mmole/g)
Pb(II) primary metal ion				
Pb(II)- Cd(II), mg/ L				
500 + 25	113.22	0.564	145.36	0.709
500 + 50	115.46	0.584	165.91	0.825
500 + 100	120.87	0.632	208.17	1.093
500 + 200	131.10	0.723	280.07	1.587
Pb(II)-Cu(II) mg/L				
500 +25	112.22	0.577	88.92	0.449
500 + 50	115.73	0.632	73.38	0.446
500 + 100	123.35	0.752	78.3	0.588
500 + 200	134.1	0.921	78.1	0.6918
Pb(II)-Co(II) mg/ L				
500 + 25	111.79	0.573	130.35	0.660
500 + 50	117.0	0.662	156.32	0.870
500 + 100	120.95	0.729	182.22	1.145
500 +200	130.0	0.882	206.3	1.346

The results presented in Table 4 show that with Pb(II) initial concentration of 500 mg/L, variation of Cd(II) concentration from 25 to 200 mg/L in the binary system resulted in increase in total metal uptake at all concentrations. The total metal uptake increased from 0.709 mmole/g to 1.587 mmole/g when Cd(II) concentration increase from 25 to 200 mg/L. In a similar for Pb(II)-Co(II) the total metal uptake is enhanced in binary solutions. The total metal uptake increased from 0.66 to 1.346 mmole/g when Co(II) concentration increased from 25 to 200 mg/L in the binary system. The presence of Cu(II) resulted in decrease of overall metal uptake.

Juang and Chung (2004) had tried to fit a a simple "one site" Langmuir competitive model to the adsorption from binary solutions and found that for Cu(II)-Zn(II) system, though Cu(II) adsorption could be reasonably predicted but Zn(II) adsorption was over estimated. Vilar *et al.* (2008) fitted a discrete and a continuous model and showed that there was inhibition of primary metal ion (high concentration) biosorption by the co-cation. The present studies have shown that it is not always the case for adsorption from binary solutions. In the present study for the binary systems Pb-Cd and Pb-Co, the uptake capacity of Pb(II) ion had increased.

4. Conclusions

1. In the present study, nano structured goethite synthesized at a pH of 3.0 using a novel additive namely hydrazine sulphate has been used to study its cation adsorption behaviour.
2. Kinetic study of Pb(II), Cd(II), Cu(II) and Co(II) adsorption on nano goethite from single cation containing solutions showed that all the four cations followed pseudo second order kinetic model.
3. The experimentally obtained maximum loading capacities were found to be ~109, 86.6, 29.15 and 37.25 mg/g of goethite at initial metal ion concentrations of 500, 500, 300 and 300 mg/L for Pb(II), Co(II), Cd(II) and Cu(II), respectively.
4. The adsorption data showed better fit to Freundlich isotherms when compared to Langmuir isotherms.
5. Adsorption behaviour from binary solutions was studied by keeping Pb(II) concentration as 500 mg/L and varying the concentration of others one at a time in the range of 25 to 200 mg/L. The uptake capacity of Pb(II) increased with the increase of Cd(II) or Co(II) concentrations while it decreased in presence of Cu(II). An increase in the overall metal uptake capacities was obtained for Pb(II)-Cd(II) and Pb(II)-Co(II) systems whereas a decrease was recorded for Pb(II)-Cu(II) binary system.

The detailed studies carried out on adsorption of Pb(II), Cd(II), Cu(II) and Co(II) have shown that the synthesized nano structured goethite exhibit high capacity for metal ion uptake. The adsorption of Pb(II) from binary solutions containing Cd(II) or Cu(II) showed higher overall loading capacities when compared to solutions containing only Pb(II). Further studies need to be carried out on (i) desorption of cations from the loaded adsorbent, (ii) reuse of the regenerated adsorbent to evaluate its use for the number of adsorption-desorption cycles and, (iii) column adsorption and further scale up with a view to determine the commercial use of the developed adsorbent.

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